Table 3. *Interatomic distances* (Å) *and angles* (°) *for* RCH$_3$ *in cell* (I)

	Uncorrected	Corrected*
C(*C*)–C(1)	1·525 (4)	1·539 (4)
C(1)–O(1)	1·386 (6)	1·405 (7)
O(1)···O(1^{i})†	2·714 (5)	
C(1)–H(11)	0·98 (6)	
C(1)–H(12)	0·96 (6)	
O(1)–H(O1)	0·75 (6)	
H(O1)···O(1^{i})†	1·99 (6)	
		Symmetry-related angles
C(1)–C(*C*)–C(1^{ii})	107·9 (4)	C(1^{iii})–C(*C*)–C(1^{iv})
C(1)–C(*C*)–C(1^{iii})	110·2 (2)	C(1)–C(*C*)–C(1^{iv}); C(1)–C(*C*)–C(1^{iii}); C(1^{ii})–C(*C*)–C(1^{iv})
C(*C*)–C(1)–O(1)	113·6 (4)	
O(1)–H(O1)···O(1^{i})†	162 (6)	

Symmetry code: (i) y, $1-x$, $-z$; (ii) $-x,-y,z$; (iii) $y,-x,-z$; (iv) $-y,x,-z$.

* Riding correction (Busing & Levy, 1964).

† Hydrogen-bonded distance.

The relationship between the high-temperature f.c.c. cell of phase (I) ($a \sim 8\cdot9$ Å) and cell (I) of phase (II) is $a = b \approx (\sqrt{2}/2)\ a_{\rm f.c.c.}$ and $c \approx a_{\rm f.c.c.}$. Cell (II), with eight times the volume of cell (I) and the same systematic absences, would not require a disordered molecule. However, as mentioned above, it is not the true cell. The monoclinic cell (III), which appears to be the true unit cell of RCH$_3$, is related to the phase (I) f.c.c. cell in a manner similar to that found in phases (I) and (II) of CCl$_4$ and CBr$_4$ (Rudman, 1979; Powers & Rudman, 1980). It has been shown that in the f.c.c. cell, a vector from an origin lattice point to an adjacent face-centered lattice point is perpendicular to a (110) plane. The vector forms the **b** direction of the monoclinic cell and the (110) plane is the *ac* plane. In an f.c.c. cell there are 12 such vectors, leading to 12 possible orientations of the ordered crystal. However, in RCH$_3$ where the contractions of the lattice result in a pseudo-tetragonal cell, there are only four possible orientations: ±*a* and ±*b*, as shown in Table 1. The lattice points from these four cells (with $Z = 4$) superimpose thereby giving rise to an average cell corresponding to a statically disordered molecule.

Each of the weak reflections was identified as belonging to only one of the four cells and a comparison of the intensity of five sets of similar reflections from each of the four cells resulted in the following percentages for the crystal from which data were collected: cell (III)*A*, 38·6; (III)*B*, 34·6; (III)*C*, 24·0; (III)*D*, 2·8%. No attempt has been made to refine the structure in cell (III).

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Molecular Conformation and Electronic Structure.
VII.* The Structure of the Isomorphic System *p*-Chloro-*N*-(*p*-methylbenzylidene)aniline and *p*-Methyl-*N*-(*p*-chlorobenzylidene)aniline

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Abstract

The isomorphous crystal structures of two hetero *para* disubstituted derivatives of benzylideneaniline, BA, have been determined. Both *p*-chloro-*N*-(*p*-methylbenzylidene)aniline, MeCl, and *p*-methyl-*N*-(*p*-chlorobenzylidene)aniline, ClMe, (C$_{14}$H$_{12}$ClN, $M_r = 229\cdot6$) crystallize in space group $P2_1/a$ with $Z = 2$. For MeCl $a = 5\cdot960$ (1), $b = 7\cdot410$ (1), $c = 13\cdot693$ (3) Å, $\beta = 99\cdot20$ (2)°, $V = 597\cdot0$ Å^3, $D_m = 1\cdot28$, $D_x = 1\cdot28$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1\cdot54184$ Å, $\mu = 2\cdot45$ mm^{-1}, $F(000) = 240$. For ClMe $a = 5\cdot969$ (2), $b = 7\cdot412$ (2),

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* Part VI: Bar & Bernstein (1982*a*).

