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APPLICATIONS OF X-RAY DIFFRACTION
TO ORGANIC REACTION MECHANISMS

M.S. Thesis Submitted to Iowa State University,
November, 1972

C. M. Lee

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Applications of X-ray diffraction to
organic reaction mechanisms

by

Chee Man Lee

A Thesis Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
MASTER OF SCIENCE

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INTRODUCTION

The study of organic reactions has advanced tremendously in the last fifty years or so. With the help of newly developed physical techniques and improved instrumentation, identification of the products is less difficult. However, understanding of a reaction is not complete without the knowledge of the reaction mechanism. Proof of the reaction mechanism is generally impossible. In most instances, the most probable pathways are inferred or indicated by kinetic studies; the products obtained; evidences from reaction catalysis; conditions of reactions; using isotopic labelling; stereochemical studies and/or physical detection of, or trapping of an intermediate, if there is one in that reaction.

Kinetic studies exhibit the order of the reaction, the kind of reaction (consecutive, parallel, etc.), nature of transition states, rate of reaction (and so gives the activation energy, $\Delta E^\ddagger$) and the rate law. The type of catalyst can reveal the nature of the intermediate. Acid catalyzed reactions often involve a cationic intermediate, while a base catalyzed reaction proceeds through an anion. Of course, the best way to detect an intermediate is by physical means through spectroscopy, cryoscopic measurements, magnetic measurements and so on; but these measurements can be carried out only if the intermediates are long lived.

By far most reaction mechanisms are indicated by stereochemical studies and the detection of products. Organic reactions are carried out on reactants capable of existing in stereoisomeric forms and yield products that are also capable of existing in stereoisomeric forms. The stereochemistry of the products gives valuable clues to the reaction mechanism.

However, determining the stereochemistry of the products is not easy. NMR studies sometimes work. When spectroscopy fails, X-ray diffraction (or sometimes also neutron diffraction) has to be used. Very often even the determination of the nature of the product requires X-ray technique. The following structures were solved by the X-ray diffraction technique to determine the stereochemistry of the products, so as to reveal reaction mechanisms.

THE CRYSTAL STRUCTURE AND MODE OF FORMATION OF A β -LACTAM

Literature Review and Theory

The study of carbonium ion chemistry has been greatly advanced by the use of uniparticulate electrophiles [1-8], (these are reagents incapable of fragmentation -- reagents like bromine and hydrogen chloride are fragmented into two particles during reaction), whose kinetic preferences for intramolecular reactions can be utilized for trapping transient carbonium ions which could otherwise pass undetected [7-10]. Moreover, they usually add in a stereocontrolled manner, providing good inferences for the geometric strains of the intermediate [7-12]. Chlorosulfonyl isocyanate (CSI) is such a reagent. Its power to elucidate mechanistic questions has been demonstrated [1,8,11]. It also provides new modes of synthesis.

The reaction mechanism of the electrophilic addition of CSI to cis-bicyclo [6.1.0]nonatriene system (1) is of particular interest, (a) because the reaction is impressively stereocontrolled (product is only one β -lactam with a trans ring fusion), (b) because of the uniqueness in positional attack, (c) because of the high level of stereoselectivity [11], (d) because of the capability of (1) to undergo thermal and photochemical pericyclic rearrangements [13,14], (e) because of the conformational flexibility of (1) (cf. 2a and 2b),

(f) because of the different alignments of $P\pi$ and cyclopropane orbitals in the different conformations [11], (g) because the breaking of the internal cyclopropyl bond, and (h) electrophilic addition to (1) has been little evaluated [15,16,17].

In order to advance a reaction mechanism that agrees with (a), (b), (c), (d), (f), and (g), one would have to assess the relationship between conformation and potential carbonium ion stabilization. Since the electrophilic addition to (1) is unconcerted [17], it must proceed through a kinetically competitive (the most stable) carbonium ion [18-23]. Relative nucleophilicity also dictates that attack at the sp^2 -hybridized C(2), C(3), C(4), C(5), C(6) and C(7) be kinetically preferred. For example, the electrophilic addition to cyclooctatetraene or its derivatives (cf. 3, 4, 5, 6) all proceed through the homotropylium ion as shown by NMR and UV [8,18-23]. Warner and Winstein have shown by NMR that protonation of (1) with $R_1 = R_2 = H$ gives a

monocyclic 1,3-bishomotropylium ion (7) [11]. This clearly indicates that electrophilic additions to (1) prefer the attack at C(3) to give the most stable carbonium ion. The 1,3-bishomotropylium should be more stable than (8) or (9), because of more charge delocalization; and should be more stable than 1,2-, 1,4-bishomotropylium ion according to Warner and Winstein [24] (more charge resides on longer skeletons). However, that 1,3-bishomotropylium ion may be more preferred could be better explained by the theory explaining the uniqueness of positional attack to C(3) from Leo A. Paquette [11].

(8)

(9)

The reason why C(3) is more preferred is based on inductive effect [25-27] arguments of the $P\pi$ orbitals of the triene, and the cyclopropyl orbitals on adjacent cationic centers. Studies on acetolysis or solvolysis of some 2-substituted derivatives of 1-adamantyl tosylate [25-27] have indicated that the orientations of cyclopropyl and vinyl groups with respect to the adjacent cationic center, affects the stability of that cationic center, and hence the reaction

rate of that species. It was found from experiments that the most favorable geometry for an olefin group is parallel (cf. 10) since conjugative stabilization between the empty p orbital and the double bond is possible. The most unfavorable one is when two groups are orthogonal as in (cf. 11).

(10)

(11)

For a cyclopropyl group, the most favorable geometry is bisected (cf. 12, 13), where conjugation between the empty p orbital and the cyclopropyl orbitals are possible, and the most unfavorable one is the perpendicular (14).

Of considerable importance in this proposed reaction mechanism is the conformation of the triene during the electrophilic attack. There is no direct evidence in the literature concerning this in the cis-bicyclo [6.1.0]nonatriene systems. However, cyclooctatetraene and the eight-membered ring in tetraphenylene prefer the tub conformation [28, 29]. It is very probably that the cis-bicyclo [6.1.0]nonatriene also prefers the tub conformation, since the behavior in electrophilic addition of the COT and the triene systems are very similar. The orientations of p orbitals are

different with a boat model, and the mechanism described is not operative. Also, a boat configuration of the triene cannot explain why the syn-9-methyl substituted derivative was unreactive, while the anti-9-methyl isomer was reactive under the same conditions. The successful explanation and prediction of the stereochemistry of products for similar reactions could be a good indication that assuming a tub model for the species during reaction is justified.

Assuming a tub model for the triene system (2a or 2b), as the electrophile attacks C(4) and forms a bond, the vacant p orbital at C(5) of the cation cannot overlap with the neighboring vinyl group (cf. 15) since the orbitals are orthogonal to each other. Thus the cation will experience destabilization by means of inductive electron withdrawal [25-27] and the transition states leading to the carbonium ion are not expected to be attainable on a kinetically competitive basis. The cyclopropane ring is too remote to have any effect. Similar considerations applies to C(2) (cf. 16). However, when C(3) is attacked, the vacant p orbital in cf. 17 is aligned just like 13 and 12, and is in good position for maximum overlap with the internal cyclopropyl bond such that stabilization of the cationic center through delocalization is operative, and formation of the low energy 1,3-bishomotropylium ion will be an easy transformation. Conversely, the same orbitals in cf. 18 will have a

(12)

(13)

(14)

(15)

(16)

perpendicular orientation (cf. 14), and pronounced destabilization of the cationic center is encountered [25-27].

(17)

(18)

So it is predicted that electrophilic addition to cis-bicyclo [6.1.0]nonatrienes should occur at C(3) via conformer 2b, and proceed through the intermediate 1,3-bishomotropylium ion. That the syn-9-methyl substituted derivative was unreactive under the same condition is a very good support for this mechanism. Because of the steric interaction, it is highly unlikely that it forms the conformer 2b, a precursor for this mechanism.

Since the 1,3-bishomotropylium ion can assume a cis or trans conformation of the methylene bridges, and also the electrophilic reagent can exhibit preferential exo or

endo bonding to 2b, there are four possible paths from here on. The four paths are described in the next page (Figure 1). The electrophile CSI behaves exactly like $CX_2 = CY_2$ in this reaction.

The simplest way to answer which one of these paths the reaction actually goes through is by reacting an anti-9-methyl substituted derivative of (1) (i.e. $R_1 = CH_3$, $R_2 = H$ in (1)). A knowledge of the stereochemistry of the product of the reaction will show which one of the paths the reaction goes through.

The cis or trans ring fusion of the four and nine member rings can be determined by NMR spectroscopy of the hydrogenated β -lactam. However, the orientation of the methyl group requires the use of the X-ray diffraction technique.

Figure 1. A scheme showing the possible reaction pathways for the electrophilic addition of $\text{CX}_2 = \text{CY}_2$ to cis-bicyclo [6.1.0]nonatriene

Experimental

Crystal Data

β -lactam, $C_{11}H_{13}NO$,

$M = 175.23$ g/mole, $F(000) = 376e^-$,

$a = 11.535(2)\text{\AA}$, $b = 5.706(4)\text{\AA}$, $c = 16.980(2)\text{\AA}$,

$\beta = 116.55(3)^\circ$, $V = 999.75\text{\AA}^3$, $D_c = 1.16\text{g/cc}$, $Z = 4$,

$\mu = 0.80\text{cm}^{-1}$, $T \approx 25^\circ\text{C}$, $\text{Mo } K_\alpha$ ($\lambda = 0.7107\text{\AA}$).

The β -lactam crystals were kindly supplied by Professor Leo A. Paquette of the Ohio State University. The crystals were colorless needles. Preliminary oscillation and Weissenberg photographs exhibited 2/m Laue symmetry, indicating a monoclinic space group. The observed systematic extinctions of the type $Ok0$, $k = 2n + 1$ and $h0l$, $l = 2n + 1$, were consistent with the space group $P2_1/c$ (C_{2h}^5). The lattice parameters and associated errors were determined by a least-squares fit [30] to twelve independent reflection angles whose centers were determined by a left-right, top-bottom beam splitting technique using a previously aligned Hilger-Watts four-circle diffractometer.

