206. Crystal and Molecular Structures of Benzylideneaniline, Benzylideneaniline-*p*-carboxylic acid and *p*-Methylbenzylidene-*p*-nitroaniline

by **H. B. Bürgi** and **J. D. Dunitz**

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

(27. VIII. 70)

Summary. The structures of the title compounds have been established by X-ray crystal structure analysis, based on three-dimensional diffractometer data. Bond lengths and angles are given, and the thermal motion of the molecules in the crystals is discussed. The most striking feature of all three molecules is the twist of the aniline ring out of the C–N=C–C plane by 41–55°.

The UV. spectrum of benzylideneaniline differs from that of the isoelectronic molecules stilbene and azobenzene [1]. In order to provide a structural basis for the interpretation of these differences, we have carried out crystal structure determinations of benzylideneaniline itself, of benzylideneaniline-*p*-carboxylic acid and of *p*-methylbenzylidene-*p*-nitroaniline. In the present paper we discuss the results of these structure analyses; the relationship of the results to the spectroscopic data will be discussed separately in a later contribution, together with the analysis of the effect of *p*-substituents on the aniline ring on the dimensions of the –N=C– group. Some of the results have been published in preliminary form [2].

1. Crystallographic data. – Crystallographic data for benzylideneaniline and for several derivatives have already been reported [3]. More accurate data are given in Table 1 for the three compounds whose crystal structures have been determined.

Table 1. *Crystallographic data*

All three crystals belong to the space group $P2_1/c$ (C^5_{2h}) with 4 molecules per unit cell

Compound	a(Å)	b(Å)	c(Å)	β(Å)	V(Å^3)
Benzylideneaniline ($C_{13}H_{11}N$)	12.157	7.921	11.944	118.38	1011.9
Benzylideneaniline-*p*-carboxylic acid ($C_{14}H_{11}NO_2$)	6.656	30.82	7.606	133.58	1130.3
p-Methylbenzylidene-*p*-nitroaniline ($C_{14}H_{12}N_2O_2$)	15.469	7.282	12.768	123.63	1197.5

The lattice constants were measured on the *Hilger & Watts* 4-circle diffractometer Y290, using Mo-Kα radiation (λ = 0.7107 Å). It should be noted that *p*-methylbenzylidene-*p*-nitroaniline crystallizes in an orthorhombic modification [3] as well as in the monoclinic modification described here.

2. Intensity measurements. – Intensity measurements for all three compounds were made on the *Y290* diffractometer. Intensities were recorded using Mo-Kα radiation with Zr/Sr balanced filters and the ω-scan technique. Background measurements (B) were made on both sides of each reflexion for one quarter of the time of the actual scan through the reflexion. The intensities were converted into relative F-values in the usual way. Absorption corrections were not carried out since the dimensions and absorption coefficients of the crystals made them unnecessary. The standard deviations of intensities (I) and F-values were calculated according to

$$\begin{aligned}\sigma(I) &= [I(\mathrm{Sr}) + B(\mathrm{Sr}) + I(\mathrm{Zr}) + B(\mathrm{Zr})]^{1/2},\\ (L.p.)^{1/2}\,\sigma(F) &= I^{1/2} - [I - \sigma(I)]^{1/2} \quad \text{if } I \geqslant \sigma(I)\,,\\ (L.p.)^{1/2}\,\sigma(F) &= I^{1/2} \qquad\qquad\qquad\; \text{if } I < \sigma(I)\,,\end{aligned}$$

where L.p. is the usual *Lorentz*-polarization factor.

For *benzylideneaniline* (M.p. 47–49°) a crystal of dimensions approximately 0.25 mm × 0.30 mm × 0.05 mm was enclosed in a *Lindemann*-glass capillary. A total of 1397 independent reflexions were measured out to a maximum θ-angle of 25°. The ω-scan angle was set between 0.41° and 0.55°, the step-size was 0.01°, and the measurement time was 1 sec. per step.

For *benzylideneaniline*-p-*carboxylic acid* (M.p. 191–193°) the crystal used had dimensions of approximately 0.15 mm × 0.28 mm × 0.40 mm. A total of 2725 independent reflexions were measured out to a maximum θ-angle of 28°. The ω-scan angle was set between 0.60 and 0.80°, the step-size was 0.01°, and the measurement time was 1 sec. per step.

For p-*methylbenzylidene*-p-*nitroaniline* (M.p. 134–135°) a crystal of approximate dimensions 0.15 mm × 0.50 mm × 0.50 mm was enclosed in a *Lindemann*-glass capillary. A total of 1846 independent reflexions were measured out to a maximum θ-angle of 22°. The ω-scan angle was set between 0.45 and 0.53°, the step-size was 0.01° and the measurement time was 1.2 sec. per step.

3. Structure analysis. – All three structures were determined with the help of direct methods. For each crystal the relative F-values were brought to an approximately absolute scale by the *Wilson* method [4]. The E-values were then obtained in the usual way. Some of the statistical results regarding the distributions of E-values are given in Table 2.

Table 2. *E-Value statistics*

Compound	$\bar{B}$ (Å^2)	Number of E's $\geqslant 1.2$	Number of allocated signs	$\langle\lvert E\rvert\rangle$	$\langle E^2\rangle$	$\langle E^2-1\rangle$	$\lvert E\rvert_{max}$	$\lvert E\rvert \geqslant 1$	$\lvert E\rvert \geqslant 2$	$\lvert E\rvert \geqslant 3$
								percentages		
Benzylidene-aniline	4.24	303	272	0.78	1.07	1.10	4.73	30.2	5.6	1.3
Benzylidene-aniline-p-carboxylic acid	4.64	386	284	0.76	1.19	1.24	5.25	34.1	8.3	1.0
p-Methyl-benzylidene-p-nitroaniline	4.06	335	269	0.72	0.95	1.04	5.36	26.6	4.7	0.8
Values for centro-symmetrical distribution				0.80	1.00	0.97		32.0	5.0	0.3

For each set of E-values, signs were allocated with the help of a computer programme [5] based on the symbolic addition procedure [6]. The resulting E-map calculated for benzylideneaniline was immediately interpretable in terms of a reasonable trial structure, but the interpretation of the corresponding maps for the other two compounds was not so simple. The difficulties that arose are connected with the amplitude termination effect, discussed elsewhere [7].