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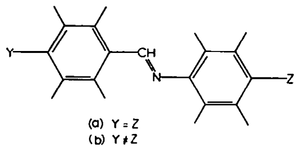
$c = 13{\cdot}747$ (4) Å, $\beta = 99{\cdot}12$ (2)°, $V = 600{\cdot}5$ Å^3, $D_x = 1{\cdot}27$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}54184$ Å, $\mu = 2{\cdot}45$ mm^{-1}, $F(000) = 240$. Final R values are 0·056 for 907, and 0·065 for 736 observed reflections respectively. The distortion from planarity is larger than that found in homo *para* disubstituted BA's which lie on a crystallographic center of symmetry. Three different types of disorder are defined and described for these systems: in addition to the positional and orientational disorder of the bridge atoms found in previously reported homo *para* disubstituted BA's, this pair of isomorphic compounds also exhibits substitutional disorder.

Introduction

One approach to studying the structural aspects of various influences on packing motifs in organic solids is to vary systematically the mode of substitution on a particular molecule and to investigate the subsequent similarities and differences in the crystal structures. Our structural investigation of a series of *para* disubstituted benzylideneanilines, BA's, (Bernstein & Bar, 1980) is part of such a study. We have previously reported the structures of dimorphic *p*-chloro-*N*-(*p*-chlorobenzylidene)aniline, ClCl (i *a*), $Z = Y = \mathrm{Cl}$ (Bernstein & Schmidt, 1972; Bernstein & Izak, 1976) and the trimorphic *p*-methyl-*N*-(*p*-methylbenzylidene)-aniline (i *a*), $Z = Y = \mathrm{CH_3}$, MeMe (Bar & Bernstein, 1977, 1982*a*; Bernstein, Bar & Christensen, 1976). In each of these two polymorphic systems significantly different conformations are found in the different crystal structures, a phenomenon known as conformational polymorphism (Corradini, 1973; Panagiotopoulos, Jeffrey, La Placa & Hamilton, 1974). These findings led to quantitative studies of the influence of crystal forces on molecular conformation (Bernstein & Hagler, 1978; Bar & Bernstein, 1982*b*).



(i)

In spite of the similarity of chlorine and methyl substituents, there is no isomorphism among the known polymorphs of these two homo-disubstituted derivates. In the trimorphic MeMe system we found that the molecule adopts the energetically preferred non-planar molecular conformation (Bernstein, Engel & Hagler, 1981) only in the one form in which disorder is not exhibited. This observation raises the possibility of engineering crystal structures of benzylideneanilines containing the energetically less favorable planar conformation by inducing disorder of the appropriate type. One obvious strategy is substitution of BA with chloro and methyl substituents in the *para* positions wherein disorder at the extremities of the molecule might be expected owing to the similarity in van der Waals radii of these two groups. This leads to two chemically unique derivatives (i *b*): $Y = \mathrm{CH_3}$, $Z = \mathrm{Cl}$, MeCl; $Y = \mathrm{Cl}$, $Z = \mathrm{CH_3}$, ClMe. The structures of this pair of derivatives were investigated to test this strategy of engineering planar molecular conformations, to compare the structures and conformations with the homo analogs, and to provide a basis for further computational studies.

Experimental

Crystals of MeCl were prepared by condensation of *p*-tolualdehyde and *p*-chloroaniline and crystallized from 1-propanol solution, m.p. 391–394 K. ClMe was prepared by condensation of *p*-chlorobenzaldehyde and *p*-toluidine and recrystallized from ethanol 95%, m.p. 397–398 K.

Systematic absences unambiguously lead to a space-group assignment of $P2_1/a$ for both compounds. Unit-cell constants for MeCl were obtained from a least-squares fit of fifteen reflections with $46 < 2\theta < 82°$ (Cu $K\bar{\alpha}$); and those for ClMe were obtained from a least-squares fit of fifteen reflections with $8 < 2\theta < 23°$ (Cu $K\bar{\alpha}$). Experimental data are summarized in Table 1. Intensities for both compounds were measured on a Syntex automatic diffractometer (Cu $K\bar{\alpha}$, graphite monochromator in parallel mode employing $\theta/2\theta$ scans with scan rate varying from 2 to 24° min^{-1}). Data were corrected for Lorentz and polarization factors; absorption corrections were not applied.

