tion boiling below 132° was collected, thus separating the dimethylaminoboron difluoride dimer as its azeotrope, b.p. 116°. The distillate and the residue were each mixed with hexane, cooled to 0°, and the crystals filtered off, giving, respectively, 10.0 g. (0.054 mole) of dimethylaminoboron difluoride dimer, subl. 135°, and 13.0 g. (0.10 mole) of crude trimethylamine–boron trifluoride, m.p. 125–135°.

Tetramethylammonium Fluoborate.—Traces of impurities were volatilized from the crude product by heating to 250° at 5 mm. The purified fluoborate melted without decomposition at 415° and did not depress the melting point of an authentic specimen. It could be distilled at 15 mm. a little above its melting point, but decomposed with charring when heated at atmospheric pressure.

Trimethylamine–boron Trifluoride.—The crude product was purified with 90% recovery by three vacuum sublimations at about 100° and 5 mm. The purified sublimate was a white crystalline solid, m.p. 140–146°; b.p. 238°; apparent molecular weight, 213 in an 0.0054 mole-fraction solution in benzene (cryoscopic). Reported constants for trimethylamine–boron trifluoride are m.p. 138°,[4] 139–147°[5]; b.p. 233° (extrapolated[5]); apparent molecular weight 228 in an 0.0054 mole fraction solution in benzene.[4]

Anal. Calcd. for $C_3H_9NBF_3$: N, 11.0. Found: N, 11.3.

Dimethylaminoboron Difluoride Dimer.—The crude product was resublimed and recrystallized from benzene to give colorless crystals having a pleasant camphor-like odor; subl. 135°, m.p. (sealed tube) 167–169° (sl. dec.). The compound was insoluble in hexane and cold water, slightly soluble in cold aromatic solvents, soluble in hot aromatic solvents, and rapidly hydrolyzed by hot water. It formed low boiling azeotropes with chlorobenzene, *m*-xylene, and probably also with benzene.

Mass spectrometric study showed no peaks corresponding to the dimeric formula. The observed parent peaks at masses 91, 92 and 93 suggested the presence of monomeric dimethylaminoboron difluoride, and the interpretation that dissociation of the dimer was complete in the high vacuum.

The compound was unstable upon standing in dry air. It rapidly acquired an unpleasant, pungent odor, the crystals became sticky, and a low melting solid of lesser volatility was formed. Because of this instability, it is doubtful whether any of the analyses were based upon particularly pure specimens of the compound.

Anal. Calcd. for $C_4H_{12}B_2N_2F_4$: C, 25.9; H, 6.5; N, 15.1; mol. wt., 186. Found: C, 24.8; H, 6.5; N, 15.0; mol. wt., 173 (Victor Meyer method at 155°, 747 mm.).

Acknowledgments.—The author is indebted to Mr. L. B. Bronk, Miss P. A. Powers and Mrs. M. B. Lennig for their assistance with the microanalyses, and to Dr. F. J. Norton for the mass spectrometric study.

SCHENECTADY, N. Y. RECEIVED JULY 13, 1951

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[4] J. R. Bright and W. C. Fernelius, THIS JOURNAL, **65**, 735 (1943).

[5] A. B. Burg and Sr. A. A. Green, *ibid.*, **65**, 1838 (1943).

[CONTRIBUTION FROM THE PHYSICS DEPARTMENT, THE UNIVERSITY OF CHICAGO]

A Study of Molecular Complexes Formed by Aniline and Aromatic Nitrohydrocarbons[1,2]

BY J. LANDAUER AND HARDEN MCCONNELL[3]

The equilibrium constants and absorption spectra of the 1:1 complexes formed by aniline and *m*-dinitrobenzene, *p*-dinitrobenzene and *s*-trinitrobenzene have been determined in chloroform solution. Evidence for the existence of 1:2 complexes has also been obtained. It is proposed that an acid-base interaction (in the Lewis sense) is responsible for the formation and coloration of these complexes. Geometrical structures for the complexes are discussed.

