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The Fourfold Disordered Structures of *p*-Chloro-*N*-(*p*-methylbenzylidene)aniline and *p*-Methyl-*N*-(*p*-chlorobenzylidene)aniline

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Abstract

p-Chloro-*N*-(*p*-methylbenzylidene)aniline, MeCl, and *p*-methyl-*N*-(*p*-chlorobenzylidene)aniline, ClMe, are isostructural, both $C_{14}H_{12}ClN$, $M_r = 229.6$, differing only in the disposition of a $—CH=N—$ linkage joining two phenyl-ring systems, one with a *p*-Cl atom attached, the other with a *p*-methyl group attached. A non-disordered prototype structure would have the space group $P2_1/n$, $Z = 4$. MeCl: $a = 5.965(2)$, $b = 7.423(3)$, $c = 27.420(3) \text{ \AA}$, $\beta = 99.22(1)^\circ$, $V = 1198(1) \text{ \AA}^3$, $D_x = 1.28 \text{ Mg m}^{-3}$, $T = 295 \text{ K}$, $\mu = 24.5 \text{ cm}^{-1}$, $Cu K\alpha$, $\lambda = 1.5418 \text{ \AA}$; ClMe: $a = 5.971(2)$, $b = 7.411(3)$, $c = 27.462(3) \text{ \AA}$, $\beta = 99.13(1)^\circ$, $V = 1200(1) \text{ \AA}^3$, $D_x = 1.27 \text{ Mg m}^{-3}$, $T = 295 \text{ K}$, $\mu = 24.3 \text{ cm}^{-1}$, $Cu K\alpha$, $\lambda = 1.5418 \text{ \AA}$. The molecules have pseudo-*mmm* symmetry, but no real symmetry. Four pseudo-equivalent orientations occur in the disordered structure. If inversion-related orientations are equally populated, then l odd data are unobserved and the average disordered structure has the space group $P2_1/a$, with $\mathbf{a}' = \mathbf{a}$, $\mathbf{b}' = \mathbf{b}$, $\mathbf{c}' = \mathbf{c}/2$, $Z = 2$. This was the case for the ClMe crystal studied, but not for MeCl. For the crystals studied, occupation ratios for the reference-, inversion-, mirror- and twofold rotation-related orientations were 0.543:0.189(3):0.095(3):0.173(3) for MeCl and 0.351:0.351:0.149:0.149(3) for ClMe. A

91-variable model (with 7 degrees of freedom restrained) was used in the constrained refinement of MeCl to refine 660 from 1784 reflections in one quadrant with $I(\mathbf{h}) > 3\sigma[I(\mathbf{h})]$. Final values for $R_1 = \sum_h |\Delta F(\mathbf{h})| / \sum_h |F_o(\mathbf{h})|$ were 0.049 for the 529 l even data, 0.079 for the 131 l odd data, and 0.052 overall. An 87-variable model (with 8 degrees of freedom restrained) was used in the constrained refinement of ClMe to refine 1387 from 2284 unmerged data with $I(\mathbf{h}) > 3\sigma[I(\mathbf{h})]$ to a value for R_1 of 0.044.

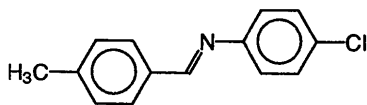
Introduction

The disorder in the structures of *p*-chloro-*N*-(*p*-methylbenzylidene)aniline, hereafter referred to as MeCl, and *p*-methyl-*N*-(*p*-chlorobenzylidene)aniline, hereafter referred to as ClMe, was first reported by Bar & Bernstein (1983), but little attempt was made at accurate refinement. We have a long-term interest in diffuse scattering from disordered crystal systems and are particularly interested in the distributions of local structure environments in disordered systems. We have already published some preliminary investigations of the diffuse scattering from MeCl (Welberry, Butler & Heerdegen, 1993; Welberry & Butler, 1994) and work is progressing on ClMe. To further our understanding we considered it useful to obtain a better description of the average cell contents of MeCl and ClMe, as obtained

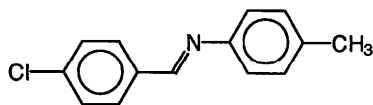
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from Bragg reflection data. This has provided a very useful working example of constrained and restrained refinement procedures.

MeCl



ClMe



(I)

A number of studies of *para*-disubstituted benzyldeneanilines have been reported. Following Bar & Bernstein (1983), we shall label these *ZY*, where *Z* is the functional group attached to the benzyldene ring and *Y* is the functional group attached to the aniline ring. A number of similar structures have been reported, but only one has a well refined ordered structure, *viz.* the second of three forms of MeMe (Bar & Bernstein, 1977), which crystallizes in space group $P2_1$, with $Z = 2$, and has been refined to $R_1 = 0.046$ for observed data. A noticeable feature of this structure is the H···H repulsion involving the H atom of the —CH=N— linkage and the aniline ring. A consequence of this repulsion is a $4.6(3)^\circ$ difference between bond angles involving the N atom and the aniline ring, and a 41.7° torsional angle about the N—C bond attached to the aniline ring. The torsional angle about the CH—C bond attached to the benzyldene ring is -3.0° . Thus, the rings are neither coplanar nor parallel, destroying the potential pseudo-inversion symmetry of the molecule. The C and N atoms of the —CH=N— linkage are *ca* 0.04 Å out of the planes of the rings to which they are attached. *Ab initio* calculations [see Bernstein, Engel & Hagler (1981)] suggest that this conformation is close to the preferred isolated molecule conformation and 6.6 kJ mol^{-1} favoured over a totally coplanar conformation. The orthorhombic form of ClCl (Bernstein & Izak, 1976) crystallizes in $Pccn$, $Z = 4$, with the molecule disordered about a twofold rotation axis parallel to *c*. The angle between the planes of the rings is 49.6° . No attempt was made to resolve the disorder. Rather a structure averaged across the rotation axis was obtained.

In contrast, crystalline forms exist in which the planes of the rings are essentially parallel, and in this situation the molecules have local pseudo-*mmm* symmetry; packing considerations, then allowing up to eight pseudo-equivalent orientations of the molecules, reducing to four if the molecule is truly coplanar. In the presence of a pseudo-inversion centre imposing parallelism on the rings, H···H repulsion can still eliminate coplanarity

by creating oppositely signed non-zero torsional angles about the single bonds of the —CH=N— linkage. Thus, in situations of reported coplanarity, *e.g.* the $P1$, $Z = 1$, structure of ClCl (Bernstein & Schmidt, 1972), a 1 : 1 disorder of mirror-related conformers across this plane is likely.

The first form of MeMe (Bar & Bernstein, 1982) crystallizes in $P2_1/c$, $Z = 4$, and would appear to allow all eight possible conformers. The third form of MeMe (Bernstein, Bar & Christensen, 1976) crystallizes in $P2_1/c$, $Z = 2$. Inversion-related planes of the rings of the average structure appear to be 0.12 Å apart, implying a $2/m11$ subgroup of the *mmm* orientation is favoured. BrBr crystallizes in space group $P2_1/a$, $Z = 2$ (Bernstein & Izak, 1975). As for the triclinic form of ClCl, a $112/m$ subgroup is likely as the rings seem to be coplanar.

Experimental

Crystals were prepared as outlined by Bar & Bernstein (1983).