4. Structure refinement. – Positional and anisotropic temperature-factor parameters for the carbon, nitrogen and oxygen atoms were refined by full-matrix least-squares analyses. The hydrogen atom parameters were not refined, but the contributions of these atoms to the calculated structure factors, based on estimated positions, were included in the later refinement cycles. For these calculations the temperature factor of each hydrogen atom was assumed to be isotropic and equal to the mean isotropic temperature factor of the carbon atom to which it was bound. The estimated positions of the hydrogen atoms were confirmed for each structure by a final difference synthesis. Atomic scattering factors were taken from a standard compilation [8].

For benzylideneaniline five cycles of least-squares refinement give an R-factor of 4.9% based on the 839 reflexions with $F \geqslant 2\,\sigma(F)$. The expectation R-factor, defined as $100 \times \Sigma\,\sigma(F)/\Sigma\,|F|$ is 4.8%. – For benzylideneaniline-*p*-carboxylic acid seven cycles of least-squares refinement gave an R-factor of 8.2% (expectation value 7.1%) based on 741 reflexions with $F \geqslant 2\,\sigma(F)$. – For *p*-methylbenzylidene-*p*-nitroaniline seven cycles of refinement gave an R-factor of 7.3% (expectation value 4.6%) based on 1031 reflexions with $F \geqslant 2\,\sigma(F)$.

In all three refinements the final cycle led to parameter shifts smaller than half of the corresponding standard deviations as calculated by inversion of the least-squares normal equations matrix. A fuller account of the refinement, including details of the weighting systems used, is given elsewhere [5].

5. Results. – Figure 1 shows the atom-numbering system on which the subsequent Tables are based.

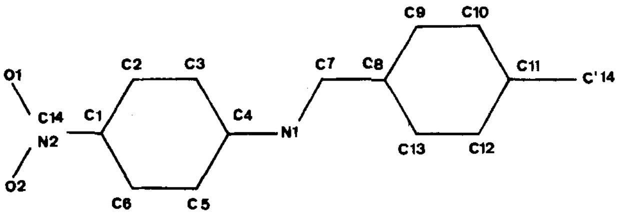

Fig. 1. *Atom-numbering system*

For *benzylideneaniline*, crystal coordinates of the non-hydrogen atoms are given in Table 3a, together with the corresponding standard deviations; in Table 3b the atomic positions are referred to an orthogonal molecular coordinate system; Table 3c gives the estimated crystal coordinates of the hydrogen atoms; Table 3d gives the anisotropic temperature-factor parameters of the heavy atoms.

The corresponding information for *benzylideneaniline*-p-*carboxylic acid* and p-*methylbenzylidene*-p-*nitroaniline* is given in Tables 4a, b, c, d and 5a, b, c, d, respectively.

Tables 6 and 7 contain bond lengths and bond angles, calculated from the positional parameters at the end of the least-squares refinement for all three crystals. Some of these values are subject to corrections for the effect of thermal motion, as discussed in the following section. Table 8 contains some torsion angles for the carboxyl and nitro substituents.

Tables of observed and calculated F-values for all three crystal structure analyses have been listed separately [5].

Table 3. *Benzylideneaniline*

Table 3a. *Crystal coordinates (and standard deviations* × *10^4)*

	x	y	z
C(1)	1.4283 (4)	0.1114 (5)	0.1303 (4)
C(2)	1.4243 (4)	0.2174 (5)	0.2191 (4)
C(3)	1.3085 (4)	0.2665 (5)	0.2083 (4)
C(4)	1.1969 (4)	0.2099 (4)	0.1088 (4)
C(5)	1.2005 (4)	0.1045 (5)	0.0191 (4)
C(6)	1.3157 (4)	0.0545 (5)	0.0306 (4)
N(1)	1.0739 (3)	0.2632 (4)	0.0889 (3)
C(7)	1.0450 (4)	0.2426 (4)	0.1743 (4)
C(8)	0.9211 (3)	0.2954 (4)	0.1608 (4)
C(9)	0.8860 (4)	0.2458 (5)	0.2500 (3)
C(10)	0.7690 (4)	0.2917 (5)	0.2375 (4)
C(11)	0.6865 (4)	0.3871 (5)	0.1376 (4)
C(12)	0.7208 (3)	0.4392 (5)	0.0482 (3)
C(13)	0.8374 (3)	0.3938 (4)	0.0595 (3)

Table 3b. *Coordinates (in Å) referred to principal axes of the atom grouping C(4), N(1), C(7), C(8)* (see Fig. 2)

	X	Y	Z
C(1)	0.0159	-0.9468	4.5415
C(2)	-0.9641	-1.3908	3.6916
C(3)	-0.9723	-0.9746	2.3486
C(4)	-0.0026	-0.1146	1.8577
C(5)	0.9763	0.3404	2.7092
C(6)	0.9913	-0.0838	4.0412
N(1)	0.0024	0.4058	0.4934
C(7)	0.0028	-0.3774	-0.4642
C(8)	-0.0026	0.0862	-1.8869
C(9)	0.2106	-0.8150	-2.9097
C(10)	0.2332	-0.3925	-4.2500
C(11)	0.0405	0.9157	-4.5863
C(12)	-0.1883	1.8275	-3.5755
C(13)	-0.2103	1.4179	-2.2315

Transformation matrix

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} -2.7114 & -7.1371 & -2.6429 \\ -1.4098 & 3.1956 & -8.8812 \\ 11.7635 & -1.2621 & -7.5412 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

Coordinates of old origin in new system: $(X, Y, Z) = (-5.0280, -1.8683, 11.1366)$

Table 3c. *Estimated hydrogen-atom coordinates, assuming bond length C–H = 1.0 Å and local C_{2v}-symmetry at each C-atom*

	x	y	z
H(C1)	1.510	0.076	0.135
H(C2)	1.509	0.256	0.295
H(C3)	1.307	0.343	0.278
H(C5)	1.116	0.062	0.056
H(C6)	1.322	0.023	0.034
H(C7)	1.108	0.186	0.258
H(C9)	0.947	0.175	0.327
H(C10)	0.744	0.251	0.305
H(C11)	0.603	0.422	0.132
H(C12)	0.660	0.511	-0.027
H(C13)	0.861	0.431	-0.009