I. Introduction

Many investigators have attributed the marked visible coloration exhibited by solutions containing aromatic amines and nitrohydrocarbons to the formation of highly colored molecular complexes. The existence of such complexes in the solid state is well known[4–7] and, in certain cases, their presence in solution has been established by spectroscopic methods.[8]

In spite of the extensive literature on this subject little quantitative information has appeared regarding the absorption spectra of the aromatic amine–polynitrohydrocarbon complexes. Part III of the present communication gives the results of a spectrophotometric determination of the equilibrium constants and absorption spectra of the 1:1 complexes present in chloroform solutions containing aniline and *m*-dinitrobenzene, *p*-dinitrobenzene and *s*-trinitrobenzene. Evidence for the existence of 1:2 complexes in these solutions is also presented.

In contrast to the earlier theories,[4,9] it is now generally recognized that the spectra and stabilities of complexes of the aniline–nitrohydrocarbon type cannot be adequately accounted for in terms of intermolecular interactions involving simple dispersion, polarization, multipole, hydrogen bond[10,11] or strong chemical bond forces.[8,11]

In Part IV it is proposed that an acid–base interaction is responsible for the formation and visible coloration of the aniline–polynitrobenzene complexes. Probable geometrical structures for these complexes are discussed in terms of the theory of acid–base interactions formulated by Mulliken.[12,13]

II. Experimental

Absorption spectra were determined with a model DU Beckman spectrophotometer. Optical densities were reproducible to 2%. Light paths of approximately 1.0, 0.1, 0.03 and 0.01 cm. were employed using 1.0-cm. quartz cells and calibrated quartz spacers. The reference cell always contained pure chloroform.

In several preliminary experiments, solutions containing

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[1] This work was assisted in part by the Office of Naval Research under Task, Order IX of Contract N6ori with the University of Chicago.

[2] Presented at the Symposium on Molecular Structure and Spectroscopy at The Ohio State University, June 11, 1951.

[3] National Research Council Postdoctoral Fellow, 1950–1951.

[4] G. Briegleb, "Zwischenmolekulare Kräfte und Molekülstructur," F. Enke, Stuttgart, 1937.

[5] P. Pfeiffer, "Organische Molekülverbindungen," F. Enke, Stuttgart, 1927.

[6] C. Shinomya, *Bull. Chem. Soc. Japan*, **15**, 137 (1940).

[7] R. Gibson and O. Loeffler, THIS JOURNAL, **62**, 1324 (1940).

[8] D. L. Hammick and R. B. Yule, *J. Chem. Soc.*, 1539 (1940).

[9] R. Hunter, *et al.*, *ibid.*, 1576 (1936)..

[10] Dr. N. D. Coggeshall has recently obtained infrared evidence indicating the absence of strong hydrogen bonding between aniline and nitrobenzene in solution (private communication).

[11] H. M. Powell, *J. Chem. Soc.*, 153 (1943).

[12] R. S. Mulliken, THIS JOURNAL, **74**, 811 (1952).

[13] R. S. Mulliken, *J. Chem. Phys.*, **19**, 514 (1951); THIS JOURNAL, **72**, 600 (1950).

chloroform, a polynitrobenzene and aniline were prepared by weighing each component and determining the total volume of the solution. It was found that for the aniline concentrations employed ([A], mole fraction aniline, = 0.01–1.0), the volumes of aniline and chloroform were additive to within 3%. Subsequent solutions were prepared by diluting weighed samples of aniline and a polynitrobenzene to a known volume, and calculating the weight of chloroform added. The errors in [A] introduced by this procedure are thought to be less than those arising from other sources (*cf.* Part III). Experiments showed that room temperature variations (22 ± 2°) resulted in negligible changes in the solution spectra.

Reagent grade aniline was distilled from zinc dust in a nitrogen atmosphere and repeated checks of its spectroscopic purity were made. The polynitrobenzenes, namely, *p*-dinitrobenzene, *m*-dinitrobenzene and *s*-trinitrobenzene, were recrystallized several times from absolute alcohol and in all cases the observed melting points were within 1° of those reported in the literature. Also, the absorption spectra of the polynitrobenzenes were determined in the 200–300 mμ range and these spectra were found to be in excellent agreement with the spectra of these compounds as reported by Kortüm.[14] Reagent grade chloroform was found to be spectroscopically pure and was used without further purification. The absorption spectra of typical solutions were unchanged over a period of one week.