Data collection

Preliminary examination and data collection used graphite monochromated $\text{Cu K}\alpha$ X-rays on a Rigaku AFC-6R diffractometer with a 12 kW rotating anode generator at 295 K. The same procedure was followed for both ClMe and MeCl. Cell constants are based on 25 accurately centred reflections in the range $77 < 2\theta < 93^\circ$. Analytic absorption corrections (de Meulenaer & Tompa, 1965) were made for parallelepiped crystals bound by $\pm(110)$, $\pm(110)$, $\pm(001)$ at distances between parallel faces of (MeCl, $\mu = 24.5 \text{ cm}^{-1}$) 0.188, 0.153, 0.115 and (ClMe, $\mu = 24.3 \text{ cm}^{-1}$) 0.208, 0.256, 0.017 mm. For MeCl [$P2_1/n$, $Z = 4$, $a = 5.965(2)$, $b = 7.423(3)$, $c = 27.420(3) \text{ \AA}$, $\beta = 99.22(1)^\circ$, $V = 1198(1) \text{ \AA}^3$, $D_c = 1.28 \text{ Mg m}^{-3}$] reflection data to $2\theta = 120^\circ$ were collected with $0 \leq h \leq 6$, $-8 \leq k \leq 0$, $-30 \leq l \leq 30$ to give 660 (529 with *l* even, 131 with *l* odd) out of 1784 merged reflections with $I(\mathbf{h}) \geq 3\sigma[I(\mathbf{h})]$. For ClMe [$P2_1/a$, $Z = 2$, $a = 5.971(2)$, $b = 7.411(3)$, $c = 13.731(2) \text{ \AA}$, $\beta = 99.13(1)^\circ$, $V = 600(1) \text{ \AA}^3$, $D_c = 1.27 \text{ Mg m}^{-3}$] all reflections to $2\theta = 80^\circ$ were collected, plus reflections with $k \leq 1$ for $80 \leq 2\theta \leq 120^\circ$, to give 1387 data out of 2284 with $I(\mathbf{h}) \geq 3\sigma[I(\mathbf{h})]$. Reflections associated with *l* odd for a cell with a doubled *c*-axis were not observed. Scattering curves, atomic absorption coefficients, and anomalous dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Refineability

The MeCl structure can be thought of as a modulation (modulation vector $\mathbf{q} = \mathbf{c}^*$), of a $P2_1/a$ parent structure corresponding to Bragg reflections $h'\mathbf{a}^* + k'\mathbf{b}^* + l'(2\mathbf{c}^*)$.

The modulation has the symmetry necessary to create the space group $P2_1/n$ for the cell \mathbf{a} , \mathbf{b} , \mathbf{c} and destroys half the inversion centres of the parent, including those at $\mathbf{r}_o = \frac{1}{2}\mathbf{a} + \frac{1}{2}\mathbf{b} + \frac{1}{4}\mathbf{c}$ and its $P2_1/n$ equivalents which locate the MeCl molecules. The structure factors for l even reflections are given by the Fourier transform of the symmetrized scattering density component $\rho_A(\mathbf{r}_o + \mathbf{r}) = [\rho(\mathbf{r}_o + \mathbf{r}) + \rho(\mathbf{r}_o + \mathbf{r} + \mathbf{c}/2)]/2$ and for l odd, $\rho_B(\mathbf{r}_o + \mathbf{r}) = [\rho(\mathbf{r}_o + \mathbf{r}) - \rho(\mathbf{r}_o + \mathbf{r} + \mathbf{c}/2)]/2$. The average scattering density, $\rho(\mathbf{r}_o + \mathbf{r}) = \sum_{i=1,4} a_i \rho_i(\mathbf{r}_o + \mathbf{r})$, is made up of four contributions, each associated with a different orientation of the MeCl molecule, the first two and final two being centrosymmetrically related pairs. Since $\rho(\mathbf{r}_o + \mathbf{r} + \mathbf{c}/2) = \rho(\mathbf{r}_o - \mathbf{r})$ by symmetry, it follows that

$$\begin{aligned} \rho_A(\mathbf{r}_o + \mathbf{r}) = & (a_1 + a_2)[\rho_1(\mathbf{r}_o + \mathbf{r}) + \rho_2(\mathbf{r}_o - \mathbf{r}) \\ & + \rho_1(\mathbf{r}_o - \mathbf{r}) + \rho_2(\mathbf{r}_o + \mathbf{r})]/4 \\ & + (a_1 - a_2)[\rho_1(\mathbf{r}_o + \mathbf{r}) - \rho_2(\mathbf{r}_o - \mathbf{r}) \\ & + \rho_1(\mathbf{r}_o - \mathbf{r}) - \rho_2(\mathbf{r}_o + \mathbf{r})]/4 \\ & + (a_3 + a_4)[\rho_3(\mathbf{r}_o + \mathbf{r}) + \rho_4(\mathbf{r}_o - \mathbf{r}) \\ & + \rho_3(\mathbf{r}_o - \mathbf{r}) + \rho_4(\mathbf{r}_o + \mathbf{r})]/4 \\ & + (a_3 - a_4)[\rho_3(\mathbf{r}_o + \mathbf{r}) - \rho_4(\mathbf{r}_o - \mathbf{r}) \\ & + \rho_3(\mathbf{r}_o - \mathbf{r}) - \rho_4(\mathbf{r}_o + \mathbf{r})]/4 \end{aligned}$$

and

$$\begin{aligned} \rho_B(\mathbf{r}_o + \mathbf{r}) = & (a_1 + a_2)[\rho_1(\mathbf{r}_o + \mathbf{r}) - \rho_2(\mathbf{r}_o - \mathbf{r}) \\ & - \rho_1(\mathbf{r}_o - \mathbf{r}) + \rho_2(\mathbf{r}_o + \mathbf{r})]/4 \\ & + (a_1 - a_2)[\rho_1(\mathbf{r}_o + \mathbf{r}) + \rho_2(\mathbf{r}_o - \mathbf{r}) \\ & - \rho_1(\mathbf{r}_o - \mathbf{r}) - \rho_2(\mathbf{r}_o + \mathbf{r})]/4 \\ & + (a_3 + a_4)[\rho_3(\mathbf{r}_o + \mathbf{r}) - \rho_4(\mathbf{r}_o - \mathbf{r}) \\ & - \rho_3(\mathbf{r}_o - \mathbf{r}) + \rho_4(\mathbf{r}_o + \mathbf{r})]/4 \\ & + (a_3 - a_4)[\rho_3(\mathbf{r}_o + \mathbf{r}) + \rho_4(\mathbf{r}_o - \mathbf{r}) \\ & - \rho_3(\mathbf{r}_o - \mathbf{r}) - \rho_4(\mathbf{r}_o + \mathbf{r})]/4. \end{aligned}$$

An assumption used in our refinement was that $\rho_2(\mathbf{r}_o + \mathbf{r}) = \rho_1(\mathbf{r}_o - \mathbf{r})$ and $\rho_4(\mathbf{r}_o + \mathbf{r}) = \rho_3(\mathbf{r}_o - \mathbf{r})$. This reduces the above expressions to

$$\begin{aligned} \rho_A(\mathbf{r}_o + \mathbf{r}) = & (a_1 + a_2)[\rho_1(\mathbf{r}_o + \mathbf{r}) + \rho_1(\mathbf{r}_o - \mathbf{r})]/2 \\ & + (a_3 + a_4)[\rho_3(\mathbf{r}_o + \mathbf{r}) + \rho_3(\mathbf{r}_o - \mathbf{r})]/2 \\ \rho_B(\mathbf{r}_o + \mathbf{r}) = & (a_1 - a_2)[\rho_1(\mathbf{r}_o + \mathbf{r}) - \rho_1(\mathbf{r}_o - \mathbf{r})]/2 \\ & + (a_3 - a_4)[\rho_3(\mathbf{r}_o + \mathbf{r}) - \rho_3(\mathbf{r}_o - \mathbf{r})]/2 \end{aligned}$$

The assumption is best tested using reflections with l odd. Only the MeCl structure showed observable intensity for these reflections, and the success of the MeCl refinement justified the assumption. The consistent lack of l odd data for CIME crystals imposes the constraints $a_1 = a_2$ and $a_3 = a_4$ on the CIME refinement. We regard the crystals studied as typical. The molecules are pseudo-centrosymmetric, and differences in scattering

density across \mathbf{r}_o are only detectable in the weaker and therefore less reliable l odd data. However, for an atom-based model, there are still detectable effects on l even reflections. Constraints and restraints allow the data to refine the more meaningful parameters by reducing the noise associated with allowing non-refineable parameter combinations to take up unrealistic values.

