# SURVEY OF THE SOLID STATE CONFORMATION OF CALIX[4]ARENES 

## THESIS

# Presented to the Graduate Council of the University of North Texas in Partial Fulfillment of the Requirements 

For the Degree of

MASTER OF SCIENCE

By

Stephen J. Obrey Denton, Texas

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The characteristics of seventy-six calix[4]arene crystal structures derived from the Cambridge Crystallographic Database are presented. This survey is a discussion of the inter and intramolecular effects on the solid state cavity shape and molecular recognition ability of the compounds. In addition to this survey, four new calix[4]arene crystal structures are presented. The conformational characteristics of these four calixarenes are determined by a complicated array of inter and intramolecular interactions in the crystal packing.

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## TABLE OF CONTENT

Page
ACKNOWLEDGEMENTS ..... ii
LIST OF TABLES .....  V
LIST OF FIGURES ..... viii
ABBREVIATIONS ..... xi
Chapter

1. INTRODUCTION TO CALIX[4]ARENES ..... 1
2. EXPERIMENTAL ..... 8
2.1. Crystallographic Data for Calix[4]arenes ..... 8
2.2. X-ray Crystallography ..... 10
3. SOLID STATE CONFORMATION OF CALIX[4]ARENES WIT'H INTRAMOLEULAR HYDROGEN BONDING ..... 15
3.1. Introduction ..... 15
3.2. Tetrahydroxycalix[4]arenes ..... 16
3.3. Trihydroxycalix[4]arenes ..... 31
3.4. 1,2-dihydroxycalix[4]arenes ..... 32
3.5. 1,3-dihydroxycalix[4]arenes ..... 39
3.6. Monohydroxycalix[4]arenes ..... 46
4. SOLID STATE CONFORMATION OF CALIX[4]ARENES WITHOUT INTRAMOLEULAR HYDROGEN BONDING ..... 52
4.1. Introduction ..... 52
4.2. Tetraalkylated Calix[4]arenes in the "Cone" Conformation ..... 53
4.3. Tetralkylated Calix[4]arenes with Small Lower Rim Substitutents ..... 60
4.4. Tetraalkylated Calix[4]arenes in the "Partial Cone" Conformation ..... 66
4.5. Tetralkylated Calix[4]arenes in the "1,2-Alternate" Conformation ..... 72
4.6. Tetraalkylated Calix[4]arenes in the "1,3-Alternate" Conformation ..... 74
4.7 Conclusions ..... 79
5. CRYSTAL STRUCTURES OF NEW CALIX[4]ARENES ..... 81
5.1. Introduction ..... 81
5.2. Structure $\mathbf{I}$ ..... 82
5.3. Structure II ..... 91
5.4. Structure III ..... 98
5.5 Structure IV ..... 103
5.6. Conclusion ..... 111
APPENDIX A ..... 114
APPENDIX B ..... 123
APPENDIX C ..... 135
APPEINDIX D ..... 147
APPENDIX E ..... 155
REFERENCES ..... 162

## LIST OF TABLES

Table Page
1 General representation of tetrahydroxy calix[4]arenes ..... 17
2 Mean Molecular plane angles of structures 1a - g. ..... 18
3 The cavity guests found in structures
1a - g. ..... 19
4 Molecular plane angles of structures
1h and 1i ..... 20
5 Molecular plane angles of structures $1 j$ and $1 k$ ..... 22
6 Molecular plane angles of structures 1q - t ..... 24
7 Molecular plane angles of structures 11 - n ..... 26
8 Molecular plane angles of structures 10 and1p ..... 28
9 Molecular plane angles of structure 1u ..... 30
10 General representation of 1,2-dihydroxy calix[4]arenes ..... 33
11 Molecular plane angles of structures
$2 a$ and $2 b$ ..... 35
12 Molecular plane angles of structures
$2 c$ and 2 d . ..... 37
13 General representation of 1,3-dihydroxy calix[4]arenes ..... 40
14 Molecular plane angles of structures 3a-f ..... 42
15 Molecular plane angles of structure 3 h ..... 42
16 General representation of monohydroxy calix[4]arenes ..... 47
17 Molecular plane angles of structures $4 b$ and $4 c$ ..... 46
18 Molecular plane angles of structure 4a ..... 50
19 General representation of tetralkylated calix[4]arenes in the "cone" conformation ..... 54
20 Desriptive plane angles for symmetric and assymetric "cone" conformations ..... 55
21 Molecular plane angles for structures 5q and 5r ..... 56
22 Mean conformation of calixarens with small para substituents ..... 58
23 Molecular plane angles for structure 5s ..... 59
24 General representation of tetrasubstituted calix[4]arenes with small lower rim substituents ..... 61
25 Mean conformation of "partial cone" structures ..... 62
26 General representation of tetralkylated calix[4]arenes in the "partial cone" conformation ..... 67
27 Molecular plane angles for structure 7a and 7d ..... 66
28 Molecular plane angles for structures $7 b$ and 7c ..... 69
29 General representation of tetralkylated calix[4]arenes in the "1,3-alternate" conformation. ..... 75
30
Molecular plane angles for structure 9b ..... 76
31 Molecular plane angles for structures 9a, 9c, 9d and 9e ..... 78
32 X-Ray Crystallographic collection and processing data for structure $I$. ..... 83
33 Molecular plane angles for structure I and mean plane angles for similar 1,3-dihydroxy calix[4]arenes ..... 87
processing data for structure II ..... 92
35 Molecular plane angles for structure II and mean plane angles for similar 1,3-dihydroxy calix[4]arenes........................ . . 9336 X-Ray Crystallographic collection andprocessing data for structure IIr................. 100
37 Molecular plane angles for structure IIIand mean plane angles for similar1,3-dihydroxy calix[4]arenes....................... . . . 102
X-Ray Crystallographic collection andprocessing data for structure IV105
39 Moleculax plane angles of structure IV ..... 106

## LIST OF FIGURES

Figure Page
1 General Representation of Calix[4]arenes ..... 1
2 Four Conformations of calix[4]arenes ..... 3
3 Crystal strucutre of p-t-butyl calix[4]arene:toluene clathrate5
4 Crystal structures of the cage complex of 1h and 11 ..... 21
5 Diagram of the trimer and molecular geometry of structures $\mathbf{1 j}$ and $\mathbf{1 k}$ ..... 23
6 Diagrams showing the inter-calixarene inclusion complexes in 1q - 1t ..... 25
7 Crystal packing diagrams showing $\pi-\pi$ interactions in structures 11 - $1 n$ ..... 27
8 Diagrams of the molecular geometry of structures 10 and 1p. ..... 29
9 Molecular geometries for structures 2a and 2b ..... 34
10 Diagrams of the intermolecular inclusion observed in 2a ..... 36
11 Molecular geometries for structures 2 c and 2d. ..... 38
12 Molecular geometries for structure 3h ..... 43
13 Crystal packing, molecular geometry and plane angles for structure 3i ..... 45
14 Molecular geometries for structures
$4 b$ and $4 c$ ..... 48
15 Molecular geometries for structures $5 r$ and $5 q$. ..... 57
16 Crystal packing and molecular geometry for 6 g . ..... 64
17
7a and 7d ..... 68181920thermal ellipsoids drawn at $50 \%$ probabilitylevel. H atoms are omitted for clarity. (sideview) . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . .101
ORTEP diagram of structure $I$ with thermal ellipsoids drawn at $50 \%$ probability level. H atoms are omitted for clarity. Hydrogen bondng interaction between 01b and the THF molecule ..... 96
ellipsoids drawn at 50\% probability level. H atoms are omitted for clarity ..... 94
A diagram of the unit cell of structure I ..... 90
ORTEP diagram of structure I with thermal ellipsoids drawn at 50\% probability level. H atoms are omitted for clarity. (topview) ..... 86 ..... 23
Diagram of the crystal packing for structure I ..... 89
9d, and 9e ..... 77
General representation of compounds I, II, III, and IV ..... 81
ORTEP diagram of structure $I$ withthermal ellipsoids drawn at 50\%probability level. $H$ atoms areomitted for clarity. (side view)85
$7 b$ and $7 c$ ..... 70
General representation, table of plane angles, and molecular geometry of $8 \mathbf{a}$. ..... 73A diagram of the unit cell for structure $I$.97
ORTEP diagram of structure III with

$\qquad$

ORTEP diagram of structure IV with thermal ellipsoids drawn at $50 \%$ probability level
H atoms are omitted for clarity. ................. 107
32 A diagram of the unit cell for structure IV.... 109
33 A diagram of the unit cell for structure IV.... 110

## ABBREEVIATIONS

THF
tetrahydrofuran

## CHAPTER 1

## INTRODUCTION TO CALIX[4]ARENES

Calixarenes are a class of cyclic bowl-shaped organic macrocycles that have become of interest over the last 25 years. 1 The general structural representation of a calixarene is shown below


Figure 1. General representation of calix[4]arenes

The general term "calix[n]arene" 2 is used to describe the calixarenes where "n" describes the ring size which is most commonly 4, 6, or 8,3 although other oligomers have been reported. 4

Much like crown ethers, ${ }^{5}$ and cyclodextrins, ${ }^{6}$ calixarenes posses large cavities that make them potential hosts for molecular recognition chemistry. Unlike cyclodextrin and crown ethers, calixarenes are readily functionalized on the upper and the lower rim of the macrocyles and the presence of methylene linkages allow rotational flexibility which makes a variety of conformations possible. Due to these functionalization and conformational properties, calixarenes may be "chemically tailored" for application as potential host-guest sites, 7 catalyst supports, ${ }^{8}$ and transport agents for the extraction of metals from aqueous media. 9

Calixarenes may be readily functionalized at both the phenolic oxygen (R), commonly known as the lowex rim, and at the para position (R'), known as the upper rim. Synthetic chemists have developed methodology for selective lower rim substitution of calix[4]arene for mono-alkylation, 10 di alkylation ${ }^{11}$ and trialkylation. 12 There is also methodology for asymmetric upper rim substitution with a variety of substrates. ${ }^{13}$

One of the requirements to use these compounds for molecular recognition is to produce and maintain a stable cavity shape and size to accommodate a guest. ${ }^{14}$ The rotational flexibility about the methylene bridges allow calix[4]arenes to adopt and maintain four different geometries based on the relative orientation of the rings. 15 These conformations are
commonly known as the "cone", "partial cone", "1,2-alternate" and the "1,3-alternate" conformations. ${ }^{16}$ The "cone" conformation involves all four aromatic rings being oriented in the same direction. The "partial cone" has three rings pointing up with the fourth ring down. Both the "1,2alternate" and the "1,3-alternate" have two rings up and two down in different isomers.


Figure 2. The four conformations of calix[4]arenes

The "1,2-alternate" has the two adjacent rings pointed down and the other two pointed up. The "1,3-alternate" has the two opposing rings up and the other two down. Synthetically, the conformation of a functionalized calixarene is most commonly controlled utilizing a template effect related to the nature of the cation used during alkylation. 17 These conformations should only be treated as idealized orientations of the rings and actually give no indication as to the cavity shape, size, or the relative angles the aromatic rings. The specific
characteristics of the aromatic rings are dependent on the functionalization of the upper and lower rim, the conformation in which the calixarene was synthesized, and a series of complicated inter and intramolecular interactions

One of the most common ways in which to produce a stable conformation is the introduction of sterically bulky substitutents attached to the lower rim phenolic oxygens. It is well documented that only substituents smaller than propyl may have the rotational freedom to allow the interconversion between one conformation to another. 18 Ethyl substituents show the ability to undergo this conformational mobility at elevated temperatures, but do not readily interconvert at room temperature. 19 In application to single crystal X-ray crystallography, it is important to note that, since most crystals used are grown at or below room temperature, we may only treat groups that are smaller than ethyl as conformationally mobile for analysis of the solid state structures.

In 1979, Adreetti et al. published the crystal structure of the inclusion complex between para t-butyl calix[4]arene and toluene shown in Figure 3.20 This crystal structure shows the calixarene in the "cone" conformation with $C_{4 v}$ symmetry. This conformation is maintained by the cyclical network of hydrogen bonds on the lower rim of the calixarene, which holds the aromatic rings so that they form a cavity or a bowl. This cavity contains one toluene molecule as a guest
which is oriented so that the methyl group is pointed into the cavity. Although the positions of the hydrogen atoms on the guest toluene were not located, it is believed that the methyl hydrogens are interacting with the $\pi$-cloud of the aromatic rings.


Figure 3. Crystal strucutre of p-t-butyl calix[4]arene: toluene clathrate

The para-t-butyl groups also show $\mathrm{CH}_{3}-\pi$ interactions with the aromatic ring of the toluene. These $\mathrm{CH}_{3}-\pi$ interactions are among the most common observed for the host guest complexes of calixarenes with neutral guest molecules.

Since this publication, there have been many studies on the inclusion behavior of calixarenes. ${ }^{21}$ Due to the fluxional behavior of calixarenes in solution there is little evidence for solution state inclusion complexes, 22 therefore solid state analysis by using single crystal x-ray diffraction is the most common way to analyze these interactions. Recently, it has been shown that the inclusion behavior of these solid
state complexes may also be analyzed by ${ }^{13} \mathrm{C}$ Cp-MAS NMR experiments but only in combination with X -ray crystallographic data. ${ }^{23}$ In the solid state, calixarenes have shown the ability to form inclusion complexes with other neutral organic molecules such as xylene, anisole, acetonitrile, acetone, chloroform, methylene chloride as well as other neutral organic molecules. In addition to this host-guest behavior, calixarenes are also capable of retaining guest species in channels and layers within the crystal lattice. These channel guest species make calixarenes particularly difficult to analyze by X-ray diffraction since these crystals tend to lose the solvent and decompose readily.

A previous analysis of calix[4]arene crystal structures was undertaken by Lipkowitz in $1993^{24}$ in an attempt to determine their architectural foundation for use with computational modeling programs. In this paper a total of 29 crystal structures of calixarenes in the "cone" conformation were analyzed, none of these contained metals or bridging linkages between the phenolic units. These were partitioned into three categories: native structures, near-native structures, and derivatized structures. Native strucutres are unsubstituted on the lower rim with either $H$, Me or t-buytl substitutents in the para position. Near-native structures also have $\mathrm{H}, \mathrm{Me}$, or t-butyl in the para position but the $4-\mathrm{OH}$ groups are replaced by a simple functionality like ethers or
esters. Derivatized calixarenes are also substituted on the lower rim and include all para substituents other than $\mathrm{H}, \mathrm{Me}$, or t-butyl. Although this paper reports in detail the important bond lengths, bond angles, and dihedral angles, it fails to describe the effect of these substituents on the cavity formed by the four aromatic rings.

In the first part of this thesis, I will describe the inter and intramolecular effects which alter the cavity shape, size, and inclusion properties of various types of calixarenes. The second part of this thesis contains a disscussion of four new calix[4]arene crystal structures which add to the limited body of knowledge concerning the solid state complexes.

## CHAPTER 2

EXPERTMENTAL
2.1. Crystallographic Data for Calix[4]arenes

All data used in the survey of crystal structures of Calix[4]arenes were obtained using the 1996 Cambridge Crystallographic Database. 25 of the two hundred thirty eight hits, ninety eight were applicable to the work. (the rest being either higher homologs, contained metal atoms or bridging linkages) Of these 98 remaining structures, twentyfour had no coordinates, incomplete coordinates, or were disordered. These were thus removed. This left a working set of 76 calix[4]arenes.

These structures were partitioned into ten categories. Five in which the conformation is determined by the presence of intramolecular hydrogen bonding between the phenolic units. These five categories are the tetrahydroxy calix[4]arenes, trihydroxy calix[4]arenes, 1,3-dihydroxy calix[4]arenes, 1,2-dihydroxy calix[4]arenes, and monohydroxy calix[4]arenes. The other five were separated by conformation and size of the lower rim substituents. The first category was defined as tetrasubstituted calix[4]arenes with lower rim substitutents which allow conformational
freedom. The other four categories were calixarenes which are frozen in the "cone", "partial cone", 1,2-alternate", and the "1,3-alternate" conformations.

For each of the 76 crystal structures, twelve pieces of data was collected using the 3D-structural option in the CCD. Six of these were distances between lower rim oxygens. The four distances between adjacent oxygen atoms may be used to indicate the location of intramolecular hydrogen bonding interactions. The two transannular oxygen-oxygen distances give an indication as to the shape of the lower rim of the cavity. The other six pieces of data were plane angles. The first four were the angles that each aromatic plane made with the mean plane of the methylene carbons which reflect the canting angle of the aromatic rings with the mean plane of the methylene carbons. These plane angles were normalized for each structure so that if the angle is less than 90 degrees, the top of the ring is pointed away from the cavity and if the angle is greater than 90 degree the top of the ring is pointed into the cavity. The other angles were between the two opposite aromatic planes. These plane angles may be used to describe the shape of the calixarene cavity which may allude to the presence of host-guest interactions. All plane angles, oxygen-oxygen distances and the database codes accumulated in this search are listed in Appendix $A$. Each of these twelve data points were reported from the ccD with three significant figures past the decimal point. Since
these values are not truely reflective of the accuracy X-ray điffraction, the angles will be truncated at one digit past the decimal place and the distances will be truncated after 2 decimal places. It is important to realize that these values are not from the crystal structure data but in fact generated by the CCD, by treating the atom as a single point rather than a sphere or an ellipsiod. All means reported were statistically analyzed at the $t_{0} .005$ probablity level to assure the statistical relavance of the data set. It is important to note that due to the small sample size used in the calculation of the means, these values may not be representative of the population. All crystallographic figures were generated using PLUTO. 26

### 2.2. X-ray Crystallography

X-ray crystallography may provide the most useful information regarding the structure of a complex furnishing information about bond lengths and angles as well as connectivity. Unfortunately, there are several drawbacks to its application. The most obvious problem is that one needs a single crystal that is at least 0.1 mm in every dimension. Some systems do not crystallise, and even if crystals can be obtained, they may not be of sufficient size or quality. Even if one manages to obtain a crystal, there is no guarantee that it represents the bulk of any precipitate, much less the predominant species in solution.

In cases where thermally stable crystals were obtained, they were mounted in thin glass capillaries with silicone grease by one of two methods. Where solvent-dependent crystals were obtained, the lattice depletion was overcome by addition of mother liquor or fresh solvent to the capillary tube. The ends were plugged with modelling clay and then sealed with an oxygen-methane torch as soon as possible. Crystals that were not solvent dependent were mounted on the bench top with the use of a microscope. In the cases where thermally unstable crystals were obtained, they were mounted on a glass fiber using Paratone-n. The crystal was held in place by passing a cold $\left(-60^{\circ} \mathrm{C}\right)$ stream of nitrogen across the crystal.

A suitable crystal was selected and mounted on the goniometer head of an Enraf-Nonius CAD-4 automated diffractometer which comprised of a four-circle kappa axis goniometer with graphite crystal monochromated Mo radiation $(\lambda=0.71073 \AA)$. The crystal-to-detector distance was 173 mm , and the take-off angle was 5.6 degrees. The diffractometer was controlled by a Digital Corporation VAXStation 3100/76. The crystal was first centered visually under the diffractometer microscope and then the program SEARCH ${ }^{27}$ was run to find up to 25 reflections and measure their angular settings. These were then used by the INDEX ${ }^{27}$ routine to calculate the primitive unit cell. Where appropriate this was transformed, either to a higher symmetry or to fulfil
,
international conventions. 28 Strong axial reflections were accurately centered and then used to refine the cell parameters.

Where the cell was reasonable and did not bear close resemblance to that of structures previously determined, data was collected. This was performed using either a $\omega-2 \theta$ or $\omega$ scan (in cases where a cell axis was greater that ca. 20 A) technique with a variable scan width as given in Eq. 2-1 (A was between 0.65 and 0.8 degrees).

Scan Width $=A+0.35 \tan (\theta)$

Backgrounds were measured by extending the calculated width on either end of the scan by 25\%. A fixed vertical detector aperture ( 4 mm ) and a variable horizontal aperture $(3+\tan \theta)$ were used. Every reflection was subjected to a prescan at a rate of 8 degrees per min. Reflections with $I / \sigma(I)<2$ for this prescan were rejected as weak, and those for which $I / \sigma(I)>10$ were accepted immediately. Reflections not falling into these two categories were rescanned at speeds ranging from 0.67 to 8 degrees per min for up to 120 s in an attempt to increase $I / \sigma(I)$ to 10 . Three reflections were measured every 3600 s of exposure time to monitor crystal decay. Crystal alignment was checked using the same reflections every 250 data points, and if the scattering vectors deviated by greater than 0.10 degrees from their
calculated values at any stage, the unit cell and orientation matrix were recalculated.

The intensity (I) and standard deviation $[\sigma(I)]$ were calculated using Eqs. 2-2 and 2-3, respectively, where $C$ is the total number of integrated counts, $B$ is the sum of the left and right backgrounds, $A$ is an attenuator factor (either 1 or 14.3), and $S$ is the scan rate.

$$
\begin{gather*}
I=A S(C-2 B)  \tag{2-2}\\
\sigma(I)=A S(C+4 B)^{1 / 2} \tag{2-3}
\end{gather*}
$$

All computations were carried out on a DEC VAXStation 3100/76. Calculations, except where noted, were performed using MolEN crystallographic software package. 29 The structures were solved using direct methods (MULTAN, $30 \mathrm{SIR}, 31$ or SHELXS-8632) and difference Fourier maps. After refinement of the entire model with isotropic thermal parameters, a Fourier absorption correction (DIFABS) 33 was applied. The extent of conversion of certain atoms to have anisotropic thermal parameters was dependent upon the quality and number of data. Hydrogen atoms were either located or generated and allowed to ride on the appropriate attached atom $\left[U(H)=1.3 \mathrm{U}_{\mathrm{eq}}\right.$ (Attached atom)]. The function minimized during refinement was $\Sigma \mathrm{W}\left(\left|\mathrm{F}_{\mathrm{O}}\right|-\left|\mathrm{F}_{\mathrm{C}}\right|\right)^{2}$ where the weight, $\mathrm{w}=$ $\left[\left(\sigma F_{\mathrm{O}}\right)^{2}-0.04 \mathrm{~F}_{\mathrm{O}}{ }^{2}\right] 1 / 2$.

The results of the final refinement are reported as three parameters: (1) $\mathrm{R}=\left(\Sigma\left(\left|\mathrm{F}_{\mathrm{O}}\right|-\left|\mathrm{F}_{\mathrm{C}}\right|\right) / \Sigma\left(\left|\mathrm{F}_{\mathrm{O}}\right|\right)\right.$, (2) $\mathrm{Rw}=$ $\left[W \Sigma\left(\left|F_{O}\right|-\left|F_{C}\right|\right)^{2} / W \Sigma\left(\left|F_{O}\right|\right)^{2}\right]^{1 / 2}$ and (3) goodness-of-fit (GOF) $=\left[\Sigma W\left(\left|F_{O}\right|-\left|F_{C}\right|\right)^{2}\right] /($ number of reflections - number of least-squares parameters).

Crystallographic diagrams were drawn with the aid of ORTEP-II ${ }^{34}$. Scattering factors and corrections for the real and imaginary components of anomalous dispersion were taken from reference 28 .

