latter equation when one is concerned with atoms or groups with low electronegativity values.[21,22]

Acknowledgment.—We wish to thank the staff of the MISTIC computer laboratory of Michigan State University for their valuable coöperation. This work was supported by a grant from the Research Corporation to whom we are particularly indebted.

EAST LANSING, MICHIGAN

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[22] P. T. Narasimhan, N. Laine and M. T. Rogers, *J. Chem. Phys.*, **28**, 1257 (1958); **29**, 1184 (1958).

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICS, LABORATORY OF MOLECULAR STRUCTURE AND SPECTRA, UNIVERSITY OF CHICAGO]

Molecular Complexes and Their Spectra. X. Molecular Complexes between Iodine and N,N-Dimethylaniline Derivatives

BY HIROSHI TSUBOMURA[1]

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n-Heptane solutions of the iodine complexes with N,N-dimethylaniline or its methyl derivatives have been found to be stable when the iodine concentrations in the solutions are quite low (of the order of 3×10^{-5} *M*). All these solutions show strong absorption bands in the near ultraviolet, which are interpreted as the charge transfer absorption bands due to the complexes. The equilibrium constants and the heats of formation of the 1:1 complexes have been determined from the intensity measurements of these bands. While the heats of formation obtained for the iodine complexes with N,N-dimethylaniline and N,N-dimethyl-*p*-toluidine are very large (−8.2 and −8.3 kcal./mole, respectively), those for the iodine complexes with N,N-dimethyl-*o*-toluidine and N,N-dimethyl-2,6-xylidine (−2.3 and −1.7 kcal./mole, respectively) are much smaller than the former two. From the inspection of the energies and shapes of the molecular orbitals of N,N-dimethylaniline, it has been concluded that the charge transfer in the complex between N,N-dimethylaniline and iodine occurs mainly from the lone pair of electrons of the nitrogen atom. In the *ortho*-methylated N,N-dimethylanilines, the *ortho* methyl group approaches the lone-pair of electrons of nitrogen, owing to the twisting of the dimethylamino group. The decrease in donor strengths of these *ortho*-methylated N,N-dimethylanilines is therefore attributed to the steric effect of the methyl group on the iodine molecule approaching the lone pair of electrons.

Introduction

The donor molecules which form donor–acceptor complexes with iodine may be divided into two groups: hydrocarbon donors such as olefins and aromatic hydrocarbons (π-donors) and compounds which contain heteroatoms such as oxygen or nitrogen atoms with lone-pair electrons (n-donors). Generally speaking, the latter group has stronger donating properties than the former, and especially aliphatic amines and aza-aromatic compounds like pyridine[2] interact very strongly with iodine.

Although the anilines are expected to have considerable donor strengths toward iodine, no study has ever been made on the molecular compounds between the anilines and iodine. As donor molecules, the anilines cannot be classified rigorously as either n- or π-donors, because the amino group and the benzene ring form nπ mixed donor orbitals, as well as a pure π-donor orbital, as a consequence of the resonance between them. (For details, see below.) It is a problem, therefore, to decide whether the anilines behave mainly as n-donors or as π-donors in complex formation with iodine; in other words, whether the orbital of the electron which is donated to the iodine molecule is mainly concentrated on the nitrogen lone-pair electron orbital or spreads over the molecule.

When the hydrogen atom at the *ortho* position of N,N-dimethylaniline is substituted by a methyl group, the dimethylamino group is rotated around the nitrogen–carbon bond, due to steric hindrance between the ring and amino methyl groups and, consequently, resonance of the lone-pair on the nitrogen atom with the benzene π-electrons will be prevented to a large extent. The twisted dimethylamino group plus the ring methyl group will also produce a steric effect toward the iodine molecule approaching the nitrogen atom. It is interesting to see what change will occur in the donor strength of this compound with iodine.

The donating properties of these hindered anilines toward aromatic acceptors such as trinitrobenzene[3] and chloranil[4] have been studied already. It was found that the complexing strength of N,N-dimethylaniline is greatly diminished by the substitution of a methyl or a larger group at the *ortho* position. Somewhat similar studies were made for the donor strengths of hindered biphenyls toward *s*-trinitrobenzene.[5] It was again concluded that the complexing power is large only when the molecule retains the coplanar structures. These results are quite reasonable from the theoretical viewpoint that the benzene rings of the donor and acceptor in these cases should lie parallel and as close as possible to each other to obtain a large binding energy. The steric requirements for the iodine–aniline complexes may be different from those of the above mentioned π-π complexes. There is evidence that, in many complexes formed between halogens and n-donors, the halogen lies in a straight line passing through the n-donor, like O—X–X or N—X–X.[6] Even in the case of benzene–halogen complexes, there are some experimental results which support the structure with the halogen mole-

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[1] On leave of absence from the Institute for Solid State Physics, University of Tokyo, Meguroku, Tokyo, Japan.

