

UV Spectral Changes from Rotational and Inversion Processes at the Nitrogen Center in Aniline Molecules

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The decoupling of π electrons by nuclear distortion and its influence on the UV spectrum are studied using CNDO/S calculations on aniline type molecules. Spectral changes with respect to the rotational angle of the amine group and the degree of hybridization at the nitrogen atom are investigated. The experimental spectrum is discussed on the basis of calculations performed for a variety of nuclear conformations. In particular, changes of the second (charge transfer) band are considered. INDO calculations of potential curves of aniline for the two degrees of freedom yield barriers of 1.2 kcal/mole for the nitrogen inversion and of 7.5 kcal/mole for the internal amine rotation at the hybridization angle $\alpha = 39.35^\circ$.

Key words: Aniline type molecules

1. Introduction

The aniline molecule is mobile with respect to two internal degrees of freedom, i.e. an inversion process at the nitrogen center and an internal rotation for twisting the amine group relative to the phenyl ring system. In both cases, double minimum potentials with relatively small potential barriers which are fairly easily surmounted by the dynamics of the system belong to the vibrations. Planar aniline belongs to the point symmetry group C_{2v} . An internal rotation about the amine to ring bond decreases this symmetry to C_2 until the amine group becomes perpendicular to the ring. Aniline with pyramidal bonds at the nitrogen center has C_s point symmetry at rotational angles $\varphi = 0$ and 90° and no symmetry for all other angles. The top symmetry group containing all feasible operations for the nonrigid molecule is isomorphous to D_{2h} [1, 2].

Any investigation which calculates physical properties of aniline and its derivatives should consider a variety of conformers and not only, as is usually done, one or two molecular geometries. Internal rotation and inversion decouples the π -electron system of aniline and, as with other properties, appreciably changes the electronic spectrum due to π -electron transitions. *Ab initio* calculations have been reported only for a single geometry in the ground state [3]. However, semiempirical investigations on the PPP, MINDO or CNDO level have been performed repeatedly [4–8]. In any case only a planar and/or a single pyramidal ground state geometry have been calculated and compared with the experimental spectrum.

A thorough investigation should, however, consider all degrees of decoupling of the π -electron system due to the various stages of rotation and inversion of the nuclear frame-

work. Such calculations may also explain the spectrum of the aniline homologues in which steric hindrance due to substituents causes conformations which differ from the common aniline ground state. Also, for more complex molecules where the aniline system is contained in an inverted or rotated form, aniline may act as a chromophore which is subject to an easier calculation than the full molecule.

In the present paper the UV spectrum of aniline and N-dimethylaniline (DMA) is calculated using the CNDO/S procedure of Del Bene and Jaffé [9] in its latest version. The substituted molecule is used for studying the inductive effect of the methyl group on the nitrogen atom. We are aware of the limited value of the results from semiempirical methods; however, it is believed that this method is able for one and the same molecule to reflect at least band changes in the UV spectrum upon variation of the geometry. Ground state calculations in the vicinity of the equilibrium geometry are performed by the INDO and CNDO/2 methods in order to determine those geometries which are energetically feasible by internal movements.

2. Ground State Equilibrium Geometries

Semiempirical ground state calculations for different inversion angles, α , and rotational angles, φ , have been performed using average values of Sutton's interatomic distances [10] from a series of compounds as geometrical parameters (C-C 1.394, C-N 1.43, C-H 1.084, N-H 1.02; for DMA H₃C-N 1.472, N · H₂C-H 1.096 in Ångström units). The rotational angle, φ , is the angle between the lone pair on nitrogen and the adjacent $2p_\pi$ orbital at the ring. The inversion angle, α , as the hybridization on the nitrogen atom is changed, is the angle between the extended C-N bond and the bisector of the plane of the amino group. The variation of the inversion angle corresponds to a change of amino group bond angle, β , which is approximated by assuming at nitrogen a pyramidal bond center with equal bond lengths and face angles. Under these conditions α and β are related by

$$\tan \alpha = \cos \frac{\beta}{2} \sqrt{\tan^2 \beta - \tan^2 \frac{\beta}{2}}$$