## CHAPTER 3

## SOLID STATE CONFORMATION OF CAIIX[4]ARENES WITH INTRAMOLEULAR HYDROGEN BONDING

### 3.1. Introduction

Hydrogen bonding is commonly believed to be the single strongest interaction in the solid state ${ }^{35}$ and therefore has a major effect on the conformation of calix[4]arenes. Calixarenes that undergo intramolecular hydrogen bonding interactions are subdivided into five categories dependent on the presence and location of alkyl substitutents on the phenolic oxygens. Introduction of alkyl substituents on the lower rim of the calixarene changes the nature of the intramolecular hydrogen bonding by the alteration of an alcohol into an ether. This introduction of an ether carbon from 0 -alkylation also requires the calixarene to adjust its conformation to accommodate the increased steric bulk. Due to selective asymmetric alkylation of calix[4]arenes there are five types of calix[4]arenes that may contain intramolecular hydrogen bonding: tetrahydroxycalix[4]arenes, trihydroxycalix[4]arenes, 1,2-dihydroxycalix[4]arenes, 1,3-dihydroxycalix[4]arenes, and monohydroxycalix[4]arenes. Although the
intramolecular hydrogen bonding affects the gross geometry of the calixarene cavity, the fine structure is affected by a series of complicated interactions in the crystal packing. This part of the survey describes the characteristics of these five structurally different calixarenes and some of the inter and intra molecular effects directing the observed conformation.

### 3.2. Tetrahydroxycalix[4]arenes

The search of the CCD resulted in twenty-one crystal structures that fall into the tetrahydroxy calix[4]arene category. The chemical representation of these twenty-one calixarenes is shown in Table 1. All of these calixarenes crystallise in the "cone" conformation due to the presence of a strong hydrogen bonding network formed by the four phenolic alcohols on the lower rim of the calixarene. The mean adjacent oxygen oxygen distance was $2.65 \AA$ for all twenty-one crystal structures which is indicative of a strong hydrogen bond. The cavity shape of tetrahydroxycalix[4]arenes appears to be directed by the intermolecular and intramolecular interactions in the crystal packing.

Intermolecular interactions observed in these calixarene crystal structures are due to inclusion of a neutral organic guest in the cavity, inclusion of a para substitutent of an adjacent calixarene, or from $\pi$ - stacking from para substituents with aromatic rings. All of these

Table 1. General representation of tetrahydroxycalix[4]arenes

$\mathrm{M}=\mathrm{H}$

| Compound | R1=R2eR3=R4 | Reference |
| :---: | :---: | :---: |
| 1a | t-butyl | 20 |
| 1b | hydroxyethylpiperazine | 36 |
| 1e | $1,1,3,3$-tetramethylbutyl | 37 |
| 1d | isopropyl | 38 |
| 1e | H | 39 |
| 1f | H | 40 |
| 1g | isopropyl | 41 |
| 1h | t-buty1 | 42 |
| 11 | isopropyl | 38 |
| 1j | H | 39 |
| 1k | H | 40 |
| 11 | phenyl | 41 |
| 1m | phenylazo | 42 |
| 1n | 4-nitrophenylazo | 43 |
| 10 | $1,1,3,3$-tetramethylbutyl | 37 |
| 1p | ethyl | 44 |


| Compound | R1 | R2 | R3 | R4 | Reference |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 1q | H | H | H | bromopropy1 | 45 |
| 1r | octyl | methyl | octyl | methyl | 46 |
| 1a | isopropyl | isopropyl | isopropyl | isopropyl | 38 |
| 1t | t-butyl | nitro | t-butyl | methyl | 47 |

intermolecular interactions may be observed in the crystal packing diagrams. The intramolecular interactions observed in tetrahydroxy calixarenes involve the self-inclusion of the para substituents or introduction of meta substituents that interact with adjacent aromatic rings of the calixarene.

There are eleven, $\mathbf{1 a}-\mathbf{k}$, crystal structures of tetrahydroxy calix[4]arenes where the shape of the calixarene cavity is affected by inclusion of a neutral organic molecule. There are three different crystallisation patterns observed which are dependent on the number of calixarenes per guest molecule.

There are seven examples, $\mathbf{1 a}-\mathrm{g}$, of tetrahydroxy crystallising with one neutral organic guest in the cavity of a single calixarene. With the exception of this host-guest interaction, these compounds show no unusual interactions in the crystal packing so the geometry of the cavity should be solely determined by the guest present. Table 2 presents a diagram of the mean geometry and plane angles for these seven structures.

Table 2. Mean molecular plane angles of structures 1a-g


These seven crystal structures are very close to $c_{4 v}$ symmetry. Each of the four aromatic rings make angles close to 55 degrees with the methylene carbons. The interplanar angles between two opposite planes are close to 69 degrees. The nature of the para substituent does not seem to affect the cavity shape and size, but does have an affect on the interaction with the guest molecule. In these seven structures there are five different guest molecules observed: toluene, xylene, acetone, acetonitrile, and 1-(2hydroxyethyl)piperazine. Table 3 shows the guests that are included in each of these seven structures.

Table 3. The cavity guests found in structures 1a-g

| Structure |
| :---: |
| $1 a$ |
| 1 b |
| 1 c |
| 1 d |
| 1 e |
| 1 f |
| $\mathbf{1 g}$ |

Guest toluene
1-(2-hydroxyethyl) piperazine toluene xylene acetonitrile acetone toluene

Each of these guests orients itself in the cavity to allow CH - $\pi$ interactions with the aromatic rings of the calixarene. The two aromatic guests, toluene and xylene, each show the presence of $\mathrm{CH}-\pi$ interactions with the para substituent. In all cases, this guest is disordered so that each of the
four aromatic rings interacts with the guest in a symmetric manner.

There are two examples, $\mathbf{1 h}$ and $1 \mathbf{1 i}$, of cage complexes where two calixarenes play host to a single neutral organic guest molecule. The two calixarenes are oriented so that the upper rim of each calixarene is facing one another with the guest molecule being trapped in the middle. Figure 4 shows these two calixarenes with the guest in the middle. Table 4 shows the relevant angles for the aromatic rings in these two structures.

Table 4. Molecular plane angles of structure $\mathbf{1 h}$ and $\mathbf{1 i}$

| Plane | $\underline{\mathbf{1 h}}$ | $\underline{\mathbf{1 i}}$ |
| :---: | :---: | :---: |
| A | 54.2 | 55.8 |
| B | 54.2 | 55.8 |
| C | 55.2 | 55.8 |
| D | 55.2 | 55.8 |
| B C D | 71.7 | 68.4 |
|  | 71.7 | 68.4 |

Although both the calixarenes are intimately joined, there appears to be no structural deviations of the individual calixarene molecules as a result of this close interaction. The observed conformation is very similar to the previously mentioned structures of one calixarene with a single guest molecule. All four of the aromatic rings are inclined close to 55 degrees and the interplanar angle between two alternating aromatic rings is close to 70 degrees

Structure of 1h


Structure of 1i


Figure 4. Crystal structures of the cage complex of 1 h and II
in both cases. The guest included in the cage is disordered in both structures, the anisole in 1 h is disordered over 8 positions and the xylene in $1 i$ is disordered over 2 positions. The disorder of the guest molecule allows it to interact with the cavity in a symmetric manner.

There are two examples, $\mathbf{1 j}$ and $\mathbf{1 k}$, of cage complexes where three calixarenes play host to a single organic guest molecule. Figure 5 shows the trimer and a representation of a single molecule. Table 5 shows the plane angles of the two calixarene molecules.

Table 5. Molecular plane angles of structure $\mathbf{1 j}$ and $\mathbf{1 k}$

| Plane | $\mathbf{1 0 \mathbf { 1 }}$ | $\underline{\mathbf{I k}}$ |
| :---: | :---: | ---: |
| A | 65.7 | 64.5 |
| B | 42.1 | $\mathbf{4 2 . 7}$ |
| C | 63.7 | 64.7 |
| A - C | 42.1 | 42.7 |
| B - D | 50.6 | 50.8 |
|  | 95.8 | 94.6 |

The crystal packing diagram shows that these calixarenes crystallise as a trimer with the single guest molecule in the center of the complex. Each calixarene has one aromatic ring that interacts with the cavity of the adjacent calixarene. Due to the asymmetric nature of this interaction there is a structural deviation observed in the cavity. Two of the aromatic rings fold up toward the center of the cavity making an interplanar angle of about 50 degrees. The other two


Representation of the molecular geometry from structures if and 1k


Figure 5. Diagram of the trimer and molecular geometry of structures 1j and 1k
rings fold down away from the center of the cavity making an interplanar angle of about 95 degrees. The structural deviation observed in this compound may be explained by the asymmetric way in which one of the calixarene rings interacts with the adjacent calixarene cavity.

There are four compounds, 1q - t, which show intermolecular interactions of the para substituent of one calixarene interacting in the cavity of another calixarene. These interactions may be observed in the crystal packing as seen in Figure 6. Table 6 shows the canting angles of the aromatic rings for the individual molecules in the structures

Table 6. Molecular plane angles of structures 1q - t

| Plane | $\underline{\underline{1 q}}$ | $\underline{\underline{\mathbf{I}}}$ | $\underline{\mathbf{1 g}}$ | $\underline{\mathbf{1 t}}$ |
| :---: | ---: | :---: | :---: | :---: |
| A | 61.4 | 55.4 | 55.0 | 56.1 |
| B | 52.3 | 56.3 | 50.4 | 48.8 |
| C | 57.8 | 58.5 | 53.8 | 53.6 |
| D | 57.8 | 53.9 | 53.3 | 55.5 |
| A - C | 60.9 | 66.1 | 71.2 | 70.4 |
| B - D | 74.9 | 69.8 | 76.3 | 75.7 |

The conformation of the calixarene cavity in the four structures is very similar to the previously mentioned calixarenes with C 4 v symmetry. The shape of the calixarene cavity is slightly deformed with two of the alternate aromatic rings folding slightly further out. Each of the four structures has different substituents interacting in the cavity and therefore the geometry is effected differently.

1a

$1 s$


Figure 6. Diagrams showing the inter-calixarene inclusion complexes in Iq - It

The minor deformation may be attributed to the asymmetric manner in which the guest resides in the cavity.

There are three crystal structures, 11 - $\mathbf{n}$, of compounds with para substituents that contain aromatic rings. Figure 7 shows the crystal packing diagrams for these three compounds and their structural representation. Table 7 lists the plane angles for these three calixarenes.

Table 7. Molecular plane angles of structure 11 - $\mathbf{n}$

| Plane | $\underline{11}$ | 1m | 1n |
| :---: | ---: | :--- | ---: |
| A | 55.5 | 51.4 | 66.0 |
| B | 48.8 | 57.0 | 34.5 |
| C | 53.6 | 49.0 | 66.0 |
| D | 55.5 | 64.6 | 34.5 |
| A C | 70.4 | 58.4 | 48.1 |
| B - D | 75.7 | 79.5 | 111.0 |

The crystal packing diagrams for these three compounds, in Figure 7, shows the presence of $\pi$ - stacking between the para aromatic substitutents. The manner in which this occurs is similar to inter-calixarene inclusion where the para substituent on an adjacent calixarene interacts with the cavity of the calixarene. In addition to the presence of the $\pi-$ stacking interaction each of these calixarenes acts as a host to a neutral guest molecule. Due to the complicated nature of these intermolecular interactions, direct correlation of these effects to the calixarene geometry would be unfounded.

Crystal packing diagram for 1 n


Crystal packing for 11
Crystal packing for 1m


Figure 7. Crystal packing diagrams showing $\pi-\pi$ interactions
in structures 11 - 1n

There are two crystal structures, 10 and $1 p$ that show no intermolecular interactions in the crystal packing but rather have intramolecular interactions with two para substituents interacting within the cavity. As can be seen in Figure 8, two of the para substituents fold into the cavity effectively blocking the cavity from inclusion of a guest molecule.

The other two para substituents fold out of the cavity and show no effect on the cavity conformation. The crystal packing of these two compounds shows a minimal amount of intermolecular interactions therefore the cavity shape may be attributed to only intramolecular interactions. Table 8 lists the angle of the aromatic planes with the methylene carbons and the interplanar angles between the two alternate aromatic rings.

Table 8. Molecular plane angles of structure 10 and $\mathbf{1 p}_{\mathbf{p}}$

| Plane |  |  |
| :---: | :--- | :--- |
| A | 58.4 | $\underline{\mathbf{1 0}}$ |
| B | 52.1 | 56.0 |
| C | 58.7 | 53.0 |
| D | 56.4 | 59.8 |
| B C | 62.8 | 55.7 |
|  | 71.5 | 64.2 |
|  |  | 71.1 |

Compared to the mean values for calixarenes with a single organic guest within the cavity there is a slight but noticeable deviation in rings $A$ and $C$ that corresponds to the aromatic rings with para substituents folding into the

Molecular geometry of 10


Molecular geometry of ip


Figure 8. Diagrams of the molecular geometry of structures 10 and 1p

Cavity. Planes $B$ and $D$ appear to maintain a similar angle to other tetrahydroxy compounds.

Introduction of a substituent in the meta position effectively changes the shape of the calixarene cavity. There is one example, $1 u$, of tetrahydroxy calixarene with meta substituents. Table 9 shows a representation of $1 u$ and its associated plane angles.

Table 9. Molecular plane angles of structure $1 \mathbf{u}$


Analysis of the cavity shape of $\mathbf{l u}$ demonstrates that introduction of meta-methyl groups has significantly distorted the conformation of the cone due to steric repulsion between the meta methyl substituent and the adjacent aromatic ring. This compound does not show the presence of a guest within the cavity since the pinching of two of the aromatic rings make inclusion sterically prohibitive.

The presence of the four hydrogen bonding sites on the lower rim of the calixarene directs the "cone" to be the preferred conformation in the solid state. Conformationally
all of these structures have similar cavity geometries with the only major distortion due to intramolecular interaction from meta substituents and intermolecular $\pi$ - stacking. With the exception of the two crystal structures where the upper rim para substituents fold in and block the cavity and calixarenes with meta substituents, all the tetrahydroxy calix[4]arenes show the presence of a guest within the cavity being held by CH - $\pi$ interactions with the aromatic rings.

### 3.3. Trihydroxycalix[4]arenes

Monosubstituted calixarenes have three hydroxyl groups and one ether oxygen on the lower rim. The replacement of one of the phenolic hydrogens with an alkyl substituent significantly reduces the strength of the overall hydrogen bonding network but these interactions still maintains a sizeable effect on the conformation. Although there are no crystal structures of monoalkylated calixarenes, there have been several synthesised in the literature. $281_{H}$ NMR analysis of these compounds shows that the "cone" conformation is observed almost exclusively. Further analysis into the solid state characteristics of this family of calixarenes should be investigated to understand the affect of the breaking one of the hydrogen bonds and the manner in which the calixarene adjusts its conformation upon the introduction of a single ether linkage. Additionally these compounds should also show
host-guest properties similar to the tetrahydroxy calix[4]arenes.
3.4. 1,2-dihydroxycalix[4]arenes

Four of the crystal structures from the CCD search are 1,2-dihydroxy calix[4]arenes. Table 10 shows the generic representation of these four calixarenes. The presence of the two hydroxyl substituents on the lower rim directs the conformation of the calixarene. These two hydroxyl substituents make two hydrogen bonds, one of which is always bonded to the other hydroxyl group which in turn interacts with the adjacent phenolic ether oxygen. This orientation assures that three of the aromatic rings will be syn and the fourth ring may be either syn or anti dependent on the manner in which the calixarene was synthesised. If both the substituted rings are syn the expected conformation is a "cone", but if they are anti the "partial cone" results.

Compounds $2 \mathbf{a}$ and $\mathbf{2 b}$ were synthesised so that the two lower rim substituents are syn. Since the size of these substituents do not allow them to rotate they have a fixed orientation and both crystallise in the "cone" conformation. Figure 9 shows the representation of the solid state structure for these three compounds. Table 11 shows the relevant plane angles for these compounds.

The structure 2a has two inequivalent calixarenes in the assymetric unit. Structure $2 \mathbf{2 a}$ (A) has two hydrogen bonds,
Table 10. General representation of 1,2-dihydroxycalix[4]arenes


Molecular Geometry of $\mathbf{2 b}$


Molecular geometry of the two inequivalent molecules in structure 2a


Figure 9. Molecular geometries for structures $2 a$ and $2 b$
one between the adjacent phenolic oxygen and a second with the ethyl ether oxygen on the lower rim substituent of the adjacent aromatic ring.

Table 11. Molecular plane angles of structure $2 \mathbf{a}$ and $\mathbf{2 b}$

| Plane | 2a (A) | $\mathbf{2 a}(B)$ | $\mathbf{2 b}$ |
| :---: | :---: | :---: | ---: |
| A | 87.5 | 75.6 | 60.5 |
| B | 35.1 | 46.0 | 61.9 |
| C | 78.8 | 60.3 | 68.9 |
| A - C | 40.8 | 51.5 | 53.0 |
| B - D | 13.7 | 54.1 | 50.6 |
|  | 75.8 | 97.5 | 65.0 |

The presence of this unusual hydrogen bonding interaction prevents inclusion of a guest within the cavity of this calixarene. Strucuture 2a (B) has the expected hydrogen bonding network with the hydrogen bonds only between the phenolic oxygens.

The symmetrical arrangement of the four aromatic rings in 2 b and 2 a ( B$)$ provides a cavity for inclusion interactions. $\mathbf{2 b}$ has an ethanol molecule acting as a guest in the cavity and 2a (B) shows an intermolecular interaction with an adjacent calixarene. The inter calixarene inclusion may be seen in the crystal packing in Figure 10.

Compounds 2c and 2d were synthesised so that the two substituted aromatic rings have an anti arrangement with lower rim substituents large enough to prevent conformational interconversion. Due to the anti arrangement of the two


Figure 10. Diagram of the intermolecular inclusion observed in $2 a$
substituted aromatic rings both of these compounds crystallise in "partial cone" conformation. Figure 11 shows the solid state conformation of these two compounds. Table 12 shows the plane angles associated with these two compounds.

Table 12. Molecular plane angles of structure 2c and 2d

| Plane | $\underline{\mathbf{2 c}}$ | $\underline{\mathbf{2 d}}$ |
| :---: | ---: | ---: |
| A | -67.0 | -68.9 |
| B | 73.5 | 73.3 |
| C | 48.8 | 39.2 |
| D - C | 58.0 | 66.4 |
| B - D | 18.7 | 28.9 |
|  | 48.4 | 40.3 |

These two structures have similar conformational characteristics. The aromatic rings that point down make an angle of about 68 degrees with the methylene carbons. Although slightly different, the other three aromatic rings that point up all have similar canting angles. Both of these compounds show self inclusion in the cavity between the three "up" aromatic rings. The lower rim substituent on the single alternate aromatic ring interacts in the cavity. For 2c the ethyl substituent points into the cavity but does not show any strong interactions. Compound 2d shows a similar interaction with the dinitrobenzoyl substituent. This aromatic ring fits further into the cavity than the ethyl on


Molecular geometry of 2d


Figure 11. Molecular geometries for structures 2c and 2d

2c and appears to be held by $\mathrm{CH}-\pi$ interactions with the $t$ butyl substituents.

Of the four crystal structures that are 1,2-dihydroxy, two crystallise in the "cone" and two crystallise in the "partial cone" conformation, directed by the up-down arrangement of the two substituted aromatic rings. The two calixarenes in the "cone" conformation both show intermolecular host guest interactions; the first showing inclusion of a guest ethanol molecule and the second with inter-calixarene inclusion. Both these guests are held by CH - $\pi$ interactions with the aromatic rings of the calixarene. The two calixarenes in the "partial cone" conformation have intramolecular host guest interactions. In both cases the lower rim substituent on the single alternate aromatic ring arranges itself so that it may interact with the cavity. In one case the ethyl substituent simply blocks the cavity. The other inclusion complex has the dinitrobenzoyl substituent held within the ring by $C H-\pi$ interactions with the t-butyl substituents.
3.5. 1,3-dihydroxycalix[4]arenes

The CCD search found nine crystal structures of calix[4]arenes that are 1,3-disubstituted on the lower rim. The general representation of these calixarenes is shown in Table 13. All of these 1,3-disubstituted calixarenes are in
Table 13. General representation of 1.3-dihydroxycalix[4]arenes


the "cone" conformation which is directed by the presence of two hydrogen bonds. The first of these two hydrogen bonds is between the phenolic oxygen and one of the two adjacent ether linkages and the second hydrogen bond occurs between the other phenolic oxygen and the other ether linkage. Since in most cases the hydrogen involved in this bond can not be found on the density map, the only indication of its existence is a short average oxygen-oxygen distance of 2.81 $\AA$. The average distance between the two oxygens that are not hydrogen bonded is $2.99 \AA$ for all nine crystal structures.

For these nine compounds the observed cavity geometry does not appear to be affected by the nature of the substituent on the upper and lower rim but by intermolecular interactions.

Seven of the nine crystal structures, $\mathbf{3 a} \mathbf{-} \mathbf{f}$, do not show the presence of a guest within the cavity or any other unusual intermolecular interaction in the crystal packing. Each of these calixarenes crystallises in a "flattened cone" conformation where two alternate aromatic rings are almost parallel and the second two make a mutual obtuse angle. A diagram of the mean conformation and a list of plane angles for these seven structures is shown in Table 14.

In all cases the two rings which are almost parallel, A and C, are substituted on the lower rim. These lower rim substituents are directed away from the center of the cavity
in a manner that reduces steric interactions. The other two rings $B$ and $D$ are unsubstituted and are flattened.

Table 14. Mean molecular plane angles of structure 3a-f

| Plane | Degrees |
| :---: | ---: |
| A | 78.2 |
| B | 40.3 |
| C | 77.5 |
| D C | 39.0 |
| B - D | 24.3 |
|  | 102.3 |



This "flattened cone" conformation does not provide a sufficient cavity to observe host guest interactions.

There are two examples of a neutral guest molecule interacting in the cavity of a 1,3-dihydroxy calixarene. In the crystal structure of $\mathbf{3 h}$ there are two inequivalent structures in each unit cell. Figure 12 shows a diagram of both of these structures and thier plane angles are listed in Table 15.

Table 15. Molecular plane angies of structure 3 h

| Plane | $\frac{3 h .(A)}{3 h .(B)}$ |  |
| :---: | :---: | :---: |
| A | 62.6 | $\frac{38.1}{58}$ |
| B | 56.5 | 56.7 |
| C | 62.7 | 60.0 |
| A - C | 52.4 | 58.3 |
| B D | 54.7 | 61.9 |

Structurally, 3h has a more open conformation than the other 1,3-aihydroxy relatives. The shape of the cavity is

Molecular Geometries of $\mathbf{3 h}$



Pigure 12. Molecular geometries for structure 3h
more symmetrical and more closely resembles the cavity shape of tetrahydroxy calixarenes. It is however less symmetrically shaped due to the presence of two alkyl substituents on the lower rim that change the hydrogen bonding network and introduce steric repulsion between the two substituents.