[2] C. Reid and R. S. Mulliken, THIS JOURNAL, **76**, 3869 (1954); S. Nagakura, *ibid.*, **80**, 520 (1958).

[3] J. Landauer and H. McConnell, *ibid.*, **74**, 1221 (1952); R. Foster and D. L. Hammick, *J. Chem. Soc.*, 2685 (1954); S. D. Ross and M. M. Labes, THIS JOURNAL, **79**, 76 (1957).

[4] N. H. Smith, Thesis, Univ. Chicago, 1955.

[5] C. E. Castro, L. J. Andrews and R. M. Keefer, THIS JOURNAL, **80**, 2322 (1958).

[6] O. Hassel, *Mol. Phys.*, **1**, 241 (1958), and earlier papers.

cule perpendicular to the benzene ring,[6,7] although for theoretical and other experimental reasons it seems more probable that the orientation is oblique, or more or less random.[8]

Experimental

Purification of Materials.—Fisher Certified iodine was resublimed under pressure of 15 mm. Phillips *n*-heptane was shaken with concentrated sulfuric acid, then washed with water, dried with sodium sulfate and distilled using a Podbielniak column. Eastman Pure Chemicals of N,N-dimethylaniline and its *o*- and *p*-methyl derivatives were dried with sodium hydroxide and fractionally distilled under reduced pressure. N,N-Dimethyl-2,6-xylidine was synthesized from 2,6-xylidine[9] and purified by fractional distillation (n^{20}D 1.5141; lit.[10] 1.51310). The ultraviolet absorption spectra of these anilines agreed with those of the same compounds given in the literature.

Method.—For absorption spectra measurements, a Warren Spectracord was used with specially designed cell holders through the inside of which water from the thermostat was passed to keep the temperature of the cell constant. It was found that the *n*-heptane solutions of iodine and the bases are unstable. Even when the concentrations of iodine and the bases are, respectively, of the order of 3 × 10^{-4} *M*, and 0.02 *M*, the solutions became turbid in five or ten min. after preparation, and, in a few hours, yellow, fine precipitates collected on the wall. In several days the solution became colorless. It was found that this difficulty could not be avoided by further purification of the bases. It seems that the iodine substitution reaction proceeds slowly at the benzene ring, leading to the formation of the N,N-dimethyl-iodo-anilinium hydroiodide or its methyl derivatives. However, when the concentration of iodine was made one tenth that of the above mentioned value, all the solutions remained clear for many days, and no change of the absorption spectra was observed at least in a day.

As was reported by Evans,[11] dimethylaniline absorbs light in the visible region when it contains oxygen. However, it has been found that this absorption intensity decreases rapidly when dimethylaniline is diluted with *n*-heptane and is quite negligible for the present experimental conditions. The dissolved oxygen might promote the substitution reaction of iodine with the anilines. In order to examine this, a *n*-heptane solution of iodine and dimethylaniline was prepared with the complete exclusion of oxygen, by removing oxygen from the heptane solutions of iodine and dimethylaniline using the vacuum line, then mixing the two solutions in an atmosphere of nitrogen. The absorption spectrum of this solution was found to be very much the same as those of the solutions prepared by the ordinary method. In preparing all other solutions, therefore, no precautions were taken for excluding oxygen.

The spectra were measured by using 10 cm. cylindrical cells made of fused silica. The 100% transmission line was adjusted for each measurement by using two such cells both filled with *n*-heptane. The absorption of the solution was measured with *n*-heptane as the reference. The absorption caused by the anilines was negligible under the present experimental conditions down to 360 mμ. In the further ultraviolet region, however, the absorption of the anilines rises rapidly, making it difficult to measure the spectra of the complexes.

Results

Some of the absorption spectra obtained for the *n*-heptane solutions of iodine and the bases are shown in Figs. 1, 2 and 3. All show that the free iodine band at 525 mμ diminishes in intensity and strong absorption appears at shorter wave lengths upon adding the base to the solution. It seems to be quite reasonable to attribute this newly appearing absorption to charge-transfer bands arising from iodine–aniline complexes. Because of the strong absorption due to the anilines themselves, it was not possible to follow these new absorptions to their maxima, which must lie at shorter wave lengths, considerably below 360 mμ.