A crystal having approximate dimensions $0.20 \times 0.25 \times 0.20$ mm mounted on a glass fibre with Du Pont Duco cement diluted with amyl acetate such that the b axis was along the spindle axis. Data were collected at room temperature utilizing a Hilger-Watts four-circle diffractometer equipped with a scintillation counter and interfaced to a SDS-910 computer in a real time mode, and using Zr-filtered $\text{Mo } K_\alpha$.

radiation. Within a two theta sphere of 60° , all data in two full octants (hkl , $h\bar{k}l$) were recorded using a stationary crystal-stationary counter technique with a take-off angle of 4.5° . A total of 3,333 peakheight data were obtained with a ten second count on each peak maximum and a five second count on each side of the peak for background measurements. About 100 reflections were taken using a θ - 2θ step-scan technique, with symmetric scan ranges of 1.00° in 2θ at low θ values to 2.20° at the high 2θ limit. An integrated intensity-peakheight conversion curve was constructed from these data; but no conversion on the data were made because the least-squares fit to this curve was almost a horizontal line, though the deviations of the $I(\text{integrated})/I(\text{peakheight})$ ratio from the mean (1.80) were greater in high 2θ reflections than those in low θ regions. Three standard reflections were observed periodically and there were no indications that decomposition had occurred during the data collection.

The intensity data were corrected for Lorentz-polarization effects. The correction for absorption was not made because of the small linear absorption coefficient of the compound ($\mu = 0.8$). The estimated error in intensity was estimated by

$$[\sigma(I)]^2 = C_T + C_B + (0.05 C_T)^2 + (0.05 C_B)^2,$$

where C_T , C_B are the total count and background count respectively. The estimated standard deviation, $\sigma(F)$, in each

structure factor was calculated from the main deviation in intensity by the method of finite differences [31]. The reciprocals of the structure factor variances, $(1/\sigma(F))^2$, were used as weights in the least-squares refinement. Exactly 1335 reflections with $|F_o|$ greater or equal to $3 \times \sigma(I)$, were considered as observed. The equivalent data had deviations ranged from 5% to 50%, with the mean at 20%, with hkl generally weaker than h $\bar{k}$ l. This is probably due to misalignments in the diffractometer.

Structure Determination and Refinement

The structure was solved by a direct method technique [32,33]. Normalized structure factors (E_h) were calculated by the formula

$$E_h^2 = (k F_o)^2 / (\epsilon \sum_{i=1}^N f_{i,o}^2 e^{-2BS^2})$$

where $|F_o|$ = measured structure factor,

k = scale factor converting $|F_o|$ to $|F_{\text{absolute}}|$,

$f_{i,o}$ = atomic scattering factor of atom i at the s value of that reflection $\vec{h}$,

N = number of atoms per unit cell,

$S = \sin \theta / \lambda$,

B = temperature factor,

ϵ = a symmetry factor which takes care of excessive intensities due to the symmetry of the reflections [34-39].

The k and B were found from a Wilson plot [40] of $\ln(\langle F_0 \rangle / \sum_i f_i^2)$ versus S^2 , to be 0.91 and 3.81 respectively. ϵ was taken as unity for all reflections; except for 0k0 and h0l reflections, which were assigned a value of 2.0 in computing the normalized structure factors.

There were 358 normalized structure factors greater than 1.5. When all the normalized structure factors greater than 1.5 were used for phasing by MULTAN [41] (a program which uses $\sum_1, \sum_2$, a weighted tangent formula, as well as a converge algorithm for choosing the starting set reflections) and also by RELA [42] (a program using only Sayre's equations), the solutions obtained were no good. Increasing the minimum $|E|$ values did not help. Finally, 156 normalized structure factors greater than 1.5 with $|F_0|$ greater than 10.0 were chosen. Both programs phased the normalized structure factors correctly. MULTAN gave the correct solution with the highest absolute figure of merit (ABS FOM), 1.014, where

$$\text{ABS FOM} = (\sum \alpha_h - \sum \alpha_r) / (\sum \alpha_e - \sum \alpha_r),$$

$$T_h = \sum_h W_h W_{h-h} |E_h E_{h-h}| \sin(\phi_h + \phi_{h-h}),$$

$$B_h = \sum_h W_h W_{h-h} |E_h E_{h-h}| \cos(\phi_h + \phi_{h-h}),$$

$$\alpha_h = |E_h| (T_h^2 + B_h^2)^{1/2},$$

$$\phi_h = \text{phase of } h,$$

$$W_h = \tanh(\frac{1}{2}\alpha_h) = \text{weight associated with the phase } \phi_{h'},$$

$$\sum \alpha_e = \sqrt{\sum_h K_{hh'}^2 + 2 \sum_{\substack{h, h'' \\ h' \neq h''}} K_{hh'} K_{hh''} \frac{I_1(K_{hh'}) I_1(K_{hh''})}{I_0(K_{hh'}) I_0(K_{hh''})}},$$

I_0, I_1 are modified Bessel functions,

$$K_{hh'} = 2 \sigma_3 \sigma_2^{-3/2} |E_h E_{h'} E_{h-h'}|,$$

$$\sigma_n = \sum_j z_j^n,$$

z = atomic number for atom j , and

$$\sum \alpha_r = \sum_n \left(\sum_h K_{hh'}^2 \right)^{1/2}.$$

Theoretically for a random phase, ABS FOM = 0. RELA gave the correct solution with the least number of cycles of iteration and the highest consistency index ($C = \langle |E_{h+h'}| \sum_{h+h'} |E_h E_{h'}| \rangle / \langle |E_{h+h'}| \sum_{h+h'} |E_h| |E_{h'}| \rangle$, where $\langle \rangle$ means 'take the average of'), when NBack = 0 (the iteration process such that newly determined signs are not used immediately in the determination of other signs not yet determined), but not when NBack = 1 (the iteration process such that newly determined signs are not used to determine additional signs until the next cycle). From the three-dimensional E synthesis [43] twelve non-hydrogen atoms were easily found (all large peaks), with reasonably good bond length and geometry. These atomic positions were refined by full matrix least-squares technique using a modified version of OR FLS [44] with refinement on $\sqrt{W} \Delta$, where W = weight, $\Delta = |F_o| - |F_c|$ (that is, minimizing $\sum W (|F_o| - |F_c|)^2$). The difference electron density map [43] revealed the thirteenth non-hydrogen atom. The 13 atoms were refined

isotropically and then anisotropically until the conventional discrepancy index of $R = (\sum (||F_o| - |F_c||)) / (\sum |F_o|)$ was 0.151 and a weighted R-factor, $R_w = (\sum w(|F_o| - |F_c|)^2) / (\sum w|F_o|^2)$, was 0.176 for the observed reflections. Eleven hydrogen atoms (except two in the methyl group) were found from the resulting difference electron density map and the atomic positions refined. The final agreement factor $R = 0.101$ and $R_w = 0.104$, with 62 reflections (4.6% of the observed data), where $|F_o - kF_c|$ were greater than five times $\sigma(F)$, were discarded. Since the symmetry equivalents are not in very good agreement, removal of these reflections seemed to be justified. The final difference electron density map showed no peaks greater than 0.3 electrons per cubic angstrom, and the agreement factor based on input parameters $(\sqrt{\sum w(|F_o| - |F_c|)^2} / (n_o - n_v))$, where n_o = number of observations, n_v = number of variables) was $1.763e^2$. The Hartree-Fock-Slater X-ray atomic scattering factor used for each element was from Hanson et al.[45].

The final positional and thermal parameters are given in Table 1, along with their standard deviations as derived from the inverse matrix of the final least-squares cycle. The largest ratio of shift to standard deviation is 0.7. A computer drawing of the molecule using ORTEP [46] with all 13 non-hydrogen atoms is shown on Figure 2. A drawing showing the inter-molecular hydrogen bonds around the screw axis is shown on Figure 3. Distances and angles with their standard

Table 1. Final atomic positional and thermal parameters with their standard deviations for the β -lactam^a

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	0.6987(5)	-0.2004(6)	-0.0281(3)	180(6)	216(12)	40(2)	9(7)	42(3)	0(4)
C(2)	0.6541(5)	-0.2854(8)	0.0365(3)	174(6)	307(16)	58(3)	-33(8)	47(3)	15(5)
C(3)	0.6788(5)	-0.1836(8)	0.1121(3)	181(6)	384(17)	52(3)	-25(9)	51(3)	15(5)
C(4)	0.7630(5)	0.0337(9)	0.1455(3)	160(6)	503(21)	48(2)	15(9)	50(3)	13(5)
C(5)	0.8973(5)	-0.0194(9)	0.1593(3)	158(6)	479(20)	44(2)	25(9)	39(3)	18(5)
C(6)	0.9579(5)	0.0587(8)	0.1121(3)	156(6)	439(19)	53(2)	26(9)	45(3)	-0(6)
C(7)	0.9109(5)	0.2097(8)	0.0345(3)	162(6)	349(17)	68(3)	-3(8)	62(4)	-4(6)
C(8)	0.7991(5)	0.2130(8)	-0.0362(3)	179(7)	274(15)	56(2)	26(8)	59(3)	19(5)
C(9)	0.6809(4)	0.0641(7)	-0.0566(2)	163(6)	265(14)	43(2)	32(7)	44(3)	12(4)
N(10)	0.6132(4)	-0.0238(8)	-0.1481(2)	209(6)	362(15)	38(2)	33(7)	32(2)	17(4)
C(11)	0.6124(5)	-0.2478(8)	-0.1244(3)	189(6)	319(17)	41(2)	42(8)	37(3)	-10(5)
C(12)	0.7678(7)	0.1155(14)	0.2354(3)	211(8)	967(39)	68(3)	-35(15)	75(4)	-104(9)
O(13)	0.5596(3)	-0.4234(5)	-0.1685(2)	246(13)	387(13)	51(2)	13(6)	33(2)	-48(4)
H(14)	0.7941(56)	-0.2291(103)	-0.0071(35)						
H(15)	0.5958(58)	-0.3894(117)	0.0190(38)						
H(16)	0.6446(50)	-0.2899(107)	0.1483(34)						
H(17)	0.7252(51)	0.1712(107)	0.0902(36)						
H(18)	0.9487(53)	-0.0934(102)	0.2124(38)						
H(19)	1.0573(59)	0.0416(98)	0.1395(35)						
H(20)	0.9827(54)	0.3181(106)	0.0404(35)						
H(21)	0.7819(52)	0.3242(109)	-0.0845(36)						
H(22)	0.6087(53)	0.1304(109)	-0.0488(34)						
H(23)	0.5647(55)	0.0292(108)	-0.2026(40)						
H(24)	0.6724(58)	0.1086(110)	0.2231(34)						

^aThe β_{ij} 's are $\times 10^4$. The hydrogen β 's are isotropic and fixed at 6.0. The form of the anisotropic temperature factor is $\exp(-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl))$. Estimated standard deviations are given in the parentheses for the least significant figure.