The other 1,3-dihydroxy calixarene that has an inclusion complex is $3 i$. In addition to the inclusion of a guest, there is an intermolecular interaction in the crystal packing. The diagram of the crystal packing, conformation of the individual molecule and a list of plane angles is shown in Figure 13. The crystal packing shows that there are two picric acid molecules stacked on the outside of the molecule. This is the only example of a molecule interacting with the exterior of the calixarene cavity. Similar to $\mathbf{3 h}, \mathbf{3 i}$ appears to open its cavity to accomidate the guest molecule.

The observed conformation of 1,3-dihydroxy calix[4] arenes is directed by the presence of two alternating hydrogen bonds and steric repulsion due to the introduction of an alkyl substituent on two of the positions. All nine of these calixarenes are found in a "flattened cone" conformation. Although seven of these nine crystal structures do not have a guest within the cavity, the fact that two do have host-guest properties indicates that these calixarenes are capable of host-guest interactions given the proper conditions.

Crystal packing of 3i


Molecular geometry and plane angles of $3 i$


| Plane |
| :---: |
| $A$ |
| $B$ |
| $C$ |
| D |
| A C |
| $B-D$ |

> | Degrees |
| :---: |
| 66.8 |
| 52.1 |
| 66.8 |
| 52.1 |
| 46.4 |
| 75.8 |

Pigure 13 Crystal packing, molecular geometry and plane angles for structure 3i
3.6. Monohydroxycalix[4]arenes

There are three crystal structures of calixarenes that are trisubstituted on the lower rim. Table 16 shows the general representation of these three compounds.

The conformation of these compounds is directed by the manner in which the calixarene is synthesised. If all three substituted aromatic rings are syn the solid state conformation is found as a "cone". If one of the three substituted rings is anti the "partial cone" conformation is found in the solid state. Two compounds, $4 b$ and $4 c$ are in the "cone" conformation and $\mathbf{4 a}$ is in the "partial cone" conformation. A diagram of the solid state structure of $\mathbf{4 b}$ and 4c are shown in Figure 14. Table 17 shows the plane angles of the aromatic rings in this conformation.

Table 17. Molecular plane angles of structure $\mathbf{4 b}$ and $4 \mathbf{c}$

| Plane | $\underline{4 b}$ |  |
| :---: | ---: | ---: |
| A | 49.0 | 43.6 |
| B | 98.5 | 81.1 |
| C | 27.9 | 45.7 |
| D | 85.2 | 87.4 |
| B - D | 103.1 | 90.7 |
|  | -4.1 | 11.5 |

Both of these compounds crystallise in a "pinched cone" conformation where two of the alternating rings are almost parallel and the other two rings are almost normal. The three lower rim alkyl substituents arrange themselves so that
Table 16. General Representation of monohydroxycalix[4]arenes


## Molecular Geometry of $\mathbf{4} \mathbf{b}$



Molecular Geometry of $\mathbf{4 c}$


Figure 14. Molecular geometries for structures $\mathbf{4 b}$ and $4 c$
they point away from the cavity of the calixarene in order to reduce steric interactions. The crystal packing of these two compounds shows no unusual intermolecular interactions and much like theix other "pinched cone" relatives there are no host guest interactions. Both $\mathbf{4 b}$ and $\mathbf{4 c}$ have a single hydrogen bond occurring between the phenolic oxygen and one of the adjacent ether oxygens.

Structure 4c has a more symmetrical cavity shape than 4b. The "parallel" rings in 4c both fold away from the cavity making an interplanar angle of 11.5 degrees. The other two aromatic rings, phenol and methyl ether, make an interplanar angle of 90.7 degrees. In compound $\mathbf{4 b}$ the "parallel" rings are asymmetric with one ring bent in toward the cavity at 98.5 degrees and the second ring bent away from the cavity at 85.2 degrees with respect to the methylene carbons. The interplanar angle between these two rings is -4.1 degrees that indicates that the para positions fold over to cover the cavity. The other two aromatic rings, phenol and methyl pyridine ether, fold out making an interplanar angle of 103.1 degrees. Although there are no solid indications as to the preference for symmetric and asymmetric conformations, it is probably related to the nature of the lower rim substituents.

There is one structure, 4a, of a calixarene, trisubstitued on the lower rim that is in a "partial cone"
conformation. Table 18 shows a diagram of the solid state structure as well as the plane angles of the aromatic rings.

Table 18. Molecular plane angles of structure 4 a

| Rlane | qa |
| :---: | ---: |
| A | -70.3 |
| B | 70.3 |
| C | 39.3 |
| A -C | 77.7 |
| B - D | 70.4 |
|  | 32.0 |



The phenolic unit and its two ac, weac aromatic rings, which are substituted with dinitrobenzoyl groups, are pointed down. The fourth aromatic ring is oriented with the lower rim substituent pointing up. The presence of a hydrogen bond between the phenolic unit and the adjacent ether oxygen, indicated by the short oxygen-oxygen distance of $2.87 \AA$, prevents rotation about the methylene bridge to form a "1,3alternate" conformation. The crystal packing shows no unusual intermolecular interactions.

The three "up" rings make angles with the methylene carbons of $70.3,39.3$ and 77.7 degrees. This orientation of these rings forms a cavity that allows a intramolecular hostguest interaction with the lower rim substituent of the "down" aromatic ring. This ring lies at an angle of -70.3 degrees. The dinitrobenzoyl substituent lies in the cavity
of the calixarene held by $\mathrm{CH}-\pi$ interactions with the para-t-butyl substituents.

The conformation of the monohydroxy calix[4]arenes is determined by the up-down arrangement of the substituted aromatic rings. Two of the calixarenes have the substituted aromatic rings all arranged syn and are found in a pinched cone" conformation. The third calixarene has one substituted aromatic ring anti which produces a "partial cone" conformation. Neither of the two calixarenes in the "pinched cone" conformation have host guest interactions which is not unusual due to the close interactions between the two upright aromatic rings. The calixarene in the "partial cone" conformation shows intramolecular host-guest interactions with the lower rim substituent on the single anti aromatic ring. The dinitrobenzoyl substituent is held in the cavity by CH - $\pi$ interactions with the upper rim t-butyl substituents.

SOLID STATE CONFORMATION OF CALIX[4]ARENES WITHOUT INTRAMOLECULAR HYDROGEN BONDING

### 4.1. Introduction

There are 39 crystal structures of calixarenes which do not show the presence of intramolecular hydrogen bonding interactions. These crystal structures may be partitioned into five different categories that are dependent on the size of the lower rim substituents, and the conformation in which the calixarene is synthesised. When the lower rim substituents are smaller than ethyl, calixarenes are conformationally mobile and may be found in any of the four conformations ("cone", "partial cone", "1,2-alternate", "1,3alternate"). When the lower rim substituents are ethyl or larger, the conformation of the calixarene may be thought of as "frozen" with no conformational mobility. These crystal structures are categorized into the four conformations dependent on the manner in which the calixarene was synthesised. Although the gross geometry is defined by the conformation, the "fine" geometry is directed by a series of complicated inter and intramolecular interactions.

### 4.2. Tetraalkylated Calix[4]arenes in the "Cone" Conformation

The CCD search resulted in twenty-one crystal structures of calix[4]arenes which are tetrasubstituted and frozen in the "cone" conformation. Table 19 shows the general representation of these compounds. The crystal packing of these calixarenes show no unusual intermolecular interactions, therefore the conformation of these compounds is directed by intermolecular effects from both the upper and lower rim substituents.

Seventeen, 5a-q, of the twenty-one compounds have a t-butyl substituent in the para position and do not form host-guest complexes. All of these crystal structures may be thought of as "pinched cone" conformations with two of the aromatic rings being "normal" and the other two rings essentially "parallel". There are two subdivisions that are observed in these compounds due to the orientation of the two "parallel" rings. Ten, 5a - $\mathbf{h}$, of the seventeen crystal structures may be described as symmetric, where the two parallel rings both fold slightly away from the center of the cavity. There are seven structures, 5i-q, that are asymmetric where one ring folds slightly into the cavity (angle $>90$ degrees) and the other folds slightly away from the cavity. The mean angles for these structures are shown in Table 20 with a descriptive diagram for the symmetric and asymmetric crystallization patterns.


## Symmetric



Asymmetric


Table 20. Descriptive plane angles for symetric and assymetric "cone" conformations

For both symmetric and asymnetric structures the lower rim substituents arrange themselves to reduce steric interactions, and these appear to have no effect on the geometry of the cavity. The lower rim substituents attached to the "parallel" rings point out away from the cavity, and the group attached to the "normal" rings point down under the cavity. There is no obvious preference for symmetric versus the assymetric conformations.

There are three calixarenes that have para substitutents that are sterically smaller than t-butyl, 5r, 5t and 5u. A comparison of the crystal structures of $5 \boldsymbol{r}$ and $5 q$ shows that, without a sterically large para substituent, the two "parallel" rings fold in over the cavity. 5q has p-t-butyl and $5 x$ has a p-hydrogen and both calixarenes have the same lower rim substituents: methyl pyridines. The crystal structures of these two compounds are shown in Figure 15. The plane angles are listed in Table 21.

Table 21. Molecular plane angles for structures 5 q and $\mathbf{5 r}$

| Plane | $5 q$ <br> Degrees | $\mathbf{5 r}$ <br> A |
| :---: | :---: | :---: |
| B | 90.0 | 101.1 |
| C | 51.8 | 26.5 |
| D | 81.3 | 99.7 |
| B C D | 52.6 | 40.3 |
|  | 8.7 | -16.0 |
|  | 75.6 | 113.2 |

Molecular Geometry of $5 \mathbf{x}$


Molecular Geometry of 5q


Figure 15. Molecular geometries for structures $\mathbf{5 r}$ and $\mathbf{5 q}$

In the p-t-butyl calixarene, 5q, the two "parallel" rings are arranged in an asymmetric fashion with one ring at greater than 90 degrees and the other ring bent away from the center of the cavity. The interplanar angle ( 8.7 degrees) of these two rings indicates that the rings fold away from the center of the cavity. Without this sterically large t-butyl substituent, in $5 x$, both aromatic rings fold into the cavity (interplanar angle of -16.0 degrees) so that the two phenolic oxygens are bent out.

The conformational characteristics of $5 x$ are also observed in the two other crystal structures of calixarenes with para substituents smaller than t-butyl. The mean geometry of these three compounds $5 x, 5 t$, and $5 u$ is shown in Table 22.

Table 22. Mean conformation of calixarenes with small para substituents

| Plane |  |
| :---: | ---: |
| A | Degrees |
| B | 100.4 |
| C | 30.9 |
| D | 99.7 |
| A C | 37.8 |
| B D | -20.2 |
|  | 111.2 |



In all four cases the two "parallel" rings fold into the cavity as observed in $5 \mathbf{r}$. The presence of meta substituents in $5 \mathbf{u}$ shows no effect on the preferred conformation. None of
these three crystal structures show the presence of a guest within the cavity.

There is one example of a tetrasubstitued calix[4]arene that shows host-guest behavior. Table 23 shows the molecular geometry and plane angles for structure $5 s$ with its $1: 1$ acetonitrile clathrate.

Table 23. Molecular plane angles for structure 58

| Plane | Degrees |
| :---: | :---: |
| A | 65.4 |
| B | 65.4 |
| C | 65.4 |
| D - C | 65.4 |
| B - D | 49.2 |
|  | 49.2 |



Unlike other tetrasubstituted calixarenes this compound shows $C_{4 v}$ symmetry. The aromatic rings are all canted at 65.4 degrees with an interplanar angle of 49.2 degrees. These canting angles show that the calixarene cavity adopts a more open shape than the other tetrasubstitued calixarenes, and most closely resembles the shape of the tetrahydroxy compounds that have an average canting angle of 55.1 degrees and an interplanar angle of 69.5 degrees. The interplanar angle for this tetrasubstituted calixarene is about 20 degrees smaller which can be rationalised by the increase in steric repulsion from the presence of lower rim ether linkages.

Iwenty of the twenty-one crystal structures that are tetrasubstituted crystallise in a "pinched cone" conformation. The calixarenes that have para t-butyl substituents on the upper rim either crystallise with both "pinched" rings bent out or one bent in and the other bent out. Sterically small para substituents allow the "pinched" rings fold into the cavity. There is only one crystal. structure, 5s, that has host guest interactions. Due to the small cavity formed in this complex, one may presume that only sterically small guests, such as acetonitrile, may be held within the cavity of these calixarenes.
4.3. Tetraalkylated Calix[4]arenes with Small

Lower Rim Substituents
Unlike the other tetrasubstituted calixarenes that are synthesised in a single conformation, these calixarenes posses lower rim substituents which are small enough to rotate though the cavity. This rotation allows the calixarene to adopt of any of the four standard conformations ("cone", "partial cone", "1,2-alternate", and "1,3alternate"). There are eight crystal structures that are tetrasubstituted and allow this freedom of rotation. The general representation of these compounds is shown in Table 24. Of these eight crystal structures, seven, $\mathbf{6 a}-\mathbf{g}$, crystallise in a "partial cone" and one, 6 h , in the "cone" conformation.
rim substitutents



These seven calixarenes that crystallise in the "partial cone" conformation all have similar geometries. A diagram of the mean geometry of these compounds and their mean plane angles are shown in Table 25.

Table 25. Mean conformation for "partial cone" structures

| Plane | Degrees |
| :---: | :---: |
| A | -90.4 |
| B | 90.6 |
| C | 30.6 |
| D | 92.2 |
| $\mathrm{~A}-\mathrm{C}$ | 8.5 |
| $\mathrm{~B}-\mathrm{D}$ | 59.8 |

As seen in Table 25, one aromatic ring is pointed down at -90.4 degrees. The two aromatic rings next to the ring pointing down make angles of 90.6 and 92.2 degrees with an interplanar angle of 8.5 degrees that means that these two planes bend in over the cavity. The fourth aromatic ring that is alternate to the one facing down lies at a mean angle of about 30.6 degrees. The crystal packing of these compounds shows no unusual intermolecular interaction.

The "partial cone" conformation provides a shelf for a guest to interact with the cavity of the calixarene but inclusion of a guest molecule is only observed in structure 6d. In 6d there is a chloroform guest residing in the cavity of the calixarene that is being held by $\mathrm{CH}-\pi$ interactions. The lack of guest molecules in the other six structures is
due to steric affects from the two alternate aromatic rings pinching over the cavity and the lower rim substituent of the aromatic ring pointing down effectively blocking the cavity.

The steric size of the para substituents appears to have no effect on the observed conformation of these structures. Structures $6 \mathbf{a}$ and $\mathbf{6 b}$ both have $t$-butyl groups in the para position and compound 6d has a sterically smaller bromine in the para position but there is no significant difference in the conformation of these two compounds.

The crystal structure of p-phenylcalix[4]arene
tetramethyl ether, $\mathbf{6 h}$, crystallises in a "pinched cone" conformation. It has been reported that this compound exists in the "partial cone" conformation in solution during room temperature NMR analysis which indicates that there was a change in conformation during crystallization. Figure 16 shows the conformation of a single molecule, plane angles and the crystal packing diagram for $\mathbf{6 h}$.

This crystal structure shows that two of the aromatic rings are bent in over the cavity at an angle of 95.8 degrees for both rings with an interplanar angle of -11.5 . The ipso carbons on the para phenyl substituents are $4.2 \AA$ apart which is indicative of $\pi-\pi$ interactions. The nature of this $\pi-$ $\pi$ interaction precludes this compound from acting as a host and no guests are observed in the cavity. The other two aromatic rings make an angle of 40.1 degrees with the mean plane of the methylene carbons. This cavity is similar to


Molecular geometry of $\mathbf{6 g}$


Figure 16. Crystal packing and molecular geometry for $6 \boldsymbol{g}$
that observed with tetrasubstituted calixarenes with small para substitutents. Although phenyl would not be classified as a small substituent, the presence of the $\pi-\pi$ interactions emulate the effect. Analysis of the crystal packing of this compound (Figure 16) shows the presence of intermolecular $\pi-\pi$ interactions between the p-phenyl rings. These $\pi$ - $\pi$ interactions may account for the preference of this compound crystallising in the "cone" conformation over the more commonly observed "partial cone" conformation.

The observed preference for calixarenes with small lower rim substituents to crystallise in a "partial cone" indicates that this conformation is the most energetically favorable, which has been substantitated by molecular orbital calculations. 52 Similar to other calixarenes in the "partial cone" conformation, these calixarenes provide a cavity for the inclusion of a guest. In all but one structure the guest interaction is precluded by the presence of the lower rim substituent on the anti ring blocking the cavity. In the single structure, 6d, with a guest, the chloroform is held in the cavity by $\mathrm{CH}-\pi$ interactions.
4.4. Tetraalkylated Calix[4]arenes in the
"Partial Cone" Conformation
Four of the compounds, 7a - d, from the CCD search are frozen in the "partial cone" conformation. The general representation of these compounds is shown in Table 26. Each of these structures are conformationally frozen due to large lower rim substituents. The crystal packing diagrams of these four structures shows no unusual intermolecular interactions. These four structures indicate that the only significant deviation in the geometry of the calixarene is due to inclusion complexes within the cavity.

The crystal structures of $\mathbf{7 a}$ and $\mathbf{7 d}$ show no inclusion properties. 7a has acetyl substituents on the lower rim and t-butyl groups on the upper rim. The crystal structure of 7d has methyl pyridine substituents on the lower rim and hydrogen on the upper rim. Figure 17 shows the structure of 7a and 7d in the solid state. The plane angles for these two structures are shown in Table 27.

Table 27. Molecular plane angles for structure 7a and 7d

| Plane | $7 \mathbf{a}$ <br> Degrees | $7 \mathbf{d}$ <br> A |
| :---: | :---: | :---: |
| B | -78.6 | -86.3 |
| C | 86.8 | 90.7 |
| D | 39.3 | 44.0 |
| A - | 82.3 | 88.1 |
| B - D | 39.4 | 42.3 |
|  | 11.0 | 1.2 |

0
0
0
0
0

Molecular geometry of 7a


Molecular geometry of 7a


Figure 17. Molecular geometries for structures 7a and 7d

Comparison of these two structures with the mean conformation of the seven "partial cone" structures with small lower rim substituents shows that there is only a slight deviation between the two preferred conformations. The lower rim substituents all arrange themselves so that they point away from the cavity of the calixarene and minimize steric interaction.

The crystal structures of 7 b and 7 c both show inclusion properties in the cavity. Figure 18 shows the structure of $\mathbf{7 b}$ and $\mathbf{7 c}$ in the solid state. The plane angles for these two structures are shown in Table 28.

Table 28. Molecular plane angles for structure $\mathbf{7 b}$ and $\mathbf{7 c}$

| Plane | 7b <br> Degrees | $\mathbf{7 c}$ <br> A |
| :---: | :---: | :---: |
| B | -59.5 | -75.3 |
| C | 72.0 | 67.2 |
| D | 61.9 | 53.2 |
| A C | 41.5 | 77.2 |
| B - D | 2.7 | 22.4 |
|  |  | 35.8 |

Structure 7 c is selectively substituted so that there is an ethyl ester substituent on rings $A$ and $C$, and methyl pyridine groups on rings $B$ and $D$. These lower rim substituents arrange themselves as to reduce steric interactions and do not appear to have an effect on the conformation of the calixarene. There is an acetonitrile

Molecular geometry of $\mathbf{7 b}$


Molecular geometry of 7c


Figure 18. Molecular geometries for structures 7 b and 7c
guest held within the cavity oriented so that the methyl group interacts with the aromatic rings of the calixarene. The presence of this guest in the cavity makes the aromatic rings fold out. This folding out was also observed with the tetrasubstituted $5 s$ that adopts a "cone" conformation with an acetonitrile guest.

The structure of $\mathbf{7 b}$ has methyl pyridine substituents on the lower rim and t-butyl groups on the upper rim. This compound shows self inclusion of the methyl pyridine attached to ring A that should account for the apparent deformation of the calixarene geometry. This inclusion complex is held together via CH - $\pi$ interactions between the methyl pyridine group and the methyls of the t-butyl substituents. Comparison of this structure with 7d, its de-butylated analog, shows that the presence of $t$-butyl substituents is necessary for this self inclusion interaction

The observed cavity of these four calixarenes appears to be dependent on the presence of a guest within the cavity. The calixarenes without guest molecules have a closed conformation with two of the opposite aromatic rings almost parallel. Upon introduction of a guest molecule in the cavity, these two aromatic rings fold out further to accommodate its presence. The comparison of $\mathbf{7 b}$ and $\mathbf{7 d}$ implies that the p-t-butyl substituents are necessary for the formation of a host guest complex with an aromatic guest.
4.5. Tetralkylated Calix[4]arenes in the
"1,2-Alternate" Conformation
One of the crystal structures from the CCD search was tetralkylated and in the "1,2-alternate" conformation. Compound 8a was synthesised in the "1,2-alternate" conformation and is held immobile by ethyl substituents which are sufficiently large as to prevent freedom of rotation. ${ }^{19}$ Figure 19 shows a diagram of the crystal structure, plane angles and a general representation of the molecule of $\mathbf{8 a}$. The two adjacent aromatic rings are syn making an angle with the methylene bridges of 83.8 and 47.8 degrees. The other two adjacent aromatic rings are also syn. These two point down making a -83.8 and -47.8 degree angle with the methylene bridges. Analysis of the crystal packing of this compound shows no intermolecular interaction. There is a cavity present but no guest is observed due to the ethyl substitutents which point into the cavity creating a selfinclusion interaction.

There is a second crystal structure of a tetrasubstituted calixarene in the "1,2-alternate" conformation that is not included in the CCD. This structure, 8b, has four butanoate substituents on the lower rim and is unfunctionalized on the upper rim. 82 Although complete data is not available for this structure, the information that is available indicates that these two structures share similar conformational properties. The two

General Representation and table of plane angles for structure 8a


Molecular geometry of $8 a$


Pigure 19. General representation, table of plane angles,
and molecular geometry of $8 \mathbf{a}$
adjacent aromatic rings make angles with the methylene carbons of 48.5 and 81.0 degrees. The other two aromatic rings are pointed down related by a plane of symmetry making angles of -48.5 and 81.0 degrees. In this complex, the lower rim substituents also block the cavity preventing the formation of an inclusion complex.

Both structures are monoclinic four asymmetric units in the unit cell. The unit cell for $\mathbf{8 a}$ is larger than $\mathbf{8 b}$ due to the presence of para-t-butyl substituents. Both $\mathbf{8 a}$ and $\mathbf{8 b}$ show the presence of a cavity that may show host-guest properties. Further investigation into the crystallisation patterns the "1,2-alternate" conformation seems warranted.
4.6. Tetraalkylated Calix[4]arenes in the
"1,3-Alternate" Conformation
There are five crystal structures from the CCD that are tetrasubstituted and adopt the "1,3-alternate" conformation. The general representations of these compounds with the various substitutents are shown in Table 29 . In the crystal packing none of these five structures show any unusual intermolecular interactions. The cavity shape of calixarenes in the "1,3-alternate" conformation appears to be dependent on the steric size of the upper and lower rim substituents.

Compound 9b has sterically small upper and lower rim substituents. A diagram of the calixarene conformation and descriptive plane angles is shown below in Table 30. Compound

$$
\begin{aligned}
& \text { Table 29. General representation of tetralkylated calix[4]arenes in the "1,3- } \\
& \text { alternate" conformation }
\end{aligned}
$$


$9 b$ is unsubstituted on the upper rim and the lower rim is tetrasubstituted by an ethyl-ethyl ether substituent.

