Molecular Conformation and Electronic Structure. Part III.[1] Crystal and Molecular Structure of the Stable Form of *N*-(*p*-Chlorobenzylidene)-*p*-chloroaniline

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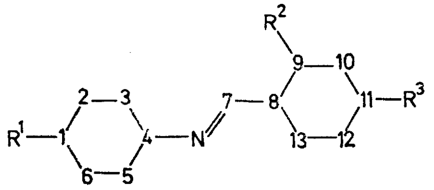
The title compound crystallizes in the orthorhombic space group *Pccn* with a = 24.503(5), b = 6.334(1), c = 7.326(1) Å, and Z = 4. The structure was solved by direct methods from 1 259 reflections measured on a Syntex P$\bar{1}$ automated diffractometer with graphite-monochromated Mo-K_α radiation, and refined anisotropically by full-matrix least-squares to R 0.056.

The structure is disordered about a crystallographic two-fold axis leading to a novel conformation of the molecule with benzene rings twisted by 24.8° in opposite directions from the plane of the central four atoms, in contrast to the metastable triclinic form, which is planar. The two structures represent a striking example of conformational polymorphism which is discussed in terms of the packing.

THE notion of ' crystal engineering ' *i.e.* utilizing the solid state as a vehicle for obtaining desired intermolecular geometric relationships or molecular conformations, was first put forward by Schmidt.[2] Although the field is still very much in its infancy, considerable progress has already been made, and the packing modes of primary amides, carboxylic acids, and their complexes have been systematically investigated.[3] Generalizations drawn from these studies can be used quite reliably to predict the crystal structures of members of these classes of compounds from unit-cell constants and symmetry relations, or to obtain crystals with structural properties suitable for solid-state chemical reactions. Furthermore, dihalogeno-substitution, in particular dichlorophenyl-substitution, has been demonstrated as a particularly reliable means for obtaining a short (4 Å) translation axis,[4] which is desirable for studying topochemical effects, including asymmetric synthesis in mixed crystals.[5]

In terms of molecular conformation, the benzylideneanilines [(I)—(VIII)] provide a good model for the further development of the principles of ' crystal engineering '. The spectral behaviour is a rather sensitive function of the molecular conformation, which to a very good approximation can be described by a single molecular parameter, the rotation of the plane of the phenyl ring about the N–C(4) bond. Hence, a systematic investigation of the spectral properties as a function of molecular conformation requires the means for obtaining a series of benzylideneanilines with differing but known molecular conformations.



	R¹	R²	R³
(I)	H	H	H
(II)	H	Cl	Cl
(III)	CO_2H	H	H
(IV)	NO_2	H	Me
(Va)	Cl	H	Cl
(Vb)	Cl	H	Cl
(VI)	Br	H	Br
(VII)	Br	H	H
(VIII)	NMe_2	H	NO_2

Accurate geometric information is most readily obtained from X-ray structural investigations, but before the advent of ' crystal engineering ' there was no means for determining *a priori* the way in which a molecule might pack in a crystal, or how its conformation might be affected by putting it into a crystal. From our continuing study of benzylideneaniline structures, we are obtaining information of this sort, as well as the structures of a series of compounds whose molecular

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[1] Part II, J. Bernstein and I. Izak, *J. Cryst. Mol. Structure*, in the press.

[2] G. M. J. Schmidt, *Pure Appl. Chem.*, 1971, **27**, 647.

[3] L. Leiserowitz and G. M. J. Schmidt, *J. Chem. Soc.* (*A*), 1969, 2372; L. Leiserowitz, *Acta Cryst.*, in the press.

[4] B. S. Green, J. Leser, and G. M. J. Schmidt, to be published.

[5] A. Elgavi, B. S. Green, and G. M. J. Schmidt, *J. Amer. Chem. Soc.*, 1973, **95**, 2058.

geometry varies systematically over a significant range, thus affording a system for the investigation of the structure–spectrum relationship.[6] The structure determination of the orthorhombic (stable) form of *N*-(*p*-chlorobenzylidene)-*p*-chloroaniline (Vb) reported here is part of this study [the triclinic form is numbered (Va)].

