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THE IMPORTANCE OF INTRAMOLECULAR CHARGE TRANSFER EFFECT ON THE MOLECULAR CONFIGURATION OF p-NITROBENZYLIDENE-p-DIMETHYLAMINOANILINE

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The structure of p-nitrobenzylidene-p-dimethylaminoaniline [I] was determined as planar transconfiguration. This is quite different from the structure of benzylideneaniline etc., which are not planar. It is stressed that the intramolecular charge transfer interaction between the substituents in [I] may play an important role for the configuration.

It is well known that charge transfer (CT) force plays an important role for the formation of molecular complexes as well as for interpreting the problems of intramolecular interaction.1,2) A typical example for the latter is for the interpretation of so-called intramolecular CT spectra.1,2) However, as far as we know, clear evidence indicating the important contribution of intramolecular CT effect on the molecular configuration seems not to be so many. In this communication we present the evidence found on the molecular structure of p-nitrobenzylidene-p-dimethylaminoaniline [I]. Molecular configuration at the ground state of benzylideneaniline [II] and its derivatives is not planar3,6) although these substances are isoelectronic with the corresponding stilbenes or azobenzenes from the viewpoint of π-electronic structures. Particularly that the angle θ_2 shown in Fig. 1 deviates largely from the planar configuration is already known from the analyses of various physicochemical data,3) X-ray crystal analyses,4) and theoretical considerations.5) The data are given in Table 1. The

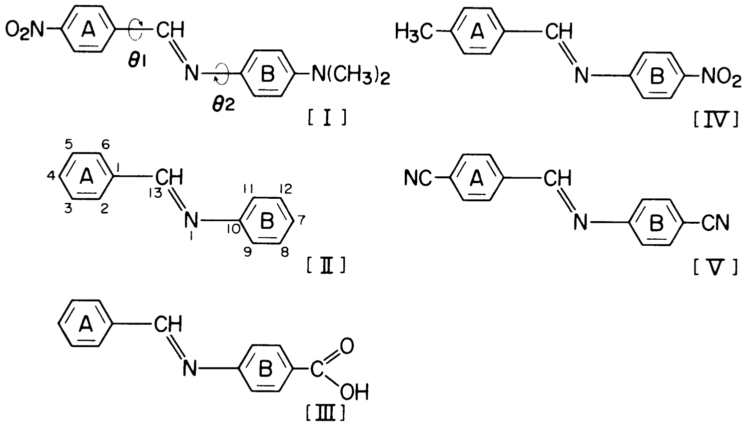

Fig. 1. Definition of numbering, twisted angles, and benzene rings of benzylideneaniline derivatives.

Table 1

Torsion Angles about C_1-C_{13} and C_{10}-N_1 Bonds[a]

	θ_1	θ_2
[I]	3.5	9.1
[II]	10.3	-53.3
[III]	12.5	-40.9
[IV]	9.9	-47.0
[V]	see text	

[a] The θ_1 and θ_2 values for [II], [III], and [IV] were re-evaluated from the data in reference 4 for denoting the torsion angle from aniline ring or benzylidene ring.