Table 30. Molecular plane angles for structure $9 \mathbf{~ b}$


The lower rim substituents are arranged so that the methylene carbon points away from the cavity but the substituent itself shows an interaction within the cavity. Due to the sterically small nature of these upper and lower rim substituents, the four aromatic rings of the calixarene fold in over the cavity effectively covering it.

Structurally the cavity shapes of 9a, 9c, 9d and 9e are similar. Diagrams of the structures of these four compounds are shown in Figure 20. Table 31 lists the descriptive plane angles for these four structures. All four of these structures posses substituents on the upper and lower rim that may be considered sterically large. In each case the lower rim substituents drape down and fill the void under the cavity. These substituents do not have any unusual intramolecular interactions but their steric size appears to be sufficiently large to alter the shape of the cavity so

9a


9d


9c

$9 e$


Figure 20. Molecular geometries of 9a, 9c, 9d, 9e
that the folding in of the aromatic rings as seen in $\mathbf{9 b}$ is not observed. It is unclear whether the upper rim

Table 31. Molecular plane angles for structure 9a, 9c, 9d,
and 9e

| Plane | 9a | 9 c | 9d | 9 e |
| :---: | :---: | :---: | :---: | :---: |
| A | 78.7 | 83.0 | 86.9 | 86.9 |
| B | -81.5 | -87.3 | 79.6 | -85.7 |
| C | 72.6 | 83.0 | 78.6 | 83.0 |
| D | -77.0 | -87.3 | -73.9 | 83.0 -86.9 |
| A - C | 28.0 | 14.0 | 26.6 | 9.0 |
| B - D | 21.5 | 5.3 | 15.1 | 8.3 |

substituents directly affect the observed conformation but only in their absence may the aromatic rings fold in over the cavity.

None of the calixarenes that crystallise in the "1,3alternate" conformation show the ability to have host-guest interactions. The arrangement of the aromatic rings so that the two opposing rings are parallel precludes a guest formation. Unlike related "pinched cone" calixarenes which may distort to accommodate a guest, the calixarenes in the "1,3-alternate" conformation do not show this flexibility. The cavity shape of these calixarenes appears to be dependent on a combination of the steric size of the upper and lower rim substituents but no conclusions of this sort may be made given the limited data set.

### 4.7. Conclusions

Of the 76 crystal structures of calix[4]arenes analysed in this survey, fifty-six were "cone", fourteen in the "partial cone", one in the "1,2-alternate", and five in the "1,3-alternate" conformation. Although the preference for these four different conformations is determined by their synthetic design, the molecular recognition properties appear to be a function of their conformation. Only compounds that are found in the "cone" and "partial cone" conformation have shown inclusion properties. The "1,2-alternate" conformation shows the presence of a cavity but no host-guest complexes have been found to date. The "1,3-alternate" conformation does not appear to be capable of host-guest interaction since there does not appear to be a cavity present in this conformation.

Calixarenes in the "cone" conformation most readily accept guests within its cavity. Of the fifty-six calixarenes in the "cone" conformation, twenty-three calixarenes show host guest interaction with small organic guest molecules, or intex-calixarene inclusion complexes. Although the nature of the upper and lower rim affects the preferred geometry in the solid state, the shape of calixarene cavity appears to be dependent on whether or not the calixarene has a host-guest interaction. In all cases where there is a guest present the aromatic rings are folded
further out to accormodate for its presence. In the absence of a guest the aromatic rings appear to be more closed.

The same host guest relationship is apparent for calixarenes in the partial cone conformation. Although calixarenes in the "partial cone" conformation are apt to self-inclusion of the lower rim substituent from the single anti aromatic ring, inclusion of small organic molecules is also observed. In cases where there is a guest present in the cavity, the three aromatic rings fold out to accommodate its presence. Alternately, without a guest present the three aromatic rings are more closed.

All guests present in these seventy-six crystal structures are held in place by $\mathrm{CH}-\pi$ interactions between the guests and the aromatic rings of the calixarene. In the cases where the guest has $\pi$ orbitals and the host has alkyl substituents on the upper rim, interaction between the calixarene alkyls substitutents and the $\pi$ orbitals of the guest are also observed.

There are indications that all calixarenes in the "cone" and "partial cone" conformations are capable of host guest interaction. The fact that in all cases where there is a guest present, the cavity opens up to accommodate the guest indicates that other host-guest complexes may be observed given proper crystallisation conditions.

### 5.1. Introduction

The solid state structures of four new calixarene compounds have been determined. The generic diagrams of these four compounds are shown in Figure 21.

Figure 21. General representation of structures I, II, III, IV.



There are two 1,3-dihydroxycalixarenes that adopt the "cone" conformation(I and II), one tetrasubstituted "cone" (III), and one calixarene in the "1,3-alternate" conformation (IV). All four of these compounds were synthesised by Dusan Hesek in Paul Beer's research group at Oxford University. Specifically these compounds are intermediates in the synthesis of calix[4]arene derivatives for use in anion extraction from aqueous media.

### 5.2. Structure $\mathbf{I}$

Crystals of. compound I were obtained from a saturated solution in chloroform. The solution was in a sealed container that was placed in a water bath with a temperature of $65^{\circ} \mathrm{C}$. Over a period of two months the bath temperature was lowered to room temperature and clear colorless crystals with block morphology were obtained. Due to the solvent dependent nature of these crystals they were analysed at -60 ${ }^{\circ} \mathrm{C}$ mounted on a glass fiber and held in position with Paratone-N. Data collection was carried out as described in the experimental section.

After collection of the diffraction data, the structure was solved with the use of SHELXS-86. Information regarding the collection and processing for structure $I$ is shown in Table 32. The crystals were found to be monoclinic and in the space group P21/c. There are four calixarenes in the unit

Table 32 - X-Ray Crystallographic Collection and Processing Data for Structure I

Structure I
Crystal System
Monociinic
Space Group $\mathrm{P} 2_{1} / \mathrm{C}$
-
Cell Constants
a, $\AA$
b. $\AA$
$29.373 \quad(2)$
c. $\AA$
9.647 (1)
18.328 (2)
b
V. $A^{3}$
mol formula
fw
formular units per cell (Z)
$29.373(2)$
$9.647(1)$
$18.328(2)$
$106.428(8)$
$4981.4 \quad(7)$
$\mathrm{C}_{48} \mathrm{H}_{44} \mathrm{Cl}_{6} \mathrm{~N}_{2} \mathrm{O}_{10} \mathrm{~S}_{2}$
1085.74
4
1.448
6340
3000
0.0491
0.0498
0.94
$[0.04$
$\mathrm{F}^{2}+(\mathrm{s} \mathrm{F})^{2} \mathrm{~J}-1$
cell with two molecules of chloroform per calixarene. No disorder was found within the lattice. All atoms with the exception of the carbons of the calixarene framework were refined with anisotropic thermal parameters. The hydrogens attached to the phenolic oxygens were found from an electron density difference map and all other hydrogen atoms were calculated in most probable positions. This refinement resulted in a final $R$ value of 0.0491 .

The structure of the individual molecule is shown in Figures 22 and 23. Information regarding the bond lengths, bond angles, and torsion angles associated with structure $I$ may be found in Appendix B. Comparison of these bond lengths and angles with other 1,3-dihydroxycalix[4]arene show no unusual deviations. This calixarene is another example of a 1,3-dihydroxycalix[4]arene which crystallises in a "flattened cone" conformation where two of the aromatic rings are almost parallel and the other two form an obtuse angle. The preference for the "cone" conformation is directed by the presence of two hydrogen bonds between the two phenolic oxygens. The hydrogens on the two phenolic oxygens were located from the difference map. The hydrogen bonds occur between 01b - O1c and 01d - O1a which is reflected by their short oxygen-oxygen distances of 2.88 and $\dot{2} .94 \AA$ respectively. The distances between the two non-hydrogen bonded oxygens is 3.21 for 01a - 01b and 3.13 for 01c - 01d. Although these differences in oxygen-oxygen distances are not


Figure 22 ORTEP diagram of structure $I$ with thermal ellipsoids drawn at 50\% probability level. H atoms are omitted for clarity. (side view)


Figure 23 ORTEP diagram of structure $I$ with thermal ellipsoids drawn at 50 of probability level. H atoms are omitted for clarity. (top view)
very large, they do indicate that two of the distances are due to stronger interactions. These oxygen-oxygen distances correspond well with other 1,3-dihydroxycalix[4]arenes.

The cavity shape of $I$ is defined by the angles between each of the four aromatic rings and the mean plane of the methylene carbons as well as the interplanar angle between the two opposite aromatic rings. The relevant angles of the aromatic rings of structure $\mathbf{I}$ and the mean values for other 1,3-dihydroxycalix[4]arenes are shown in Table 33.

Table 33. Molecular plane angles of structure $\mathbf{I}$ and mean plane angles for similar 1,3-aihydroxycalix[4]arenes
Plane
$\frac{a}{b}$
$c$
$d$
$a-c$
$b-d$

Structure I
80.3 (2)
42.1 (2)
81.2 (2)
40.1 (2)
19.4 (3)
97.8 (2)
mean
78.2
40.3
77.5
39.0
24.3
102.3

The plane angles of the calixarene cavity are very similar to the mean plane angles of other 1,3-dihyrdroxy calix[4]arenes. The two "parallel" aromatic rings make an interplanar angle of $19.41(3)$ (24.3 mean value) degrees and the two "flattened" rings make an interplanar angle of 97.84(2) degrees (102.3 mean value). The two tosylate substituents on the lower rim point away from the cavity. As seen in Figure 23 (the top view of the calixarene molecule),
the tosylates appear to twist around in a counter clockwise direction.

The crystal packing of $I$ is directed by series of intermolecular hydrogen bonds and $\pi$-stacking between adjacent calixarene molecules. Figure 24 shows a projection of the crystal packing looking down the C axis. The calixarenes are oriented so that they are in an "up-down" arrangement with the aromatic ring $b$ stacking on top of aromatic ring $d$ of $a n$ adjacent calixarene $(x, y, z) \rightarrow(x, 3 / 2-y, z-1 / 2)$. The atoms in these two rings show close interactions ranging between 3.34 to $3.57 \AA$. A strong hydrogen bonding interaction occurs between $N 4 b$ and 041 d related by the transformation of $(x, y, z)$ -> ( $x, 5 / 2-y, z+1 / 2$ ).

The "up-down" relationship of these calixarenes in the crystal packing creates long threads of molecular calixarenes which extend the length of the crystal. Figure 25 shows a diagram of the unit cell projected down the $b$ axis. There are four calixarenes and eight molecules of chloroform in the cell. This packing diagram shows a series of layers. The top layer has two chloroform molecules followed by two calixarenes in the next layer, then another layer of chloroform. This layering effect of calixarene: solvent: calixarene is very common to the crystal packing of calixarenes in general. These unique clathrate interactions were first observed by Atwood in a series of papers regarding the the crystal structures of a series of calix[4]arene


Figure 24 A diagram of the crystal packing of structure $I$


Figure 25 A diagram of the unit cell of structure $I$
sulfonate salts where the calixarenes form layers which are separated by a sheet of water molecules. 86 This layering affect may also be seen looking down the a-axis.

### 5.3. Structure II

Crystals of compound II were grown from a saturated solution in THF by slow evaporation of the mother liquor at $10^{\circ} \mathrm{C}$. Clear colorless crystals were obtained. These crystals were solvent dependent, quickly decomposing when left in the open air. The crystals were mounted in a capillary tube with the addition of a small amount of mother liquor prior to sealing the capillary. Data were collected as described in the experimental section.

After collection of the diffraction data, the structure was solved using SHELXS-86. The crystals were found to be monoclinic in the $\mathrm{P} 21 / \mathrm{n}$ space group. Information regarding the collection and processing of the data for structure II is given in Table 34. There are four calixarene molecules in the unit cell with 2 molecules of THF per calixarene. The solvent molecules in the lattice were disordered and their absolute positions were difficult to identify. Hydrogen atoms were generated and also found on the difference map. The hetero atoms and methyl groups were turned anisotropic prior to the final refinement which resulted in an $R$ value of 0.0698.

Table 34 - X-Ray Crystallographic Collection and Processing Data for Structure II

## Structure II

Crystal System
Space Group
Cell Constants
a, A
b, $\AA$
c. $\AA$
b
$\mathrm{V}, \mathrm{A}^{3}$
mol formula
fw
formular units per cell (Z)
r. $g \mathrm{~cm}-3$
total data collected
Independent data $I>3 \mathrm{~s}(\mathrm{I})$
R
-
$\mathrm{R}_{\mathrm{W}}$
GOF
wieghts

Monoclinic
P2 $1_{1}$ n
11.7184 (8)
15.023 (1)
27.687 (3)
$99.333(7)$
4809.6 (7)
$\mathrm{C}_{50} \mathrm{H}_{56} \mathrm{~N}_{2} \mathrm{O}_{14} \mathrm{~S}_{2}$
967.09

4
1.335

6159
2994
0.0698
0.0701
1.39
$\left[0.04 F^{2}+(S F)^{2}\right]^{-1}$

The structure of the individual calixarene molecule resembles other 1,3-dihydroxycalix[4]arenes. Tables of bond lengths, bond angles, and torsion angles are shown in Appendix C. These distances and angles correlate well with other 1,3-dihydroxycalix[4]arenes. Figure 26 shows the geometry of a single calixarene molecule in this structure. Table 35 shows the relevant plane angles of structure II and the mean values for other 1,3-dihydroxycalix[4]arenes.

Table 35. Molecular plane angles of structure II and mean plane angles for similax 1,3-dihydroxycalix[4]arenes

| Plane | Structure IT |  |
| :---: | :---: | :---: |
| a | 81.2 (2) | $\frac{\text { mean }}{78.2}$ |
| b | 31.7 (3) | 40.3 |
| c | 78.7 (2) | 77.5 |
| ${ }_{\text {a }}^{\text {d }}$ - | 32.2 (4) | 39.0 |
| a-c $b-d$ | 20.1 (6) | 24.3 |
| b-d | 116.0 (3) | 102.3 |

The plane angles of the two parallel rings are slightly deviated from the mean conformation of other 1,3-dihydroxycalix[4]arenes. The two "flattened" rings are bent out further making an angle of $116.0(3)$ degree angle compared to the mean value of 102.3 degrees usually observed for these calixarenes. The other two "upright" rings are reasonably similar to the mean.

This deviation in the plane angles of the two "flattened" rings is due to an intermolecular hydrogen bonding interaction of the phenolic oxygens with one of the


Figure 26 ORTEP diagram of structure II with thermal ellipsoids drawn at 50 o probability level. $H$ atoms are omitted for clarity.

THF molecules. The normal arrangement of the hydrogen bonding network which involves two hydrogen bonds between the phenolic oxygens and the oxygens of the ether linkages is not present in this structure. In structure II there is one intramolecular hydrogen bond which occurs across the bottom of the cavity between 01d to 01b (2.91 A). The second phenolic oxygen, 01b, has an intermolecular hydrogen bond to oxygen of a THF molecule which resides under the cavity of the calixarene with an oxygen-oxygen distance of $2.77 \AA$ as shown in Figure 27. This is the only example of a 1,3dihydroxycalix[4]arene which prefers an intermolecular over an intramolecular hydrogen bond. Due to the presence of this intramolecular hydrogen bond across the cavity, the two phenolic rings may fold further into the ring, as demostrated by the increased dihedral angle between planes $b$ and $d$.

The two lower rim tosylate substituents arrange themselves under the cavity as to minimize steric interactions. The presence of the THF under the cavity appears to have no significant affect on the arrangement of these substituents. One of the tosylates is directed so that it points down and the other tosylate sticks out away from the cavity.

The crystal packing in the unit cell is shown in Figure 28. The unit cell contains four calixarene molecules and eight molecules of THF. Although the packing arrangement of the individual calixarene molecules is different from that


Figure 27 ORTEP diagram of structure II with thermal ellipsoids drawn at $50 \%$ probability level. H atoms are omitted for clarity. Hydrogen bonding interaction between the O1b and the THF molecule.


Figure 28 A diagram of the unit cell for structure II
observed in structure $\mathbf{I}$, the same layering effect is observed. The layers of clathrate guest molecules and calixarenes alternate along the $c$ and a axis. Similar to Structure $I$, the calixarenes are lined in long threads which extend the full length of the crystal. Although one of the solvent molecules is held in position by a strong hydrogen bond, the second THF is held in place by weak Van der walls forces in a cavity formed between the calixarenes. This second molecule of THF which is weakly held in position is presumably responsible for the solvent dependent nature of these crystals.

The nitro substituent on the para position is twisted slightly out of plane with the aromatic ring by four degrees. This twisting is due to a strong intercalixarene interaction between $04 a 1$ and $C 7 b(3.27 \AA)$. These two calixarenes are related by the transformation $(x, y, z)$ to $(3 / 2-x, y-1 / 2,1 / 2-$ $z)$. The oxygen of the nitro substituent appears to have an interaction with one or both of the methylene hydrogens.

### 5.4. Structure III

The compound in structure III is tetrasubstituted and adopts the "cone" conformation. The lower rim substituents are large enough to prevent conformational mobility. Crystals of structure III were grown from a saturated solution of THF at $10{ }^{\circ} \mathrm{C}$ over a period of two months. Clear colorless crystals in the shape of long blocks were obtained.

These crystals were found to be solvent dependent and were mounted with mother liquor in the capillary prior to sealing. Data collection proceeded as outlined in the experimental section.

The crystals were found to be orthorhombic and in the space group C2221. Specific information on the collection and processing of this structure is shown in Table 36. The structure was solved using SHELXS-86 where four calixarenes and twelve THF molecules were found in the unit cell. The solvent molecules in the lattice showed a significant amount of disorder which was treated by fixing the bond lengths and angles for these molecules prior to final refinement. All non hydrogen atoms were treated with isotropic thermal parameters and the positions of the hydrogen atoms were calculated in most probable positions prior to the last refinement which resulted in an $R$ value of 0.065 .

The molecular structure of III, Figure 29, is in a "pinched cone" conformation in which two aromatic rings with lower rim benzyl substituents lie flattened and the two rings with lower rim tosylate substituents are pinched in over the cavity of the calixarene. The molecule lies on a two fold miror plane. Specific information regarding bond lengths and angles for structure may be found in Appendix D. The conformational characteristics of this structure match well with other tetrasubstitueted calixarene in the "cone" conformation without sterically bulky para substituents.

Table 36 - X-Ray Crystallographic Collection and Processing Data for Structure III

| Crystal System | Structure IJI |
| :--- | :---: |
| Space Group | Orthrombic |
| Cell Constants | C2221 |

a, A
19.044
b, A
21.522
c, $\AA$
15.362

V, $\mathrm{A}^{3}$
6296 (1)
mol formula
f w
$\mathrm{C}_{68} \mathrm{H}_{70} \mathrm{~N}_{2} \mathrm{O}_{15} \mathrm{~S}_{2}$
1219.45
formular units per cell (Z) 4
$r, \mathrm{~g} \mathrm{~cm}-3$
1.286
total data collected
2143
Independent data I>3 $\mathrm{s}(\mathrm{I})$
1074
R
0.0565
$\mathrm{R}_{\mathrm{W}}$
0.0742

GOF
weights
$\left[0.04 F^{2}+(s F)^{2}\right]^{-1}$


Figure 29 ORTEP diagram of structure III with thermal ellipsoiđs drawn at $50 \%$ probability level. H atoms are omitted for clarity.

Table 37 shows the planes of the axomatic rings for structure III and also the mean value of similar structures.

Table 37. Molecular plane angles of structure III and mean plane angles for similar calix[4]arenes

| Plane | Mean |  |
| :---: | ---: | :---: |
| A | 37.8 | Structure III |
| B | 100.4 | $37.6(3)$ |
| C | 30.9 | $37.56(8)$ |
| D | 99.7 | $102.1(3)$ |
| A C | 111.2 | $104.8(2)$ |
|  | -20.1 | $-24.5(4)$ |

The two flattened rings are canted at angles of about 37 degrees with an interplanar angle of $104.8(2)$ degrees. The two parallel aromatic rings fold over the center of the cavity with an interplanar angle of $-24.5(4)$ degrees. These angles are very similar to the mean values for calixarenes of this type. The methylene carbon attached to the phenolic oxygens point away from the cavity and their substituents arrange themselves under the cavity to reduce steric interactions.

The arrangement of the lower rim substituents shows no unusual charecteristics. The two benzyl groups are attached to the rings which are folded out at an obtuse angle and the two tosylate substituents are attached to the rings which are pinched over the cavity. The two benzyl substituents occupy the area under the cavity with one bent to the right and the other bent to the left. If one were to look at a top view of
this structure, the tosylates would both be pointed out from the underside of the cavity and would appear to twist in a clockwise direction similar to their arrangement in structure I.

The crystal packing diagram of the unit cell, Figure 30 , shows four calixarene molecules and twelve THF molecules. The calixarene molecules in the crystal lattice may be thought of as occupying octahedral positions and there are two THF molecules in the tetrahedral holes in the lattice. There are several close contacts between each calixarene with other calixarene and the solvent molecules but none appear to have a significant effect on the observed geometry of the calixarene molecule.

### 5.5. Structure IV

Compound IV was synthesised in the "1,3-alternate" conformation where both of the lower rim substituents are iarge enough to prevent rotation about the methylene bridges. Crystals of IV were grown by slow evaporation of a saturated THF solution at room temperature. The clear colorless crystals with a block morphology were mounted in a capillary and held in place using silicon grease. The data collection proceeded as outlined in the experimental section.

The structure was solved using SHELXS-86. Specific information regarding the collection and processing of the data for structure IV is shown in Table 38. The crystals


Figure 30 A diagram of the unit cell for Structure III

Table 38 - X-Ray Crystallographic Collection and Processing Data for Structure vI

|  | Structure IV |
| :---: | :---: |
| Crystal System | Monoclinic |
| Space Group | C2/c |
| Cell Constants |  |
| a, A | 22.835 (3) |
| b, A | 15.885 (1) |
| c, A | 15.582 (2) |
| b | 117.067 (9) |
| V, $\mathrm{A}^{3}$ | 5033.1 (9) |
| mol formula | $\mathrm{C}_{56} \mathrm{H}_{46} \mathrm{~N}_{2} \mathrm{O}_{12} \mathrm{~S}_{2}$ |
| 'fw | 1003.13 |
| formular units per cell (Z) | 4 |
| $r, \mathrm{~g} \mathrm{~cm}-3$ | 1.324 |
| total data collected | 3225 |
| Independent data $I>3 \mathrm{~s}(\mathrm{I})$ | 1601 |
| R | 0.0567 |
| $\mathrm{R}_{\mathrm{W}}$ | 0.0548 |
| GOF | 1.34 |
| wieghts | $04 \mathrm{~F}^{2}+(\mathrm{sF})^{2} \mathrm{l}^{-1}$ |

were found to be monoclinic and in the space group $\mathrm{c} 2 / \mathrm{c}$. Four calixarenes occupied the unit cell and no disorder was found in the lattice. Hydrogen atoms were found on the difference map as well as being assigned positions. All sulfurs, oxygens, nitrogens, and methyls were turned anisotropic which resulted in a final $R$ value of 0.0567 .

