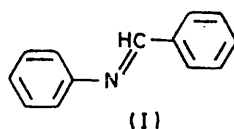


Conformational Studies. Part IV.¹ Crystal and Molecular Structure of the Metastable Form of *N*-(*p*-Chlorobenzylidene)-*p*-chloroaniline, a Planar Anil

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The title compound crystallises in the triclinic system with cell constants $a = 5.986(2)$, $b = 3.933(1)$, $c = 12.342(2)$ Å, $\alpha = 87.38(3)$, $\beta = 78.40(3)$, $\gamma = 89.53(3)^\circ$, and $Z = 1$. The crystal and molecular structures were solved from 1458 intensities measured on a diffractometer, and refined anisotropically to R 0.062. The structure is disordered about a crystallographic inversion centre, which requires that the two aromatic rings must be parallel, the dihedral angles about the exocyclic bonds being equal but of opposite sign, in contrast to the structures of previously analysed benzylideneanilines. The metastable nature of the crystal is discussed in terms of the packing arrangement.

In the crystal structure analyses of benzylideneaniline (I) and two substituted benzylideneanilines² the



molecules were found to be twisted about the N-C(Ph) bond by *ca.* 45°, with a small and opposite twist (*ca.* 10°) about the CH-C(Ph) bond. These results are in accord with the predictions of the molecular conformation based on spectroscopic arguments³⁻⁸ which arose from the observation that the u.v. absorption spectrum of (I) differs markedly from that of the isoelectronic nearly planar analogues *trans*-stilbene and *trans*-azobenzene. In a previous paper,¹ we reported the structure of *N*-(2,4-dichlorobenzylidene)aniline in which the degree of out-of-plane rotation about the single bonds is smaller and in the same sense for the two rings. We now report the structure of *N*-(*p*-chlorobenzylidene)-*p*-chloroaniline, which is planar within experimental accuracy.

EXPERIMENTAL

Crystals (m.p. 114–116 °C) were obtained from a nearly saturated boiling ethanolic solution which was allowed to cool rapidly to room temperature in a desiccator charged with fresh calcium chloride. The crystals are white to very pale yellow needles which extinguish white light under crossed polarisers at an angle of *ca.* 30° to the needle axis.† When set aside, or cleaved, most crystals turn yellow and fail to extinguish; X-ray photographs of such crystals indicate that very little order remains after the transformation.

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‡ Crystals of the orthorhombic 6.7 Å form are obtained by slow cooling from methylcyclohexane solutions. They are yellow rhombs which extinguish white light under crossed polarizers along the crystal edges.

§ The absorption factor was computed with a Gaussian grid containing 16 sampling points.

¹ Part III, J. Bernstein, preceding paper.

² H. B. Bürgi and J. D. Dunitz, *Chem. Comm.*, 1969, 472; *Helv. Chim. Acta*, 1970, **52**, 1747.

³ V. A. Ismailski and E. A. Smirnov, *Zhur. obshchei Khim.*, 1956, **26**, 3389.

The crystals are elongated along [010]; well formed specimens show the {011}, {102}, and {001} forms. The lattice constants were determined by least squares from 44 high-order ($\theta > 20^\circ$) reflections measured on the Siemens diffractometer with Mo- K_α radiation, $\lambda = 0.7107$ Å.

Crystal Data.— $C_{13}H_9Cl_2N$, $M = 250.13$, Triclinic, $a = 5.986(2)$, $b = 3.933(1)$, $c = 12.342(2)$ Å, $\alpha = 87.38(3)$, $\beta = 78.40(3)$, $\gamma = 89.53(3)^\circ$, $U = 284.3$ Å³, $D_c = 1.46$, $Z = 1$, D_m (floatation) = 1.42, $F(000) = 128$. Mo- K_α radiation, $\lambda = 0.7107$ Å; $\mu(\text{Mo-}K_\alpha) = 5.39$ cm⁻¹. Space group either $P1$ or $P\bar{1}$; the latter confirmed in the course of the analysis, requires disorder.

A crystal of dimensions 0.07 × 0.54 × 0.18 mm measured perpendicular to the (001), (102), and (011) faces was mounted along b^* on an IBM 1800 controlled Siemens diffractometer. Two independent sets of $I(hkl)$ were recorded for $\sin \theta/\lambda \leq 0.68$ with Mo- K_α radiation and balanced zirconium and yttrium filters.