EXPERIMENTAL

Crystals of (Vb) (m.p. 114—116 °C) were obtained as yellow rhombs by slow cooling from methylcyclohexane. Spectra of ethanolic solutions were measured on a Cary 17 recording spectrophotometer. Cell constants and space-group assignment agree with those reported earlier,[7] and are based on a least-squares fit of 15 reflections with 2θ values ranging between 18 and 37° (Mo-K_α).

Crystal Data.—$C_{13}H_9Cl_2N$, $M = 250.13$. Orthorhombic, $a = 24.503(5)$, $b = 6.334(1)$, $c = 7.326(1)$ Å, $U = 1\,136.98$ Å^3, $D_c = 1.46$, $Z = 4$, D_m (flotation) $= 1.42$, $F(000) = 512$; λ(Mo-K_α) $= 0.710\,69$ Å; μ(Mo-K_α) $= 5.38$ cm^{-1}. Space group *Pccn*. The presence of four molecules in the unit cell implies disorder about a crystallographic centre of symmetry or two-fold axis. The former requires parallelism of the two aromatic rings, the dihedral angles about the exocyclic bonds being of equal but opposite sign. In the latter case the dihedral angles are equal, but the restriction on parallelism of the aromatic rings is relaxed.

Intensities of diffraction maxima were measured on a Syntex P$\bar{1}$ autodiffractometer with graphite-monochromatized Mo radiation on a crystal measuring 0.18 × 0.20 × 0.30 mm. 1 259 reflections were measured by a θ—2θ scan, for which $2\theta \leqslant 54°$. The scan rate varied from 2 to 24° min^{-1} and was determined for each reflection by a rapid prescan of the diffraction maximum.

TABLE 1

Final positional and thermal parameters * for non-hydrogen (10^4) and hydrogen (10^3) atoms, with estimated standard deviations in parentheses. Hydrogen atoms are numbered according to the atoms to which they are bonded.

Atom	x	y	z	U_{11} or U_{iso}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Cl	402(0)	1 819(2)	6 574(2)	519(6)	647(6)	774(8)	−149(5)	71(7)	−26(6)
X	2 257(1)	7 802(6)	6 462(6)	488(19)	475(21)	834(29)	−214(16)	40(23)	−139(18)
C(1)	947(1)	3 568(5)	6 576(6)	479(20)	469(21)	530(22)	−56(16)	−73(22)	80(19)
C(2)	1 442(2)	2 922(7)	7 250(6)	523(22)	463(24)	642(28)	24(19)	81(21)	−4(20)
C(3)	1 875(2)	4 298(6)	7 210(6)	450(21)	458(21)	691(30)	36(18)	48(20)	−21(20)
C(4)	1 817(1)	6 326(5)	6 471(6)	468(20)	428(20)	552(24)	38(15)	14(20)	−46(19)
C(5)	1 313(2)	6 935(6)	5 839(6)	482(22)	439(21)	599(25)	57(17)	26(21)	−25(19)
C(6)	874(2)	5 588(6)	5 880(6)	404(20)	546(22)	580(25)	63(18)	1(20)	−26(19)
H(2)	150(2)	147(7)	777(6)	29(13)					
H(3)	226(2)	408(6)	792(6)	32(12)					
H(5)	127(2)	841(6)	530(6)	34(12)					
H(6)	52(2)	599(6)	536(5)	16(10)					
H(X) †	214	871	750	30					

* Anisotropic thermal parameters are in the form $\exp[-2\pi^2(\Sigma_i a^2_{ii} h^2_i U_{ii} + 2\Sigma_i\Sigma_j a_i a_j h_i h_j U_{ij})]$: isotropic, $\exp[-8\pi^2 U \sin^2\theta/\lambda^2]$.
† Final positional and thermal parameters not included in refinement.

Intensities were corrected for absorption according to the method of ref. 8. After Lorentz and polarization corrections, 577 reflections had $F_o < 2.5\,\sigma(F_o)$ and were considered unobserved.