Structure solution and refinement

MeCl

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1972). The presence of only two molecules in the unit cell in space group $P2_1/a$ requires crystallographic orientational disorder (see below) about a center of symmetry similar to that found in two other BA's (Bernstein & Schmidt, 1972; Bernstein & Izak, 1975). Hence, at this stage the scattering factor of the two bridge atoms, denoted by X, was taken as the

Table 1. *Experimental data*

	MeCl	ClMe
Number of intensities measured	1142	1192
Range (2θ°)	0–54	0–54
Number of intensities considered observed	907 [$I > 2{\cdot}0\sigma(I)$]	736 [$I > 1{\cdot}5\sigma(I)$]
R	0·056	0·065
R_w	0·070	0·062

average of C and N. The location of the molecule on a center of symmetry leads to substitutional disorder, with respect to the methyl and chlorine *para* substituents (see below), which was not present in the previously determined homo-disubstituted BA's, but results from the hetero-substitution in these compounds. The *para* substituents were also assigned half occupancy ($\frac{1}{2}$Cl,$\frac{1}{2}$C) and refined in separate blocks. Least-squares refinement with isotropic temperature factors converged at $R = 0{\cdot}181$ for all data. The difference map revealed a new peak in the neighborhood of the bridge atom, suggesting an additional positional disorder (see below) in the region of this atom. Positional disorder combined with orientational disorder about a center of symmetry, similar to that observed here, was found previously in MeMe form III (Bernstein, Bar & Christensen, 1976). Anisotropic refinement of the non-hydrogen atoms and isotropic of the H atoms (which were calculated from geometric considerations) with all ring atoms in a block, and the bridge and substituent atoms one atom per block with bond-length constraints, converged with $R = 0{\cdot}056$, $R_w = 0{\cdot}070$ for observed data and $R = 0{\cdot}065$, including unobserveds. The final difference map did not exceed 0·13 e Å^{-3} at any point.

ClMe

The similarity of cell constants and observed structure amplitudes of ClMe and MeCl suggests that the two compounds are truly isomorphic. Hence, a least-squares refinement of a trial structure based on the coordinates obtained in the MeCl structure, with only one X on the bridge (*i.e.* not including positional disorder), yielded an R of 0·23 for reflections of $\sin\theta <$ 0·7 with only positional parameters permitted to vary. Symmetry considerations require that the methyl and chlorine substituents be assigned a fixed occupancy of 0·5; these and the bridge atom ($\frac{1}{2}$C,$\frac{1}{2}$N) were refined in separate blocks. The refinement was continued with isotropic temperature factors, then anisotropic and H atoms calculated and included in the refinement to $R =$ 0·089 for all data. The difference map exhibited a new peak of 0·61 e Å^{-3} in the vicinity of the bridge, suggesting the presence of the positional disorder observed above. Further block-diagonal least squares led to $R = 0{\cdot}065$, $R_w = 0{\cdot}062$ for observed data and $R = 0{\cdot}108$, including unobserveds. The final difference map exhibited no peak higher than 0·25 e Å^{-3}.

H atoms on the bridge and methyl group were not located for either structure. Final positional and equivalent isotropic temperature factors for both compounds are given in Table 2.[*] Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1968). Refinement of both structures was carried out with *SHELX* (Sheldrick, 1976), employing weights $w = 1/\sigma^2(F_o)$ in the least-squares calculations.

Table 2. *Atomic coordinates* ($\times 10^4$ *for non-hydrogen atoms*, $\times 10^3$ *for hydrogen atoms*) *and* U_{eq} (Å^2 $\times 10^4$) *expressed as* $(U_{11}\,U_{22}\,U_{33})^{1/3}$

E.s.d.'s quoted in this and subsequent tables are probably underestimated owing to the disorder in the structure.

