

## 127. Molecular Conformation of Benzylideneanilines

by H. B. Bürgi and J. D. Dunitz

Laboratorium für organische Chemie der Eidg. Technischen Hochschule, 8006 Zürich

(21. IV. 71)

*Summary.* The non-planar conformations of benzylideneanilines and the almost planar conformations of stilbene and azobenzene are consistently reproduced by a simple model, which takes into account the dependence of  $\pi$ -electron energy and non-bonded interactions on molecular conformation. Other aspects of the molecular geometry of benzylideneanilines (bond angles, influence of *p*-substituents) are also discussed.

In a recent paper [1] we have described the crystal and molecular structures of benzylideneaniline, benzylideneaniline-*p*-carboxylic acid and *p*-methylbenzylidene-*p*-nitroaniline. The most striking feature exhibited by all three molecules is the twist of the aniline ring out of the C–N=C–C plane by 41–55°. Several authors [2] [3] had previously invoked such distortions (30–90°) in order to explain the UV.-spectrum of benzylideneaniline, which differs from that of the isoelectronic and essentially planar molecules stilbene [4] and azobenzene [5]. In the absence of direct information the twist angle had to be estimated by strain-minimization calculations [3] in which variation of the  $\pi$ -electron energy and non-bonded interaction energy were taken into account. The variation of the  $\pi$ -electron energy was evaluated from Hückel-Molecular-Orbital (HMO) calculations, that of the non-bonded interactions from a scheme of assumed bond lengths and angles and from various sets of potential functions [6].

Although such calculations are based on a greatly oversimplified model containing several arbitrary parameters, they provide some insight into the delicate balance of forces operating in this class of molecules. The observed differences between the conformations of benzylideneaniline on the one hand and stilbene or azobenzene on the other, now provide the opportunity to adjust some of the energy parameters. In particular, it seems worth-while to estimate an appropriate value of the HMO exchange integral  $\beta_0$  which, when used with a specified set of potential functions, will reproduce the experimental results.

**1. Molecular conformations.** – *Estimate of  $\pi$ -electron energies (HMO-Model):* The  $\pi$ -electron energy of benzylideneaniline has been calculated on the assumption that the lone-pair electrons of the imino-nitrogen atom interact with the  $\pi$ -electrons of the aniline ring in the non-planar conformations. Energy differences between the planar and the perpendicular conformations of benzylideneaniline have been given by several authors [3] for different choices of the *Coulomb* and exchange integrals associated with the nitrogen atom. Systematic variation of these parameters [7] confirms that the planar conformation becomes energetically more favourable with increasing *Coulomb* integral  $\alpha$  of the lone pair and with decreasing coupling between the lone pair and the aniline ring. Using *Coulomb* integrals recommended by *Streitwieser* [8] and exchange integrals estimated from overlap calculations, the planar conformation is more stable than the perpendicular by about  $0.2 \beta_0$ .

The dependence of the  $\pi$ -electron energy on the twist angle  $\tau$  can be approximated to within 0.01  $\beta_0$  by the expression

$$\Delta E_\pi = \{E_\pi(90^\circ) - E_\pi(0^\circ)\} \cdot \sin^2 \tau.$$

Analogous considerations show that twisting a phenyl ring in azobenzene requires about the same amount of energy as in benzylideneaniline. For stilbene it is assumed that the perpendicular conformation is not stabilized by any interaction of the phenyl rings with the olefinic C–H group. The twisting then requires about twice as much energy as in the other two molecules.

*Non-bonded interactions:* Non-bonded distances were calculated from idealized models (Fig. 1) as a function of the twist angle  $\tau$ . Bond lengths and angles shown in Fig. 1 are those found by X-ray analyses [1] [4] [5], except for the C=C angle in stilbene, where the experimental value of  $128^\circ$  was thought to be too large and an angle of  $124^\circ$  was assumed instead; C–H bond lengths and X–C–H bond angles were taken as 1.1 Å and  $120^\circ$  respectively, except as noted in Fig. 1. The distances for which non-bonded interaction energies were taken into account are shown in Fig. 1 as dotted lines. The interaction energies were calculated from the potential functions given by Bartell [9]. For distances  $d(N \dots X)$  the potential curves  $V(C \dots X)$  were used with effective distances given by  $d_{\text{eff}} = d(N \dots X) + 0.1 \text{ \AA}$ .