Structure Determination and Refinement.—The structure was solved by direct methods with the program MULTAN.[9] A total of 531 Σ_2 relationships among the 89 reflections with E values > 1.79 were included in the phase determination by the weighted tangent formula.

Six reflections were included in the starting set. Of the 64 resulting solutions 21 had identical residual, and absolute and weighted figures of merit. Examination of these 21 solutions indicated that they could be reduced to four sets, which in turn were related by a shift in origin and a corresponding change in the sign of one of the reflections in the starting set. Hence, all 21 solutions are equivalent. The chlorophenyl moiety appeared in the E map corresponding to this solution in an orientation which requires disorder about the two-fold axis rather than the centre of symmetry. The bridge atom was included from geometric considerations.

Least-squares refinement of the heavy atoms proceeded smoothly through two cycles to R 0.18 for 254 reflections with $\sin\theta/\lambda \leqslant 0.4$ Å, with only positional parameters permitted to vary. Because of the disorder about the two-fold axis, the scattering factor for the bridge atom was taken to be the mean of those for carbon and nitrogen at all stages of refinement. For the next two cycles all data were included with individual isotropic temperature factors. Expected hydrogen atom positions on the ring were calculated from geometric considerations (assuming C–H 1 Å) and were included in the following two cycles with individual anisotropic temperature factors for all heavy atoms and isotropic thermal parameters for the hydrogen atoms. At this stage a difference electron density map in the vicinity of the bridge exhibited a peak of 0.30 eÅ^{-3}, slightly exceeding $\sigma(\rho)$, at the chemically expected position of the disordered bridge hydrogen atom. Consequently, in the final stage of refinement a hydrogen atom of half-occupancy with isotropic temperature factor 0.03 Å^2 was included in the structure-factor calculation but was not refined.

In all stages of refinement the weight (w) of an individual reflection was $1.0/\sigma^2(F_o{}^2)$. The final stage resulted in R 0.056 (0.063 including unobserved intensities) and R' 0.016, with goodness-of-fit 1.43. The function minimized was $\Sigma\, w(|kF_o|^2 - |F_c{}^2|)^2$.

A difference electron-density map based on the final parameters of all atoms was virtually featureless and at no

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[6] C. J. Eckhardt and J. Bernstein, *J. Amer. Chem. Soc.*, 1972, **94**, 3247.

[7] H. B. Bürgi, J. D. Dunitz, and C. Zust, *Acta Cryst.*, 1968, **B24**, 463.

[8] P. Coppens, L. Leiserowitz, and D. Rabinovich, *Acta Cryst.*, 1965, **18**, 497.

[9] G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.*, 1971, **A27**, 368.

point exceeded 0.28 eÅ^{-3}. Scattering factors were taken from ref. 10. Local versions of ORFLS [11] and FORDAP [12] were used in the least-squares and Fourier calculations respectively.

Final positional parameters and temperature factors are given in Table 1. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21553 (7 pp., 1 microfiche).*

Thermal Motion.—A rigid-body analysis was carried out according to ref. 13 on the chlorophenyl moiety and the entire molecule. The fit was decidedly better in the former case with root-mean-square discrepancy of U_{ij} of 0.0100 Å^2 and discrepancy index $\{[\Sigma(U_o - U_c)^2/U^2{}_o]^{\frac{1}{2}}\}$ of 0.057 compared to the mean σ of U_{ij} values $\overline{\sigma U_{ij}}$ 0.0019 Å^2. Even this fit is only fair, with the largest deviations between observed and calculated thermal parameters occurring in the off-diagonal terms of the vibration tensors, especially U_{13}. The diagonal values all agree to within 10% and since the directional properties of the librational motion are consistent with those found for (Va)[14] and (VI),[1] the results of the analysis are given in Table 2.