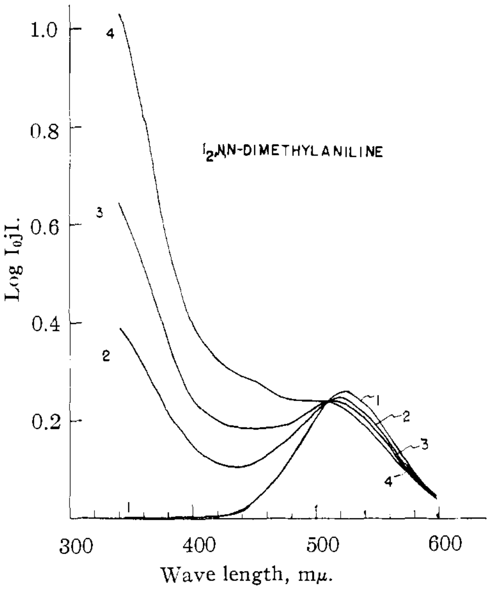

Fig. 1.—The visible absorption spectra of the *n*-heptane solutions of iodine and N,N-dimethylaniline at 27°. The path length is 10 cm. The concentration of iodine is 2.88 × 10^{-5} *M*. The concentrations of N,N-dimethylaniline are zero for solution 1, 0.00993 *M* for solution 2, 0.01986 *M* for solution 3 and 0.03972 *M* for solution 4, respectively.

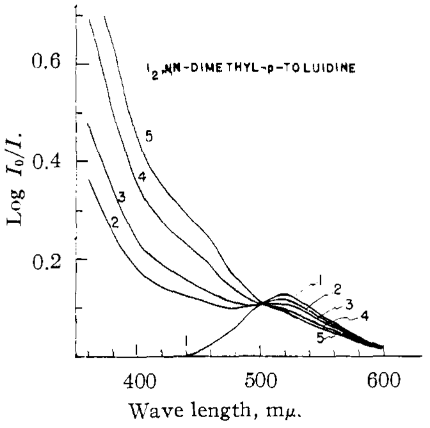

Fig. 2.—The visible absorption spectra of the *n*-heptane solutions of iodine and N,N-dimethyl-*p*-toluidine at 12°. The path length is 10 cm. The concentration of iodine is 2.88 × 10^{-5} *M*. The concentrations of N,N-dimethyl-*p*-toluidine are zero for solution 1, 0.005460 *M* for solution 2, 0.008190 *M* for solution 3, 0.01638 *M* for solution 4 and 0.02730 *M* for solution 5, respectively.

In the cases of N,N-dimethylaniline (Fig. 1), and N,N-dimethyl-*p*-toluidine (Fig. 2), there are shoulders at about 440 mμ, which may be attributed to the visible iodine band strongly shifted by the complexing. This assignment is reasonable in view of the fact that the pyridine–iodine and triethylamine–iodine complexes show strongly shifted peaks at 422 and 414 mμ, respectively, corresponding to the visible iodine bands.

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[7] E. E. Ferguson, *J. Chem. Phys.*, **25**, 577 (1956); **26**, 1357 (1957); *Spectrochim. Acta*, **10**, 123 (1957).

[8] L. E. Orgel and R. S. Mulliken, THIS JOURNAL, **79**, 4839 (1957).

[9] E. Bamberger and L. Rudolf, *Ber.*, **39**, 4291 (1906).

[10] H. Ley and G. Pfeiffer, *ibid.*, **54**, 377 (1921).

[11] D. F. Evans, *J. Chem. Soc.*, 345 (1953).

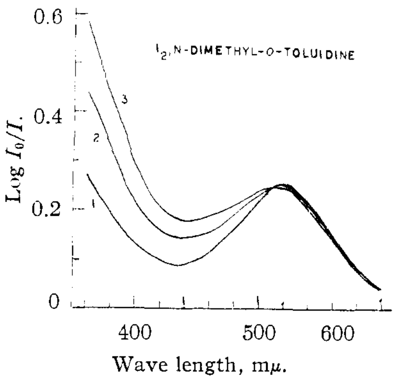

Fig. 3.—The visible absorption spectra of the *n*-heptane solutions of iodine and N,N-dimethyl-*o*-toluidine at 17°. The path length is 10 cm. The concentration of iodine is 2.88×10^{-5} *M*. The concentrations of N,N-dimethyl-*o*-toluidine are 0.0542 *M* for solution 1, 0.0948 *M* for solution 2 and 0.1353 *M* for solution 3, respectively.

As is seen in Fig. 3, no shoulder was observed in the case of N,N-dimethyl-*o*-toluidine. Also, no shoulder was observed in the case of N,N-dimethyl-2,6-xylidine, although the spectrum is not shown because it is so similar to that of the iodine–N,N-dimethyl-*o*-toluidine complex. That the spectra in these cases show no shoulder may be explained by the small concentration of the complexes in the solutions, corresponding to their smaller equilibrium constants (see below).