	x	y	z	U_{eq}
MeCl				
C(1)	2670 (4)	9797 (3)	8043 (2)	691 (12)
C(2)	1359 (4)	9164 (3)	7190 (2)	709 (12)
C(3)	2107 (5)	9336 (3)	6297 (2)	729 (13)
C(4)	4191 (4)	10145 (3)	6239 (2)	750 (13)
C(5)	5453 (4)	10803 (3)	7095 (2)	783 (14)
C(6)	4719 (4)	10629 (3)	7984 (2)	768 (14)
Cl*	1830 (11)	9576 (9)	9190 (3)	1115 (20)
C(7)*	1539 (38)	9563 (25)	8945 (10)	835 (62)
X(1)†	5338 (10)	10423 (5)	5383 (4)	640 (23)
X(2)†	4034 (25)	9912 (13)	5135 (8)	645 (61)
H(2)	−6 (4)	855 (4)	715 (2)	
H(3)	129 (4)	882 (4)	587 (2)	
H(5)	697 (5)	1136 (4)	711 (2)	
H(6)	555 (5)	1128 (4)	858 (3)	
ClMe				
C(1)	2678 (5)	9792 (4)	8038 (2)	616 (17)
C(2)	1371 (5)	9171 (4)	7195 (2)	638 (19)
C(3)	2141 (6)	9348 (4)	6311 (2)	671 (21)
C(4)	4194 (6)	10150 (4)	6243 (2)	667 (19)
C(5)	5429 (6)	10789 (4)	7092 (3)	712 (22)
C(6)	4712 (5)	10610 (4)	7971 (2)	695 (20)
Cl*	1827 (17)	9556 (11)	9190 (5)	1120 (33)
C(7)*	1440 (52)	9577 (29)	8923 (14)	705 (91)
X(1)†	5345 (18)	10427 (8)	5371 (6)	673 (42)
X(2)†	3961 (51)	9907 (26)	5150 (16)	381 (112)
H(2)	4 (4)	866 (3)	723 (2)	
H(3)	122 (4)	895 (3)	584 (2)	
H(5)	671 (4)	1133 (3)	708 (2)	
H(6)	564 (5)	1099 (3)	852 (2)	

* Occupancy of 0·5 owing to disorder.

† Atoms X(2) are the disordered pairs of the atoms X(1) which have occupancy of 0·7 in MeCl and 0·8 in ClMe.

Results and discussion

For the purposes of this discussion it is necessary to define and to distinguish three different types of disorder which are exhibited by benzylideneanilines and similar molecules: *orientational*, *positional* and *substitutional* disorder.

For *orientational* disorder[*] the molecule at any one crystallographic site may be disposed in different ways [*e.g.* (i *a*) and (ii)] but in the two dispositions each atom is essentially superimposed on another. The disorder is due to the fact that dissimilar atoms (*e.g.* C and N)

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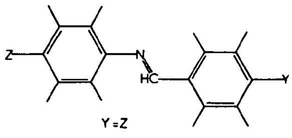
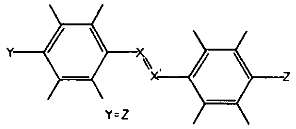
[*] Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38259 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

[*] We earlier (Bernstein, Bar & Christensen, 1976) called this 'crystallographic' disorder; we believe 'orientational' is more descriptive and unique.

may occupy the same site. If crystallographic symmetry is higher than the molecular point symmetry (which is 1 in this case), such a disorder is statistical, as represented by (iii), in which the site symmetry is either $\bar{1}$ or 2 and X (and X') is defined by $[x\text{C} + (1 - x)\text{N}; x = 0{\cdot}5]$. Examples of such structures are the two forms of ClCl (Bernstein & Schmidt, 1972; Bernstein & Izak, 1976) and the dibromo analog (i *a*), $Y = Z =$ Br (Bernstein & Izak, 1975). In the absence of a crystallographic symmetry element $0 \le x \le 1$.

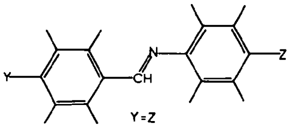


(ii)



(iii)

For *positional* disorder, the C and N atoms occupy different positions as represented by (i *a*) and (iv) [or alternatively by (ii) and (v)]. Combining (i *a*) and (iv) leads to (vi), and similarly for (ii) and (v) leading to (vii), with, of course, equal occupancies of atoms which are bonded chemically.* A number of distinct possibilities arise for the disposition of the molecules in the two positions. In one type, represented by (vi) and (vii), the *para* substituents are superimposed, while in a second possibility the substituted *para* carbon atoms are superimposed as in (viii) and (ix). In the former type, about 0·1 Å displacement is expected for the *para* carbon from the average position of the two dispositions while this increases to a maximum of about 0·4 Å for the phenyl carbon bonded to the bridge atoms. In the latter case the substituent atoms are displaced about 0·3–0·35 Å from their average positions [depending on the length of the C(phenyl)–substituent bond] while displacements around the ring are in the range 0·1–0·3 Å. In any case the displacements of ring atoms and substituents from average positions are below the resolution of the structure determination within the limits of the copper sphere. The atoms in the bridge are at least 0·6 Å apart in all cases and hence may be legitimately resolved in the refinement. It is most likely that the true situation is a combination of these dispositions (and possibly others as well), and depends to a large extent upon the intermolecular energetics.