TABLE 2

Summary of Rigid-body analysis of chlorophenyl moiety. The calculation is referred to the origin which symmetrizes **S** and reduces the trace of **T**. Centre of mass of axial system of inertia referred to crystal axes:

$x = 0.1058, \quad y = 0.3918, \quad z = 0.6549$

Transformation matrix from crystal system to axial system of inertia:

18.8856	4.0349	−0.0995
14.2858	−4.4116	3.0646
6.2981	−2.0924	−6.6530

Tensor elements (× 10^4)

Tensor	11	22	33	12	23	13
L/rad^2	141(36)	54(10)	17(8)	3(16)	−9(10)	5(22)
T/Å^2	467(22)	432(25)	402(49)	−5(21)	−56(25)	4(29)
S/rad-Å	−4(17)	1(17)	3(24)	−10(12)	−19(8)	5(7)

	Root-mean-squares amplitudes	Components on molecular axes		
		L	*M*	*N*
L	6.8°	0.9986	0.0324	0.0410
	4.3°	0.0223	−0.9720	0.2339
	2.2°	0.0475	−0.2326	−0.9714
T	0.22 Å	−0.4990	0.6891	−0.5255
	0.22	−0.8666	−0.3975	0.3016
	0.19	−0.0010	0.6059	0.7955

For both (Va) and (VI) we argued that the large root-mean-square amplitude about the principal axis, C(1) · · ·(Y = halogen) (8.9 and 8.6° respectively) was probably not due entirely to a true librational motion. In those structures, where the molecules are essentially planar, the disorder is about a crystallographic inversion centre, and the steric repulsion due to short contacts between the bridge carbon and ortho-hydrogens can be relieved by a small static rotation clockwise or counterclockwise about the X–C (arom) bonds in a statistical manner leading to an apparently high librational motion about the principal axis. The smaller librational motion in this case is more likely a molecular property. The translational motion is nearly isotropic in both (Va) and (Vb). Bond lengths corrected for rigid-body motion are given in Figure 1.

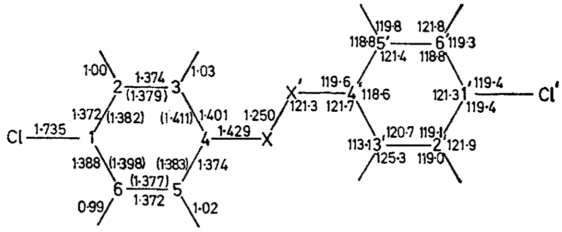

FIGURE 1 Experimental bond distances (Å) and angles (°); mean σ: C–C 0.005, C–Cl 0.005, C–H 0.04, C–C–C 0.4 and C–C–Cl 0.3, and C–C–H 2.3. Those for X included an average for C. Bond distances in parentheses are those corrected for rigid-body motion

RESULTS AND DISCUSSION

Molecular Geometry.—Bond lengths and angles are given in Figure 1. The features of the chlorophenyl group are consistent with earlier studies. The internal angle C(2)–C(1)–C(6) (121.3°) is identical to that found for (Va), but the distortion of the aromatic ring noted there is not apparent here.

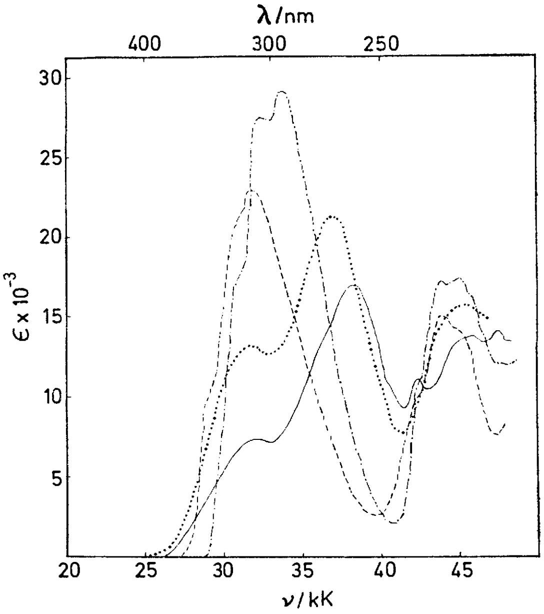

FIGURE 2 Solution spectra at 298 K for: stilbene (dash dot); azobenzene (dashed); benzylideneaniline (I) (full line); *N*-(*p*-chlorobenzylidine)-*p*-chloroaniline (dotted) (V)

The solution absorption spectrum (Figure 2) shows the features characteristic of (I) rather than those of *trans*-stilbene or *trans*-azobenzene, strongly suggesting a

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* See Notice to Authors No. 7, in *J.C.S. Perkin II*, 1975, Index issue.

