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INFRARED DICHROISM STUDIES OF SOME MOLECULAR COMPLEXES

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Infrared Dichroism Studies of Some Molecular Complexes

by

R. D. Kross, K. Nakamoto and V. A. Fassel

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Ames Laboratory
at
Iowa State College
F. H. Spedding, Director
Iowa State College
Ames, Iowa

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Infrared Dichroism Studies of Some Molecular Complexes

R. D. Kross, K. Nakamoto* and V. A. Fassel

Institute for Atomic Research and Department of Chemistry
Iowa State College, Ames, Iowa

Abstract

The results of a study on the polarized infrared spectra of the hexamethylbenzene-picryl chloride, anthracene-sym-trinitrobenzene, and p,p'-dinitrodiphenyl-p-hydroxydiphenyl molecular compounds show agreement with published x-ray crystal structures. On the basis of the observed dichroism, molecular orientations are suggested for the complexes of picric acid with β -methyl-naphthalene and piperidine.

Introduction

When polarized infrared radiation passes through an anisotropic material, maximum absorption will occur if the electric vector of the incident polarized radiation is parallel to the direction of the transition moment vector of a molecular vibration. Similarly, when the vector directions are perpendicular, minimum absorption will occur. If the two vectors are at some intermediate angle, the amount of absorption depends on the magnitude of the parallel projection of the transition moment on the E-vector. Polarization data obtained from oriented single crystals are therefore very useful in determining the orientation of various bonds with respect to the crystal axes.¹⁻⁷ These data may be

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Corn Industries Research Foundation Post Doctoral Fellow, on leave from Department of Chemistry, Osaka University, Osaka, Japan.

1. R. J. Francel, J. Am. Chem. Soc., 74, 1265 (1952).
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used to confirm x-ray structural predictions and, in some cases, provide structural information which is difficult to obtain by x-ray or neutron diffraction methods. Thus Francel,¹ by studying an aggregate of oriented crystals with infrared polarized radiation, was able to determine the orientations of nitro groups substituted ortho to various groups on the benzene ring. Similarly, Waldron and Badger⁴ showed that the urea molecule is completely planar, a fact only recently ascertained through neutron diffraction studies.⁸

8. J. E. Worsham, Jr., H. A. Levy, and S. W. Peterson, paper presented at meeting of American Chemical Society, September 12-17, 1954.
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Single crystals of the well-known molecular complexes of the type formed between nitro-substituted benzenes and aromatic hydrocarbons should be particularly amenable to infrared polarization studies. Pertinent information on (1) the relative spatial configurations of the two molecules composing the complex,

(2) the arrangement of the individual complex molecules with relation to the crystal axes, and (3) the changes of orientation of individual groups due to the complex formation can be directly obtainable from the polarized spectra. In this paper the polarized spectra of five complexes of this type are presented. The crystal structure of three of these compounds were known; their polarized spectra served as a guide in interpreting the spectra of the other two molecular compounds whose structures have not been determined.

Experimental

A Perkin-Elmer Model #112 single beam universal monochromator equipped with a reflecting type microscope attachment, and a Perkin-Elmer Model #13 double beam infrared spectrophotometer, both equipped with an AgCl polarizer were used in obtaining the polarized spectra of single crystals. The optical path within the instruments were flushed with dry nitrogen.

The hexamethylbenzene-picryl chloride complex was prepared from a 1:1 mole ratio solution of both components in hot chloroform. Cooling and evaporation of the solution yielded the yellow crystalline adduct (m.p. 148°). The same procedure was followed for the anthracene-sym-trinitrobenzene complex, with the substitution of methanol for chloroform (orange, m.p. 164°). The β -methylnaphthalene and piperidine picric acid complexes were prepared by addition of β -methylnaphthalene and piperidine to hot saturated solutions of picric acid in ethanol, followed by cooling (both yellow, m.ps. 116° and 147°, respectively). The p,p'-dinitrodiphenyl-p-hydroxydiphenyl complex was prepared by cooling a warm solution of acetone containing equal amounts of

both components (yellow, m.p. 228°). The first four crystals were acicular and the latter were rectangular plates. Polarization studies were made along and perpendicular to the long axis.

Results and Discussion

In general, the infrared spectra of these molecular complexes appear to be summations of the spectra of the two components. However, small frequency shifts and band splittings of a rather complex nature do occur on complex formation.

