

where the interaction between the substituent groups seems to be stronger.

The orientation of the methanesulfonamide group with respect to the benzene ring, deduced from the torsion angles reported in Table 2, is not different for the three derivatives; the position adopted by the SO<sub>2</sub> group with respect to the N(4) atom is comparable with the N lone pair bisecting the O—S—O angle.

Short N(4)⋯O(31) contacts [(I) N(4)⋯O(31) 2.847 (5), H(4)⋯O(31) 2.26 (5) Å, N(4)—H(4)⋯O(31) 125 (4)°; (III) N(4)⋯O(31) 2.610 (4), H(4)⋯O(31) 1.86 (5) Å, N(4)—H(4)⋯O(31) 137 (4)°] suggest the presence of an intramolecular hydrogen bond between the sulfonamide N and a sulfonyl O atom of the vicinal methanesulfonyl group.

The molecular packing is determined by hydrogen bonds of the type N—H⋯O [(I) N(4)⋯O(42<sup>i</sup>) 3.176 (5), H(4)⋯O(42<sup>i</sup>) 2.62 (4) Å, N(4)—H(4)⋯O(42<sup>i</sup>) 123 (4)°, (i) = 1 - x, 1 - y, 2 - z; (II) N(4)⋯O(32<sup>ii</sup>) 2.887 (4), H(4)⋯O(32<sup>ii</sup>) 2.01 (4) Å, N(4)—H(4)⋯O(32<sup>ii</sup>) 166 (4)°, (ii) =  $\frac{3}{2} - x, -y, -\frac{1}{2} +$

z]. Other contacts are consistent with van der Waals interactions.

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## Crystallographic Studies and Physicochemical Properties of $\pi$ -Electron Systems. 21. Structure of *N,N'*-Bis(*p*-chlorophenyl)formamidine

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**Abstract.** C<sub>13</sub>H<sub>10</sub>Cl<sub>2</sub>N<sub>2</sub>, *M<sub>r</sub>* = 265.0, monoclinic, *C2/c* or *Cc*, *a* = 11.450 (2), *b* = 22.992 (7), *c* = 9.720 (3) Å,  $\beta$  = 93.81 (2)°, *V* = 2553.2 Å<sup>3</sup>, *Z* = 8, *D<sub>x</sub>* = 1.378 g cm<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha)$  = 1.54178 Å,  $\mu$  = 42.37 cm<sup>-1</sup>, *F*(000) = 1088, *T* = 293 K, *R* = 0.0628, *wR* = 0.0687 for *C2/c*, for 1934 observed reflections. The crystal structure contains dimers of the title compound with two intermolecular N—H⋯N hydrogen bonds, 2.958 (3) Å, linking the two molecules in the dimer. The planes defining the amidine moieties in the dimer are inclined at a dihedral angle of 27.3 (2)°.

**Introduction.** Amidine derivatives have recently been extensively studied both chemically (Oszczapowicz & Ciszowski, 1987; Gilli & Bertolasi, 1979; Häfelinger, 1975) and crystallographically (Bellucci,

Bertolasi, Ferretti & Gilli, 1985; Norrestam, 1984*a,b*; Alcock, Barker & Kilner, 1988; Kratochvil, Ondracek, Krechl & Hasek, 1987; Ciszak, Gdaniec & Kosturkiewicz, 1987; Tykarska, Jaskólski & Kosturkiewicz, 1986*a,b*; Oszczapowicz, Tykarska, Jaskólski & Kosturkiewicz, 1986) to investigate their chemical (Shriner & Neumann, 1944; Schwenker & Bösl, 1969) and in particular biological (Grout, 1975) properties. One particular feature of some amidine derivatives is their tautomerism (Oszczapowicz & Ciszowski, 1987, 1989; Häfelinger, 1975) and this paper is a continuation of our studies (Anulewicz, Krygowski & Pniewska, 1987; Anulewicz, Krygowski, Jaroszevska-Manaj & Pniewska, 1989). Geometrical analysis of the amidine skeleton seems to be of great interest because of its dependence on the hydrogen bonding in dimers of formamidine

derivatives. Owing to ambiguity in space groups of the crystals of the title compound, *C2/c* and *Cc*, the crystallographic aspect becomes even more interesting.