[10] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1965, p. 202.

[11] W. R. Busing, K. O. Martin, and H. A. Levy, ORFLS: A Fortran Crystallographic Least-squares Program, 1963, Report ORNL TM 305, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

[12] A. L. Zalkin, FORDAP, A Fourier Synthesis Program, 1962, Lawrence Radiation Laboratories, Livermore, California.

[13] V. Schomaker and K. N. Trueblood, *Acta Cryst.*, 1968, **B24**, 63.

[14] J. Bernstein and G. M. J. Schmidt, *J.C.S. Perkin II*, 1972, 951.

conformation in the solution phase where ($\alpha \approx 50°$, $\beta \approx -10°$) (Figure 3).[15,16]

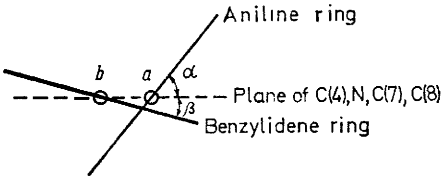

FIGURE 3 Schematic representation of benzylideneaniline. Points *a* and *b* represent the view down the N–C(4) bond and down the C(8)–C(7) bond respectively. α and β are the angles of rotation of the aniline and benzylidene rings, respectively, the positive direction being a counterclockwise rotation

In the previously investigated structures of benzylideneanilines [(I)—(Va), (VI)] the trend in bond lengths in the bridge group (Table 3) was quite consistent with the electron-withdrawing power of *ortho*- or *para*-substituents on the molecule, which are expected to contribute to resonance quinoid structures, at least for low values of the torsion angle about N–C(4) (α) (Figure 3). The X=X′ bond length* (1.250 Å) is in accord with this, being longer than that in the unsubstituted parent compound (1.237 Å) but shorter than in the planar triclinic modification (1.262 Å). However, the C(4)–X bond length (1.429 Å) is shorter than in the triclinic form by almost 2σ.

TABLE 3

Comparison of some geometric features of benzylideneanilines, with estimated standard deviations in parentheses

	Bond lengths (Å)			Torsion angles (°)	
	C(4)–N	N–C(7)	C(7)–C(8)	α	β
(I) [a]	1.460(3)	1.237(3)	1.496(3)	55.2	−10.3
(II) [b]	1.407(11)	1.268(11)	1.482(12)	37.9	6.1
(III) [a]	1.431(7)	1.281(12)	1.461(9)	41.1	−13.7
(IV) [a]	1.400(3)	1.269(5)	1.474(3)	50.2	−8.1
(Va) [c]	1.437(4)	1.262(4)	(1.437)(4)	0.4	0.4
(Vb) [d]	1.429(5)	1.250(5)	(1.429)(5)	24.8	−24.8
(VI) [e]	1.445(14)	1.241(14)	(1.445)(14)	1.9	1.9
(VII) [f]	1.414(11)	1.287(10)	1.475(10)	39.0	−11.1
	1.410(10)	1.275(10)	1.475(11)	46.2	−9.4
(VIII) [g]	1.416(5)	1.258(5)	1.460(5)	−9.1	−3.5

[a] Ref. 16. [b] Ref. 17. [c] Ref. 14. [d] Present work. [e] Ref. 1. [f] Ref. 18. [g] Ref. 19.

The trend breaks down for compound (VIII), which owing to its near planarity and strong donor and acceptor groups at opposite ends of the molecule, would be expected to have significant contributions from quinonoid resonance structures. However, C(4)–N and C(7)–C(8) are not the shortest and N–C(7) is not the longest of the bond lengths in the series. The relationship among bond length, torsion angles α and β, and electron-donating or -withdrawing power of substituents is clearly more complex than indicated by the first few structures in the series.