In all cases, the intensities of the strong bands decrease at elevated temperature, and at the same time the free iodine band gains in intensity. This indicates that these bands are due to the complex which is in equilibrium with free components.

As a next step, the usual Benesi–Hildebrand plot was made using extinction coefficient data for two or three wave lengths in the region of the strong absorption attributed to the complexes. (The shifted iodine band overlaps the charge-transfer band at these wave lengths, while the free iodine band does not. The Benesi–Hildebrand method is still applicable here in spite of the fact that the absorption is a superposition of the charge-transfer band and the shifted visible iodine band, because both arise from the complex.) In all cases, straight lines were obtained to within the experimental error of the optical density. This definitely indicates the formation of 1:1 molecular complexes. From these results the equilibrium constants for the formation of complexes were calculated by the least-squares method, using the modified Benesi–Hildebrand equation

$$C(\mathrm{D})/d = 1/C(\mathrm{I_2})K\epsilon + C(\mathrm{D})/C(\mathrm{I_2})\epsilon$$

where $C(\mathrm{D})$ and $C(\mathrm{I_2})$ are the concentrations of the donor and iodine in mole/l., respectively, and *d*, *K* and ϵ mean the optical density of the band, the equilibrium constant and the molar extinction coefficient, respectively. This equation seems to give more accurate results, because it takes into consideration the individual optical density measurements more than the Benesi–Hildebrand equation does.[12] The results are given in Table I, where the equilibrium constants are given in units of l./mole and the molar extinction coefficients in units of mole/l. cm.

TABLE I

EQUILIBRIUM CONSTANTS OBTAINED AT DIFFERENT WAVE LENGTHS AND TEMPERATURES

N,N-Dimethylaniline

Wave length, mμ	Temp., °C. 11	27	40	Temp., °C. 11	27	40
	K (l./mole)			ϵ (mole/l. cm.)		
370	39.0	19.7	11.0[a]	6090	5520	(5800)
400	43.0	17.8	11.0[a]	3170	3330	(3250)
Av.	41.0	18.8	11.0			

N,N-Dimethyl-*p*-toluidine

Wave length, mμ	Temp., °C. 12	21.3	33	Temp., °C. 12	21.3	33
	K (l./mole)			ϵ (mole/l. cm.)		
360	69.0	42.7	23.1	9190	8780	9370
380	64.4	40.9	23.1	6970	6550	6910
400	63.8	42.2	25.9	4810	4440	4510
Av.	65.7	41.9	24.0			

N,N-Dimethyl-*o*-toluidine

Wave length, mμ	Temp., °C. 17	32	Temp., °C. 17	32
	K (l./mole)		ϵ (mole/l. cm.)	
360	2.49	2.04	8020	5790

N,N-Dimethyl-2,6-xylidine

Wave length, mμ	Temp., °C. 16	33	Temp., °C. 16	33
	K (l./mole)		ϵ (mole/l. cm.)	
356	1.95	1.70	3180	2620

[a] The data at this temperature showed large deviations from the Benesi–Hildebrand equation. Hence these *K* values were calculated by assuming that the molar extinction coefficients were the average of those obtained at 11 and 27°, that is, 5800 and 3250 mole/l. cm., respectively, because better results can be obtained by this procedure when the accuracy of the data is not good.

The plots of ln *K* against $1/T$ (*T* being the absolute temperature) lead to straight lines as shown in Fig. 4 in the case of the two bases. For the remaining two bases, equilibrium constants were determined only at two temperatures. Heats of formation of the complexes and the entropy change were calculated from these results as shown in Table II.

TABLE II

ΔH AND ΔS FOR THE MOLECULAR COMPLEX FORMATION WITH I_2

Base	$-\Delta H$ (kcal./mole)	$-\Delta S$ (e.u.)
N,N-Dimethylaniline	8.2 ± 0.3	21.6 ± 0.6
N,N-Dimethyl-*p*-toluidine	8.3 ± .2	20.8 ± 0.4
N,N-Dimethyl-*o*-toluidine	2.3 ± .5	6.2 ± 1.0
N,N-Dimethyl-2,6-xylidine	1.7 ± .3	3.6 ± 0.6

Discussion

It will be illuminating to examine the donor properties of dimethylaniline by the molecular orbital theory. In Fig. 5a and Fig. 5c are shown the energy levels of the six π-orbitals of benzene, ϕ_0, ϕ_1, ϕ_{-1}, ϕ_2, ϕ_{-2} and ϕ_3, and the lone-pair electron orbital of nitrogen, ψ_N. The energy levels of ϕ_1 and ϕ_{-1} in benzene may be taken equal to the ionization potential of benzene, 9.24 e.v.[13] and that of ψ_N to that of trimethylamine 7.82 e.v.[14] If the dimethylamino group in N,N-dimethylaniline is assumed to lie in the plane of the benzene ring, the lone pair orbital on the nitrogen atom should be a π-atomic or-

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(12) H. Tsubomura, *Bull. Chem. Soc. Japan*, **27**, 1 (1954); R. L. Scott, *Rec. trav. chim. Pays-Bas*, **75**, 787 (1956).

