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# Steric Effects in Azo Compounds. The Electric Dipole Moments and the Absorption Spectra of Azobenzene Derivatives

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The electric dipole moments of *trans*-4-*N*,*N*-dimethylaminoazobenzene and its derivatives, and the absorption spectra of azobenzene derivatives and their conjugate acids have been measured. The dipole moment and the intensity of the $\pi$–$\pi^*$ band are clearly reduced by introduction of methyl groups into ortho positions to azo group. The twisting angle of the benzene rings with respect to the azo group has been estimated for 2,2′-disubstituted azobenzenes and their conjugate acids by means of the Braude equation. From the spectral intensity and transition energy, it was concluded that the conjugate acids are generally more susceptible than the bases to the steric effect.

It is well known that steric hindrance affects certain physical and chemical properties of organic compounds.[1] The twist of molecule about a *single* bond in a conjugated system is of particular interest, the physical properties being susceptible to the twist.[2–4] This makes experimental approach possible.

Minkin *et al.*[5] showed that aromatic azomethines have a nonplanar conformation in which the dihedral angle between the amino nucleus and the rest of the molecule plane is 40—60°. Acoplanarity of the molecule is supported by the following: low intensity of $\pi$–$\pi^*$ conjugation band and absence of fluorescence in contrast to the isoelectronic analogues—stilbenes and azobenzenes; low basicity, nonisolation of *cis*-isomers.

The dipole moments of aromatic amines[6] and nitro compounds[7,8] are greatly reduced by ortho substitution. A similar effect has been reported for biphenyls,[9] stilbenes,[10] and other aromatic compounds.[11] The reduction in dipole moment by ortho substitution is interpreted as due to the reduced conjugation which arises from the twisting of molecule about a single bond in a conjugated system.[2]

It has been recognized that when the molecule is sufficiently crowded to render coplanarity of the conjugated atoms difficult or impossible, the electronic spectra differ from those expected for a planar model.

In a conjugated system X–Y, change in steric conformation about the single bond can give rise to three types of spectral effects[12]: (A) Slight twisting about the single bond, the spectroscopic result being hypochromic effect only. (B) moderate twisting resulting in both a hypochromic effect and a hypsochromic shift. (C) Severe twisting resulting in complete steric inhibition of resonance, and giving rise to the cumulative spectra of the two isolated chromophores X and Y.

Good example of type (A) are provided by alkylated benzaldehydes, acetophenones, cyclic aromatic ketones, and related compounds.[2] The angle of twist $\theta$ can be calculated according to the Braude equation,[2] by which Finar[13] evaluated the angle of twist for some sterically hindered pyrazoles. Jaffé and Orchin[12] attempted an unified explanation for the spectra of (A) and (B); the observed hypochromic effect exhibited by both slightly hindered and moderately hindered stilbenes could be explained by their interpretation.

Azobenzene and its meta- and para-substituted derivatives have planar structure which is due to the energy stabilization by extended $\pi$-electron conjugation.[14] However, if substituents are introduced into one or both benzene rings on the ortho positions to the azo group, a steric hindrance between the substituents and the lone-pair electrons on the N-atoms will make the molecule twist around the –N=N– bonds,[15,16] the extent of twist being determined by a compromise of the mesomeric stabilization with the steric factor.

The spectra of substituted azobenzenes have been reported by many workers,[17,18] and systematic studies of the effects of substituents on the spectra have been carried out. Gore and Wheeler[15] measured the

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[1] M. S. Newman, "Steric Effects in Organic Chemistry," ed. by M. S. Newman, John Wiley, New York (1956), pp. 164, 479.

[2] E. A. Braude and F. Sondheimer, *J. Chem. Soc.*, **1955**, 3754.

[3] H. Suzuki, This Bulletin, **32**, 1340 (1959).

[4] H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley, New York (1962). pp. 384—449.

[5] V. I. Minkin, Yu. A. Zhdanov, E. A. Medyantzeva, and Yu. A. Ostroumov, *Tetrahedron*, **23**, 3651 (1967).

[6] R. H. Birtles and G. C. Hampson, *J. Chem. Soc.*, **1937**, 10; C. E. Ingham and G. C. Hampson, *ibid.*, **1939**, 981.

[7] H. Koford, L. E. Sutton, P. E. Verkade, and B. M. Wepster, *Rec. trav. chim.*, **78**, 790 (1959).

[8] R. Nakashima, *Nippon Kagaku Zasshi*, **83**, 672 (1962).

[9] K. B. Everard, L. Kumar, and L. E. Sutton, *J. Chem. Soc.*, **1951**, 2807.

[10] K. B. Everard and L. E. Sutton, *ibid.*, **1951**, 2816.

[11] J. W. Baker and W. T. Tweed, *ibid.*, **1941**, 796.

[12] H. H. Jaffé and M. Orchin, *ibid.*, **1960**, 1078.

[13] I. L. Finar, *ibid.*, **1968**. 725.

[14] J. M. Robertson, *ibid.*, **1939**, 232.

[15] P. E. Gore and O. H. Wheeler, *J. Org. Chem.*, **26**, 3295 (1961).

[16] D. Gegiou, K. A. Muszkat, and E. Fischer, *J. Amer. Chem. Soc.*, **90**, 3907 (1968).

[17] a) W. R. Brode, *ibid.*, **48**, 1984 (1926); *Ber.* **61**, 1722 (1928). b) A. H. Cook, D. G. Jones, and J. B. Polya, *J. Roy. Chem. Soc.*, **1939**, 1315; D. G. Jones, *J. Roy. Coll. Sci.*, **10**, 52 (1940). c) W. R. Brode, J. H. Gould, and G. M. Wyman, *J. Amer. Chem. Soc.*, **74**, 4641 (1952). d) G. M. Badger and R. G. Buttery, *J. Chem. Soc.*, **1953**, 2156.