III. Spectra and Equilibrium Constants of Aniline–Polynitrobenzene Complexes

Solutions of *m*-dinitrobenzene, *p*-dinitrobenzene or *s*-trinitrobenzene in aniline are strongly colored in the visible wave length region. Chloroform solutions containing either aniline or a polynitrobenzene alone are comparatively transparent at these wave lengths. This effect of aniline on the absorption spectra of the polynitrobenzenes is illustrated in Fig. 1. The formal extinction coefficients in Fig. 1 are defined by the equation, $\bar{\epsilon} = D/(N)_0 l$, where D is the total optical density ($D = \log_{10} I_0/I$) of a solution containing a formal polynitrobenzene concentration of $(N)_0$ moles/liter and l is the light path. The polynitrobenzenes, *m*-dinitrobenzene, *p*-dinitrobenzene and *s*-trinitrobenzene, are abbreviated by mN, pN and sN.

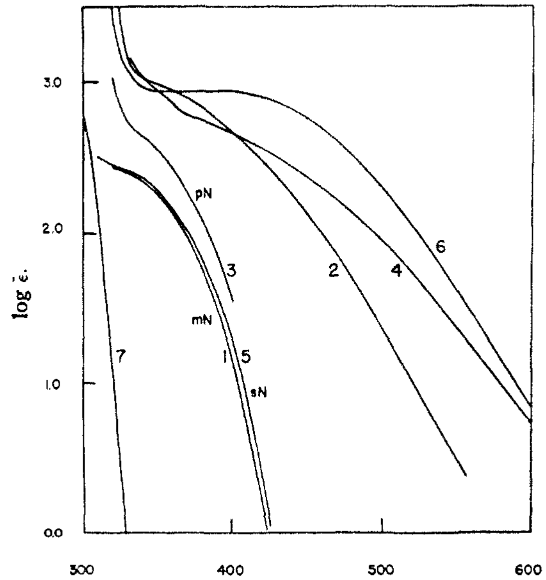

Fig. 1.—Effect of aniline on the formal extinction coefficients, $\bar{\epsilon}$, of the polynitrobenzenes: (1), (3) and (5): molar extinction coefficients, ϵ_0, of *m*-dinitrobenzene (mN), *p*-dinitrobenzene (pN) and *s*-trinitrobenzene (sN) in pure chloroform solvent. (2), (4) and (6): formal extinction coefficients of mN, pN and sN in solutions with aniline mole fractions of 0.50, 0.50 and 0.202, respectively. The formal polynitrobenzene concentrations are (mN) = 10^{-2}, (pN) = 10^{-2} and (sN) = 2.5×10^{-3} mole/liter. (7): molar extinction coefficients of aniline.

It is seen in Fig. 1 that the formal extinction coefficients, $\bar{\epsilon}$, are much greater in the presence of aniline. An examination of the spectra of a large number of solutions showed that $\bar{\epsilon}$ increases with increasing aniline concentration. Our results show that the quantitative dependence of $\bar{\epsilon}$ on aniline concentration can be interpreted in terms of light absorption by the complexes represented in the equilibria

$$\mathrm{N} + \mathrm{A} \rightleftharpoons \mathrm{NA},\ K_1 = (\mathrm{NA})/(\mathrm{N})[\mathrm{A}] \qquad (1)$$

$$\mathrm{N} + 2\mathrm{A} \rightleftharpoons \mathrm{NA_2},\ K_2 = (\mathrm{NA_2})/(\mathrm{N})[\mathrm{A}]^2 \qquad (2)$$

In (1) and (2), A and N represent aniline and one of the polynitrobenzenes, mN, pN or sN. The mole fraction of aniline is [A]. Parentheses denote molar concentrations. The mass action equilibrium constants, K_1 and K_2, are functions of the activity coefficients of the molecular species appearing in (1) and (2). In the following discussion, we first develop the equations used to relate the observed spectra, $\bar{\epsilon}$, to the spectra of the 1:1 and 1:2 complexes.