(13) K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957).

(14) K. Watanabe and J. R. Mottle, *ibid.*, **26**, 1773 (1957).

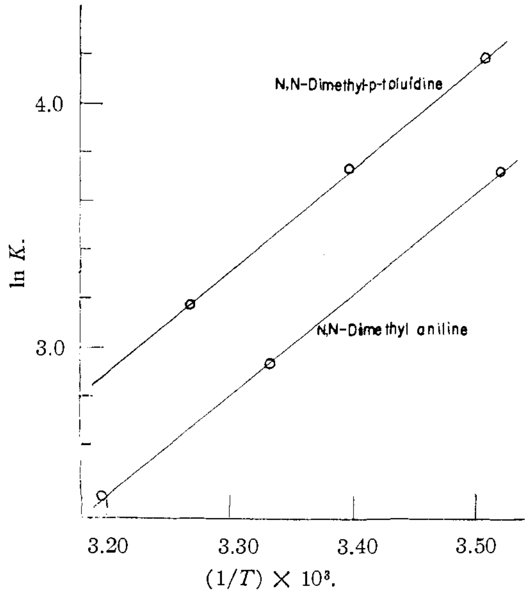

Fig. 4.—The plot of ln K against $1/T$ for the iodine complexes with N,N-dimethylaniline and N,N-dimethyl-*p*-toluidine.

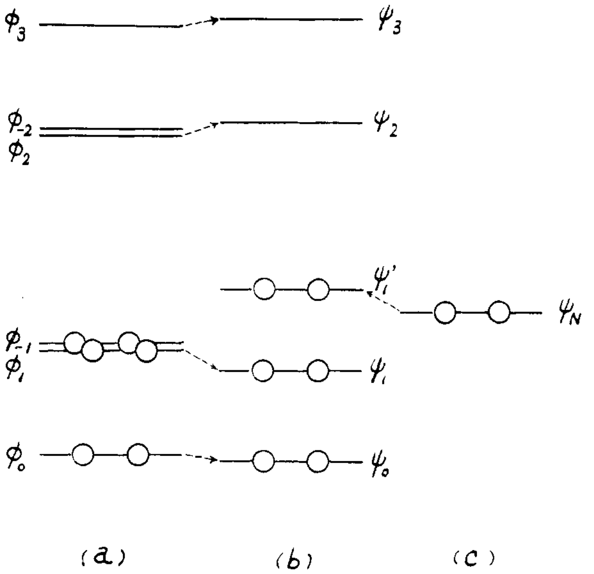

Fig. 5.—Electronic energy levels for benzene and amino group.

bital and perpendicular to the plane of the benzene ring, and, when the minor effect of the methyl groups is neglected, the symmetry of the molecule may be considered as C_{2v}. In view of the experimentally established pyramidal structure of amines, however, it may be considered that the amino group in dimethylaniline does not lie in the plane of the benzene ring, although no experimental verification has been made on the structure of this molecule. If this is true, the lone pair on the nitrogen atom should be an s-p hybridized orbital with its direction a little different from the π-atomic orbitals of the benzene ring, but still lying in the plane of symmetry which passes through the nitrogen atom and the center of the benzene ring, and perpendicular to the ring. The symmetry of the molecule is then considered to be C_s. It can be immediately understood that the above-mentioned orbitals are divided into two groups a′ and a″, which are, respectively, symmetric and antisymmetric with respect to reflection in the plane of the symmetry.[15] The orbitals in the benzene ring with a″ symmetry, ϕ_{-1} and ϕ_{-2}, do not interact with ψ_N and remain unchanged in energy, while the orbitals with a′ symmetry, ϕ_0, ϕ_1, ϕ_2 and ϕ_3, interact with ψ_N forming five orbitals, ψ_0, ψ_1, ψ_1', ψ_2 and ψ_3, as illustrated qualitatively in Fig. 5b, the lowest three being filled with electrons.

Among the filled orbitals, the donor strength of ψ_0 may be considered to be quite small because of its low energy. Also the donor strength of ϕ_{-1} orbital, which must be very similar to that of benzene and may be designated as a pure π-donor orbital, should be much smaller than those of ψ_1 and ψ_1'. The orbitals ψ_1 and ψ_1' may be called nπ-mixed donor orbitals because these consist of π-molecular orbitals of benzene mixed with the nonbonding orbital of the nitrogen atom (for details, see below). Of the two orbitals, ψ_1' will have the higher donor strength because of its higher energy. However, ψ_1 may also have considerable donor strength, especially when its form is favored for an overlapping with the orbital of the acceptor molecule.

