Conformational Studies. Part III.[1] Crystal and Molecular Structures of *N*-(2,4-Dichlorobenzylidene)aniline

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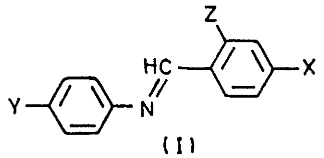
The title compound crystallises in the orthorhombic system $P2_12_12_1$ with cell constants a = 11·202, b = 3·934, c = 26·077 Å, and Z = 4. The crystal and molecular structures were determined by direct methods from 1524 intensities measured on a diffractometer, and refined anisotropically (except hydrogen) to R 0·082. The possible influence of the packing arrangement on the molecular conformation, which differs significantly from that of earlier reported benzylideneanilines, is discussed.

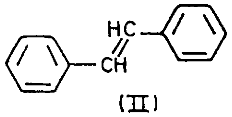
SPECTRAL investigations into the cause of the marked dissimilarity between the u.v. spectra of benzylideneaniline (Ia) and the isoelectronic analogues *trans*-stilbene (II) and *trans*-azobenzene (III)[2] led to the conclusion that the difference was due to the non-planarity of (Ia), (II) and (III) being nearly planar molecules.[3,4]

X-Ray structure determinations of (Ia), (Ib), and (Ic)[5] verified that the aniline ring is twisted out of the plane of C(4)–N=C(7)–C(8) by 55, 41, and 50°, with a smaller and opposite twist of the benzylidene ring by 10, 14, and 8°. MO calculations based on the observed geometry in the solid and correspondence between the solution and crystal reflectance spectra[6] are consistent with the conclusions of the earlier spectral studies.

Recent investigations[7] have indicated that two chlorine substituents in the aromatic nucleus of a molecule are very likely to lead to packing arrangement with a 4 Å translation axis. *N*-(2,4-Dichlorobenzylidene)aniline (Id) and the metastable form of *N*-(*p*-

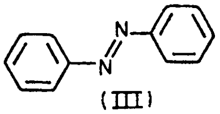


(I)



(II)

a; X = Y = Z = H
b; X = Z = H; Y = CO_2H
c; X = CH_3, Y = NO_2, Z = H
d; X = Z = Cl; Y = H
e; X = Y = Cl; Z = H



(III)

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† *Present address:* Department of Chemistry, University of the Negev, Beersheva, Israel.

[1] Part II, A. E. Jungk and G. M. J. Schmidt, *J. Chem. Soc.* (*B*), 1970, 1427.

[2] V. A. Ismailski and E. A. Smirnov, *Zhur. obshchei Khim.*, 1956, **26**, 3389; N. Ebara, *Bull. Chem. Soc. Japan*, 1960, **33**, 534; P. Brocklehurst, *Tetrahedron*, 1962, **18**, 299; G. Favini and A. Gamba, *J. Chim. phys.*, 1965, **62**, 995; E. Haselbach and E. Heilbronner, *Helv. Chim. Acta*, 1968, **51**, 16.

[3] J. M. Robertson and I. Woodward, *Proc. Roy. Soc.*, 1937, *A*, **162**, 568.

[4] J. J. deLange, J. M. Robertson, and I. Woodward, *Proc. Roy. Soc.*, 1939, *A*, **171**, 398; C. J. Brown, *Acta Cryst.*, 1966, **21**, 146.

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

[6] H. B. Bürgi, Thesis, ETH, Zurich, 1969.

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

chlorobenzylidene)-*p*-chloroaniline (Ie) * were found to crystallise with a 4 Å axis. The structure analyses of (Id) and (Ie) were undertaken to investigate whether the close interplanar packing along the 4 Å axis would be sufficient to force the benzylideneaniline skeleton into a nearly planar conformation. The results of the structure analysis of (Id) are given here; those of (Ie) are reported in the following paper.

EXPERIMENTAL

Crystals (m.p. 88—89 °C) were grown from slowly cooled methylcyclohexane solution, as thin yellow needles elongated along [010], and showing the {102} and {$\bar{1}$03} forms. The lattice constants were determined by least squares from 22 high-order ($2\theta > 103°$) reflections measured on a General Electric diffractometer with Cu-K_α radiation, $\lambda = 1{\cdot}548$ Å.

