

[CONTRIBUTION FROM THE STAMFORD RESEARCH LABORATORIES, AMERICAN CYANAMID COMPANY]

Polarized Infrared Radiation in the Study of the Molecular Structure of Substituted Nitrobenzenes

BY RUDOLPH J. FRANCEL

Infrared spectra are presented for five ortho-substituted nitrobenzene compounds in the solid phase using polarized radiation and linearly oriented preparations. The molecular structure of these compounds is interpreted on the basis of known vibrational assignments of certain absorption bands and the behavior of these bands toward polarized infrared radiation. *o*-Nitrophenol, 2-nitroresorcinol and *o*-nitroaniline are found to be planar molecules while *o*-nitrobromobenzene and *o*-nitrochlorobenzene are found to be non-planar.

Introduction

The interaction between unpolarized infrared radiation and a particular transition moment is a function of the component of that moment in a plane perpendicular to the direction of propagation of the radiation. When unpolarized infrared radiation traverses a random arrangement of molecules (a gas, a liquid or a powdered or amorphous solid), there is an equal probability of interaction between the E-vector of the radiation and the transition moments associated with each of the various vibrational modes. However, this condition may not prevail when an anisotropic material (*e.g.*, a single crystal) is examined with unpolarized radiation. In this case it is possible for the transition moment arising from a given vibration to have a preferred orientation parallel to the direction of propagation of the radiation which would prohibit any absorption by that particular mode. This effect was used by Barnes, *et al.*,¹ to explain a discrepancy in the analysis of penicillin which resulted from orientation of the sample.

When plane polarized infrared radiation and an anisotropic material are used, the component of the transition moment along the E-vector of the incident radiation will determine their interaction. The intensity of the absorption will be a maximum when the transition moment is parallel to the E-vector and no absorption will occur when they are perpendicular. The polarization data which may be obtained in this manner have been applied in various ways in the recent literature. In this connection the classification and selection rules of Halford^{2,3} and Hornig⁴ are frequently useful in the interpretation of crystalline spectra.

The use of polarized infrared radiation has led to information regarding the position of various bonds with respect to the crystal axes.^{5,6} Newman and Halford⁷ were able to correlate the polarization data for single crystals of certain nitrates with the structure reported from X-ray data. By using polarized infrared radiation and micro techniques, Waldron and Badger⁸ showed that urea was a planar molecule because four NH stretching frequencies were observed. Elliott, Ambrose and Temple⁹ have investigated the structure of poly-

mers in the form of stretched or rolled films. Polarization data have also been used to check the classification of vibrational frequencies into their respective symmetry species.¹⁰ In the present work the behavior of certain absorption bands of known assignment toward polarized infrared radiation is used to determine the molecular structure of some substituted nitrobenzene compounds. No attempt has been made to obtain quantitative results or to determine the position of the molecules with respect to the crystal axes.

Experimental

As an ideal case it would be desirable to examine with polarized infrared radiation a single crystal of a given compound in the form of several thin sections each containing the various pairs of crystal axes. However, it is quite difficult to prepare a sufficiently thin section (*ca.* 0.01 mm.) of a single crystal with the requisite area. Newman and Halford⁷ have succeeded in obtaining certain ionic crystals which were somewhat suitable for study. In principle, this difficulty may be overcome by the use of a reflecting microscope^{8,11,12} which would decrease the sample area required. However, with the instrumentation available in these laboratories the introduction of both a polarizer and a reflecting microscope into the optical path resulted in an excessive attenuation of the energy.

The preparations used for the spectra described here were obtained by allowing the molten material to crystallize while subject to a temperature gradient. This method, which usually resulted in a linearly oriented solid, was similar to that previously described¹⁰ except that the temperatures used were adjusted to allow for differences in melting points. The success of this rather simple method was found to vary considerably among the compounds tried. The sample thickness in each of the spectra reported here is estimated to be about 0.01 mm.

The polarizer, which was constructed in a manner similar to that described by Elliott, Ambrose and Temple,¹³ consisted of five selenium films inclined at an angle of *ca.* 25° to the optical path. Its efficiency was indicated by the fact that certain intense absorption bands completely disappeared as the plane of polarization was rotated.

All spectra were obtained with a Perkin-Elmer spectrometer, Model 12A, using a sodium chloride prism. Polarized visible light was used to select the most desirable area of the preparation to place in the spectrometer beam. Various orientations of the E-vector and sample with respect to each other were accomplished by rotation of the polarizer while the sample was kept in a fixed position with the direction of crystal growth parallel to the spectrometer slit. This procedure eliminated any ambiguity that might result from variations in sample thickness if the sample were rotated.