A sensible constraint or restraint is to approximate the value of some parameter combination, where the approximation determines the value more accurately than would be the case using the unconstrained refinement. Assumptions about thermal vibration, planarity and equality of geometry are very sensible options, as they leave the evaluation of average geometric values largely unrestricted. As a constraint, the assumed value is imposed exactly, but this requires appropriate parameterization. The use of refineable local orthogonal coordinates relative to refineable local axial systems greatly assists this process (see Appendices 1 and 2). When applied as a restraint, *i.e.* an extra observational requirement is added to the least-squares equations, the resulting mismatch in the parameter combination should be less than the standard deviation obtained from the inverted least-squares matrix with the restraints included. A standard deviation calculated in this way can become very small if the weight applied to the restraint is increased. Errors evaluated from the least-squares refinement of models which include constraints and restraints exclude errors associated with the inappropriateness of the restraints and constraints. Unrealistic parameter values indicate unresolved difficulties, including the self-consistency of the various restraints used. If the value of a parameter combination cannot be determined with reasonable accuracy using unrestrained refinement, it follows that the R -factor does not depend on this value and thus a restrained value should hold with very good precision, even when the weight given to the restraint is reduced.

Rigid-body thermal parameters were used (Rae, 1975). The molecules each have two torsional degrees of freedom, *viz.* rotations about the single bonds on either side of the CH=N double bond. For CIME, inversion-related molecules showed inversion-related thermal parameters because of a refinement in space group $P2_1/a$, corresponding to the $l = 2n$ only data of space group $P2_1/n$. This constraint was also imposed on the MeCl structure using equal parameter and equal but opposite parameter instructions (Rae, 1984). The component $\rho_1(\mathbf{r}_o + \mathbf{r})$ is pseudo-mirror-related to $\rho_3(\mathbf{r}_o + \mathbf{r})$, but they were treated independently. Each had a separate nine-parameter LX component for each half of the molecule and an overall six-parameter T component to give a total of 48 independent thermal parameters. The refinement relocated the origin and orientation of the principal libration axes each cycle, to aid visualization. Final values are given in Table 4. By choice, the T parameters were described relative to $P = 3$

Table 1. Local coordinates of MeCl and ClMe (Å)

Atom	<i>M</i>	<i>S(M)</i> ₁	MeCl <i>S(M)</i> ₂	<i>S(M)</i> ₃	<i>S(M)</i> ₁	ClMe <i>S(M)</i> ₂	<i>S(M)</i> ₃
C11	1	0	0	0	0	0	0
C11	2	4.507 (5)	0	0	4.510 (9)	0	0
C12	3	3.790 (5)	-1.194 (2)	0	3.801 (8)	-1.195 (2)	0
C13	4	2.421 (4)	-1.194 (2)	0	2.423 (9)	-1.195 (2)	0
C14	5	1.704 (5)	0	0	1.714 (9)	0	0
C15	6	2.421 (4)	1.194 (2)	0	2.423 (9)	1.195 (2)	0
C16	7	3.790 (5)	1.194 (2)	0	3.801 (8)	1.195 (2)	0
N1/Cl*	8	5.913 (6)	-0.150 (7)	-0.051 (8)	5.964 (14)	0.007 (7)	-0.021 (8)
C27	9	0	0	0	0	0	0
C21	10	4.314 (7)	0	0	4.314 (9)	0	0
C22	11	3.596 (7)	-1.194 (2)	0	3.605 (10)	-1.195 (2)	0
C23	12	2.227 (7)	-1.194 (2)	0	2.226 (9)	-1.195 (2)	0
C24	13	1.511 (7)	0	0	1.518 (10)	0	0
C25	14	2.227 (7)	1.194 (2)	0	2.226 (9)	1.195 (2)	0
C26	15	3.596 (7)	1.194 (2)	0	3.605 (10)	1.195 (2)	0
C2/N2*	16	5.759 (9)	-0.013 (8)	0.004 (9)	5.725 (15)	-0.147 (8)	0.059 (8)

* The first atom label is for MeCl, the second is for ClMe.

and $P = 6$ axes (see Appendix), but no unusual features were observed. H atoms were recalculated every cycle to ensure their positions were chemically reasonable. Atoms of molecule n were assigned occupancy a_n , $n = 1-4$, and the occupancy a_1 constrained to be $1 - a_2 - a_3 - a_4$ using parameter-coupling instructions (Rae, 1984).

Refinement results

The ClMe structure was refined in space group $P2_1/a$ with $\mathbf{a}' = \mathbf{a}$, $\mathbf{b}' = \mathbf{b}$, $\mathbf{c}' = \mathbf{c}/2$, $Z = 2$, relative to $P2_1/n$ used for MeCl. Four pseudo-equivalent orientations occur, and for the crystals studied occupation ratios for the reference-, inversion-, mirror- and twofold rotation-related molecules were 0.543:0.189 (3):0.095 (3):0.173 (3) for MeCl and 0.351:0.351:0.149:0.149 (3) for ClMe. A hierarchy of appropriate variables for constrained refinement was employed using the program RAELS92 (Rae, 1992). The number of variables was increased as refinement progressed. For MeCl a 91-variable model (with 7 degrees of freedom restrained) was used to refine 660 from 1943 data in one quadrant with $I(\mathbf{h}) > 3\sigma[I(\mathbf{h})]$. Final values for $R_1 = \sum_{\mathbf{h}} |\Delta F(\mathbf{h})| / \sum_{\mathbf{h}} |F_o(\mathbf{h})|$ were 0.049 for the 529 l even data, 0.079 for the 131 l odd data and 0.052 overall. For ClMe an 87-variable model (with 8 degrees of freedom restrained) was used to refine 1387 from 2404 unmerged data with $I(\mathbf{h}) > 3\sigma[I(\mathbf{h})]$ to an R_1 -value of 0.044. An uncorrelated 4% error in $|F_o(\mathbf{h})|$ was included with the counting statistics error to estimate least-squares weights, $w_{\mathbf{h}} = 1/\text{var}[|F_o(\mathbf{h})|]$. This gave a uniform distribution of weighted residuals for reflections of various intensity. Final values for $[\sum_{\mathbf{h}} w_{\mathbf{h}} |\Delta F(\mathbf{h})|^2 / (n - m)]^{1/2}$ were 1.31 for the 529 l even and 1.38 for the 131 l odd reflections used in the MeCl refinement, and 1.20 for the 1387 reflections used in the ClMe refinement.

Local coordinates are given in Table 1, and the axial systems to which they refer are in Table 2. The corre-

sponding fractional coordinates are given in Table 3. The axial systems for the LX thermal parameter component of atomic thermal parameters are given in Table 4. Origins of axial systems are relative to orthonormal crystal axes parallel to \mathbf{a} , \mathbf{b} , \mathbf{c}^* , centred on the unit-cell origin. A description of the axial systems used is given in the Appendices. Tables of bond lengths and angles are given in Table 5. Due to the restraints and constraints used, the only differences in geometry between pseudo-mirror-related molecules are in the torsional angles listed. H atoms were included in geometrically sensible positions with a bond length of 1 Å and were included in the rigid-body descriptions for thermal parameterization. Values of fractional coordinates and thermal parameters for H atoms have been deposited. Values of non-H atom thermal parameters U_{ij} , relative to orthonormal crystal axes parallel to \mathbf{a} , \mathbf{b} , \mathbf{c}^* , have also been deposited, as have values of observed and calculated structure factors.†

Fig. 1 gives the atom labelling system for both molecules and defines the axial systems used for refinement (see Appendices 1 and 2). Fig. 2 shows the relative positions of different orientations of the MeCl molecules. Fig. 3 shows a projection down \mathbf{b} of the MeCl structure, idealized to include only molecules associated with the occupancy 0.543. Fig. 4 shows a projection of the same structure down $-2\mathbf{a} + \mathbf{c}$, and clearly shows the pseudo-hexagonal close packing of molecules in a layer perpendicular to \mathbf{c}^* . Four of the six adjacent molecule sites relative to a reference site are related by 2_1 screw axis operations, the remaining two by translations of $\pm\mathbf{a}$. The shortest contacts between phenyl-ring C atoms of screw axis-related molecules in

† Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: BK0015). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *The six axial systems used for local coordinates of MeCl and ClMe*

Columns describe direction cosines and origins of the orthonormal axes relative to another orthonormal axial system. Systems 3 and 6 are relative to the standard orthonormal crystal axes.