The forms of the orbitals of ψ_1 and ψ_1' are qualitatively illustrated in Fig. 6, where the diameters of the circles are proportional to the approximately calculated coefficients of the atomic orbitals in these orbitals and the shadowed circles mean that the coefficients at these atoms are negative. In both these orbitals, the electron density is largest at the nitrogen atom and, in the orbital of ψ_1', which supposedly has the highest donor strength, the electron density is especially large at the nitrogen atom. Therefore, it can be seen that the nitrogen atom will take the most important role in the charge transfer.

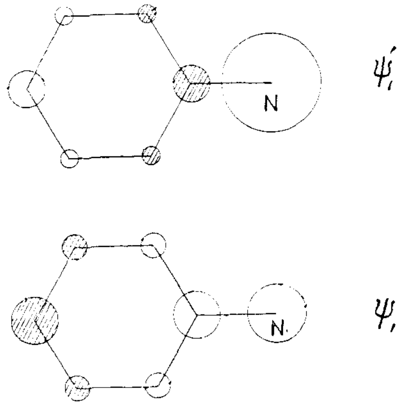

Fig. 6.—Molecular orbitals of ψ_1 and ψ_1'.

Furthermore, if charge transfer occurs from both ψ_1' and ψ_1 orbitals, with strengths somewhat different from each other, it is probable that the role of the lone-pair of nitrogen electrons is greater than

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(15) If the molecule has approximate C_{2v} symmetry, the orbitals can be divided into two groups with symmetry of b_1 and a_2, which correspond, respectively, to a′ and a″ for the case of C_s symmetry. The following argument based on the C_s symmetry of the molecule can be applied exactly in the same way for the case of C_{2v} symmetry.

if only ψ_1' were involved. To understand this, we neglect the interactions between ψ_N and all benzene π-orbitals except ϕ_1, this approximation being justified since the interaction between ψ_N and ϕ_1 is considered to be especially large because of their proximity in terms of energy. Then, ψ_1' and ψ_1 can be expressed as

$$\psi_1' = a\psi_N - b\phi_1 \qquad 1 > a > b > 0$$
$$\psi_1 = b^*\psi_N + a^*\phi_1 \qquad a^* \approx a,\ b^* \approx b$$

Now if the charge transfer from both these orbitals is significantly large, it may be more appropriate to describe the charge transfer as occurring from a donor orbital which is derived by the linear combination of ψ_1' and ψ_1, so that it is effectively the ψ_N orbital itself. Although this "relocalized" orbital has a larger ionization potential than ψ_1', it may be more favored for overlap with the orbital of a σ-acceptor such as iodine, because of its localized nature, and hence may play a dominant part in the complex formation.

Therefore, it is highly probable that dimethylaniline acts mainly as an n-donor, with its nitrogen atom as an attaching center toward acceptor molecules such as iodine. The possible structure of the complex is predicted as shown in Fig. 7 (a or b). The structure of the complex is more likely to be a than b, if the accepting orbital of iodine has the large directing property along the I–I straight line, as is suggested by the structures of many halogen complexes with n-donors such as ethers and amines as determined by Hassel.

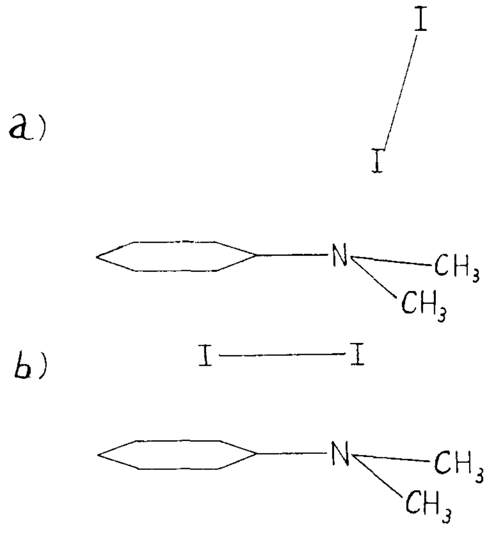

Fig. 7.—Assumed structures of N,N-dimethylaniline–iodine complex.

In relation to the conclusion reached here, it may be interesting to point out that the ΔH values for the complexes with pyridine[2] ($\Delta H = -7.8$ kcal./mole), N,N-dimethylaniline ($\Delta H = -8.2$ kcal./mole), and triethylamine[2] ($\Delta H = -12.0$ kcal./mole) are parallel to the basicity of these bases, defined by their pK values, which are 5.19, 5.21 and 10.72, respectively. Presumably these bases all act alike as n-donors in their interactions with a proton, and the present results indicate a parallel behavior with iodine as an acceptor.