Hexamethylbenzene-Picryl Chloride Molecular Complex

According to x-ray crystal structure data,⁹ the structure of

9. H. M. Powell and G. Huse, *Nature* 144, 77 (1939); *J. Chem. Soc.* 1943, 435.

this complex consists of alternate layers of hexamethylbenzene and picryl chloride molecules, with the planes of the molecules being perpendicular to the needle axis. Both the picryl chloride and hexamethylbenzene molecules are planar except for the ortho-nitro groups of picryl chloride, which are turned out of the plane of the ring because of the steric effect of the chlorine atom.⁹ The angle of rotation can be estimated through comparison with the 64° rotational angle of the nitro group ortho to a chlorine atom in 3,5-dichloro-4-nitroaniline.¹⁰

10. G. S. Zhdanov and G. A. Gol'der, *Zhur. fiz. Khim.* 29, 1248 (1955).

The polarization spectra of this complex shown in Figure 1 and the polarization properties summarized in Table I are in agreement with this structure. The absorption of polarized

Fig. 1 - Polarized spectra of hexamethylbenzene-picryl chloride complex.

Table I

Hexamethylbenzene (H.B.)-Picryl Chloride (P.C.)

No. of Band	Frequency (cm ⁻¹)	Assignment	Predominant Polarization ^a	Vibration Type
1	3030	Arom. C-H stretch (P.C.)	⊥	planar
2	2886 2857	Aliph. C-H stretch (H.B.)	≈ ^b	
3	1522	Asymm. NO ₂ stretch	≈	
4	1450	CH ₃ deform.	≈	
5	1338	Symm. NO ₂ stretch	⊥	planar
6	1174	C-N stretch		planar
7	1060 1054	C ₆ ring plan. degen. vib. of both rings ^c		planar
8	994	C ₆ out-of-plane (H.B.) ^c		non-planar
9	824	C ₆ out-of-plane (P.C.)		non-planar
10	784	C-H out-of-plane bend (P.C.)		non-planar
11	7717	C ₆ out-of-plane mode of both rings		non-planar

^aDenotes orientation of the electric vector, with respect to the needle axis, which shows greater absorption intensity.

^bApproximately equal intensity.

^cBased on the assignments of Mann and Thompson.²

radiation by the asymmetric and symmetric nitro stretching vibrations (bands 3 and 5) is of interest. An asymmetric nitro stretching vibration has its transition moment parallel to a line between the two nitro oxygens. If a nitro group is rotated out of the plane of the ring, the transition moment vector will have a component perpendicular to the ring, and the magnitude of the component vector is directly proportional to the cosine of the degree of rotation of that group. Since the p-nitro group in picryl chloride is probably coplanar with the benzene ring within a few degrees, its asymmetric stretching vibration should show almost pure perpendicular polarization. The o-nitro groups, however, are rotated out of the plane and should contribute to both polarization spectra. Experimentally, the sum of these absorptions appears approximately equal (band 3), confirming the appreciable rotation of the o-nitro groups out of the plane of the ring. A symmetric nitro vibration, on the other hand, has its transition moment along a line bisecting the O-N-O angle and in the plane of the ring, regardless of the angle of rotation of the group. Thus, band 5, the symmetric nitro stretching vibration, appears predominantly in the component of light perpendicular to the needle axis. The slight degree of absorption in the parallel component probably arises from imperfect orientations of the molecules.

Anthracene-sym-Trinitrobenzene Molecular Complex

In this complex, the molecules are alternately stacked in columns parallel to the needle axis and tilted about 6° from a plane perpendicular to that axis.¹¹ The polarization spectra

11. S. C. Wallwork, *Acta Cryst.*, 7, 648 (1954).

of the complex shown in Figure 2 and the polarization assignments summarized in Table II are in agreement with the published structure. The polarized spectra of the nitro stretching vibrations are again worthy of special comment, because both the symmetric and asymmetric frequencies exhibit absorption in both planes of polarization.

The nitro symmetric stretching vibration should appear solely as a planar vibration if the following conditions are fulfilled: (a) the molecules are parallel to each other; (b) the molecules are perpendicular to the needle axis; and (c) the crystal is perfect, as well as perfectly oriented with respect to the incident polarized radiation. The significant absorption of radiation which has its E-vector parallel to the needle axis (band 5) suggests that one or more of these conditions are not fulfilled. The 6° molecular tilt of the molecules with respect to the needle axis should lead to a small absorption of parallel radiation, but not to the extent indicated in the spectrum. It is therefore probable that the greatest part of the absorption arises from orientational and/or crystalline imperfections. It is generally observed that unhindered nitro groups are rotated about 6 to 10° with respect to the ring,^{2,12} but this rotation

12. E. W. Hughes, Private Communication.

would not contribute to absorption of radiation which has the E-vector parallel to the needle axis because of the reasons previously stated. However, the rotation of the nitro groups as well as the molecular tilt and the crystalline and orientational

Fig. 2 - Polarized spectra of anthracene-sym-trinitrobenzene complex.