	MeCl				ClMe			
$Q = 1$								
-0.9996	0.0280	0.0096	6.307	-0.9997	-0.0245	-0.0084	6.349	
-0.0276	-0.9991	0.0311	0.416	0.0245	-0.9997	0.0002	0.393	
0.0105	0.0308	0.9995	0.057	-0.0084	-0.0000	1.0000	0.182	
$Q = 2$								
0.9996	0.0273	-0.0113	-6.086	0.9997	-0.0245	0.0084	-6.059	
-0.0277	0.9991	-0.0306	-0.422	0.0245	0.9997	0.0002	-0.455	
0.0104	0.0309	0.9995	-0.300	-0.0084	0.0001	1.0000	-0.211	
$P = 3$								
-0.5026	0.7396	-0.4477	1.884	-0.5052	0.7304	-0.4596	1.896	
-0.1106	0.4586	0.8817	3.711	-0.1147	0.4710	0.8747	3.706	
0.8574	0.4926	-0.1487	6.766	0.8553	0.4946	-0.1542	6.779	
$Q = 4$								
-0.9997	0.0203	-0.0126	6.317	-0.9994	-0.0168	0.0296	6.289	
-0.0203	-0.9998	0.0012	0.436	0.0168	-0.9999	-0.0006	0.449	
-0.0126	0.0014	0.9999	0.389	0.0296	-0.0001	0.9996	0.165	
$Q = 5$								
0.9997	0.0201	0.0124	-6.075	0.9994	-0.0168	-0.0296	-6.117	
-0.0201	0.9998	-0.0015	-0.384	0.0168	0.9999	-0.0006	-0.416	
-0.0124	0.0012	0.9999	-0.020	0.0296	0.0001	0.9996	-0.157	
$P = 6$								
-0.3485	0.8426	-0.4106	1.884	-0.3329	0.8628	-0.3805	1.896	
-0.0276	0.4287	0.9030	3.711	-0.0227	0.3961	0.9179	3.706	
0.9369	0.3260	-0.1261	6.766	0.9427	0.3142	-0.1123	6.779	

Table 3. *Fractional coordinates and U_{eq} (\AA^2) for MeCl and ClMe*

	MeCl				ClMe			
	x	y	z	U_{eq}	x	y	z	U_{eq}
Cl1	0.1685 (7)	0.4384 (6)	0.4571 (1)	0.093 (2)	0.1476 (8)	0.4482 (9)	0.9128 (3)	0.104 (2)
Cl4	0.2644 (6)	0.4630 (5)	0.4021 (2)	0.060 (1)	0.2600 (9)	0.4757 (10)	0.8064 (6)	0.076 (1)
Cl5	0.1359 (8)	0.4035 (10)	0.3581 (2)	0.056 (1)	0.1461 (12)	0.4116 (11)	0.7170 (6)	0.066 (1)
Cl6	0.2129 (9)	0.4233 (11)	0.3140 (1)	0.047 (1)	0.2366 (15)	0.4337 (14)	0.6314 (6)	0.054 (1)
Cl11	0.4221 (7)	0.5034 (7)	0.3118 (2)	0.043 (1)	0.4433 (16)	0.5205 (16)	0.6328 (6)	0.051 (1)
Cl12	0.5506 (8)	0.5629 (10)	0.3557 (2)	0.047 (1)	0.5571 (13)	0.5847 (15)	0.7222 (6)	0.060 (1)
Cl13	0.4736 (8)	0.5432 (10)	0.3999 (2)	0.055 (1)	0.4667 (10)	0.5626 (12)	0.8078 (6)	0.073 (1)
N1	0.5263 (9)	0.5263 (9)	0.2693 (2)	0.052 (1)				
C1					0.5394 (24)	0.5409 (20)	0.5425 (10)	0.047 (1)
C27	0.8366 (11)	0.5289 (9)	0.0512 (2)	0.076 (3)	0.8286 (16)	0.5400 (15)	0.1035 (7)	0.078 (3)
C24	0.7377 (8)	0.5057 (7)	0.0981 (2)	0.057 (2)	0.7412 (14)	0.5173 (12)	0.2007 (6)	0.054 (1)
C25	0.8497 (8)	0.5723 (9)	0.1430 (2)	0.057 (2)	0.8643 (16)	0.5832 (14)	0.2879 (7)	0.060 (1)
C26	0.7600 (8)	0.5513 (9)	0.1855 (2)	0.050 (2)	0.7849 (22)	0.5626 (17)	0.3762 (6)	0.061 (1)
C21	0.5541 (7)	0.4627 (7)	0.1853 (2)	0.045 (2)	0.5802 (23)	0.4756 (17)	0.3798 (6)	0.054 (1)
C22	0.4421 (9)	0.3961 (10)	0.1404 (2)	0.055 (2)	0.4572 (18)	0.4098 (15)	0.2927 (7)	0.056 (1)
C23	0.5317 (9)	0.4171 (9)	0.0979 (2)	0.061 (2)	0.5365 (14)	0.4304 (12)	0.2043 (6)	0.057 (1)
C2	0.4573 (12)	0.4401 (11)	0.2300 (3)	0.050 (2)				
N2					0.4741 (28)	0.4522 (20)	0.4645 (10)	0.076 (2)
Cl11'	0.1985 (22)	0.4987 (18)	0.4616 (3)	0.109 (4)	0.2293 (16)	0.4772 (23)	0.9255 (5)	0.115 (4)
Cl14'	0.2614 (18)	0.5044 (16)	0.4031 (4)	0.064 (2)	0.2735 (15)	0.4871 (18)	0.8053 (8)	0.078 (3)
Cl15'	0.4661 (25)	0.5759 (29)	0.3937 (4)	0.065 (3)	0.4752 (17)	0.5552 (20)	0.7819 (9)	0.071 (2)
Cl16'	0.5165 (25)	0.5805 (32)	0.3468 (4)	0.055 (3)	0.5108 (20)	0.5632 (22)	0.6852 (10)	0.053 (2)
Cl11'	0.3647 (20)	0.5138 (23)	0.3070 (3)	0.044 (3)	0.3457 (22)	0.5034 (21)	0.6092 (9)	0.043 (2)
Cl12'	0.1600 (19)	0.4423 (26)	0.3164 (3)	0.039 (3)	0.1440 (21)	0.4354 (21)	0.6326 (8)	0.048 (2)
Cl13'	0.1095 (18)	0.4377 (24)	0.3633 (4)	0.048 (3)	0.1084 (17)	0.4274 (20)	0.7293 (8)	0.064 (3)
N1'	0.3978 (23)	0.5035 (28)	0.2571 (4)	0.060 (3)				
C1'					0.3857 (31)	0.5096 (28)	0.5075 (11)	0.037 (2)
C27'	0.7590 (29)	0.5423 (28)	0.0444 (4)	0.080 (10)	0.7599 (35)	0.5215 (30)	0.0856 (9)	0.074 (6)
C24'	0.7152 (24)	0.5362 (21)	0.0971 (4)	0.053 (5)	0.7069 (30)	0.5211 (23)	0.1901 (9)	0.048 (3)
C25'	0.5144 (27)	0.4644 (35)	0.1086 (4)	0.077 (7)	0.5000 (30)	0.4571 (22)	0.2098 (10)	0.057 (3)
C26'	0.4747 (26)	0.4589 (36)	0.1563 (4)	0.054 (5)	0.4518 (30)	0.4567 (20)	0.3047 (11)	0.054 (3)
C21'	0.6340 (21)	0.5248 (24)	0.1949 (4)	0.044 (5)	0.6093 (32)	0.5203 (20)	0.3826 (10)	0.041 (3)
C22'	0.8349 (26)	0.5966 (32)	0.1835 (4)	0.075 (7)	0.8162 (31)	0.5843 (23)	0.3629 (9)	0.050 (3)
C23'	0.8746 (27)	0.6021 (30)	0.1357 (5)	0.061 (7)	0.8644 (30)	0.5847 (24)	0.2680 (10)	0.054 (3)
C2'	0.5937 (24)	0.5201 (34)	0.2455 (4)	0.061 (5)				
N2'					0.5785 (33)	0.5350 (21)	0.4827 (11)	0.058 (4)

$U_{eq} = (U_{11} + U_{22} + U_{33})/3$ for U_{ij} defined relative to orthonormal crystal axes.