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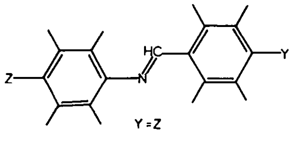

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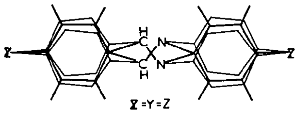

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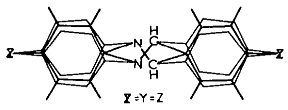

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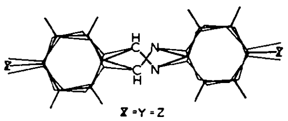

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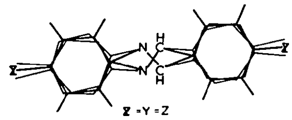
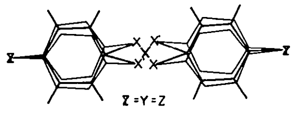
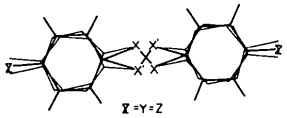


(ix)

In the absence of crystallographic site symmetry, the disorder is not required to be statistical, and the situation depicted in (vi) (and vii) is represented in the structure of form I of MeMe (Bar & Bernstein, 1982*a*). The presence of, say, a center of symmetry ($\bar{1}$) leads to the situation portrayed in (x) and (xi) in which the *orientational* disorder is now superimposed on the *positional* disorder but the occupancy of X and X' may differ [however $X = X' = (\text{C} + \text{N})/2$]. The situation represented in (x) is found, for instance, in the structure of form III of MeMe (Bernstein, Bar & Christensen, 1976) and *p*-azoxyanisole (Brown, 1966).

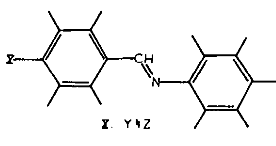


(x)



(xi)

For *substitutional* disorder the atoms of the parent molecule occupy constant positions but the substituents may be interchanged owing to their similar steric properties and bond lengths with the parent molecule. Among the classic examples is *p*-bromochlorobenzene (Klug, 1947) in which the disorder is statistical owing to the location of the molecule on a crystallographic center of symmetry. Other bromochlorobenzenes exhibit similar behavior (Costines, Pies & Weiss, 1981). An additional case recently studied in some detail by a combination of thermal diffuse scattering and computational modeling is 9-bromo-10-methylanthracene (Jones & Welberry, 1980; Welberry & Jones, 1980) in which the disorder is not statistical but is characterized by domains of molecules packed in a regular way. Pure *substitutional* disorder in the systems studied here would be represented by $Y \neq Z$ in (i)–(iv), where these two substituents are disordered but the remainder of the atoms would not be disordered. *One* of the possible situations (derived from i) is shown in (xii).



(xii)

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* In (vi)–(xi) the two distinct dispositions are represented by lighter lines. The averaged positions as would be observed in the refinement are represented by heavy lines. For clarity, all double bonds and hydrogens in the two distinct dispositions have been omitted in these views.

In the case of the hetero-disubstituted benzylideneanilines, and in particular for the isomorphic structures MeCl and ClMe studied here, the observed disorder represents a combination of these three different modes.

Molecular geometry

Atomic numbering for both molecules is given in Fig. 1. Although many of the coordinates in Table 2 have e.s.d.'s which may be considered 'normal', the complex mode of disorder in both structures suggests that geometric features be treated with caution and that these e.s.d.'s are probably significantly underestimated. The bond lengths and bond angles based on the refined coordinates are in Table 3.