*Potential curves:* Composite potential curves were calculated by adding  $\pi$ -electron and non-bonded interaction energy terms (Fig. 2). The numerical values used for the exchange integral  $\beta_0$  were 20 and 30 kcal/mole [10]. The results are consistent with the experimental observations. Stilbene and azobenzene show a potential minimum at a twist angle of  $0^\circ$  or close to  $0^\circ$ . For azobenzene the strain due to non-bonded interactions is small, owing to the absence of hydrogen atoms on the central double bond, so that the  $\pi$ -electron energy dominates the potential. For stilbene the C=C-double-bond length (1.33 Å), the C–C-single-bond length (1.44 Å) and the C–C=C angle ( $124^\circ$ ) are all somewhat larger than corresponding quantities in azobenzene (1.24 Å, 1.43 Å,  $114^\circ$ ) and, as a result, the strain due to non-bonded interactions is still relatively small, and the potential is again dominated by the  $\pi$ -electron energy. Benzylideneaniline has a short C=N double bond (1.24 Å), an intermediate C–N=C angle ( $120^\circ$ ) and therefore a relatively short H...H contact in the planar conformation. Strain due to non-bonded interactions and  $\pi$ -electron energy are roughly equally important and give a potential with a distinct minimum between  $0^\circ$  and  $90^\circ$ .

Fig. 2 might suggest that for benzylideneaniline the barrier to internal rotation at  $0^\circ$  is slightly lower than that at  $90^\circ$ . It should be emphasized that it is not known at present which of these barriers is the lower. Slight changes in the model or in the arbitrary constants could easily reverse the relative heights of the barriers, but they could hardly change the qualitative features of the potential curves given in Fig. 2, which are based on the choice of 20 kcal/mole for  $\beta_0$ . Similar calculations for biphenyl, based on this value, reproduce the experimental gas-phase parameters [11] quite well, whereas the higher value  $\beta_0 = 30$  kcal/mole leads to a twist angle  $7^\circ$  lower than the observed value [12]. We find that in general the higher  $\beta_0$  value leads to twist angles that are typically  $5$ – $10^\circ$  smaller than those calculated from  $\beta_0 = 20$  kcal/mole and found experimentally.

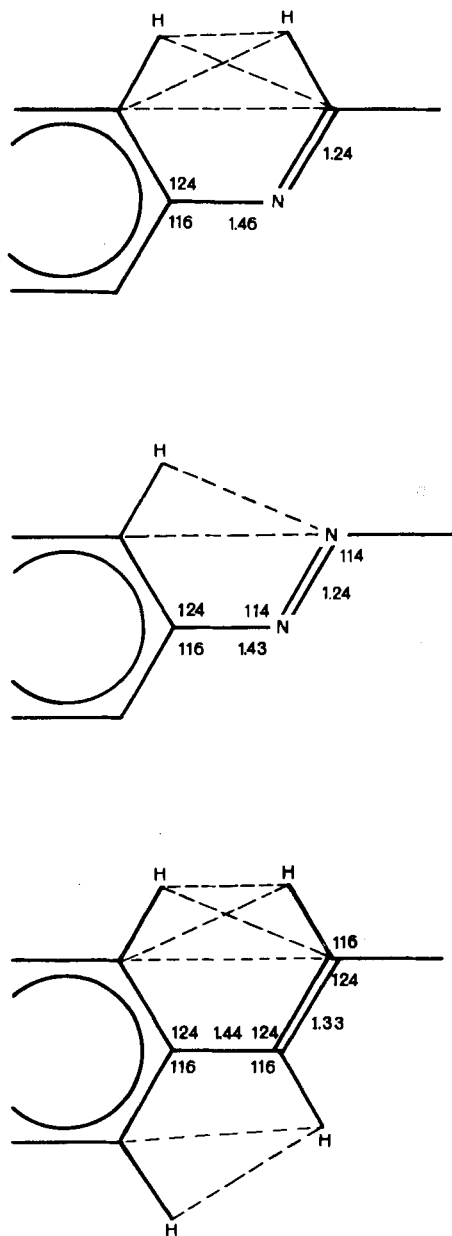


Fig. 1. Idealized partial models of benzylideneaniline, azobenzene, and stilbene, for calculating non-bonded distances for different twist angles

Bond angles are  $120^\circ$ , bond lengths are 1.39 Å (C-C) or 1.10 Å (C-H), except where another value is given in the figure