Table 3d. *Anisotropic temperature factor parameters*
$T = \exp - (b_{11} h^2 + b_{22} k^2 + b_{33} l^2 + b_{12} hk + b_{13} hl + b_{23} kl)$

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C (1)	0.0119	0.0207	0.0208	0.0045	0.0188	0.0077
C (2)	0.0107	0.0250	0.0158	-0.0012	0.0102	-0.0004
C (3)	0.0115	0.0214	0.0124	-0.0023	0.0101	-0.0027
C (4)	0.0096	0.0158	0.0124	0.0021	0.0119	0.0046
C (5)	0.0127	0.0192	0.0124	0.0018	0.0125	-0.0005
C (6)	0.0149	0.0206	0.0166	0.0031	0.0197	0.0013
N (1)	0.0129	0.0217	0.0115	0.0021	0.0130	0.0013
C (7)	0.0118	0.0182	0.0100	0.0003	0.0101	0.0011
C (8)	0.0093	0.0157	0.0101	-0.0010	0.0087	-0.0015
C (9)	0.0116	0.0237	0.0094	-0.0019	0.0090	0.0032
C (10)	0.0136	0.0274	0.0116	-0.0020	0.0150	-0.0012
C (11)	0.0121	0.0205	0.0162	0.0008	0.0163	-0.0050
C (12)	0.0113	0.0209	0.0126	0.0019	0.0113	0.0015
C (13)	0.0106	0.0188	0.0097	0.0002	0.0092	-0.0001

Table 4. *Benzylideneaniline-*p*-carboxylic acid*

Table 4a. *Crystal coordinates (and standard deviations × 10^4)*

	x	y	z
C(1)	0.3795 (20)	0.4441 (3)	0.4282 (19)
C(2)	0.3096 (19)	0.4482 (3)	0.2071 (17)
C(3)	0.4599 (20)	0.4257 (4)	0.1742 (17)
C(4)	0.6758 (20)	0.3989 (3)	0.3559 (19)
C(5)	0.7525 (18)	0.3957 (3)	0.5807 (16)
C(6)	0.6024 (21)	0.4185 (3)	0.6143 (18)
N(1)	0.8302 (16)	0.3739 (3)	0.3243 (14)
C(7)	0.6897 (19)	0.3556 (4)	0.1173 (18)
C(8)	0.8193 (19)	0.3295 (3)	0.0577 (16)
C(9)	0.6497 (18)	0.3038 (4)	-0.1516 (17)
C(10)	0.7675 (22)	0.2780 (3)	-0.2117 (17)
C(11)	1.0526 (22)	0.2783 (4)	-0.0651 (20)
C(12)	1.2201 (19)	0.3048 (4)	0.1393 (20)
C(13)	1.1034 (20)	0.3301 (3)	0.1991 (17)
C(14)	0.2083 (20)	0.4679 (4)	0.4551 (19)
O(1)	0.0009 (20)	0.4890 (3)	0.2816 (12)
O(2)	0.2816 (20)	0.4647 (2)	0.6623 (11)

Table 4b. *Coordinates (in Å) referred to principal axes of the atom grouping C(4), N(1), C(7), C(8)* (see Fig. 2)

	X	Y	Z
C(1)	-0.1023	-1.2512	-4.3491
C(2)	0.7388	-1.8132	-3.3696
C(3)	0.7888	-1.2466	-2.1191
C(4)	0.0038	-0.1436	-1.8202
C(5)	-0.8089	0.4493	-2.8088
C(6)	-0.8516	-0.1154	-4.0697
N(1)	-0.0033	0.4414	-0.5146
C(7)	-0.0045	-0.3744	0.4729
C(8)	0.0040	0.0767	1.8619
C(9)	-0.2681	-0.8551	2.8718
C(10)	-0.2850	-0.4514	4.2083
C(11)	-0.0195	0.8711	4.5356
C(12)	0.2865	1.7883	3.5336
C(13)	0.2969	1.3890	2.2120
C(14)	-0.1564	-1.9091	-5.6778
O(1)	0.4745	-2.9653	-5.8870
O(2)	-0.9053	-1.3518	-6.5720

Transformation matrix

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} 3.1338 & 25.1127 & -4.3324 \\ 3.9854 & -\ 0.4114 & 1.2736 \\ 4.3141 & -17.8621 & -6.1204 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

Coordinates of old origin in new system: $(X, Y, Z) = (10.5890, 3.1264, -4.5673)$

Table 4c. *Estimated hydrogen-atom coordinates, assuming bond length C–H = 1.0 Å and local C_{2v}-symmetry at each C-atom*

The position of the carboxyl-H atom was estimated from difference synthesis

	x	y	z
H(C2)	0.151	0.467	0.075
H(C3)	0.413	0.429	0.018
H(C5)	0.913	0.377	0.714
H(C6)	0.655	0.417	0.773
H(C7)	0.484	0.360	-0.009
H(C9)	0.444	0.304	-0.258
H(C10)	0.646	0.259	-0.360
H(C11)	1.137	0.259	-0.108
H(C12)	1.425	0.306	0.242
H(C13)	1.226	0.349	0.347
H(O2)	0.200	0.494	0.717

Table 4d. *Anisotropic temperature factor parameters*

$$T = \exp - (b_{11}\, h^2 + b_{22}\, k^2 + b_{33}\, l^2 + b_{12}\, hk + b_{13}\, hl + b_{23}\, kl)$$