Table 3. *Molecular geometry*

(*a*) Bond lengths (Å) and angles (°) excluding 'bridge' atoms

	MeCl	ClMe		MeCl	ClMe
C(1)–C(2)	1·379 (4)	1·370 (4)	C(1)–C(2)–C(3)	120·1 (2)	119·4 (3)
C(2)–C(3)	1·373 (4)	1·372 (4)	C(2)–C(3)–C(4)	120·7 (2)	121·8 (3)
C(3)–C(4)	1·393 (4)	1·378 (5)	C(3)–C(4)–C(5)	118·3 (2)	117·2 (3)
C(4)–C(5)	1·378 (4)	1·363 (5)	C(4)–C(5)–C(6)	121·1 (2)	121·8 (3)
C(5)–C(6)	1·363 (4)	1·351 (5)	C(5)–C(6)–C(1)	120·5 (2)	120·8 (3)
C(6)–C(1)	1·382 (3)	1·373 (4)	C(6)–C(1)–C(2)	119·2 (2)	118·9 (3)
C(1)–Cl	1·731 (5)	1·747 (8)	Cl–C(1)–C(2)	122·0 (3)	121·7 (4)
C(1)–C(7)	1·51 (2)	1·53 (2)	Cl–C(1)–C(6)	118·8 (3)	119·5 (4)
			C(7)–C(1)–C(2)	113 (1)	111 (1)
			C(7)–C(1)–C(6)	128 (1)	130 (1)

(*b*) Geometric features of the bridge atoms (average values)

The numbers in square brackets are the two values from which the average value was calculated.

MeCl					
C(4)–X	1·49 Å	[1·46 (1), 1·51 (1)]	C(3)–C(4)–X	112°	[95·4 (6), 129·9 (3)]
X–X'	1·25	[1·23 (1), 1·27 (2)]	C(5)–C(4)–X	129	[111·8 (3), 146·2 (6)]
			C(4)–X–X'	115	[118·6 (5), 111·4 (10)]
ClMe					
C(4)–X	1·49	[1·49 (1), 1·50 (2)]	C(3)–C(4)–X	112	[130·0 (4), 94·2 (11)]
X–X'	1·29	[1·22 (1), 1·38 (4)]	C(5)–C(4)–X	131	[112·7 (4), 148·5 (11)]
			C(4)–X–X'	114	[117·8 (8), 110·1 (20)]

The disorder model least affects the phenyl rings whose geometric characteristics are compatible with those obtained for the trimorphic MeMe (Bar & Bernstein, 1977, 1982*a*; Bernstein, Bar & Christensen, 1976) and the dimorphic ClCl (Bernstein & Izak, 1976; Bernstein & Schmidt, 1972), except for the internal bond angle at the C atom at which substitution takes place. The angle at C(1) has a value of 119° in both compounds. This is the average of the values obtained in MeMe, 117·3°, and in ClCl, 121·3°, within experimental error, as might be expected from the disorder. Owing to the disorder, the e.s.d.'s of the geometric features about C(1) are all at least double those of the remainder of the ring. Nevertheless, the C(1)–C(7) and C(1)–Cl bond distances are very close to the values expected (Domenicano, Vaciago & Coulson, 1975*a*,*b*). The situation illustrated in Fig. 1, showing these bonds, simply represents the final coordinates as obtained from the least-squares refinement; again, this is an average of the ideal modes of the type shown in (vi) and (ix) and clearly no special chemical significance should be attached to them. The fact that the bond lengths do closely approximate normal values serves to justify the disorder model employed.

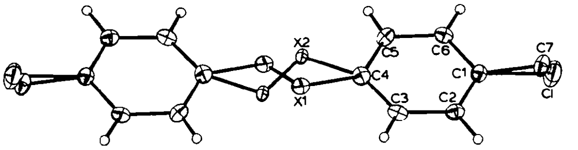

Fig. 1. Atomic numbering for both structures, showing disorder and the positions obtained in the least-squares refinement. X is defined in the text. Thermal ellipsoids are at the 30% probability level.

One of the important features of these structures is the molecular conformation as defined by the torsion angles about the exocyclic bonds. Benzylideneaniline itself (Bürgi & Dunitz, 1970) adopts the more energetically preferred non-planar conformation and the existence of planar homo-disubstituted benzylideneanilines led to the quantitative studies of conformational polymorphism. The disorder described above involves essentially no out-of-plane displacements of the phenyl groups (as evidenced also by the form of the anisotropic temperature factors)* and in both structures they are planar to within 0·01 Å (Table 4). The atoms in the 'bridge' region (plane II, Table 4) are significantly less planar, the maximum deviation from the best plane being 0·21 Å in MeCl and 0·13 Å in ClMe. The location of the molecule on a crystallographic center of symmetry requires the two phenyl rings to be parallel, but not necessarily coplanar (Bunn, 1961). The angle of twist about C(4)–X is −16° in both compounds for one orientation of the disordered model, while for the second orientation it is 18°. The angle of twist of the phenyl ring about the single bond obtained by computing the angle between the normals to planes I and II is −11° in MeCl and −9° in ClMe. Thus a reasonable estimate for the deviation from planarity is 12–15° (e.s.d.'s *ca* 1°).