Intensities were measured by a $\omega/2\theta$ scan technique as described in ref. 9. The procedure for the treatment of data, including correction for absorption, was as in ref. 10. § Averaging of the two sets of data yielded 1458 independent reflections in the copper sphere, of which 453 had intensities $< 2\sigma$ of the mean value, or $< 2\sigma$ (mean) for equivalent reflections, and were treated as 'unobserved'.

Structure Determination and Refinement.—Intensity statistics, based on the second and third moment tests of Forster and Hargreaves,¹¹ as well as the $N(z)$ test, indicated a centrosymmetric space group. Statistics of normalised structure factors (E) supported this assignment. Since D_c corresponds to one non-centrosymmetric molecule per unit cell of space group, the structure must be disordered about the C=N group.

The structure was solved by Patterson methods and packing considerations. The length of the vector connecting the lattice points 1,0,0 and $\bar{1},1,1$ (16 Å) suitably allows for the intramolecular Cl...Cl distance (12.5 Å) and the expected intermolecular van der Waals contact of 3.6 Å.

⁴ N. Ebara, *Bull. Chem. Soc. Japan*, 1960, **33**, 534.

⁵ P. Brocklehurst, *Tetrahedron*, 1962, **18**, 299.

⁶ G. Favini and A. Gamba, *J. Chim. phys.*, 1965, **62**, 995.

⁷ V. I. Minkin, Y. A. Zhdanov, E. A. Medyantzeva, and Y. A. Ostroumov, *Tetrahedron*, 1967, **23**, 3651.

⁸ E. Haselbach and E. Heibronner, *Helv. Chim. Acta*, 1968, **51**, 16.

⁹ H. Irngartinger, L. Leiserowitz, and G. M. J. Schmidt, *J. Chem. Soc. (B)*, 1970, 1035.

¹⁰ P. Coppens, L. Leiserowitz, and D. Rabinovich, *Acta Cryst.*, 1965, **18**, 497.

¹¹ F. Foster and A. Hargreaves, *Acta Cryst.*, 1963, **16**, 1124, 1133.

Furthermore, these points were both found to lie within 0.5 Å of the least-squares plane of the 19 strongest Patterson peaks, which showed good correspondence with the Patterson function predicted for a planar molecule.

A trial structure based on these considerations yielded a conventional R factor of 0.36 for 36 reflections of lowest $\sin \theta/\lambda$. Rigid-body least-squares refinement of one-half of the molecule in space group $P\bar{1}$ allowing only the orientation of the group and the overall scale factor to vary, led to R of 0.30 after 6 cycles, with no marked inconsistencies between observed and calculated structure factors.

Full-matrix least-squares refinement of this centrosymmetric model proceeded by stages. In the first stage (3

map based on the final parameters of all atoms was virtually featureless and at no point exceeded $|0\cdot20| \text{ e}\text{\AA}^{-3}$. Refinement of the structure in space group $P\bar{1}$ was also carried out; to limit the number of parameters, the chloroaromatic moieties were refined as rigid bodies while C, H, and N on the bridge were refined as individual atoms. No significant improvement in R was obtained. It therefore appears that the statistically disordered centrosymmetric model is the correct one.

Thermal Motion. Rigid-body analysis according to the method of ref. 13 was carried out separately on the chlorophenyl moiety and on the full molecule. The respective root-mean-square discrepancies of ΔU_{ij} are 0.0022 Å² and

TABLE 1

Summary of rigid-body analysis of chlorophenyl moiety

The calculation is referred to the origin which symmetrises \mathbf{S} and reduces the trace of \mathbf{T} . Centre of mass of axial system of inertia referred to crystal axes:

$$x = 0.4919, y = -0.2612, z = -0.2804.$$

Transformation matrix from crystal system to axial system of inertia:

$$\begin{array}{ccc} -3.6241 & 1.2089 & 7.5083 \\ -3.9971 & 1.1634 & -9.7150 \\ -2.5935 & -3.5568 & -1.2489 \end{array}$$

Tensor elements $\times 10^5$.