Table II

Anthracene (A.)-sym-Trinitrobenzene (T.B.)

No. of Band	Frequency (cm ⁻¹)	Assignment	Predominant Polarization	Vibration Type
1	3030	Arom. C-H stretch of both mols.	⊥	planar
2	1620	C-C stretch of both rings	⊥	planar
3	1526	Asymm. NO ₂ stretch	⊥	planar
4	1439	C-H in plane bend of both mols.	⊥	planar
5	1341	Symm. NO ₂ stretch	⊥	planar
6	1167	C-N stretch	⊥	planar
7	1147	Ring stretch (A.)	⊥	planar
8	1068	Degen. ring stretch (T.B.)	⊥	planar
9	998	Out-of-plane ring vib. of both mols.		non-planar
10	966	Ring stretch (A.)	⊥	planar
11	917	C-H out-of-plane bend (T.B.)		non-planar
12	882	Ring stretch (A.)	⊥	planar
13	825	C ₆ out-of-plane (T.B.)		non-planar

imperfections would contribute to the absorption of this radiation by the asymmetric nitro stretching vibrations. If the rotation of the nitro groups is within the usual limits of 6 to 10°, the absorption of the parallel radiation by this vibration should not be significantly greater than the corresponding absorption by the symmetric vibration. The approximate equal intensity of the symmetric and asymmetric nitro stretching modes (bands 5 and 3, respectively) suggests that the nitro groups retain their basic coplanarity in the complex.

p,p'-Dinitrodiphenyl-p-Hydroxydiphenyl Molecular Complex

In this structure the dinitrodiphenyl molecules are in a 3:1 ratio with respect to the hydroxydiphenyl molecules,¹³ and

13. D. H. Saunder, Proc. Roy. Soc. (London), A188, 31 (1946).

there are no apparent strong intermolecular interactions. The dinitrodiphenyl molecules lie in the ab plane of the crystal and the hydroxydiphenyl molecules are arranged with their lengths nearly normal to that plane (i.e. along the c-axis). A large single crystal of the complex was placed over the slit of the Model #13 instrument and the polarizer was mounted between the sample and the source. The resulting strongly polarized spectra, as shown in Figure 3 and summarized in Table III, completely agree with the published structure.

β-Methyl Naphthalene-Picric Acid Molecular Complex

The over-all strong dichroism shown by the polarized spectra of this complex in Figure 4 indicates that the molecular components are stacked closely perpendicular to the needle axis of the

Fig. 3 - Polarized spectra of p,p'-dinitrodiphenyl-p-hydroxydiphenyl complex.

Table III

p,p'-Dinitrodiphenyl (D.D.)-p-Hydroxydiphenyl (H.D.)

No. of Band	Frequency (cm ⁻¹)	Assignment	Predominant Polarization	Vibration Type
1	3315	O-H stretch	⊥	planar
2	3088	C-H stretch (H.D.)		planar
3	3150	C-H stretch (D.D.)	⊥	planar
4	1505	Asymm. NO ₂ stretch	⊥	planar
5	1352	Sym. NO ₂ stretch	⊥	planar
6	1178	C-N stretch	⊥	planar
7	7770	C-H out-of-plane bend (H.D.)	⊥	non-planar
8	7740 7733	C ₆ out-of-plane deform. (D.D.)		non-planar

crystal. The polarization properties of the individual bands as listed in Table IV give more information pertinent to the structure of the complex. The O-H group of picric acid is surrounded by two ortho-nitro groups, one of which forms a hydrogen bond with the O-H group, while the other is rotated out of the plane of the ring by the steric influence of the O-H group. The para nitro group of picric acid is expected to be basically coplanar with the ring. Some idea as to the magnitude of rotation of the one ortho nitro group can be obtained from the fact that the dihedral angle for the two ortho nitro groups in potassium picrate is about 27°. ¹² This rotation results in absorption, by the asymmetric stretching vibration of one ortho nitro group, of radiation which has an E-vector parallel to the needle axis (band 4, Fig. 4 and Table IV). The symmetric nitro stretching vibrations

Fig. 4 - Polarized spectra of β -methyl naphthalene-picric acid complex.

Table IV

 β -Methyl Naphthalene (M.N.)-Picric Acid (P.A.)