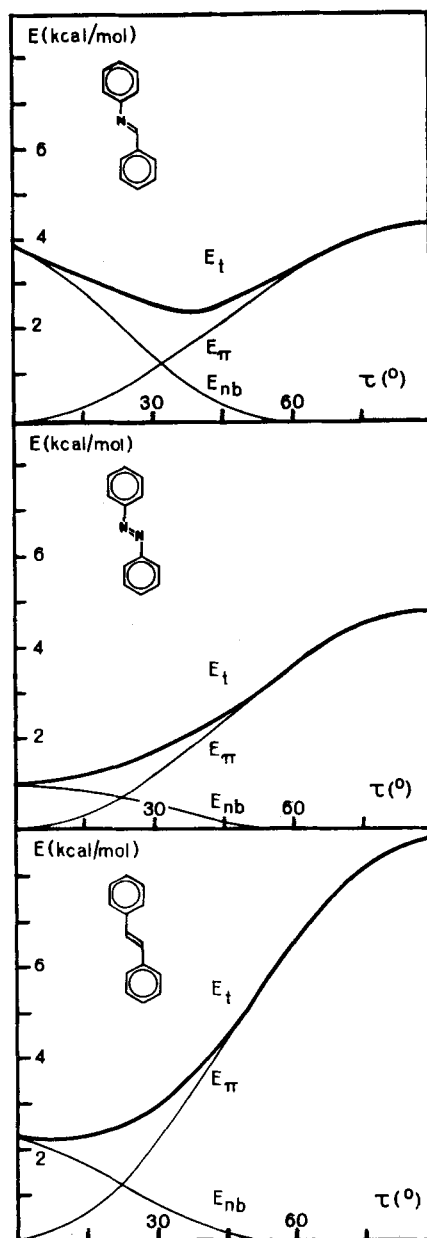


Fig. 2. Potential energy ( $E_t$ ), non-bonded interaction energy ( $E_{nb}$ ) and  $\pi$ -electron energy ( $E_\pi$ ) as function of the twist angle for benzylideneaniline, azobenzene and stilbene

Although crystal packing forces can sometimes give rise to quite drastic changes in molecular conformation, it is unlikely that this is the case for the three crystalline benzylideneaniline derivatives discussed here. The electronic absorption spectrum of a solution of benzylideneaniline in ethanol is very similar to the reflectance spectrum of a powdered mixture of benzylideneaniline with barium sulfate [7], suggesting that the twist angle in the solid state ( $55^\circ$ ) is very similar to that in solution. Nearly the same twist angles ( $49^\circ$  and  $51^\circ$ ) have also been observed for other molecules (4-isopropylideneaminophenol [13] and a phenyl-iminotriazine derivative [14]) containing a similar phenyl-substituted imino group, in spite of considerable differences in overall molecular shape.

The twist angles observed for the benzylidene rings range from  $8^\circ$ – $14^\circ$  and are adequately accounted for by a potential curve similar to that of stilbene (Fig. 2).

*EHMO-Calculation:* Extended-Hückel-Molecular-Orbital calculations (EHMO) for benzylideneaniline lead to a potential curve in which the perpendicular conformation is more stable than the planar by about 6.5 kcal/mole and hence fail to reproduce the qualitative features of the curve shown in Fig. 2. The energy difference between the perpendicular and planar conformations can be reduced only by the rather drastic device of arbitrarily omitting the two protons that are in fairly close non-bonded contact ( $H\dots H \sim 1.7 \text{ \AA}$ ) in the planar conformation (Fig. 1), *i.e.* replacing the C–H bonds by lone pairs of electrons. In another series of EHMO-calculations, in which the benzylideneaniline molecule was constrained to be planar [15], energy minimization led to a structure with an abnormally large C–N–C angle ( $156^\circ$ ) and non-bonded distances of  $d(H\dots H) \sim 2.9 \text{ \AA}$ ,  $d(C\dots H) \sim 3.2$ – $3.4 \text{ \AA}$ ,  $d(C\dots C) \sim 3.4 \text{ \AA}$ . These results suggest that, for the molecular geometries considered, the EHMO-model tends to exaggerate non-bonded repulsion energies, which then dominate the potential curve in an unrealistic way. This tendency to overemphasize steric effects was pointed out in an early paper on the application of EHMO-theory [16].

**2. Bond angles.** – The C–N=C angles found in the three benzylideneaniline derivatives lie in the range  $116^\circ$  to  $121^\circ$ , somewhat larger than the C–N=N angle in azobenzene ( $112^\circ$ – $114^\circ$ ) [5]. The increase could be attributed to non-bonded strain or to an intrinsic difference between a C=N and a N=N double bond. Angle strain should be produced by the same non-bonded interactions as govern the conformational behaviour and is undoubtedly responsible for the inequality of the two C–C–N angles at the phenyl rings of both benzylideneanilines and azobenzenes, where the ‘outer’ angle ranges between  $115^\circ$  and  $118^\circ$ , the ‘inner’ between  $121^\circ$  and  $126^\circ$  (see Fig. 3 for examples). A similar widening of the C–N=C (C–N=N) angle by about  $8^\circ$  can be assumed to have occurred. An alternative explanation of the difference between C–N=N and C–N=C angles can be based on the valence-shell-electron-pair-repulsion (VSEPR) model [17]. The argument would imply that the change from N=N to N=C double bond increases the volume occupied by the bonding electron pairs of the double bond, thereby reducing the effectiveness of angle compression by the nitrogen lone-pair electrons. A quantitative assessment of the two possible effects cannot be made from the present results.