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C (1)	0.0384	0.0008	0.0410	0.0021	0.0569	0.0007
C (2)	0.0563	0.0012	0.0332	0.0021	0.0640	0.0018
C (3)	0.0494	0.0014	0.0317	0.0039	0.0580	0.0014
C (4)	0.0449	0.0009	0.0393	-0.0010	0.0681	-0.0022
C (5)	0.0384	0.0012	0.0258	0.0016	0.0381	0.0007
C (6)	0.0495	0.0011	0.0427	0.0032	0.0715	0.0014
N (1)	0.0478	0.0012	0.0325	0.0008	0.0627	0.0001
C (7)	0.0481	0.0013	0.0369	0.0004	0.0658	0.0004
C (8)	0.0363	0.0010	0.0293	-0.0010	0.0484	-0.0006
C (9)	0.0386	0.0012	0.0293	0.0003	0.0365	-0.0002
C (10)	0.0754	0.0010	0.0482	0.0003	0.0913	-0.0028
C (11)	0.0562	0.0013	0.0599	0.0025	0.0962	0.0010
C (12)	0.0449	0.0010	0.0500	0.0009	0.0647	0.0015
C (13)	0.0423	0.0008	0.0468	0.0005	0.0681	-0.0002
C (14)	0.0457	0.0010	0.0364	-0.0033	0.0568	-0.0008
O (1)	0.0538	0.0017	0.0427	0.0093	0.0708	0.0060
O (2)	0.0607	0.0012	0.0379	0.0049	0.0735	0.0025

The overall shapes of the three molecules are represented in Figure 2. For the first two molecules, the four atoms C(4), N(1), C(7), C(8) lie almost exactly in a plane (maximum deviation less than 0.005 Å). For *p*-methylbenzylidene-*p*-nitroaniline the deviation from planarity is somewhat larger (maximum deviation 0.0135 Å), but still barely significant. The most striking feature of all three molecules is the twist of the aniline ring out of the C–N=C–C plane by 41–55°. The twist of the benzylidene ring out of this plane is much smaller (8–14°).

6. Thermal motion. – A detailed analysis of the thermal-motion parameters in terms of rigid-body translational and librational motions has been carried out with two distinct models:

a) The entire molecule is regarded as a rigid body.

b) Each benzene ring, with the carbon or nitrogen atom directly bonded to it, is regarded as a rigid body that vibrates independently of the other benzene ring in the molecule. This model is obviously also grossly oversimplified, since the motions of the two benzene rings must be coupled through the –C=N– double bond.

The librational, translational and screw motions were analysed by the method of *Schomaker & Trueblood* [9] in terms of both models for each of the three crystals.

Table 5. p-*Methylbenzylidene*-p-*nitroaniline*

Table 5a. *Crystal coordinates* (*and standard deviations* × 10^4)

	x	*y*	*z*
C(1)	-0.3500 (4)	0.1775 (8)	0.3420 (5)
C(2)	-0.3484 (3)	0.2842 (8)	0.2543 (5)
C(3)	-0.2547 (4)	0.3094 (7)	0.2660 (5)
C(4)	-0.1655 (4)	0.2255 (8)	0.3629 (5)
C(5)	-0.1710 (4)	0.1162 (8)	0.4470 (5)
C(6)	-0.2633 (5)	0.0878 (8)	0.4374 (5)
N(1)	-0.0666 (3)	0.2599 (7)	0.3882 (4)
C(7)	-0.0493 (4)	0.2440 (7)	0.3023 (5)
C(8)	0.0540 (4)	0.2875 (8)	0.3286 (5)
C(9)	0.0779 (4)	0.2440 (8)	0.2417 (5)
C(10)	0.1776 (4)	0.2761 (8)	0.2701 (5)
C(11)	0.2544 (4)	0.3478 (8)	0.3849 (5)
C(12)	0.2294 (4)	0.3922 (7)	0.4704 (5)
C(13)	0.1308 (4)	0.3630 (7)	0.4429 (5)
N(2)	-0.4480 (4)	0.1574 (8)	0.3343 (6)
O(1)	-0.5278 (3)	0.2149 (8)	0.2405 (5)
O(2)	-0.4449 (3)	0.0875 (7)	0.4231 (5)
C'(14)	0.3636 (4)	0.3749 (8)	0.4176 (5)

Table 5b. *Coordinates (in Å) referred to principal axes of the atom grouping C(4), N(1), C(7), C(8)* (see Fig. 2)

	X	Y	Z
C(1)	0.1296	-0.7310	-4.4843
C(2)	1.0207	-1.6261	-3.6228
C(3)	0.9655	-0.9930	-2.2798
C(4)	0.0133	-0.0981	-1.8220
C(5)	-0.8810	0.4517	-2.7142
C(6)	-0.8545	0.1335	-4.0560
N(1)	-0.0134	0.3901	-0.5101
C(7)	-0.0125	-0.4078	0.4771
C(8)	0.0126	0.1158	1.8551
C(9)	-0.1920	-0.7345	2.9310
C(10)	-0.2422	-0.2212	4.2269
C(11)	-0.1158	1.1326	4.4630
C(12)	0.0994	1.9697	3.3838
C(13)	0.1654	1.4723	2.0992
N(2)	0.2234	-1.0246	-5.9230
O(1)	0.9656	-1.9271	-6.2844
O(2)	-0.4249	-0.3365	-6.6922
C'(14)	-0.2291	1.6928	5.8627

The root-mean-square (r.m.s.) deviations between observed and calculated thermal-motion parameters U_{ij} are:

	Entire molecule Å	Aniline ring Å	Benzylidene ring Å
Benzylideneaniline	0.0056	0.0048	0.0042
Benzylideneaniline-*p*-carboxylic acid	0.0086	0.0079	0.0075
p-Methylbenzylidene-*p*-nitroaniline	0.0063	0.0042	0.0039

It is suggested by these numbers, and it can be shown from a statistical *F*-test, that for *p*-methylbenzylidene-*p*-nitroaniline and, to a lesser extent, also for benzylideneaniline, model b) with independently vibrating rings fits the observations better than model a). For benzylideneaniline-*p*-carboxylic acid the two models a) and b) give roughly equal goodness of fit to the observations.