The most remarkable finding of the present experimental results is the *ortho* effect of the methyl group upon the complexing strengths of dimethylaniline derivatives. As is well known, the methyl group attached to the benzene ring gives rise to a slight increase of donor strength. According to the present results, N,N-dimethyl-*p*-toluidine has a ΔH value almost equal to that of N,N-dimethylaniline and a K value more than twice as large as that of N,N-dimethylaniline. For the case of N,N-dimethyl-*o*-toluidine, on the other hand, both $-\Delta H$ and K values are greatly diminished and a still larger reduction is seen in the case of N,N-dimethyl-2,6-xylidine.

In these molecules, there are large steric repulsions between methyl groups with the result that the dimethylamino group is rotated and the line connecting the two carbon atoms in this group is almost perpendicular to the benzene ring. Klevens and Platt[16] concluded, from discussions on the ultraviolet absorption spectra of these molecules, that the angle of rotation of the dimethylamino group in N,N-dimethyl-2,6-xylidine is 90°, which corresponds to a complete destruction of the resonance between the π-electrons of the ring and the lone-pair of nitrogen electrons, and that the angle of rotation in N,N-dimethyl-*o*-toluidine is 60°, which corresponds to a reduction of the resonance energy to one quarter. The same problem has been discussed more recently by other authors,[17] but no substantial change in the conclusions was made.

By the rotation of the dimethylamino groups, the nπ-mixed donor orbitals discussed above are converted (either completely or less completely) to pure π and pure n-donor orbitals. On grounds of electronic structure alone, it should be expected that the donor properties of these hindered anilines become more or less like the superposition of those of the aliphatic amine and the methylated benzene, of which the former should play the dominant part, owing to its larger donor strength. The I_2 complexes of these hindered anilines should then have nearly the same ΔH values as that of trimethylamine, whose $-\Delta H$ value is considered to be larger than that of N,N-dimethylaniline.[18] However, this is true only when there is no steric hindrance around the nitrogen lone-pair electron orbital toward the approaching iodine molecule. As can be seen in Fig. 8, which shows the molecular model of N,N-dimethyl-*o*-toluidine (rotation of the dimethylamino group by 60°), the two methyl groups in the dimethylamino group and one methyl group[19] at the *ortho* position in the benzene ring may well produce a considerable steric effect around the nitrogen atom and the neighboring carbon atom in the benzene ring. It should be pointed out that this steric effect does not seem to be appreciably large in the formation of substituted

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(16) H. B. Klevens and J. R. Platt, THIS JOURNAL, **71**, 1714 (1949).

(17) J. N. Murrell, *J. Chem. Soc.*, 3779 (1956); E. C. McRae and L. Goodman, *Mol. Spectroscopy*, **2**, 464 (1958).

(18) Trimethylamine has a larger pK than N,N-dimethylaniline.

(19) The isomer which can be obtained by the rotation of the dimethylamino group by 180° from the position shown in Fig. 8 is considered to be less stable, because, if a pyramidal structure of the dimethylamino group is assumed, the repulsion between its methyl groups and the methyl group at the *ortho* position appears to be very large.

anilinium cations, as can be seen from the larger *pK* value of N,N-dimethyl-*o*-toluidine than that of N,N-dimethylaniline. However, taking into account the difference in size between an iodine molecule and a proton (or perhaps more correctly, a proton in an H_3O^+ group), we may conclude that this steric effect is responsible for the large reduction of the donor strength of N,N-dimethyl-*o*-toluidine toward iodine, even though from the molecular model it is not obvious that the steric interference with I_2 complexing would be as great as the ΔH values seem to indicate. In the case of N,N-dimethyl-2,6-xylidine, the steric repulsion around the nitrogen atom will be a little larger, because of the larger angle of rotation of the dimethylamino group and the presence of two *ortho* methyl groups.

As for the structures of the complexes of these hindered anilines with iodine, two isomeric forms may be considered. The first one involves the nitrogen atom as n-donor, with perhaps one end of the iodine molecule in touch with the nitrogen atom, and the second one involves the benzene as π-donor, with the iodine molecule lying transversely somewhere above the benzene ring and away from the dimethylamino group.

It should be noted that the equilibrium constants for the iodine complexes with the *ortho*-substituted dimethylanilines are considerably larger than those of the iodine–toluene complex ($K = 0.16$ l./mole at 25°) and the iodine–*m*-xylene complex ($K = 0.31$ at 25°). From the molecular models of N,N-dimethyl-*o*-toluidine and N,N-dimethyl-2,6-xylidine, it is reasonable that the iodine molecule may approach at least fairly close to the nitrogen atom in spite of considerable steric hindrance, so that the aniline groups are probably still functioning more as n-donors on the nitrogen atom than as π donors on the ring.