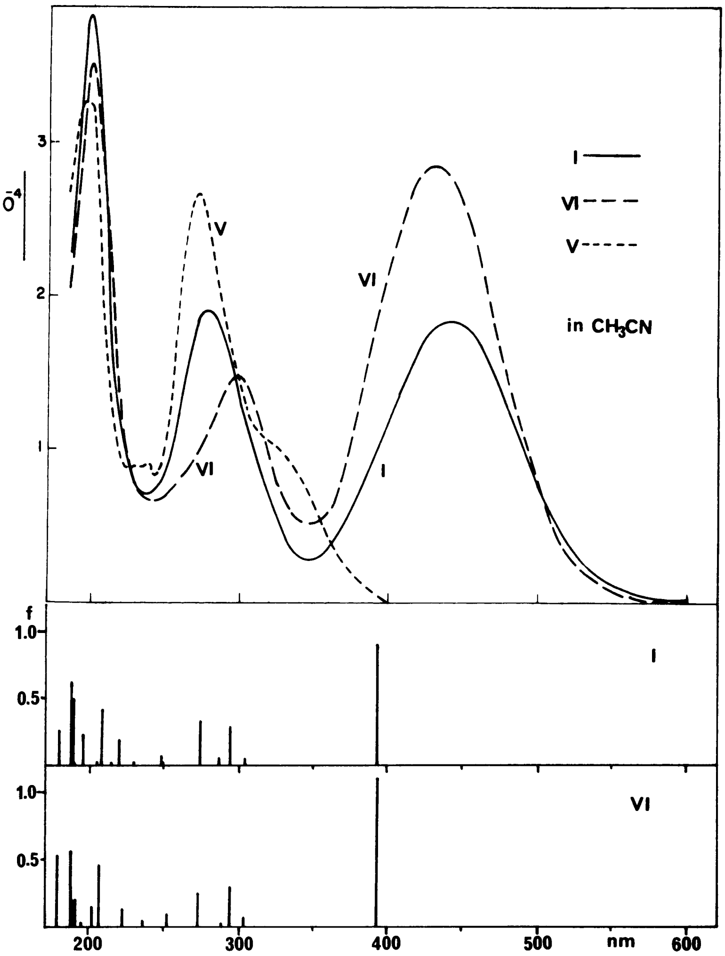

Fig. 2. Electronic spectra of p-nitrobenzylidene-p-dimethylamino-aniline [I], p-nitro-p'-dimethylaminostilbene [VI], and p-cyanobenzylidene-p-cyanoaniline [V], and calculated transition energies and intensities of [I] and [VI].

resonance interaction between the N-lone pair electrons in bridge part and the B benzene ring (Fig. 1) may be one of important reasons for the large value of the angle θ_2.6,7) So benzylideneaniline N-oxide is considered as planar structure.8)

The above mentioned fact on benzylideneanilines seems to be a good example for testing the effect of intramolecular charge transfer on molecular configuration at ground state. Needless to say, the delocalization of π-electrons through a whole molecule makes it possible to obtain the planar structure. Therefore, if the intramolecular CT energy from the strong electron donor substituent, $N(CH_3)_2$, to the strong electron acceptor one, NO_2, through the -CH=N- bridge in the molecule [I] is large enough, the compound [I] is reasonably expected to become planar configuration. And, if so, this may be a good evidence that the intramolecular CT force plays an important role at ground state.7) From this viewpoint we have determined the molecular structure of [I] by using the techniques of UV and ESR spectra and X-ray analysis.

The compound [I] was synthesized in the usual manner from p-nitrobenzaldehyde and p-dimethylaminoaniline, the single crystal (dark brown: mp 226°C) being obtained by recrystallizing from benzene. The electronic spectrum of [I] is given in Fig. 2 with the corresponding stilbene derivative p-nitro-p'-dimethylaminostilbene [VI]. Both the spectra are quite similar. The PPP-SCFMO-CI calculation as the trans-type planar molecule reproduced well the observed spectra, where the parametrization for heteroatoms is the same as was reported in the foregoing papers.9,10) From these results it is expected that the compound [I] has the trans-type planar structure at ground state. On the other hand, the spectrum (see Fig. 2) of p-cyanobenzylidene-p-cyanoaniline [V] is a very similar type to that of [II].3) The angle θ_2 in the [V] seems to deviate very much from the $\theta_2 = 0$, since large intramolecular CT interaction is not expected between both the C≡N groups at p- and p'-positions. The above mentioned planar structure of [I] was confirmed as follows by the aid of X-ray crystal analysis.

Dark brown crystals of $C_{15}H_{15}N_3O_2$ are formed in the monoclinic space group $P2_1/c$: $a = 11.065(2)$, $b = 7.759(2)$, $c = 16.488(2)$ Å, $\beta = 106.53°(3)$, $Z = 4$, $D_m = 1.32$, $D_x = 1.32$ g/cm^3. Three dimensional intensity data were collected on a Hilger and Watts Y-290. Integrated intensities were measured up to $\theta = 27.5°$ by the θ-2θ scan technique with Mo-K_α radiation and scintillation counter. A pulse height analyser and a zirconium filter were used. A total 2475 independent non-zero reflections were obtained. The signs of 243 reflections ($E \geqq 1.1$) were determined by the method of Beurskens,11) from which the correct structure was deduced. The positional and thermal parameters were refined by a block-diagonal least squares method. The anisotropic temperature factors were used for non-hydrogen atoms and an over-all isotropic one for hydrogen atoms. The conventional R-factor was 8.1% for 1675 reflections ($|F_c| > 2\sigma F_o$).