The results for aniline calculated with the INDO method, which is considered to be well adapted for reproducing bond lengths and bond angles [11], are plotted in Fig. 1. The calculated values of $\alpha = 39^\circ$ for the inversion angle and 1.2 kcal/mole for the inversion barrier correspond very well with the experimental values. Lister and Tyler reported $\alpha = 37.48^\circ$ in 1974 [12] and in 1966 [13] they measured $\alpha = 39.35^\circ$. Quack and Stockburger [14] obtained from resonance fluorescence measurements an $\alpha = 42^\circ$ and an inversion barrier of $450 \text{ cm}^{-1} = 1.3 \text{ kcal/mole}$. The excellent agreement is fortuitous. Indeed, higher energy barriers ought to be calculated if real agreement is to be obtained, since experimental values also contain tunnelling effects. However, the good agreement with experiment sheds some confidence on theoretical results obtained for the rotational barrier which is calculated for different degrees of nitrogen hybridization to be 10.3 kcal/mole for $\alpha = 0$ (sp^2 hybridization), 7.5 kcal/mole for $\alpha = 39.35$ (using the Lister and Tyler bond angles of 1966 [13]) and 5.6 kcal/mole for $\alpha = 54.74^\circ$ (the standard tetrahedral sp^3 hybridization). From these numbers it is concluded that a rotational mobility around the amine-ring axis could also take place since it is well within the energy range of usual chemical and physical processes. INDO calculations for DMA yield molecules with a planar bond structure at nitrogen. From experimental results which are, however, not very conclusive, a bent structure for DMA is pre-

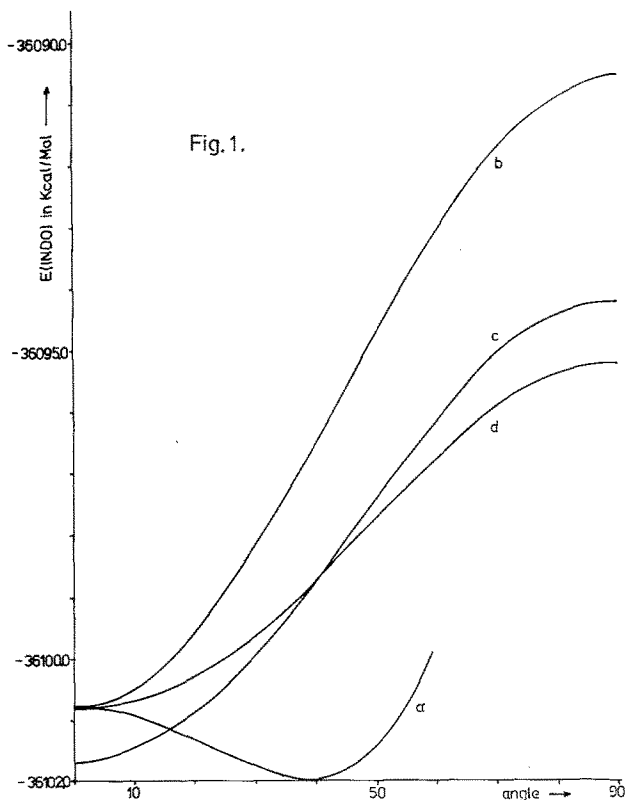


Fig. 1. INDO calculations of potential curves for varying angles α and φ for aniline. (a) $\varphi = 0$, α varied, (b) $\alpha = 0$, φ varied, (c) $\alpha = 39.35$, φ varied, (d) $\alpha = 54.74$, φ varied

dicted [15]. A variation of the twisting angle, φ , for different inversion angles, α , shows more complicated dependencies. CNDO/2 calculations also predict bent molecules, i.e. bent aniline ($\alpha = 54^\circ$) is favoured to planar aniline by 7.6 kcal/mole.