[18] a) L. Skulski, *Bull. Acad. Polon. Sci., ser. Sci. Chim.*, **12**, 719 (1956). b) P. P. Birnbaum, J. H. Linford, and D. W. G. Style, *Trans. Faraday Soc.*, **49**, 735 (1953).

spectra of some of 2,2′-disubstituted azobenzenes and calculated the angle of distortion from coplanarity by means of the Braude equation. However, no wide spectral investigation seems to have been made on these substances in relation to the steric effect. Only a few studies were made on how the steric effect causes the change in their dipole moments. This paper presents the dipole moment and the spectral data of azobenzene derivatives. The spectral data of their conjugate acids are also given, from which the molecular conformation is discussed.

## Experimental

*Compounds.* Symmetrically substituted azobenzenes were prepared by the following procedures.[19]

*4,4′-Dimethylazobenzene*: A solution of 13.8 g of sodium nitrite in 200 m*l* of water was added dropwise with stirring to a solution of 20 g of *p*-toluidine in 136 m*l* of 13% hydrochloric acid, the temperature of the solution being kept below 5°C with ice bath. The diazonium solution was added to a stirred solution containing 70 g of cupric sulfate, 30 g of hydroxylamine hydrochloride, 48 m*l* of 50% solution of potassium hydroxide and 100 m*l* of 33% aqueous solution of ammonia. The product was dissolved in benzene, and the solution was passed through an alumina column, and then crystallized from benzene.

Azobenzene: mp 68°C (lit, 68°C)

2,2′-Dimethylazobenzene: mp 55°C (lit, 55°C)

3,3′-Dimethylazobenzene: mp 53°C (lit, 54—55°C)

4,4′-Dimethylazobenzene: mp 144°C (lit, 144°C)

2,2′-Dichloroazobenzene: mp 137°C (lit, 137°C)

3,3′-Dichloroazobenzene: mp 103.5°C (lit, 102—103.5°C)

4,4′-Dichloroazobenzene: mp 185°C (lit, 183—184°C)

2,2′-Dimethoxyazobenzene: mp 154°C (lit, 154—155°C)

4,4′-Dimethoxyazobenzene: mp 163.5°C (lit, 160.5—162.5°C)

2,3,2′,3′-Tetramethylazobenzene: mp 110—110.5°C (lit, 110—111°C)

2,4,2′,4′-Tetramethylazobenzene: mp 128—128.5°C (lit, 125—126°C)

2,5,2′,5′-Tetramethylazobenzene: mp 119—119.5°C (lit, 119°C)

3,4,3′,4′-Tetramethylazobenzene; mp 157°C (Found: C, 80.50; H, 7.86; N, 11.89%. Calcd: C, 80.63; H, 7.61; N, 11.76%).

2,2′-Dimethyl-3,3′-dichloroazobenzene: mp 154°C (lit, 153—154°C)

2,2′-Dimethyl-4,4′-dichloroazobenzene: mp 164—165°C (Found: C, 60.19; H, 4.59; N, 10.12%. Calcd: C, 60.23; H, 4.33; N, 10.04%).

The derivatives of 4-*N*,*N*-dimethylaminoazobenzene were prepared and purified by the following procedure.

4-N,N-*Dimethylaminoazobenzene*[20]: 4-*N*,*N*-Dimethylaminoazobenzene was prepared by diazotizing aniline and coupling the resulting diazonium salt with dimethylaniline in an acetate buffer. Other compounds of Types II and II′ were prepared in a similar way. The products were dissolved in benzene, and the solutions were passed through an alumina column, and then crystallized from benzene.

4-*N*,*N*-Dimethylaminoazobenzene: mp 118—119°C (lit, 119—120°C)

4-Methyl-4′-*N*,*N*-dimethylaminoazobenzene: mp 170—171°C (lit, 169.5—170°C)

4-Chloro-4′-*N*,*N*-dimethylaminoazobenzene: mp 158—158.5°C (lit, 158—158.5°C)

3-Nitro-4′-*N*,*N*-dimethylaminoazobenzene: mp 157—157.5°C (lit, 157—158°C)

4-Nitro-4′-*N*,*N*-dimethylaminoazobenzene: mp 228°C (lit, 230—231°C)

2,2′-Dimethyl-4-*N*,*N*-dimethylaminoazobenzene: mp 79—80°C (Found: C, 75.62; H, 7.97; N, 16.60%. Calcd: C, 75.85; H, 7.56; N, 16.59%).

2,4,2′-Trimethyl-4′-*N*,*N*-dimethylaminoazobenzene: mp 120—121°C (Found: C, 76.15; H, 7.94; N, 15.93%. Calcd: C, 77.37; H, 7.92; N, 15.72%).

2,2′-Dimethyl-4-chloro-4′-*N*,*N*-dimethylaminoazobenzene: mp 115—116°C (Found: C, 66.98; H, 6.56; N, 14.55%. Calcd: C, 66.77; H, 6.30; N, 14.60%).

2,2′-Dimethyl-5-nitro-4′-*N*,*N*-dimethylaminoazobenzene: mp 148—148.5°C (Found: C, 64.20; H, 6.23; N, 18.97%. Calcd: C, 64.41; H, 6.08; N, 18.78%).

2,2′-Dimethyl-4-nitro-4′-*N*,*N*-dimethylaminoazobenzene: mp 147—148°C (Found: C, 64.58; H, 6.38; N, 18.95%. Calcd: C, 64.41; H, 6.08; N, 18.78%).

*Benzene*: Benzene was purified successively by shaking with concentrated sulfuric acid and water, drying over sodium wire, and distillation.

*Cyclohexane*: Cyclohexane was washed several times with a mixture of concentrated nitric and sulfuric acids. After repeated washing with distilled water it was distilled over sodium.

*Ethyl Alcohol*: Ethyl alcohol was of reagent grade and was used without further purification.

*Sulfuric Acid*: Sulfuric acid of commercial special grade was used without purification.