The molecular structure of $\mathbf{I V}$, shown in Figure 31, is in the "1,3-alternate" conformation in which two alternate aromatic rings are pointed up and the other two rings are pointed down. The calixarene lies on a crystallographic two fold rotational axis. Table 39 shows the angles of the planes with the methylene carbons and the interplanar angle between the two alternate planes.

Table 39. Molecular plane angles of structure IV

| Planes | Degrees |  |
| :---: | :---: | :---: |
| A | 87.6 |  |
| B | -87.2 | $(2)$ |
| $A^{\prime}$ | 87.76 | $(7)$ |
| $B^{\prime}$ | -87.29 | $(5)$ |
| A - A' | 4.6 | $(4)$ |
| B $^{\prime}-B^{\prime}$ | 5.5 | $(5)$ |

Each of the four aromatic rings make an angle of about 87 degrees with the methylene carbon plane. The resulting angle between alternate aromatic rings is about 5 degrees. The shape of this cavity is very similar to other "1,3alternate" crystal structures which have large lower rim


Figure 31 ORTEP diagram of structure IV with thermal
ellipsoids drawn at $50 \%$ probability level. H atoms are omitted for clarity.
substituents. The methylene carbons of the lower rim substituents point away from the cavity and the substituents themselves drape down filling the void under the cavity. The cavity geometry in this structure most closely resembles structure 9a. 9a has three sterically large substituents on the lower rim. The addition of the fourth sterically large substituent on the lower rim in IV may account for the decreased interplanar angle between planes A and C. The close interaction between these aromatic planes does not provide a cavity for host-guest interactions. Due to the strained nature of the "1,3-alternate" conformation, it is unlikely that these rings may fold open to accommodate a guest as observed in calixarenes in the "cone" and "partial cone" conformations.

The crystal packing which is shown in Figure 32 shows that these calixarenes arrange themselves in layers. The layer shown at the top of the diagram has two calixarenes oriented so that the benzyl substituents on both calixarenes are interacting in the center and the tosylate substituents are on the exterior. The second layer down has the alternate arrangements with the tosylates in the center and the benzyl groups point out. These layers alternate along the $C$ axis of the unit cell forming a series of long threads in the crystal. The projection down the A axis, as seen in Figure 33, shows an top view of these "molecular threads". The close packing arrangement of these threads provides very few


Figure 32 A diagram of the unit cell for structure IV


Figure 33 A diagram of the unit cell for structure IV
voids in the lattice that would usually be occupied by lattice solvent.

### 5.6. Conclusions

Of the four new crystal structures of calix[4]arenes, two are examples of calixarenes where the preferred conformation is determined by intramolecular hydrogen bonding. The conformation of the other two calixarene structures is determined by the manner in which they are synthesised.

Structure I is a typical example of a 1,3-dihydroxycalix[4]arenes. This calixarene is found in the "cone" conformation which is directed by two intramolecular hydrogen bonds between the two phenolic oxygens and the adjacent ether linkages. Structurally this compound has no unusual characteristics; the cavity shape and size is very similar to the mean conformation of calixarenes of this type. One of the unique characteristics of this structure is the presence of intermolecular $\pi$-stacking and hydrogen bonding interactions observed in the crystal packing. The presence of these intermolecular interactions appears to have no effect on the preferred conformation of the individual molecule. The calixarenes arrange themselves in long threads which extend the length of the crystal. Each of these threads is separated by clathrate solvent molecules.

Structure II is an atypical example of a 1,3-dihydroxycalix[4]arene. The calixarene is in the "cone" conformation which is directed by the presence of a single intramolecular hydrogen bond which occurs transannularly between the two phenolic oxygens. There is also a second hydrogen bond occurring between the second phenolic oxygen and a single THF molecule. This is the only example of a $1,3-$ dihydroxycalix[4]arene which prefers an intermolecular hydrogen bond over an intramolecular hydrogen bond. The presence of this single tranannular intramolecular hydrogen bond allows the two phenolic oxygens to fold fuxther into the cavity making the two aromatic rings more flattened. The calixarene molecules are arranged in threads separated by solvent molecules similar to structure $I$.

Structure III is a typical example of a tetralkylated calix[4]arene in the "cone" conformation with small para substituents. This calixarene is tetrasubstituted with sterically large lower rim substituents which prevent conformational interconversion. The cavity shape and size is typical for these calixarenes; two of the aromatic rings are pinched, folding over the cavity and the other two aromatic rings are folded out with an interplanar angle of about 90 degrees. The calixarenes are found in octahedral positions in the crystal packing with two solvent molecules found in the tetrahedral holes.

Structure Iv is a typical example of a calix[4]arene in the "1,3-alternate" conformation. The lower rim substituents are sterically large which prevents conformational interconversion. Both of the two alternate aromatic rings have an interplanar angle of about five degrees which is common for calixarenes in the "1,3-alternate" conformation. The calixarenes arrange themselves in a head to tail fashion forming long threads. The close packing arrangement of these compounds prevents the presence of clathrate solvent in the lattice.

None of these four calixarene crystal structures show the presence of host guest interactions. After examining structural characteristics of calix[4]arenes, the absence of intracavity host guest interactions is not particularly surprising. There are no examples of host guest interactions with compounds similar to structures III and IV. There are two examples of 1,3-dihydroxycalix[4]arenes, similar to structure $I$ and II, which have inclusion complexes but there are no examples of THF inclusion complexes in any of these structures. Further research will be necessary to determine the chemical characteristics necessary for host guest interactions.

APPENDIX A
CDS SEARCH RESULTS

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CDS Structural Data and Codes (cont.)

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APPENDIX B
BOND LENGTHS, BOND ANGLES, AND TORSION ANGLES FOR STRUCTURE I

Bond Distances for Structure I

| Atom 1 | Atom 2 | Distance $\AA$ <br> $($ e.s.d. $)$ | Atom 1 | Atom 2 | Distance $\AA$ <br> $(\mathrm{e} . \mathrm{s} . \mathrm{d})$ |
| :--- | :--- | :--- | :--- | :--- | :--- |
| S8a | O1a | $1.614(5)$ | C1c | C2c | $1.39(1)$ |
| S8a | O8a1 | $1.427(6)$ | C1c | C6c | $1.39(1)$ |
| S8a | O8a2 | $1.416(7)$ | C1d | C2d | $1.39(1)$ |
| S8a | C9a | $1.735(8)$ | C1d | C6d | $1.40(1)$ |
| S8c | O1c | $1.621(6)$ | C2a | C3a | $1.39(1)$ |
| S8c | O8c1 | $1.425(6)$ | C2a | C7a | $1.52(1)$ |
| S8c | O8c2 | $1.402(6)$ | C2b | C3b | $1.39(1)$ |
| S8c | C9c | $1.751(8)$ | C2b | C7b | $1.51(1)$ |
| O1a | C1b | $1.410(9)$ | C2c | C3c | $1.36(1)$ |
| O1b | C1b | $1.386(9)$ | C2c | C7c | $1.51(1)$ |
| O1c | C1c | $1.412(9)$ | C2d | C3d | $1.39(1)$ |
| O1c | C1c | $1.37(1)$ | C2d | C7d | $1.51(1)$ |
| O4a1 | N4a | $1.22(1)$ | C3a | C4a | $1.38(1)$ |
| O4a2 | N4a | $1.21(1)$ | C3b | C4b | $1.39(1)$ |
| O4c1 | N4c | $1.21(1)$ | C3c | C4c | $1.37(1)$ |
| O4c2 | N4c | $1.23(1)$ | C3d | C4d | $1.37(1)$ |
| N4a | C4a | $1.47(1)$ | C4a | C5a | $1.37(1)$ |
| N4c | C4c | $1.47(1)$ | C4b | C5b | $1.37(1)$ |
| C1a | C2a | $1.40(1)$ | C4c | C5c | $1.37(1)$ |
| C1a | C6a | $1.39(1)$ | C4d | C5d | $1.37(1)$ |
| C1b | C2b | $1.38(1)$ | C5a | C6a | $1.39(1)$ |
| C1b | Cb6 | $1.39(1)$ | C5b | C6b | $1.39(1)$ |
| C5c | C6c | $1.38(1)$ | C12a | C15a | $1.54(2)$ |
| C5d | C6d | $1.38(1)$ | C12c | C13c | $1.38(1)$ |
| C6a | C7a | $1.51(1)$ | C12c | C15c | $1.52(1)$ |
| C6b | C7b | $1.53(1)$ | C13c | C14c | $1.38(1)$ |
| C6c | C7c | $1.52(1)$ | C13a | C14a | $1.38(2)$ |
| C6d | C7d | $1.50(1)$ | O1s | C2s | $1.46(2)$ |
| C9a | C10a | $1.37(1)$ | O1s | C5s | $1.61(3)$ |

Bond Distances for Structure I (cont)

| Atom 1 | Atom 2 | Distance $\AA$ <br> (e.s.d.) | Atom 1 | Atom 2 | Distance $\AA$ <br> (e.s.d.) |
| :--- | :--- | :--- | :--- | :--- | :--- |
| C9a | C14a | $1.37(1)$ | C2s | C3s | $1.50(3)$ |
| C9c | C10c | $1.36(1)$ | C3s | C4s | $1.46(5)$ |
| C9c | C14c | $1.39(1)$ | C4s | C5s | $1.29(4)$ |
| C10a | C11a | $1.44(2)$ | O6s | C7s | $1.42(2)$ |
| C10c | C11c | $1.38(1)$ | O6s | C10s | $1.40(2)$ |
| C11a | C12a | $1.37(2)$ | C7s | C8s | $1.48(3)$ |
| C11c | C12c | $1.38(1)$ | C8s | C9s | $1.50(3)$ |
| C12a | C13a | $1.29(2)$ | C9s | C10s | $1.44(3)$ |
| C3a | H3a | 0.95 | C13c | H13c | 0.95 |
| C3b | H3b | 0.95 | C13a | H13a | 0.95 |
| C3c | H3c | 0.95 | C14a | H14a | 0.95 |
| C3d | H3d | 0.95 | C14c | H14c | 0.95 |
| C4b | H4b | 0.95 | C15a | H15a1 | 0.95 |
| C4d | H4d | 0.95 | C15a | H15a2 | 0.95 |
| C5a | H5a | 0.95 | C15a | H15a3 | 0.95 |
| C5b | H5b | 0.95 | C15c | H15c1 | 0.95 |
| C5c | H5c | 0.95 | C15c | H15c2 | 0.95 |
| C5d | H5d | 0.95 | C15c | H15c3 | 0.95 |
| C7a | H7a1 | 0.95 | C2s | H2s1 | 0.95 |
| C7a | H7a2 | 0.95 | C2s | H2s2 | 0.95 |
| C7b | H7b1 | 0.95 | C3s | H3s1 | 0.95 |
| C7b | H7b2 | 0.95 | C3s | H3s2 | 0.95 |
| C7c | H7c1 | 0.95 | C4s | H4s1 | 0.95 |
| C7c | H7c2 | 0.95 | C4s | H4s2 | 0.95 |
| C7d | H7d1 | 0.95 | C5s | H5s1 | 0.95 |
| C7d | H7d2 | 0.95 | C5s | H5s2 | 0.95 |
| C10a | H10a | 0.95 | C7s | H7s1 | 0.95 |
| C10c | H10c | 0.95 | C7s | H7s2 | 0.95 |
| C11a | H11a | 0.95 | C8s | H8s1 | 0.95 |
|  |  |  |  |  |  |

Bond Distances for Structure I (cont)

| Atom 1 | Atom 2 | Distance $\AA$ <br> (e.s.d.) | Atom 1 | Atom 2 | Distance $\AA$ |
| :--- | :--- | :--- | :--- | :--- | :--- |
| C11c | H11c | 0.95 | C8s | H8s2 | 0.95 |
| C9s | H9s1 | 0.95 | C10s | H10s1 | 0.95 |
| C9s | H9s2 | 0.95 | C10s | H10s2 | 0.95 |

Bond Angles for Structure I

| Atom 1 | Atom 2 | Atom 3 | Angle | Atom 1 | Atom 2 | Atom 3 | Angle |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| O1a | S8a | O8a | $107.2(3)$ | C2a | C1a | C6a | $123.4(7)$ |
| O1a | S8a | O8a | $109.0(3)$ | O1b | C1b | C2b | $117.9(6)$ |
| O1a | S8a | C9a | $98.8(3)$ | O1b | Clb | C6b | $119.9(7)$ |
| O8a | S8a | O8a | $118.3(4)$ | C2b | C1b | C6b | $122.1(7)$ |
| O8a | S8a | C9a | $111.4(4)$ | Olc | C1c | C2c | $117.1(7)$ |
| O8a | S8a | C9a | $110.2(4)$ | Olc | C1c | C6c | $118.8(7)$ |
| Olc | S8c | O8c | $108.1(3)$ | C2c | C1c | C6c | $124.1(7)$ |
| O1c | S8c | O8c | $101.9(3)$ | O1d | C1d | C2d | $119.2(7)$ |
| O1c | S8c | C9c | $106.7(4)$ | O1d | C1d | C6d | $119.7(7)$ |
| O8c | S8c | O8c | $120.9(4)$ | C2d | C1d | C6d | $121.1(7)$ |
| O8c | S8c | C9c | $107.8(4)$ | C1a | C2a | C3a | $117.2(7)$ |
| O8c | S8c | C9c | $110.4(4)$ | C1a | C2a | C7d | $123.4(7)$ |
| S8a | Ola | C1a | $115.0(4)$ | C3a | C2a | C7d | $119.4(7)$ |
| S8c | O1c | C1c | $119.7(5)$ | C1b | C2b | C3b | $117.9(7)$ |
| O4a | N4a | O4a | $124.0(8)$ | C1b | C2b | C7a | $121.5(7)$ |
| O4a | N4a | C4a | $118.5(8)$ | C3b | C2b | C7a | $120.5(7)$ |
| O4a | N4a | C4a | $117.5(7)$ | C1c | C2c | C3c | $117.5(7)$ |
| O4c | N4c | O4c | $123.3(7)$ | C1c | C2c | C7b | $122.2(6)$ |
| O4c | N4c | C4c | $119.0(7)$ | C3c | C2c | C7b | $120.1(7)$ |
| O4c | N4c | C4c | $117.7(7)$ | C1d | C2d | C3d | $118.8(7)$ |
| Ola | C1a | C2a | $117.7(5)$ | C1d | C2d | C7c | $119.1(7)$ |
| O1a | C1a | C6a | $118.9(7)$ | C3d | C2d | C7c | $121.8(7)$ |

Bond Angles for Structure I (cont.)

| Atom 1 | Atom 2 | Atom 3 | Angle | Atom 1 | Atom 2 | Atom 3 | Angle |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| C2a | C3a | C4a | $119.5(8)$ | C1c | C6c | C5c | $116.2(7)$ |
| C2b | C3b | C4b | $120.8(8)$ | C1c | C6c | C7c | $123.0(6)$ |
| C2c | C3c | C4c | $119.4(7)$ | C5c | C6c | C7c | $120.7(7)$ |
| C2d | C3d | C4d | $120.4(8)$ | C1d | C6d | C5d | $118.0(7)$ |
| N4a | C4a | C3a | $118.8(8)$ | C1d | C6d | C7d | $119.6(7)$ |
| N4a | C4a | C5a | $118.8(7)$ | C5d | C6d | C7d | $122.3(7)$ |
| C3a | C4a | C5a | $122.4(8)$ | C2b | C7a | C6a | $113.1(6)$ |
| C3b | C4b | C5b | $120.5(8)$ | C2c | C7b | C6b | $112.4(7)$ |
| N4c | C4c | C3c | $119.2(7)$ | C2d | C7c | C6c | $113.7(7)$ |
| N4c | C4c | C5c | $118.7(7)$ | C2a | C7d | C6d | $111.3(6)$ |
| C3c | C4c | C5c | $122.1(7)$ | S8a | C9a | C10a | $119.0(7)$ |
| C3d | C4d | C5d | $120.0(9)$ | S8a | C9a | C14a | $119.4(7)$ |
| C4a | C5a | C6a | $120.0(8)$ | C10a | C9a | C14a | $121.5(9)$ |
| C4b | C5b | C6b | $120.4(7)$ | S8c | C9c | C10c | $119.6(7)$ |
| C4c | C5c | C6c | $120.2(8)$ | S8c | C9c | C14c | $118.7(6)$ |
| C4d | C5d | C6d | $121.7(8)$ | C10c | C9c | C14c | $121.4(8)$ |
| C1a | C6a | C5a | $117.1(7)$ | C9a | C10a | C11a | $116(1)$ |
| C1a | C6a | C7a | $122.6(7)$ | C9c | C10c | C11c | $119.5(8)$ |
| C5a | C6a | C7a | $120.2(7)$ | C10a | C11a | C12a | $120(1)$ |
| C1b | C6b | C5b | $118.2(7)$ | C10c | C11c | C12c | $120.6(8)$ |
| C1b | C6b | C7b | $121.3(7)$ | C11a | C12a | C13a | $120(1)$ |
| C5b | C6b | C7b | $120.5(7)$ | C11a | C12a | C15a | $116(1)$ |
| C13a | C12a | C15a | $124(1)$ | O1s | C2s | C3s | $98(1$ |
| C11c | C12c | C13c | $118.8(9)$ | C2s | C3s | C4s | $93(2$ |
| C11c | C12c | C15c | $120.5(8)$ | C3s | C4s | C5s | $104(3$ |
| C14c | C12c | C15c | $120.6(9)$ | O1s | C5s | C4s | $91(2$ |
| C12c | C13c | C14c | $121.8(9)$ | C7s | C6s | C10s | $105(1$ |
|  |  |  |  |  |  |  |  |

Bond Angles for Structure I (cont.)

| Atom 1 | Atom 2 | Atom 3 | Angle | Atom 1 | Atom 2 | Atom 3 | Angle |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| C2a | C13a | C14a | $123(1)$ | O6s | C7s | C8s | $111(1$ |
| C9a | C14a | C13a | $118.7(9)$ | C7s | C8s | C9s | $98(2$ |
| C9c | C14c | C13c | $117.6(8)$ | C8s | C9s | C10s | $109(2$ |
| C2s | O1s | C5s | $107(1)$ | O6s | C10s | C9s | $109(2$ |
| C2a | C3a | H3a | 120 | C6a | C7a | H7a1 | 109 |
| C4a | C3a | H3a | 120 | C6a | C7a | H7a2 | 109 |
| C2b | C3b | H3b | 120 | H7al | C7a | H7a2 | 110 |
| C4b | C3b | H3b | 120 | C2c | C7b | H7b1 | 109 |
| C2c | C3c | H3c | 120 | C2c | C7b | H7b2 | 109 |
| C4c | C3c | H3c | 120 | C6b | C7b | H7b1 | 109 |
| C2d | C3d | H3d | 120 | C6b | C7b | H7b2 | 109 |
| C4d | C3d | H3d | 120 | H7bl | C7b | H7b2 | 110 |
| C3b | C4b | H4b | 120 | C2d | C7c | H7c1 | 108 |
| C5b | C4b | H4b | 120 | C2d | C7c | H7c2 | 108 |
| C3d | C4d | H4d | 120 | C6c | C7c | H7c1 | 108 |
| C5d | C4d | H4d | 120 | C6c | C7c | H7c2 | 110 |
| C4a | C5a | H5a | 120 | H7c1 | C7c | H7c2 | 109 |
| C6a | C5a | H5a | 120 | C2a | C7d | H7d1 | 109 |
| C4b | C5b | H5b | 120 | C2a | C7d | H7d2 | 109 |
| C6b | C5b | H5b | 120 | C6d | C7d | H7d1 | 109 |
| C4c | C5c | H5c | 120 | C6d | C7d | H7d2 | 109 |
| C6c | C5c | H5c | 120 | H7d1 | C7d | H7d2 | 110 |
| C4d | C5d | H5d | 119 | C9a | C10a | H10a | 122 |
| C6d | C5d | H5d | 119 | C11a | C10a | H10a | 122 |
| C2b | C7a | H7al | 109 | C9c | C10c | H10c | 120 |
| C2b | C7a | H7a2 | 109 | C11c | C10c | H10c | 120 |
| C10a | C11a | H11a | 120 | H15cl | C15c | H15c3 | 109 |
| C12a | C11a | H11a | 120 | H15c2 | C15c | H15c3 | 109 |
| C10c | C11c | H11c | 120 | O1s | C2s | H2s1 | 112 |
|  |  |  |  |  |  |  |  |

Bond Angles for Structure 1 (cont.)

| Atom 1 | Atom 2 | Atom 3 | Angle | Atom 1 | Atom 2 | Atom 3 | Angle |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| C12c | C11c | H11c | 120 | O1s | C2s | H2s2 | 112 |
| C12c | C13c | H13c | 119 | C3s | C2s | H2s1 | 112 |
| C14c | C13c | H13c | 119 | C3s | C2s | H2s2 | 112 |
| C12a | C13a | H13a | 119 | H2s | C2s | H2s2 | 109 |
| C14a | C13a | H13a | 119 | C2s | C3s | H3s1 | 113 |
| C9a | C14a | H14a | 121 | C2s | C3s | H3s2 | 113 |
| C13a | C14a | H14a | 121 | C4s | C3s | H3s1 | 113 |
| C9c | C14c | H14c | 121 | C4s | C3s | H3s2 | 113 |
| C13c | C14c | H14c | 121 | H3s | C3s | H3s2 | 109 |
| C12a | C15a | H15a1 | 109 | C3s | C4s | H4s1 | 111 |
| C12a | C15a | H15a2 | 109 | C3s | C4s | H4s2 | 111 |
| C12a | C15a | H15a3 | 109 | C5s | C4s | H4s1 | 111 |
| H15a1 | C15a | H15a2 | 109 | C5s | C4s | H4s2 | 111 |
| H15a1 | C15a | H15a3 | 109 | H4s | C4s | H4s2 | 109 |
| H15a2 | C15a | H15a3 | 109 | O1s | C5s | H5s1 | 114 |
| C12c | C15c | H15c1 | 109 | O1s | C5s | H5s2 | 114 |
| C12c | C15c | H15c2 | 109 | C4s | C5s | H5s1 | 114 |
| C12c | C15c | H15c3 | 110 | C4s | C5s | H5s2 | 114 |
| H15c1 | C15c | H15c2 | 109 | H5s | C5s | H5s2 | 109 |
| O6s | C7s | H7s1 | 109 | C8s | C9s | H9s1 | 110 |
| O6s | C7s | H7s2 | 109 | C8s | C9s | H9s2 | 110 |
| C8s | C7s | H7s1 | 109 | C10s | C9s | H9s1 | 110 |
| C8s | C7s | H7s2 | 109 | C10s | C9s | H9s2 | 110 |
| H7s1 | C7s | H7s2 | 109 | H9s1 | C9s | H9s2 | 109 |
| C7s | C8s | H8s1 | 112 | O6s | C10s | H10s1 | 110 |
| C7s | C8s | H8s2 | 112 | O6s | C10s | H10s2 | 110 |
| C9s | C8s | H8s1 | 112 | C9s | C10s | H10s1 | 110 |
|  |  |  |  |  |  |  |  |

