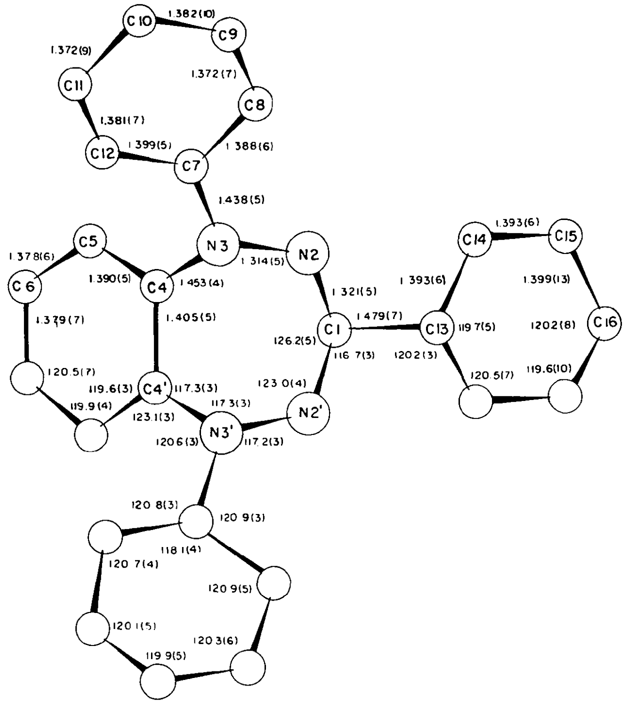

Fig. 1. A perspective view of the molecule showing the numbering system.

Discussion. The molecule including atom labels, bond distances and angles is shown in Fig. 1. Atoms C(1), C(13) and C(16) lie on the mirror plane at $x = 0{\cdot}25$. Because the molecule cannot possess symmetry [see (I)] a disordered structure has to be assumed, the present model being the average of two orientations. The disorder is also suggested by some high temperature parameters, mainly in ring *C*.

The C(1)–N(2) and N(2)–N(3) distances are longer than the corresponding double bond and much shorter than the corresponding single bond, as might be expected from the molecular disorder. The mean bond angle at N(3) is 118·3°. The molecular conformation is described in terms of torsion angles (Table 2), the seven-membered ring having the boat conformation. Rings *A*, *B* and *A*, *C* and *B*, *D* make angles of 59·7, 70·3 and 63·1° respectively.

Table 2. *Main torsion angles* (°)

N(2)–N(3)–C(7)–C(8)	−1·5 (5)
C(4)–N(3)–C(7)–C(12)	28·2 (4)
N(2)–C(1)–C(13)–C(14)	−4·0 (5)
N(2')–C(1)–N(2)–N(3)	−25·9 (6)
C(1)–N(2)–N(3)–C(4)	−41·8 (4)
N(2)–N(3)–C(4)–C(4')	63·3 (4)
N(3)–C(4)–C(4')–N(3')	0

No intermolecular contacts shorter than the sum of the van der Waals radii were found.

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Salicylideneaniline

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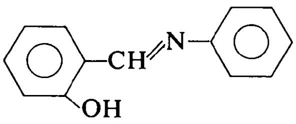
Abstract. $C_{13}H_{11}NO$, orthorhombic, space group *Fd2d*; $a = 27{\cdot}968$ (16), $b = 5{\cdot}941$ (2), $c - 12{\cdot}882$ (3) Å, $Z = 8$, $D_m = 1{\cdot}22$, $D_c = 1{\cdot}22$ g cm^{-3}. The number of equivalent positions being 16, orientational disorder simulates symmetry around a twofold axis, and prevents the determination of accurate molecular

parameters, although the structure can be refined to $R = 0{\cdot}053$ with an average molecular model. The angles between the main planes in the molecule are given.

Introduction. Salicylideneaniline (SAL):



was discovered (Cohen, Schmidt & Flavian, 1964) to be a photochromic crystal, *i.e.* to exhibit a marked change in color under UV irradiation, due to a solid state reaction possibly leading to a quinonic derivative (Cohen & Green, 1973). The space group and cell dimensions, somewhat less accurate than ours, were also determined (Cohen *et al.*, 1964). Because of our interest in solid state reactivity (Gavezzotti & Simonetta, 1978) we undertook a full crystal structure analysis of SAL. Due to the lability of the irradiated product, its structural analysis has not been undertaken.

