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AN INFRARED STUDY OF PICRIC ACID MOLECULAR COMPLEXES

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An Infrared Study of Picric Acid Molecular Complexes

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An Infrared Study of Picric Acid Molecular Complexes

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Abstract

The infrared spectra of 42 picric acid molecular complexes show that the nitro asymmetric stretching and the out-of-plane C-H bending vibrations of the picric acid component are sensitive to complex formation. The frequencies of these vibrations can be correlated with the type of complex formed, i.e. $\pi-\pi$ or $n-\pi$ type charge transfer. Many of the $\pi-\pi$ complexes were found to contain localized intermolecular interactions which give rise to an additional asymmetric stretching vibration. The frequency of the C-H out-of-plane bending vibration of complexed picric acid is an indication of the type of complex formed.

I. Introduction

The existence of molecular complexes between nitro-substituted benzenes and aromatic hydrocarbons has long been recognized. Many theories have been advanced to explain the nature of these complexes but only recently has one been proposed which is completely acceptable. This theory is found in a series of papers by R. S. Mulliken¹ whose

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1. (a) R. S. Mulliken, J. Am. Chem. Soc., 72, 600 (1950);
(b) 74, 811 (1952); (c) J. Phys. Chem., 56, 801 (1952).
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general quantum-mechanical treatment of molecular complexes encompassed all of the preceding major, classical theories.^{2,3,4}

2. J. Weiss, J. Chem. Soc., 245 (1942).
 3. W. Brackmann, Rec. trav. chim., 68, 147 (1949).
 4. M. J. S. Dewar, Nature, 156, 784 (1945); J. Chem. Soc., 406, 777 (1946).
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Mulliken suggested that the formation of molecular complexes from two aromatic molecules can arise from the transfer of an electron from a π -molecular orbital of a Lewis base to a vacant π -molecular orbital of a Lewis acid, with resonance between this dative structure and the no-bond structure stabilizing the complex. He also noted the possibility of complex formation through the donation of an electron from a non-bonding molecular orbital in a Lewis base to a vacant π -orbital of an acceptor (n - π interaction)^{1b}, with resonance stabilization of the combination.

Mulliken's ideas have been supported by spectroscopic evidence. The dichroism studies by K. Nakamoto⁵ of molecular complexes of a

5. K. Nakamoto, J. Am. Chem. Soc., 74, 1739 (1952).
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type similar to those treated in this paper clearly indicate the existence of charge transfer forces operating between the two components of the complex. The original attraction of the two components, according to Nakamoto, arose from mutual polarizing

forces which caused attracting dipoles. When the two molecules approached each other closely enough so as to be in the effective π -electron fields of each other, the electron transfer could then occur.

The intermolecular charge transfer predicted by Mulliken gives rise to intense electronic absorption bands in many complexes. These bands were examined by McConnell, Ham and Platt⁶ who used

6. H. McConnell, J. S. Ham and J. R. Platt, J. Chem. Phys., 21, 66 (1953).

them to set up empirical methods which would predict the wavelengths and intensities of these charge transfer absorptions.

Whereas the ultraviolet region can be used to study the electronic characteristics of these complexes, the infrared spectra can be utilized to examine the result of the charge transfers. Since the stability of these complexes arises from a shift of electron density from the donor to the electron deficient acceptor molecule, the infrared region should show the effect of the change of electron density in the components upon the vibrations of the atoms within the individual molecules. Study of vibrational spectra may also reveal which parts of the molecules play an active role in complex formation.

II. Experimental

The forty-two picric acid complexes listed in Table I were studied in nujol mulls with a Perkin-Elmer Model 13 Infrared Spectrophotometer, using sodium chloride optics. Four other