A full account of the results of the thermal-motion analysis (with all relevant numerical data) is given elsewhere [5] and need not be reproduced here. The results may be summarized as follows: for the aniline rings, the largest eigenvector of the libration tensor runs approximately parallel to the axis C(1)...C(4), corresponding

Transformation matrix

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} -2.2410 & 6.9511 & -1.7451 \\ 1.8528 & 2.0265 & 9.2841 \\ 15.1935 & 0.7781 & -8.5894 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

Coordinates of old origin in new system: $(X, Y, Z) = (1.2916, 3.6173, -3.6335)$

Table 5c. *Estimated hydrogen-atom coordinates, assuming bond length C–H = 1.0 Å and local C_{2v}-symmetry at each C-atom, except the methyl carbon*

For the disordered methyl group six hydrogen atoms, each with weight 0.5 and $B = 4$ Å^2, were included in the structure factor calculation.

	x	y	z
H(C2)	-0.4135	0.3430	0.1841
H(C3)	-0.2515	0.3885	0.2039
H(C5)	-0.1063	0.0561	0.5169
H(C6)	-0.2672	0.0057	0.4972
H(C7)	-0.1062	0.2024	0.2162
H(C9)	0.0239	0.1888	0.1589
H(C10)	0.1936	0.2473	0.2063
H(C12)	0.2838	0.4456	0.5534
H(C13)	0.1143	0.3970	0.5059
H(C'14) 1	0.4189	0.3766	0.5198
H(C'14) 2	0.3704	0.5065	0.3814
H(C'14) 3	0.3854	0.2667	0.3790
H(C'14) 4	0.3652	0.3766	0.3339
H(C'14) 5	0.4145	0.2667	0.4796
H(C'14) 6	0.3950	0.5065	0.4666

to a torsional vibration about this axis with r.m.s. amplitude 7.2°, 7.5° and 5.6° for the three crystals investigated. For the benzylidene ring of benzylideneaniline and *p*-methylbenzylidene-*p*-nitroaniline, the largest eigenvector of the libration tensor runs approximately parallel to the axis C(8)...C(11) and corresponds to an r.m.s. amplitude of 6.9° and 6.1° respectively. The r.m.s. amplitudes corresponding to the remaining eigenvalues of the libration tensors lie in the range 1° to 4°, and their directions have no simple interpretation in terms of easily describable molecular motions. The thermal motions of the carboxyl and nitro groups are made up mainly from torsional vibrations about the single bonds C(1)–C(14) and C(1)–N(2), respectively.

The bond lengths in the three molecules have been corrected to allow for the systematic error arising from displacement of the apparent atomic positions towards the librational axes [10]. The corrected values are given in Table 9, together with the

Table 5d. *Anisotropic temperature factor parameters*

$$T = \exp - (b_{11}\,h^2 + b_{22}\,k^2 + b_{33}\,l^2 + b_{12}\,hk + b_{13}\,hl + b_{23}\,kl)$$

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C (1)	0.0058	0.0246	0.0111	-0.0053	0.0111	-0.0041
C (2)	0.0055	0.0269	0.0090	0.0001	0.0075	-0.0011
C (3)	0.0063	0.0224	0.0086	-0.0014	0.0079	0.0034
C (4)	0.0053	0.0212	0.0086	-0.0032	0.0075	-0.0017
C (5)	0.0063	0.0245	0.0107	0.0011	0.0092	0.0024
C (6)	0.0071	0.0215	0.0109	-0.0011	0.0100	0.0037
N (1)	0.0061	0.0248	0.0104	-0.0029	0.0091	-0.0004
C (7)	0.0060	0.0176	0.0094	-0.0005	0.0074	-0.0002
C (8)	0.0048	0.0198	0.0067	0.0009	0.0055	0.0029
C (9)	0.0070	0.0209	0.0085	-0.0023	0.0083	-0.0018
C (10)	0.0078	0.0229	0.0108	0.0024	0.0122	0.0013
C (11)	0.0059	0.0220	0.0099	0.0015	0.0091	0.0055
C (12)	0.0062	0.0226	0.0088	-0.0030	0.0077	-0.0008
C (13)	0.0056	0.0222	0.0075	-0.0021	0.0063	-0.0021
N (2)	0.0082	0.0339	0.0138	-0.0053	0.0144	-0.0059
O (1)	0.0067	0.0587	0.0166	-0.0009	0.0103	0.0070
O (2)	0.0102	0.0447	0.0172	-0.0048	0.0195	0.0003
C'(14)	0.0059	0.0377	0.0160	0.0028	0.0127	0.0111

corrections applied. For benzylideneaniline, the corrections are considerably larger than the estimated standard deviations (e.s.d.) in bond lengths due to random error; for the other two molecules, the corrections are roughly similar in magnitude to the standard deviations. The overall effect of the corrections is to level out somewhat the differences between individual bond lengths in the benzene rings, particularly in the case of benzylideneaniline.

However, the differences between the corrected lengths of individual bonds in the benzene rings are still much larger than the corresponding e.s.d.'s and appear to be distributed somewhat erratically. Although differences certainly must occur through the influence of substituents and molecular packing, it is difficult to believe that the observed pattern of bond distances corresponds to the real one. It seems more likely that the e.s.d.'s are considerably underestimated. More realistic values for the standard deviations in bond length and bond angle are roughly 0.01 Å and 1.0° for benzylideneaniline and *p*-methylbenzylidene-*p*-nitroaniline, and 0.02 Å and 2.0° for benzylideneaniline-*p*-carboxylic acid.

7. Planarity of various groupings. – For all three molecules, the best planes through the six atoms of each benzene ring and through the four atoms of the central grouping C(4), N(1), C(7), C(8) have been calculated. Table 10 shows the displacements

Table 6. *Bond lengths in Å (and standard deviations* $\times 10^3$*) calculated from coordinates in Tables 3, 4 and 5*