3. Ultraviolet Spectra

The electronic spectra of aniline and DMA were calculated for various rotated and inverted molecules using the CNDO/S procedure of Del Bene and Jaffé [5, 9]. A 100 term configuration interaction expansion consisting of one electron excitations was used in the present calculations. The two center Coulomb repulsion integrals are approximated by the formula of Nishimoto and Mataga [16], which improves the position of the second (so called charge transfer) band. The calculations were performed with two sets of parameters proposed by Jaffé *et al.* in 1968 [9] and 1972 [17]. However, qualitatively no significant differences have been observed for the two parameter sets, although band positions and oscillator strengths differ by small amounts. All results of present interest, therefore, are derived from the calculations using the parametrization from 1968. Usually the 1972 parametrization yields some higher transition energies for the whole UV spectrum. In the calculation of electronic transition moments not all integrals containing overlapping orbital functions are neglected as in the strict zero differential overlap approximation. Overlaps of functions on the same center are included in the present program [17].

Table 1. UV spectrum of DMA for different inversion and rotation angles α and ψ as calculated with the parametrization of 1968 [9] (transition energies in eV, oscillator strengths in parentheses, and main polarization axes)

α	$\psi = 0$	32	64.5	70	90
0					
$N(sp^2)$	B_2 4.38(0.030) ^x A_1 5.16(0.341) ^y B_2 6.23(0.565) ^x A_1 6.36(0.607) ^y B_1 6.44(0.000) ^z A_2 6.50(0.000) ⁻ A_2 6.72(0.000) ⁻ B_1 6.94(0.014) ^z	B 4.40(0.025) ^x A 5.08(0.268) ^y B 6.02(0.278) ^x A 6.20(0.117) ^y A 6.54(0.523) ^y B 6.57(0.350) ^x A 6.70(0.007) ^y B 6.96(0.019) ^z	B 4.53(0.014) ^x A 4.92(0.084) ^y B 5.62(0.037) ^{zx} A 5.90(0.012) ^y B 6.51(0.822) ^x A 6.58(0.854) ^y A 6.64(0.025) ^y B 6.88(0.005) ^x	B 4.56(0.012) ^x A 4.90(0.054) ^y B 5.55(0.022) ^{zx} A 5.84(0.023) ^y B 6.50(0.863) ^x A 6.59(0.859) ^y A 6.63(0.064) ^y B 6.87(0.002) ^x	B_2 4.62(0.008) ^x A_2 4.86(0.000) ⁻ B_1 5.43(0.002) ^z A_1 5.85(0.055) ^y B_2 6.45(0.941) ^x A_2 6.60(0.000) ⁻ A_1 6.61(1.036) ^y B_1 6.85(0.000) ⁻
39.35 ($\beta = 113.9$)	A'' 4.46(0.020) ^x A' 5.39(0.256) ^y A'' 6.32(0.627) ^x A' 6.34(0.486) ^y A'' 6.41(0.009) ^x A' 6.48(0.192) ^y A'' 6.70(0.104) ^x A' 6.98(0.093) ^y	4.48(0.020) ^x 5.33(0.212) ^y 6.08(0.166) ^x 6.18(0.130) ^y 6.50(0.403) ^x 6.53(0.652) ^y 6.60(0.173) ^x 6.85(0.102) ^y	4.54(0.015) ^x 5.33(0.086) ^y 5.87(0.024) ^y 5.95(0.049) ^x 6.46(0.831) ^x 6.56(0.939) ^y 6.66(0.009) ^x 6.81(0.013) ^y	4.55(0.014) ^x 5.35(0.060) ^y 5.84(0.034) ^y 5.92(0.029) ^{zx} 6.49(0.851) ^x 6.56(0.973) ^y 6.65(0.008) ^x 6.80(0.009) ^y	A' 4.58(0.013) ^x A'' 5.37(0.000) ^z A' 5.78(0.080) ^y A'' 5.85(0.001) ^z A' 6.50(0.915) ^x A' 6.58(1.014) ^y A'' 6.64(0.000) ^z A'' 6.78(0.000) ^z
54.74 $N(sp^3)$	A'' 4.47(0.017) ^x A' 5.50(0.178) ^y A'' 6.33(0.606) ^x A' 6.34(0.539) ^y A'' 6.39(0.085) ^x A' 6.49(0.280) ^y A'' 6.69(0.145) ^x A' 6.88(0.112) ^y	4.51(0.020) ^x 5.50(0.169) ^y 6.00(0.047) ^x 6.14(0.034) ^y 6.36(0.443) ^x 6.49(0.709) ^y 6.50(0.414) ^x 6.72(0.090) ^y	4.52(0.019) ^x 5.54(0.112) ^y 5.91(0.005) ^y 6.14(0.068) ^{xy} 6.45(0.764) ^x 6.53(0.926) ^y 6.64(0.078) ^{xy} 6.79(0.000) ^{xy}	4.52(0.019) ^x 5.57(0.104) ^y 5.86(0.011) ^y 6.14(0.041) ^{xy} 6.45(0.814) ^x 6.53(0.951) ^y 6.64(0.044) ^{xy} 6.79(0.001) ^x	A' 4.53(0.018) ^x A' 5.68(0.112) ^y A'' 5.71(0.000) ^z A'' 6.12(0.001) ^z A' 6.46(0.896) ^x A' 6.55(0.979) ^y A'' 6.63(0.000) ^z A'' 6.77(0.000) ^z