The chemicals were obtained from the Eastman Kodak Company and used without further purification. All spectra were corrected for scattering losses and replotted to a per cent. transmittance scale.

Discussion

The interpretation of the polarization data is

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- (2) R. S. Halford, *J. Chem. Phys.*, **14**, 8 (1946).
- (3) H. Winston and R. S. Halford, *ibid.*, **17**, 607 (1949).
- (4) D. F. Hornig, *ibid.*, **16**, 1063 (1948).
- (5) D. A. Crookes, *Nature*, **160**, 17 (1947).
- (6) A. V. Jones and G. B. M. Sutherland, *ibid.*, **160**, 567 (1947).
- (7) R. Newman and R. S. Halford, *J. Chem. Phys.*, **18**, 1276 (1950).
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- (9) A. Elliott, E. J. Ambrose and R. B. Temple, *ibid.*, **18**, 877 (1948); *Proc. Roy. Soc. (London)*, **A198**, 188 (1949).

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- (11) J. R. Loofbourow, *J. Optical Soc. Am.*, **40**, 317 (1950).
- (12) E. R. Blout, G. R. Bird and D. S. Grey, *ibid.*, **40**, 304 (1950).
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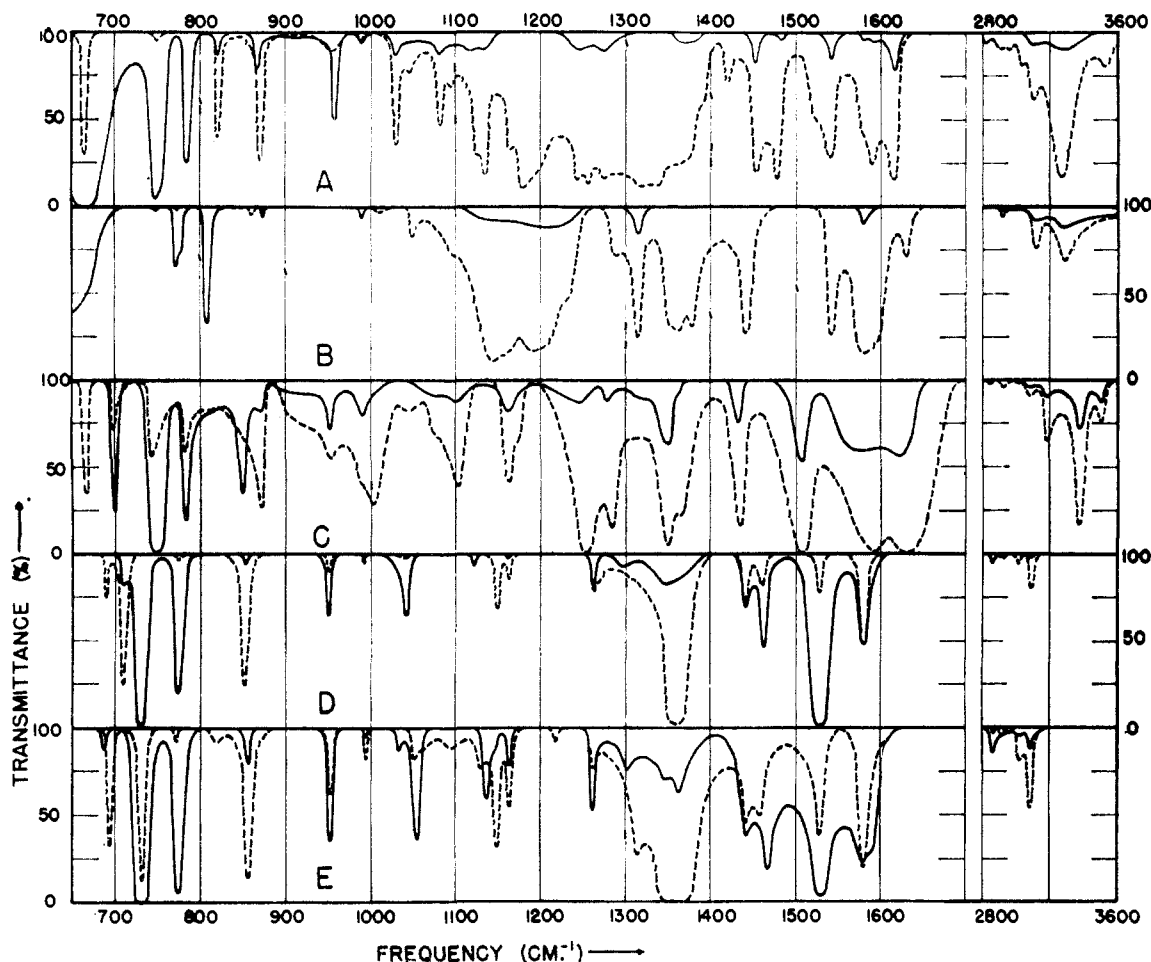