**Experimental.** *N,N'*-Bis(*p*-chlorophenyl)formamidine (CDIF) was recrystallized from anhydrous ethanol. A crystal, dimensions 0.30 × 0.17 × 0.10 mm, was used with an Enraf-Nonius CAD-4 diffractometer. Unit-cell parameters were obtained from the least-squares refinement of 25 reflections in the range  $10 \leq 2\theta \leq 26^\circ$ . Intensities were collected using Cu *K*α radiation monochromated by graphite up to a  $\theta$  angle of  $70^\circ$  ( $h \leq 14$ ,  $k \leq 25$ ,  $-10 \leq l \leq 10$ ),  $\omega$ - $2\theta$  scan mode. Two standards monitored every 200 reflections, 3% variation. Of 2352 unique reflections ( $R_{\text{int}} = 0.0191$ ), 1934 were classified as observed on the basis of the criterion  $F_o \geq 3\sigma(F_o)$ . Intensities were corrected for Lorentz-polarization factors, and for absorption, using *DIFABS* (Walker & Stuart, 1983). Max., min. absorption correction 1.406, 0.562, average absorption correction 0.975. The structure was solved by routine application of *SHELX76* (Sheldrick, 1976) and *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) in space groups *C2/c* and *Cc*. Refinement was carried out by block-matrix least squares using *F*'s. All non-H atoms were refined anisotropically, atoms H(7) (I), H(7) (II), HN and HN' located from difference map and refined isotropically. The phenyl hydrogens were included at calculated positions, C—H = 1.08 Å, and allowed to ride on their parent atoms. Final  $R = 0.0628$ ,  $wR = 0.0687$ ,  $w = 4.0503[\sigma^2(F_o) + 0.000267(F_o)^2]^{-1}$  for *C2/c* and  $R = 0.0600$ ,  $wR = 0.0654$ ,  $w = 3.6097[\sigma^2(F_o) + 0.000263(F_o)^2]^{-1}$  for *Cc*, 22 and 11 reflections per parameter, respectively;  $(\Delta/\sigma)_{\text{max}} = 0.06$  and 0.07, respectively; residual density within max. +0.33, min. -0.53 and +0.23, -0.27 e Å<sup>-3</sup>, respectively for *C2/c* and *Cc*. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Atomic coordinates are given in Table 1\* for *C2/c* and significant bond lengths and angles in Table 2. Table 3 contains details of the least-squares planes. Two independent molecules of CDIF in an asymmetric unit form the dimer presented in Fig. 1.

**Discussion.** Analysis of the normalized structure factors calculated by *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), shows a distribution consistent with the centrosym-

Table 1. Final fractional coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters ( $\text{\AA}^2 \times 10^3$ ) with *e.s.d.*'s in parentheses

$$U_{\text{eq}} = (U_{11} + U_{22} + U_{33})/3.$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
<b>Molecule (I)</b>				
Cl(1)	2593 (1)	2398 (1)	6712 (3)	57 (3)
C(1)	1041 (3)	1617 (1)	10440 (3)	33 (8)
C(2)	1892 (30)	1321 (1)	9768 (4)	44 (10)
C(3)	2373 (3)	1558 (2)	8622 (4)	47 (10)
C(4)	2002 (30)	2096 (1)	8169 (3)	39 (10)
C(5)	1163 (3)	2395 (2)	8807 (4)	46 (10)
C(6)	669 (3)	2155 (2)	9944 (4)	43 (10)
N(1)	575 (2)	1340 (1)	11584 (3)	37 (7)
C(7)	0	1621 (2)	12500	35 (12)
H(7)	0	2059 (20)	12500	—
<b>Molecule (II)</b>				
Cl(1)	4712 (1)	-1159 (1)	9437 (2)	76 (5)
C(1)	1797 (3)	-229 (1)	11410 (3)	36 (8)
C(2)	2933 (3)	-52 (2)	11655 (4)	44 (10)
C(3)	3842 (3)	-335 (2)	11056 (4)	48 (11)
C(4)	3582 (3)	-803 (1)	10205 (4)	46 (11)
C(5)	2463 (3)	-985 (2)	9938 (4)	48 (11)
C(6)	1551 (3)	-695 (1)	10535 (4)	43 (10)
N(1)	892 (2)	75 (1)	12021 (3)	41 (8)
C(7)	0	-198 (2)	12500	42 (13)
H(7)	0	2059 (20)	12500	—
H(N1)	949 (60)	534 (28)	12042 (71)	—

Table 2. Bond lengths (Å) and angles (°)