Crystal Data.—$C_{13}H_9Cl_2N$, $M = 250{\cdot}13$. Orthorhombic, $a = 11{\cdot}202_8(4)$, $b = 3{\cdot}934_5(1)$, $c = 26{\cdot}077_8(10)$ Å, $U = 1149{\cdot}4$ Å^3. $D_c = 1{\cdot}45$, $Z = 4$, D_m (flotation) $= 1{\cdot}45$, $F(000) = 128$. Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å, μ(Mo-K_α) $= 5{\cdot}3$ cm.$^{-1}$ Space group: $P2_12_12_1$ from systematic absences: $h00$ for h odd, $0k0$ for k odd, $00l$ for l odd.

A crystal of dimensions $0{\cdot}21 \times 0{\cdot}10 \times 0{\cdot}14$ mm, measured normal to the faces (010), ($\bar{1}0\bar{2}$), and ($10\bar{3}$) was mounted along $-a^* + 3b^*$ on an IBM 1800 controlled Siemens diffractometer; the $I(hkl)$ and $I(\bar{h}k\bar{l})$ were recorded for $\sin\theta/\lambda \leqslant 0{\cdot}68$ with Mo-K_α radiation and balanced zirconium and yttrium filters.

Intensities were measured by a $\omega/2\theta$ scan technique, the details of which have been described elsewhere.[9] The procedure for the treatment of data, including correction for absorption, has been reported previously.[10] † Of the 1524 unique reflections recorded in the copper sphere, 621 had intensities which were $<2\sigma$ of the mean value or $<2\sigma$ (mean) for equivalent reflections, and were treated as ' unobserved '; this large number is attributed primarily to the small size of the crystal used.

Structure Determination and Refinement.—The structure was solved by the multisolution procedure of the tangent formula [11] method outlined by Germain and Woolfson [12] as modified by Kaufman and Leiserowitz.[13] Phases assigned to three zonal reflections fixed the origin; five additional reflections were selected and assigned starting phases (Table 1). The phase angles of 100 reflections with the highest E values were determined for each of the 320 possible models. Examination of the 60 models with the highest figure of merit C[12] indicated that many of these had converged to the same or the enantiomorphic set. Of these top models, 21 were utilized to generate the phases of 300 reflections. The resulting model which had the highest C and the lowest R index (0·28) was also the model with maximum C after the generation of the first 100 phases. An E-map based on the phases of this model clearly showed 14 of the 16 atom positions of the molecule; small peaks were found at the expected positions of the remaining two atoms.

The structure was refined by three cycles of least-squares with isotropic temperature factors followed by three cycles with anisotropic temperature factors. A difference synthesis based on the heavy atoms revealed the nine hydrogen atoms in the chemically expected positions. The hydrogen position parameters were refined in the final stages; since the data were not sufficiently good to permit refinement of individual temperature factors for the hydrogen atoms, an overall temperature factor of 0·045 Å ^{2} was assigned to these atoms. The weight (w) assigned to each reflection in the refinement scheme was $w = 1/\sigma^2(F^2)$. The final values of R and R' were 0·082 and 0·02; $R' = [\Sigma w(kF_o - |F_c|)^2/\Sigma wF_o{}^2]^{\frac{1}{2}}$. Scattering factor curves were taken from ref. 14. The calculated and observed structure factors are listed in Supplementary Publication No. SUP 20312 (3 pp., 1 microfiche).‡

TABLE 1

Initial phase set used for the multisolution phase-determination method

	h	k	l	Phase (deg.)	E_h
Origin-determining set	8	0	9	90	2·53
	0	1	15	90	2·53
	5	3	0	90	1·76
Starting phases for application of tanϕ formula	1	1	4	30, 60	2·53
	7	1	11	45, 135, 225, 315	2·32
	7	2	3	45, 135, 225, 315	2·08
	4	2	6	30, 102, 174, 246, 318	2·39
	5	0	2	0, 180	1·75

RESULTS AND DISCUSSION

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

Bond Lengths and Angles.—Bond lengths and angles are given in Figure 1. The mean phenyl C–C bond lengths of 1·386 Å in the aniline ring and of 1·384 Å in the benzylidene ring are normal; the mean deviation of 0·007 Å in each case is less than the mean σ of the C–C bond lengths. These values are also consistent with the comparable mean C–C aromatic bond lengths reported in ref. 5.

Both C–Cl bond lengths (1·782 and 1·750 Å) are longer than the mean ($1{\cdot}737 \pm 0{\cdot}016$ Å) for twenty-six aromatic molecules,[15] although many values greater

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* Cell constants for the stable form, in which the shortest axis is 6·8 Å, as well as for 12 additional benzylideneanilines have been given earlier.[8] Only one of these, *N*-(*p*-nitrobenzylidene)-*p*-nitroaniline, crystallises with a short (4·21 Å) axis.

