

O(2)	0.3696 (4)	0.4947 (3)	0.1837 (3)	0.072 (2)
C(3)	0.4802 (4)	0.2601 (4)	0.2691 (4)	0.037 (2)
C(4)	0.3708 (5)	0.1255 (5)	0.3820 (4)	0.038 (2)
O(3)	0.3885 (3)	0.0024 (3)	0.3853 (3)	0.056 (1)
O(4)	0.2464 (3)	0.1700 (3)	0.4842 (3)	0.042 (1)
C(5)	0.1204 (5)	0.0775 (5)	0.6018 (4)	0.037 (2)
O(5)	0.1006 (4)	-0.0487 (3)	0.6217 (3)	0.058 (1)
C(6)	0.0181 (4)	0.1668 (4)	0.6939 (4)	0.039 (2)
C(7)	0.1433 (5)	0.2418 (5)	0.7424 (4)	0.046 (2)
O(6)	0.1319 (5)	0.3611 (4)	0.7525 (5)	0.104 (2)
O(7)	0.2646 (4)	0.1569 (3)	0.7753 (3)	0.056 (1)
C(8)	0.3968 (6)	0.2144 (5)	0.8183 (5)	0.069 (2)
C(9)	0.6046 (5)	0.2123 (4)	0.1460 (4)	0.055 (2)
C(10)	0.5795 (5)	0.3286 (4)	0.3448 (5)	0.059 (2)
C(11)	-0.0773 (6)	0.2795 (5)	0.6041 (5)	0.063 (2)
C(12)	-0.1100 (5)	0.0641 (5)	0.8310 (4)	0.062 (2)

Table 2. Selected geometric parameters (Å, °)

O(7)—C(7)	1.308 (5)	C(3)—C(4)	1.526 (5)
O(7)—C(8)	1.436 (7)	C(3)—C(9)	1.530 (6)
O(1)—C(2)	1.326 (6)	C(3)—C(10)	1.526 (7)
O(1)—C(1)	1.434 (6)	C(6)—C(5)	1.508 (6)
O(4)—C(5)	1.389 (4)	C(6)—C(7)	1.519 (7)
O(3)—C(4)	1.182 (6)	C(6)—C(12)	1.529 (5)
C(4)—O(4)	1.373 (5)	C(6)—C(11)	1.530 (6)
O(5)—C(5)	1.178 (6)	C(2)—O(2)	1.200 (6)
C(3)—C(2)	1.505 (6)	C(7)—O(6)	1.183 (7)
C(7)—O(7)—C(8)	118.4 (4)	C(12)—C(6)—C(11)	111.1 (3)
C(2)—O(1)—C(1)	118.1 (3)	O(1)—C(2)—C(3)	111.4 (4)
C(5)—O(4)—C(4)	124.8 (3)	O(1)—C(2)—O(2)	123.3 (4)
C(2)—C(3)—C(4)	108.0 (3)	C(3)—C(2)—O(2)	125.3 (4)
C(2)—C(3)—C(9)	109.4 (3)	O(4)—C(5)—O(5)	124.0 (4)
C(4)—C(3)—C(9)	108.4 (3)	O(4)—C(5)—C(6)	108.4 (3)
C(2)—C(3)—C(10)	111.1 (3)	O(5)—C(5)—C(6)	127.6 (3)
C(4)—C(3)—C(10)	108.6 (3)	O(4)—C(4)—O(3)	124.3 (3)
C(9)—C(3)—C(10)	111.3 (3)	O(4)—C(4)—C(3)	108.6 (3)
C(5)—C(6)—C(7)	108.5 (3)	O(3)—C(4)—C(3)	127.1 (3)
C(5)—C(6)—C(12)	108.8 (3)	O(7)—C(7)—C(6)	111.8 (4)
C(7)—C(6)—C(12)	108.1 (3)	O(7)—C(7)—O(6)	123.5 (5)
C(5)—C(6)—C(11)	109.6 (4)	C(6)—C(7)—O(6)	124.7 (4)
C(7)—C(6)—C(11)	110.7 (4)		

A variable scan rate, with a scan width of 0.6° below $K\alpha_1$ and 0.6° above $K\alpha_2$ to a maximum 2θ value of 40°, was used. Refinement was completed using full-matrix least-squares methods. H atoms were included in fixed positions with isotropic U values determined by assuming that they were riding on the methyl C atoms.

Data collection: XSCANS (Siemens, 1991). Cell refinement: XSCANS. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXS86. Molecular graphics: XP (Siemens, 1990). Software used to prepare material for publication: XP.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1201). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Cambridge Structural Database (1994). Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, England.
- Ibers, J. & Hamilton, W. C. (1984). *International Tables for X-ray Crystallography*, Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- Sheldrick, G. M. (1990). *Acta Cryst.* A46, 467–473.
- Siemens (1990). *XP. Interactive Molecular Graphics Program*. Version 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1991). *XSCANS User's Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Valle, G., Crisma, M., Toniolo, C., Sen, N., Sukumar, M. & Balam, P. (1988). *J. Chem. Soc. Perkin Trans. 2*, pp. 393–398.

Valle, G., Toniolo, C. & Jung, G. (1986). *Liebigs Ann. Chem.* pp. 1809–1822.