Table 2. Orbital energies (eV) and main orbital transitions (%) for DMA at Lister and Tyler configuration [13] for different rotational angles

	$\varphi = 0$	32	64.5	70	90
<i>h</i>	$\pi a'$ -0.25	π -0.26	π -0.28	π -0.29	$\pi a''$ -0.29
<i>g</i>	$\pi a''$ -0.36	π -0.37	π -0.39	π -0.39	$\pi a''$ -0.40
<i>f</i>	$\pi a'$ -8.90	π -8.95	π -9.14	π -9.18	$\pi a''$ -9.26
<i>e</i>	$\pi a''$ -9.68	π -9.71	π -9.73	π -9.73	$\pi a''$ -9.74
<i>d</i>	$\pi a'$ -11.27	$\sigma + \pi$ -10.87	$\sigma + \pi$ -10.35	$\sigma + \pi$ -10.28	$\sigma a'$ -10.13
<i>c</i>	$\sigma a''$ -11.77	σ -11.97	σ -12.17	σ -12.16	$\sigma a'$ -12.12
<i>b</i>	$\sigma a'$ -12.29	σ -12.39	σ -12.47	σ -12.48	$\sigma a'$ -12.49
	A'' 65.1f-g	64.7f-g	60.9f-g	59.7f-g	A' 58.1f-g
	33.4e-h	33.3e-h	35.9e-h	36.4e-h	36.6e-h
	A' 88.1f-h	8.1d-h	48.5f-h	45.6d-h	A'' 76.8d-h
	8.2e-g	8.1d-h	35.3d-h	36.1f-h	8.9d-i
	A'' 55.1e-h	30.5f-g	26.6f-h	37.5f-h	A' 69.9f-h
	30.5f-g	16.9d-h	19.7e-g	20.6d-h	24.3e-g
	13.6f-g	13.6f-g	17.2d-g	11.8d-g	
	A' 61.5e-g	22.1c-g	47.9d-g	58.1d-g	A'' 76.2d-g
	22.1c-g	26.4d-h	15.6d-h	12.6d-h	12.6b-g
	26.4d-h	14.3d-g	7.1e-h	11.0b-g	7.4f-g
	7.1e-h	14.3d-g	7.1e-h	54.9e-h	A' 59.5e-h
	A'' 89.8c-h	45.3c-g	25.5e-h	28.6f-g	34.5f-g
	25.5e-h	11.9f-g	9.0d-g	7.4f-g	
	9.0d-g	11.9f-g	9.0d-g	69.8e-g	A' 72.1e-g
	A' 70.8c-g	21.3e-g	49.7e-g	20.7f-h	25.0f-h
	21.3e-g	22.2c-h	18.0f-h	88.8c-g	A'' 88.3c-g
	22.2c-h	43.4b-g	26.1c-g	91.2c-h	
	26.1c-g	11.8d-g	9.5e-h	90.4c-h	A'' 92.3c-h
	9.5e-h	11.8d-g	9.5e-h		
	A' 71.1b-h	17.1d-h	55.4c-h		
	17.1d-h	17.1d-h	19.5b-h		
	19.5b-h				