Table 4. Axial systems for four sets of LX thermal parameters for MeCl and ClMe defined relative to standard orthonormal crystal axes

Column values describe the direction cosines of libration axes. At the top of each column values of L_{11} , L_{22} and L_{33} (10^4 radians²) are given.

MeCl			ClMe				
Atoms 1–8 plus attached H							
29 (3)	45 (2)	56 (4)		13 (2)	33 (1)	21 (1)	
0.2228	-0.9329	-0.2828	0.998	-0.0856	-0.9962	-0.0133	1.802
0.7964	0.0070	0.6047	3.642	0.5809	-0.0608	0.8117	3.573
-0.5622	-0.3600	0.7446	8.747	-0.8094	0.0618	0.5839	7.013
Atoms 9–16 plus attached H							
12 (3)	40 (4)	120 (17)		69 (6)	33 (7)	167 (14)	
-0.7369	-0.2931	0.6092	2.350	-0.5037	-0.5950	0.6264	3.027
-0.4204	0.9034	-0.0735	4.049	-0.8225	0.5512	-0.1370	3.891
-0.5293	-0.3103	-0.7896	4.977	-0.2642	-0.5842	-0.7674	3.924
Atoms 17–24 plus attached H							
10 (8)	73 (15)	105 (8)		22 (2)	15 (6)	48 (3)	
-0.6908	0.3378	0.6393	-0.248	-0.0560	0.1219	0.9910	1.307
0.6243	-0.1672	0.7630	2.863	0.9218	-0.3751	0.0983	3.345
0.3647	0.9262	-0.0954	8.680	0.3837	0.9190	-0.0913	6.775
Atoms 25–32 plus attached H							
0 (8)	37 (13)	521 (77)		27 (12)	52 (11)	267 (34)	
-0.7279	-0.3271	0.6026	2.568	-0.7949	0.4245	0.4335	3.386
-0.2729	0.9445	0.1830	3.597	0.3001	0.8961	-0.3272	3.668
-0.6290	-0.0312	-0.7768	5.066	-0.5273	-0.1300	-0.8396	4.091

Table 5. Bond lengths (Å) and angles (°) for MeCl and ClMe

	MeCl	ClMe		MeCl	ClMe
C11—C14	1.705 (5)	1.714 (9)	C27—C24	1.510 (7)	1.518 (10)
C14—C15	1.392 (2)	1.389 (1)	C24—C25	1.392 (2)	1.389 (1)
C15—C16	1.369 (3)	1.379 (2)	C25—C26	1.369 (3)	1.379 (2)
C16—C11	1.393 (2)	1.389 (1)	C26—C21	1.393 (2)	1.389 (1)
C11—C12	1.393 (2)	1.389 (1)	C21—C22	1.393 (2)	1.389 (1)
C14—C13	1.392 (2)	1.389 (1)	C24—C23	1.392 (2)	1.389 (1)
C12—C13	1.369 (3)	1.379 (2)	C22—C23	1.369 (3)	1.379 (2)
C11—N1	1.415 (7)		C21—C2	1.446 (8)	
C11—C1		1.455 (13)	C21—N2		1.420 (12)
N1—C2	1.265 (5)		C1—N2		1.265 (—)
	MeCl	ClMe		MeCl	ClMe
C11—C14—C15	121.0 (1)	120.6 (1)	C27—C24—C25	121.0 (1)	120.6 (1)
C11—C14—C13	121.0 (1)	120.6 (1)	C27—C24—C23	121.0 (1)	120.6 (1)
C15—C14—C13	118.1 (2)	118.7 (1)	C25—C24—C23	118.1 (2)	118.7 (1)
C14—C15—C16	121.0 (1)	120.6 (1)	C24—C25—C26	121.0 (1)	120.6 (1)
C15—C16—C11	121.0 (1)	120.7 (1)	C25—C26—C21	121.0 (1)	120.7 (1)
C16—C11—C12	118.0 (2)	118.7 (1)	C26—C21—C22	118.0 (2)	118.7 (1)
C11—C12—C13	121.0 (1)	120.7 (1)	C21—C22—C23	121.0 (1)	120.7 (1)
C14—C13—C12	121.0 (1)	120.6 (1)	C24—C23—C22	121.0 (1)	120.6 (1)
C16—C11—N1	127.1 (3)		C26—C21—C2	121.5 (3)	
C16—C11—C1		120.4 (3)	C26—C21—N2		126.6 (3)
C12—C11—N1	114.9 (3)		C22—C21—C2	120.5 (3)	
C12—C11—C1		120.9 (3)	C22—C21—N2		114.7 (3)
C11—N1—C2	121.0 (4)		N1—C2—C21	123.0 (5)	
C11—C1—N2		123.9 (4)	C1—N2—C21		120.8 (4)
	MeCl				
C11—N1—C2—C21	178.2 (6)		C11'—N1'—C2'—C21'	-175.0 (9)	
C2—N1—C11—C16	-15.2 (7)		C2—N1—C11—C12	162.3 (5)	
N1—C2—C21—C26	14.0 (7)		N1—C2—C21—C22	-165.8 (5)	
C2'—N1'—C11'—C16'	15.5 (12)		C2'—N1'—C11'—C12'	-162.0 (12)	
N1'—C2'—C21'—C26'	-19.5 (16)		N1'—C2'—C21'—C22'	160.3 (15)	
	ClMe				
C11—C1—N2—C21	-178.2 (7)		C11'—C1'—N2'—C21'	173.2 (7)	
N2—C1—C11—C16	-15.8 (5)		N2—C1—C11—C12	163.2 (4)	
C1—N2—C21—C26	13.7 (6)		C1—N2—C21—C22	-163.4 (4)	
N2'—C1'—C11'—C16'	13.8 (12)		N2'—C1'—C11'—C12'	-165.2 (11)	
C1'—N2'—C21'—C26'	-8.8 (11)		C1'—N2'—C21'—C22'	168.3 (10)	

the same layer are given in Table 6. Adjacent layers are related by an inversion centre so the structure (see Fig. 4) can be described as a pseudo-hexagonal close packing of columns parallel to $-2a + c$. Table 7 gives contact distances involving Cl and Me atoms between adjacent molecules in such columns.

Discussion and comparison of the structures

The molecular geometry obtained is in good agreement with expectation, the only truly reliable structure for comparison being that of the second form of MeMe (Bar & Bernstein, 1977). The MeCl and ClMe molecules have local coordinates that agree within standard deviation, except for the $-\text{CH}=\text{N}-$ connection where the C and N atoms interchange to switch from MeCl to ClMe. From Table 5 we see that the C11—N1 and C21—C2 bonds of MeCl are consistent with the C21—N2 and C11—C1 bonds of ClMe and the corresponding distances of 1.411 (4) and 1.456 (4) Å for MeMe. The local Y and Z coordinates of the C atom of the $-\text{CH}=\text{N}-$ connections show a much larger displacement from local fragment $mm2$ symmetry values of 0.0 Å than does the

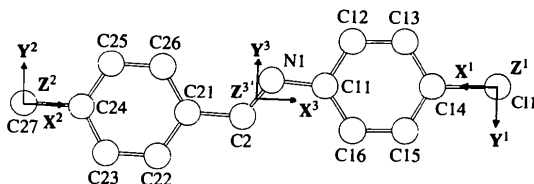


Fig. 1. The atom labelling and local axial systems used for the reference MeCl molecule. In the prototype the origins of systems (1) and (2) are inversion-related through the origin of system (3). The X^2, Y^2, Z^2 axes parallel the X^3, Y^3, Z^3 axes and the X^1, Y^1, Z^1 directions are twofold rotation-related about Z^3 to the X^2, Y^2, Z^2 directions. For the ClMe molecule, C1 and N2 atoms replace N1 and C2.