The optical density of a solution containing the molecular species of (1) and (2) is

$$D = \bar{\epsilon}(\mathrm{N})_0 = \epsilon_0(\mathrm{N}) + \epsilon_1(\mathrm{NA}) + \epsilon_2(\mathrm{NA_2}) \qquad (3)$$

where the ϵ_i's are the appropriate molar extinction coefficients. By combining (1)–(3) with the equation representing the conservation of polynitrobenzene,

$$(\mathrm{N})_0 = (\mathrm{N})(1 + K_1[\mathrm{A}] + K_2[\mathrm{A}]^2) \qquad (4)$$

one obtains

$$Q = \frac{1 + K_1[\mathrm{A}] + K_2[\mathrm{A}]^2}{(\epsilon_1 - \epsilon_0)\,K_1 + (\epsilon_2 - \epsilon_0)K_2[\mathrm{A}]} \qquad (5)$$

where

$$Q \equiv [\mathrm{A}]/(\bar{\epsilon} - \epsilon_0)$$

The derivation of (5) makes use of the adequate approximation $(\mathrm{A}) >> (\mathrm{N})_0$. The use of (5) to determine the equilibrium constants and extinction coefficients is based on the approximation that these quantities are independent of the aniline concentration. The validity of this approximation is examined later.

The absorption spectra and equilibrium constants of the 1:1 complexes were determined from plots of the experimental values of Q (*cf.* (5)) against [A]. Some of the results are given in Fig. 2. In order to clarify the discussion of these results, we point out here that for the solutions used, *ca.* 10–40% of the polynitrobenzenes were in the form of 1:1 complexes. It was not possible to determine the *concentration* of the 1:2 complexes. That is, in all cases the spectrophotometric data showed the $K_2[\mathrm{A}]^2$ term in (5) to be negligible.

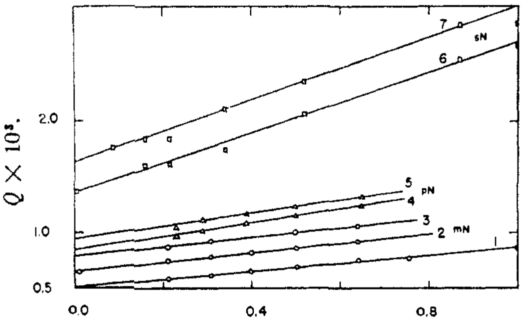

Fig. 2.—Typical plots used in the graphical determination of the equilibrium constants and extinction coefficients: ○, mN-aniline solutions, (1) 360, (2) 380, (3) 390 mμ; △, pN-aniline solutions, (4) 370, (5) 400 mμ; □, sN-aniline solutions, (6) 380 and 420, mμ (7) 340 mμ. For □, abscissa = [A] × 50.

For solutions of sN with [A] = 0.01–0.10, plots similar to those in Fig. 2 were made for a dozen wave lengths in the

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[14] G. Kortüm, *Z. physik. Chem.*, **B42**, 39 (1939).

340–500 mμ range. All these plots were found to be straight lines to within the experimental error, 5%. The experimental values of K_1 calculated from these plots (by setting $K_2 = 0$ in (2)) are given in Table I. The extinction coefficients of the sNA complex, also obtained from these plots, are given in Fig. 4.

For sN solutions with larger aniline mole fractions, $[A] = 0.1–0.2$, the values of ϵ_1 (Fig. 4) and K_1 can account for the observed spectra in the 350–410 mμ range, but not in the 430–500 mμ range. Thus: (a) plots of Q *vs.* [A] in Fig. 2 (curves (6) and (7)) are linear for 340, 380 and 420 mμ when $[A] = 0.01–0.20$ but (b) the value of ϵ_1 at 500 mμ ($\epsilon_1 = 2.5 \times 10^2$) accounts for only *ca.* 60% of $\bar{\epsilon}$ in curve (6) of Fig. 1 for 500 mμ and $[A] = 0.202$. Since K_1 and ϵ_1 for sNA could be determined from the spectra of solutions with $[A] = 0.01–0.10$, the dependence of $\bar{\epsilon}$ on [A] for $[A] > 0.1$ was not studied extensively. The fact that the calculated K_1's (Table I) are constants to within the experimental error shows that the approximations used in the derivation of (5) are adequate for $[A] = 0.01–0.10$.