	Molecule (I)	Molecule (II)
C(1)—C(2)	1.387 (5)	1.369 (5)
C(2)—C(3)	1.387 (5)	1.388 (5)
C(3)—C(4)	1.371 (5)	1.378 (5)
C(4)—C(5)	1.364 (5)	1.356 (5)
C(5)—C(6)	1.389 (5)	1.397 (5)
C(6)—C(1)	1.384 (4)	1.385 (4)
C(1)—N(1)	1.416 (4)	1.413 (4)
N(1)—C(7)	1.312 (4)	1.309 (3)
Cl(1)—C(4)	1.752 (3)	1.739 (4)
Cl(1)—C(4)—C(3)	119.3 (3)	119.2 (3)
Cl(1)—C(4)—C(5)	119.3 (3)	119.5 (3)
C(1)—C(2)—C(3)	120.1 (3)	121.2 (4)
C(2)—C(3)—C(4)	119.9 (4)	118.7 (3)
C(3)—C(4)—C(5)	121.5 (3)	121.3 (4)
C(4)—C(5)—C(6)	118.8 (3)	119.7 (4)
C(5)—C(6)—C(1)	120.9 (3)	119.8 (3)
C(6)—C(1)—C(2)	118.9 (3)	119.3 (3)
C(6)—C(1)—N(1)	117.5 (3)	121.0 (3)
C(2)—C(1)—N(1)	123.5 (3)	119.7 (3)
C(1)—N(1)—C(7)	122.9 (3)	121.6 (3)
N(1)—C(7)—N(2)	121.0 (4)	122.8 (4)

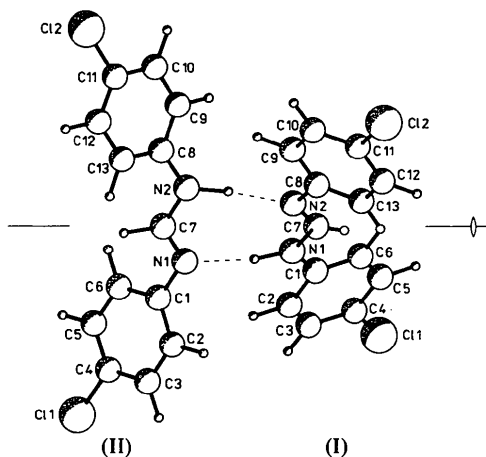
metric space group *C2/c* and refinement in this space group is satisfactory. There is, however, an inherent disadvantage in this refinement since the positions of the H atoms involved in intermolecular hydrogen bonding are constrained to belong to the same molecule of the asymmetric unit dimer by the crystallographic twofold axis. Chemical considerations (see Fig. 1) would indicate that each amidine group would have one H atom in an arrangement consistent with the noncentrosymmetric space group *Cc*. However, refinement in this latter space group gives an unacceptable variation in the bond lengths

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52958 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Deviations from mean planes (Å)

Starred atoms define planes; e.s.d.'s 0.004 Å.

Molecule (I)			
Plane 1			
C(1)*	0.005	C(5)*	0.002
C(2)*	0.001	C(6)*	0.007
C(3)*	0.008	Cl(1)	0.001
C(4)*	0.004		
Plane 2			
N(1); C(7); N(2)			
Molecule (II)			
Plane 3			
C(1)*	0.004	C(5)*	0.002
C(2)*	0.003	C(6)*	0.007
C(3)*	0.005	Cl(1)	0.002
C(4)*	0.004		
Plane 4			
N(1); C(7); N(2)			
Angles between plane normals (°) (e.s.d.'s 1.2°)			
1:1'	51.8	3:4	42.7
1:2	27.0	2:4	27.3
3:3'	76.6		

Fig. 1. Projection of the CIDF dimer on the *ab* plane with the atomic numbering scheme.

of the amidine moieties. A possible explanation of this behaviour, in terms of statistical disorder, is indicated in Fig. 2; the average structure shown in this figure would be expected to have N(1)—C(7) and N(1)—C(1) bond lengths consistent with those observed in the *C2/c* refinement (see Table 2). The N—H...N distance in the dimer is 2.958 (3) Å and the dihedral angle between the planes of both amidine moieties, N(1)—C(7)—N(2) (I) and (II), is 27.3 (3)°. In comparison, in the crystal structure of *N,N'*-bis(*p*-bromophenyl)formamidine (Anulewicz, Krygowski, Jaroszewska-Manaj & Pniewska, 1989) these data are 2.963 (4) Å and 27.3 (3)°, respectively. Table 3 lists all dihedral angles in both units of the dimer.

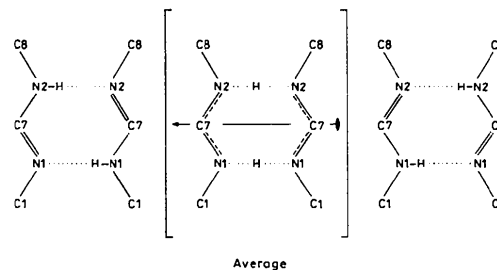


Fig. 2. Scheme of the amidine structural fragment illustrating the disorder of the central part.

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