In Table 1 the DMA calculation for the eight lowest electronic singlet-singlet transitions is presented. The coordinate system is chosen such that the benzene ring is in x, y -plane with the z -axis perpendicular to it. The corresponding aniline table shows quite similar features in the spectra; therefore, a presentation of these results is omitted. Table 2 compiles orbital energies and main orbital transitions for the bands of Table 1 at the Lister and Tyler inversion angle. Thus, shifts of orbital transitions on rotation of the dimethylamine group relative to the ring are exhibited. In order to maintain equal point groups for DMA and aniline, the methyl groups are chosen in all cases to be in eclipsed position to each other. Test calculations performed for staggered conformations yield no essential differences in band shifts and oscillator strengths.

A close inspection of the tables shows that there are only two transitions with large oscillator strengths giving rise to strong bands, which remain remarkably close together in energy when varying the angles, α , and φ , even by large amounts. At the long wave length side a low intensity band is found for all nuclear configurations as well as another transition further towards the visible range which always has the smallest oscillator strength. For lower symmetries at φ angles about 30 – 70° more than two lower bands are observed due to the lack of symmetry restrictions. The calculated spectra for the higher symmetries, C_{2v} and C_s (angles $\varphi = 0$ and 90°), are very similar to the benzene spectrum or, because of the inductive effect of the amine group, to the toluene spectrum. The two bands with high oscillator strengths, polarized along the x - and y -axes, have almost equal energies for all conformations. These bands originate from a nearly degenerate excited state which corresponds to the ${}^1E_{1u}$ state in benzene. The two lower bands correspond to the benzene ${}^1B_{2u}$ and ${}^1B_{1u}$ states, which arise from the

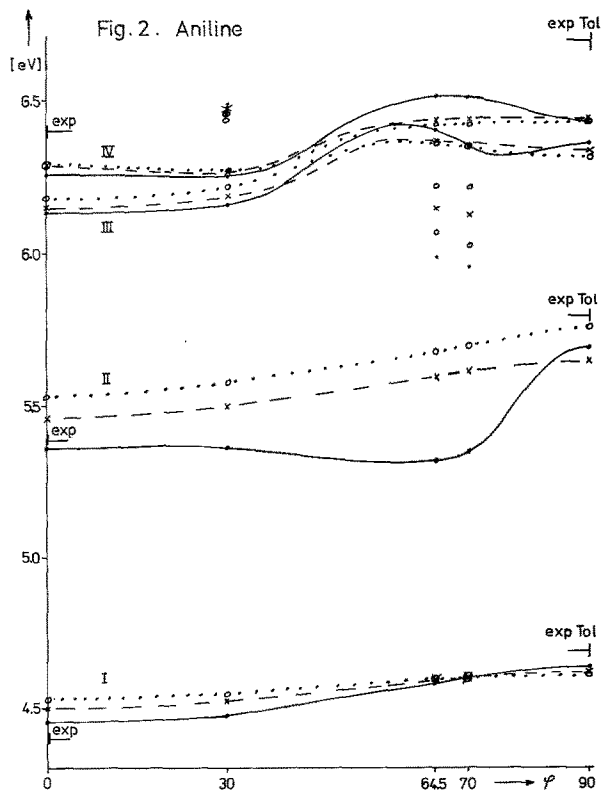


Fig. 2. Calculated near UV transitions for aniline with varying rotational angles of φ . The curves indicate connections between bands with main contribution of equal orbital transitions. --- $\alpha = 0^\circ$ -- x -- $\alpha = 39.35^\circ$ $\alpha = 54.74^\circ$