Best planes for various molecular fragments are given in Table 4. The four bridge atoms [(Plane (IV)] comprise an almost planar group, the torsion angle about X–X′ being 0.7°. Owing to symmetry both angles between the plane of the four bridge atoms and the planes of the aromatic rings are 24.8° in contrast to all other previously studied benzylideneanilines (Table 3).

TABLE 4

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

Plane	A	B	C	D
Plane (I): C(1)—C(6)	−6.043	2.149	6.650	−4.576

[C(1) −0.009, C(2) 0.002, C(3) 0.008, C(4) −0.011, C(5) 0.004, C(6) 0.006, X 0.034, Cl −0.057, H(2) 0.006, H(3) 0.204, H(5) −0.013, H(6) −0.038, C(1′) −0.196, C(2′) 0.689, C(3′) 0.630, C(4′) −0.332, C(5′) −1.188, C(6′) −1.137, X′ −0.390, Cl′ −0.154, H(2′) 1.383, H(3′) 1.379, H(5′) −1.891, H(6′) −1.786]

Plane	A	B	C	D
Plane (II): All heavy atoms of one ring	6.264	−2.103	−6.652	4.522

[C(1) −0.010, C(2) −0.012, C(3) −0.003, C(4) 0.025, C(5) 0.001, C(6) −0.017, X −0.003, Cl 0.018, H(2) −0.022, H(3) −0.192, H(5) 0.024, H(6) 0.021, C(1′) 0.283, C(2′) −0.611, C(3′) −0.567, C(4′) 0.387, C(5′) 1.251, C(6′) 1.216, X′ 0.428, Cl′ 0.258, H(2′) −1.299, H(3′) −1.324, H(5′) 1.949, H(6′) 1.871]

Plane	A	B	C	D
Plane (III): All heavy atoms	0.000	0.000	−7.326	4.786

[C(1) −0.031, C(2) −0.525, C(3) −0.496, C(4) 0.045, C(5) 0.508, C(6) 0.478, X 0.052, Cl −0.030, H(2) −0.910, H(3) −1.017, H(5) 0.905, H(6) 0.860]

Plane	A	B	C	D
Plane (IV): C(4), X, C(4′), X′	0.000	0.000	−7.326	4.737

[C(1) −0.080, C(2) −0.574, C(3) −0.544, C(4) −0.004, C(5) 0.460, C(6) 0.430, X 0.004, Cl −0.078, H(2) −0.958, H(3) −1.065, H(5) 0.856, H(6) 0.812]

Table 3[1,14,16-19] shows that this structure fills the gap which had previously existed in the range of observed conformations of benzylideneanilines. In the additional sense that this is the largest β yet observed, the present geometry represents an entirely new molecular conformation for this family of compounds. Except for (VIII),[19] throughout the series the rather small variation in the solution absorption spectrum suggests a near constancy of molecular geometry in solution and further indicates that in solution, at least in the absence of intramolecular charge-transfer, the substituents play a minimal role on determining the molecular geometry.

On the basis of a calculation for the free molecule which takes into account the non-bonded H(X′) · · · H(3) interaction and the π-electron energy as a function of α, the planar molecule is estimated to be *ca.* 2—3 kcal^{-1} mol^{-1} above the minimum for which $\alpha \approx 45°$.[20] The function

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* $X = (C + N)/2$, and is used to designate the heavy atoms in the bridge.

[15] E. Haselbach and E. Heilbronner, *Helv. Chim. Acta.*, 1968, **51**, 16.

[16] H. B. Bürgi and J. D. Dunitz, *Helv. Chim. Acta.*, 1970, **52**, 1747.

[17] J. Bernstein, *J.C.S. Perkin II*, 1972, 946.

[18] B. T. Blaylock and R. F. Bryan, Amer. Cryst. Assocn., Winter Meeting, 1972, Abstract C2; R. F. Bryan, personal communication.