*Measurement of Dielectric Constant and Density.* Six solutions of each compound with weight fractions between 0 and 0.015 were used. The solutions were allowed to stand in the dark for a few hours in order to avoid contamination with *cis*-isomers.

The dielectric constants were determined with a Dielectric Analyzer, Type FAM-3A, manufactured by Yamato Scientific Instrument Co. The oscillator, controlled by a quartz crystal, was operated at frequency of 2MHz. The accuracy of the precision variable condenser, taken from the average of several readings, was about one part in 10000 for the cell filled with air.

The densities of the same solutions were measured in an Ostwald type pycnometer of about 5 m*l*. All the measurements were carried out in a thermostat regulated at 25± 0.01°C.

Further, to insure that the instruments were properly calibrated and that the method of calculation was appropriate, the dipole moments of *p*-chloroaniline and chlorobenzene were determined. The results were 2.99 D for *p*-chloroaniline, and 1.58 D for chlorobenzene, and were in good agreement with literature values (2.99 D for *p*-chloroaniline and 1.55 D and 1.58 D for chlorobenzene) which were obtained under similar condition.

*Measurement of Absorption Spectra.* Absorption spectra were measured with a Hitachi double beam spectrophotometer, Model 124. The absorption spectra of the bases were measured in cyclohexane solutions. The measurements for the conjugate acids were made in a mixture of ethyl alcohol and sulfuric acid. The solutions were kept to stand in the dark until the absorbance became constant. All the measurements were made at room temperature.

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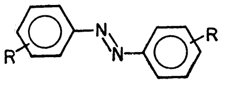
19) F. Meyer and E. Trampedach, *Ann.*, **320**, 125 (1902).

20) M. Isaks and H. H. Jaffé, *J. Amer. Chem. Soc.*, **86**, 2209 (1964).

## Results

Azobenzene derivatives and their conjugate acids of the following types were used.



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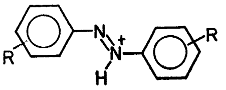
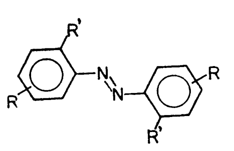
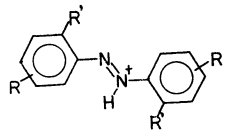


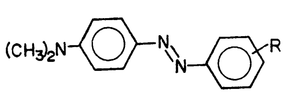
Ia



I′



Ia′



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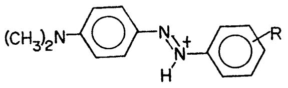
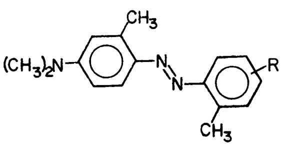


IIa



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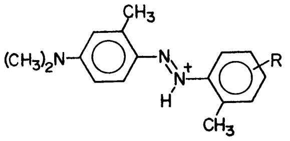

IIa′

*Dipole Moment.* It is generally recognized that both dielectric constant $\varepsilon$ and density $d$ of a solution are linearly related to the weight fraction $w$ of the solute for dilute solutions. If these relationships hold, as was the case in this experiment, the molar polarization $P$ can be calculated by means of the following Halverstadt-Kumler equation.[21]

$$P=\frac{(\varepsilon_0-1)}{(\varepsilon_0+2)}\cdot\frac{M}{d_0}\left\{1+\frac{3a}{(\varepsilon_0+1)(\varepsilon_0+2)}-\frac{b}{d_0}\right\} \quad (1)$$

where $d_0$ and $\varepsilon_0$ are the density and the dielectric constant of the solvent, respectively, and the constants $a$ and $b$ are the slopes of the linear plots of $\varepsilon$, and $d$ against $w$, respectively.

The electric dipole moment of a solute is related to the molar polarization by the following well-known equation.

$$\mu^2=(9kT/4\pi N)(P-P_E-P_A) \quad (2)$$

where $P_E$ and $P_A$ are the electronic and atomic polarizations, respectively. It is generally accepted that the sum $(P_E+P_A)$ can be put equal to 1.05 $R_M$ in good approximation,[22] where $R_M$ is the molar refractivity estimated from bond refractivities.[23,25]

The dipole moments of various substituted azobenzenes have been obtained on the basis of Eqs. (1) and (2), and are listed in Table 1 with relevant data. The calculated dipole moments $(\mu_0+\mu_g)$, where $\mu_0$ is the dipole moment of a reference compound (R=H for Types II and II′), and $\mu_g$ denotes the group moment of the substituent R, are listed in the last column. We see that the choice of reference compound gives the relationship $\mu_{obsd}\approx(\mu_0+\mu_g)$. For *p*-nitro compound, however, the agreement is poor. This may arise from the large contribution of the type

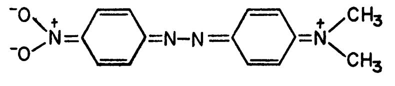

Table 1. Dipole moments of 4-*N*,*N*-dimethylaminoazobenzene derivatives with relevant data

| Substituent R | $a$ | $b$ | $R_M$ cc | $P$ cc | $\mu_{obsd}$ D | $\mu_0+\mu_g$[a,b] D |
|---|---|---|---|---|---|---|
| Type II | | | | | | |
| H | 5.27 | 0.19 | 75.5 | 281.6 | 3.17 | 3.17 |
| 4′-$CH_3$ | 3.50 | 0.15 | 76.5 | 225.2 | 2.66 | 2.77 |
| 4′-Cl | 9.20 | 0.22 | 76.7 | 516.3 | 4.61 | 4.71 |
| 3′-$NO_2$ | 16.80 | 0.24 | 78.3 | 922.5 | 6.41 | 6.19 |
| 4′-$NO_2$ | 25.50 | 0.28 | 78.3 | 1361.7 | 7.91 | 7.13 |
| Type II′ | | | | | | |
| H | 3.60 | 0.20 | 85.3 | 237.6 | 2.73 | 2.73 |
| 4′-$CH_3$ | 2.80 | 0.34 | 85.9 | 196.8 | 2.28 | 2.33 |
| 4′-Cl | 7.60 | 0.29 | 86.0 | 467.3 | 4.29 | 4.27 |
| 5′-$NO_2$ | 14.40 | 0.24 | 87.6 | 883.0 | 6.22 | 5.83 |
| 4′-$NO_2$ | 21.60 | 0.24 | 87.6 | 1284.3 | 7.63 | 6.69 |

a) Vector combination
b) $\mu_g$=0.40D for $CH_3$, 1.54D for Cl, and 3.96D for $NO_2$