SAL is readily prepared from salicylaldehyde and aniline in an ether solution. The bright yellow crystals were washed in ethanol, and a suitable specimen was mounted on the tip of a glass capillary. No sublimation or decay was observed during the data collection, carried out on a Syntex diffractometer [λ(Mo $K\alpha$) = 0·7107 Å; graphite monochromator], and monitored by the periodic measurement of two standard reflections. A variable-rate θ–2θ scan technique was employed; the background was monitored at each extremity (for one-half of the scan time). Out of 677 measured reflections ($2\theta \leq 55°$), 32 (having negative net intensities) were assigned zero weight; all other reflections were assigned variances $\sigma^2(I)$ based on counting statistics plus the additional term (0·03 scan count)^2. The data were corrected for Lorentz and polarization factors but not for absorption ($\mu = 0{\cdot}84$ cm^{-1}).

MULTAN (Germain, Main & Woolfson, 1971) gave the solution of the structure and a map with nine significant peaks, one more than expected [see Fig. 1(*a*)]. It was soon realized that a positional disorder similar to that found in *p*-(*N*-methylbenzylidene)-*p*-methylaniline (Bernstein, Bar & Christensen, 1976) was present. The asymmetric unit consists of two positions obtained by rotation in the plane of the benzene ring. The situation is sketched in Fig. 1; atoms 1–6 form an 'average' benzene ring, to which 'half substituents' and H atoms are attached. A few refinement cycles using anisotropic C(1)–C(6), $\frac{1}{2}$C(7), $\frac{1}{2}$N, $\frac{1}{2}$O, and isotropic H(2)–H(5), $\frac{1}{2}$H(8), $\frac{1}{2}$H(7), and $\frac{1}{2}$H(6) gave $R = 0{\cdot}053$ (for $I > 0$); Table 1 shows the final atomic parameters.*

The quantity minimized was $\sum w(|F_o| - |F_c|)^2$, with weights w equal to $4\,F_o^2/\sigma^2(F_o^2)$. Other details on atomic form factors and programs used can be found in Destro, Pilati & Simonetta (1974). A final difference Fourier synthesis showed no peaks higher than 0·13 e Å^{-3}.

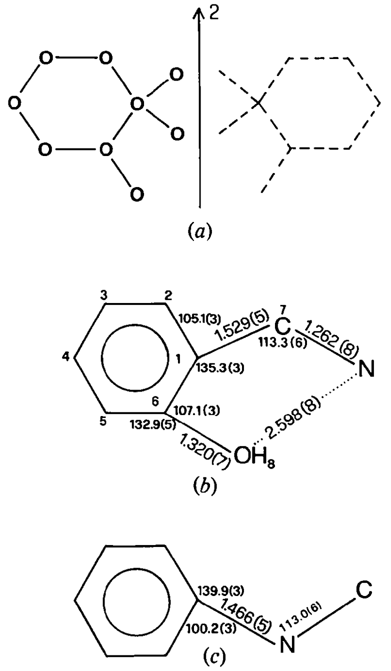


Fig. 1. (*a*) Schematic representation of the nine peaks appearing in the maps after the use of the *MULTAN* program (Germain, Main & Woolfson, 1971). The crystal structure is the superposition of (*b*) and (*c*), the benzene ring being an average of the one that would fit the aniline moiety and that which would fit the salicylaldehyde moiety.

Table 1. *Final atomic parameters*

Fractional coordinates for C, N and O (× 10^4) and for H (× 10), and isotropic B's of the H atoms (× 10) are given.

