Molecular Conformation of Benzylideneanilines; Relation to Electronic Structure and Spectra

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Summary   X-Ray analysis of benzylideneaniline and of two para-substituted derivatives has shown that the aniline ring is twisted out of the C–N=C–C plane by 40—55°, a result that bears on the apparently anomalous u.v. spectrum of benzylideneaniline derivatives.

THE u.v. spectrum of benzylideneaniline (II) differs markedly from that of stilbene (I) or trans-azobenzene (III), which are very similar to each other[1] (Figure 1). Whereas
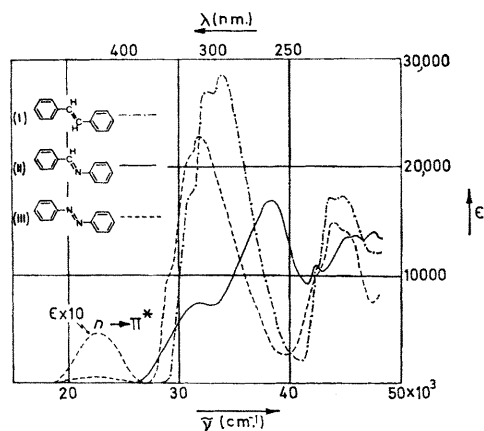

FIGURE 1.   U.v. spectrum of stilbene (I), benzylideneaniline (II) and azobenzene (III) (ref. 9 by kind permission of Prof. E. Heilbronner).

(I) and (III) are known to be almost planar, centrosymmetric molecules[2,3] structural information for (II) has not been available up till now, and the different spectral behaviour of (II) has been attributed to various factors—to the lower molecular symmetry,[4] to a postulated linearity of the C=N–C grouping,[1] and to a postulated rotation of the aniline ring out of the molecular plane by various amounts[5,6] In order to define the actual molecular geometry and to investigate the effect of electron-withdrawing groups, we have now determined the crystal structures of benzylideneaniline itself, of benzylideneaniline-p-carboxylic acid (IV) and of p-methylbenzylidene-p-nitroaniline (V) (monoclinic modification). Since the crystal reflectance spectra are in all three cases similar to the solution spectra, it seems likely that the stable conformations of the free molecules are not too different from those occuring in the crystalline state.

Crystallographic data for (II), (IV), and (V) have been given previously.[7] Intensity data were collected on the Hilger and Watts 4-circle diffractometer under the control of a PDP8 computer. The structures were solved by direct methods and refined by full-matrix least-squares analysis. The final bond distances have e.s.d.'s in the range 0·003—0·005 Å (II), 0·008—0·015 Å (IV) and 0·003—0·007 Å (V) and are shown, together with bond angles, in Figure 2. The most striking feature of the molecular

geometries is the pronounced twist of the aniline ring out of the C–N=C–C plane, by 55°(II), 41°(IV), and 50°(V); the benzylidene rings are twisted in the opposite sense, but by much smaller amounts (10°, 14°, and 8° respectively).
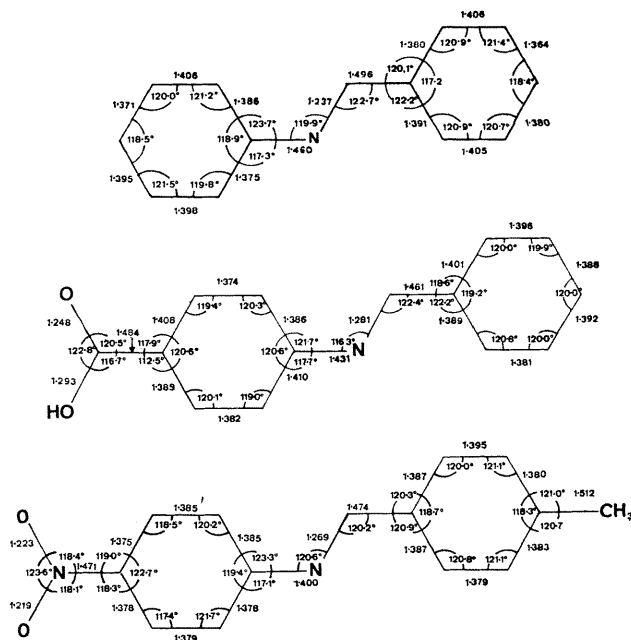

FIGURE 2.   Bond lengths and angles in benzylideneaniline (II), benzylideneaniline-p-carboxylic acid (IV), p-methyl-benzylidene-p-nitroaniline (V).

Calculations based on the simple HMO-model, with allowance for conjugation of the lone-pair electrons with the aniline ring, suggest that, for a reasonable choice of adjustable parameters, the π-electron energy is ca. 6 kcal. mole^{-1} lower for the planar than for the perpendicular conformation. On the other hand, the repulsive interactions between non-bonded atoms are relieved by twisting the aniline ring out of the plane, and the overall energy is minimized for some intermediate angle of twist, in agreement with the arguments of Minkin et al.[6] In stilbene, with no lone-pair electrons available, the difference between the π-electron energies in the planar and perpendicular conformations must be much greater than in benzylideneaniline, and hence the molecule is approximately planar.[2] In azobenzene, with two electron pairs available, the energy difference should be quite small, but here the repulsive interactions are virtually absent in the planar geometry.[3]

Figure 2 shows that the C–N single bond distance decreases with increase in electronegativity of the para-substituent, in accordance with expectations based on quinonoid structures or on the appropriate bond–atom polarizabilities π[C–N, C(para)] in the HMO-treatment.

Analogous considerations lead to an expected increase in the C=N distance with increasing electronegativity of the substituent. As expected, this distance is shortest in (II) but it appears to be slightly longer in the p-CO_2H compound than in the p-NO_2 compound. However, the C=N bond order is also a function of the torsion angle, increasing with increasing torsion angle, so that a combination of the two effects (substitution and torsion) could be invoked to explain the observed behaviour. Moreover, the smaller torsion angle in the p-CO_2H derivative implies diminished conjugation by the lone-pair electrons and, following arguments of Gillespie,[8] should be associated with a smaller C–N–C bond angle, as observed. In planar azobenzene the C–N–C angle is reduced to 112°.[3]

The energies of the two lowest lying absorption maxima in the u.v. spectrum of benzylideneaniline are adequately reproduced by HMO-calculations based on the observed torsion angle of 55°.

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