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

‡ 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. will be supplied as full size copies).

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

[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] J. Karle and I. L. Karle, *Acta Cryst.*, 1966, **21**, 849.

[12] G. Germain and M. M. Woolfson, *Acta Cryst.*, 1968, *B*, **24**, 91.

[13] H. W. Kaufman and L. Leiserowitz, *Acta Cryst.*, 1970, *B*, **26**, 442.

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

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

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)	4444(9)	3416(36)	5877(3)	503(66)	687(96)	426(60)	−128(88)	29(82)	−118(53)
C(2)	5225(8)	3522(30)	5468(3)	450(55)	474(80)	512(65)	109(82)	0(70)	−8(54)
C(3)	4819(8)	4512(28)	4991(3)	388(58)	496(87)	439(56)	32(66)	25(62)	9(49)
C(4)	3613(8)	5301(28)	4918(3)	559(63)	405(74)	266(47)	120(64)	−6(56)	−34(45)
C(5)	2831(7)	5089(30)	5330(3)	392(58)	654(93)	347(48)	−21(70)	28(69)	29(46)
C(6)	3251(9)	4172(30)	5813(3)	624(65)	605(94)	398(54)	−124(87)	1(68)	146(56)
C(7)	3699(8)	8046(33)	4140(3)	549(62)	509(91)	283(50)	85(78)	20(68)	−29(46)
C(8)	3226(8)	8855(27)	3623(3)	450(52)	283(67)	362(49)	10(62)	−1(53)	124(48)
C(9)	3889(6)	10520(26)	3257(3)	162(44)	340(71)	506(52)	−1(52)	−98(58)	−157(41)
C(10)	3489(7)	11337(29)	2771(3)	426(56)	279(68)	348(51)	−18(62)	106(59)	0(43)
C(11)	2343(8)	10296(29)	2656(3)	532(58)	489(90)	226(42)	170(65)	−144(58)	−137(43)
C(12)	1626(7)	8598(31)	3006(3)	305(49)	736(94)	406(51)	−136(71)	−40(78)	10(47)
C(13)	2063(7)	7891(29)	3487(3)	282(53)	582(90)	408(54)	−27(68)	−59(64)	−5(40)
N	3100(6)	6202(24)	4445(2)	368(44)	510(65)	342(40)	32(58)	66(51)	−27(37)
Cl(1)	5363(2)	11951(8)	3396(1)	357(12)	550(23)	519(15)	−77(18)	51(18)	4(11)
Cl(2)	1791(2)	11255(9)	2045(1)	620(15)	749(26)	426(14)	97(22)	70(19)	−152(13)
H(1) *	478(7)	310(31)	618(3)						
H(2)	613(7)	357(29)	554(3)						
H(3)	539(7)	419(26)	463(3)						
H(5)	198(7)	550(28)	526(3)						
H(6)	262(6)	402(28)	615(3)						
H(7)	455(7)	873(29)	419(3)						
H(10)	401(6)	1235(34)	248(3)						
H(12)	78(6)	752(31)	285(3)						
H(13)	155(7)	671(31)	375(3)						

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

than 1·75 Å have been reported.[16,17] In 3-nitroperchlorylbenzene[15] the C(Ph)–Cl distance of 1·786 Å was attributed to the high degree of substitution on the chlorine atom. The rather long distance of 1·782 Å found for C(9)–Cl(1) in the present study may result in part from the repulsion between H(7) and Cl(1). The non-bonded distance is 2·61 Å, significantly shorter than that found in 2-chlorobiphenyl-4-carboxylic acid (2·72 Å),[18] 2′-chlorobiphenyl-4-carboxylic acid (2·80 Å),[19] and 4-acetyl-2′-chlorobiphenyl (2·79 Å),[20] in which the molecule apparently may adopt the conformation which minimizes the *ortho*-repulsion. The strain is partly relieved by a significant decrease from trigonal configuration in the Cl(1)–C(9)–C(10) angle to 114·5° and a displacement of 0·03 Å of the Cl(1) atom out of the plane of the benzylidene ring [plane (III), Table 4) in the direction away from the hydrogen. Additional strain energy may be taken up by lengthening of the C(9)–Cl(1) bond. An alternate orientation of the benzylidene ring obtained by a 180° rotation about C(7)–C(8) would lead to an unacceptably short N ··· Cl distance.