	x	y	z	B (Å^2)
C(1)	2847 (1)	6790 (0)	3711 (2)	
C(2)	2860 (1)	8572 (8)	4387 (2)	
C(3)	3150 (1)	8533 (9)	5241 (2)	
C(4)	3432 (1)	6669 (9)	5419 (2)	
C(5)	3423 (1)	4874 (9)	4752 (2)	
C(6)	3129 (1)	4928 (8)	3896 (2)	
C(7)	2503 (2)	7512 (13)	2851 (3)	
O	3056 (2)	3501 (12)	3128 (4)	
N	2427 (2)	5992 (12)	2187 (3)	
H(2)	267 (1)	986 (7)	425 (2)	44 (8)
H(3)	314 (1)	985 (7)	569 (2)	49 (6)
H(4)	363 (1)	665 (5)	601 (2)	51 (6)
H(5)	362 (1)	346 (9)	484 (3)	65 (9)
H(6)	311 (3)	330 (17)	357 (6)	62 (25)
H(7)	236 (1)	899 (9)	284 (3)	23 (9)
H(8)	275 (5)	413 (18)	237 (14)	85 (33)

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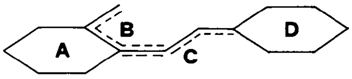
* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33568 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.



	B	C	D
A	2	5	49
B		6	49
C			44

Fig. 2. Angles (°) between the main planes in the molecule.

Discussion. Crystal structures of similar compounds, available for comparison, are: *N*-(5-chlorosalicylidene)-aniline (I) (Bregman, Leiserowitz & Schmidt, 1964); 2-chloro-*N*-salicylideneaniline (II) (Bregman, Leiserowitz & Osaki, 1964); *p*-nitrobenzylidene-*p*-dimethylamino-aniline (III) and *p*-dimethylaminobenzylidene-*p*-nitro-aniline (IV) (Nakai, Shiro, Ezumi, Sakata & Kubota, 1976); benzylideneaniline and two substituted derivatives (V–VII) (Bürgi & Dunitz, 1970).

The geometry of the 'average' benzene ring is almost perfectly regular [C—C bond lengths 1·366 (4) to 1·381 (5) Å; C—C—C bond angles 119·1 (4) to 121·0 (4)°; C—H distances and H—C—C angles are reasonable]. In contrast, the C(5)—C(6)—O, C(1)—C(6)—O, C(6)—C(1)—C(7) and C(2)—C(1)—C(7) angles are too far from 120° to be acceptable (see Fig. 1); the geometry at the corresponding molecular sites in I and II is regular. Deviation from 120° of the aniline moiety C—C—N angles is more common (116·3 and 126·8° in III; 124·3 and 116·1° in I). However, the C(1)—C(7) distance (1·529 Å) looks too long (1·444 in I, 1·452 in II, and 1·452 to 1·496 Å in III–VII). The C(1)—N distance (1·466 Å) is also somewhat long (1·419 in I, 1·421 in II, 1·399 to 1·460 Å in III–VII). However, the C(6)—O bond length (1·320 Å) is too short (1·351 in I, 1·365 Å in II). Finally, the C(1)—C(7)—N and C(1)—N—C(7′) angles are out of the expected range, all the corresponding values in I–VII being in the region of 120°. The C(7)—N′ distance (1·262 Å), however, is within the usual range (1·237 to 1·288 Å in I–VII). Also, the O—N′ distance (2·598 Å) is within the usual dimensions for a hydrogen bond, although the position of the H atom involved was not accurately determined (see the exceedingly high *B* thermal factor for this atom, Table 1).

This evidence points to the conclusion that the geometrically regular benzene ring is an artifact, due to the fit (obtained by the use of anisotropic ellipsoids) of the atoms of two nearly superposing rings separated by a small rotation in their common plane. When this 'average' ring is placed in front of the pattern of the substituents, which has been shown to be geometrically consistent within itself, an obvious misfit appears. This makes further attempts to refine the structure, even by different models such as rigid benzene rings with half population, probably misleading and pointless. However, the key molecular parameters in the study of the spectroscopic properties and solid state reactivity of such compounds are the angles between the main molecular planes (Cohen & Green, 1973). These can confidently be extracted from our treatment, and are shown in Fig. 2. They prove that SAL was correctly assigned to the family of anils whose benzene rings are not coplanar in the solid state, on the basis of their behavior under UV irradiation (Cohen & Green, 1973).

Finally, the ease with which the structure was refined to a very low discrepancy index by a clearly unrealistic use of anisotropic thermal parameters should be pointed out, with the implications of this fact in the ordinary application of X-ray crystal structure analysis.

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