	Benzylidene-aniline	Benzylidene-aniline-*p*-carboxylic acid	*p*-Methyl-benzylidene-*p*-nitroaniline
C(1) - C(2)	1.371 (5)	1.408 (12)	1.375 (7)
C(2) - C(3)	1.406 (3)	1.374 (8)	1.385 (3)
C(3) - C(4)	1.386 (4)	1.386 (13)	1.385 (6)
C(4) - C(5)	1.375 (4)	1.410 (12)	1.378 (7)
C(5) - C(6)	1.398 (4)	1.382 (8)	1.379 (4)
C(6) - C(1)	1.395 (5)	1.389 (13)	1.378 (7)
C(4) - N(1)	1.460 (3)	1.431 (7)	1.400 (3)
N(1) - C(7)	1.237 (3)	1.281 (12)	1.269 (5)
C(7) - C(8)	1.496 (3)	1.461 (9)	1.474 (3)
C(8) - C(9)	1.380 (4)	1.401 (13)	1.387 (5)
C(9) - C(10)	1.406 (3)	1.396 (10)	1.395 (4)
C(10)- C(11)	1.364 (5)	1.388 (10)	1.380 (7)
C(11)- C(12)	1.380 (4)	1.392 (15)	1.383 (5)
C(12)- C(13)	1.405 (3)	1.381 (9)	1.379 (4)
C(13)- C(8)	1.391 (4)	1.389 (9)	1.387 (7)
C(14)- C(1)		1.484 (8)	
C(14)- O(1)		1.293 (10)	
C(14)- O(2)		1.248 (11)	
C(11)- C'(14)			1.512 (3)
C(1) - N(2)			1.471 (3)
N(2) - O(1)			1.223 (7)
N(2) - O(2)			1.219 (7)

of individual atoms from these planes. Neither the benzene rings nor the double-bond systems deviate significantly from planarity, but the substituents are displaced from these planes by as much as 0.13 Å.

8. Molecular packing. – 8.1. *Benzylideneaniline* (Fig. 3). The molecules are arranged in the crystal with their long axes approximately parallel to [100] and their mean molecular plane approximately parallel to (010). The molecular centres lie approximately at $(x, y, z) = (0.06, 0.25, 0.125)$. There are no distances shorter than 3.5 Å, between carbon atoms of different molecules *i.e.* no contacts shorter than the sum of the *van der Waals* radii given by *Pauling* [11]. The molecular volume of benzylideneaniline is 253 Å^3, approximately equal to the molecular volume of stilbene (256 Å^3)

Table 7. *Bond angles (and standard deviations) in degrees*

	Benzylidene-aniline	Benzylidene-aniline-*p*-carboxylic acid	*p*-Methyl-benzylidene-*p*-nitroaniline
C(6) -C(1) -C(2)	118.5 (0.4)	120.6 (1.0)	122.7 (0.6)
C(1) -C(2) -C(3)	120.0 (0.4)	119.4 (0.9)	118.5 (0.6)
C(2) -C(3) -C(4)	121.2 (0.4)	120.3 (0.9)	120.2 (0.5)
C(3) -C(4) -C(5)	118.9 (0.4)	120.6 (0.9)	119.4 (0.5)
C(3) -C(4) -N(1)	123.7 (0.3)	121.7 (0.9)	123.3 (0.5)
C(4) -C(5)--N(1)	117.3 (0.3)	117.7 (0.9)	117.1 (0.5)
C(4) -C(5) -C(6)	119.8 (0.4)	119.0 (0.9)	121.7 (0.5)
C(5) -C(6) -C(1)	121.4 (0.4)	120.1 (0.9)	117.4 (0.5)
C(4) -N(1) -C(7)	119.9 (0.3)	116.3 (0.8)	120.6 (0.5)
N(1) -C(7) -C(8)	122.7 (0.3)	122.4 (0.9)	120.2 (0.5)
C(7) -C(8) -C(9)	120.1 (0.3)	118.6 (0.9)	120.3 (0.5)
C(7) -C(8)--C(13)	122.2 (0.3)	122.2 (0.8)	120.9 (0.5)
C(9) -C(8) -C(13)	117.7 (0.3)	119.2 (0.9)	118.7 (0.5)
C(8) -C(9) -C(10)	120.9 (0.3)	120.0 (0.9)	120.0 (0.5)
C(9) -C(10)-C(11)	121.4 (0.4)	119.9 (0.9)	121.1 (0.5)
C(10)-C(11)-C(12)	118.4 (0.4)	120.0 (1.0)	118.3 (0.5)
C(11)-C(12)-C(13)	120.7 (0.4)	120.0 (1.0)	121.1 (0.5)
C(12)-C(13)-C(8)	120.9 (0.3)	120.8 (0.9)	120.8 (0.5)
C(2) -C(2) -C(14)		117.9 (0.9)	
C(6) -C(1) -C(14)		121.5 (0.9)	
C(1) -C(14)-O(1)		120.5 (0.9)	
C(1) -C(14)-O(2)		116.7 (0.9)	
O(1) -C(14)-O(2)		122.8 (0.9)	
C(10)-C(11)-C'(14)			121.0 (0.5)
C(12)-C(11)-C'(14)			120.7 (0.5)
C(2) -C(1) -N(2)			119.0 (0.6)
C(6) -C(1) -N(2)			118.3 (0.6)
C(1) -N(2) -O(1)			118.4 (0.6)
C(1) -N(2) -O(2)			118.1 (0.6)
O(1) -N(2) -O(2)			123.6 (0.6)

Table 8. *Torsion angles in degrees*

	Benzylidene-aniline-*p*-carboxylic acid	*p*-Methyl-benzylidene-*p*-nitroaniline
O(1) - C(14) - C(1) - C(2)	-3.6	
O(1) - C(14) - C(1) - C(6)	176.5	
O(2) - C(14) - C(1) - C(2)	178.0	
O(2) - C(14) - C(1) - C(6)	-1.9	
O(1) - N(2) - C(1) - C(2)		10.1
O(1) - N(2) - C(1) - C(6)		-169.8
O(2) - N(2) - C(1) - C(2)		-168.6
O(2) - N(2) - C(1) - C(6)		11.4