*Absorption Spectra.* Azobenzene derivatives have two distinct absorption bands in the near ultraviolet and visible regions. The band at 320—360 m$\mu$ is relatively intense ($\varepsilon$, 10000—30000), whereas the band at 430—460 m$\mu$ is considerably weaker ($\varepsilon$, 400—1000). The former is known to be the $\pi$-$\pi^*$ band (conjugation band) and the latter $n$-$\pi^*$ band.[26] The absorption maxima and the molar extinction coefficients for Types I and I′ are collected in Table 2.

It can be seen that both the position and intensity of the conjugation band are considerably affected by substitution. As far as these data are concerned, the substitution in azobenzene always produces a bathochromic shift as compared with the spectrum of azobenzene. For 3,3′-dimethyl- and 3,3′-dichloroazobenzenes, however, the shift is very small, since the mesomeric effect is inoperative in meta positions. In addition, the molar extinction coefficients of these substances do not differ much from the parent compound. Similar findings have been reported by Gore and Wheeler for azoxybenzene derivatives.[27]

## Discussion

Braude and Sondheimer[2] proposed the following equation, which relates the interplanar angle $\theta$ between the aryl and the carbonyl chromophores of benzalde-

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[21] W. D. Kumler and I. F. Halverstadt, *J. Amer. Chem. Soc.*, **64**, 1941 (1942).

[22] L. G. Groves and S. Sugden, *J. Chem. Soc.*, **1935**, 971.

[23] For nitro group, the group refractivity of 8.5 cc was used.[24]

[24] T. Shimozawa and U. Morino, *Nippon Kagaku Zasshi*, **81**, 20 (1960).

[25] A. I. Vogel, W. T. Cresswell, G. H. Jeffery, and J. Leicester, *J. Chem. Soc.*, **1952**, 514.

[26] H. H. Jaffé, Si-Jung Yeh, and R. M. Gardner, *J. Mol. Spectrosc.*, **2**, 120 (1958).

[27] P. H. Gore and O. H. Wheeler, *J. Amer. Chem. Soc.*, **78**, 2160 (1956).

TABLE 2. ABSORPTION SPECTRA OF AZOBENZENES AND THEIR CONJUGATE ACIDS

| No. | Base | | Conjugate Acid $\pi$-$\pi^*$ band | | |
|---|---|---|---|---|---|
| | $\pi$-$\pi^*$ band $\lambda_{max}$ (m$\mu$) ($\varepsilon$) | $n$-$\pi^*$ band $\lambda_{max}$ (m$\mu$) ($\varepsilon$) | $\lambda_{max}$ (m$\mu$) 45%$H_2SO_4$ | $\lambda_{max}$ (m$\mu$) 90%$H_2SO_4$ | ($\varepsilon$) |
| 1 | 317 (22,100) | 447 (450) | 417 | 426 | (26,400) |
| 2 | 331 (18,900) | 464 (550) | 435 | 447 | (24,900) |
| 3 | 323 (20,900) | 447 (470) | 428 | 437 | (26,400) |
| 4 | 330 (27,000) | 444 (630) | 446 | 458 | (36,400) |
| 5 | 328 (15,000) | 467 (450) | 435 | 443 | (20,500) |
| 6 | 318 (19,300) | 449 (430) | 412 | 423 | (22,400) |
| 7 | 331 (26,400) | 444 (640) | 443 | 457 | (34,700) |
| 8 | 366 (10,300)[a] | 454 (470) | 492 | 491 | (29,900) |
| 8 | 310 ( 7,400)[a] | | | | |
| 9 | 353 (24,700) | 418[b] | 501 | 493 | (37,000) |
| 10 | 332 (19,400) | 458 (610) | 437 | 453 | (26,700) |
| 11 | 346 (22,800) | 458 (810) | 464 | 476 | (34,200) |
| 12 | 336 (16,900) | 463 (660) | 447 | 467 | (20,700) |
| 13 | 333 (24,700) | 441 (650) | 460 | 470 | (36,400) |
| 14 | 329 (19,500) | 461 (560) | 428 | 441 | (24,000) |
| 15 | 346 (25,200) | 461 (870) | 461 | 476 | (35,700) |

a) Apparent molar extinction coefficient b) Shoulder

| No. | Substituent |
|---|---|
| 1 | —— |
| 2 | 2,2′-dimethyl |
| 3 | 3,3′-dimethyl |
| 4 | 4,4′-dimethyl |
| 5 | 2,2′-dichloro |
| 6 | 3,3′-dichloro |
| 7 | 4,4′-dichloro |
| 8 | 2,2′-dimethoxy |
| 9 | 4,4′-dimethoxy |
| 10 | 2,3,2′,3′-tetramethyl |
| 11 | 2,4,2′,4′-tetramethyl |
| 12 | 2,5,2′,5′-tetramethyl |
| 13 | 3,4,3′,4′-tetramethyl |
| 14 | 2,2′-dimethyl-3,3′-dichloro |
| 15 | 2,2′-dimethyl-4,4′dichloro |

hyde and acetophenone derivatives to the dipole moment.

$$\cos^2\theta = (\mu_{obsd}-\mu_{90°})/(\mu_{0°}-\mu_{90°}) \qquad (3)$$

where $\mu_{90°}$ is the moment for completely deconjugated system in which the phenyl and carbonyl planes are at right angle. This equation may hold for any system in which a change in dipole moment arises from a twist by which conjugation is broken.