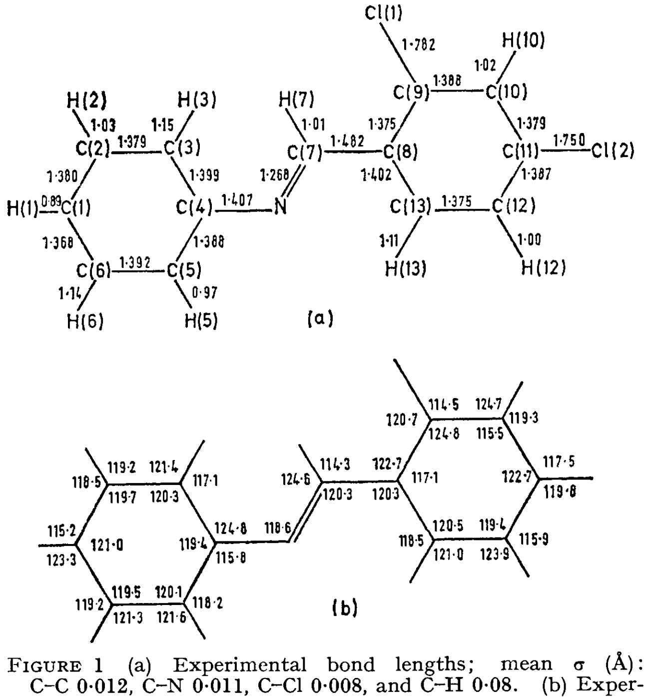

FIGURE 1 (a) Experimental bond lengths; mean σ (Å): C–C 0·012, C–N 0·011, C–Cl 0·008, and C–H 0·08. (b) Experimental bond angles; mean σ (°): C–C–C and C–N–C 0·8, Cl–C–C 0·6, and angles involving hydrogen 4·3

Bürgi and Dunitz observed that the C–N single bond distance is shortened and the C=N distance lengthened with increase in the electronegativity of the *para*-substituent on the aniline ring owing to the proportionally higher contribution of quinoid structures to the resonance forms. Thus, bond lengths in the 'bridge' atoms C(4), N, C(7), C(8) provide some measure of the contribution of resonance forms to the electronic structure (Table 3; see also Figure 2 for definitions). The bond lengths found in the present structure closely resemble those in (Ic), the compound with the strongest electronegative substituent in the *para*-position. As the disposition of the two chlorine substituents stabilises two equivalent resonance forms, each chlorine may be

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[16] P. L. Orioli, E. C. Lingafelter, and B. W. Brown, *Acta Cryst.*, 1964, **17**, 1113; K. Folting, W. N. Lipscomb, and B. Jerslev, *Acta Cryst.*, 1964, **17**, 1263; A. T. McPhail and G. A. Sim, *J. Chem. Soc.*, 1965, 227; G. Ferguson and G. A. Sim, *J. Chem. Soc.*, 1962, 1767; G. Y. Chao and J. D. McCullough *Acta Cryst.*, 1962, **15**, 887; J. Bregman, L. Leiserowitz, and G. M. J. Schmidt, *J. Chem. Soc.*, 1964, 2086.

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

[18] H. H. Sutherland, *Acta Cryst.*, 1969, *B*, **25**, 1013.

[19] H. H. Sutherland, *Acta Cryst.*, 1969, *B*, **25**, 171.

[20] H. H. Sutherland and T. G. Hoy, *Acta Cryst.*, 1968, *B*, **24**, 1207.

considered to contribute approximately half the resonance energy of one nitro-group. This observation is compatible with the relative effect of resonance on bond and group moments for chloro- and nitro-substituents[21] (–Cl 1·7, –NO_2 4·20D), although the relationship of the two rings to the plane of the four central atoms and the fact that substitution in this case is on the benzylidene rather than on the aniline ring no doubt also affect the relative contribution of resonance forms.

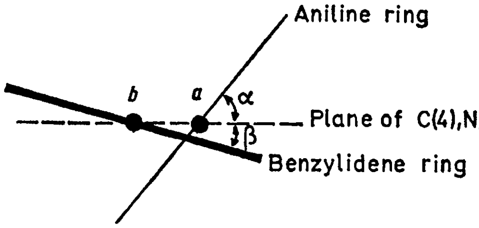

FIGURE 2 Schematic representation of benzylideneaniline. Points *a* and *b* represent the view down the N–C(4) bond and down the C(8)–C(7) bond respectively. α and β are the angles of rotation of the aniline and benzylidene rings, respectively, the positive direction being a counter clockwise rotation