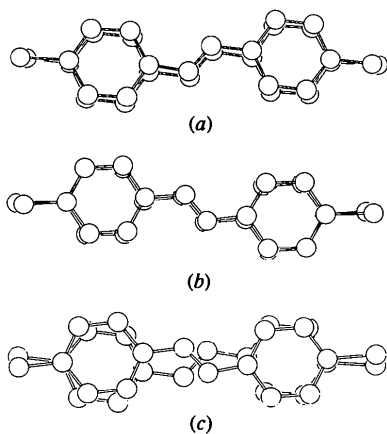


Fig. 2. The relative positions of different orientations of the MeCl molecules: (a) inversion-related molecules of the major component; (b) inversion-related molecules of the pseudo-mirror-related component; (c) the major component and the pseudo-mirror-related component.

N atom. This is because of a repulsion between the H atom and an H atom from the aniline ring, *i.e.* H atoms attached to C2 and C16 (MeCl), C1 and C26 (ClMe). The components of the 0.15 Å displacement, seen for both structures, are consistent with a mutual repulsion. The signs of local coordinates are related to the directions of the local axial systems. This results in differences of 12.2 (6) (MeCl) and 11.9 (6)° (ClMe) between the two angles subtended by the C atom to the benzylidene ring. The differences in Z coordinates of the origins of the axial systems (1) and (2) (and

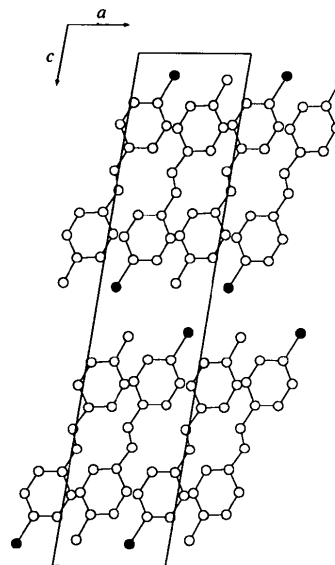


Fig. 3. A projection down b of the MeCl structure only including the molecules associated with the occupancy 0.543. Cl atoms are filled in to distinguish them from methyl C atoms. The reference molecule lies about a pseudo-inversion centre at $\frac{1}{2}, \frac{1}{2}, \frac{1}{4}$. Three other orientations of lesser occupancy also occur at this site. The space group $P2_1/n$ describes an average structure that contains four molecules per unit cell.

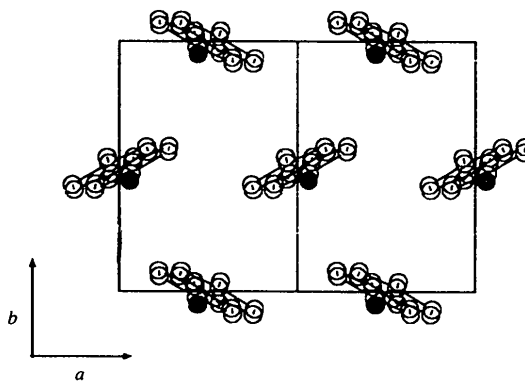


Fig. 4. A projection down $2a + c$ of the MeCl structure showing only one layer of the major component. Four adjacent molecules are related by screw axis operations, the other two by translations parallel to a . Cl atoms are filled in to distinguish them from methyl C atoms. An adjacent layer is related by an inversion through a unit-cell origin.

Table 6. Shortest contacts between phenyl-ring C atoms of molecules adjacent in a layer perpendicular to c^* and related by a 2_1 screw axis

Values are differences in Å from 3.6 Å, entries marked > have no contacts less than 4.0 Å

MeCl		A'		B'		C'		D'	
Position	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)	
Ring	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)	
Position A	0.00	-0.03	-0.16	-0.25	-0.18	-0.29	0.04	0.00	
Position B	0.29	0.17	0.07	0.01	0.03	0.00	0.32	0.22	
Position C	0.13	>	-0.01	0.23	-0.03	0.18	0.18	>	
Position D	0.26	-0.08	0.05	-0.27	0.00	-0.27	0.31	-0.06	

Pseudo-equivalent positions A, B, C and D for MeCl centred at $\frac{1}{2}, \frac{1}{2}, \frac{1}{4}; x, y, z; 1-x, 1-y, \frac{1}{2}-z; x', y', z'; 1-x', 1-y', \frac{1}{2}-z'$. Pseudo-equivalent positions A', B', C' and D' for MeCl centred at 0, 0, $\frac{1}{4}; \frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z; -\frac{1}{2}+x, \frac{1}{2}-y, z; \frac{1}{2}-x', -\frac{1}{2}+y', \frac{1}{2}-z'$; $-\frac{1}{2}+x', \frac{1}{2}-y', z'$. (1) refers to the ring with p -Cl and (2) refers to the ring with p -Me for A', B', C' and D'.

ClMe		A'		B'		C'		D'	
Position	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)	
Ring	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)	
Position A	0.08	0.05	-0.06	-0.04	-0.19	-0.02	0.01	0.12	
Position B	0.01	0.08	-0.07	-0.06	-0.06	-0.17	0.08	0.04	
Position C	0.07	0.29	-0.03	0.23	-0.19	0.23	0.09	0.36	
Position D	0.26	0.04	0.20	-0.07	0.20	-0.20	0.34	0.06	

Pseudo-equivalent positions A, B, C and D for ClMe centred at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}; x, y, z; 1-x, 1-y, 1-z; x', y', z'; 1-x', 1-y', 1-z'$. Pseudo-equivalent positions A', B', C' and D' for ClMe centred at 0, 0, $\frac{1}{2}; \frac{1}{2}-x, -\frac{1}{2}+y, 1-z; -\frac{1}{2}+x, \frac{1}{2}-y, z; \frac{1}{2}-x', -\frac{1}{2}+y', 1-z'$; $-\frac{1}{2}+x', \frac{1}{2}-y', z'$. (1) refers to the ring with p -Cl and (2) refers to the ring with p -Me for A', B', C' and D'.

Table 7. Intermolecular contacts (Å) between adjacent molecules in columns parallel to $-a + \frac{1}{2}c(\text{MeCl})$ or $-a + c(\text{ClMe})$

	MeCl	ClMe		MeCl	ClMe
C11...C11 ⁱ	3.455 (6)	3.282 (7)	C27—27 ⁱⁱ	3.689 (12)	3.804 (18)
C11...C27 ⁱⁱⁱ	3.765 (12)	3.609 (14)	C27—C11 ^{iv}	3.527 (9)	3.711 (11)
C11...C11 ⁱ	3.399 (8)	3.448 (7)	C27—C27 ⁱⁱ	3.872 (15)	3.874 (19)
C11...C27 ⁱⁱⁱ	3.559 (6)	3.540 (8)	C11'—C27 ⁱⁱⁱ	3.747 (14)	3.841 (13)
C11'—C11 ⁱ	3.412 (18)	3.685 (15)	C27'—C27 ⁱⁱ	4.103 (26)	3.998 (30)

Symmetry codes: MeCl: (i) $-x, 1-y, 1-z$; (ii) $2-x, 1-y, -z$; (iii) $-1+x, y, \frac{1}{2}+z$; (iv) $1+x, y, -\frac{1}{2}+z$. ClMe: (i) $-x, 1-y, 2-z$; (ii) $2-x, 1-y, -z$; (iii) $-1+x, y, 1+z$; (iv) $1+x, y, -1+z$.