[19] K. Ezumi, H. Nakai, S. Sakata, K. Nishikida, M. Shiro, and T. Kubota, *Chem. Letters*, **1974**, 1393.

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

itself is broad with a shallow minimum and the rather large value of β found here suggests that the function is of a similar form for this parameter. The wide variation of geometries found in the crystal structures coupled with the almost constant solution absorption spectrum leads to the conclusion that the ' crystal forces ' play a significant role in the determination of the molecular conformation in the solid.

The feature common to those molecules which are disordered in the crystal and show the largest change in molecular conformation from that assumed as normal in solution is the pseudo-centrosymmetric mode of substitution. The analogous dimethyl compound is trimorphic,[7,21] with space-group symmetry requiring disorder about an inversion centre in one form. Furthermore, the difference in cell constants between the other two polymorphs suggests that the molecular conformation differs in the two crystalline forms. The corresponding dinitro-derivative is also disordered, most likely in the same manner.[7]

Although we have not yet acquired a means for selecting *a priori* a particular molecular geometry, we have clearly demonstrated that a wide range of geometries may be obtained for this relatively simple system. Nonetheless, it is possible to make some generalizations about the relationship between the crystal structure and molecular geometry.

Packing Arrangement.—The packing arrangement, as viewed along [010] and [001] is shown in Figure 4. Short intermolecular distances are given in Table 5. Although none of these distances is unusually short, the concentration of those which are less than the sum of the van der Waals radii in a particular region of the structure suggests that the packing is dominated by the chain of chlorine atoms running perpendicular to *a*. Similar concentrations of halogen atoms are evident in the structures of (Va) and (VI) and the disorder observed in all three of these structures is consistent with the notion that the forces acting at the extremities of the molecules are those which play the most significant role in determining the structure. In these cases, in the process of crystal growth a molecule approaching the surface of a crystal is influenced predominantly by the halogens on the surface and there is virtually no preference for either of the two possible orientations about the –CH=N– bridge. The disorder may also be reinforced by alternating opposite orientations of the molecule since the dipoles of the –CH=N– then serve as an attractive rather than a repulsive force.

TABLE 5

Intermolecular distances

Atom pair	Translation along			Distance (Å)
	a	*b*	*c*	
Cl · · · H(5)	0	−1	0	3.17
Cl · · · H(6)$^{\mathrm{I}}$	0	1	1	3.00
Cl · · · Cl$^{\mathrm{II}}$	0	0	−1	3.76
Cl · · · Cl$^{\mathrm{III}}$	0	0	1	3.81

Symmetry: I $\bar{x},\frac{1}{2}+y,\bar{z}$ II $x,\frac{1}{2}-y,+z$ III $\bar{x},\bar{y},\bar{z}$

The two structures (Va) and (Vb) represent one of the more extreme examples of conformational polymorphism.[22] The molecular volumes are identical in the two structures (284.3 Å^3), consistent with the notion of close-packing requirements.[23] As we noted previously, (Va) is metastable.[14] Although we have not directly observed a single-crystal transformation there is sufficient evidence that there is a phase transformation (Va)→(Vb) which may now be qualitatively understood on the molecular level.

In (Va) we observed spontaneous transformation of the crystal from the triclinic phase, although the product phase has not been positively identified as orthorhombic. The process may last over a period of weeks for a physically undisturbed batch of crystals, but once initiated, spreads through all crystals. Very pale yellow to colourless crystals of (Va) turn yellow during the process and fail to extinguish light under crossed polarizers or to give *X*-ray photographs typical of single crystals. The transformation may also be initiated in single crystals by cleaving perpendicular to the needle (*b*) axis, which is the stack axis in the triclinic form (see Figure 2 of ref. 14).