Torsion Angles for Structure I

| Atom1 | Atom 2 | Atom 3 | Atom 4 | Angle |
| :---: | :---: | :---: | :---: | :---: |
| O8al | S8a | Ola | C1a | 61.31(0.56) |
| O8a2 | S8a | Ola | Cla | -67.92(0.55) |
| C9a | S8a | O1a | Cla | 177.08(0.51) |
| O1a | S8a | C9a | C10a | -68.89(0.79) |
| Ola | S8a | C9a | C14a | 113.92(0.73) |
| O8a1 | S8a | C9a | C10a | 43.60(0.86) |
| O8a1 | S8a | C9a | C14a | -133.59(0.72) |
| O8a2 | S8a | C9a | C10a | 177.05(0.74) |
| O8a2 | S8a | C9a | C14a | -0.14(0.85) |
| $\mathrm{O8c} 1$ | S8a | O1c | C1c | -45.71(0.60) |
| O8c2 | S8c | O1c | Clc | -174.17(0.53) |
| C 9 c | S8c | Olc | C1c | $70.03(0.59)$ |
| Olc | S8c | C9c | C10c | -100.89(0.72) |
| O1c | S8c | C9c | C14c | 84.80(0.75) |
| O8cl | S8c | C9c | C10c | 15.05(0.81) |
| O8c1 | S8c | C9c | C14c | -159.26(0.69) |
| O8c2 | S8c | C9c | C10c | 149.10(0.69) |
| O8c2 | S8c | C9c | C14c | -25.21(0.85) |
| S8a | O1a | Cla | C2a | -90.95(0.71) |
| S8a | O1a | Cla | C6a | 92.09(0.72) |
| S8c | Olc | Clc | C2c | -101.94(0.72) |
| S8c | O1c | C1c | C6c | 80.69(0.79) |
| O4al | N4a | C4a | C3a | 176.39(0.77) |
| O4a1 | N4a | C4a | C5a | -3.68(1.17) |
| O4a2 | N4a | C4a | C3a | -5.15(1.17) |
| O 4 a 2 | N4a | C4a | CSa | 174.78(0.81) |
| O 4 cl | N4c | $\mathrm{C4c}$ | C3c | 2.94(1.20) |
| O4c1 | N4c | C 4 c | $\mathrm{C5c}$ | $-176.70(0.81)$ |
| O 4 c 2 | N4c | C 4 c | C3c | -176.56(0.81) |

Torsion Angles for Structure I (cont.)

| Atom1 | Atom 2 | Atom 3 | Atom 4 | Angle |
| :---: | :---: | :---: | :---: | :---: |
| O 4 c 2 | N4c | C4c | C5c | 3.81(1.18) |
| Ola | Cla | C 2 a | C3a | 176.46(0.66) |
| O1a | Cla | C 2 a | C7d | -7.44(1.09) |
| C6a | Cla | C2a | C3a | -6.73(1.16) |
| C6a | Cla | C 2 a | C7d | 169.37(0.75) |
| Ola | Cla | C6a | C5a | -175.25(0.68) |
| Ola | Cla | C6a | C7a | 6.98(1.12) |
| C 2 a | Cla | C6a | C5a | 7.98(1.18) |
| C 2 a | Cla | C6a | C7a | -169.79(0.74) |
| Olb | Clb | C 2 b | C3b | 177.52(0.67) |
| Olb | Clb | C2b | C7a | 1.02(1.08) |
| C6b | Clb | C 2 b | C3b | -1.23(1.14) |
| C6b | C1b | C2b | C7a | -177.73(0.71) |
| Olb | Clb | C6b | C5b | -178.09(0.68) |
| Olb | Clb | C6b | C7b | 1.59(1.09) |
| C 2 b | Clb | C6b | C5b | 0.63 (1.13) |
| C 2 b | Clb | C6b | C7b | -179.69(0.70) |
| Olc | Clc | C2c | C3c | 175.83(0.69) |
| Olc | Clc | C2c | C7b | -8.58(1.10) |
| C6c | Clc | C2c | C3c | -6.96(1.21) |
| C6c | Clc | C2c | C7b | 168.64(0.76) |
| O1c | Clc | C6c | C5c | -177.10(0.69) |
| Olc | Clc | C6c | C7c | 6.24(1.15) |
| C2c | Clc | C6c | C5c | 5.73 (1.20) |
| C2c | Clc | C6c | C7c | -170.93(0.76) |
| Old | C1d | C2d | C3d | $176.21(0.71)$ |
| Old | C1d | C2d | C7c | 2.02(1.10) |
| C6d | C1d | C2d | C3d | -2.13(1.18) |
| C6d | Cld | C2d | C7c | -176.32(0.72) |

Torsion Angles for Structure I (cont.)

| Atom1 | Atom 2 | Atom 3 | Atom 4 | Angle |
| :--- | :--- | :--- | :--- | :--- |
| O1d | C1d | C6d | C7d | $2.31(1.12)$ |
| C2d | C1d | C6d | C5d | $1.86(1.170$ |
| C2d | C1d | C6d | C7d | $-179.36(0.73)$ |
| C1a | C2a | C3a | C4a | $0.82(1.14)$ |
| C7d | C2a | C3a | C4a | $-175.45(0.74)$ |
| C1a | C2a | C7d | C6d | $-112.63(0.83)$ |
| C3a | C2a | C7d | C6d | $63.40(0.96)$ |
| C1b | C2b | C3b | C4b | $1.04(1.16)$ |
| C7a | C2b | C3b | C4b | $177.57(0.74)$ |
| C1b | C2b | C7a | C6a | $-68.93(0.97)$ |
| C3b | C2b | C7a | C6a | $114.66(0.83)$ |
| C1c | C2c | C3c | C4c | $1.58(1.17)$ |
| C7b | C2c | C3c | C4c | $-174.11(0.75)$ |
| C1c | C2c | C7b | C6b | $-107.90(0.85)$ |
| C3c | C2c | C7b | C6b | $67.58(0.94)$ |
| C1d | C2d | C3d | C4d | $1.32(1.24)$ |
| C7c | C2d | C3d | C4d | $175.35(0.79)$ |
| C1d | C2d | C7c | C6c | $-72.58(0.92)$ |
| C3d | C2d | C7c | C6c | $113.42(0.85)$ |
| C2a | C3a | C4a | N4a | $-176.49(0.72)$ |
| C2a | C3a | C4a | C5a | $3.58(1.26)$ |
| C2b | C3b | C4b | C5b | $-0.26(1.26)$ |
| C2c | C3c | C4c | N4c | $-174.92(0.74)$ |
| C2c | C3c | C4c | C5c | $4.70(1.28)$ |
| C2d | C3d | C4d | C5d | $-0.27(1.36)$ |
| N4a | C4a | C5a | C6a | $177.78(0.74)$ |
| C3a | C4a | C5a | $-2.29(1.29)$ |  |
| C3b | C4b | C5b | $-0.37(1.24)$ |  |
| N4c | C5c | $173.67(0.74)$ |  |  |
|  | C6b |  |  |  |
|  |  |  |  |  |

Torsion Angles for Structure $\mathbf{I}$ (cont.)

| Atom1 | Atom 2 | Atom 3 | Atom 4 | Angle |
| :---: | :---: | :---: | :---: | :---: |
| C3c | C4c | C5c | C6c | -5.95(1.29) |
| C3d | C4d | C5d | C6d | 0.00(1.38) |
| C4a | C5a | C6a | Cla | -3.33 (1.19) |
| C4a | C5a | C6a | C7a | 174.50(0.77) |
| C4b | C5b | C6b | C1b | 0.19(1.17) |
| C 4 b | C5b | C6b | C7b | -179.49(0.73) |
| $\mathrm{C4c}$ | C5c | C6c | C1c | 0.79(1.18) |
| C4c | C5c | C6c | C7c | 177.53(0.76) |
| C4d | C5d | C6d | C1d | -0.77(1.26) |
| C4d | C5d | C6d | C7d | -179.52(0.82) |
| Cla | C6a | C7a | C2b | 108.77(0.86) |
| C5a | C6a | C7a | C2b | -68.94 (1.00) |
| C1b | C6b | C7b | C2c | 70.14(0.92) |
| C5b | C6b | VC7b | C2c | -110.18(0.81) |
| Clc | C6c | C7c | C2d | 109.73(0.86) |
| $\mathrm{C5c}$ | C6c | C7c | C2d | -66.78(0.98) |
| C1d | C6d | C7d | C2a | 70.24(0.94) |
| C5d | C6d | C7d | C2a | -111.03(0.86) |
| S8a | C9a | C10a | C11a | -177.64 (0.81) |
| C14a | C9a | C10a | C11a | -0.51(1.46) |
| S8a | C9a | C14a | C13a | 178.96(0.77) |
| C3c | C4c | C5c | C6c | -5.95(1.29) |
| C3d | C4d | C5d | C6d | 0.00(1.38) |
| C4a | C5a | C6a | Cla | -3.33 (1.19) |
| C 4 a | C5a | C6a | C7a | 174.50(0.77) |
| $\mathrm{C4b}$ | C5b | C6b | Clb | 0.19(1.17) |
| C4b | C5b | C6b | C7b | -179.49(0.73) |
| $\mathrm{C4c}$ | C5c | C6c | Clc | 0.79(1.18) |
| $\mathrm{C4c}$ | C5c | C6c | C7c | 177.53(0.76) |

Torsion Angles for Structure I (cont.)

| Atoml | Atorn 2 | Atom 3 | Atom 4 | Angle |
| :--- | :--- | :--- | :--- | :--- |
| C4d | C5d | C6d | C1d | $-0.77(1.26)$ |
| C4d | C5d | C6d | C7d | $-179.52(0.82)$ |
| C1a | C6a | C7a | C2b | $108.77(0.86)$ |
| C5a | C6a | C7a | C2b | $-68.94(1.00)$ |
| C1b | C6b | C7b | C2c | $70.14(0.92)$ |
| C5b | C6b | VC7b | C2c | $-110.18(0.81)$ |
| C1c | C6c | C7c | C2d | $109.73(0.86)$ |
| C5c | C6c | C7c | C2d | $-66.78(0.98)$ |
| C1d | C6d | C7d | C2a | $70.24(0.94)$ |
| C5d | C6d | C7d | C2a | $-111.03(0.86)$ |
| S8a | C9a | C10a | C11a | $-177.64(0.81)$ |
| C14a | C9a | C14a | C13a | $178.96(0.77)$ |
| S8a | C9a | C14a | C13a | $1.85(1.44)$ |
| C10a | C9c | C10c | C11c | $-170.07(0.69)$ |
| S8c | C9c | C10c | C11c | $4.08(1.32)$ |
| C14c | C9c | C14c | C13c | $171.69(0.74)$ |
| S8c | C9c | C14c | C13c | $-2.50(1.37)$ |
| C10c | C13a | C12a | $-1.88(1.68)$ |  |
| C9a | C10a | C11a | C12c | $-2.36(1.36)$ |
| C9c | C10c | C11c | C12a | C12a |
| C10a | C11a | C13a | $2.95(1.84)$ |  |
| C10a | C11a | C12a | C15a | $179.48(1.16)$ |
| C10c | C11c | C12c | C13c | $-0.85(1.42)$ |
| C10c | C12c | C15c | $176.45(0.90)$ |  |
| C11a | C12a | C14a | $-1.60(1.82)$ |  |
| C15a | C12a | C14a | $-177.84(1.17)$ |  |
| C11c | C13c | C14c | $2.45(1.51)$ |  |
| C15c | C13c | C14c | $-174.85(0.97)$ |  |
| C12c | C14c | $-0.81(1.49)$ |  |  |
|  | C12a | $-0.81(1.65)$ |  |  |

APPENDIX C
BOND LENGTHS, BOND ANGLES, AND TORSION ANGLES FOR STRUCTURE II

Bond Distances for Structure II

| Atom 1 | Atom 2 | $\begin{aligned} & \text { Distance } \AA \\ & \text { (e.s.d.) } \end{aligned}$ | Atom 1 | Atom 2 | $\begin{aligned} & \text { Distance } \AA \\ & \text { (e.s.d.) } \end{aligned}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| S8a | Ola | 1.595(5) | Clc | C2c | 1.385(9) |
| S8a | O8a1 | 1.427(6) | C1c | C6c | 1.398(9) |
| S8a | O8a2 | 1.427(5) | C1d | C2d | 1.368(8) |
| S8a | C9a | 1.751(6) | C1d | C6d | 1.41(1) |
| S8c | Olc | 1.593(5) | C2a | C3a | 1.39(1) |
| S8c | O8c1 | 1.431(6) | C2a | C7d | 1.511(9) |
| S8c | O8c2 | 1.420(5) | C2b | C3b | 1.394(9) |
| S8c | C9c | 1.742(6) | C2b | C7a | 1.49(1) |
| Ola | Cla | 1.432(8) | C2c | C3c | 1.40(1) |
| O1b | C1b | 1.383(8) | C2c | C7b | 1.525(9) |
| O1c | Clc | 1.422(8) | C2d | C3d | 1.401(9) |
| Old | C1d | 1.390(9) | C2d | C7c | 1.53(1) |
| O41b | C41b | 1.216(7) | C3a | C4a | 1.379(9) |
| O41d | C41d | 1.226(7) | C3b | C4b | 1.39(1) |
| N4b | C4b | 1.429(9) | C3c | C4c | 1.38(1) |
| N4b | C41b | 1.352(9) | C3d | C4d | 1.39(1) |
| N4d | C4d | 1.439(9) | C4a | C5a | 1.38(1) |
| N4d | C41d | 1.344(9) | C4b | C5b | 1.381(8) |
| Cla | C2a | 1.395(9) | C4c | C5c | 1.37(1) |
| C1a | C6a | 1.388(9) | C4d | C5d | 1.360(8) |
| C1b | C2b | $1.390(8)$ | C5a | C6a | 1.39(1) |
| C1b | C6b | 1.41(1) | C5a | C6b | 1.378(9) |
| $\mathrm{C5a}$ | C6c | 1.38(1) | C12a | C13a | 1.38 (1) |
| C5d | C6d | 1.393(9) | C12a | C15a | 1.50(1) |
| C6a | C7a | 1.52(1) | C12c | Cl 3 c | 1.38(1) |
| C6b | C7b | 1.505(8) | C12c | C15c | 1.52(1) |
| C6c | C7c | 1.52 (1) | C13a | C14a | 1.384(9) |
| C6d | C7d | 1.489(8) | C13c | C14c | 1.36(1) |

Bond Distances for Structure II (cont.)

| Atom 1 | Atom 2 | Distance $\AA$ <br> (e.s.d. $)$ | Atom 1 | Atom 2 | Distance $\AA$ <br> $($ e.s.d. $)$ |
| :--- | :--- | :--- | :--- | :--- | :--- |
| C9a | C10a | $1.360(9)$ | C41b | C42 | $1.50(1)$ |
| C9a | C14a | $1.39(1)$ | C41d | C42 | $1.50(1)$ |
| C9c | C10c | $1.37(1)$ | C1s | C11 | $1.774(8)$ |
| C9c | C14c | $1.39(1)$ | C1s | C12 | $1.750(9)$ |
| C10a | C11a | $1.375(9)$ | C1s | C13 | $1.718(8)$ |
| C10c | C11c | $1.38(1)$ | C2s | C14 | $1.734(9)$ |
| C11a | C12a | $1.39(1)$ | C2s | C15 | $1.76(1)$ |
| C11c | C12c | $1.39(1)$ | C2s | C16 | $1.743(8)$ |
| O1b | H1b | 0.95 | C10a | H10a | 0.95 |
| O1d | H1d | 1.06 | C10c | H10c | 0.95 |
| N4b | H4b | 0.99 | C11a | H11a | 0.95 |
| N4d | H4d | 1.16 | C11c | H11c | 0.95 |
| C3a | H3a | 0.95 | C13a | H13a | 0.95 |
| C3b | H3b | 0.95 | C13c | H13c | 0.95 |
| C3c | H3c | 0.95 | C14a | H14a | 0.95 |
| C3d | H3d | 0.95 | C14c | H14c | 0.95 |
| C4a | H4a | 0.95 | C15a | H15a1 | 0.85 |
| C4c | H4c | 0.95 | C15a | H15a2 | 0.95 |
| C5a | H5a | 0.95 | C15a | H15a3 | 0.95 |
| C5b | H5b | 0.95 | C15c | H15c1 | 0.92 |
| C5c | H5c | 0.95 | C15c | H15c2 | 0.95 |
| C5d | H5d | 0.95 | C15c | H15c3 | 0.95 |
| C7a | H7a1 | 0.95 | C42b | H42b1 | 0.84 |
| C7a | H7a2 | 0.95 | C42b | H42b2 | 0.95 |
| C7b | H7b1 | 0.95 | C42b | H42b3 | 0.95 |
| C7b | H7b2 | 0.95 | C42d | H42d2 | 1.00 |
| C7c | H7c1 | 0.95 | C42d | H42d3 | 0.95 |
| C7c | H7c2 | 0.95 | C42d | H42d3 | 0.95 |
|  |  |  |  |  |  |

Bond Distances for Structure II (cont.)

| Atom 1 | Atom 2 | Distance $\AA$ <br> (e.s.d.) | Atom 1 | Atom 2 | Distance $\AA$ <br> (e.s.d.) |
| :--- | :--- | :--- | :--- | :--- | :--- |
| C7d | H7d1 | 0.95 | C1s | H1s | 0.95 |
| C7d | H7d2 | 0.95 | C2s | H2s | 0.95 |

Bond Angles for Structure II

| Atom 1 | Atom 2 | Atom 3 | Angle | Atom 1 | Atom 2 | Atom 3 | Angle |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| O1a | S8a | O8a1 | $108.8(3)$ | O1c | C1c | C2c | $118.2(6)$ |
| O1a | S8a | O8a2 | $102.5(3)$ | O1c | C1c | C6c | $118.4(6)$ |
| O1a | S8a | C9a | $103.8(3)$ | C2c | C1c | C6c | $123.2(6)$ |
| O8a1 | S8a | O8a2 | $120.8(3)$ | O1d | C1d | C2d | $121.1(6)$ |
| O8a1 | S8a | C9a | $109.0(3)$ | O1d | C1d | C6d | $117.4(5)$ |
| O8a2 | S8a | C9a | $110.5(3)$ | C2d | C1d | C6d | $121.5(6)$ |
| O1c | S8c | O8c1 | $109.2(3)$ | C1a | C2a | C3a | $115.8(6)$ |
| O1c | S8c | O8c2 | $103.4(3)$ | C1a | C2a | C7d | $123.5(6)$ |
| O1c | S8c | C9c | $103.9(3)$ | C3a | C2a | C7d | $120.1(6)$ |
| O8c1 | S8c | O8c2 | $119.5(3)$ | C1b | C2b | C3b | $117.6(6)$ |
| O8c1 | S8c | C9c | $108.6(3)$ | C1b | C2b | C7a | $120.6(6)$ |
| O8c2 | S8c | C9c | $111.0(3)$ | C3b | C2b | C7a | $121.8(5)$ |
| S8a | O1a | C1a | $118.9(4)$ | C1c | C2c | C3c | $116.8(6)$ |
| S8c | O1c | C1c | $118.7(4)$ | C1c | C2c | C7b | $123.5(6)$ |
| C4b | N4b | C41b | $125.8(6)$ | C3c | C2c | C7b | $119.5(6)$ |
| C4d | N4d | C41d | $124.8(5)$ | C1d | C2d | C3d | $119.2(6)$ |
| O1a | C1a | C2a | $117.9(5)$ | C1d | C2d | C7c | $120.6(6)$ |
| O1a | C1a | C6a | $117.5(6)$ | C3d | C2d | C7c | $120.2(5)$ |
| C2a | C1a | C6a | $124.5(6)$ | C2a | C3a | C4a | $121.8(6)$ |
| O1b | C1b | C2b | $121.6(6)$ | C2b | C3b | C4b | $121.3(6)$ |

Bond Angles for Structure II (cont.)

| Atom 1 | Atom 2 | Atom 3 | Angle | Atom 1 | Atom 2 | Atom 3 | Angle |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| O1b | C1b | C6b | $116.6(5)$ | C2c | C3c | C4c | $120.9(7)$ |
| C2b | C1b | C6b | $121.6(6)$ | C2d | C3d | C4d | $119.7(6)$ |
| C3a | C4a | C5a | $119.8(6)$ | C1d | C6d | C7d | $120.5(6)$ |
| N4b | C4b | C3b | $117.9(5)$ | C5d | C6d | C7d | $121.6(6)$ |
| N4b | C4b | C5b | $122.0(6)$ | C2b | C7a | C6a | $112.8(5)$ |
| C3b | C4b | C5b | $119.9(6)$ | C2c | C7b | C6b | $110.5(6)$ |
| C3c | C4c | C5c | $120.6(7)$ | C2d | C7c | C6c | $111.7(5)$ |
| N4d | C4d | C3d | $116.8(5)$ | C2a | C7d | C6d | $110.4(6)$ |
| N4d | C4d | C5d | $122.6(6)$ | S8a | C9a | C10a | $120.1(6)$ |
| C3d | C4d | C5d | $120.5(6)$ | S8a | C9a | C14a | $118.6(5)$ |
| C4a | C5a | C6a | $121.4(6)$ | C10a | C9a | C14a | $121.0(6)$ |
| C4b | C5b | C6b | $120.5(6)$ | S8c | C9c | C10c | $119.0(6)$ |
| C4c | C5c | C6c | $120.8(7)$ | S8c | C9c | C14c | $119.8(5)$ |
| C4d | C5d | C6d | $121.3(7)$ | C10c | C9c | C14c | $120.7(6)$ |
| C1a | C6a | C5a | $116.4(6)$ | C9a | C10a | C11a | $120.6(7)$ |
| C1a | C6a | C7a | $123.0(6)$ | C9c | C10c | C11c | $119.3(7)$ |
| C5a | C6a | C7a | $120.4(6)$ | C10a | C11a | C12a | $120.1(7)$ |
| C1b | C6b | C5b | $118.9(6)$ | C10c | C11c | C12c | $120.8(7)$ |
| C1b | C6b | C7b | $119.2(6)$ | C11a | C12a | C13a | $118.4(6)$ |
| C5b | C6b | C7b | $121.7(6)$ | C11a | C12a | C15a | $120.4(7)$ |
| C1c | C6c | C5c | $117.3(6)$ | C13a | C12a | C15a | $121.2(7)$ |
| C1c | C6c | C7c | $123.1(6)$ | C11c | C12c | C13c | $118.6(7)$ |
| C5c | C6c | C7c | $119.5(6)$ | C11c | C12c | C15c | $119.7(7)$ |
| C1d | C6d | C5d | $117.8(5)$ | C13c | C12c | C15c | $121.8(8)$ |
| C12a | C13a | C14a | $121.9(7)$ | O41d | C41d | C42d | $121.9(7)$ |
| C12c | C13c | C14c | $121.5(8)$ | N4d | C41d | C42d | $113.9(5)$ |
| C9a | C14a | C13a | $117.9(6)$ | C11 | C1s | C12 | $109.6(5)$ |

Bond Angles for Structure II (cont.)