3 and 4 for the pseudo-mirror-related molecule) show that the rings are not coplanar, again consistent with this repulsion. Values are 0.393 (7) and 0.409 (20) Å for MeCl and 0.357 (13) and 0.322 (20) Å for ClMe. The other feature associated with the repulsion is a bending of the molecule, as is seen by the non-parallelism of the local axial systems describing the halves of the molecules that are pseudo-inversion-related. MeCl shows opposite signs for the deviations from parallelism for the rings compared with ClMe, consistent with the deviations being induced by a repulsion involving an atom that is on ring (2) for MeCl and ring (1) for ClMe. The bending of the mirror-related molecules is consistent with the above description.

The major consequence of these distortions is that intermolecular contacts are quite different for the two structures. The shortest contacts between phenyl-ring C atoms on molecules at 2_1 related sites at $\frac{1}{2}, \frac{1}{2}, z$ and $0, 0, z$, $z = \frac{1}{4}$ (MeCl) or $\frac{1}{2}$ (ClMe) are given in Table 6. Contacts between molecules at $\frac{1}{2}, \frac{1}{2}, z$ and $0, 1, z$ or $1, 0, z$ or $1, 1, z$ are

symmetry-related distances. Contacts between molecules at $0, 1, z$ and $\frac{1}{2}, \frac{1}{2}, z$ are related by a 2_1 screw-axis, contacts between molecules at $\frac{1}{2}, \frac{1}{2}, z$ and $1, 1, z$ are related by inversion and contacts between molecules at $1, 0, z$ and $\frac{1}{2}, \frac{1}{2}, z$ are related by an a -glide.

In contrast, there are very few short intermolecular contacts between molecules on sites related by a translation of $+a$, there being just three/four (MeCl/ClMe) values of contact distances less than 3.6 Å, viz. 3.44/3.46 Å for a contact between molecules in orientations A and C, 3.51/3.56 Å for a contact between molecules in orientations A and D, and 3.55/(3.39 and 3.45 Å) for a contact between molecules in orientations D and C. The second molecule is translated by a relative to the first (see Appendix 2 for a description of A, B, C and D). Contacts between layers also occur but it is felt that these contacts do not determine the ordering in a layer perpendicular to c^* , see later.

The observed occupancies for MeCl are not too different from the ratio 0.543:0.215:0.069:0.173 that would

result from making the $B:C$ ratio equal that for $A:D$. From Table 6 it is seen that for molecules adjacent to the 2_1 screw axis relating $\frac{1}{2}, \frac{1}{2}, \frac{1}{4}$ to $0, 0, \frac{1}{4}$, contacts are too small for A or D to B' or C' compared with A or D to A' or D' . It is therefore reasonable to assume that if we start with molecule A , then B, C, B' or C' will not occur next to this screw axis. For the adjacent screw axis relating $\frac{1}{2}, \frac{1}{2}, \frac{1}{4}$ to $1, 1, \frac{1}{4}$, we are looking at an inversion-related environment. Thus, A, B, C, D, A', B', C' and D' are transformed into B, A, D, C, B', A', D' and C' , in order to use Table 6. The table shows that no contacts from B or C are too short, but contacts to A' and D' are possibly too long. A layer that excludes B and C would only have molecules of a single hand, A being related to D by an approximate local twofold rotation. Adjacent layers are inversion-related.

For ClMe contact distances within a layer are more confused. Contacts from A and D to C' are still quite short, but contacts to B' are acceptable. Contacts from B and C to C' are now too short, while those to A' and D' are not as long. These observations suggests that layers of MeCl should be dominantly A and D or B and C , but this is probably not so for ClMe.

The only significant contacts between layers are given in Table 7, between adjacent molecules in columns parallel to $-a + c/2$ for MeCl ($-a + c$ for ClMe). The first row gives the distances for an ordered $P2_1/n$ structure involving only the main component. The second row gives the additional major to minor component contacts associated with introducing reoriented molecules, so that alternate layers contain molecules A and D in odd layers and molecules B and C in even layers. The sum of the contact distances in a row increases by 0.15 \AA for MeCl and 0.23 \AA for ClMe. This clearly shows that the alternative orientation allows the density of the crystal to increase by shortening the average repeat along the column direction. The magnitude of this vector is 15.804 \AA for MeCl and 15.818 \AA for ClMe. The minor component–minor component contacts are given in line 5 of Table 7 and indicate an unfavourably long contact for $C27'—C27'b$. Lines 3 and 4 give contact distances should further disordering possibly occur. For MeCl this introduces the shortest interlayer contact, but for ClMe it allows a way of avoiding the shortest interlayer contact.

Concluding remarks

The refined structural parameters obtained from the constrained refinement of the fourfold disordered structures, using parameters chosen for their chemical significance, has allowed useful structural information to be obtained, even when l odd reflections were unobserved, as was the case for ClMe. We believe that the structural features described are typical of all crystals of these compounds, in particular the disordering in layers perpendicular to c^* . We associate the observation of the extra weak

reflections for the MeCl structure with the ability of this structure (in contrast to the ClMe structure) to form individual layers, which predominantly use only two of the four molecular orientations available per site, and so do not contain an inversion centre when averaged using the lattice translations $ma + nb$. A stacking fault corresponding to a translation of $1/2c$ (i.e. an adjacent 'average layer' is translation-related rather than inversion-related) reduces the intensity of the l odd reflections and could explain the occupancy for the other two orientations. It is hoped that this knowledge of the average structure will lead us to a better understanding of the diffuse scattering associated with the local variations away from this average structure.

Appendix 1. Local axial systems

The program *RAELS92* (Rae, 1992) was used to describe and refine the MeCl and ClMe structures. This program uses ideas espoused by Rae (1975) to allow an atom position (described using *orthonormal crystal coordinates* relative to a standard reference set of *orthonormal crystal axes*, centred at the unit cell origin and parallel to $a, c^* \times a, c^*$) to be defined using five integers (N, M, P, R and Q). The orthonormal crystal coordinates of atom number N in the asymmetric unit of a crystal is obtained from entry number M in a list of local coordinates via three sequential transformations identified by integers P, R and Q . The same values for M, P, R or Q can appear in more than one recipe. Equal object constraints simply require the use of the same set of M values for different sets of P, R and Q . If P, R or Q is zero then no axis transformation is made for this step in the sequence. If M is zero, atom N is then described using only crystal coordinates. Thus

$$X(N)_i = T(P)_i + \sum_j U(P)_{ij} \sum_k V(R)_{jk} [T(Q)_k + \sum_l U(Q)_{kl} S(M)_l]. \quad (1)$$

The P th rotation–translation transformation $[U(P), T(P)]$ defines the orthonormal crystal coordinates of an object developed relative to the P axial system in the asymmetric unit of the unit cell by the R and Q transformations. The transformation is defined by the coordinates $T(P)_i$, $i = 1-3$, of the origin and the direction cosines $U(P)_{ij}$, $i = 1-3$, of the axes, $j = 1-3$, described relative to the standard orthonormal crystal axes defined above. Subsequent least-squares refinement of this axial system updates $[U(P), T(P)]$ using rotational increments $\epsilon_1(P)$, $\epsilon_2(P)$, $\epsilon_3(P)$ about the existing axis directions of the P axial system. This corresponds to a rotation by $\epsilon = [\epsilon_1(P)^2 + \epsilon_2(P)^2 + \epsilon_3(P)^2]^{1/2}$ radians about an axis that passes through the origin of the P axial system with direction cosines $l, m, n = \epsilon_1(P)/\epsilon, \epsilon_2(P)/\epsilon, \epsilon_3(P)/\epsilon$ relative to the initial position of the P axial system, i.e. the matrix

$$\begin{pmatrix} l^2(1-c) + c & lm(1-c) - ns & ln(1-c) + ms \\ lm(1-c) + ns & m^2(1-c) + c & mn(1-c) - ls \\ ln(1-c) - ms & mn(1-c) + ls & n^2(1-c) + c \end{pmatrix}$$

where $c = \cos \epsilon$, $s = \sin \epsilon$. The R transformation $\mathbf{V}(R)$ is a point symmetry operation defined relative to the P axial system. It locates an equivalent position $\sum_k \mathbf{V}(R)_{jk} s_k$, $j = 1-3$, of an object described in local coordinates, $s_k = [T(Q)_k + \sum_i U(Q)_{ki} S(M)_i]$, $k = 1-3$, relative to the P axial system by the Q th rotation-translation transformation $[U(Q), T(Q)]$. Unlike the P and Q transformations, which are refineable and define right-handed axial systems, the R transformation is fixed and may be either a rotation or a rotation inversion. $[U(Q), T(Q)]$ locates an object developed relative to the Q axial system in the space of the P axial system. It is defined by the coordinates $T(Q)_k$, $k = 1-3$, of the origin and the direction cosines $U(Q)_{ki}$, $k = 1-3$ of the axes, $l = 1-3$, described relative to the P axial system.