TABLE 3

Comparison of some geometric features of benzylideneanilines *

	Bond lengths/Å			Rotation/deg. of aromatic rings †	
	C(4)–N	N–C(7)	C(7)–C(8)	α	β
Benzylideneaniline ‡	1·460	1·237	1·496	55·2	–10·3
Benzylideneaniline-*p*-carboxylic acid ‡	1·431	1·281	1·461	41·1	–13·7
N-(2,4-Dichlorobenzylidene)aniline	1·407	1·268	1·482	50·2	–8·1
N-(4-Methylbenzylidene)-*p*-nitroaniline ‡	1·400	1·269	1·474	37·9	6·1

* Atom numbering corresponds to Figure 1. † *See* Figure 2 for definition of α and β. ‡ Ref. 5.

The internal angles on the chlorine-substituted aromatic carbon atoms are both significantly greater than the value expected for sp^2 hybridisation. An internal angle greater than 120° appears to be general for a large number of chlorine-substituted aromatics.[17,22,23] The distortion is consistent with the electron-withdrawing effect of chlorine discussed earlier. In aromatic compounds, it has been observed[23,24] that substitution by electron-withdrawing groups leads to an internal angle greater than 120° on the substituted carbon, while electron-dontaing groups have the opposite effect. The opposing effects are dramatically illustrated in the structure of 1,3,5-triamino-2,4,6-trinitrobenzene[25] where the internal angles at positions of nitro-substitution are all greater than (Mean 122·0°) and at those of amino-substitution are all less than 120° (Mean 117·9°). The pattern is also observed in *NN*-(dimethylamino)-*p*-nitroaniline[25] in which non-bonded interactions between *ortho*-hydrogens and methyl or oxygen are expected to be nearly similar, indicating that the direction of change in internal angle is indeed a function of the electronegativity of the substituent. The decrease from 120° of the internal angles at C(8) and C(10) results from the distortion due to chlorine substitution at C(9) and C(11).

Table 4 gives the best planes for each of the two aromatic rings and for the four central atoms of the molecule; both benzene rings are planar to within 0·01 Å, while C(4), N, C(7), C(8) lie within 0·023 Å of their best plane. The displacements of Cl(1), C(2), H(10), and H(12) from the plane of the benzylidene ring apparently serve to relieve the strain caused by repulsion of neighbouring atoms.

Molecular Shape and Packing Considerations.—The most striking feature of the molecular geometry is the relationship of the planes of the aromatic rings to plane (II) (Table 3): namely the angle of twist of the aniline ring about the N–C(4) bond (37·9°) and of the benzylidene ring about the C(7)–C(8) bond (6·1°). The degree of rotation is smaller for both rings than in previously reported examples;[5] moreover, the sense of rotation in the present case is the same for the two rings whereas in other benzylideneanilines the two rotations are opposite in sense.

TABLE 4

Equations of some best 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

	A	*B*	*C*	*D*
Plane (I): C(1)—(6)	2·133	3·769	5·591	–5·510
[C(1) 0·009, C(2) –0·014, C(3) 0·006, C(4) 0·006, C(5) –0·011, N –0·029, H(1) 0·14, H(2) 0·24, H(3) –0·19, H(5) –0·07, H(6) 0·01]				
Plane (II): C(4), C(7), C(8), N	–4·694	3·221	10·235	–5·026
[C(1) –0·040, C(4) –0·024, C(7) 0·024, C(8) –0·023, C(11) –0·133, N 0·023, H(7) –0·10]				
Plane (III): C(8)—(13)	3·909	–3·443	8·738	4·158
[C(7) 0·012, C(8) 0·000, C(9) 0·005, C(10) –0·007, C(11) 0·003, C(12) 0·002, C(13) –0·004, Cl(1) –0·033, Cl(2) –0·009, H(10) 0·06, H(11) 0·10, H(12) 0·18, H(13) –0·03]				

This significant change in molecular shape compared to other benzylideneanilines appears to be primarily a manifestation of packing considerations rather than

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[21] G. W. Wheland, ' Resonance in Organic Chemistry,' Wiley, New York, 1955, p. 223.

[22] See *e.g.* refs. in Table 7 of ref. 15.

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

[24] H. Hope, *Acta Cryst.*, 1969, *B*, **25**, 78.