Table I

Compound Complexed with Picric Acid	Frequency of Normal Nitro Asymmetric Stretching Vibration (cm ⁻¹)	Frequency of "bonded" Nitro Asymmetric Stretching Vibration (cm ⁻¹)	C-H out- of-plane Type Bending Frequency (cm ⁻¹)	Complex
Mesitylene	1526	----	780.6	↑-↑
m-Chloroanisole	1527	----	783.3	↑-↑
o-Chloroanisole	1527	----	783.4	↑-↑
Fluorene (dipicrate)	1528	----	783.1	↑-↑
Indene	1528	----	overlap	↑-↑
Phenanthrene	1534	----	780.0	↑-↑
Tetralin	1539	----	780.6	↑-↑
Naphthalene	1541	----	779.0	↑-↑
Anthracene	1542	----	777.7	↑-↑
Hexamethylbenzene	1543	----	783.1	↑-↑
o-Phenanthroline	1545	----	784.9	↑-↑
Anisole	1524	1514	783.8	↑-↑
Aniline	1525	1491	792.1	↑-↑
Phenetole	1526	1508	783.0	↑-↑
p-Iodoaniline	1531	1513	789.1	↑-↑
β-Naphthylamine	1536	1521	792.5	↑-↑
β-Naphthol	1536	1507	780.4	↑-↑
β-Naphthyl ethyl ether	1536	1507	779.6	↑-↑
α-Naphthyl methyl ether	1537	1504	779.5	↑-↑
β-Methyl Naphthalene	1537	1504	779.4	↑-↑
2-Aminodibenzofuran	1540	1525	785.7	↑-↑
β-Naphthyl methyl ether	1542	1507	779.5	↑-↑
Guaiacol	1542	1513	783.1	↑-↑
α-(α-naphthyl) Pyrroline	1532	1508	780.2	↑-↑
		1548	790.6	n-↑
α-Benzylpyrroline	1530	1549	785.4	n-↑
Strychine	1506	1523	787.8	n-↑
	1506			
Pyridine	1520	1548	786.0	n-↑
α-(p-tolyl) Pyrroline	1513	1551	787.4	n-↑
Atropine	1515	1560	787.5	n-↑
β-Picolylamine	1515	1540	792.2	n-↑
4,7-Dichloroquinoline	1520	1536	789.3	n-↑
7-Chloro-4-(N-morpholino-amino) quinoline	1520	1548	789.7	n-↑
α-(p-tolyl) Pyrrolidine	1523	1545	791.3	n-↑
Piperidine	1524	1548	786.9	n-↑
α-Ethylpyrroline	1525	1543	789.7	n-↑
α-(p-chlorophenyl) Tetrahydro- pyridine	1526	1546	787.0	n-↑

Table I (Continued)

Compound Complexed with Picric Acid	Frequency of Normal Nitro Assymmetric Stretching Vibration (cm ⁻¹)	Frequency of "bonded" Nitro Assymmetric Stretching Vibration (cm ⁻¹)	C-H out- of-plane Bending Frequency (cm ⁻¹)	Type of Com- plex
α -Phenylpyrroline	1528	1535	789.8	n- π
Nicotine	1529	1543	787.4	n- π
β -(p-tolyl) Tetrahydropyridine	1532	1541	786.6	n- π
Tetramethylpyrazine (dipicrate)	1536	1540	788.0	n- π
N-(p-tolyl) Pyrrolidine	*	1548	787.3	n- π
2,3-Diaminobutane (dipicrate)	1514	1541	793.7	h.b.**
Picric Acid	1525	----	783.3	----
Picryl chloride; hexamethylbenzene complex				
m-Bromoaniline; 2,4-Dinitrochlorobenzene complex				
Aniline; 2,4-Dinitrochlorobenzene complex				
p-Iodoaniline; sym-trinitrobenzene complex				

*Peak frequency masked

**Hydrogen bonded complex

complexes of a similar nature which were examined for comparison purposes are listed at the bottom of Table I.

Approximately half of the complexes were prepared by the authors using a number of different methods, depending upon the individual compound. Many were crystallized from a hot saturated solution of picric acid in ethanol or chloroform to which was added the second component. In other cases where the latter component was

a liquid, the picric acid was added directly to the hot liquid and the excess solvent evaporated under reduced pressure. The complexes which were not prepared were obtained from the Iowa State College Chemistry Department.

III. Results and Discussion

In general, the spectra of all the molecular complexes appear to be a summation of the spectra of the two components, with the vibrational bands of picric acid appearing more strongly than those of the other components. Because of the large differences in the spectra of the various hydrocarbon (Lewis base) components of the complexes, it was difficult to uncover any systematic spectral changes in their spectra when complexes were formed. For this reason, emphasis was placed on noting whether any significant changes occurred in the spectra of the picric acid component. In the wavelength region investigated only the nitro asymmetric stretching vibrations and the C-H out-of-plane bending vibrations of the picric acid component showed significant changes.