Appendix 2. Application of constraints

The structure of MeCl was described in $P2_1/n$ using four orientations about $\frac{1}{2}, \frac{1}{2}, \frac{1}{4}$ to describe the asymmetric unit. Axial systems are given in Table 2. The non-H atoms for each of the molecules A, B, C and D were described by the following recipes (see Appendix 1) for N, M, P, R and Q .

- A $[(N = M, M = 1 - 8, 3, 0, 1);$
 $(N = M, M = 9 - 16, 3, 0, 2)]$
- B $[(N = M + 32, M = 1 - 8, 7, 1, 1);$
 $(N = M + 32, M = 9 - 16, 7, 1, 2)]$
- C $[(N = M + 16, M = 1 - 8, 6, 2, 4);$
 $(N = M + 16, M = 9 - 16, 6, 2, 5)]$
- D $[(N = M + 48, M = 1 - 8, 8, 3, 4);$
 $(N = M + 48, M = 9 - 16, 8, 3, 5)],$

where $R = 1, 2, 3$ correspond to local equivalent positional operations $-x, -y, -z; x, -y, z; -x, y, -z$, respectively. The fractional coordinates for the atoms $N = 1-32$ are given in Table 3. The prototype molecule was considered to be made up of two halves, each of local $2mm$ symmetry, with atom positions for the two halves related by an inversion through the origin of the $P = 3$ axial system, the axes of which are aligned with the symmetry axes of the local $2mm$ symmetry of each half of the molecule. Only atom type breaks the inversion symmetry in the prototype. The $Q = 1$ axial system is centred on the Cl1 atom and the $Q = 2$ axial system is centred on C27. The $Q = 2$ axes are parallel to the $P = 3$ axes and the $Q = 1$ axes are twofold rotation-related to the $Q = 2$ axes (see Fig. 1). The origins of the axial systems (1) and (2) are inversion-related through the

origin of axial system (3). Refinement allowed these initial conditions to be relaxed.

Since (1) in Appendix 1 is an equality, the program is capable of evaluating an initial estimate of one of the following four components of atom description, given the values for the other three [see Rae (1976)]. The four components are (i) the atom coordinates $X(N)_i$, (ii) the P th axial system, (iii) the Q th axial system or (iv) the local coordinates $S(M)_1$. The program is capable of editing before structure-factor computation and an instruction to proceed with 1 cycle of the least-squares calculations results in parameter file editing, with the listing of resulting parameters being the only output.

The program automatically changes fractional coordinates to orthonormal crystal coordinates and renormalizes axial systems whenever this information is input, singular matrices being replaced by unit matrices. Thus, after an initial pass to obtain orthonormal crystal coordinates, and hence approximate vectors, the input of approximate non-normalized vectors \mathbf{X}, \mathbf{Y} (and \mathbf{Z}) will automatically be replaced with orthonormal vectors parallel to $\mathbf{X}, (\mathbf{X} \times \mathbf{Y}) \times \mathbf{X}$ and $(\mathbf{X} \times \mathbf{Y})$. Thus, the $P = 3$ axial system for MeCl could be centred at the fractional coordinates $\frac{1}{2}, \frac{1}{2}, \frac{1}{4}$, and the $Q = 1$ (likewise $Q = 2$) axial system located by fitting an idealized structure fragment fitting $S(M)_1$ coordinates to an initial set of crystal coordinates $X(N)_i$. Options are available in this step. A weight per atom is supplied, and a dubious atom can be given zero weight, located anywhere, then correctly inserted using the appropriate local coordinates. The crystal coordinates $X(N)_i$ of an atom used in the fitting process can be either replaced or not by the description implied from the fitting process. The transformation that best fits local coordinates $S(M)_1$ to crystal coordinates $X(N)_i$ can occur constraining either the weighted mean position or a designated atom to be coincident. If the axial systems and crystal coordinates are known, then subsidiary coordinates $S(M)_1$ can be obtained from specifying recipes (N, M, P, R and Q). Subsidiary coordinates can be idealized, e.g. local symmetry can be imposed by file editing.

Molecules A (and D) were related to molecules B (and C) by an exact local inversion centre by keeping the axial system $P = 7$ identical to $P = 3$, and $P = 8$ identical to $P = 6$ with their origins fixed at fractional coordinates $\frac{1}{2}, \frac{1}{2}, \frac{1}{4}$. This constraint was never relaxed. Local coordinates were constrained to have $mm2$ symmetry for the first 7 of 8 atoms in each of the two segments, allowing only the atoms of the $-\text{CH}=\text{N}-$ linkage to show the effects of $\text{H} \cdots \text{H}$ repulsion. Values in Table 1 with the same magnitude were constrained to hold the implied relationships exactly. Quoted errors in Table 1 are standard deviations in mean coordinates, excluding any error associated with the appropriateness of the constraints or restraints. The use of restraints, corresponding to 4 degrees of freedom, caused the two

six-membered C-atom rings to approach a common geometry. This left just 11 unrestrained degrees of freedom in the description of the local coordinates.

The axis of the pseudo- $2/m$ disordering was refined by allowing the orientations of axis systems $P = 3$ and 6 to refine independently. The rotational adjustments of axis systems $Q = 1$ and 2 covary with the rotational adjustments of axis system $P = 3$ and the rotational adjustments of axis systems $Q = 4$ and 5 covary with the rotational adjustments of axis system $P = 6$. It is necessary to impose rotational constraints $\epsilon_1(1) = \epsilon_1(2)$, $\epsilon_2(1) = \epsilon_2(2)$, $\epsilon_3(1) = -\epsilon_3(2)$ and $\epsilon_1(4) = \epsilon_1(5)$, $\epsilon_2(4) = \epsilon_2(5)$, $\epsilon_3(4) = -\epsilon_3(5)$ to remove the redundant degrees of freedom. Non-zero values correspond to distortions that misalign the ring systems. The origin shifts for axial systems $Q = 1, 2$ (and 4, 5) control the positions of the molecules and the $-\text{CH}=\text{N}-$ linkages between the halves of each molecule. The two angles and one distance of this linkage were restrained to be the same for each molecule by restraining distance differences between molecules to approach zero. Thus, 24 rotation-translation degrees of freedom effectively reduce to 21. For ClMe, the effective degrees of freedom

were further reduced by restraining the $\text{CH}=\text{N}$ distance to be the same as for the MeCl structure and making $\epsilon_1(1) = \epsilon_1(2) = 0$ and $\epsilon_1(4) = \epsilon_1(5) = 0$.

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Electron Density Study by X-ray and Neutron Diffraction of an NLO Compound: *N*-(4-Nitrophenyl)-*L*-prolinol. Description of Quadratic Hyperpolarizability

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Abstract

The study of the electron density and the determination of the dipolar moment of the molecule in the crystalline compound *N*-(4-nitrophenyl)-*L*-prolinol have been completed using X-ray and neutron diffraction. The deformation maps and the calculations of the atomic net charges demonstrate the character of the donor-acceptor couple (DA) linked to the phenyl transmitter. The dipolar

molecular moments obtained by several methods have similar values, except the method of kappa refinement. The kappa refinement appears inadequate to solve the phase problem. Accurate knowledge of the first molecular moment reduces the ambiguity on the quadratic polarizability coefficient β , measured from electric field-induced second-harmonic generation (EFISHG). The coefficients of the cubic moment (third-order semi-invariant) of the electronic distribution in the crystal state are compared with those of the quadratic hyperpolariz-

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