Tensor	11	22	33	12	23	13
\mathbf{L}/rad^2	2393(153)	534(39)	279(31)	113(63)	60(39)	188(85)
$\mathbf{T}/\text{\AA}^2$	3749(88)	4994(101)	4850(197)	-27(88)	-51(101)	181(117)
$\mathbf{S}/\text{rad \AA}^{-1}$	-117(69)	77(76)	40(103)	-39(50)	-104(38)	-77(30)
R.m.s. amplitudes						
\mathbf{L}	{	8.9°		0.9941	0.0625	0.0891
		4.2		0.0772	-0.9820	-0.1724
		2.9		0.0767	-0.1782	-0.9810
\mathbf{T}	{	0.224 Å		-0.0715	0.9294	-0.3620
		0.220		-0.1415	-0.3687	-0.9187
		0.193		-0.9874	-0.1451	0.1579

cycles) data were limited to $\sin \theta/\lambda \leq 0.4$ and only positional parameters and individual isotropic temperature factors permitted to vary; hydrogen atoms on the ring were included in the structure-factor calculation and the bridge atom was assigned a nitrogen scattering-factor curve. For the second stage (6 cycles) all data were included, the scattering factor for the bridge atom was taken to be the mean of those for carbon and nitrogen, and all heavy atoms were refined with anisotropic temperature factors. In the final stage (3 cycles) a hydrogen of half-occupancy was inserted at the chemically expected position on the bridge and the positional parameters and isotropic temperature factors for all hydrogen atoms were refined as well as all heavy-atom parameters. In all stages of refinement the weight (w) of a particular reflection was $1/\sigma^2(F_o^2)$. Refinement converged for R 0.062 and R' 0.030 $\{R' = [(\Sigma w F_o - |F_c|)^2 / \Sigma w F_o^2]^{1/2}\}$. The scattering-factor curves were taken from ref. 12. The calculated and observed structure factors are listed in Supplementary Publication No. SUP 20313 (3 pp., 1 microfiche).*

The centrosymmetric model was subjected to a number of tests. All temperature factors for the hydrogen atoms are quite normal, including that of the hydrogen of half-occupancy on the bridge. A difference electron-density

* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc. (A)*, 1970, Issue No. 20 (items less than 10 pp. are supplied as full page copies).

† $\mathbf{X} = (\mathbf{C} + \mathbf{N})/2$, and is used to designate the heavy atoms in the bridge.

0.0053 Å² compared to the mean σ of the observed U_{ij} values of $\overline{\sigma U_{ij}} = 0.0014 \text{ \AA}^2$. The fit for a single chlorophenyl portion of the molecules is quite good; calculated values of the diagonal elements of the vibration tensor agree with the observed values to within 10% and in most cases the agreement is better than 5%. Results of the rigid-body analysis are summarised in Table 1. The directional properties of the motion described by the analysis are physically reasonable, the axis of largest libration being almost coincident with the axis corresponding to the smallest moment of inertia. However, it is unlikely that the rather large principal root-mean-square amplitude of 8.9° represents a true librational motion. The structure analysis established that at any particular molecular site the molecule may adopt one of two possible orientations which differ only with respect to the disposition of the -CH=N- bridge. In either of the two orientations the repulsion due to the short contact (2.01 Å) between H(6) and H(X') † may be partially relieved by a small (static) displacement of H(6) due to rotation about the X-C(1) bond, the clockwise and counterclockwise rotations being equally probable. Hence, in the space-average crystallographic refinement with a centrosymmetric model, the four possible displacements are included in the anisotropic temperature factors and yield an

¹² 'International Tables for X-ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1965, p. 202.

¹³ V. Schomaker and K. N. Trueblood, *Acta Cryst.*, 1968, B, 24, 63.

apparently high librational motion about the X-C(1) axis in the rigid-body analysis. Bond lengths corrected for rigid-body motion are given in Figure 1.

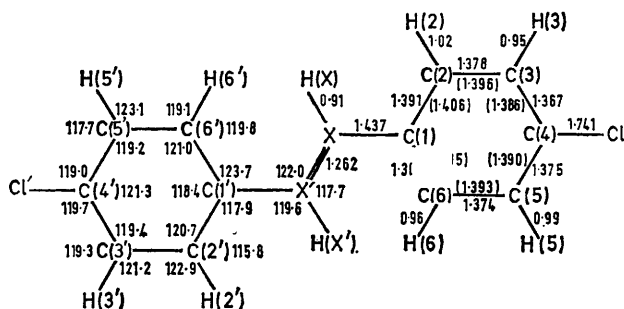


FIGURE 1 Experimental bond distances (Å) and angles (°); mean σ : C-C 0.004, C-Cl 0.003, C-H 0.034 Å, C-C-C and C-C-Cl 0.3, and C-C-H 1.8°. Bond distances in parentheses are those corrected for rigid-body motion

RESULTS AND DISCUSSION

The experimental positional and thermal parameters together with their estimated standard deviations are listed in Table 2.