Orgel and Mulliken[8] have pointed out that, even if two or more isomeric configurations for a 1:1 complex, with different absorption spectra, are present in solution and give an observed spectrum which is a superposition of bands corresponding to the isomeric configurations, the equilibrium constants obtained by the Benesi–Hildebrand plot at different wave lengths should give the same values, but the extinction coefficients obtained at different temperatures will not in general coincide. As is seen in Table I, the molar extinction coefficients obtained at different temperatures in the cases of N,N-dimethylaniline and N,N-dimethyl-*p*-toluidine agree to within the estimated experimental error (about 10%), suggesting that these complexes have only one configuration. On the other hand, in the cases of N,N-dimethyl-*o*-toluidine and N,N-dimethyl-2,6-xylidine, the molar extinction coefficients obtained at higher temperatures show a definite decrease. According to the above mentioned theory, this might indicate the existence of two or more isomeric configurations for these complexes, which may well be the two structures of the complex discussed above. However, the observed decrease of molar extinction coefficients at higher temperature may be due, at least in part, to a different cause. The amplitudes of internal vibrations of molecules are generally enhanced at higher temperature. This enhancement will be particularly large for the hindered rotation of the methyl groups and the amino group and for other low frequency motions. Consequently, the average position of the complexed iodine molecule should be pushed away from the nitrogen atom at higher temperature, and thus the molar extinction coefficients be reduced.

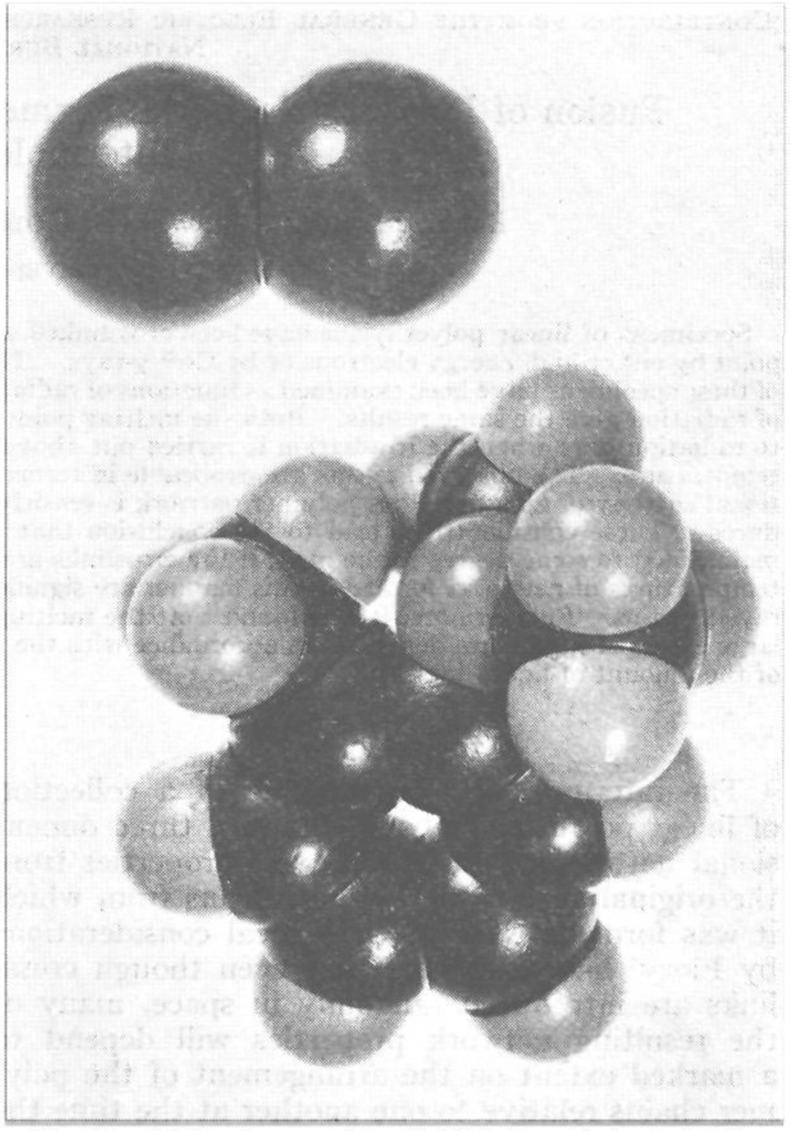

Fig. 8.—Molecular model of N,N-dimethyl-*o*-toluidine: the model of iodine molecule is shown for convenience to compare the sizes of these molecules.

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