Fig. 1.—Infrared spectra of linearly oriented preparations with: (1) E-vector parallel to the direction of crystal growth ---, and (2) E-vector perpendicular to the direction of crystal growth ——. Estimated thickness: *ca.* 0.01 mm.; A, *o*-nitrophenol; B, 2-nitroresorcinol; C, *o*-nitroaniline; D, *o*-nitrochlorobenzene; E, *o*-nitrochlorobenzene.

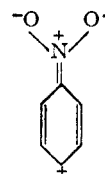
somewhat simplified when the molecules in a crystal have similar orientations, since then it is sufficient to consider only the directions of the individual molecular transition moments. For this reason the present study has been confined to substituted benzene compounds since their rings are frequently parallel or nearly parallel in the crystal. In particular, it was desired to demonstrate the application of the method in the determination of the geometry of the nitro group on a benzene ring in the presence of ortho substituents.

In the compounds studied it is assumed that the CN bond is in the plane of the ring and collinear with a line bisecting the ONO angle. Therefore, the symmetric NO₂ stretching vibration is planar regardless of the angle of twist of the plane of the nitro group about the CN axis.

Since the transition moment for the asymmetric NO₂ stretching vibration is parallel to a line connecting the two oxygen atoms, it is possible to determine whether or not the nitro group and the ring are coplanar. If the absorption band associated with the asymmetric NO₂ stretching vibration exhibits the same polarization characteristics as those bands arising from known planar vibrations, it is concluded that the nitro group is coplanar with the benzene ring and *vice versa*. The

intermolecular coupling exhibited by the nitro group and by the phenyl group may be expected to have the same geometrical form for a planar molecule, and to be different for the non-planar case. Thus by directly comparing the band polarizations arising from these groups, the effect of intermolecular coupling on direction of the transition moment largely cancels out. Similarly, it should be possible to obtain information regarding the geometry of the amine group for ring-substituted aniline compounds which could not be determined from X-ray diffraction data.

In the absence of steric effects the nitro group would be expected to be coplanar with the ring because of resonance with structures typified by¹⁴



However, it is well known that sufficiently large ortho substituents would cause the nitro group to

(14) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1942, p. 222.

rotate about the CN axis so that the oxygen atoms would be out of the plane of the ring.¹⁴ These effects are illustrated by the structure of picryl iodide (2,4,6-trinitroiodobenzene) where it has been shown¹⁵ by X-ray diffraction methods that the two nitro groups adjacent to the iodine atom are out of the plane of the ring while the nitro group which is para to the iodine is coplanar with the ring.

From a study of the lower nitro-paraffins, Smith, Pan and Nielsen¹⁶ have assigned the absorption band at about 1580 cm^{-1} to the asymmetric NO_2 stretching vibration and that at about 1375 cm^{-1} to the symmetric stretching vibration. Empirical correlations obtained in these laboratories have shown that the symmetric and asymmetric NO_2 stretching vibrations absorb at about 1360 and 1530 cm^{-1} , respectively, for nitrobenzene-type compounds.

Observed Spectra and Results

o-Nitrophenol.—The spectra obtained for *o*-nitrophenol are shown in Fig. 1A (the region from 1700 to 2800 cm^{-1} has been omitted to conserve space). In Table I certain key absorption bands are tabulated together with their respective assignments, polarization characteristics, and type (*i.e.*, planar or non-planar). In addition to the tabulated absorption bands, other correlations may be observed such as the ring vibrations which absorb at 1475, 1580 and 1620 cm^{-1} . Incomplete polarization of some of the absorption bands may be due to imperfect orientation of the sample upon crystallization or to a slightly non-parallel arrangement of the planes of the benzene rings in the crystal.

The planar or non-planar nature of the following tabulated vibrations is independent of the geometry of the nitro or hydroxyl groups: CH bend, symmetric NO_2 stretch and CH stretch. By comparison of the polarization characteristics of the absorption bands associated with these vibrations and that for the asymmetric NO_2 stretching vibration, the latter vibration is found to be either planar or non-planar. In the case of *o*-nitrophenol the absorption band at 1540 cm^{-1} , attributed to the asymmetric stretching vibration, has the same polarization characteristics (in a qualitative sense) as those absorption bands associated with planar vibrations. Similarly, the bonded OH stretching vibration, which absorbs at 3270 cm^{-1} , is found to be planar. It is concluded that both the nitro group and the OH bond are in the plane of the benzene ring. This conclusion is in agreement with the well-known fact that the hydroxyl group forms a strong intramolecular hydrogen bond with the oxygen atom of an adjacent nitro group.¹⁷ Since no steric effects are present in this case, the nitro group would also be expected to be coplanar with the ring because of resonance.