TABLE 2

Atomic co-ordinates (fractional $\times 10^4$) and thermal parameters ($10^4 U_{ij}$), with standard deviations									
Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
C(1)	1870(4)	-912(7)	-1341(2)	460(13)	529(18)	443(13)	60(13)	-71(12)	-27(11)
C(2)	1712(5)	-386(9)	-2445(2)	484(14)	791(23)	494(15)	110(16)	-28(15)	-94(12)
C(3)	3447(5)	-1383(9)	-3282(2)	572(17)	859(25)	417(14)	90(17)	-67(15)	-44(12)
C(4)	5359(5)	-2851(8)	-3019(2)	3019(2)	605(19)	487(13)	42(14)	-112(13)	38(11)
C(5)	5571(5)	-3390(9)	-1936(2)	520(16)	724(22)	539(15)	188(16)	-51(15)	-31(12)
C(6)	3829(5)	-2415(9)	-1104(2)	509(15)	788(23)	434(13)	158(16)	-47(15)	-78(12)
X	-6(4)	172(8)	-509(2)	469(13)	711(19)	478(12)	129(14)	-57(14)	-39(11)
Cl	7568(1)	-4100(3)	-4071(1)	615(5)	1016(8)	570(5)	148(4)	-204(4)	94(3)
$10^3 U_{iso}$									
H(2) *	16(6)	46(9)	-258(2)	H(2)	41(9)				
H(3)	339(5)	-90(9)	-403(3)	H(3)	43(9)				
H(5)	701(6)	-441(10)	-179(3)	H(5)	53(10)				
H(6)	396(5)	-285(8)	-34(3)	H(5)	36(8)				
H(X)	-133(11)	85(17)	-70(5)	H(X)	37(17)				

* Hydrogen atom co-ordinates $\times 10^3$.

Molecular Dimensions.—Bond lengths and angles are given in Figure 1. The C(4)-Cl length (1.741 Å) agrees well with the mean value (1.737 ± 0.016 Å) given in ref. 14. A small but regular distortion of the aromatic ring is apparent and is due principally to the presence of the electron-withdrawing chlorine substituent. The angle C(3)-C(4)-C(5) (121.3°) is larger than that expected for pure sp^2 hybridisation at C(4). Aromatic substitution by electron-withdrawing groups generally leads to an increase in the internal angle at the position of substitution¹⁴⁻¹⁶ and the effect has been observed in the case of chlorine substitution as well.^{17,18} The resulting strain in the ring is relieved by a symmetric distortion as evidenced by the close correspondence of chemically equivalent bonds and internal angles.

¹⁴ G. J. Palenik, J. Donohue, and K. N. Trueblood, *Acta Cryst.*, 1968, B, **24**, 1139.

¹⁵ O. L. Carter, A. T. McPhail, and G. A. Sim, *J. Chem. Soc. (A)*, 1966, 822.

Geometric features of the four atoms [C(1), X, X', C(1')] which comprise the link between the two phenyl rings are compatible with those of other benzylideneanilines. The X=X' bond length (1.262 Å) closely resembles the C=N distance found in *N*-(2,4-dichlorobenzylidene)-aniline (1.268 Å) and *N*-(*p*-methylbenzylidene)-*p*-nitroaniline (1.269 Å). Bürgi and Dunitz argued that the C=N bond length depends principally on two opposing effects: (i) the electron-withdrawing power of a *para*-substituent which leads to lengthening of the bond due to increased contribution of quinoid resonance structures over the unsubstituted molecule, and (ii) the torsion angle about the N-C(Ph) bond which increases the overlap between the non-bonding orbital on N and the π -system of the aniline ring and thus reduces the contribution of quinoid resonance structures. In the benzylideneaniline structures, the various C=N bond lengths generally follow a pattern expected if the first effect is dominant at least at torsion angles up to about 40° , at which point the π -delocalisation energy is still 75% of its value at 0° .⁷ By use of the length of the C=N bond as a measure, we previously showed¹ that two chlorine substituents, in the *ortho*- or *para*-positions, are approxi-