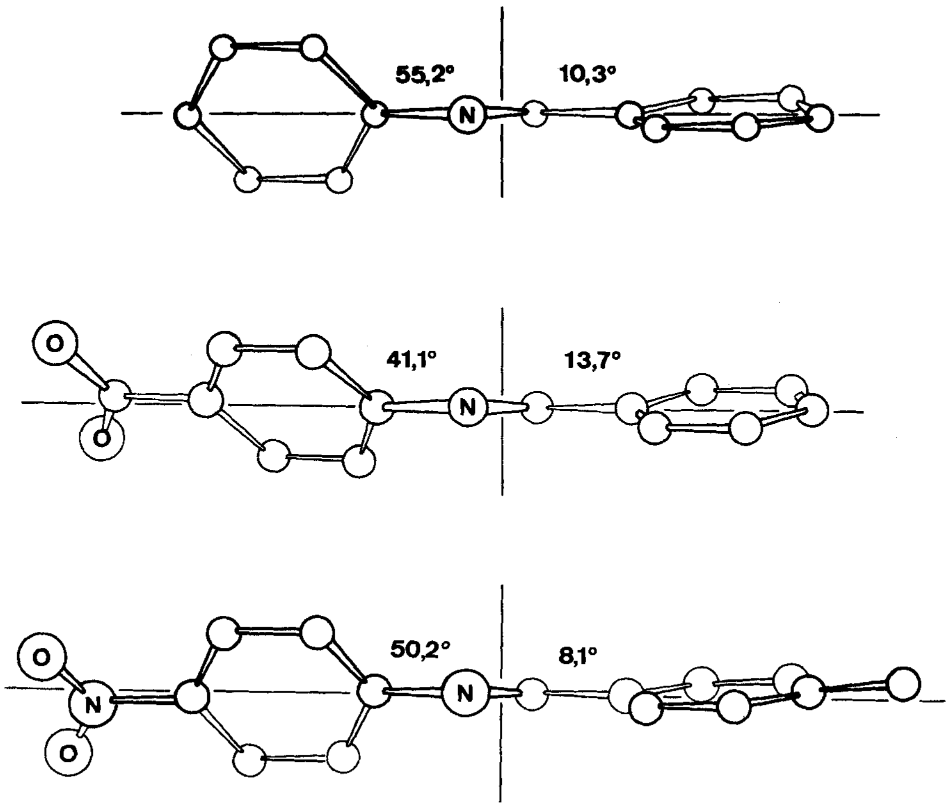

Fig. 2. *The three molecules shown in projection down the principal axis Y of the atom-grouping C(4), N(1), C(7), C(8) (compare Tables 3b, 4b, 5b)*

The benzene rings are twisted out of the plane of this atom-grouping by the amounts indicated.

Table 9. *Bond lengths (in Å) corrected for thermal motion (corrections applied, standard deviations, both × 10^3)*

	Benzylidene-aniline	Benzylidene-aniline-*p*-carboxylic acid	*p*-Methyl-benzylidene-*p*-nitroaniline
C(1) -C(2)	1.383(12;5)	1.416(8;12)	1.383(8;7)
C(2) -C(3)	1.412(6;3)	1.375(1; 8)	1.389(4;3)
C(3) -C(4)	1.399(13;4)	1.393(7;13)	1.392(7;6)
C(4) -C(5)	1.387(12;4)	1.421(11;12)	1.386(8;7)
C(5) -C(6)	1.404(6;4)	1.383(1; 8)	1.383(4;4)
C(6) -C(1)	1.408(13;5)	1.397(8;13)	1.386(8;7)
C(4) -N(1)	1.467(7;3)	1.431(1; 7)	1.403(3;3)
N(1) -C(7)			
C(7) -C(8)	1.501(5;3)	1.467(6; 9)	1.479(5;3)
C(8) -C(9)	1.389(9;4)	1.408(7;13)	1.396(9;5)
C(9) -C(10)	1.413(7;3)	1.402(6;10)	1.400(5;4)
C(10)-C(11)	1.374(10;5)	1.395(7;10)	1.389(9;7)
C(11)-C(12)	1.389(9;4)	1.401(9;15)	1.392(9;5)
C(12)-C(13)	1.410(5;3)	1.387(6; 9)	1.384(5;4)
C(13)-C(8)	1.400(9;4)	1.396(7; 9)	1.396(9;7)
C(14)-C(1)		1.487(3; 8)	
C(11)-C'(14)			1.517(5;3)
C(1) -N(2)			1.475(4;3)

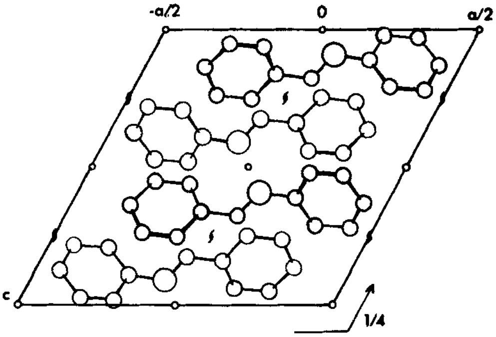

Fig. 3. *Crystal structure of benzylideneaniline, seen in projection along the* b *axis*

and azobenzene (247 Å^3) in spite of the differences in molecular conformation and crystal structure.

8.2. p-*Methylbenzylidene*-p-*nitroaniline* (Fig. 4). The cell constants show close similarities to those of benzylideneaniline. Although the c-axes and the angles β are slightly different, the expressions $c \sin\beta$ are almost identical: 10.63 Å and 10.51 Å respectively. As suggested by these similarities, the molecular packing is rather similar to that in benzylideneaniline itself. Again, the long axis of the molecule is approximately parallel to [100] and the mean molecular plane to (010). The extra space required by the *p*-substituents is provided by the elongation of the *a*-axis by about 3.3 Å. The length of the molecule without its substituents, when projected on the *a*-axis, is the same as in benzylideneaniline, the distances $a\,\Delta x$(C(1)...C(11)) being 9.05 Å and 9.06 Å, respectively. The tilt of *p*-methylbenzylidene-*p*-nitroaniline around c^*, away from the direction of the *a*-axis, is somewhat less than the corresponding tilt of benzylideneaniline, thus leading to the slightly shorter *b*-axis in the nitro

Table 10. *Deviations of various atoms from certain planes*

Atoms in brackets were not included in the calculation of the best planes, but their deviations are listed

Table 10a. *Aniline ring*

	Benzylideneaniline	Benzylideneaniline-*p*-carboxylic acid	*p*-Methylbenzylidene-*p*-nitroaniline
C(1)	0.0008	0.0142	0.0172
C(2)	0.0018	-0.0040	-0.0094
C(3)	-0.0008	-0.0188	-0.0023
C(4)	-0.0028	0.0172	0.0062
C(5)	0.0055	-0.0069	0.0012
C(6)	-0.0045	-0.0088	-0.0129
(N(1)	0.0632	0.0575	0.1541)
(C(14)		0.0561	)
(N(2)			0.0796)
(O(1)		0.1419	-0.0823)
(O(2)		0.0323	0.3154)