The molecular structure of p-nitrobenzylidene-p-dimethylaminoaniline is shown in Fig. 3 with the numbering for each atom. The average e.s.d. is 0.005 Å for bond length and 0.5° for bond angle. No librational corrections are applied. The average C-C bond lengths in benzylidene and aniline rings are 1.371 and 1.390 Å, respectively. The distances (see Fig. 3) C_1-C_{13}, C_{13}=N_1, and N_1-C_{10} in [I] are compared with those (in the given order 1.496, 1.237 and 1.460 Å, respectively) of [II].4) There is seen some tendency of the quinoidal structure for the bridge part of [I] compared with that of [II]. Each benzene ring and the central grouping atoms (C_1, C_{13}, N_1, C_{10}) are planar within 0.01 Å deviation, respectively, and both rings are twisted slightly out of the plane $\gg$C-C=N-C$\ll$ ($\angle\theta_2 = 9.1°$ and $\angle\theta_1 = 3.5°$). The N atom of dimethylamino group deviates only 0.16 Å from the plane connecting C_7, C_{14} and C_{15} atoms.

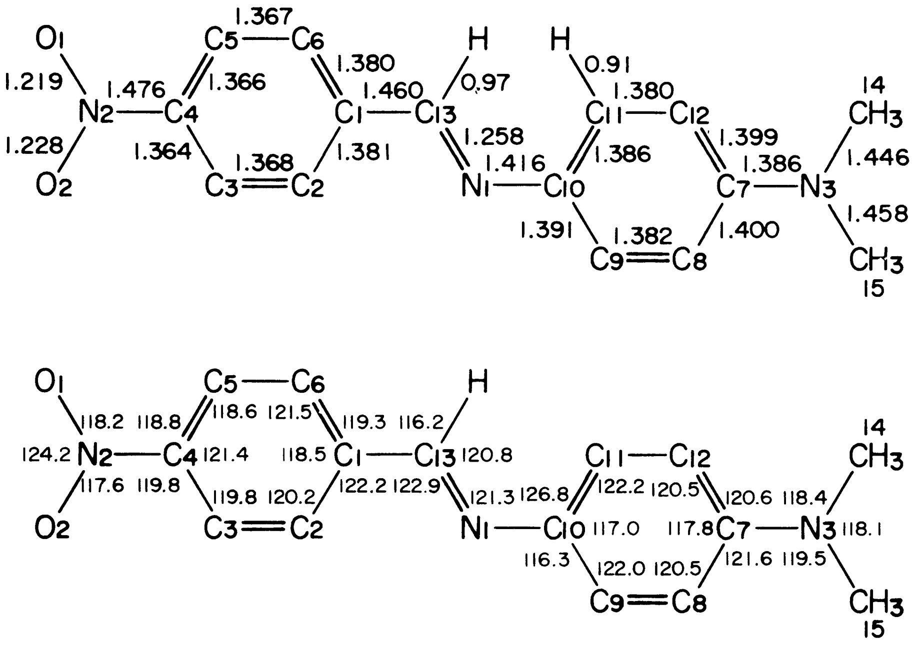

Fig. 3. Bond lengths and bond angles of the compound [I].