[25] T. C. W. Mak and J. Trotter, *Acta Cryst.*, 1965, **18**, 68.

intramolecular forces. The packing (Figures 3 and 4) is rather efficient, with no unusually short intermolecular distances (Table 5). The majority of ' short ' distances are between Cl and H, and for each chlorine there is a contact with hydrogen on at least two neighbouring molecules. Two regions of intermolecular relationship dominate the structure, both roughly parallel to the *a* axis: the first contains contacts only of the type Cl · · · Cl and Cl · · · H, while the second may be visualised as a chain of alternate aniline rings and inter-ring bridges. In addition to the two Cl · · · Cl distances which arise from the *b* translation (3·94 Å) there is a Cl(1) · · · Cl(2) distance of 3·79 Å (Table 3). This separation corresponds to the minimum energy equilibrium distance of 3·82 Å for Cl · · · Cl.[26] A calculation of the intermolecular distances which result from a twist of the benzylidene ring in the opposite sense and by the same amount as in the present structure leads to many short intermolecular distances especially between carbon atoms of two benzylidene rings related by a *b* translation; moreover the Cl(1) · · · Cl(2) distance increases to 4·18 Å. The intramolecular distances C(9) · · · H(7), C(13) · · · H(7), N · · · H(13), and Cl(1) · · · H(7) are virtually unaffected by the alteration in molecular geometry. Although such calculations are tenuous at best, in this case they indicate that the change in molecular conformation from earlier structures is compatible with a minimum energy situation in this crystal, and that the molecule of opposite twist about C(7)–C(8), for the same packing arrangement, would lead to an unfavourable situation. These packing considerations strongly indicate that this structure is one in which intermolecular forces, predominantly those of the Cl · · · Cl attractive type, are responsible for a change of molecular geometry from the expected pattern.

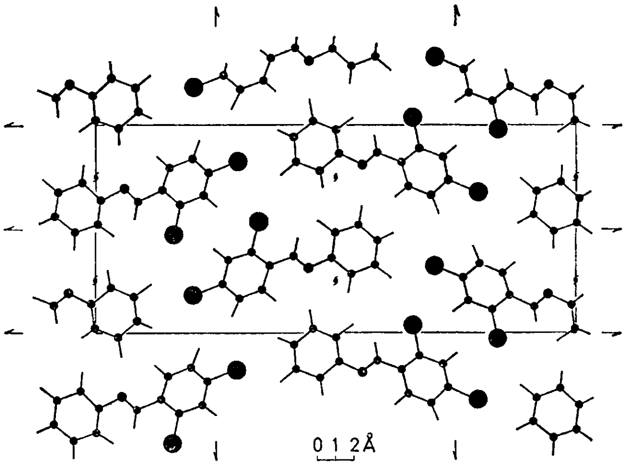

FIGURE 3 The structure viewed down the *b* axis

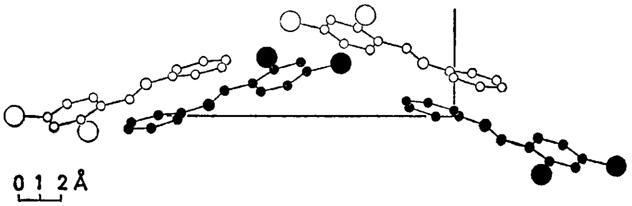

FIGURE 4 Molecular packing viewed down the *a* axis

TABLE 5
Intermolecular distances *

Symmetry elements

A x, y, z
B $\frac{1}{2} - x, -y, \frac{1}{2} + z$
C $\frac{1}{2} + x, \frac{1}{2} - y, -z$
D $-x, \frac{1}{2} + y, \frac{1}{2} - z$

Atom pair	Symmetry element	Translation along			Distance/ Å
		a	*b*	*c*	
N · · · H(2)	C	−1	0	1	2·90
C(4) · · · C(7)	A	0	−1	0	3·50
C(8) · · · C(9)	A	0	−1	0	3·50
H(3) · · · H(5)	C	0	0	1	2·58
Cl(2) · · · H(12)	D	0	0	0	2·94
Cl(2) · · · H(6)	B	0	1	−1	3·18
Cl(1) · · · H(6)	C	0	1	1	2·82
Cl(2) · · · H(6)	B	0	2	−1	3·04
Cl(1) · · · H(10)	D	1	−1	0	3·01
Cl(1) · · · Cl(2)	D	1	0	0	3·79

* All distances less than sum of van der Waals radii plus 0·2 Å. First atom of pair is located at *x*, *y*, *z*; the second is obtained by the appropriate symmetry transformation and translation.

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[26] M. A. Newman, *Trans. Amer. Cryst. Assoc.*, 1970, **6**, 111.