Table 10b. *Atom grouping C(4), N(1), C(7), C(8)*

	Benzylideneaniline	Benzylideneaniline-*p*-carboxylic acid	*p*-Methylbenzylidene-*p*-nitroaniline
C(4)	-0.0026	-0.0038	0.0133
N(1)	0.0024	0.0032	-0.0134
C(7)	0.0028	0.0045	-0.0125
C(8)	-0.0026	-0.0040	0.0126
(C(1)	0.0159	0.1023	0.1296)
(C(11)	0.0405	0.0195	-0.1158)

Table 10c. *Benzylidene ring*

	Benzylidene-aniline	Benzylidene-aniline-*p*-carboxylic acid	*p*-Methyl-benzylidene-*p*-nitroaniline
C(8)	0.0048	0.0124	-0.0047
C(9)	-0.0034	-0.0083	-0.0021
C(10)	-0.0009	-0.0029	0.0086
C(11)	0.0038	0.0101	0.0081
C(12)	-0.0024	-0.0060	0.0012
C(13)	-0.0019	-0.0052	0.0052
(C(7)	0.0286	0.0250	-0.0964)
(C'(14)			-0.0555)

compound. The molecular centres lie approximately at $(x, y, z) = (0.06, 0.25, 0.16)$, that is, the molecules are slightly displaced in the [001] direction. The net result is to provide a somewhat tighter packing, the mean volume per heavy atom being reduced to 16.6 Å^3 compared with 18.0 Å^3 in benzylideneaniline. The shortest intermolecular contacts occur between nitro groups of different molecules related by the screw axes. The distances O(1)...O'(1) and O(1)...N'(2) are 3.30 and 3.32 Å, respectively. All C...C and C...N distances are greater than 3.6 Å.

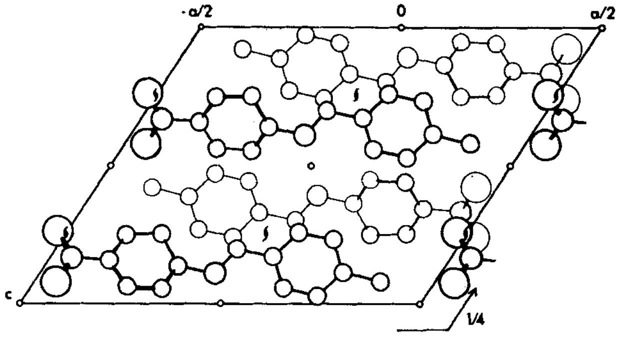

Fig. 4. *Crystal structure of* p-*methylbenzylidene*-p-*nitroaniline, seen in projection along the* b *axis*

8.3. *Benzylideneaniline*-p-*carboxylic acid* (Fig. 5). The molecules are linked across inversion centers into dimers by hydrogen bonding between the carboxyl groups (O–H...O distance 2.62 Å). Polar layers, formed by the carboxy-substituted aniline rings, are separated by less polar layers formed by the benzylidene rings. Distances between carbon atoms in different benzylidene rings are all greater than 3.5 Å. The polar layers are characterized by several shorter intermolecular distances, mostly involving the atoms with unshared electron pairs:

O(1)...C(2)	3.35 Å	C(14)...C(2)	3.49 Å	O(2)...C(3)	3.41 Å
O(1)...C(14)	3.40 Å	C(14)...N(1)	3.50 Å	O(2)...C(14)	3.42 Å
O(1)...O(1)	3.40 Å			O(2)...C(2)	3.44 Å
				O(2)...O(2)	3.48 Å

The distance between best planes through aniline rings is 3.398 Å and is found between molecules at (x, y, z) and at $(1 - x, 1 - y, 1 - z)$ (Tab. 4). The mean volume per heavy atom is 16.6 Å³, the same as in *p*-methylbenzylidene-*p*-nitroaniline.

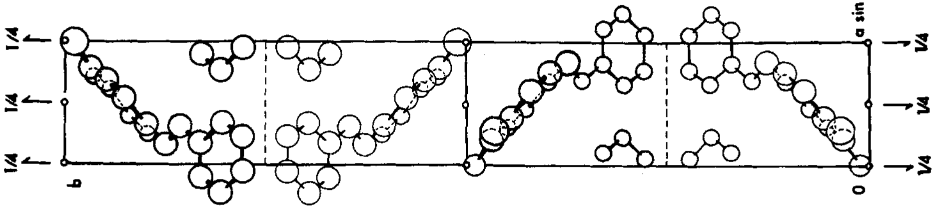

Fig. 5. *Crystal structure of benzylideneaniline*-p-*carboxylic acid, seen in projection along the* c *axis*

We are grateful to Dr. *M. Dobler*, Dr. *O. Ermer* and Mr. *B. Dürr* for help with computer programmes, and to the staff of the *ETH Computer Centre* for carrying out the calculations. 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] See, for example, *N.F. Smith*, Tetrahedron, *19*, 445 (1963); *E. Haselbach & E. Heilbronner*, Helv. *51*, 16 (1968).

[2] *H.B. Bürgi & J.D. Dunitz*, Chem. Commun. *1969*, 472.

[3] *H.B. Bürgi, J.D. Dunitz & C. Züst*, Acta crystallogr. *B24*, 463 (1968).

[4] *A.J.C. Wilson*, Nature *150*, 152 (1942).

[5] *H.B. Bürgi*, E.T.H. Zürich, Dissertation Nr. 4334 (1969).

[6] *J. Karle & I.L. Karle*, Acta crystallogr. *21*, 849 (1966).

[7] *H.B. Bürgi & J.D. Dunitz*, Acta crystallogr., in press.

[8] International Tables for X-ray Crystallography, Volume III, p. 202, the Kynoch Press, Birmingham (England) 1962.

[9] *V. Schomaker & K.N. Trueblood*, Acta crystallogr. *B24*, 63 (1968).

[10] *D.W.J. Cruickshank*, Acta crystallogr. *9*, 757 (1956); *W.R. Busing & H.A. Levy*, *ibid.* *17*, 142 (1964).

[11] *L. Pauling*, The Nature of the Chemical Bond, 3rd edition, p. 260, Cornell University Press, Ithaca (New York) 1960.