For 2,2′-disubstituted *trans*-azobenzene derivatives, the situation becomes more complicated. For example, if the molecular frame takes a coplanar structure, conformations of the following types are possible.

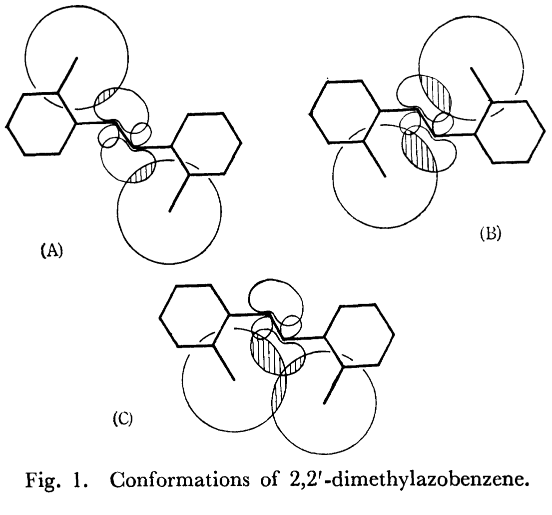
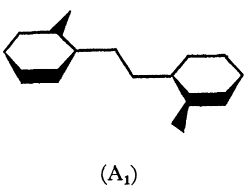
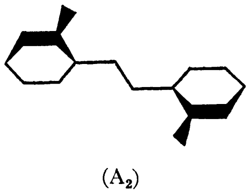


Fig. 1. Conformations of 2,2′-dimethylazobenzene.

In the above conformations, each mushroom-shaped region represents the $sp^2$-density function ($\psi^2$=0.01). The probability of finding the lone pair electrons within this region is *ca.* 0.95. The van der Waals radius for methyl group is assumed to be 2.0 Å.[28] The interaction energy between the methyl group and the $n$-electrons cannot be estimated in a simple manner. However, the steric hindrance will become severer in the order A<B<C. In conformation C, the van der Waals radii of the methyl groups also overlap. Thus, comformation A is the most likely, and conformation C is the least likely. In this case, the molecule will be twisted to some extent relative to conformation A, owing to the steric hindrance. It is noted that if the repulsion between the methyl group and the nitrogen atom is considered using van der Waals radii, there would arise no advantage by twisting. Actually, two types of twist may be possible as indicated:



$(A_1)$



$(A_2)$

If one neglects both the long-range force between

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[28] L. Pauling, "The Nature of the Chemical Bond," 3rd ed., Cornell Univ. Press, New York, (1959), p. 260.

methyl groups and the resonance and overlap integrals between non-adjacent atoms, an equal number of isomer molecules of the above types will exist, and the observed dipole moment $\mu_{\text{obsd}}$ may be given by

$$\mu^2_{\text{obsd}} = (\mu^2_1+\mu^2_2)/2 \qquad (4)$$

where $\mu_1$ and $\mu_2$ are the dipole moments of the isomers $A_1$ and $A_2$, respectively. In conformation $A_1$, the moments due to the two methyl groups, $\mu_{CH_3}$, cancel each other. In conformation $A_2$, these moments do not cancel. If this is taken into account, Eq. (4) can be modified as

$$\mu^2_{\text{obsd}} = \mu^2_1 + 2\mu^2_{CH_3}\sin^2\theta \qquad (5)$$

The group moment of methyl group is 0.40D.[29] If the angle of twist $\theta$ is small, as will be indicated later, the contribution of the second term can be neglected.[30]

We might conclude that ortho disubstituted azobenzenes are twisted in a way to take either one or both conformations of $A_1$ and $A_2$. It is generally accepted that the value of $\sigma$-moment is not affected considerably by twisting.[31] Hence, it is the $\pi$-moment that is affected by the twisting, and this will make the estimation of twisting angle possible by means of Eq. (3). However, in 2,2′-disubstituted azobenzenes, there are two bands around which the molecules are twisted. In order to examine the validity of the use of Eq. (3), in such cases, the $\pi$-moments of 4-*N*,*N*-dimethylaminoazobenzene and its derivatives were calculated as a function of $\theta$, by means of the equation

$$\boldsymbol{\mu}_\pi = e\sum Q_r\boldsymbol{r}_r \qquad (6)$$

where $e$ is the electronic charge, and $Q_r$ and $\boldsymbol{r}_r$ are the net charge and the position vector of $r$th atom, respectively. In calculating $\boldsymbol{r}_r$, the following values for bond length were used: C–C=1.39 Å, C–N=1.45 Å, N=N=1.23 Å, C–Cl=1.70 Å, C–CH$_3$=1.53 Å; all the bond angles being assumed to be 120°. The net charge $Q_r$ was estimated by means of the simple LCAO MO method. The displacement of the lone-pair electrons on the azo-nitrogens has been neglected, since these electrons would flow into both benzene rings symmetrically and would not change the dipole moment considerably.

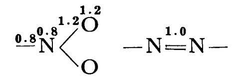
In Table 3, the variation of the $\pi$-moments are shown as a function of the assumed twisting angle. Using $\mu(\theta)$-values, the twisting angle was calculated by means of Eq. (3). We see that the assumed and calculated twisting angles agree very well, showing that the Braude equation is applicable in the present case.