This value indicates that the molecules are more distorted from planarity than the homo-disubstituted BA's which are located on a center of symmetry: form III of MeMe in which the phenyl rings are rotated by 4·6° about the N–phenyl and CH–phenyl bonds (Bernstein, Bar & Christensen, 1976); the *para* disubstituted bromo and chloro (triclinic form) derivatives in which the rotation is 1·9° and 0·4° respectively (Bernstein & Schmidt, 1972; Bernstein & Izak, 1975); and form I of MeMe which is located at a general position with a torsion angle of 4·9° (Bar & Bernstein, 1982*a*). The conformation also differs from that of ClCl (orthorhombic form) with torsion angles of ±24·8° for the two exocyclic bonds (Bernstein & Izak, 1976), and that of MeMe form II with a torsion

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* See deposition footnote.

Table 4. *Best planes*

Equations of weighted least-squares planes in the form $Ax + By + Cz + D = 0$, where x,y,z are fractional coordinates, with deviations (Å) of relevant atoms from the planes. E.s.d.'s of the deviations are probably underestimated (see heading to Table 2).

	A	*B*	*C*	*D*
Plane I C(1)–C(6)	0·443	−0·885	0·142	−4·962 MeCl
	0·442	−0·886	0·138	−4·999 ClMe
Plane II C(4), *X*(2), *X*(1), C(4′), *X*(2′), *X*(1′)	−0·524	0·801	−0·290	2·986 MeCl
	−0·328	0·914	−0·239	4·530 ClMe

	Plane I		Plane II	
	MeCl	ClMe	MeCl	ClMe
C(1)	0·008 (2)	0·007 (3)	−0·235 (2)	−0·454 (3)
C(2)	−0·005 (2)	−0·007 (3)	0·036 (2)	0·406 (3)
C(3)	−0·005 (2)	−0·007 (3)	0·151 (2)	0·213 (3)
C(4)	0·010 (2)	0·008 (3)	−0·004 (2)	−0·055 (3)
C(5)	−0·007 (2)	−0·008 (3)	−0·245 (2)	−0·079 (3)
C(6)	−0·002 (2)	−0·001 (3)	−0·365 (2)	−0·282 (3)
Cl	0·040 (7)	0·043 (9)	−0·421 (6)	−0·739 (8)
C(7)	−0·05 (2)	−0·10 (2)	−0·27 (2)	−0·58 (2)
X(1)	0·049 (4)	0·050 (7)	0·039 (5)	0·128 (7)
X(2)	0·02 (1)	0·01 (2)	0·21 (1)	0·10 (2)
C(1′)	0·394 (2)	0·405 (3)	0·235 (2)	0·454 (3)
C(2′)	0·399 (2)	0·419 (3)	−0·030 (2)	−0·406 (3)
C(3′)	0·406 (2)	0·412 (3)	−0·151 (3)	−0·213 (3)
C(4′)	0·392 (2)	0·404 (3)	0·004 (2)	0·055 (3)
C(5′)	0·408 (2)	0·420 (3)	0·245 (2)	0·079 (3)
C(6′)	0·403 (2)	0·411 (3)	0·365 (2)	0·282 (3)
Cl′	0·371 (7)	0·369 (8)	0·421 (6)	0·739 (8)
C(7′)	0·45 (2)	0·51 (2)	0·27 (2)	0·58 (2)
X(1′)	0·352 (4)	0·361 (7)	−0·039 (5)	−0·128 (7)
X(2′)	0·39 (1)	0·41 (2)	−0·21 (1)	−0·10 (2)

angle of 41·7° about the N—phenyl bond and −3·0° about the C—phenyl bond (Bar & Bernstein, 1977), which is the minimum-molecular-energy conformation for these molecules (Bernstein, Engel & Hagler, 1981). The conformations of the two structures reported here have a higher energy than the minimum-energy conformation by approximately 5·0 kJ mol^{-1}; hence the lattice (crystal environment) and disorder must supply sufficient energy to stabilize this relatively unfavorable conformation (Bar & Bernstein, 1982*b*; Bernstein & Hagler, 1978).