The observed absorption bands arising from planar vibrations are of maximum intensity when the E-vector is perpendicular to the direction of crystal growth. Therefore, the plane of the benzene ring must be approximately perpendicular to the

(15) G. Huse and H. M. Powell, *J. Chem. Soc.*, 1398 (1940).

(16) D. C. Smith, C. Y. Pan and J. R. Nielsen, *J. Chem. Phys.*, **18**, 708 (1950).

(17) Reference 14, p. 318.

TABLE I
ASSIGNMENT, POLARIZATION AND TYPE OF OBSERVED ABSORPTION BANDS

Compound	Vibration	Frequency (cm^{-1})	Polarization ^a	Type
	CH bend	{ ~650 } 748 784		Non-planar
<i>o</i> -Nitrophenol	Symm. NO_2 stretch	~1360	⊥	Planar
	Asymm. NO_2 stretch	1540	⊥	Planar
	CH stretch	3110	⊥	Planar
	OH stretch (bonded)	3270	⊥	Planar
	CH bend	{ 772 } 808		Non-planar
	Symm. NO_2 stretch	1360	⊥	Planar
2-Nitroresorcinol	Asymm. NO_2 stretch	1540	⊥	Planar
	CH stretch	3100	⊥	Planar
	OH stretch (bonded)	3280	⊥	Planar
	CH bend	{ 699 } 747 782		Non-planar
	Symm. NO_2 stretch	1350	⊥	Planar
	Asymm. NO_2 stretch	1510	⊥	Planar
<i>o</i> -Nitroaniline	NH_2 bend	1625	⊥	Planar
	CH stretch	3180	⊥	Planar
	Symm. NH_2 stretch	3370	⊥	Planar
	Asymm. NH_2 stretch	3500 (?)	⊥	Planar
	CH bend	{ 731 } 773		Non-planar
<i>o</i> -Nitrobromobenzene	Symm. NO_2 stretch	1358	⊥	Planar
	Asymm. NO_2 stretch	1528		Non-planar
	CH stretch	3090	⊥	Planar
	CH bend	{ 732 } 776		Non-planar
<i>o</i> -Nitrochlorobenzene	Symm. NO_2 stretch	1360	⊥	Planar
	Asymm. NO_2 stretch	1528		Non-planar
	CH stretch	3090	⊥	Planar

^a Denotes the orientation of the E-vector with respect to the direction of crystal growth which shows the greater absorption intensity.

direction of crystal growth. Since *o*-nitrophenol would be expected to have more planar than non-planar vibrations, this conclusion is in agreement with the fact that a preponderance of absorption bands in Fig. 1 exhibit maximum intensity when the E-vector is perpendicular to the direction of crystal growth. Similarly, in each of the succeeding examples the plane of the benzene ring can be shown to be perpendicular to the direction of crystal growth.

2-Nitroresorcinol.—The spectra for 2-nitroresorcinol are given in Fig. 1B and data for the key absorption bands are given in Table I. Applying the same reasoning used for *o*-nitrophenol, it is seen that the nitro group and the OH groups are approximately in the plane of the benzene ring. This configuration is expected in this case since each of the oxygen atoms of the nitro group is bonded by the adjacent hydroxyl groups. In addition, resonance of the nitro group would tend to restrict the plane of the nitro group to that of the benzene ring.

o-Nitroaniline.—Absorption bands of interest in the spectra of *o*-nitroaniline (Fig. 1C) are listed in Table I. Since the asymmetric stretching vibration absorbing at 1510 cm^{-1} is polarized in the same direction as the planar vibrations, the nitro group is assumed to be coplanar with the benzene ring. The relatively small difference in the intensity of the 1510 cm^{-1} absorption band in the two spectra is probably the result of an imperfect orientation of the preparation. The peculiar appearance

of the absorption bands arising from the NH_2 stretching vibrations probably results from the fact that one of the hydrogen atoms of the amine group is bonded to the adjacent oxygen atom of the nitro group. As a result there is some uncertainty regarding the assignment of the 3500 cm.^{-1} absorption band to the asymmetric NH_2 stretching vibration. However, since all of the absorption bands in the vicinity of 3500 cm.^{-1} which could be assigned to this vibration have the same polarization characteristics as those bands due to known planar vibrations, the NH_2 group is assumed to be planar. This configuration would be expected for the NH_2 group in this case because of bonding and resonance.