TABLE 3. MESOMERIC DIPOLE MOMENTS OF 4-*N*,*N*-DIMETHYLAMINOAZOBENZENES AS A FUNCTION OF THE ANGLE OF TWIST

| R | $\theta_{\text{assumed}}$ degree | $\mu(\theta)$ | $\theta_{\text{calcd}}$ degree |
|---|---|---|---|
| H | 0 | 6.78 | 0 |
| | 15 | 6.60 | 13 |
| | 30 | 5.79 | 31 |
| | 45 | 4.88 | 46 |
| | 60 | 3.78 | 64 |
| | 75 | 3.19 | 78 |
| | 90 | 3.05 | 90 |
| 4′-CH$_3$ | 0 | 4.51 | 0 |
| | 15 | 4.38 | 15 |
| | 30 | 3.89 | 32 |
| | 90 | 2.29 | 90 |
| 4′-NO$_2$ | 0 | 14.69 | 0 |
| | 15 | 13.89 | 20 |
| | 30 | 13.21 | 28 |
| | 90 | 7.91 | 90 |

Parameters used here are:[38]

| X | *h* | *k* | *l* |
|---|---|---|---|
| N(azo) | 0.5 | cos $\theta$ | 0 |
| CH$_3$[13] | 1.8 | 0.54 | 0 |
| Cl[37] | 1.8 | 0.8 | 0.18 |
| N(CH$_3$)$_2$ | 0.8 | 1.0<br>(1.2)[a] | 0 |



where *h*, *k*, and *l* are the coefficients of the following integrals:
$\alpha_X=\alpha+h\beta$, $\beta_{C-X}=k\beta$, $\alpha_{adj}=\alpha+l\beta$

a) In the nitrodimethylaminoazobenzenes

TABLE 4. ANGLE OF TWIST OF 2,2′-DIMETHYL-4-*N*,*N*-DIMETHYLAMINOAZOBENZENE AND ITS DERIVATIVES

| R | $\mu_{0°}$(D) | $\mu_\theta$(D) | $\mu_{90°}$(D) | $\theta$(°) |
|---|---|---|---|---|
| H | 3.17 | 2.73 | 1.55 | 27 |
| 4′-CH$_3$ | 2.66 | 2.28 | 1.15 | 30 |
| 4′-Cl | 4.61 | 4.29 | 3.09 | 27 |
| 4′-NO$_2$ | 7.91 | 7.63 | 5.51 | 20 |
| 5′-NO$_2$ | 6.41 | 6.22 | 4.92 | 21 |

As Table 1 shows the dipole moment is clearly reduced by 0.19—0.44 D by the introduction of two methyl groups into ortho positions to azo-group. Thus the twisting angles were estimated by means of Eq. (3). They are listed in Table 4 which shows that $\theta$ is about 10° smaller for nitro compounds than for other compounds. For a 4-nitro compound, this might be ascribed to the large contribution of canonical resonance forms. However, it is difficult to express such a contribution for a 3 (or 5)-nitro compound. From Table 1 we see that observed values of $\mu$ are always larger than the expected values for nitro compounds, irrespective of the position of the substituent, suggesting the existence of a kind of combined contribution of the nitro group and the dimethylamino group. As Table 6 shows, the large red shift of the $\pi$-$\pi^*$ band ($\Delta\lambda$=20 m$\mu$ for 3-nitro and 46 m$\mu$ for 4-nitro) with respect to the parent 4-*N*,*N*-dimethylaminoazobenzene may support this view.

From Table 2 we see that 2,2′-disubstituted azobenzenes have absorption maxima of the $\pi$-$\pi^*$ band in a similar position but with lower intensities, as compared with the corresponding 4,4′-disubstituted ones.

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[29] C. P. Smyth and S. O. Morgan, *J. Amer. Chem. Soc.*, **49**, 1030 (1927).

[30] Very recently, we found by means of X-ray analysis that 2,2′-dichloroazobenzene is symmetrically twisted about 12° relative to conformation A.

[31] E. G. McRae and L. Goodman, *J. Chem. Phys.*, **29**, 334 (1958).

When four substituents are introduced into azobenzene, the situation becomes complicated. However, an ortho effect on the intensity of the $\pi$–$\pi^*$ band is clearly seen in the table.

Gegiou *et al.*[16], studied sterically hindered azobenzenes (2,4,6- and 2,4,6,2′,4′,6′-methylsubstituted azobenzenes) and found that ortho methylation causes shifts of the $n$–$\pi^*$ band to longer wavelengths and higher intensities. They suggested that the increase in intensity is due to the increase in the conjugation between phenyl ring and the lone pair electrons of a nitrogen atom. In the present case, a clear red shift by ortho substitution has been observed, but the increase in intensity is obscure. Introduction of substituent generally causes an increases in intensity of absorption band, even if the steric effect is absent (Table 2). Gegiou *et al.* compared the intensity for 2,4,6- and 2,4,6,2′,4′,6′-methylsubstituted azobenzenes with that for azobenzene. However, the comparison should have been made between sterically hindered azobenzenes and the corresponding unhindered ones. Hence, their suggestion is questionable.

A simple method for evaluating the ortho effect of the substituent at the 2 and 2′ positions from the intensity of the conjugation bands is to use the Braude equation $\varepsilon/\varepsilon_0 = \cos^2\theta$ where $\varepsilon_0$ is the value of the extinction coefficient of a reference, unhindered parent compound and $\theta$ is the angle of twist to be calculated.[32] The values of $\theta$, calculated according to the Braude equation for a number of azobenzene derivatives of the Type I′ are given in Table 5.

Table 5. Angle of twist of benzene rings in 2,2′-disubstituted azobenzenes and their conjugate acids[a]

| No. | Base | | Conjugate acid | |
|---|---|---|---|---|
| | $\varepsilon/\varepsilon_0$ | $\theta$ | $\varepsilon/\varepsilon_0$ | $\theta$ |
| 2 | 0.698 | 33° | 0.684 | 34° |
| 10 | 0.787 | 27° | 0.734 | 31° |
| 12 | 0.684 | 34° | 0.569 | 41° |
| 5 | 0.567 | 41° | 0.590 | 40° |
| 8 | 0.417 | 50° | 0.808 | 26° |

a) The parent compounds are corresponding 4,4′disubstituted azobenzenes.