Packing

The packing arrangement is shown in Fig. 2. It is different from the packing observed in any of the structures of the trimorphic MeMe and dimorphic ClCl. For a situation in which neighboring molecules have opposite orientation of the *para* substituent the shortest intermolecular distances are between the atoms at the extremities, being 3·41 (1) Å in MeCl and 3·42 (1) Å in ClMe between the Cl atoms, and 3·72 (3) Å in MeCl and 3·71 (4) Å in ClMe between the C(7) atoms. The shortest Cl · · · Cl distance that was found in this family of compounds is similar to that observed here, being 3·42 Å in the triclinic form of ClCl (Bernstein & Schmidt, 1972), while the shortest contact between the C atoms of two methyl groups was 3·75 Å in MeMe form I and 3·80 Å in MeMe form III. Because of the hetero substituents that are present in these molecules there is the possibility of an additional short distance between Cl and C(7) of two neighboring molecular sites of identical orientation of 3·55 (2) Å in MeCl and 3·54 (3) Å in ClMe.

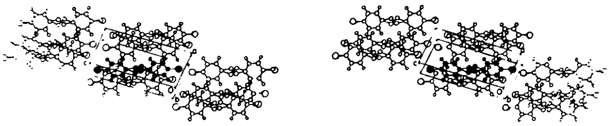

Fig. 2. Stereoview of the structure in a direction perpendicular to the best plane of the bridge atoms of the reference molecule (indicated by filled circles). The disordered atoms both at the bridge (—CH=N) and at the *para* positions (Cl,CH_3) are shown.

The molecular volumes in the three forms of MeMe are 307·5, 303·0 and 289·9 Å^3, while in both forms of ClCl the molecular volume is 284·2 Å^3. Since forms I and III of MeMe are planar, and have significantly different molecular volumes, we suggested that the planarity does not influence the packing efficiency. The pair of isomorphic structures reported here strengthens this proposition. The C—Cl group has a lower volume increment than the C—Me group (Kitaigorodskii, 1973) so we would expect that the molecular volumes of MeCl and ClMe would be intermediate between those of MeMe and ClCl, but they are 298·5 and 300·3 Å^3, respectively, both higher than form III of MeMe.

A quantitative investigation of lattice energetics of this isomorphic system will be reported elsewhere.

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Structures of Modified Cardenolides. IV. [20*S*]20(22)-Dihydrodigitoxigenin Analogues

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Abstract

Many often-conflicting models have been proposed to describe the biological roles of digitalis structure and conformation. In an effort to resolve these conflicts, the structures of two 20(22)-dihydro analogues of digitalis genins have been determined as part of a continuing study of the effects changes in the C(17)β side chain have on biological activity. A double bond in this side group has been considered important for biological activity and binding at the receptor. The structural and biological data from three analogues, [20*R*]- and [20*S*]3β,14-dihydroxy-5β,14β-cardanolide (I), [20*R*]- and [20*S*]3β,14-dihydroxy-22-methylene-5β,14β-cardanolide (II), and [20*R*]- and [20*S*]3β-hydroxy-22-methylene-5β-card-14-enolide (III) indicate that the double bond is not necessary for activity, but rather plays a geometric role in positioning the lactone carbonyl O relative to the steroid backbone. The relative position of this functional O is the major determinant in each analogue's biological activity. Crystal and molecular structures for two of these analogues, (I_S) and (II_S), are reported here. The crystals obtained for analogue (I_S)($C_{23}H_{36}O_4$, M_r = 376·54) were triclinic with space group $P1$ and a = 7·726 (1), b = 10·224 (2), c = 6·379 (1) Å, α = 84·55 (1), β = 97·46 (1), γ = 90·92 (1)°, V = 497·33 Å^3, Z = 1 and D_x = 1·257 Mg m^{-3}. The final R factor was 0·049 for all the independent reflection data (2030) with $\theta < 75°$. Analogue (II_S) ($C_{24}H_{36}O_4$, M_r = 388·56) crystallized in the monoclinic space group $P2_1$ with a = 21·474 (2), b = 13·444 (2), c = 7·279 (1) Å, β = 94·98 (2)°, V = 2093·49 Å^3, Z = 4 and D_x = 1·233 Mg m^{-3}. The final R factor was 0·078 for all of the independent reflection data (4477) with $\theta < 75°$.

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