These frequency changes are not simple in nature as shown by the summary of data in Table I. Both the nitro asymmetric stretching and the C-H out-of-plane bending vibrations exhibit frequencies less than, approximately equal to, or greater than the corresponding frequencies in picric acid. An additional nitro asymmetric stretching vibration also appears in most of the complexes.

Before discussing the spectra of specific complexes it is advisable to consider the nitro asymmetric stretching vibrations in picric acid itself. Figure 1A shows that these vibrations

Fig. 1 - Nitro asymmetric stretching absorption bands in picric acid and picrate complexes.

produce a rather broad band at 1525 cm^{-1} . At first glance one might attribute this broad band to the fact that picric acid contains an intramolecular hydrogen bond between the phenolic hydrogen and an oxygen of an ortho-nitro group. Because of this interaction, the frequency of the asymmetric stretching vibration of the bonded o-nitro group would be lower than the asymmetric stretching vibration of an unbonded coplanar nitro group, and the resulting absorption band would be expected to be broad. However, the spectrum of picryl chloride manifests the same broad band, so that some other explanation for the observed broadness must exist. E. W. Hughes⁷ pointed out that the ortho nitro groups in potassium

7. Private communication.

picrate, as well as in four or five other picryl derivatives, are not coplanar with the benzene ring. In potassium picrate, for example, the dihedral angle for the ortho nitro groups is 27° . The hydrogen bond in picric acid can be expected to stabilize one ortho nitro group in the plane of the ring, but there is no reason why the other ortho group should be coplanar with the ring. Because of a lower degree of resonance with the benzene ring, the frequency of the non-coplanar nitro group will be lower than that of the para nitro group, which is known to be nearly coplanar with the ring in all picryl derivatives. In addition to the two frequencies arising from these dissimilar nitro groups, another lower frequency vibration can be expected for the nitro group involved in the hydrogen bond. The three nitro asymmetric stretching frequencies are manifested as one broad band which has its maximum at 1525 cm^{-1} (Fig. 1A).

A. π - π Complexes

It is rather significant that only the nitro asymmetric stretching vibrations and not the nitro symmetric stretching vibration should undergo marked alteration in frequency on the formation of π - π complexes. Apparently, the transfer of charge to a π -orbital of the picric acid component does not significantly alter the charge distribution in the π -orbitals of the nitro groups in the picric acid molecule. An increase in π -electron density in the nitro groups would probably result in a slight rehybridization of the N-O bonds and a frequency increase for both symmetric and asymmetric modes, which is not observed. The formation of π - π complexes does place a large charge density between the rings, which may be expected to interact with non-planar vectors of any vibration of the complex. Figure 2 shows that planar nitro symmetric or asymmetric stretching vibrations have no vector component perpendicular to the plane of the ring. The same argument applies to non-planar nitro symmetric stretching vibrations, since the resultant vector remains in the plane of the ring. Only the asymmetric stretching vibrations of non-planar nitro groups possess a transition moment vector component perpendicular to the plane of the ring. In the presence of the high charge density between the rings, the repulsive forces between the perpendicular vector dipole component of the nitro asymmetric vibration and this charge density may be expected to increase the frequency of the vibration. The data in Table I show that virtually all of the complexes formed from components which should

Fig. 2 - Direction of transition moment vectors for (left) nitro symmetric and (right) nitro antisymmetric stretching vibrations.

undergo $\pi-\pi$ interactions have a nitro asymmetric stretching frequency greater than in picric acid itself. The only exceptions are the anisole and aniline complexes which show no frequency change.

In addition to the nitro asymmetric stretching vibration which usually shows an increase in frequency, another nitro asymmetric stretching vibration appears in the spectra of many of the $\pi-\pi$ complexes. Except for two cases, this additional band falls in the region 1500-1520 cm^{-1} . These vibrations appear only when the hydrocarbon component of the complex contains an electrodotic group (NH_2 , OH, etc.) (Fig. 1C). The relative intensities of the additional band vary directly with the basic strength (in the Lewis sense) of the substituent, as shown by the spectra of four β -substituted naphthalenes in Figure 3 and by the relative intensity tabulation in Table II.