Figure 2. A computer generated drawing of the final X-ray model of the β -lactam

Figure 3. A computer generated drawing showing hydrogen-bonding between molecules

deviations were calculated using the variance-covariance matrix from the final least-squares cycle and ORFFE program [47]. They are shown on Tables 2 and 3. A table containing the magnitude (times ten) of the observed structure factors compared with those of the calculated structure factors are shown on Table 4.

Description and Discussion of the Result

As stated in previous discussion, the most important aspects of the structure are (1) whether the nine-and four-membered rings are trans or cis-fused, and (2) the geometry of the methyl group. As shown by the drawing and the atomic positions, the nine-and four-membered rings are clearly trans-fused, in agreement with NMR investigations, and the methyl group is cis to the α -carbonyl hydrogen. This result and further investigations with other compounds [12] indicate that the reaction pathway clearly proceeds in the 1,3-bishomotropylium ion (20) and results in the product 24.

In general, the bond lengths of the molecule agree well with previously reported values [48,49]. The C(11)-N(10) bond distance is longer than that of a normal amide (1.341Å vs. 1.325Å). Presumably contracting the C(11)-N(10)-C(9) bond angle from 122° to 94° gives the C(11)-N(10) bond more p character and consequential lengthening.

It should be noted that the N(10)-C(9) bond is lengthened from the expected 1.46Å to 1.48Å and the C(1)-C(11) bond

Table 2. Selected bond distances^a for the β -lactam

C(1)-C(2)	1.484(6)	C(7)-C(8)	1.319(6)
C(2)-C(3)	1.320(6)	C(8)-C(9)	1.500(6)
C(3)-C(4)	1.519(6)	C(9)-N(10)	1.479(5)
C(4)-C(5)	1.491(6)	C(11)-O(13)	1.236(5)
C(4)-C(12)	1.573(6)	C(11)-N(10)	1.341(5)
C(5)-C(6)	1.353(6)	C(1)-C(9)	1.570(5)
C(6)-C(7)	1.461(6)	C(1)-C(11)	1.511(5)

^aEstimated standard deviations are given in parentheses for the least significant figure. The bond distances are given in Å.

Table 3. Table of selected bond angles^a for the β -lactam

Atom	Angle in degrees
C(5)-C(4)-C(3)	109.8(4)
C(5)-C(4)-C(12)	108.9(4)
C(3)-C(4)-C(12)	110.1(4)
C(4)-C(5)-C(6)	128.0(4)
C(5)-C(6)-C(7)	130.3(5)
C(6)-C(7)-C(8)	130.4(5)
C(7)-C(8)-C(9)	128.5(4)
C(8)-C(9)-N(10)	115.7(3)
C(8)-C(9)-C(1)	119.6(4)
N(10)-C(9)-C(1)	86.1(3)
C(9)-N(10)-C(11)	94.6(3)
N(10)-C(11)-O(13)	131.2(4)
N(10)-C(11)-C(1)	93.7(3)
O(13)-C(11)-C(1)	135.1(4)
C(9)-C(1)-C(11)	84.6(3)
C(11)-C(1)-C(2)	117.6(4)
C(9)-C(1)-C(2)	120.1(3)
C(1)-C(2)-C(3)	125.4(4)
C(2)-C(3)-C(4)	123.1(4)

^aEstimated standard deviations are given in parentheses for the least significant figure.

Table 4. Observed and calculated structure factors ($\times 10$) for the β -lactam

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80																				

is the anticipated $1.51\text{\AA}$. The relatively short N(10)-H bond of $0.89\text{\AA}$ (expected $1.02\text{\AA}$) supports this analysis although the experimental uncertainty is high ($0.06\text{\AA}$) (cf. 28). The β -lactam grouping is essentially planar with an average standard deviation of $0.04\text{\AA}$ from the best least-squares plane. The internal ring angles with vertices at atoms C(11) and N(10) are 94° while those at C(1) and C(9) are 85° (cf. 29).

In the nine-membered ring, extensive conjugation with the neighboring carbon atoms can be seen. A C(2)-C(3) bond length of $1.320\text{\AA}$ agrees with a simple double C-C bond ($1.34\text{\AA}$). But the neighbors' bond lengths (C(3)-C(4), $1.519\text{\AA}$; C(1)-C(2), $1.485\text{\AA}$) clearly indicated their partial double bond character. The same kind of conjugation also exists in C(4)-C(5) ($1.491\text{\AA}$), C(5)-C(6) ($1.353\text{\AA}$), C(6)-C(7) ($1.460\text{\AA}$), C(7)-C(8) ($1.319\text{\AA}$), and C(8)-C(9) ($1.500\text{\AA}$).

C(5)-C(6) and C(7)-C(8) are double bonds. The single bond lengths of $1.570\text{\AA}$ and $1.573\text{\AA}$ for C(1)-C(9) and C(4)-C(12) respectively are slightly higher than the ordinary value of $1.54\text{\AA}$.

The bond angles in the nine-membered ring are somewhat distorted. The tetrahedrally bonded C(4) agrees well with the expected 109° , but the others have strains of from 4 to 10° . The deviations from the sp^2 -hybridized C-C-C angles in the butadiene C(5)-C(6)-C(7)-C(8) are more pronounced (about 130°) than in the double bond C(2)-C(3) (ca. 123 - 125°). The tetrahedral angles with vertices at C(9) and C(1) in the four-membered ring have a strain of about 8 - 10° . The torsional angle in the butadiene is about 42° . The torsional angle for the double bonds are $180 \pm 2^\circ$.

From the least-squares plane calculations as shown in Tables 5-9, the planes C(1)-C(2)-C(3)-C(4), C(4)-C(5)-C(6)-C(7), C(6)-C(7)-C(8)-C(9) are planar within $0.01\text{\AA}$ (torsional angles are $0.0 \pm 3.0^\circ$).

There is very extensive hydrogen bonding of the type N-H...O between molecules. The 2_1 screw along the lines $(\frac{1}{2}, y, \frac{1}{2})$ and $(\frac{1}{2}, y, \frac{1}{2})$ contain the planes of all N-H...O hydrogen bonds as shown in Figure 3. The N-H bond length was $0.89 \pm 0.06\text{\AA}$, the O-H bond length was $2.03 \pm 0.06\text{\AA}$ and the N-H-O bond length was $2.92 \pm 0.06\text{\AA}$, with angle N-H-O to

be ca. 167.5° . The interatomic distance between N and O was $2.908 \pm 0.006 \text{ \AA}$. No other abnormally short inter-molecular contacts are present.

Table 5. Least-squares plane^a for the β -lactam

Equation of least-squares plane for

C(1), C(9), N(10), C(11), O(13)

is

$$0.985X - 0.1335Y - 0.1225Z - 8.2876 = 0$$

in $\text{\AA}$ in Cartesian coordinates relative to a, b, c

Atomic distances from plane ($\text{\AA}$):

C(1)	0.05	C(9)	-0.08
N(10)	0.07	C(11)	0.01
O(13)	-0.05	H(23)	-0.01

^aThe coordinate system used for all the least-squares planes computed was:

$$X = xa \sin \gamma + cz (\cos \beta - \cos \alpha \cos \gamma) / \sin \gamma$$

$$Y = xa \cos \gamma + by + cz \cos \alpha$$

$$Z = zV / ab \sin \gamma.$$

Table 6. Least-squares plane for the β -lactam

Equation of least-squares plane for

C(1), C(9), N(10), C(11)

is

$$0.9909X - 0.0934Y - 0.0974Z - 8.3024 = 0$$

in Å in Cartesian coordinates relative to $\underline{a}$, $\underline{b}$, $\underline{c}$

Atomic distances from plane (Å):

C(1)	0.04	C(9)	-0.04
N(10)	0.05	C(11)	-0.05
H(23)	-0.04		

Table 7. Least-squares plane for the β -lactam

Equation of least-squares plane for

C(1), C(2), C(3), C(4)

is

$$0.6924X - 0.5694Y + 0.4433Z - 6.1941 = 0$$

in Å in Cartesian coordinates relative to $\underline{a}$, $\underline{b}$, $\underline{c}$

Atomic distances from plane (Å):

C(1)	-0.005	C(2)	0.011
C(3)	-0.011	C(4)	0.005

Table 8. Least-squares plane for the β -lactam

Equation of least-squares plane for

C(4), C(5), C(6), C(7)

is

$$0.076X + 0.8002Y + 0.5949Z - 2.0530 = 0$$

in Å in Cartesian coordinates relative to a, b, c

Atomic distances from plane (Å):

C(4)	0.002	C(5)	-0.005
C(6)	0.005	C(7)	-0.003

Table 9. Least-squares plane for the β -lactam

Equation of least-squares plane for

C(6), C(7), C(8), C(9)

is

$$-0.5972X + 0.6631Y + 0.4513Z + 5.0960 = 0$$

in Å in Cartesian coordinates relative to a, b, c

Atomic distances from plane (Å):

C(6)	-0.003	C(7)	0.008
C(8)	-0.008	C(9)	0.003
H(20)	-0.010	H(21)	-0.025

THE CRYSTAL STRUCTURES AND MODE OF FORMATIONS OF
 SYM-1,2,3,4-TETRACHLOROPENTACYCLO
 $[8.4.2.2^{4,9}.0^{2,10}.0^{3,9}]$ OCTADECA-6,12-DIENE
 AND
 SYM-1,2,3,4-TETRACHLOROPENTACYCLO
 $[8.4.2.2^{4,9}.0^{2,10}.0^{3,9}]$ OCTADECANE

Introduction

The study of the nature of strained carbon-carbon single bonds [50-56] and strained carbon-carbon double bonds [57-65] has aroused much interests in recent years. It is hoped that an understanding of the nature and origin of the strain, and its relationship with reactivity, can lead us to understand the nature of chemical bond in such a strained system. Reactivity is usually proportional to the degree of strain [65]. This is often explained by a lesser degree of overlap between orbitals involved, thus producing a high energy ground state. Hence breaking of this strained bond is kinetically favored. The geometry and chemical properties of some strained cycloalkanes were explained by the formation of "banana bonds" [66-69]; however, the proof is still lacking.