Our determination of K_1 and ϵ_1 for the pNA and mNA complexes required large aniline concentrations, $[A] = 0.1 - 1.0$. To account for the observed dependence of Q on [A] in the 350–500 mμ range it is necessary to include the K_2 $(\epsilon_2 - \epsilon_0)$ term in (5) in addition to the terms due to 1:1 complexes. As indicated in Fig. 2, the plots of Q against [A] for the shorter wave lengths of the 350–500 mμ range are very nearly straight lines. If the terms in K_2 in (5) are neglected, the values of K_1 calculated from these linear plots show some tendency to drift to smaller values as the wave length used for the calculation is increased. This variation in the calculated values of K_1 can be accounted for in terms of $K_2(\epsilon_2 - \epsilon_0)$ by noting that for

$$(\epsilon_2 - \epsilon_0)K_2/(\epsilon_1 - \epsilon_0)K_1 < 0.2$$

(5) may be written

$$Q = \{1 + [K_1 - K_2(\epsilon_2 - \epsilon_0)/K_1(\epsilon_1 - \epsilon_0)][A]\}\,/\,K_1(\epsilon_1 - \epsilon_0) \quad (6)$$

to within an accuracy of *ca.* 5% for $[A] = 0.1 - 1.0$. The fact that the plots are straight lines to within the experimental error, in accordance with (6), shows that the values of K_1 for mNA and pNA in Table *I* are probably too low, but by not more than 0.2. Other investigators have estimated the stabilities of the mNA and pNA complexes. Their results agree with ours as well as can be expected in view of the different experimental conditions.[15,16]

TABLE I

DETERMINATIONS OF THE EQUILIBRIUM CONSTANTS, K_1

Wave length, mμ	mNA	pNA	sNA
340			4.2
50	0.75		5.0
60	.79		6.5
70	.70	0.72	5.7
80		.70	4.8
90		.69	5.5
400			5.0
10			5.6
20			4.8
40			5.4
60			4.9
80			4.9
500			4.2
Most probable K_1 =	0.74 ± 0.05	0.70 ± 0.05	5.1 ± 0.7

For solutions of mN or pN in aniline, plots of Q against [A] in the 420–600 mμ range yield curves with maxima. To account for these results, we rewrite (5) to give

$$(1 + K_1[A])/Q = K_1(\epsilon_1 - \epsilon_0) + K_2(\epsilon_2 - \epsilon_0)[A] \quad (7)$$

Typical plots of the left-hand member of (7) against [A] are given in Fig. 3. Values of the ordinates in Fig. 3 were calculated using the approximate values of K_1 determined at the shorter wave lengths ($K_1 = 0.74$ for mNA, $K_1 = 0.70$ for pNA). The linearity of these plots affords no indication of the accuracy of the K_1 determined at the shorter wave lengths. It is estimated that the intercepts of these plots, $K_1(\epsilon_1 - \epsilon_0)$, are accurate to 5% but the error in the slopes is approximately the same as that in K_1 (*cf.* Table I and discussion immediately following (6)). The extinction coefficients of the mNA and pNA complexes, ϵ_1, were determined using both (6) and (7) and are given in Fig. 4. The values of the coefficient of [A] in the right-hand member of (7) are also given in Fig. 4.