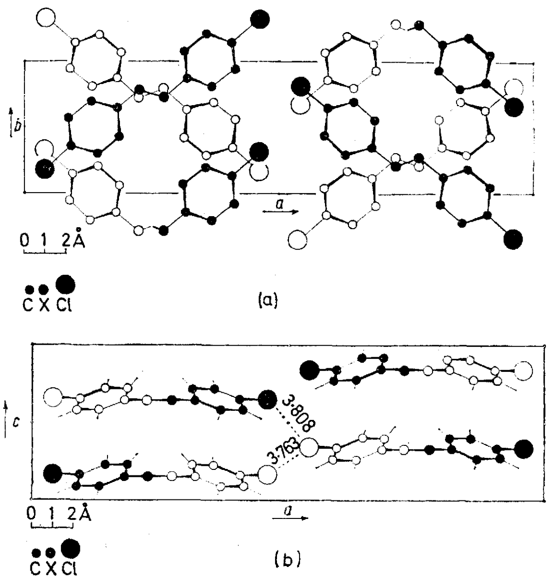

FIGURE 4 The structure viewed (a) down the *c* axis, with hydrogen atoms omitted for clarity, and (b) down the *b* axis, showing intermolecular Cl · · · Cl distances

On the basis of these observations we previously postulated that the transformation involved, on the molecular level, a relaxation of the molecule from the planar to an energetically more favourable non-planar conformation, by rotation about an X–C(4) bond.[14] This picture is consistent with the results of the rigid-body analysis of the anisotropic temperature factors for the triclinic form.

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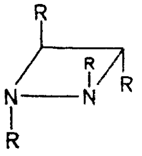
[21] J. Bernstein and I. Izak, unpublished results.

[22] N. C. Panagiotopoulos, G. A. Jeffrey, S. J. La Placa, and W. C. Hamilton, *Acta Cryst.*, 1974, **B30**, 1421.

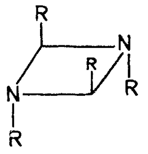
[23] A. I. Kitaigorodskii, ' Organic Chemical Crystallography,' Consultants Bureau, New York, 1961, pp. 111—112.

The packing modes of the two forms (Figure 4 and ref. 14) suggest that additional molecular movements are required. With respect to the reference molecule, molecule (B) must slide parallel to the *a* axis and rotate about the *b* axis to acquire the orientation observed in the orthorhombic form [Figure 4(a)]. This process probably takes place in a concerted fashion concomitant to the intramolecular rotations. Statistically the relaxation may involve equal rotations in two opposite senses and would lead to the molecular conformation observed in the present structure. Evidence from the crystal-cleaving experiments strongly suggests that the transformation from the triclinic form is initiated at dislocations and it does not seem unreasonable to assume that it ceases at them as well. Hence, relatively small domains of the orthorhombic form develop within the triclinic form and these in turn may have at least two different orientations depending on the sense of the initial rotation about the N-phenyl bond involved in the relaxation from planar to non-planar molecule. Such a mechanism provides a partial explanation for the loss of single crystalline character in the product phase.

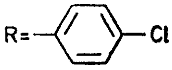
Failure of Solid-state Photoreaction.—The registry of the –CH=N– groups due to the packing arrangement along the *c* axis is in principle favourable for solid-state photocyclodimerization in accordance with topochemical principles.[2] Owing to the disorder both cyclic dimers (IX) and (X) are possible, and disproportionation of (IX) could lead to the *trans*-azobenzene and stilbene derivatives. Prolonged irradiation of the solid (2 weeks) at $\lambda > 320$ nm led to no change in the starting material, suggesting that either (IX) and (X) are not formed at all, or that if they are formed the cyclic and further products are not stable in the host lattice and disproportionate to the initial benzylideneaniline.



(IX)



(X)



Although the distance between the potentially reactive double-bonds is consistent with that necessary for photoreaction, the geometric relationship between them may not be suitable for reaction. The situation here closely resembles that in the methyl ester of *m*-bromocinnamic acid[24] where the glide plane related double bonds are also not parallel and no photoreaction is observed.[2]

[5/985 *Received, May 23rd*, 1975]

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[24] L. Leiserowitz and G. M. J. Schmidt, *Acta Cryst.*, 1965, **18**, 1058.