Strained propellances [70-79] have been given much attention because of this. Warner and LaRose had recently synthesized two new strained $[4.2.1]$ propellances (I,II) from 3,6-dihydrobenzocyclobutene, IV [80]. The reaction is outlined on the following page:

Satisfactory identification of the products I, II, III by NMR, IR, and mass spectroscopy were obtained [80]. I and II were found to be thermally stable. III, however, reacted with itself exothermically if allowed to warm to room temperature when it is neat, or when dissolved in a dipolar aprotic solvent (e.g., DMSO, DMF, acetone, acetonitrile). The reaction was found to be acid catalyzed. When III is in solution such as hexane, ether etc., it is quite stable.

The results from elementary analysis of the product indicated three chlorines, eighteen carbons and twenty hydrogens per molecule (mass spectrum, $m/e = 343$), and the existence

of at least one double bond. (NMR shows a doublet centered at τ 4.53, olefinics; multiplet at τ 6.68-8.21, aliphatics; later mass spectrum of the hydrogenated dimer shows an increase of two moles of hydrogen, $m/e = 347$, indicating two double bonds). The existence of double bonds in the product indicates that a simple $[2 + 2]$ cyclo-addition is inoperative. The reaction must involve breaking of the strained propellane bond. The mechanism of the reaction will surely dictate the stereochemistry of the product here. In order to understand what really had happened, the stereochemistry of the product has to be known. NMR, IR, UV, and mass spectroscopy failed to do this. A single crystal X-ray diffraction analysis must be carried out.

Experimental

Sym-1,2,3,4-tetrachloropentacyclo[8.4.2.2^{4,9}.
0^{2,10}.0^{3,9}] octadeca-6,12-diene, $\text{Cl}_4\text{C}_{18}\text{H}_{20}$,
Monoclinic $P2_1/n$, $a = 7.484(3) \text{ \AA}$, $b = 16.787(4) \text{ \AA}$, (A)
 $c = 13.100(3) \text{ \AA}$, $\beta = 91.05(3)^\circ$, $V = 1,645.5 \text{ \AA}^3$,
 $M = 378.17 \text{ g/mole}$, $D_c = 1.53 \text{ g/cm}^3$, $Z = 4$,
 $\mu = 7.10 \text{ cm}^{-1}$, $T = 25^\circ\text{C}$, $F(000) = 784 e^-$,
Mo K_α ($\lambda = 0.7107 \text{ \AA}$)

Crystals in the form of colorless plates of the unknown compound (A) were grown by slow evaporation of a CH_2Cl_2 solution. Weissenberg and precession photographs of

the crystal displayed 2/m Laue symmetry, indicating a monoclinic space group. Systematic extinctions of the reflection type $0k0$, $k = 2n + 1$ and $h0l$, $l = 2n + 1$ were consistent with the space group $P2_1/n$ (C_{2h}^5 alternate setting). The unit cell parameters and their standard deviations were obtained from a least-squares fit [30] to twelve independent reflection angles, whose centers were determined by a left-right, top-bottom beam splitting technique, using a previously aligned Hilger-Watts four-circle diffractometer. The crystals were observed to be air stable, and one with approximate dimensions $0.20 \times 0.10 \times 0.20$ mm was mounted along a axis (0.20 mm) on a glass fibre with Du Pont Duco cement diluted with amyl acetate. Intensity data were collected at ca. 25°C utilizing a Hilger-Watts four-circle diffractometer equipped with a scintillation counter and interfaced to a SDS-910 computer in a real time mode, and using Zr-filtered $\text{Mo K}\alpha$ radiation. Using a θ - 2θ step scan technique, $0.01^\circ/\text{step}$ counting for 0.4096 sec./step, with a take-off angle of 4.5° , two octants of data (hkl , $\bar{h}kl$) within a two theta sphere of 50° were taken. Symmetric scan ranges of 1.00° in 2θ at low 2θ values to 2.0° at high 2θ limits were used, corresponding to steps of $50 + 2$ per degree θ for each reflection. Background measurements were obtained using stationary crystal-stationary counter method for one-half the total scan time at each end of the scan. The intensities of three standard reflections were

measured periodically during the data collection. Monitoring options based on these standard counts were used to maintain crystal alignment and to test for decomposition of the crystal. No decomposition was observed during data collection. A total of 3,408 reflections were collected, and 2,897 were found to be unique. The intensity data were corrected for Lorentz-polarization effects. Because of the small linear absorption coefficient, no absorption correction was made. There were 1,630 independent reflections having $|F_o|$ greater than or equal to three times the standard deviation of intensities ($\sigma(I)$), where

$$[\sigma(I)^2] = C_T + C_B + (0.05C_T)^2 + (0.05C_B)^2$$

C_T and C_B are the total count and the background count respectively. The estimated standard deviation in each structure factor was calculated from the main deviation in intensity by the method of finite differences [31].

(i.e., $\sigma(F) = \sqrt{(I_{\text{net}} + \sigma(I))/L_p - |F_o|}$, where I_{net} is the net count, L_p is the Lorentz-polarization factor [33], and was calculated by $L_p = (1 + \cos^2(2\theta))/2\sin(2\theta)$ for each reflection.) The reciprocal of the structure factor variances were used as weights in the least-squares refinements. The equivalent reflections in the two octants were found to vary from 20% to 50% in intensity. This is probably due to misalignments in the diffractometer.

Sym-1,2,3,4-tetrachloropentacyclo[8.4.2.2^{4,9}.

0^{2,10}.0^{3,9}] octadecane, Cl₄C₁₈H₂₄,

Monoclinic P2₁/n, $a = 9.295(5) \text{ \AA}$, $b = 7.469(5) \text{ \AA}$,
 $c = 24.741(6) \text{ \AA}$, $\beta = 94.70(7)^\circ$, $V = 1,711.8 \text{ \AA}^3$, (B)

$M = 382.2 \text{ g/mole}$, $D_c = 1.48 \text{ g/cm}^3$, $Z = 4$,

$\mu = 7.17 \text{ cm}^{-1}$, $T = 25^\circ\text{C}$, $F(000) = 800 e^-$,

Mo K α ($\lambda = 0.7107 \text{ \AA}$)

The crystals of the hydrogenated form of (A) were colorless prisms. Preliminary photographs showed that it had the same Laue symmetry as well as systematic extinctions as (A), and so it belongs to the same space group P2₁/n. The crystal turned brown upon exposure to X-ray. The cell parameters and associated errors were determined by a least-squares fit to twelve independent reflection angles whose centers were determined by a left-right, top-bottom beam splitting technique, using a previously aligned Hilger-Watts four-circle diffractometer. In (B), a axis was about the same as in (A), b was about halved and c was about doubled. The packing of the molecules in the unit cell should be different in both cases. A crystal of approximate dimensions 0.13 x 0.34 x 0.26 mm was mounted on a glass fibre with Du Pont Duco cement diluted with amyl acetate such that the b axis (0.34 mm) was along the spindle. Data collection procedure was exactly the same as in (A). A total of 3,231 pieces of scanned reflection data was

collected and 2,759 were found to be unique. The intensities of three standard reflections were observed periodically by a stationary crystal-stationary counter technique on the peak maxima, and it is found that the intensities of the standards were about halved after half of the data had been collected. Since there were no further decomposition after that, and that the equivalent data (scanned data) as a whole showed no significant decrease in intensities, no decomposition correction for the scanned data was made. This phenomenon may be explained by that the effect of decomposition in this crystal mainly altered the mosaic structure of the crystals, thus spreading the peak maxima, so that only peakheight measurement was affected. Scanning over the peak maxima should still give the same integrated intensities. The intensity data were corrected for Lorentz-polarization effects. Correction for absorption was not made because of the small linear absorption coefficient of the compound. The estimated standard deviation of intensities was calculated by

$$[\sigma(I)]^2 = C_T + C_B + (0.05C_T)^2 + (0.05C_B)^2$$

where C_B and C_T are the background count and total count respectively. The estimated standard deviation in each structure factor ($\sigma(F)$) was calculated from the mean deviation in intensity by the method of finite differences [31]. The weights in the least-squares refinements were

$1/\sigma^2(F)$. Exactly 1,970 reflections with $|F_o|$ greater than or equal to three times $\sigma(I)$ were considered as observed. The intensities of equivalent reflections in both octants had deviations from 20% to 50%, with no one octant stronger than the other. This was probably due to misalignments in the diffractometer.

Solution and Refinement

Since the results from elementary analysis indicated these were three chlorine atoms, attempts to solve the structure were at first based on only three heavy atoms. The Patterson map [43] showed extensive overlapping of peaks so that interpretation of the Patterson function was difficult even after sharpening [81] to reduce the peak width. The sharpened coefficients were computed by

$$(|F_h^S|)^2 = [|F_h^O| / (\hat{f}k)]^2 \exp [(2B - B') \sin^2 \theta / \lambda^2]$$

where

$$f = \sum f_{0,j} / \sum Z_j,$$

$f_{0,j}$ is the X-ray atomic scattering factor for atom j ,

Z is the atomic number for atom j ,

k is the scale factor,

B is the overall isotropic temperature factor

B' is a variable used to minimize rippling resulting from sharpening.

Estimates of the overall temperature factor and scale factor were obtained from a Wilson plot. Using $(2B - B')$

= 3.0, the Patterson map with the best resolution was obtained. The atomic coordinates of two or three chlorines that checked out from the Patterson map were input to OR FLS [44] for refinement and the refined coordinates of these heavy atoms were used in electron density map calculations [43]. However, all these electron density maps either did not give fragments with good bond lengths or angles, or the resulting fragments chosen did not refine further, producing anything that looked like a realistic model. Hoping that direct method [32,33] could come to the rescue, a direct method solution to this problem was attempted. Normalized structure factors (E_h) were calculated by the formula

$$|E_h|^2 = |F_h|^2 / \xi \sum_{j=1}^N f_{o,j}^2$$

where

$$|F_h|^2 = K(s) I_h,$$

$F_h = \sum_{j=1}^N f_{o,j} \exp(2\pi i \vec{h} \cdot \vec{r}_j)$, is a structure factor of reflection $\vec{h}$, in absolute scale;

$f_{o,i}$ = X-ray atomic scattering factor of atom i ,

ξ = a symmetry factor [32-39],

I_h = observed intensity of reflection $\vec{h}$,

$K(s)$ = a scale factor converting I_h to $|F_h|^2$.