mately equivalent, in electron-withdrawing power, to one nitro-substituent. Correspondence between the C=N bond length in the present structure and the dichloro- and the nitro-methyl-compounds is in accord with this description. While the disordered model employed here obviates a direct comparison of other geometric features of the bridge with earlier structures, as expected from the foregoing arguments the bond length C(1)-X (1.437 Å) is similar to that for the mean of the C-C(Ph), N-C(Ph) distances in the dichloro- (1.444 Å) and nitro-methyl-compounds (1.437 Å).

The best planes through the six carbon atoms of the ring, the four atoms at the bridge, and all heavy atoms of the molecule are given in Table 3. Measured against any of these criteria the molecule is planar within at least 0.02 Å. This planarity is in striking contrast to

¹⁶ H. Hope, *Acta Cryst.*, 1969, B, **25**, 78.

¹⁷ S. K. Arora and L. M. Pant, *Acta Cryst.*, 1969, B, **25**, 1045.

¹⁸ See, e.g., refs. in Table 7 of ref. 14.

the conformations of previously studied benzylideneanilines in which the twists about the N-C(Ph) and CH-C(Ph) are *ca.* 45 and 10°. Short intramolecular contacts H(2)···H(X) 2.32, H(6)···X' 2.62, and H(6)···H(X') 2.01 Å are present as a result of this conformation. The fact that the potential energy for a planar molecule is roughly estimated to be 1.5–2.0

TABLE 3

Equations of some least-squares planes in the form $Ax + By + Cz = 0$ where x , y , and z are fractional coordinates. Deviations (Å) of relevant atoms from the planes are given in square brackets

	<i>A</i>	<i>B</i>	<i>C</i>
Plane (I): C(1)—C(6)	2.592	3.557	1.251
[C(1) 0.003, C(2) -0.005, C(3) 0.004, C(4) -0.002, C(5) 0.000, C(6) 0.000, X -0.001, Cl 0.002, C(1') -0.012, C(2') -0.005, C(3') -0.014, C(4') -0.008, C(5') -0.009, C(6') -0.010, X' -0.009, Cl' -0.011, H(2) 0.112, H(3) -0.057, H(5) -0.026, H(6) 0.025, H(X) 0.123]			
Plane (II): C(1), X, C(1'), X'	-2.581	-3.560	-1.176
[C(1) 0.000, C(2) 0.017, C(3) 0.011, C(4) 0.013, C(5) 0.003, C(6) -0.001, X 0.000, Cl 0.015, C(1') 0.000, X' 0.000, H(2) -0.097, H(3) 0.079, H(5) 0.026, H(6) -0.033, H(X) -0.124]			
Plane (III): All heavy atoms	-2.594	-3.556	-1.237
[C(1) -0.005, C(2) 0.004, C(3) -0.004, C(4) 0.003, C(5) 0.000, C(6) -0.002, X -0.003, Cl 0.001, C(1') 0.005, C(2') -0.004, C(3') 0.004, C(4') -0.003, C(5') 0.000, C(6') 0.002, X' 0.003, Cl' -0.001, H(2) -0.113, H(3) 0.059, H(5) 0.025, H(6) 0.029, H(X) -0.130]			

kcal mol⁻¹ higher than for a twisted molecule¹⁹ helps to explain the metastable nature of the crystals. Presumably, the lower-energy twisted form is obtained by molecular relaxation which is initiated at suitable dislocations where the immediate environment provides enough space for the initial molecular relaxation to occur. Confirmation of this notion comes from the observation that when crystals are cleaved perpendicular to the needle axis (*b*) the transformation from the metastable crystal form usually commences at the cleaved surface where the population of dislocations is expected to be high. These dislocations are expected to be of the type which perturb molecules from the normal stack to stack relationship (Figure 2) and create sufficient room for a molecular relaxation by simple rotation about a C(1)—X bond.