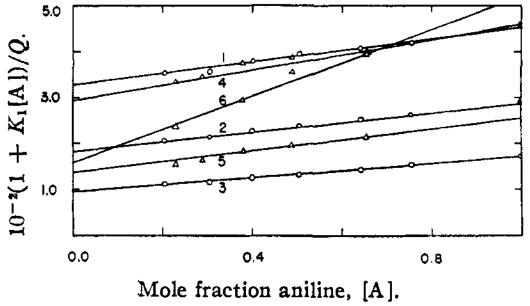

Fig. 3.—Determination of the light absorption by 1:2 complexes: O, mN-aniline solutions, (1) 420; (2) 440 (3) 460 mμ; Δ, pN-aniline solutions, (4) 480, (5) 510 (6) 570 mμ. For curves (1)-(3), divide ordinates by 0.5; for curve (6), divide by 5.0.

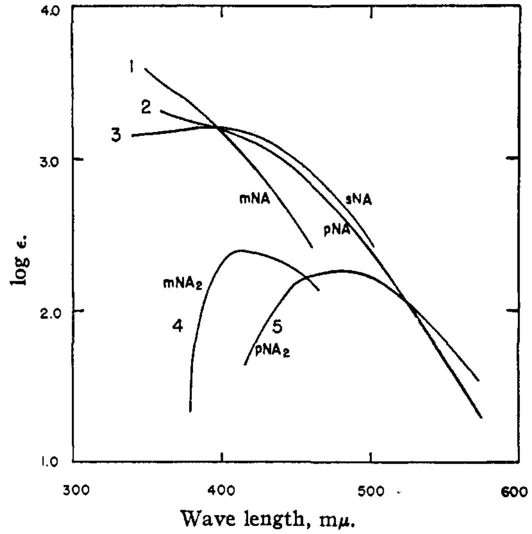

Fig. 4.—Absorption spectra of the complexes: (1), (2) and (3): logs of the molar extinction coefficients, ϵ_1, of the 1:1 complexes. (4) and (5): plots of log $\epsilon_2 K_2$ for the 1:2 complexes. These curves differ from the actual absorption spectra of the 1:2 complexes by the unknown additive constants, log K_2.

Since variations in K_1 and ϵ_1 with aniline concentration can contribute to the experimental value of $K_2(\epsilon_2 - \epsilon_0)$ in (5), the experimental results in the cases of the mNA and pNA complexes afford no indication as to whether these variations are negligible.

The extinction coefficients of the pNA and mNA complexes (Fig. 4) indicate the pNA complex to be the more colored. This is similar to the observation that, of a num-

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[15] L. W. Pickett, H. M. McClure and M. A. Jacobs, ONR report under contract N8 onr—74100 with Mount Holyoke College (Oct. 1, 1949–June 30, 1951), have used a spectrophotometric method to estimate the stability of mNA in ethyl alcohol solvent. In the units of equation (1) their result is: $K_1(\text{mNA}) = 1.3$.

[16] T. S. Moore, F. Shepard and E. Goodall, *J. Chem. Soc.*, 1447 (1931), have used a distribution method to estimate the stabilities of mNA and pNA in chloroform with $[A] = 0.027 - 0.037$. In the units of equation (1) their results are: $K_1(\text{mNA}) = 2.2$ and $K_1(\text{pNA}) = 2.1$.

ber of solid 1:1 molecular compounds containing mN or pN, the pN compound is generally the more colored.

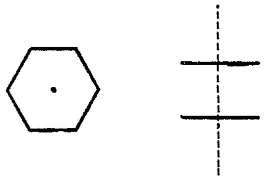
IV. Discussion

Mulliken[12,13] has pointed out that an acid–base or charge-transfer type intermolecular bond appears qualitatively well suited to account for the stabilities, spectra, dipole moments and structures of a number of molecular complexes. The 1:1 acid–base complexes which have been studied most extensively from this point of view are those between halogens and aromatic hydrocarbons.[12,13,17]

It appears likely that an acid–base interaction is also responsible for the formation of the highly colored NA complexes. In this case both acid and base molecules are aromatic: A is the electron donor or base and N is the electron acceptor or acid. The weak intermolecular binding is due to resonance between the no-bond structure, (A, N), and the charge transfer or ionic structure, ($A^+ - N^-$), in addition to the ordinary polarization and multipole forces. The contribution of the ionic structure to the wave function for the ground electronic state of the complex must be small (*ca.* a few per cent.) since the energy of ($A^+ - N^-$) is at least several electron volts greater than that of (A, N). The stabilization of a NA complex arising from resonance between (A,N) and ($A^+ - N^-$) can be shown to depend, in part, on the electron affinity of N. This dependence indicates the greater stability of the sNA complex, relative to the mNA and pNA complexes (*cf.* Table I), to be due to the greater electron affinity of sN, relative to mN or pN.