A possible explanation for the appearance and relative intensity of the additional band can be derived from the crystal structure determination of p-nitroaniline⁸ by Abrahams and Robertson.

8. S. C. Abrahams and J. M. Robertson, *Acta Cryst.*, 1, 252 (1948).

p-Nitroaniline was found to be a self complex, with the nitro group of any one molecule forming an exceptionally strong intermolecular bond with a ring carbon of an adjacent molecule, to give an O...C distance of 2.66 Å. The spectrum of this compound shows the nitro asymmetric stretching vibration at 1502 cm^{-1} , in the same region of the additional bands found in these studies.

Mulliken^{1c} has suggested that this intermolecular bond is a localized $\pi-\pi$ interaction, similar to the dative: no-bond

Fig. 3 - Variation in intensity of additional nitro stretching band in π - π complexes.

Table II

Ratio of Logs of Intensities of Additional Band to Normal Nitro
Asymmetric Stretching Vibration

β -Methylnaphthalene Picrate	0.29
β -Naphthyl Methyl Ether Picrate	0.56
β -Naphthol Picrate	0.71
β -Naphthylamine Picrate	0.83

structure of the π - π complexes. Thus, in the case of picric acid complexes, the greater the electrodotic tendency of the substituent on the hydrocarbon component of the complex, the greater the electron density on the carbon atoms ortho to that group. As the charge density is increased there should be a greater tendency for one of the ortho carbons to donate its π -electron charge to an accepting π -orbital of a nitro group on an adjacent picric acid molecule. Since the interaction involves the resonance between a dative and no-bond structure, with the latter probably predominating, and since it can be expected that the dative to no-bond ratio of the bond will increase with increasing electrodotic tendency of the substituent, the polarity of the N-O bond should also be directly related to the basicity of the group. As the N-O bond stretches, its dipole moment should also vary in accord with this dependence. Since the intensity of a band depends upon the dipole moment change involved in the vibration, the intensity of the nitro band should increase with the electrodotic tendency of the substituent group.

The observed lower asymmetric stretching frequency of the nitro group involved in the localized bond suggests the following interactions. Since the intermolecular link is basically a no-bond resonance structure, as is the case for all π - π interactions, on a time average only a fraction of a single transferred charge is located in a nitro orbital. Concomitant with the localized bonding is the close approach of a single nitro oxygen to the donating ring carbon, and a subsequent attractive interaction between the partially negative oxygen and partially positive carbon. This oxygen is also in a position to form a hydrogen bond with the hydrogen atom of that ring carbon, so that the oxygen is involved in two simultaneous bonds. This double interaction may weaken the N-O bond to the extent that the coupling of its stretching vibration with the stretching vibration of the other, unaffected, N-O bond of the nitro group to form the asymmetric vibration, more than overcomes the tendency of the group vibration to have a higher frequency as a result of the partial charge transferred to it. The vibration therefore is of a lower frequency.

The existence of a localized interaction of this type has also been found in the crystal structure of the π -complex of p-iodoaniline with sym-trinitrobenzene.⁹ In this complex one

9. H. M. Powell, G. Huse and P. W. Cooke, J. Chem. Soc., 153 (1943).

nitro group approaches the ring of the p-iodoaniline more closely than do the other two. The infrared spectrum of this complex also shows the additional band found in the spectra of the picric acid complexes.

Localized $\pi-\pi$ bonds by themselves are probably not strong enough to constitute the sole binding energy of molecular compounds, but their existence in the π -complexes undoubtedly constitutes a stabilizing factor. In accord with this, it has been noticed that the melting points of the complexes containing the additional interaction were generally higher than the melting points of the complexes that did not contain the localized bonds.

B. $n-\pi$ Complexes

The spectra of these complexes invariably exhibit two nitro asymmetric stretching vibrations, one stronger than the other. The more intense band is located in the region in which the nitro vibration is found in picric acid, and the weaker band is found at considerably higher frequencies (around 1545 cm^{-1}) (Table I and Fig. 1D). Piperidine exemplifies the type of compound yielding $n-\pi$ complexes, since the nitrogen atom in piperidine is capable of donating an electron from a non-bonding orbital to a vacant π -orbital of a nitro group.