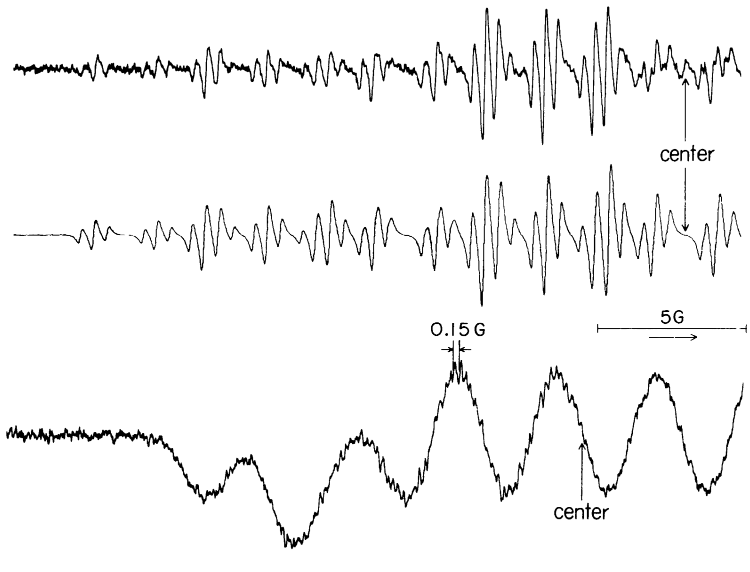

Fig. 4. Observed (top) and simulated (middle) ESR spectra of p-cyanobenzylidene-p-cyanoaniline anion radical, and the observed ESR spectrum (bottom) of the anion radical of [I].

It may be concluded that the molecule [I] as a whole has good planarity compared to the other related compounds. The H_{11}-H_{13} distance in [I] is quite short (2.1 Å), in spite of the deformation of the angle N_1-C_{10}-C_{11} (126.8°). The intramolecular CT force mentioned hitherto seems to stabilize the molecule [I] in the planar geometry against the repulsive interaction among protons.

Alternatively our studies have indicated that the conclusion discussed till now is also held for the anion radicals of [I] and [V]. As is understood from Fig. 4, the good resolved ESR spectrum of the anion radical of [I] was obtained electrochemically at -40°C in DMF solvent, the total width being about 30 gauss with the minimum hyperfine coupling (hfc) constant of 0.15 gauss. Although the analysis is not completed, the absorption lines more than 200 are expected to be hidden in this spectrum. This fact is consistent with only the case that the unpaired π-electron distributes over all atoms in [I] having planar structure, since the simpler hyperfine structure would be expected for the non-planar configuration where the unpaired electron may spread mainly on the p-nitrobenzylideneamino part in [I]. On the other hand the ESR spectrum (see Fig. 4) of V, observed electrochemically in hexamethyl phosphoramide at about 10°C, led to the conclusion that the angle θ_2 is almost 90°. This is because the spectrum can be completely analyzed as the unpaired electron is localized in the p-cyanobenzylideneamino part in V with the hfc constants (in gauss): $a_N^{-CH=N-} = 9.38$, $a_H^{-CH=N-} = 9.38$, $a_N^{C\equiv N} = 2.10$, $a_H^{o} = 3.70$, and $a_H^{m} = 0.44$. This assignment was made by the aid of molecular orbital calculation.[12] Now it may be said that the molecular configuration of the anion radicals of [I] and [V] is almost the same as that of their neutral species, and that the intramolecular CT interaction between $N(CH_3)_2$ and NO_2 groups makes the anion radical of [I] planar trans-structure.

At the present the structure analysis of p-dimethylaminobenzylidene-p-nitroaniline is in progress in our laboratory for comparison with the experimental results reported here.

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6) On the molecules such as N-salicylideneanilines there is a possibility to make those planar configuration, since strong intramolecular hydrogen bond O···H···N will keep the A and the B rings (see Fig. 1) in planar structure. This is because the intramolecular charge transfer from the N-lone pair orbital to the O-H antibonding orbital may prevent the resonance interaction of the N-lone pair electrons with the π electrons of the twisted B benzene ring. See the following paper for crystal analysis data. J. Bregman, L. Leiserowitz, and M. J. Schmidt, J. Chem. Soc., 1964, 2068.

7) In the compound [III] or [IV] quite strong intramolecular CT interaction is also possible, even at the twisted configuration about C_{10}-N_1 bond, between the substituent at the B benzene ring and the bridge nitrogen lone pair electrons. This may be one of reasons for large θ_2 values of these compounds.

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