$K(s)$ was obtained for each reflection from a K-curve [82,83], where the observed $K(s)$ was approximated for a certain range of s ($\sin \theta / \lambda$) values by the formula

$$K(s_i) = \left[\xi \sum_{j=1}^N f_{o,j}^2 / \sum_h I_h \right]$$

where $s_i = (s_{\text{maximum}} + s_{\text{minimum}}) / 2$, for that group of

reflections, assuming $K(s)$ is constant in that s range. In this way, $K(s_i)$ can be found for a number of s intervals. Plotting these observed $K(s_i)$ versus s_i , one can obtain a curve similar to Figure 4, and the $K(s)$ for any s of the reflection can be read directly from the curve. What was actually done was that all the reflections were sorted on descending order of s . $K(s)$ was calculated as before from the observed intensities for each set of 100 reflections (except in the lowest s range, the number may be less than 100), and setting s for each set in the middle of the range. This was repeated using 150, 200 reflections per s interval. Then using the least-squares fit method, the best values of k , B and x for the analytical function $k \exp(2Bs^x)$, which is in general a good approximation to the $K(s)$ function, were found. Thus $K(s)$ for each reflection h can be approximated by

$$K(s) = k \exp(2Bs^x).$$

The finding of $K(s)$, conversion to $|F_h|$ and calculation of normalized structure factors had been coded in Fortran IV and performed by computer. The advantage of a K -curve over a Wilson plot is its ability to reveal (and so to correct) unusual qualities of the intensity distribution owing to (1) special features of the structure, or (2) errors in data taking process.

Figure 4. A K-curve

From K-curve, k (equal to Wilson plot scale factor) was 1.46, B was 4.59 and x was 1.58 (as compared with Wilson plot values: $\sqrt{k} = 1.82$, $B = 5.17$, $x = 2$). The values of $\langle E^2 \rangle$, $\langle E \rangle$ and $\langle E^2 - 1 \rangle$ after renormalization [84] as seen in Table 10 agrees with theoretical centric values [33]. Exactly 363 normalized structure factors greater or equal to 1.5 were obtained. These normalized structure factors were input to MULTAN [41] and RELA [42] for phasing. Examining the E-maps using the phased normalized structure factors from the best solutions as Fourier coefficients [43] revealed no realistic model. All these maps contained twice

Table 10. List of $\langle E^2 \rangle$, $\langle E \rangle$, $\langle E^2 - 1 \rangle$ values

	$\langle E^2 \rangle$	$\langle E \rangle$	$\langle E^2 - 1 \rangle$
Centric, theoretical	1.000	0.798	0.968
Acentric, theoretical	1.000	0.886	0.736
Diene	1.000	0.786	0.954
Hydrogenated dimer	0.965	0.788	0.922

as many peaks as it should have. Hoping that some of these maps did contain the real model, the biggest three peaks which checked in the Patterson map were put in as chorines.

Most of them gave agreement factors over 57%, but one, after refinement, gave $R = 50\%$. However, only two more atoms with reasonable bond length apart can be found. Afraid that some kind of crystallographic trap may be present, a chemical solution to this problem was sought. Since bromination or chlorination of the dimer yielded too many isomers and were difficult to isolate, the dimer was simply hydrogenated. It took up two moles of hydrogen per molecule of dimer. The hydrogenated compound formed good crystals. Although it was in the same space group, it has very different cell parameters.

The solution of this compound was also attempted by direct method. The normalized structure factors were calculated using a K-curve and the same formulae as described before. It was found that $\sqrt{k} = 1.37$, $B = 4.22$ and $x = 1.93$. The values of $\langle E^2 \rangle$, $\langle E \rangle$, $\langle E^2 - 1 \rangle$ in Table 10 were consistent with that of a centric space group. There were 342 normalized structure factors greater or equal to 1.5. The best solutions also contained too many peaks, and no realistic models could be recognized. However, all the electron density maps from the best solutions had four big peaks (those solutions were obtained from RELA or MULTAN by varying the minimum E values input). Putting three of those in as chlorines for least squares refinement led to nowhere just like the previous one. At this point, the possibility of having four chlorine atoms in the dimer was considered.

The number of chlorine was determined from the mass spectrum of the product, and it was very possible that one chlorine atom dissociated so easily that the signal at $m/e = 382$ could hardly be seen. On re-examining the mass spectrum, this conjecture was totally possible. The peak with the maximum m/e ratio of 382 was there, though the intensity was very weak. So the four big peaks in the electron density map were then taken as chlorines, and their atomic coordinates refined by OR FLS. The discrepancy index base on all observed data was 0.474. From the resulting electron density map, five more peaks with good geometry were taken as carbon atoms. After further refinements, the R-factor ($R = (\sum ||F_o| - |F_c||) / \sum |F_o|$) was 0.431. From the electron density map based on the phases produced by the input atoms, all twenty-two non-hydrogen atoms were found. The atomic positions of all twenty-two atoms were refined by full matrix least squares technique by a modified version of OR FLS [44] with refinement on $\sqrt{w}\Delta$, where $\Delta = ||F_o| - |F_c||$ and w = weight for that F_o . After refinement, first isotropically, and then anisotropically, the R-factor was 0.127. Seventy-nine observed reflections with $|F_o - kF_c|$ greater than six times $\sigma(F)$ were discarded, the final R-factor was 0.09, and the final weighted R-factor was 0.102 ($R_w = \sqrt{(\sum w\Delta^2) / (\sum w|F_o|^2)}$) for the observed data. The final difference electron density map showed no peaks greater than 0.8 electrons/ $\text{\AA}^3$. The final value of

$(\sum w\Delta^2 / (\text{NO}-\text{NV}))^{1/2}$ was 1.89. (NO = number of observed, NV = number of variables.) The Hartree-Fock-Slater X-ray atomic scattering factor used for each element were from Hanson et al [45]. The final positional and thermal parameters are given in Table 11 along with their standard deviations, as derived from the inverse matrix of the final least-squares cycle. The largest shift/standard deviation ratio is 0.12. A computer drawing of the molecule using ORTEP [46] is shown on Figure 5. Distances and angles with their standard deviations were calculated using the variance-covariance matrix from the final least-squares cycle and ORFFE [47] program. They are shown on Tables 12 and 13. Table 14 contains the magnitudes ($\times 10$) of the observed and calculated structure factors. The signs of the calculated structure factors are also shown.

With the realization that there are four chlorines per molecule instead of three, new attempts to solve the structure of the diene were made. Using the atomic positions of the three chlorines from the least-squares refinement with $R = 0.50$, an electron density map was calculated. From the number of electrons of the peaks, there were two possibilities for the fourth chlorine. But the choice could be easily made since one choice increased the R-factor, while the other lowered it. From the electron density map phased by the four chlorines, fragments of the molecule could be found. Subsequent least-squares refinement and electron

Table 11. Final atomic positional and thermal parameters with their standard deviations for the hydrogenated dimer^a

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C1(1)	-0.2559(3)	0.5779(3)	0.1810(1)	235(4)	198(5)	20(1)	18(3)	1(1)	-17(1)
C1(2)	-0.1587(2)	0.4837(3)	0.0518(1)	154(3)	197(4)	16(1)	-33(3)	-8(1)	17(1)
C1(1')	0.1194(3)	0.5127(3)	0.1903(1)	229(4)	183(4)	23(1)	-72(3)	-29(1)	1(1)
C1(2')	0.1049(2)	0.2925(3)	0.0666(1)	136(3)	279(5)	15(1)	-31(3)	-1(1)	17(1)
C(1)	-0.2967(8)	0.3864(10)	0.1373(3)	138(11)	176(16)	18(2)	-1(10)	-6(3)	-4(4)
C(2)	-0.4231(9)	0.4419(12)	0.0968(3)	172(13)	266(21)	19(2)	44(13)	-3(4)	6(5)
C(3)	-0.4844(8)	0.3053(11)	0.0522(3)	128(10)	228(18)	23(2)	-15(11)	-7(3)	-1(5)
C(4)	-0.3835(10)	0.2109(11)	0.0141(4)	184(13)	209(18)	23(2)	-26(12)	-26(4)	-6(5)
C(5)	-0.2562(8)	0.0801(11)	0.0367(3)	127(10)	236(18)	18(2)	11(11)	-19(3)	-11(4)
C(6)	-0.2144(8)	0.1204(10)	0.0959(3)	126(10)	155(15)	18(2)	-25(10)	-12(3)	1(4)
C(7)	-0.3363(8)	0.0718(11)	0.1328(3)	130(11)	198(16)	19(2)	-13(11)	-3(3)	10(4)
C(8)	-0.3479(9)	0.2279(11)	0.1712(3)	161(11)	220(18)	17(2)	2(12)	2(3)	9(4)
C(9)	-0.1682(8)	0.3231(9)	0.1060(3)	146(11)	160(14)	13(1)	-38(10)	-6(3)	5(4)
C(1')	0.0912(8)	0.2797(9)	0.1750(3)	150(11)	149(14)	14(1)	-36(10)	-10(3)	2(4)
C(2')	0.2418(8)	0.1927(11)	0.1735(3)	126(10)	264(21)	20(2)	-50(12)	-12(3)	17(5)
C(3')	0.2535(9)	-0.0038(12)	0.1656(3)	160(12)	256(20)	18(2)	-7(13)	-9(3)	-3(5)
C(4')	0.1902(8)	-0.0899(12)	0.1103(3)	137(11)	263(20)	18(2)	-2(12)	-5(3)	-4(5)
C(5')	0.0246(8)	-0.0857(11)	0.0969(3)	145(11)	213(17)	19(2)	18(11)	-6(3)	-15(4)
C(6')	-0.0621(7)	0.0577(10)	0.1242(3)	113(9)	185(15)	14(1)	-22(9)	-6(3)	3(4)
C(7')	-0.0566(8)	0.0198(10)	0.1860(3)	140(10)	186(16)	16(1)	36(10)	-4(3)	3(4)
C(8')	0.0053(9)	0.1851(11)	0.2173(3)	177(11)	204(17)	16(1)	-57(12)	-13(3)	7(4)
C(9')	-0.0042(7)	0.2524(3)	0.1224(3)	137(10)	156(14)	13(1)	-20(9)	-11(3)	1(3)

^aThe β_{ij} 's are $\times 10^4$. The hydrogen β 's are isotropic and fixed at 6.0. The form of the anisotropic temperature factor is $\exp(-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{13}hl + 2\beta_{23}kl))$. Estimated standard deviations are given in parentheses for the least significant figure.