The parallelism of the rings in the $\pi-\pi$ complexes imposes the condition that only one oxygen of a nitro group can approach the adjacent molecule to form a localized $\pi-\pi$ bond. However, if the components are not arranged in a parallel fashion this condition is not demanded. If the electron donor and acceptor are sterically arranged either in a coplanar fashion, or with their rings perpendicular, the two molecules can approach each other more closely than the $\pi-\pi$ distances permit and the donation of an electron from the basic group to a nitro orbital is now possible. This transfer yields a stable datively-bonded complex,

as compared with the basically no-bond nature of the $\pi-\pi$ complexes^{1c}. Whereas the localized $\pi-\pi$ interaction involves an N-O...C bond, the n- π interaction now takes the form, say, an N...(NO₂) bond, and the restriction to a single oxygen is no longer imposed. This suggests that both N-O bonds in the nitro group are of the same energy and the resulting asymmetric vibration should be at a higher frequency and possess a greater intensity than the other two non-bonded nitro group vibrations, in agreement with experimental observation.

C. Hydrogen-Bonded Complexes

This type of complex is exemplified by the interaction product of picric acid with 2,3-diaminobutane. The pronounced shift of the NH₂ stretching vibrations to lower frequencies (3420 to 3207 cm⁻¹) in the spectrum of the complex clearly indicates that the product is stabilized by hydrogen bonds between the amino hydrogens of one component and the nitro oxygens of the other component. The appearance of two nitro asymmetric stretching frequencies and their relative intensities (Fig. 1E) indicates that two of the three nitro groups of picric acid are involved in hydrogen bonds in this complex. There are cases where hydrogen bonding further stabilizes already formed π -complexes, as in the picrates of aniline, and β -naphthylamine.

D. The C-H Out-of-Plane Bending Vibration of Picric Acid

Although the behavior of this vibration with relation to the type of complex formed is not understood, a few general correlations can be obtained, so that the position of the band might be used as

an indication of the nature of the complex. In $\pi-\pi$ complexes, the frequency of the C-H out-of-plane bending vibration of a picric acid molecule involved in the complex is generally of lower frequency than in pure picric acid (783.3 cm^{-1}) (see Table I). The exceptions, for the most part, occur in cases where the electron donor molecule contains an amino group. The latter probably gives rise to strong localized interactions which effectively weaken the molecular $\pi-\pi$ bonds. On the other hand, in the $n-\pi$ complexes the C-H out-of-plane bending vibration invariably appears at a higher frequency than in pure picric acid. Therefore, in order to determine if a complex is of the $\pi-\pi$ or $n-\pi$ type, one must merely note the position of the C-H out-of-plane bending frequency with respect to 783.3 cm^{-1} . Excluding compounds with an amino group, a higher value indicates an $n-\pi$ complex while a lower value indicates a $\pi-\pi$ complex.

E. General Comments

It is interesting to note that pyridine, which can act as either a π or n base, apparently interacts in the latter fashion. This is probably true because the $n-\pi$ bond is more strongly localized than the $\pi-\pi$ bond and is undoubtedly more stable.

The type of complex resulting from the interaction of a specific compound with picric acid (or any similar nitrohydrocarbon) can be predicted beforehand by merely noting if the compound contains an atom which would permit it to act as an n -base. If it is possible to complex in that manner than it invariably does. An apparent, though not real, exception to this rule occurs in the

case of o-phenanthroline, where steric factors inhibit the formation of an n- π complex in favor of a π - π complex. A similar case is presented by the α -(α -naphthyl)pyrroline complex. The spectrum indicates two types of nitro and C-H band systems, one characteristic of predominantly π - π bonding and one suggestive of n- π bonding. Examination of the structure of the compound clearly indicates the possibility for the formation of both types of complex. The naphthalene ring provides a site for π - π bonding and the nitrogen of the pyrroline possesses an electron which can be donated to an accepting orbital of a nitro group to form an n- π bond.