Gore and Wheeler[15] have used this equation to calculate the angle of twist for some 2,2′-disubstituted azobenzene. The values they estimated for 2,2′-dimethyl-, 2,2′-dichloro-, and 2,2′-dimethoxyazobenzenes are 23°, 35°, and 18°, respectively. It can be seen that for 2,2′-dimethoxyazobenzene, the twisting angle is considerably different from that of Gore *et al.* We have examined the possible causes of this disagreement and concluded that their $\varepsilon$-value (13100) for 4,4′-dimethoxyazobenzene was too small (compare $\varepsilon$-values for other compounds in the corresponding table).

Table 6. Absorption spectra of 4-*N*,*N*-dimethylaminoazobenzenes and their conjugate acids

| No. | Base | | Conjugate acid | |
|---|---|---|---|---|
| | $\lambda_{\max}$(m$\mu$) | $\varepsilon$ | $\lambda_{\max}$(m$\mu$) | $\lambda_{\max}$(m$\mu$) |
| 16 | 400 | 30400 | 315 | 516 |
| 17 | 400 | 28800 | 329 | 510 |
| 18 | 400 | 31800 | 326 | 528 |
| 19 | 399 | 29900 | 341 | 520 |
| 20 | 410 | 34100 | 323 | 520 |
| 21 | 411 | 31000 | 338 | 510 |
| 22 | 420 | 31600 | 306 | 503 |
| 23 | 425 | 29800 | 319 | 492 |
| 24 | 446 | 33500 | 328 | 510 |
| 25 | 452 | 32000 | 335 | 504 |

| No. | Substituent | No. | Substituent |
|---|---|---|---|
| 16 | —— | 21 | 2,2′-dimethyl-4′chloro |
| 17 | 2,2′-dimethyl | 22 | 3′-nitro |
| 18 | 4′-methyl | 23 | 2,2′-dimethyl-5′-nitro |
| 19 | 2,2′,4′-trimethyl | 24 | 4′-nitro |
| 20 | 4′-chloro | 25 | 2,2′-dimethyl-4′-nitro |

Table 7. Angle of twist of benzene rings in 2,2′-dimethyl-4-*N*,*N*-dimethylaminoazobenzenes[a]

| No. | $\varepsilon/\varepsilon_0$ | $\theta$ | $\theta$[b] |
|---|---|---|---|
| 17 | 0.945 | 13° | 27° |
| 19 | 0.940 | 14° | 30° |
| 21 | 0.909 | 17° | 27° |
| 23 | 0.942 | 14° | 20° |
| 25 | 0.957 | 12° | 21° |

a) The parent compounds are corresponding ones which have no methyl groups in ortho positions.
b) Estimated from dipole moment.

According to Gabor and Bar-Eli,[33] there are two conformational trans isomers for 2,2′-dimethoxyazobenzene which have peaks at 370 and 310 m$\mu$. In our case the twisting angle of 50°C for this compound was estimated using the apparent molar extinction coefficient at 370 m$\mu$. Hence, the value must have been overestimated.

The absorption maxima and the molar extinction coefficients for molecules of Types II and II′ are shown in Table 6. The values of $\theta$ calculated by means of the Braude equation are given in Table 7. It should be noted that the values are about 10° smaller than those estimated from the dipole moments of these molecules. In both cases, the twisting angles of the species of Type II′ were calculated with the species of Type II as references. The group moments of the two methyl groups in ortho positions act so as to cancel each other. Introduction of methyl groups gives rise to an extra hyperchromic effect. The spectroscopic $\theta$-values have not been taken into account for this effect, and this might be the cause for the discrepancy.

The twisting angles of the molecules of Type I′ are 10—20° larger than those of Type II′, as seen in Tables 5 and 7. Since the hyperchromic effect in Types I and I′ is almost the same in the absence of the steric effect, the values in Table 7 must have been underestimated.

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[32] S. Tabak, I. I. Grandberg, and A. N. Kost, *Tetrahedron*, **22**, 2703 (1966).

[33] G. Gabor and K. H. Bar-Eli, *J. Phys. Chem.*, **72**, 153 (1968).

The conjugate acids of azobenzenes (Types $I_a$ and $I_a'$) show a very strong band in the visible region. Its absorption maxima and extinction coefficients are collected in Table 2. The band has been attributed to the conjugation band. The substitution effect on it is larger for the acids than for the original bases. Further, the absorption spectra of the conjugate acids of azobenzenes are markedly affected by solvents. As the concentration of sulfuric acid in ethanol-sulfuric acid mixture increases, the conjugation band shifts to a longer wave-length. Thus the transition energy should be extrapolated to zero concentration of sulfuric acid for the discussion of steric effect. Actually, however, the comparison of the transition energies of the species of Type $I_a$ with those of species of Type $I_a'$ was made in a ethanol-sulfuric acid mixture (45 : 55 in volume), since the solvent effect is almost the same for these compounds.

All these compounds are protonated almost completely in 90 vol% sulfuric acid.[34] $\varepsilon$-Values in this condition are listed in Table 2. The angle of twist of these acids were calculated according to the Braude equation and are listed in Table 5. We see that the values are appreciably larger than those for free bases, indicating that the conjugate acids are more susceptible to the steric effect than the original bases. This is supported by the effect of substituents on the transition energies.

The influence of substituents on the transition energy was examined on the basis of the data in Table 2. The relationship between the transition energies of the conjugation band of the bases and those of the conjugate acid is shown in Fig. 2. The points for compounds of Types I and $I_a$ give a straight line with a slope larger than unity. This indicates that the change in the transition energy of the base upon introduction of substituents is proportional to that for the acids and that this change is larger for the acid than for the base. The points for compounds of Types I′ and $I_a'$, however, deviate upward from the line. The transition energies of compounds of Type I′ are similar to those of Type I. The deviation, therefore, arises from the fact that the effect of substituents on the transition energy for compounds of Type $I_a'$ is smaller than that for compounds of Type $I_a$. This suggests that the steric effect on the transition energy for the base is negligible, but not for the acid.