Figure 5. A computer generated drawing of the final X-ray model of the hydrogenated dimer

Table 12. Selected bond lengths for the hydrogenated dimer^a

C(6)-C(9)	1.59	C(6')-C(9')	1.55
C(6)-C(5)	1.51	C(6')-C(5')	1.53
C(5)-C(4)	1.60	C(5')-C(4')	1.55
C(4)-C(3)	1.55	C(4')-C(3')	1.57
C(3)-C(2)	1.57	C(3')-C(2')	1.52
C(2)-C(1)	1.54	C(2')-C(1')	1.55
C(1)-C(9)	1.55	C(1')-C(9')	1.53
C(1)-C(8)	1.55	C(1')-C(8')	1.54
C(8)-C(7)	1.51	C(8')-C(7')	1.55
C(7)-C(6)	1.55	C(7')-C(6')	1.55
C(1)-Cl(1)	1.81	C(1')-Cl(1')	1.80
C(9)-Cl(2)	1.81	C(9')-Cl(2')	1.80
C(9)-C(9')	1.63		
C(6)-C(6')	1.60		

^aThe bond lengths are given in Å. Estimated standard deviations for all the bond lengths are 0.01 Å.

Table 13. Table of selected bond angles for the hydrogenated dimer^a

Atom	Angle in degrees	Atom	Angle in degrees
C(2')-C(1')-C(8')	110.3(6)	C(2)-C(1)-C(8)	107.9(6)
C(2')-C(1')-C(9')	112.8(6)	C(2)-C(1)-C(9)	109.7(6)
C(8')-C(1')-C(9')	102.8(6)	C(8)-C(1)-C(9)	108.7(6)
C(2')-C(1')-Cl(1')	107.2(5)	C(2)-C(1)-Cl(1)	106.7(5)
C(8')-C(1')-Cl(1')	111.8(5)	C(8)-C(1)-Cl(1)	109.8(5)
C(9')-C(1')-Cl(1')	111.9(5)	C(9)-C(1)-Cl(1)	114.0(5)
C(1')-C(2')-C(3')	119.5(7)	C(1)-C(2)-C(3)	119.7(7)
C(2')-C(3')-C(4')	118.0(7)	C(2)-C(3)-C(4)	121.2(6)
C(3')-C(4')-C(5')	118.4(6)	C(3)-C(4)-C(5)	122.0(7)
C(4')-C(5')-C(6')	118.0(5)	C(4)-C(5)-C(6)	110.0(6)
C(5')-C(6')-C(9')	116.6(6)	C(5)-C(6)-C(9)	112.8(6)
C(5')-C(6')-C(7')	109.4(6)	C(5)-C(6)-C(7)	112.3(6)
C(5')-C(6')-C(6)	119.4(6)	C(5)-C(6)-C(6')	120.9(6)
C(7')-C(6')-C(6)	116.2(6)	C(6')-C(6)-C(7)	109.7(6)
C(7')-C(6')-C(9')	102.5(5)	C(7)-C(6)-C(9)	109.3(6)
C(6)-C(6')-C(9')	90.5(5)	C(6')-C(6)-C(9)	89.5(5)
C(6')-C(7')-C(8')	109.1(6)	C(6)-C(7)-C(8)	106.4(6)
C(7')-C(8')-C(1')	102.6(6)	C(7)-C(8)-C(1)	102.0(6)
C(9)-C(9')-C(6')	89.5(5)	C(9')-C(9)-C(6)	88.0(5)
C(1')-C(9')-C(6')	106.2(5)	C(1)-C(9)-C(6)	99.3(6)
C(1')-C(9')-C(9)	129.3(6)	C(9')-C(9)-C(1)	135.8(6)
C(1')-C(9')-Cl(2')	107.8(5)	C(1)-C(9)-Cl(2)	104.8(5)
C(9)-C(9')-Cl(2')	109.2(4)	C(9')-C(9)-Cl(2)	107.3(5)
C(6')-C(9')-Cl(2')	113.3(5)	C(6)-C(9)-Cl(2)	123.0(5)

^aEstimated standard deviations are given in parentheses for the least significant figure.

Table 14. Observed and calculated structure factors (x10) for the hydrogenated dimer

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80																				

density map calculations revealed the whole molecule. The final R-factor with all non-hydrogen atoms was 0.150 based on full matrix least-squares refinements on $\sqrt{w}\Delta$ for all the observed reflections. Exactly 38 of the observed reflections with $|F_o - kF_c|$ are greater than six times $\sigma(F)$ were thrown out. This final R-factor was 0.111 and $R_w = 0.117$. The final value of $(\sum w\Delta^2 / (NO-NV))^{1/2}$ was 1.95. No peaks in the final difference electron density map were greater than 0.9 electrons/ $\text{\AA}^3$. Except the differences in bond length and bond angles, the ORTEP drawings of the non-hydrogen atoms of the diene and the hydrogenated dimer were alike. The two double bonds of the diene at C(3)-C(4) and C(3')-C(4') were judged from their bond lengths. The final positional and thermal parameters and its standard deviations, the bond lengths, bond angles, and the measured and calculated structure factors are shown in Tables 15, 16, 17, 18 and 19 respectively. The largest (shift/standard deviation) ratio for the positional parameters is 0.38. Methods used for calculation of all these are the same as for the hydrogenated dimer.

Table 15. Final atomic positional and thermal parameters with their standard deviations for the diene^a

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C1(1)	-0.0514(6)	0.1296(2)	0.5406(3)	556(13)	91(2)	109(3)	104(4)	-115(5)	-1(2)
C1(2)	-0.5026(5)	0.1755(2)	0.5111(2)	370(8)	58(1)	92(2)	-19(3)	77(4)	-5(1)
C1(1')	0.0647(4)	0.3320(2)	0.5008(2)	190(6)	113(2)	87(2)	-31(3)	-38(3)	-10(2)
C1(2')	-0.3862(3)	0.3338(2)	0.5466(2)	253(6)	54(1)	64(2)	16(2)	32(3)	-7(1)
C(1)	-0.1844(17)	0.1314(7)	0.4259(8)	350(32)	59(6)	77(9)	56(12)	-30(13)	-6(6)
C(2)	-0.2847(21)	0.0482(8)	0.4273(11)	500(45)	55(7)	137(13)	18(14)	0(20)	-7(8)
C(3)	-0.4473(24)	0.0348(9)	0.0348(9)	461(49)	55(8)	152(16)	-42(15)	121(23)	-24(8)
C(4)	-0.5574(19)	0.0820(11)	0.3000(13)	320(37)	68(9)	163(15)	-30(14)	24(18)	-27(9)
C(5)	-0.5553(14)	0.1679(9)	0.2830(10)	183(24)	83(8)	129(11)	-38(11)	-7(13)	-23(7)
C(6)	-0.3820(12)	0.2095(6)	0.3162(6)	160(19)	62(5)	43(6)	-13(8)	6(8)	-4(4)
C(7)	-0.2274(13)	0.1683(7)	0.2517(8)	195(22)	69(6)	77(7)	25(9)	-4(10)	-6(5)
C(8)	-0.0809(15)	0.1407(7)	0.3322(9)	268(27)	68(6)	83(9)	20(10)	5(12)	-7(6)
C(9)	-0.3202(13)	0.2005(6)	0.4260(7)	259(24)	46(5)	48(6)	-4(8)	20(10)	-5(4)
C(1')	-0.1197(14)	0.3507(8)	0.4124(8)	227(25)	81(7)	71(8)	-21(11)	-31(11)	1(6)
C(2')	-0.1759(17)	0.4371(8)	0.4288(9)	300(30)	54(6)	127(11)	0(11)	25(14)	-7(6)
C(3')	-0.3600(22)	0.4680(8)	0.3933(10)	407(40)	67(7)	120(12)	33(14)	77(18)	22(7)
C(4')	-0.5131(18)	0.4351(9)	0.3557(10)	308(33)	71(8)	105(10)	49(13)	44(15)	33(7)
C(5')	-0.5504(13)	0.3509(8)	0.3261(8)	169(21)	64(7)	93(9)	35(9)	-2(11)	4(6)
C(6')	-0.3770(11)	0.3013(6)	0.3224(6)	126(17)	60(5)	44(6)	17(7)	-3(8)	11(4)
C(7')	-0.2454(12)	0.3409(6)	0.2471(8)	142(18)	70(6)	70(7)	-15(8)	17(9)	17(5)
C(8')	-0.0638(12)	0.3370(7)	0.3048(7)	145(19)	74(6)	74(6)	-16(9)	2(9)	6(5)
C(9')	-0.2880(12)	0.2936(6)	0.4314(6)	159(19)	60(5)	60(5)	11(8)	4(9)	-1(4)

^aThe β_{ij} 's are $\times 10^4$. The hydrogen β 's are isotropic and fixed at 6.0. The form of the anisotropic temperature factor is $\exp(-(\beta_{11}h^2 + \beta_{22}k^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl))$. Estimated standard deviations are given in parentheses for the least significant figure.

Table 16. Selected bond distances^a for the diene

C(6)-C(9)	1.51(1)	C(6')-C(9')	1.57(1)
C(6)-C(5)	1.53(1)	C(6')-C(5')	1.54(1)
C(5)-C(4)	1.46(2)	C(5')-C(4')	1.49(2)
C(4)-C(3)	1.33(2)	C(4')-C(3')	1.36(2)
C(2)-C(3)	1.56(2)	C(2')-C(3')	1.54(2)
C(2)-C(1)	1.58(2)	C(2')-C(1')	1.52(2)
C(1)-C(9)	1.54(1)	C(1')-C(9')	1.61(1)
C(1)-C(8)	1.47(2)	C(1')-C(8')	1.50(1)
C(8)-C(7)	1.58(1)	C(8')-C(7')	1.54(1)
C(7)-C(6)	1.60(1)	C(7')-C(6')	1.55(1)
C(1)-Cl(1)	1.79(1)	C(1')-Cl(1')	1.81(1)
C(9)-Cl(2)	1.83(1)	C(9')-Cl(2')	1.82(1)
C(9')-C(9)	1.58(1)		
C(6)-C(6')	1.54(1)		

^aThe bond distances are in Å. Estimated standard deviations are given in parentheses for the least significant figure.