**3. Influence of *para*-substituents.** – The present series of crystal structure determinations shows the influence of *p*-substituents on the molecular packing. The

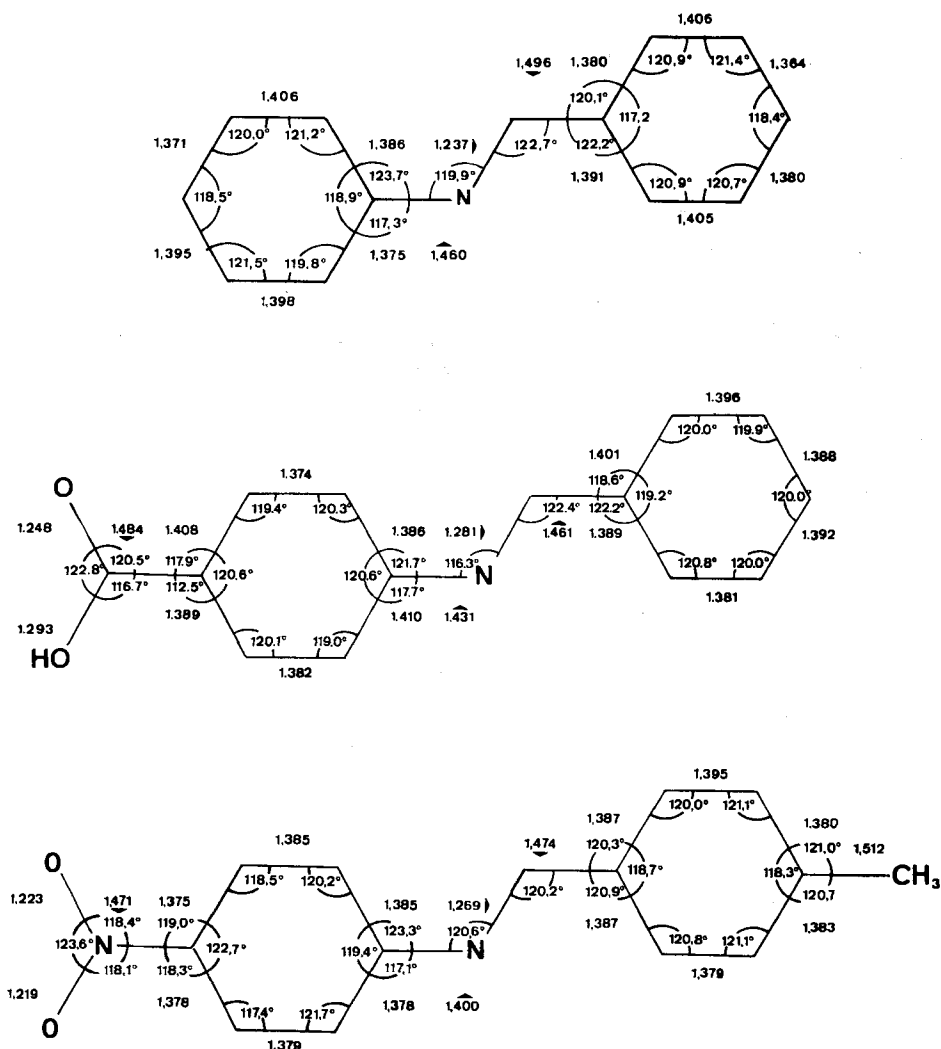


Fig. 3. Bond lengths and angles, uncorrected for thermal motion, of some benzylideneanilines  
 The twist angle of the aniline ring is (from top to bottom): 55.2°, 41.1°, 50.2°; of the benzylidene ring: 10.3°, 13.7°, 8.1°

formation of dimers by benzylideneaniline-*p*-carboxylic acid results in a packing arrangement completely different from that of benzylideneaniline or *p*-methylbenzylidene-*p*-nitroaniline [1]. The concomitant change of 10–15° in the twist angle is far smaller than the difference of 42° between planar biphenyl [18] and twisted bitolyl [19], both in the crystalline state.