| Atom 1 | Atom 2 | Atom 3 | Angle | Atom 1 | Atom 2 | Atom 3 | Angle |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| C9c | C14c | C13c | $119.1(6)$ | Cl1 | C1s | C13 | $110.1(5)$ |
| C(c | C14c | C13c | $119.1(6)$ | C11 | C1s | Cl3 | $110.1(5)$ |
| O41b | C41b | N4b | $123.5(6)$ | Cl2 | C1s | Cl3 | $111.5(4)$ |
| O41b | C41b | C42b | $122.6(7)$ | Cl4 | C2s | Cl5 | $110.5(4)$ |
| N4b | C41b | C42b | $113.9(6)$ | Cl4 | C2s | C16 | $110.5(5)$ |
| O41d | C41d | N4d | $124.1(6)$ | C15 | C2s | C16 | $110.2(5)$ |
| C1b | O1b | H1b | 121 | C4c | C5c | H5c | 120 |
| C1d | O1d | H1d | 108 | C6c | C5c | H5c | 120 |
| C4b | N4b | H4b | 127 | C4d | C5d | H5d | 119 |
| C41b | N4b | H4b | 107 | C6d | C5d | H5d | 119 |
| C4d | N4d | H4d | 124 | C2b | C7a | H7a1 | 109 |
| C4ld | N4d | H4d | 111 | C2b | C7a | H7a2 | 109 |
| C2a | C3a | H3a | 119 | C6a | C7a | H7a1 | 109 |
| C4a | C3a | H3a | 119 | C6a | C7a | H7a2 | 109 |
| C2b | C3b | H3b | 119 | H7a1 | C7a | H7a2 | 110 |
| C4b | C3b | H3b | 119 | C2c | C7b | H7b1 | 109 |
| C2c | C3c | H3c | 120 | C2c | C7b | H7b2 | 109 |
| C4c | C3c | H3c | 120 | C6b | c7b | H7b1 | 109 |
| C2d | C3d | H3d | 120 | C6b | C7b | H7b2 | 109 |
| C4d | C3d | H3d | 120 | H7b1 | C7b | H7b2 | 110 |
| C3a | C4a | H4a | 120 | C2d | C7c | H7c1 | 109 |
| C5a | C4a | H4a | 120 | C2d | C7c | H7c2 | 109 |
| C3s | C4c | H4c | 120 | C6c | C7c | H7c1 | 109 |
| C5c | C4c | H4c | 120 | C6c | C7c | H7c2 | 109 |
| C4a | C5a | H5a | 119 | H7c1 | C7c | H7c2 | 110 |
| C6a | C5a | H5a | 119 | C2a | C7d | H7d1 | 109 |
| C4b | C5b | H5b | 120 | C2a | C7d | H7d1 | 109 |
| C6b | C5b | H5b | 120 | C6d | C7d | H7d1 | 109 |
| C6d | C7d | H7d2 | 109 | H15a1 | C15a | H15a3 | 108 |

Bond Angles for Structure II (cont.)

| Atom 1 | Atom 2 | Atom 3 | Angle | Atom 1 | Atom 2 | Atom 3 | Angle |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| H7d1 | C7d | H7d2 | 110 | H15a2 | C15a | H15a3 | 110 |
| C9a | C10a | H10a | 120 | C12c | C15c | H15c1 | 119 |
| C11a | C10a | H10a | 120 | C12c | C15c | H15c2 | 107 |
| C9c | C10c | H10c | 120 | C12c | C15c | H15c3 | 107 |
| C11c | C10c | H10c | 120 | H15c1 | C15c | H15c2 | 107 |
| C10a | C11a | H11a | 120 | H15c1 | C15c | H15c3 | 107 |
| C12a | C11a | H11a | 120 | H15c2 | C15c | H15c3 | 110 |
| C10c | C11c | H11c | 120 | C41b | C42b | H42b1 | 110 |
| C12c | C11c | H11c | 120 | C41b | C42b | H42b2 | 109 |
| C12a | C13a | H13a | 119 | C41b | C42b | H42b3 | 109 |
| C14a | C13a | H13a | 119 | H42b1 | C42b | H42b2 | 109 |
| C12c | C13c | H13c | 119 | H42b2 | C42b | H421b3 | 110 |
| C9a | C14a | H14a | 121 | C41d | C42d | H42d1 | 122 |
| C13a | C14a | H14a | 121 | C41d | C42d | H42d2 | 106 |
| C9c | C14c | H14c | 121 | C41d | C42d | H42d3 | 106 |
| C13c | C14c | H14c | 121 | H42d1 | C42d | H42d2 | 106 |
| C12a | C15a | H15a1 | 117 | H42d1 | C42d | H42d3 | 106 |
| C12a | C15a | H15a2 | 108 | H42d2 | C42d | H42d3 | 110 |
| C12a | C15a | H15a3 | 108 | Cl1 | C1s | H1s | 110 |
| H15a1 | C15a | H15a2 | 108 | C12 | C1s | H1s | 1081 |
| C13 | C1s | H1s | 108 | C15 | C2s | H2s | 109 |
| C14 | C2s | H2s | 108 | C16 | C2s | H2s | 109 |

Torsion Angles for Structure II

| Atom 1 | Atom 2 | Atom 3 | Atom 4 | Angle |
| :---: | :---: | :---: | :---: | :---: |
| O8al | S8a | Ola | C1a | -36.93(0.46) |
| O8a2 | S8a | O1a | Cla | -165.86(0.42) |
| C9a | S8a | O1a | Cla | 79.01(0.46) |
| Ola | S8a | C9a | C10a | -88.71 (0.62) |
| O1a | S8a | C9a | C14a | 86.33(0.60) |
| O8al | S8a | $\mathrm{C9} a$ | C10a | 27.09(0.69) |
| O8al | S8a | C9a | C14a | -157.86(0.55) |
| O8a2 | S8a | C9a | C10a | 162.03(0.59) |
| O8a2 | S8a | C9a | C14a | -22.92(0.69) |
| O8c1 | S8c | O1c | C1c | -37.38(0.47) |
| O8c2 | S8c | Olc | C1c | -165.63(0.41) |
| C9c | S8c | O1c | C1c | 78.37(0.46) |
| O1c | S8c | C9c | C10C | -88.77(0.62) |
| Olc | S8c | C9c | C 14 c | 83.66(0.61) |
| O8c1 | S8c | C9c | C10c | 27.43(0.69) |
| O8c1 | S8c | C9c | C14c | -160.15(0.57) |
| O8c2 | S8c | C9c | C10c | 160.69(0.58) |
| O8c2 | S8c | C9c | Cl4c | -26.89(0.70) |
| S8a | Ola | C1a | C2a | 82.66(0.63) |
| S8a | O1a | C1a | C6a | -99.67(0.60) |
| S8c | Olc | Clc | C2c | 84.82(0.64) |
| S8c | O1c | Clc | C6c | $-100.47(0.61)$ |
| C41b | N4b | C4b | C3b | -138.52(0.67) |
| C41b | N4b | C4b | C5b | 46.37(0.94) |
| C4b | N4b | C41b | O41b | 8.30(1.03) |
| C 4 b | N4b | C41b | C42b | -173.31(0.58) |
| C41d | N4d | C4d | C3d | 149.55(0.68) |
| C41d | N4d | C4d | C5d | -32.64(1.03) |

Torsion Angles for Structure II (cont.)

| Atom 1 | Atom 2 | Atom 3 | Atom 4 | Angle |
| :--- | :--- | :--- | :--- | :--- |
| C4d | N4d | C42d | O41d | $-5.77(1.11)$ |
| C4d | N4d | C41d | C42d | $174.40(0.65)$ |
| O1a | C1a | C2a | C3a | $-177.20(0.56)$ |
| Ola | C1a | C2a | C7d | $11.24(0.95)$ |
| C6a | C1a | C2a | C3a | $5.31(1.00)$ |
| C6a | C1a | C2a | C7d | $-166.24(0.64)$ |
| O1a | C1a | C6a | C5a | $177.64(0.56)$ |
| O1a | C1a | C6a | C7a | $-7.53(0.94)$ |
| C2a | C1a | C6a | C5a | $-4.87(1.01)$ |
| C2a | C1a | C6a | C7a | $169.97(0.63)$ |
| O1b | C1b | C2b | C3b | $-178.39(0.57)$ |
| O1b | C1b | C2b | C7a | $2.41(0.94)$ |
| C6b | C1b | C2b | C3b | $-3.89(0.95)$ |
| C6b | C1b | C2b | C7a | $176.90(0.60)$ |
| O1b | C1b | C6b | C5b | $178.03(0.57)$ |
| Olb | C1b | C6b | C7b | $-6.23(0.88)$ |
| C2b | C1b | C6b | C5b | $3.27(0.98)$ |
| C2b | C1b | C6b | C7b | $179.01(0.60)$ |
| O1c | C1c | C2c | C3c | $-178.99(0.57)$ |
| O1c | C1c | C2c | C7b | $7.04(0.97)$ |
| C6c | C1c | C2c | C3c | $6.58(1.01)$ |
| C6c | C1c | C2c | C7b | $-167.39(0.64)$ |
| O1c | C1c | C6c | C5c | $179.72(0.57)$ |
| Olc | C1c | C6c | C7c | $-3.63(0.96)$ |
| C2c | C1c | C6c | C5c | $-5.85(1.02)$ |
| C2c | C1c | C6c | C7c | $170.79(0.64)$ |
| O1d | C1d | C2d | C3d | $177.69(0.59)$ |
| Old | C1d | C7c | $-1.32(0.97)$ |  |
|  |  | C2d |  |  |

Torsion Angles for Structure II (cont.)

| Atom 1 | Atom 2 | Atom 3 | Atom 4 | Angle |
| :--- | :--- | :--- | :--- | :--- |
| C6d | C1d | C2d | C3d | $-1.45(1.00)$ |
| C6d | C1d | C2d | C7c | $179.55(0.60)$ |
| O1d | C1d | C6d | C5d | $-178.30(0.57)$ |
| O1d | C1d | C6d | C7d | $1.07(0.93)$ |
| C2d | C1d | C6d | C5d | $0.87(0.99)$ |
| C2d | C1d | C6d | C7d | $-179.76(0.63)$ |
| C1a | C2a | C3a | C4a | $-1.30(0.99)$ |
| C7d | C2a | C3a | C4a | $170.56(0.64$ |
| C1a | C2a | C7d | C6d | $106.06(0.73)$ |
| C3a | C2a | C7d | C6d | $-65.15(0.81)$ |
| C1b | C2b | C3b | C4b | $2.09(0.96)$ |
| C7a | C2b | C3b | C4b | $-178.71(0.61)$ |
| C1b | C2b | C7a | C6a | $78.82(0.78)$ |
| C3b | C2b | C7a | C6a | $-100.36(0.71)$ |
| C1c | C2c | C3c | C4c | $-1.66(1.01)$ |
| C7b | C2c | C3c | C4c | $172.56(0.65)$ |
| C1c | C2c | C7b | C6b | $107.82(0.74)$ |
| C3c | C2c | C7b | C6b | $-65.99(0.81)$ |
| C1d | C2d | C3d | C4d | $1.43(0.99)$ |
| C7c | C2d | C3d | C4d | $-179.56(0.61)$ |
| C1d | C2d | C7c | C6c | $77.04(0.79)$ |
| C3d | C2d | C7c | C6c | $-101.96(0.70)$ |
| C2a | C3a | C4a | C5a | $-2.81(1.06)$ |
| C2b | C3b | C4b | N4b | $-174.89(0.58)$ |
| C2b | C3b | C4b | C5b | $0.32(0.99)$ |
| C2c | C3c | C4c | C5c | $-3.78(1.10)$ |
| C2d | C3d | C4d | $177.00(0.59)$ |  |
| C2d | C3d | C4d | C5d | $-0.86(1.01)$ |
|  |  |  |  |  |

Torsion Angles for Structure II (cont.)

| Atom 1 | Atom 2 | Atom 3 | Atom 4 | Angle |
| :--- | :--- | :--- | :--- | :--- |
| C3a | C4a | C5a | C6a | $3.31(1.06)$ |
| N4b | C4b | C5b | C6b | $174.00(0.60)$ |
| C3b | C4b | C5b | C6b | $174.00(0.60)$ |
| C3c | C4c | C5c | C6c | $4.58(1.11)$ |
| N4d | C4d | C5d | C6d | $-177.45(0.61)$ |
| C3d | C4d | C5d | C6d | $0.28(1.04)$ |
| C4a | C5a | C6a | C1a | $0.37(0.99)$ |
| C4a | C5a | C6a | C7a | $-174.61(0.64)$ |
| C4b | C5b | C6b | C1b | $-0.73(0.98)$ |
| C4b | C5b | C6b | C7b | $-176.37(0.61)$ |
| C4c | C5c | C6c | C1c | $0.09(1.01)$ |
| C4c | C5c | C6c | C7c | $-176.68(0.65)$ |
| C4d | C5d | C6d | C1d | $-0.27(1.00)$ |
| C4d | C6a | C6d | C7d | $-179.63(0.63)$ |
| C1a | C7a | C2b | $-112.23(0.72)$ |  |
| C5a | C6a | C7a | C2b | $62.41(0.82)$ |
| C1b | C6b | C7b | C2c | $-72.20(0.78)$ |
| C5b | C6b | C7b | C2c | $103.42(0.72)$ |
| C1c | C6c | C7c | C2d | $-112.16(0.72)$ |
| C5c | C6c | C7c | C2d | $64.42(0.80)$ |
| C1d | C6d | C7d | C2a | $-75.97(0.78)$ |
| C5d | C6d | C7d | C2a | $103.38(0.71)$ |
| S8a | C9a | C10a | C11a | $175.05(0.60)$ |
| C14a | C9a | C10a | C11a | $0.12(1.13)$ |
| S8a | C9c | C14a | C13a | $-175.21(0.57)$ |
| S8c | C9c | C11c | $0.49(1.12)$ |  |
| C14c | C9c | C11c | $0.49(1.12)$ |  |
| S8a | C13c | $-171.85(0.59)$ |  |  |
|  | C14c |  |  |  |

Torsion Angles for Structure II (cont.)

| Atom 1 | Atom 2 | Atom 3 | Atom 4 | Angle |
| :--- | :--- | :--- | :--- | :--- |
| C10c | C9c | C14c | C13c | $0.44(1.11)$ |
| C9a | C10a | C11a | C12a | $-1.59(1.17)$ |
| C9c | C10c | C11c | C12c | $-2.31(1.20)$ |
| C10a | C11a | C12a | C13a | $3.10(1.15)$ |
| C10a | C11a | C12a | C15a | $-178.07(0.75)$ |
| C10c | C11c | C12c | C13c | $3.15(1.22)$ |
| C10c | C11c | C12c | C15c | $-177.23(0.78)$ |
| C11a | C12a | C13a | C14a | $-3.26(1.17)$ |
| C15a | C12a | C13a | C14a | $177.92(0.75)$ |
| C11c | C12c | C13c | C14c | $-2.22(1.22)$ |
| C15c | C12c | C13c | C14c | $178.17(0.79)$ |
| C12a | C13a | C14a | C9a | $1.82(1.13)$ |
| C12c | C13c | C14c | C9c | $0.46(1.18)$ |

## APPENDIX D

BOND LENGTHS, BOND ANGLES, AND TORSION ANGLES FOR STRUCTURE III

Bond Distances for Structure III

| Atom 1 | Atom 2 | $\begin{aligned} & \text { Distance } \AA \\ & \text { (e.s.d.) } \end{aligned}$ | Atom 1 | Atom 2 | $\begin{aligned} & \text { Distance } \AA \\ & \text { (e.s.d.) } \end{aligned}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| S | Ola | 1.631(7) | $\overline{\mathrm{C} 5} \mathrm{a}$ | C6a | 1.48(1) |
| S | O8a | $1.391(9)$ | C5b | C6b | 1.37(2) |
| S | O8b | 1.392(8) | C6a | C7a | 1.51(1) |
| S | C9a | 1.78(1) | C6b | C7b' | 1.50(1) |
| Ola | Cla | 1.40(1) | C8b | C9b | 1.53(2) |
| O1b | C1b | 1.39(1) | C9a | C14a | 1.43(2) |
| O4a | N4 | 1.42(1) | C 9 b | C10b | 1.29(1) |
| O4b | N4 | 1.22(1) | C9b | C14b | 1.35(2) |
| N4 | C4a | 1.19(1) | C10a | C11a | 1.32(2) |
| C1a | C2a | 1.51(1) | C10b | C11b | 1.40(2) |
| C1a | C6a | 1.38(1) | C11a | C12a | 1.46(2) |
| C1b | C 2 b | 1.38(1) | C11b | C12b | 1.36(2) |
| C1b | C6b | 1.37(1) | C12a | C13a | 1.28(2) |
| C2a | C3a | 1.38(1) | C12a | C15a | 1.36(2) |
| C2a | C7b | 1.30(1) | C12b | C13b | 1.58(2) |
| C 2 b | C3b | 1.54(1) | C13a | C14a | 1.40(2) |
| C2b | C3b | 1.37(1) | C13a | C14a | 1.37(2) |
| C2b | C7a | 1.54(1) | C13b | C14b | 1.36(2) |
| C3a | C4a | 1.37(1) | C1s | C 2 s | 1.36(3) |
| C3b | C4b | 1.38(2) | C 1 s | C5s | 1.42(4) |
| C4a | C5a | 1.33(1) | C 2 s | C3s | 1.55(3) |
| C4b | C5b | 1.40(2) | C3s | C4s | 1.42(3) |
| C4s | C5s | 1.44(4) | C7s | C 8 s | 1.62(4) |
| C6s | C7s | 1.42(3) | C8s | C8s' | 1.57(3) |
| C3a | H3a | 0.95 | C14a | H14a | 0.95 |
| C3b | H3b | 0.95 | C14b | H14b | 0.95 |
| C4b | H4b | 0.95 | C15a | H15al | 0.95 |
| C5a | H5a | 0.95 | C15a | H15a2 | 0.95 |

Bond Distances for Structure III (cont.)

| Atom 1 | Atom 2 | Distance $\AA$ <br> (e.s.d.) | Atom 1 | Atom 2 | Distance $\AA$ <br> (e.s.d.) |
| :--- | :--- | :--- | :--- | :--- | :--- |
| C5b | H5b | 0.95 | C15a | H15a3 | 0.95 |
| C7a | H7a1 | 0.95 | C2s | H2s1 | 0.95 |
| C7a | H7a2 | 0.95 | C2s | H2s2 | 0.95 |
| C7b | H7b1 | 0.95 | C3s | H3s1 | 0.95 |
| C7b | H7b2 | 0.95 | C3s | H3s2 | 0.95 |
| C8b | H8b1 | 0.95 | C4s | H4s1 | 0.95 |
| C8b | H8b2 | 0.95 | C4s | H4s2 | 0.95 |
| C10b | H10a | 0.95 | C5s | H5s1 | 0.95 |
| C10b | H10b | 0.95 | C5s | H5s2 | 0.95 |
| C11a | H11a | 0.95 | C7s | H7s1 | 0.95 |
| C11b | H11b | 0.95 | C7s | H7s2 | 0.95 |
| C12b | H12b | 0.95 | C8s | H8s1 | 0.95 |
| C13a | H13a | 0.95 | C8s | H8s2 | 0.95 |
| C13b | H13b | 0.95 |  |  |  |

Bond Angles for Structure III

| Atom 1 | Atom 2 | Atom 3 | Angle | Atom 1 | Atom 2 | Atom 3 | Angle |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| Ola | S | O8a | $101.9(5)$ | C3b | C2b | C7a | $119.7(8)$ |
| O1a | S | O8b | $109.6(4)$ | C2a | C3a | C4a | $120.1(9)$ |
| Ola | S | C9a | $103.2(4)$ | C2b | C3b | C4b | $122(1)$ |
| O8a | S | O8b | $122.7(5)$ | N4 | C4a | C3a | 118.69 |
| O8a | S | C9a | $108.2(5)$ | N4 | C4a | C5a | $115.2(9)$ |
| O8b | S | C8a | $109.4(5)$ | C3a | C4a | C5a | $125.9(9)$ |
| S | O1A | C9a | $116.0(5)$ | C3b | C4b | C5b | $119(1)$ |
| C1b | O1B | C1b | $113.8(7)$ | C4a | C5a | C6a | $114.7(9)$ |
| O4a | N4 | O8b | $123(1)$ | C4b | C5b | C6b | $119(1)$ |
| O4a | N4 | C4a | $117.6(9)$ | Cla | C6a | C5a | 116.79 |
| O4b | N4 | C4a | $118(1)$ | C1a | C6a | C7a | $128.4(9)$ |

Bond Angles for Structure III (cont.)

| Atom 1 | Atom 2 | Atom 3 | Angle | Atom 1 | Atom 2 | Atom 3 | Angle |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Ola | Cl | C2a | 119.2(8) | C5a | C6a | C7a | 114.9(8) |
| Ola | Cla | C6a | 116.9(8) | Clb | C6b | C5b | 119.6(9) |
| C2a | Cla | C6a | 122.8(9) | C 2 b | C7a | C6a | 109.8(8) |
| Olb | Cla | C2b | 120.4(8) | C 2 a | C7b | C6b' | 109.8(7) |
| Olb | C1b | C6b | 117.5(8) | C1b | C8b | C9b | 113.2(9) |
| C2b | Clb | C6b | 121.7(8) | S | C9a | C10a | 116.2(8) |
| Cla | C2a | C3a | 119.1(9) | S | C9a | C14a | 121.8(8) |
| Cla | C2a | C7b | 119.8(8) | C10a | C9a | C14a | 122(1) |
| C3a | C2a | C7b | 121.0(9) | C 8 b | C9b | C10b | 116(1) |
| Clb | C2b | C3b | 117.7(9) | C8b | C9b | C14b | 123(1) |
| Clb | C 2 b | C7a | 122.1(8) | C 10 b | C9b | C14b | 121(1) |
| C9a | C10a | Clla | 117(1) | C9a | C14a | C13a | 122(1) |
| C9b | C10b | Cllb | 119(1) | C9b | C14b | C13b | 119(1) |
| ClOa | C11a | C12a | 119(1) | C 2 s | Cls | C5s | 96(2) |
| Cl0b | C11b | C12b | 119(1) | C1s | C2s | C3s | 102(2) |
| C11a | C12a | C13a | 123(1) | C2s | C3s | C4s | 98(2) |
| Cl1a | C12a | C15a | 116(1) | C3s | C4s | C5s | 98(2) |
| C13a | C12a | C15a | 122(1) | C1s | C5s | C4s | 91(2) |
| Cllb | C12b | C13b | 120(1) | C6s | C7s | C8s | 84(2) |
| C12a | C13a | C14a | 118(1) | C7s | C8s | C8s' | 75(2) |
| C12a | C13b | C14b | 121(1) | C9b | C8b | H8b1 | 109 |
| C 2 a | C3a | H3a | 120 | C9b | C8b | H8b2 | 109 |
| C 4 a | C3a | H3a | 120 | H8b1 | C8b | H8b2 | 109 |
| C2b | C3b | H3b | 119 | C9a | C10a | H10a | 122 |
| C4b | C3b | H3b | 119 | C11a | C10a | H10a | 122 |
| C3b | C4b | H4b | 120 | C9b | C10b | H10b | 120 |
| C5b | C4b | H4b | 120 | C11b | Cl0b | H10b | 120 |
| C4a | C5a | H5a | 123 | C10a | Clla | HIla | 121 |
| C6a | C5a | H5a | 123 | C12a | Clla | H11a | 121 |
| C3s | C 4 s | H4s2 | 112 | H8s 1 | C8s | H8s | 109 |