Table 17. Table of selected bond angles for the diene^a

Atom	Angle in degrees	Atom	Angle in degrees
C(1')-C(9')-C1(2')	103.7(7)	C(1)-C(9)-C1(2)	109.2(8)
C(6')-C(9')-C1(2')	123.5(7)	C(6)-C(9)-C1(2)	112.7(7)
C(1')-C(9')-C(6')	97.5(7)	C(1)-C(9)-C(6)	105.3(8)
C1(1')-C(1')-C(9')	112.8(7)	C1(1)-C(1)-C(9)	111.6(7)
C1(1')-C(1')-C(8')	110.7(7)	C1(1)-C(1)-C(8)	114.2(9)
C1(1')-C(1')-C(2')	106.5(7)	C1(1)-C(1)-C(2)	103.4(8)
C(2')-C(1')-C(8')	111.1(1.0)	C(2)-C(1)-C(8)	111.1(1.0)
C(2')-C(1')-C(9')	109.1(1.0)	C(2)-C(1)-C(9)	110.5(1.0)
C(8')-C(1')-C(9')	106.8(8)	C(8)-C(1)-C(9)	106.2(9)
C(1')-C(2')-C(3')	121.7(1.1)	C(1)-C(2)-C(3)	118.0(1.1)
C(2')-C(3')-C(4')	136.0(1.3)	C(2)-C(3)-C(4)	135.0(1.4)
C(3')-C(4')-C(5')	129.4(1.1)	C(3)-C(4)-C(5)	131.4(1.4)
C(4')-C(5')-C(6')	111.5(9)	C(4)-C(5)-C(6)	114.8(1.1)
C(9')-C(6')-C(7')	110.4(7)	C(9)-C(6)-C(7)	104.3(8)
C(9')-C(6')-C(5')	111.0(8)	C(9)-C(6)-C(5)	117.9(9)
C(7')-C(6')-C(5')	109.4(8)	C(7)-C(6)-C(5)	105.7(9)
C(6')-C(7')-C(8')	103.6(7)	C(6)-C(7)-C(8)	106.0(8)
C(7')-C(8')-C(1')	101.3(8)	C(7)-C(8)-C(1)	102.6(9)
C1(2')-C(9')-C(9)	109.8(7)	C1(2)-C(9)-C(9')	108.3(6)
C(1')-C(9')-C(9)	134.6(8)	C(1)-C(9)-C(9')	130.0(9)
C(6')-C(9')-C(9)	88.8(7)	C(6)-C(9)-C(9')	89.2(7)
C(9')-C(6')-C(6)	88.5(7)	C(9)-C(6)-C(6')	92.5(7)
C(7')-C(6')-C(6)	114.1(8)	C(7)-C(6)-C(6')	116.2(8)
C(5')-C(6')-C(6)	121.4(9)	C(5)-C(6)-C(6')	119.4(9)

^aEstimated standard deviations are given in parentheses for the least significant figure.

Table 18. Table of selected torsional angles for the diene

Atom	Angle in degrees	Atom	Angle in degrees
C(6')-C(9')-C(9)-C(6)	7.1	C(2')-C(3')-C(4')-C(5')	6.1
C(5)-C(4)-C(3)-C(2)	7.9	C(1')-C(8')-C(7')-C(6')	36.2
C(1)-C(8)-C(7)-C(6)	25.0	C(9')-C(1')-C(8')-C(7')	46.9
C(9)-C(1)-C(8)-C(7)	38.7	C(1')-C(9')-C(6')-C(7')	12.7
C(1)-C(9)-C(6)-C(7)	20.8	C(8')-C(7')-C(6')-C(9')	13.8
C(9)-C(6)-C(7)-C(8)	2.0	C(8')-C(1')-C(2')-C(3')	78.5
C(8)-C(1)-C(2)-C(3)	71.1	C(7')-C(6')-C(5')-C(4')	56.9
C(7)-C(6)-C(5)-C(4)	59.0	C(3')-C(2')-C(1')-C(9')	39.0
C(9)-C(6)-C(5)-C(4)	57.0		
C(3)-C(2)-C(1)-C(9)	46.5	C(6')-C(5')-C(4')-C(3')	11.3
C(7)-C(6)-C(6')-C(9')	-80.0	C(4')-C(3')-C(2')-C(1')	9.1
C(1)-C(9)-C(6)-C(6')	-41.3	C(1')-C(9')-C(9)-C(6)	-87.7
		C(7')-C(6)-C(9')-C(9)	-57.9
C(7)-C(6)-C(9)-C(9')	-69.3	C(5')-C(6')-C(9')-C(9)	-63.7
C(5)-C(6)-C(9)-C(9')	-47.4		

Table 19. Observed and calculated structure factors (x10) for the diene

[illegible]

Table 20. Table of selected torsional angles for the hydrogenated dimer

Atom	Angle in degrees	Atom	Angle in degrees
C(6')-C(5)-C(9)-C(9')	11.4	C(7)-C(8)-C(1)-C(9)	39.7
C(9')-C(1')-C(8')-C(7')	38.4	C(6)-C(7)-C(8)-C(1)	28.4
C(1')-C(8')-C(7')-C(6')	23.1	C(8)-C(7)-C(6)-C(9)	9.1
C(8')-C(7')-C(6')-C(9')	1.2		
C(7')-C(6')-C(9')-C(1')	25.7	C(6)-C(9)-C(1)-C(8)	32.8
C(6')-C(9')-C(1')-C(8')	40.9	C(7)-C(6)-C(9)-C(9')	-57.9
C(7')-C(6')-C(9')-C(9)	-74.6	C(1)-C(9)-C(6)-C(6')	-55.2
C(1')-C(9')-C(6')-C(6)	-37.3	C(5)-C(4)-C(3)-C(2)	62.2
C(5')-C(4')-C(3')-C(2')	67.6	C(4)-C(3)-C(2)-C(1)	52.8
C(4')-C(3')-C(2')-C(1')	65.1	C(3)-C(2)-C(1)-C(9)	55.5
C(3')-C(2')-C(1')-C(9')	61.0	C(2)-C(1)-C(9)-C(6)	84.9
C(2')-C(1')-C(9')-C(6')	78.0		
C(1')-C(9')-C(6')-C(5')	-86.3	C(6)-C(5)-C(4)-C(3)	22.0
C(9')-C(6')-C(5')-C(4')	48.3	C(5)-C(6)-C(9)-C(9')	-67.7
C(6')-C(5')-C(4')-C(3')	24.6	C(1)-C(9)-C(6)-C(6')	-55.2
C(5')-C(6')-C(9')-C(9)	-44.8		
C(1')-C(9')-C(6')-C(6)	-37.3		

Description of the Structures

The general features of the dimer and its hydrogenated form are similar except those dihedral angles, bond angles and bond lengths associated with the existence of the double bonds in the diene. A lot of the description will be common to both compounds except those explicitly stated.

Figure 5 shows the hydrogenated form. Probably because the data were not very good for both compounds, the estimated standard deviations for the bond lengths were about 0.01Å to 0.02Å. The accuracy of the bond lengths was only two decimal places. Both compounds are symmetrical on either side of the cyclobutyl ring. It is not understood, however, why the torsional angles of similar atoms on different sides showed differences of 10° or more. Comparisons of the bond lengths and bond angles for the two compounds are shown on Figures 6 and 7 respectively. The C-C single and double bonds in general agree with the reported literature values of 1.54Å for the single bond and 1.33Å for the double bond. A Cl-C distance of 1.80 to 1.83Å is slightly higher than the literature value of 1.77Å. In the diene, C(4)-C(5) and C(4')-C(5') have an interatomic distance of 1.46-1.49Å. This is more likely due to errors in the atomic positions since C(5) or C(5') does not have any π orbitals for conjugation with C(3)-C(4) or C(3')-C(4').

(A) The Diene

(B) The Hydrogenated Dimer

Figure 7. Comparison of bond angles between the diene and the hydrogenated dimer

The same kind of errors can be seen at C(1)-C(8) (1.47Å) and C(1')-C(8') (1.50Å). There are also bonds longer than normal, namely, C(1')-C(9') (1.61Å), C(6)-C(7) (1.60Å), C(7)-C(8) (1.58Å) of the diene, and C(9)-C(9') (1.63Å), C(6)-C(6') (1.60Å) and C(5)-C(4) (1.60Å) of the hydrogenated dimer, the bonds are far too long. This may be all due to slight errors in atomic positions of C(1'), C(9'), C(6'), C(6), C(7), C(8) and C(9).

As expected from the strain exerted by the four-, five-, and seven-membered rings, the bond angles are distorted from the conventional sp^3 -hybridized tetrahedral angle of 109.5° , or the sp^2 -hybridized angle of 120° . In both compounds, the angles of the cyclobutyl ring are close to 90° . The internal angles of the five-membered rings are about 104° . In the seven-membered rings, the sp^2 -hybridized angles are ca. 10° above 120° . Those sp^3 -hybridized angles are 3 to 13° greater than 109° . The angles common to both five- and seven-membered rings have values of 98° to 106° . The angles at C(1), C(1'), C(6), C(6') between the five- and seven-membered rings are close to tetrahedral. Those between the four- and five-membered ring at C(9), C(9'), C(6), C(6') showed a great deviation (C(1)-C(9)-C(9') or C(1')-C(9')-C(9) angle ca. 130° ; C(5)-C(6)-C(6') and C(5')-C(6')-C(6) are about 120° .) Cl(2) and Cl(2') are closer to the plane of the four-membered

ring than normal, as seen from the angles C(6)-C(9)-C1(12) (113°). This is true in both compounds.

The dihedral angle between the five-membered rings and four-membered ring is about 114°, that between the seven- and four-membered rings is about 140°, and that between the five- and seven-membered ring is about 74°. From the least-squares plane calculations as shown in Tables 21-28, as well as the torsional angles, the atoms C(6), C(7), C(8), C(9) (or C(6'), C(7'), C(8'), C(9')) in the five-membered ring are probably planar, with standard deviations of atoms from the plane less than 0.01, 0.01, 0.08, 0.05 Å for the four five-membered rings in two compounds.

The best least-squares plane of the four-membered rings has standard deviations for the atoms from 0.05 to 0.08 Å. The distance of any atom in the four-membered ring from the planes formed by any other three atoms was about 0.19 Å for the diene and 0.32 Å for the hydrogenated dimer. The dihedral angles between any two planes sharing an edge in the four-membered ring (as shown in Figure 8) was about 163° in the hydrogenated dimer, and about 170° in the diene. It is obvious that the four-membered ring is non-planar.