The packing arrangement is shown in Figure 2. Short intermolecular contacts are given in Table 4. The packing arrangement is dominated by the short Cl···Cl distance (3.42 Å), with infinite stranded chains of molecules along the line connecting the real lattice points 0,0,0 and -2,1,1. Apparently the planar conformation does not lead to a significant increase in packing efficiency since the molecular volume (284.3 Å³) is nearly identical with that of *N*-(2,4-dichlorobenzylidene)aniline (289.5 Å³).

The question arises as to whether the planar conformation found here is a manifestation of inter- or intra-

¹⁹ H. B. Bürgi and J. D. Dunitz, *Helv. Chim. Acta*, 1971, **54**, 1255.

molecular interactions. If the former were the principal factor, on the basis of this structure the presence of either a 4 Å axis and/or two chlorine substituents might

TABLE 4

Intermolecular distances *

Atom pair	Translation along			Distance/Å
	<i>a</i>	<i>b</i>	<i>c</i>	
H(5)···H(X) †	1	-1	0	2.55
H(6)···H(6')	1	-1	0	2.32
Cl···H(3')	1	0	-1	3.13
Cl···Cl'	2	-1	-1	3.42

* All distances less than the sum of van der Waals radii plus 0.2 Å. First atom of pairs is located at x, y, z ; primed

atoms located at $\bar{x}, \bar{y}, \bar{z}$. † $X = \frac{C + N}{2}$.

appear to be sufficient conditions for planarity; both of these restrictions are obviated by the structure of 2,4-dichlorobenzylideneaniline in which the two conditions are satisfied, but the molecule is not planar.

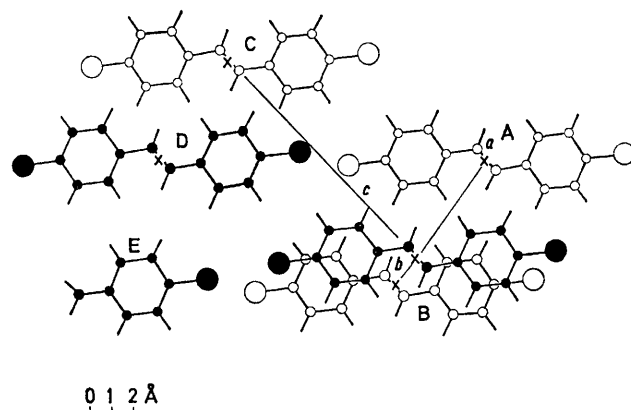


FIGURE 2 Molecular packing arrangement perpendicular to best plane of the full molecule at the origin. Elevations of other molecules (Å) with respect to the plane of the origin molecule: A -2.54, B -3.56, C -1.24, D 1.36, and E, 0.40. Molecular pseudo-centres of symmetry are marked with a cross. The vectors denoted by a, b, c , are unit-cell translations; a and b are, of course, not collinear

On the other hand, there is some evidence that the position of substitution (*i.e.* with respect to the pseudo-centre of symmetry in the C=N bond) as well as the polarity of the substituent may be a necessary condition for planarity, even in the absence of a 4 Å axis. Since the barrier to rotation about the N-C(Ph) bond is rather small, as the molecules are laid down during crystal growth, the forces which dominate are those due to intermolecular interactions between polar substituents symmetrically disposed about the pseudo-centre of symmetry and there is statistical probability for packing in the two possible orientations. Such a crystal growth process would then favour the planar molecular conformation. Unit-cell measurements on *N*-(*p*-nitrobenzylidene)-*p*-nitroaniline²⁰ indicate a hexagonal space group with only three molecules per unit cell thus

²⁰ H. B. Bürgi, J. D. Dunitz, and C. Züst, *Acta Cryst.*, 1968, **B**, **24**, 463.

implying disorder. Although systematic extinctions indicate $P6$, $P\bar{6}/m$, and $P\bar{6}$ as possible space groups, packing considerations apparently favour the centrosymmetric assignment $P\bar{6}$.²⁰ Hence it is likely that the parallel arrangement of aromatic rings will be found in this structure. In the stable orthorhombic form of *N*-(*p*-chlorobenzylidene)-*p*-chloroaniline (6.8 Å shortest axis),²⁰ the space group ($Pccn$) requires eight equivalent positions, while there are four molecules in the cell;

thus disorder is required about the space-group centre of symmetry. The question of whether the molecule adopts a conformation similar to that of the present structure in the absence of a 4 Å axis is currently under investigation.

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