Other effects of *p*-substituents on the molecular geometry are evident from the observed patterns of bond lengths (Fig. 3). The C–N distance decreases steadily with increasing electron-affinity of the *p*-substituent, the difference of 0.06 Å between benzylideneaniline and its nitro derivative being significant. A similar trend is found

for the C–N distances in aniline-*p*-carboxylic acid (1.38 Å [20] → 1.40 Å on correction for riding motion) and *p*-nitroaniline (1.371 Å) [21]. Fig. 3 also shows that the C=N-double-bond length becomes slightly greater (1.24 → 1.27 Å), the C–C-single-bond length slightly shorter (1.50 → 1.47 Å), in passing from the unsubstituted to the *p*-nitro derivative. The changes are statistically not significant, but all the trends are as expected from consideration of quinoid resonance structures and from HMO-perturbation calculations. Some influence of the molecular conformation on the bond lengths is hinted at by the dimensions of the carboxylic acid, where the C=N-double-bond length is the largest in the series, the C–C-single-bond length the smallest. In view of the rather large standard deviations estimated for the bond lengths of this compound and the uncertain rôle of crystal packing forces, any further discussion of this influence would appear to be superfluous at present.

This work was supported by the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung*. One of us (H. B. B.) would like to thank the *Stipendienfonds zur Unterstützung von Doktoranden auf dem Gebiete der Chemie* and the *Federal Institute of Technology* for additional financial assistance.

#### BIBLIOGRAPHY

- [1] H. B. Bürgi & J. D. Dunitz, *Helv.* 53, 1747 (1970).
- [2] V. A. Ismailski & E. A. Smirnov, *Ž. Obšč. Chim. USSR* 26, 3389 (1956); N. Ebara, *Bull. chem. Soc. Japan* 33, 534 (1960); P. Brocklehurst, *Tetrahedron* 18, 299 (1962); W. F. Smith, *ibid.* 19, 445 (1963); E. Haselbach & E. Heilbronner, *Helv.* 51, 16 (1968).
- [3] G. Favini & A. Gamba, *J. Chim. physique* 62, 995 (1965); V. I. Minkin, Y. A. Zhdanov, E. A. Medyantzeva & Y. A. Ostroumov, *Tetrahedron* 23, 3651 (1967).
- [4] J. M. Robertson & I. Woodward, *Proc. Roy. Soc. A* 162, 568 (1937).
- [5] C. J. Brown, *Acta crystallogr.* 21, 146 (1966); A. G. Amit & H. Hope, *Acta chem. scand.* 20, 835 (1966).
- [6] J. B. Hendrickson, *J. Amer. chem. Soc.* 83, 4537 (1961); A. I. Kitaygorodsky, *Tetrahedron* 14, 230 (1961); H. E. Simmons & J. K. Williams, *J. Amer. chem. Soc.* 86, 3222 (1964).
- [7] H. B. Bürgi, ETH Zürich, Dissertation Nr. 4334 (1969).
- [8] A. Streitwieser, 'Molecular Orbital Theory for Organic Chemists', Chapter 5, Wiley, N. Y. 1961.
- [9] L. S. Bartell, *J. chem. Physics* 32, 827 (1960).
- [10] M. Simonetta, G. Favini, C. Mariani & P. Gramaccioni, *J. Amer. chem. Soc.* 90, 1280 (1968).
- [11] O. Bastiansen, *Acta chem. scand.* 3, 408 (1949); A. Almendingen & O. Bastiansen, *Kgl. norske Videnskab. Selskabs. Skrifter*, Nr. 4 (1958).
- [12] G. Casalone, C. Mariani, A. Mugnoli & M. Simonetta, *Molec. Physics* 15, 339 (1968).
- [13] D. R. Holmes & H. M. Powell, *Acta crystallogr.* 6, 256 (1953).
- [14] J. Karle, J. Flippin & I. L. Karle, *Z. Kristallogr.* 125, 201 (1967).
- [15] S. A. Houlden & I. G. Csizmadia, *Tetrahedron* 25, 1137 (1969).
- [16] R. Hoffmann, *J. chem. Physics* 39, 1397 (1963).
- [17] R. J. Gillespie, *J. chem. Education* 47, 18 (1970), and references therein.
- [18] J. Trotter, *Acta crystallogr.* 14, 1135 (1961); A. Hargreaves & S. H. Rizvi, *ibid.* 15, 365 (1962).
- [19] G. Casalone, C. Mariani, A. Mugnoli & M. Simonetta, *Acta crystallogr. B* 25, 1741 (1969).
- [20] T. F. Lai & R. E. Marsh, *Acta crystallogr.* 22, 885 (1967).
- [21] K. N. Trueblood, E. Goldish & J. Donohue, *Acta crystallogr.* 14, 1009 (1961).