No. of Band	Frequency (cm ⁻¹)	Assignment	Predominant Polarization	Vibration Type
1	3030	Arom. C-H stretch of both mols.	$\perp$	planar
2	2884	Aliph. C-H stretch	$\approx$	
3	1630 1608	C-C stretch of both rings	$\perp$	planar
4	1533 1505	Asymm. NO ₂ stretch	$\perp$	planar
5	1422	Arom. C-H in-plane bend of both mols.	$\perp$	planar
6	1339	Symm. NO ₂ stretch	$\perp$	planar
7	1259	O-H in-plane bend	$\perp$	planar
8	1148	C-N stretch	$\perp$	planar
9	1082	Degen. ring stretch (P.A.)	$\perp$	planar
10	1038	Degen. ring stretch (M.N.)	$\perp$	planar
11	960 944	Ring stretch (M.N.)	$\perp$	planar
12	913	Ring stretch (P.A.)	$\perp$	planar
13	895	C _{ar} -CH ₃ stretch	$\perp$	planar
14	865	Ring stretch (M.N.)	$\perp$	planar
15	823	C-H out-of-plane bend (M.N.) and C ₆ out-of-plane bend (P.A.)	$\parallel$	non-planar
16	778	C-H out-of-plane bend (P.A.)	$\parallel$	non-planar

(band 6) show little absorption of the parallel radiation because the nitro group rotation does not alter the orientation of the vector moment.

Piperidine-Picric Acid Molecular Complex

Because of the probable non-planarity of the piperidine molecule, the dichroism of this complex, as shown in Figure 5, is not very strong. There are, however, a few bands from which the approximate structure of the complex can be inferred. These are the bands numbered 1, 3 and 4 in Figure 5 and Table V. The overlap of the planar C-N stretching vibration in picric acid with the non-dichroic CH₂ twisting vibration in piperidine¹⁴

14. H. Voetter and H. T. Shamler, *Monatsh.* 84, 134 (1953).

probably accounts for the greater intensity of band 4 in the a-spectrum. The predominant appearance of bands 1 and 4 in the a-direction indicates that the N-H bond in piperidine is parallel to the C-N bond and therefore the picric acid ring. Since the N-H frequency in the complex (3267 cm⁻¹) is shifted to a lower frequency as compared with its value in dilute solution (3344 cm⁻¹), a hydrogen bond involving the N-H and a nitro group is suggested. If this is so, the appearance of the N-H vibration only in the a-direction requires that the N-H bond not only be parallel to but actually coplanar with the picric acid ring. It has been shown¹⁵ that the stability of the piperidine-picric acid complex

15. R. D. Kross and V. A. Fassel, unpublished.

arises from the transfer of a lone-pair electron from the nitrogen atom of piperidine to an accepting orbital of a nitro group in picric acid. It was further indicated that the nitro group

Fig. 5 - Polarized spectra of piperidine-picric acid complex.

Table V

Piperidine (P.)-Picric Acid (P.A.)

No. of Band	Frequency (cm ⁻¹)	Assignment	Predominant Polarization	Vibration Type
1	3267	N-H stretch (P.)	⊥	planar
2	2967 2915	Overlap of C-H and CH ₂ stretch of both mols. with bonded O-H stretch	⊥	planar
3	a1544 b1527 c1515	Asymm. NO ₂ stretch	⊥	planar
4	1159	Overlap of CH ₂ twist. (P.) with C-N stretch (P.A.)	⊥	planar
5	786	Overlap of CH ₂ rock. (P.) with C-H out-of-plane bend (P.A.)		non-planar

involved in the charge-transfer interaction had the highest asymmetric stretching frequency of the three nitro groups in picric acid. Figure 5 shows that the highest nitro asymmetric frequency (band 3a) is perfectly polarized in the a-direction. This indicates that the nitro group involved in the interaction is coplanar with the N-H bond, and with the picric acid ring. Since one of the ortho nitro groups is involved in an intramolecular hydrogen bond, and the other is rotated out of the plane of the ring, the para nitro group appears to be the one involved in the intermolecular bond.

The small absorption of parallel radiation shown by band 3 arises from the rotated ortho nitro group. The dichroic nature of bands 2 and 5 agree with the above-proposed structure.*

*X-ray crystallographic data were obtained by one of the authors (K. N.) for the piperidine-picric acid complex. The crystal was found to be triclinic, of space group P_1 or $P_{\bar{1}}$, and of approximate density 1.60. The dimensions of the unit cell are as follows; $a = 8.8\text{\AA}$, $b = 12.1\text{\AA}$, $c = 6.92\text{\AA}$ (needle axis), $\alpha = 92^\circ$, $\beta = 93^\circ$, $\gamma = 108^\circ$, and the number of complex molecules per unit cell is 2.