Bond Angles for Structure III (cont.)

| Atom 1 | Atom 2 | Atom 3 | Angle | Atom 1 | Atom 2 | Atom 3 | Angle |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| C4b | C5b | H5b | 120 | C5s | C4s | H4s1 | 112 |
| C6b | C5b | H5b | 120 | C10b | C11b | H11b | 121 |
| C2b | C7a | H7a1 | 109 | C12b | C11b | H11b | 121 |
| C2b | C7a | H7a2 | 109 | C11b | C12b | H12b | 120 |
| C6a | C7a | H7a1 | 109 | C13b | C12b | H12b | 120 |
| C6a | C7a | H7a2 | 109 | C12a | C13a | H13a | 121 |
| H7a1 | C7a | H7a2 | 109 | C14a | C13a | H13a | 121 |
| C2a | C7b | H7b1 | 109 | C12b | C13b | H13b | 120 |
| C2a | C7b | H7b2 | 109 | C14b | C13b | H13b | 120 |
| C6b | C7b | H7b1 | 109 | C9a | C14a | H14a | 119 |
| C6b | C7b | H7b2 | 109 | C13a | C14a | H14a | 119 |
| H7b | C7b | H7b2 | 109 | C9b | C14b | H14b | 120 |
| O1b | C8b | H8b1 | 109 | C13b | C14b | H14b | 120 |
| O1b | C8b | H8b2 | 109 | C12a | C15a | H15a1 | 109 |
| C12a | C15a | H15a2 | 109 | C5s | C4s | H4s | 112 |
| C12a | C15a | H15a3 | 109 | H4s1 | C4s | H4s | 109 |
| H15a1 | C15a | H15a2 | 109 | C1s | C5s | H5s | 114 |
| H15al | C15a | H15a3 | 109 | C1s | C5s | H5s | 114 |
| H15a2 | C15a | H15a3 | 109 | C4s | C5s | H5s | 114 |
| C1s | C2s | H2s1 | 111 | C4s | C5s | H5s | 114 |
| C1s | C2s | H2s2 | 111 | H5s1 | C5s | H5s | 109 |
| C3s | C2s | H2s1 | 111 | C6s | C7s | H7s | 115 |
| C3s | C2s | H2s2 | 111 | C6s | C7s | H7s | 115 |
| H2s1 | C2s | H2s2 | 109 | C8s | C7s | H7s | 115 |
| C2s | C3s | H3s1 | 112 | C8s | C7s | H7s | 115 |
| C2s | C3s | H3s2 | 112 | H7s1 | C7s | H7s | 109 |
| C4s | C3s | H3s1 | 112 | C7s | C8s | H8s | 117 |
| C4s | C3s | H3s2 | 112 | C7s | C8s | H8s | 117 |
| H3s1 | C3s | H3s2 | 109 | C8s' | C8s | H8s | 117 |
| C3s | C4s | H4s1 | 112 | C8s' | C8s | H8s | 117 |

Torsion Angles for Structure III

| Atoml | Atom 2 | Atom 3 | Atom 4 | Angle |
| :---: | :---: | :---: | :---: | :---: |
| O8a | S | Ola | Cla | -167/93(0.64) |
| O8b | S | Ola | Cla | -36.57(0.70) |
| C9a | S | Ola | Cla | 79.93(0.66) |
| Ola | S | C9a | C10a | -96.21(0.83) |
| Ola | S | C9a | C14a | 76.60(0.96) |
| O8a | S | C9a | C10a | 156.33(0.84) |
| O8b | S | C9a | C10a | 20.46(0.96) |
| O8b | S | C9a | C14a | -166.73(0.88) |
| S | Ola | Cla | C2a | -106.44(0.80) |
| S | Ola | Cla | C6a | 85.09(0.86) |
| C8b | O1b | Clb | C2b | -72.25(1.06) |
| C8b | Olb | C1b | C6b | 114.79(0.94) |
| Clb | Olb | C8b | C9b | -73.66(1.05) |
| O4a | N4 | C4a | C3a | -175.05(0.96) |
| O4a | N4 | C4a | C5a | -0.75(1.39) |
| O4b | N4 | C4a | C3a | 14.38(1.45) |
| O4b | N4 | C4a | C5a | -171.32(0.99) |
| O1a | Cla | C2a | C3a | -175.46(0.82) |
| Ola | Cla | C2a | C7b | 0.03(1.24) |
| C6a | Cla | C2a | C3a | -7.71(1.42) |
| C6a | Cla | C2a | C7b | 167.79(0.88) |
| Ola | Cla | C6a | C5a | 176.86(0.76) |
| Ola | Cla | C6a | C7a | -2.25(1.42) |
| C2a | Cla | C6a | C5a | 8.85(1.35) |
| C2a | Cla | C6a | C7a | -170.26(0.93) |
| Olb | C1b | C2b | C3b | 177.23(0.82) |
| O1b | C1b | C2b | C7a | -10.40(1.31) |
| C6b | C1b | C2b | C3b | -10.11(1.37) |
| C6b | Clb | C2b | C7b | 162.26(0.88) |

Torsion Angles for Structure III (cont.)

| Atoml | Atom 2 | Atom 3 | Atom 4 | Angle |
| :---: | :---: | :---: | :---: | :---: |
| O1b | Clb | C6b | C5b | -177.79(0.87) |
| O1b | Clb | C6b | C7b ${ }^{\text {' }}$ | 2.47(1.25) |
| C 2 b | Clb | C6b | C5b | 9.34(1.44) |
| C2b | Clb | C6b | C7b' | -170.40(0.87) |
| Cla | C2a | C3a | C4a | 0.37(1.44) |
| C7b | C2a | C3a | C4a | -175.06(0.89) |
| Cla | C 2 a | C7b | C6b' | -131.19(0.90) |
| C3a | C2a | C7b | C6b | 44.22(123) |
| Clb | C2b | C3b | C 4 b | 7.01(1.50) |
| C7a | C2b | C3b | C4b | -165.55(0.97) |
| Clb | C2b | C7a | C6a | -59.40(1.15) |
| C3b | C2b | C7a | C6a | 112.82(1.00) |
| C2a | C3a | C4a | N4 | 179.40(0.91) |
| C2a | C3a | C4a | C5a | 5.77(1.61) |
| C2b | C3b | C4b | C5b | -3.15(1.68) |
| N4 | C4a | C5a | C6a | -178.01(0.83) |
| C3a | C4a | C5a | C6a | -4.19(1.49) |
| C3b | C4b | C5b | C6b | 2.10(1.68) |
| C4a | C5a | C6a | Cla | -2.92(1.30) |
| C4a | C5a | C6a | C7a | 176.31(0.87) |
| C4b | C5b | C6b | C1b | -5.10(1.57) |
| C4b | C5b | C6b | C7b' | 174.63(1.00) |
| Cla | C6a | C7a | C 2 b | 121.76(1.04) |
| C5a | C6a | C7a | C2b | -57.37(1.07) |
| Clb | C6b | C7b | C2a' | 74.86(1.09) |
| C5b | C6b | C7b' | C2a' | -104.87(1.10) |
| Olb | C8b | C9b | C10b | -102.96(1.15) |
| Olb | C8b | C9b | C14b | 82.77 (1.31) |
| S | C9a | C10a | C11a | 175.22(0.85) |

Torsion Angles for Structure III (cont.)

| Atoml | Atom 2 | Atom 3 | Atom 4 | Angle |
| :--- | :--- | :--- | :--- | :--- |
| C14a | C9a | C10a | C11a | $2.39(1.63)$ |
| S | C9a | C14a | C13a | $-175.76(0.87)$ |
| C10a | C9a | C14a | C13a | $-3.33(1.69)$ |
| C8b | C9b | C10b | C11b | $-177.14(1.12)$ |
| C14b | C9b | C10b | C11b | $-2.77(1.80)$ |
| C8b | C9b | C14b | C13b | $-178.88(1.14)$ |
| C10b | C9b | C14b | C13b | $7.16(1.80)$ |
| C9a | C10a | C11a | C12a | $-0.13(1.65)$ |
| C9b | C10b | C11b | C12b | $1.77(2.06)$ |
| C10a | C11a | C12a | C13a | $-1.21(1.78)$ |
| C10a | C11a | C12a | C15a | $-174.01(1.06)$ |
| C10b | C11b | V12b | V13b | $-5.11(2.22)$ |
| C11a | C12a | C13a | C14a | $0.43(1.77)$ |
| C15a | C12a | C13a | C14a | $172.80(1.07)$ |
| C12a | C13a | C14a | C9a | $1.91(1.72)$ |
| C12b | C13b | C14b | C9b | $-10.55(1.99)$ |

## APPENDIX E

BOND LENGTHS, BOND ANGLES, AND TORSION ANGLES FOR STRUCTURE IV

Bond Distances for Structure IV

| Atom 1 | Atom 2 | Distance $\AA$ | Atom 1 | Atom 2 | Distance $\AA$ |
| :--- | :--- | :--- | :--- | :--- | :--- |
| S8a | Ola | $1.602(4)$ | C4a | C5a | $1.37(1)$ |
| S8a | O8a | $1.422(6)$ | C4b | C5b | $1.377(8)$ |
| S8a | O8b | $1.423(5)$ | C5a | C6a | $1.386(9)$ |
| S8a | C8a | $1.734(7)$ | C5b | C6b | $1.379(9)$ |
| O1a | C9a | $1.424(7)$ | C6a | C7a | $1.51(1)$ |
| O1b | C1b | $1.395(7)$ | C6b | C7b' | $1.51(1)$ |
| O1b | C8b | $1.431(9)$ | C8a | C9b | $1.49(1)$ |
| O4a | N4 | $1.220(8)$ | C9a | C10a | $1.39(1)$ |
| O4b | N4 | $1.220(8)$ | C9a | C14a | $1.365(8)$ |
| N4 | C4a | $1.470(8)$ | C9b | C10b | $1.36(1)$ |
| C1a | C2a | $1.384(9)$ | C9b | C14b | $1.39(1)$ |
| C1a | C6a | $1.397(9)$ | C10a | C11a | $1.41(1)$ |
| C1b | C2b | $1.385(7)$ | C10b | C11b | $1.42(1)$ |
| C1b | C6b | $1.400(7)$ | C11a | C12a | $1.36(1)$ |
| C2a | C3a | $1.399(9)$ | C11b | C12b | $1.38(1)$ |
| C2a | C7b | $1.51(1)$ | C12a | C13a | $1.36(1)$ |
| C2b | C3b | $1.390(9)$ | C12a | C15a | $1.53(1)$ |
| C2b | C7a | $1.517(8)$ | C12b | C13b | $1.31(1)$ |
| C3a | C4a | $1.37(1)$ | C13a | C14a | $1.39(1)$ |
| C3b | C4b | $1.374(8)$ | C13b | C14b | $1.38(1)$ |
| C3a | H3a | 0.95 | C10b | H10b | 0.95 |
| C3b | H3b | 0.95 | C11a | H11a | 0.95 |
| C4b | H4b | 0.95 | C11b | H11b | 0.95 |
| C5a | H5a | 0.95 | C12b | H12b | 0.95 |
| C5b | H5b | 0.95 | C13a | H13a | 0.95 |
| C7a | H7a1 | 0.95 | C13b | H13b | 0.95 |
| C7a | H7a2 | 0.95 | C14a | H14a | 0.95 |
| C7b | H7b1 | 0.95 | C14b | H14b | 0.95 |
| C7b | H7b1 | 0.95 | C15a | H15al | 0.95 |
| C8b | H8b1 | 0.95 | C15a | H15a2 | 0.95 |
|  |  |  |  |  |  |

Bond Distances for Structure IV (cont.)

| Atom 1 | Atom 2 | Distance $\AA$ | Atom 1 | Atom 2 | Distance $\AA$ |
| :--- | :--- | :--- | :--- | :--- | :--- |
| C8b | H8b2 | 0.95 | C15a | H15a3 | 0.95 |
| C10a | H10a | 0.95 |  |  |  |

Bond Angles for Structure IV

| Atom 1 | Atom 2 | Atom 3 | Angle | Atom 1 | Atom 2 | Atom 3 | Angle |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| Ola | S8a | O8a | 108.1 | C3b | C2b | C7a | 119.8 |
| O1a | S8a | O8b | 109.4 | C2a | C3a | C4a | 119.5 |
| O1a | S8a | C9a | 98.1 | C2b | C3b | C4b | 120.3 |
| O8a | S8 | O8b | 118.2 | N4 | C4a | C3a | 118.9 |
| O8a | S8a | C9a | 110.6 | N4 | C4a | C5a | 117.7 |
| O8b | S8a | C9a | 110.6 | C3a | C4a | C5a | 123.4 |
| S8a | O1a | C1a | 118.1 | C3b | C4b | C5b | 120.1 |
| C1b | O1b | C1b | 113.2 | C4a | C5a | C6a | 119.3 |
| O4a | N4 | O8b | 123.0 | C4b | C5b | C6b | 121.7 |
| O4a | N4 | C4a | 118.2 | C1a | C6a | C5a | 116.4 |
| O4b | N4 | C4a | 118.8 | C1a | C6a | C7a | 123.0 |
| O1a | C1a | C2a | 118.8 | C5a | C6a | C7a | 120.4 |
| O1a | C1a | C6a | 116.0 | C1b | C6b | C5b | 117.2 |
| C2a | C1a | C6a | 125.2 | C1b | C6b | C7b | 121.5 |
| O1b | C1b | C2b | 119.9 | C5b | C6b | C7b | 121.3 |
| O1b | C1b | C6b | 117.9 | C2b | C7a | C6a | 112.4 |
| C2b | C1b | C6b | 122.0 | C1a | C7b | C6b | 114.1 |
| C1a | C2a | C3a | 115.9 | O8b | C8b | C9b | 110.2 |
| C1a | C2a | C7b | 123.2 | S8a | C9a | C10a | 117.2 |
| C3a | C2a | C7b | 120.9 | S10a | C9a | C14a | 121.3 |
| C1b | C2b | C3b | 118.4 | C8b | C9a | C14a | 121.4 |
| C1b | C2b | C7a | 121.8 | C8b | C9b | C10b | 122.8 |
| C10b | C9b | C14b | 118.9 | C13a | C12a | C15a | 120.5 |
| C9a | C10a | C11a | 117.0 | C11b | C12b | C13b | 120.9 |
| C9b | C10b | C11b | 121.0 | C12b | C13b | C14a | 121.6 |

Bond Angles for Structure IV (cont.)

| Atom 1 | Atom 2 | Atom 3 | Angle | Atom 1 | Atom 2 | Atom 3 | Angle |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| C10a | C11a | C12a | 122.5 | C12b | C13b | C14b | 122.5 |
| C10b | C11b | C12b | 117.9 | C9a | C14a | C13a | 119.2 |
| C11a | C12a | C13a | 118.2 | C9b | C14b | C13b | 118.8 |
| C2a | C3a | H3a | 120 | C9b | C8b | H8b1 | 109 |
| C4a | C3a | H3a | 120 | C9b | C8b | H8b2 | 109 |
| C2b | C3b | H3b | 120 | H8b1 | C8b | H8b2 | 110 |
| C4b | C3b | H3b | 120 | C9a | C10a | H10a | 122 |
| C3b | C4b | H4b | 120 | C11a | C10a | H10a | 122 |
| C5b | C4b | H4b | 120 | C9b | C10b | H10b | 120 |
| C4a | C5a | H5a | 120 | C11b | C10b | H10b | 120 |
| C6a | C5a | H5a | 120 | C10a | C11a | H11a | 119 |
| C4b | C5b | H5b | 119 | C12a | C11a | H11a | 119 |
| C6b | C5b | H5b | 119 | C10b | C11b | H11b | 121 |
| C2b | C7a | H7a1 | 109 | C12b | C11b | H11b | 121 |
| C2b | C7a | H7a2 | 109 | C11b | C12b | H12b | 120 |
| C6a | C7a | H7a1 | 109 | C13b | C12b | H12b | 120 |
| C6a | C7a | H7a2 | 109 | C12a | C13a | H13a | 119 |
| H7al | C7a | H7a2 | 110 | C14a | C13a | H13a | 119 |
| C2a | C7b | H7b1 | 108 | C12b | C13b | H13b | 119 |
| C2a | C7b | H7b1 | 108 | C14b | C13b | H13b | 119 |
| H7b | C7b | H7b1 | 110 | C9a | C14a | H14a | 120 |
| H7b | C7b | C6b | 108 | C13a | C14a | H14a | 120 |
| H7b | C7b | C6b | 108 | C9b | C14b | H14b | 121 |
| O1b | C8b | H8b1 | 109 | C13b | C14b | H14b | 121 |
| O1b | C8b | H8b2 | 109 | C12a | C15a | H15a1 | 109 |
| C12a | C15a | h15a2 | 109 | H15al | C15a | H15a3 | 109 |
| C12a | C15a | H15a3 | 109 | H15a2 | C15a | H15a3 | 109 |
| H15al | C15a | H15a2 | 109 |  |  |  |  |

Torsion Angles for Structure IV

| Atom1 | Atom 2 | Atom 3 | Atom 4 | Angle |
| :---: | :---: | :---: | :---: | :---: |
| O8a | S8a | Ola | Cla | -85.79(0.48) |
| O8b | S8a | O1a | Cla | 44.17(0.51) |
| C9a | S8a | Ola | Cla | 159.41(0.47) |
| Ola | S8a | C9a | C10a | -138.25(0.59) |
| Ola | S8a | C9a | C14a | $45.71(0.63)$ |
| O8a | S8a | C 9 a | C10a | 108.92(0.61) |
| O8a | S8a | C9a | C14a | -67,12(0.63) |
| O8b | S8a | C9a | C10a | -23.99(0.67) |
| O8b | S8a | C9a | C14a | 159.97(0.57) |
| S8a | Ola | Cla | C2a | 91.17(0.56) |
| S8a` | Ola | Cla | C6a | -92.43(0.52) |
| C8b | Olb | C1b | C2b | -90.90(0.67) |
| C8b | Olb | C1b | C6b | 92.06(0.66) |
| C1b | O1b | C8b | C9b | -178.66(0.45) |
| O4a | N4 | C4a | C3a | 12.34(0.77) |
| O4a | N4 | C4a | C5a | -166.24(0.53) |
| O4b | N4 | C4a | C3a | -165.61(0.53) |
| O4b | N4 | C4a | C5a | 15.82(0.77) |
| Ola | C1a | C2a | C3a | -178.22(0.45) |
| Ola | Cla | C2a | C7b | $2.50(0.76)$ |
| C6a | Cla | C2a | C3a | $5.75(0.80)$ |
| C6a | Cla | C2a | C7b | -173.53(0.51) |
| O1a | Cla | C6a | C5a | 176.99(0.45) |
| Ola | Cla | C6a | C7a | -7.78(0.74) |
| C2a | Cla | C6a | C5a | -6.87(0.81) |
| C2a | Cla | C6a | C7a | 168.36(0.52) |
| Olb | Clb | C2b | C3b | 178.80(0.58) |
| O1b | C1b | C2b | C7a | -1.33(0.97) |
| C6b | C1b | C2b | C3b | -4.29(1.00) |
| C6b | C1b | C2b | C7a | 175.58(0.62) |
| Olb | Clb | C6b | C5b | -177.72(0.57) |

Torsion Angles for Structure IV (cont.)

| Atom1 | Atom 2 | Atom 3. | Atom 4 | Angle |
| :---: | :---: | :---: | :---: | :---: |
| O1b | Clb | C6b | C7b' | 4.08(0.93) |
| C2b | Clb | C6b | C5b | 5.31(0.98) |
| C 2 | Clb | C6b | C7b' | -172.89(0.62) |
| Cla | C2a | C3a | C4a | -0.18(0.76) |
| C7b | C2a | C3a | C4a | 179.12(0.50) |
| Cla | C2a | C7b | C6b' | $60.51(0.73)$ |
| C3a | C23a | C7b | C6b' | -118.74(0.59) |
| C1b | C 2 b | C3b | C4b | 0.29(1.02) |
| C7a | C2b | C3b | C4b | -179.58(0.65) |
| C 1 b | C 2 b | C7a | C6a | -60.02(0.81) |
| C3b | C2b | C7a | C6a | 119.85(0.66) |
| C2a | C3a | C4a | N4 | 177.48(0.48) |
| C 2 a | C3a | C4a | C5a | -4.04(0.85) |
| C 2 b | C3b | C4b | C5b | 2.49(1.10) |
| N4 | C4a | C5a | C6a | -178.62(0.48) |
| C3a | C4a | C5a | C6a | 2.88(0.86) |
| C3b | C4b | C5b | C6b | -1.38(1.11) |
| C 4 a | C5a | C6a | Cla | 2.35(0.77) |
| C 4 a | C5a | C6a | C7a | -173.02(0.51) |
| C4b | C5b | C6b | C1b | -2.42(1.02) |
| C4b | C5b | C6b | C7b | 175.78(0.66) |
| C1a | C6a | C7a | C 2 b | -64.19(0.70) |
| C5a | C6a | C7a | C2b | 110.85(0.62) |
| Clb | C6b | C7b | C2a' | $67.75(0.80)$ |
| C5b | C6b | C7b | C2a' | -110.37(0.69) |
| C 2 a | C7b | C6b' | Clb' | $67.75(0.80)$ |
| C2a | C7b | C6b' | C5b | -110.37(0.69) |
| O1b | C8b | C9b | C10b | $7.19(0.80)$ |
| O1b | C8b | $\mathrm{C9b}$ | C14b | -174.75(0.53) |
| S8a | C9a | C10a | C11a | -176.10(0.66) |
| C14a | C9a | C10a | C11a | -0.07(1.14) |

Torsion Angles for Structure IV (cont.)

| Atom1 | Atom 2 | Atom 3 | Atom 4 | Angle |
| :--- | :--- | :--- | :--- | :--- |
| S8a | C9a | C14a | C13a | $175.94(0.59)$ |
| C10a | C9a | C14a | C13a | $0.07(1.08)$ |
| C8b | C9b | C10b | C11b | $177.86(0.60)$ |
| V14b | C9b | C10b | C11b | $-0.19(0.95)$ |
| C8b | C9b | C14b | C13b | $-178.32(0.62)$ |
| C10b | C9b | C14b | C13b | $-0.19(0.98)$ |
| C9a | C10a | C11a | C12a | $-0.04(1.49)$ |
| C9b | C10b | C11b | C12b | $0.41(1.02)$ |
| C10a | C11a | C12a | C13a | $0.14(1.48)$ |
| C10a | C11a | C12a | C15a | $178.49(0.97)$ |
| C10b | C11b | C12b | C13b | $-0.25(1.10)$ |
| C11a | C12a | C13a | C14a | $-0.14(1.37)$ |
| C15a | C12a | C13a | C14a | $-178.50(0.90)$ |
| C11b | C12b | C13b | C14b | $-0.13(1.20)$ |
| C12a | C13a | C14a | C9a | $0.03(1.08)$ |
| C12b | C13b | C14b | C9b | $0.36(1.13)$ |

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