$e_{1g}^3 e_{2u}$ π -electron configuration and which are symmetry forbidden electric dipole transitions from the ground state. Although the corresponding transitions for aniline, i.e. A'' and A' , respectively, are allowed due to the lower symmetry, the bands maintain their small intensity as observed in the benzene spectrum. Also, as in benzene, the observed bands in the aniline spectrum are due to mainly π - π^* transitions which are only slightly perturbed by the p_π nitrogen orbital. Orbitals e and g of Table 2 (using Platt's notation [18]), which have a nodal plane in the y, z -plane by symmetry reason, do not contain any π -orbital component from nitrogen, For the $\alpha = 39.35, \varphi = 0$ DMA molecule the π -orbital contribution to the f orbital is 20% and to the h orbital only 2%. These contributions decrease gradually with increasing rotational angle, φ ; at $\varphi = 90^\circ$ only the f orbital has an appreciable p_π nitrogen component of 1.5%. According to Table 2 all transitions contain certain amounts of charge transfer contributions; however, the largest charge transfer contribution by π -orbital interaction from the nitrogen atom into the ring is observed in the second band. A charge transfer from the nitrogen lone pair into the π -electron system of the ring (in the usual notation $n \rightarrow \pi^*$) should originate from the d orbital, which has the largest σ orbital component of nitrogen. Any transitions into the π ring orbitals, however, have vanishing transition probabilities in our calculation. This can be due to the approximation used which does not include overlaps between orbitals of different atomic centers. With increasing rotational angle, φ , the d orbital moves to higher energy and attains more σ contribution from the nitrogen atom. Hence, the transitions from this orbital occur at lower energy in the spectrum and at $\varphi = 90^\circ$ mix into the common sequence of π - π^* bands. The second band is then found at the third transition in Table 2 and the two strong bands are now moved to transitions V and VI. By interaction of levels with equal symmetry,

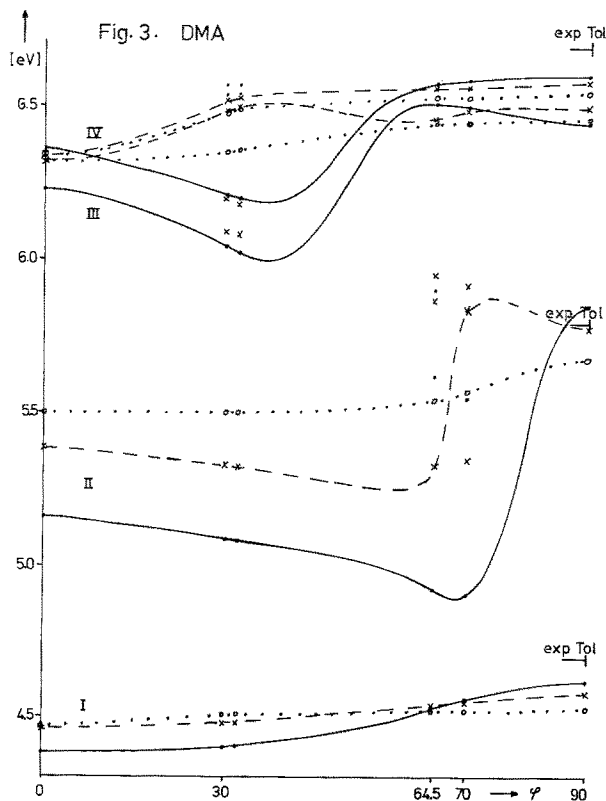


Fig. 3. Calculated near UV transitions for DMA with varying rotational angles of φ