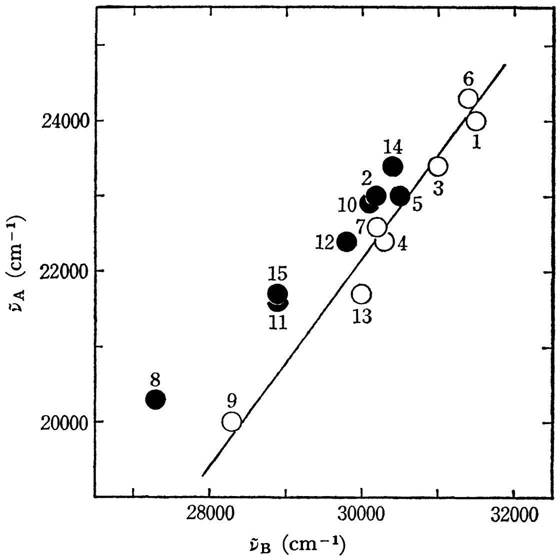
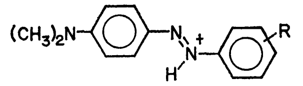
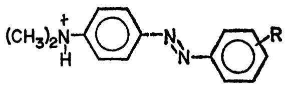


Fig. 2. The relationship between the transition energy of the conjugation band of the base ($\tilde{\nu}_B$) and that of the conjugate acid ($\tilde{\nu}_A$).
(○) Types I and $I_a$ (●) Types I′ and $I_a'$

From the analysis of the spectral data, it has been clarified[35] that following two types of the conjugate acids for 4-*N*,*N*-dimethylaminoazobenzenes coexist in an acidic solution:



A



B

Absorption bands near 500 m$\mu$ and 320 m$\mu$ have been assigned to the conjugation bands of A and B, respectively (Table 6). As the former band is isolated, its position can be determined precisely. The latter band appearing in a ultraviolet region is rather obscure both in position and intensity. The equilibrium constant between A and B has been discussed, but no precise value has been obtained.[35] Hence the molar extinction coefficients of A and B could not be determined.

Although the twisting angles for the species of Type $II_a'$ could not be estimated, the conjugate acids are

TABLE 8. INFLUENCE OF METHYL GROUPS ON TRANSITION ENERGIES

| No | Substituent in 3′- or 4′-position | Two substituents in 2,2′-positions | $\tilde{\nu}_{max}$(cm$^{-1}$) | $\Delta\tilde{\nu}$(cm$^{-1}$) |
|---|---|---|---|---|
| a ) | 4-*N*,*N*-Dimethylaminoazobenzene Derivatives | | | |
| 16 | H | H | 25000 | 0 |
| 17 | H | $CH_3$ | 25000 | |
| 18 | 4′-methyl | H | 25000 | +100 |
| 19 | 4′-methyl | $CH_3$ | 25100 | |
| 20 | 4′-chloro | H | 24400 | −100 |
| 21 | 4′-chloro | $CH_3$ | 24300 | |
| 22 | 3′-nitro | H | 23800 | −300 |
| 23 | 5′-nitro | $CH_3$ | 23500 | |
| 24 | 4′-nitro | H | 22400 | −300 |
| 25 | 4′-nitro | $CH_3$ | 22100 | |
| b ) | Conjugate Acids | | | |
| 16 | H | H | 19400 | +200 |
| 17 | H | $CH_3$ | 19600 | |
| 18 | 4′-methyl | H | 18900 | +400 |
| 19 | 4′-methyl | $CH_3$ | 19300 | |
| 20 | 4′-chloro | H | 19300 | +300 |
| 21 | 4′-chloro | $CH_3$ | 19600 | |
| 22 | 3′-nitro | H | 19900 | +400 |
| 23 | 5′-nitro | $CH_3$ | 20300 | |
| 24 | 4′-nitro | H | 19600 | +200 |
| 25 | 4′-nitro | $CH_3$ | 19800 | |

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[34] Si-Jung Yeh and H. H. Jaffé, *J. Amer. Chem. Soc.*, **81**, 3274 (1959).

[35] a) Si-Jung Yeh and H. H. Jaffé, *ibid.*, **81**, 3283 (1959). b) F. Gerson and E. Heilbronner, *Helv. Chim. Acta*, **45**, 42 (1962).

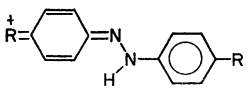
susceptible to the steric effect than the bases are, in this case too (Table 8), since the introduction of methyl groups into 2 and 2′ positions increases the transition energy in the case of the conjugate acids, while it decreases in the case of the bases. Thus, the steric effect of the conjugate acids on the transition energy is similar to that of stilbene[12] which has no *n*-electron.

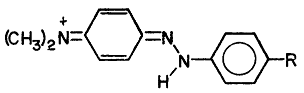
Possible explanations for the above findings are as follows:

a) The delocalization of the lone pair electrons of azo nitrogens into the phenyl rings is partly suppressed by the protonation to a nitrogen atom.

b) The repulsion energy between an ortho methyl group and the proton is larger than that between a methyl group and the lone pair electrons.[36]

c) For the conjugate acids the contribution of the following resonance forms is large in the excited state when the molecule is planar.





For the bases, however, such contribution may be smaller. As Beale and Roe have pointed out,[37] hindrance to planarity, in the absence of other effects, should increase the energy of the excited state more than that of the ground state, with a shift of the corresponding absorption to higher frequencies.

The authors are deeply grateful to Miss Hiromi Ohtani for elemental analysis.

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[36] N. L. Allinger and J. C. Tai, *J. Amer. Chem. Soc.*, **87**, 1227 (1965).

[37] R. N. Beale and E. M. F. Roe, *ibid.*, **74**, 2302 (1952).

[38] J. Kroner and H. Bock, *Chem. Ber.*, **101**, 1922 (1968).

[39] H. H. Jaffé, *J. Chem. Phys.*, **20**, 279 (1952).