The double bonds in the diene are planar within 0.02 Å. It is interesting to see that in the diene, the standard deviations in the atoms of the planes C(3)-C(4)-C(5)-C(6), C(3')-C(4')-C(5')-C(6'), C(1)-C(2)-C(3)-C(4) and C(1')-C(2')-C(3')-C(4') are less than 0.08 Å from the least-squares

Table 21. Least-squares plane for the diene^a

Equation of least-squares plane for

C(6'), C(9'), C(6), C(9) for the diene in $\overset{\circ}{A}$
in Cartesian coordinates relative to a, b, c
is

$$0.9316X - 0.0661Y - 0.3574Z + 4.4964 = 0$$

Atomic distances from plane ($\overset{\circ}{A}$):

*C(6')	-0.05	*C(9')	0.05
*C(9)	-0.05	*C(6)	0.05
C(1)	0.98	C(2)	0.36
C(3)	-0.39	C(4)	-0.95
C(5)	-0.95	C(1')	1.25
C(2')	0.68	C(3')	-0.46
C(4')	-1.31	C(5')	-1.33

^aThe coordinate system used for all the least-squares planes computed was:

$$X = xa \sin \gamma + cz (\cos \beta - \cos \alpha \cos \gamma) / \sin \gamma$$

$$Y = xa \cos \gamma + by + cz \cos \alpha$$

$$Z = zV / ab \sin \gamma$$

Table 22. Least-squares plane for the diene

Equation of least-squares plane for

C(2), C(3), C(4), C(5) of the diene in Å⁰
 in Cartesian coordinates relative to a, b, c
 is

$$-0.6222X + 0.1037Y + 0.7759Z - 5.8068 = 0$$

Atomic distances from plane (Å):

*C(2)	0.01	*C(3)	-0.02
*C(4)	0.02	*C(5)	-0.01
C(1)	-0.33	C(6)	-0.40
C(9)	0.43		

Equation of least-squares plane for

C(2'), C(3'), C(4'), C(5') of the diene in Å⁰
 in Cartesian coordinates relative to a, b, c
 is

$$-0.3541X - 0.1646Y + 0.9206Z - 4.4574 = 0$$

Atomic distances from plane (Å):

*C(2')	0.01	*C(3')	-0.02
*C(4')	0.02	*C(5')	-0.01
C(6')	-0.38	C(1')	-0.10
C(6)	-0.18	C(8)	-0.60
C(5)	-0.01	C(9')	0.73

Table 23. Least-squares plane for the diene

Equation of least-squares plane for

C(6), C(7), C(8), C(9) of the diene in Å^o
 in Cartesian coordinates relative to a, b, c
 is

$$0.4592X + 0.8863Y - 0.0599Z - 1.5097 = 0$$

Atomic distances from plane (Å):

*C(9)	-0.01	*C(6)	0.01
*C(7)	-0.01	*C(8)	0.01
Cl(1)	-0.24	C(1)	-0.57

Equation of least-squares plane for

C(6'), C(7'), C(8'), C(9') of the diene in Å^o
 in Cartesian coordinates relative to a, b, c
 is

$$-0.2006X + 0.9424Y + 0.2679Z - 6.5603 = 0$$

Atomic distances from plane (Å):

*C(6')	-0.08	*C(7')	0.08
*C(8')	-0.05	*C(9')	0.05
Cl(1')	0.38	C(1')	0.63

Table 24. Least-squares plane for the diene

Equation of least-squares plane for

C(3), C(4), C(5), C(6) of the diene in Å⁰
 in Cartesian coordinates relative to a, b, c
 is

$$-0.4496X + 0.2035Y + 0.8697Z - 5.6550 = 0$$

Atomic distances in Å from plane:

*C(6)	-0.02	*C(5)	0.04
*C(4)	-0.05	*C(3)	0.02
C(6')	0.35	C(1)	0.31
C(2)	0.38	C(9)	1.01

Equation of least-squares plane for

C(3'), C(4'), C(5'), C(6') of the diene in Å⁰
 in Cartesian coordinates relative to a, b, c
 is

$$-0.1971X - 0.2864Y + 0.9376Z - 3.1014 = 0$$

Atomic distances from plane (Å):

*C(6')	-0.02	*C(5')	0.04
*C(4')	-0.05	*C(3')	0.03
C(6)	0.35	C(1')	0.47
C(2')	0.34	C(9')	1.23
C(8)	0.43		

Table 25. Least-squares plane for the diene

Equation of least-squares plane for

$C(1')$, $C(2')$, $C(3')$, $C(4')$ of the diene in $\overset{\circ}{A}$
in Cartesian coordinates relative to $\underline{a}$, $\underline{b}$, $\underline{c}$
is

$$-0.3423X - 0.265Y + 0.9166Z - 4.0885 = 0$$

Atomic distances from plane ($\overset{\circ}{A}$):

*C(1')	-0.01	*C(2')	0.03
*C(3')	-0.03	*C(4')	0.02
C(5')	0.05	C(6')	-0.27
C(9')	0.85	Cl(1')	0.65
C(6)	-0.01	C(8)	-0.35
C(5)	0.17		

Equation of least-squares plane for

$C(1)$, $C(2)$, $C(3)$, $C(4)$ of the diene in $\overset{\circ}{A}$
in Cartesian coordinates relative to $\underline{a}$, $\underline{b}$, $\underline{c}$
is

$$-0.5675X + 0.2509Y + 0.7842Z - 5.7955 = 0$$

Atomic distances in $\overset{\circ}{A}$ from plane:

*C(1)	-0.03	*C(2)	0.06
*C(3)	-0.08	*C(4)	0.04
Cl(1)	0.59	C(5)	0.22
C(6)	-0.00	C(9)	0.84
C(6')	0.43		

Table 26. Least-squares plane for the diene

Equation of least-squares plane for

C(1), C(9), C(6), C(7) of the diene in $\overset{\circ}{A}$
 in Cartesian coordinates relative to a, b, c
 is

$$0.6554X + 0.7533Y + 0.0553Z - 1.0785 = 0$$

Atomic distances from plane ($\overset{\circ}{A}$):

*C(9)	0.13	*C(6)	-0.12
*C(7)	0.08	*C(1)	-0.08

Equation of least-squares plane for

C(1'), C(9'), C(6'), C(7') of the diene in $\overset{\circ}{A}$
 in Cartesian coordinates relative to a, b, c
 is

$$-0.5023X + 0.8429Y + 0.1930Z - 6.4547 = 0$$

Atomic distances from plane ($\overset{\circ}{A}$):

*C(7')	-0.05	*C(6')	0.08
*C(9')	-0.07	*C(1')	1.05

Table 27. Least-squares plane for the hydrogenated dimer

Equation of least-squares plane for

C(6'), C(6), C(9), C(9') of the hydrogenated dimer
 in Å in Cartesian coordinates relative to a, b, c
 is

$$-0.3459X + 0.0444Y + 0.9372Z - 3.0934 = 0$$

Atomic distances from plane (Å):

*C(9')	-0.08	*C(6')	0.08
*C(9)	0.08	*C(6)	-0.08
C(1')	0.87	C(2')	0.32
C(3')	0.03	C(5')	-0.89
C(2)	0.72	C(3)	-0.19
CC(1)	1.26	C(5)	-1.37

Table 28. Least-squares plane for the hydrogenated dimer

Equation of least-squares plane for

C(8), C(7), C(6), C(9) of the hydrogenated dimer
 in Å in Cartesian coordinates relative to a, b, c
 is

$$0.6785X - 0.3457Y + 0.6482Z + 0.3142 = 0$$

Table 28(continued)

Atomic distances from plane ($\text{\AA}$):

*C(9)	-0.03	*C(8)	0.03
*C(6)	0.05	*C(7)	-0.05
C(1)	-0.55	Cl(1)	-0.15

Equation of least-squares plane for

C(8'), C(7'), C(6'), C(9') of the hydrogenated dimer
in $\text{\AA}$ in Cartesian coordinates relative to $\underline{a}$, $\underline{b}$, $\underline{c}$
is

$$0.9338X - 0.3565Y - 0.0300Z + 1.0266 = 0$$

Atomic distances from plane ($\text{\AA}$):

*C(7')	-0.01	*C*8')	0.01
*C(9')	-0.01	*C(6')	0.01
C(1')	0.61	Cl(1')	0.20

planes, although C(1) and C(6), or C(1') and C(6') are 0.10 to 0.33 $\text{\AA}$ away from the plane of C(2)-C(3)-C(4)-C(5) (or C(2')-C(3')-C(4')-C(5')). That is to say, C(1)-C(2)-C(3)-C(4)-C(5)-C(6) of the seven-membered ring is almost flat. In the hydrogenated dimer, the seven-membered ring is pluckered.

(A) The Diene

(B) The Hydrogenated Dimer

Figure 8. Comparison of dihedral angles in the four-membered rings

The packing of the molecules are different. The length of the molecules lie along the b axis in the dimer, but they were along the a axis in the hydrogenated compound.

Discussion

The product of the reaction has now been identified by X-ray diffraction, the next question is what the most probably mechanism would be.

In the above reaction, the following should be noted:

1. V is exactly twice the molecular weight of III, there is no loss in the number of atoms.
2. Instead of bonding to the same carbon atom as in III, the chlorines are bonded to different carbon atoms in V.
3. Existence of two double bonds in V.
4. There is no three-membered rings in the dimer, but the existence of seven-, eight- and five-membered rings on either side of the cyclobutyl ring. These rings can be formed by simply breaking the propellane bond.
5. The reaction is acid catalyzed. The reaction of III in acetic acid is very vigorous, producing a liquid

product. This is indicative for carbonium ion process.

6. The reaction proceeds in dark. This ruled out the possibility of photolysis.

7. III does not react with β -naphthyl phenyl imide,

which is a good free radical reagent [85,86]. This indicates that dimerization of III does not go through a free radical intermediate.

A logical mechanism which does not violate any of the above is outlined below:

VII, however, is to our knowledge, the first example of a bridgehead double bond in a one carbon bridge in this small a ring. Because of the geometry of the species, the $p\pi$ orbitals at C(6), and C(9) are not oriented in a very favorable position for maximum overlap. This double bond should be highly strained and very easy to break. Addition reaction is highly favored through this double bond. It is obvious that V is a $(\pi_{2s} + \pi_{2s})$ -type dimer, although the concertedness and non-concertedness of the dimerization is unestablished [87].

To establish that VII is indeed an intermediate for III, Warner and LaRose had attempted to trap VII with a diene. When one equivalent of furan was added to cold, neat V, a mixture of 1:1 adducts was formed as the reaction mixture was warmed to room temperature. VIII has been judged by NMR and mass spectroscopy to be the major product (ca. 90%) [88].

The formation of VIII in this reaction clearly indicates that III does form the intermediate VII during addition reactions of the type described.

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