the $\pi\text{-}\pi^*$ bands are shifted to higher energy with increasing φ . This phenomenon is observed for all bands for all geometries of aniline and DMA. Figs. 2 and 3 illustrate the described effects although not all calculated values can be shown in graphic representations like this. The curves drawn in the figures are connections between points of the same transition with a transition classified according to its main orbital contributions. For low symmetries (φ range $30\text{--}70^\circ$) such a plot is, of course, not straightforward, since each transition may in principle contain every possible orbital transition. However, the largest intensity of the band may serve as a guide when investigating the dependence of a band on the rotational angle, φ .

Some other results can be derived from the figures. As it was pointed out, the transitions III and IV with the highest intensities are found, particularly in aniline, for all geometries considered, at almost equal energies. This suggests an assignment of the corresponding bands *C* and *D* in the experimental spectrum of aniline [4, 19] which differs from those made on the basis of earlier calculations [4–8]. The band *C* at 6.40 eV should be due to the almost degenerate transitions III and IV and the shoulder *D*, localized at 6.88 eV by curve analysis, should originate from side bands due to deviations from the equilibrium geometry by molecular vibrations. According to our calculation on aniline based on an elongation of $\varphi = 30^\circ$ along the rotational normal coordinate, side bands which are off by some 0.3 eV at the short wave length side of the calculated transition pair III, IV (see Fig. 2) should arise with comparable intensity. In DMA these bands are spread further as indicated by the better resolved spectrum of DMA in this region [4, 19]. The separation of 0.48 eV experimentally found for the two high intensity bands could not be calculated from only one geometric configuration by any semiempirical method with the various sets of empirical parameters used up to now.

In the literature much attention has been attributed to the behaviour of the second (so called charge transfer) band [20–22]. Due to steric hindrance the second band (B band in Kimura notation [19]) of any orthosubstituted DMA should decrease in oscillator strength with a rotation of the amine group by the angle φ . Also an analytical formula has been proposed [20, 21]

$$f_\varphi/f_0 = \cos^2 \varphi$$

according to which the oscillator strength f_φ for the distorted molecule should vanish for $\varphi = 90^\circ$. Other authors prefer a $\cos^5 \varphi$ dependence [23, 24]. Our calculation does not confirm any such variation. Since the corresponding transition retains its $\pi\text{-}\pi^*$ character, the oscillator strength does not vanish for a completely distorted amine group. The transition only loses oscillator strength and shifts to higher energy (see Fig. 3). The decrease of oscillator strength found in the experiment in the region 5.1–5.5 eV with rising distortion angle, φ , must be explained by considering several transitions with different transition probabilities that cross each other at large values of φ leading to almost zero intensities for the undistorted ($\varphi = 0$) molecule (see Table 1).

A decrease of intensity in the charge transfer region has also been found in the spectra of solutions at low temperatures where solvent stiffening occurs [22]. Band shapes of N-diethylaniline measured for various temperatures clearly show that at low temperatures the charge transfer band is composed of more than one transition. This indicates a deviation from the equilibrium symmetry due to a rotation of the amine group in the solvent above the freezing point.

A comparison of the spectra of aniline and DMA at equilibrium configurations with corresponding experimental results shows remarkable agreement. The first two transitions, I and II, upon methyl substitution move to larger wave lengths; the oscillator strengths for transition II are increased; the transitions III and IV in DMA, on the other hand, are shifted to higher energy and lose some of their oscillator strengths. All of the above agrees well with the experimental findings [4, 19].