o-Nitrobromobenzene.—The information listed in Table I for *o*-nitrobromobenzene, obtained from the spectra in Fig. 1D, illustrate the effect of a large ortho substituent upon the geometry of the nitro group. The absorption band at 1582 cm.^{-1} arising from the asymmetric NO_2 stretching vibration is polarized in the same direction as the absorption bands due to non-planar vibrations and opposite to those from planar vibrations. Therefore, the plane of the nitro group is rotated well out of the plane of the benzene ring due to the steric influence of the adjacent bromine atom and is probably almost perpendicular to the ring. This steric effect is usually observed indirectly by measuring the change in properties (*e.g.*, dipole moments, ultraviolet spectra, rates of reaction, etc.) resulting

from the inhibition of resonance¹⁸ or by more direct X-ray diffraction methods.¹⁵

o-Nitrochlorobenzene.—The observed spectra of *o*-nitrochlorobenzene are given in Fig. 1E and the polarization data are presented in Table I. The absorption band at 1528 cm.^{-1} corresponding to the asymmetric NO_2 stretching vibration has polarization characteristics more similar to the absorption bands from the non-planar rather than the planar vibrations. Therefore, it is assumed that the plane of the nitro group is not coplanar with the benzene ring. The polarization of the 1528 cm.^{-1} absorption band does not compare as closely to the 776 cm.^{-1} band as for the analogous absorption bands in *o*-nitrobromobenzene. This difference may be assumed to indicate a smaller angle between the benzene ring and the nitro group in *o*-nitrochlorobenzene than in *o*-nitrobromobenzene, which would be expected because of the difference in van der Waals radii between chlorine and bromine. However, it is difficult to attempt such quantitative comparisons in view of the non-ideal nature of the preparations used.

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(18) G. W. Wheland, "The Theory of Resonance and its Application to Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1944.

STAMFORD, CONNECTICUT

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Kinetics of Competitive Consecutive Second-order Reactions: The Saponification of Ethyl Adipate and of Ethyl Succinate¹

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The differential rate equations for the kinetics of the reactions of the type $\text{A} + \text{B} \xrightarrow{k_1} \text{C} + \text{E}$ and $\text{A} + \text{C} \xrightarrow{k_2} \text{D} + \text{E}$ have been integrated for the special case of stoichiometrically equivalent amounts of the reactants A and B. Numerical tables and graphs have been prepared that enable (a) the determination of whether a reaction is of this kinetic type, and (b) the evaluation of the rate constants. Measurements of the rate of saponification of ethyl adipate and ethyl succinate have been made and used as an illustration of the application of the theory.

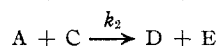
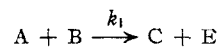
Competitive consecutive (series) second-order reactions, as usually exemplified by the saponification of diesters were first accurately handled by Ingold² who used a successive approximation method to obtain the rate constants. Ritchie³ made use of a procedure of graphical differentiation while the work of Westheimer, Jones and Lad⁴ involved graphical integration. French⁵ has recently handled this kinetic problem in more general fashion but still requiring a graphical integration for each kinetic run.

The aim of the present work was to integrate this

kinetic system once and for all in terms of general variables that would apply to any future experimental results.

Theoretical Treatment

The chemical equations of the system are



and the pertinent rate equations are

$$dA/dt = -k_1AB - k_2AC \quad (1)$$

$$dB/dt = -k_1AB \quad (2)$$

$$dC/dt = k_1AB - k_2AC \quad (3)$$

where A, B and C represent the molar concentrations of the corresponding chemical species. Let the initial concentrations of A and B be A_0 and B_0 , respectively, and the initial concentrations of C

(1) Abstracted in part from the Ph.D. thesis of Warren C. Schwemer at Northwestern University, August, 1950. Presented at the XIIth International Congress of Pure and Applied Chemistry, New York, N. Y., September, 1951. See also W. C. Schwemer and A. A. Frost, *THIS JOURNAL*, **73**, 4541 (1951).

(2) C. K. Ingold, *J. Chem. Soc.*, 2170 (1931).

(3) M. Ritchie, *ibid.*, 3112 (1931).

(4) F. H. Westheimer, W. A. Jones and R. A. Lad, *J. Chem. Phys.*, **10**, 478 (1942).

(5) D. French, *THIS JOURNAL*, **72**, 4806 (1950).