The intense light absorptions by the NA complexes in the 350–600 mμ range (Fig. 4) can be interpreted as *intermolecular charge-transfer spectra.* Such spectra represent electronic transitions which are essentially $\rightarrow(A,N)\rightarrow(A^+ - N^-)$. A rough theoretical estimate of the intensity of this transition is in accord with the spectra in Fig. 4.[18]

Crystal structure investigations[11,19,20] of a variety of 1:1 solid acid–base complexes suggest that, in a NA complex (1) all intramolecular distances correspond to normal bond radii, (2) the shortest intermolecular distances are approximately the sums of van der Waals radii, and (3) the N and A molecules are closely packed, with one molecule above the other so that the molecular planes are approximately parallel.[21] However, both theoretical and experimental evidence indicates that in the closely packed structure of a NA complex, the two aromatic rings do not have the coaxial orientation shown in (I).



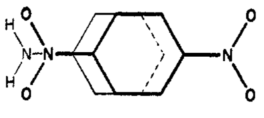
(I)

For the hypothetical benzene–benzene complex, $(C_6H_6)_2$, group theoretical arguments show that structure (I) above (with D_{6h} symmetry) is not the most favorable for acid–base intermolecular binding.[22] Similar conclusions apply to structures with C_3 or C_{3v} symmetries. Closely packed structures with lower symmetries are more favorable. The more favorable structures can be obtained from (I) by sliding one ring parallel to the other for a distance of the order of, say, an ångström. Similar arguments hold approximately for the NA complexes, so that the strongest binding should occur when the centers of the aromatic rings are not directly above one another.

The crystal structures of several acid–base molecular complexes are in accord with the above conclusions. In these structures, adjacent acid and base molecules are "pancaked" on top of one another, but the centers of the aromatic rings are not directly above each other.[11,19,20]

In the 1:1 crystal complex of *p*-iodoaniline and sN, the shortest intermolecular distance is between the nitrogen atom of an amino group and its oxygen neighbors.[11] The nitrogen atom of the amino group is nearly equidistant from the two oxygen atoms of a nitro group. This evidence for specific amino-nitro group interactions suggests that in the closely packed structure of NA, the amino group of A is directly above a nitro group of N.

This suggestion, if correct, shows that the mNA complex has no plane of symmetry. Symmetrical structures for pNA and sNA appear likely. As seen from above, the pNA complex probably has the appearance



II

A structure similar to (II) is predicted for sNA.

Acknowledgments.—We wish to acknowledge many helpful discussions with Professors R. S. Mulliken and J. R. Platt. One of us (H. Mc.) has been supported by the National Research Council.

CHICAGO 37, ILLINOIS RECEIVED AUGUST 3, 1951

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[17] J. S. Ham, J. R. Platt and H. McConnell, *J. Chem. Phys.*, **19**, 1301 (1951).

[18] Theoretical equations used for this estimate are given in Part II of ref. (12). For NA, reasonable values for Mulliken's $|r_B - r_A|$ and a^*b, 4 Å. and 0.1, respectively, give an oscillator strength, $f = 0.05$, equal to the f's estimated from the spectra of Fig. 4 for pNA and sNA.

[19] E. Hertel and G. Römer, *Z. physik. Chem.*, **B11**, 77 (1930); **B22**, 267 (1939).

[20] E. Hertel and H. Kleu, *ibid.*, **B11**, 59 (1930).

[21] Evidence on the effect of steric factors in inhibiting complex formation in solution also points to this packing of acid and base aromatic molecules. See E. Bowen and E. Coates, *J. Chem. Soc.*, 130 (1947).

[22] For details, see Part VIII of ref. (12).