The present calculations may also be used to discuss the spectra of more complicated molecules in which aniline in some distorted nuclear framework is contained as a chromophore. For instance, molecules of indoline type or benzochinoclidin contain the aniline framework with fixed rotational angles $\varphi = 70^\circ$ and 90° , respectively [25, 26], and with a nitrogen inversion angle, α , corresponding to an approximate sp^3 hybridization. It is possible that the drastic changes around $\alpha = 70^\circ$ of the second band in the DMA spectrum (see Fig. 3) explain the experimentally observed spectral changes between $\varphi = 65^\circ$ and 70° for the two indoline compounds [25]. For sp^3 hybridization ($\alpha = 54.74^\circ$) the corresponding curve does not exhibit substantial variation in this narrow region. However, the earlier claimed change from an aniline type to a benzene type spectrum could not be detected. All calculated spectra in the near UV have benzene type structure; differences in the spectra are exhibited only by band shifts more or less towards the visible. For distorted DMA quantitative agreement is found with the near UV spectrum of toluene, which, according to Fig. 3, is approximately obtained at about $\varphi = 70^\circ$ if pyramidal bond properties at nitrogen are assumed.

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References

1. Longuet-Higgins, H. C.: *Mol. Phys.* **6**, 445 (1963)
2. Watson, J. K. G.: *Can. J. Phys.* **43**, 1996 (1965)
3. Hehre, W. J., Radom, L., Pople, J. A.: *J. Am. Chem. Soc.* **94**, 1496 (1972)
4. Kimura, K., Nagakura, S.: *Mol. Phys.* **9**, 117 (1965)
5. Del Bene, J., Jaffé, H. H.: *J. Chem. Phys.* **49**, 1221 (1968)
6. Shanshal, M.: *Theoret. Chim. Acta (Berl.)* **21**, 149 (1971)
7. Mishra, P. C., Rai, D. K.: *Intern. J. Quantum Chem.* **6**, 47 (1972)
8. King, G. W., Van Putten, A. A. G.: *J. Mol. Spectry.* **44**, 286 (1972)
9. Del Bene, J., Jaffé, H. H.: *J. Chem. Phys.* **48**, 1807, 4050 (1968)
10. Sutton, L. E.: *Tables of interatomic distances*. London: The Chemical Society 1958
11. Klopman, G., O'Leary, B.: *Fortschr. Chem. Forsch.* **15**, 445 (1970)
12. Lister, D. G., Tyler, J. K., Høgg, J. H., Wessel Larsen, N.: *J. Mol. Spectry.* **23**, 253 (1974)
13. Lister, D. G., Tyler, J. K.: *Chem. Commun. Chem. Soc. [London]* 152 (1966)
14. Quack, M., Stockburger, M.: *J. Mol. Spectry.* **43**, 87 (1972)
15. Vilkov, L. V., Timasheva, T. P.: *Dokladi Akademii Nauk SSSR, Chemistry* **161**, 261 (1965)
16. Nishimoto, K., Mataga, N.: *Z. physik. Chem. (Frankfurt)* **12**, 335; **13**, 140 (1957)
17. Ellis, R. L., Kuehnlenz, G., Jaffé, H. H.: *Theoret. Chim. Acta (Berl.)* **26**, 131 (1972)
18. Platt, J. R.: *J. Chem. Phys.* **17**, 484 (1949)
19. Kimura, K., Tsubomura, H., Nagakura, S.: *Bull. Chem. Soc. Japan* **37**, 1336 (1964)
20. Jaffé, H. H., Orchin, M.: *Theory and applications of ultra violet spectroscopy*. New York: John Wiley 1964
21. Wepster, B. M.: *Recueil Trav. Chim. Pays-Bas* **76**, 335, 357 (1957)

22. Dubroca, C.: Chem. Phys. Letters **15**, 207 (1972)
23. Guy, J.: J. Chim. Phys. **46**, 469 (1949)
24. Brown, R. D.: J. Chem. Soc. [London] 2229 (1952)
25. Fritz, H., Fischer, O.: Angew. Chem. **76**, 581 (1964)
26. Göttlicher, S., Habermehl, G., Kießing, W., Fritz, H.: Chem. Ber. **103**, 46 (1970)

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