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N-(4-Bromophenyl)-5,6-dichloro-nicotinamide and 6-Chloro-5-fluoro-N-(3-pyridyl)nicotinamide

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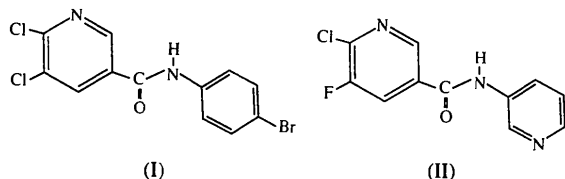
Abstract

The title compounds, *N*-(4-bromophenyl)-5,6-dichloro-nicotinamide, C₁₂H₇BrCl₂N₂O, and 6-chloro-5-fluoro-*N*-(3-pyridyl)nicotinamide, C₁₁H₇ClFN₃O, crystallize as almost planar molecules held together by intermolecular hydrogen bonding. The dichloro compound shows C—Cl distances of 1.69 (2) and 1.725 (15) Å at C6 and C5, respectively. These compounds are representatives of a class of compounds biologically important as herbicidal, pesticidal or fungicidal agents.

Comment

Substituted nicotinamides (Heaney, Shephard, Crowley & Shearing, 1988), 2,5- and 5,6-disubstituted nicotinic acids (Setliff & Huie, 1981), and benzamidopyridine derivatives (Setliff & Palmer, 1987) have shown fungicidal and herbicidal activities towards barnyard grasses and wheat leaf rust. It has been observed that halogenated derivatives show increased activity. One compound, a halogenated benzamidopyridine derivative (Setliff & Rankin, 1988), effected a 70% growth reduction of giant foxtail weed. Substituted 5-bromo-6-chloronicotinic acid derivatives (Setliff & Caldwell, 1991) have proven to show activity towards the apple scab fungus and fall army worm. Based on the promise of these earlier studies, a series of halonicotinamide derivatives (Setliff & Soman, 1992; Soman, 1992) were synthesized to allow evaluation of their potential as active fungicides and herbicides, among them, *N*-

(4-bromophenyl)-5,6-dichloronicotinamide (I) and 6-chloro-5-fluoro-*N*-(3-pyridyl)nicotinamide (II). Single-crystal X-ray analyses of these materials have been undertaken to provide parameters for structure–activity relationship studies.



N-(4-Bromophenyl)-5,6-dichloronicotinamide and 6-chloro-5-fluoro-*N*-(3-pyridyl)nicotinamide crystallize with the amide carbonyl group and the pyridine N atom of the nicotinamide moiety *trans* to each other. In *N*-phenylnicotinamide (Gdaniec, Jaskolski & Kosturkiewicz, 1979), the opposite conformation of the pyridine N atom is observed.

Both are almost planar molecules: the angle between the plane of the two aromatic rings is 12.7° in (I) and 7.3° in (II). Angles between the planes of the nicotinamide aromatic ring and the C3, N2, C7, O1 amide linkage are 3.9° in (I) and 2.0° in (II), while the angle between the planes of the amide linkage and the second aromatic ring are 8.8° in (I) but 6.3° in (II). These interplanar angles may be compared with the 64.5° angle between the planes of the aromatic rings and the 31.3 and 33.3° angles observed between those planes and the plane of the amide linkage in *N*-phenylnicotinamide (Gdaniec *et al.*, 1979).

In (I), the C—Cl bond lengths are 1.69 (2) and 1.725 (15) Å at the C atoms α and β to the N atom of the nicotinamide ring, respectively. The C—Cl distance at the β -C atom is longer than the other. The distance between the respective C atoms is 1.43 (2) Å. Comparative distances in other dichloropyridine derivatives are $C\alpha$ —Cl, $C\beta$ —Cl and $C\alpha$ — $C\beta$ distances: 1.734 (5), 1.706 (5) and 1.378 (7) Å for heptachloro-5*H*-1-pyridine (Carter & Boer, 1974); average 1.76 (1), 1.74 (1) and 1.43 (1) Å for 1,3,5,6,8-hexachlorothieno[2,3-*c*:5,4-*c'*]dipyridine (Redhouse, 1974); and 1.716 (5), 1.721 (5) and 1.368 (7) Å in tetrachloro-4-hydroxypyridine (Boer, Turley & van Remoortere, 1972). These compounds all have more highly halogenated pyridine rings than (I).

The $C\alpha$ —Cl distance of 1.725 (1) Å seen in (II) is within the range of values given above and the $C\beta$ —F distance of 1.342 (1) Å is close to the value of 1.335 (5) Å in *N*-(2,3,5,6-tetrafluoropyridyl)-*N'*-phenylurea (Yamaguchi, Matsumura, Haga & Shudo, 1992).

There are no reported crystal structures of α -chloro, β -fluoro pyridine derivatives. The single α -fluoro, β -chloro compound reported (4,5-dichloro-1,3,6,8-tetrafluoro-2,7-naphthylpyridine; van den Ham & van Hummel, 1977) has $C\alpha$ —F 1.333 (5), $C\beta$ —Cl 1.719 (4), and $C\alpha$ — $C\beta$ 1.359 (6) Å.

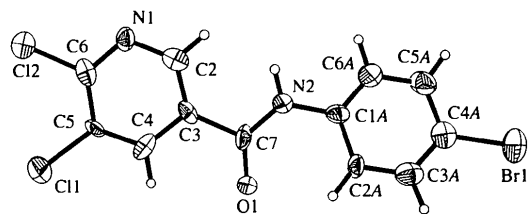


Fig. 1. View of *N*-(4-bromophenyl)-5,6-dichloronicotinamide. Displacement ellipsoids are plotted at the 30% probability level for non-H atoms; H atoms are represented as spheres of arbitrary radii.

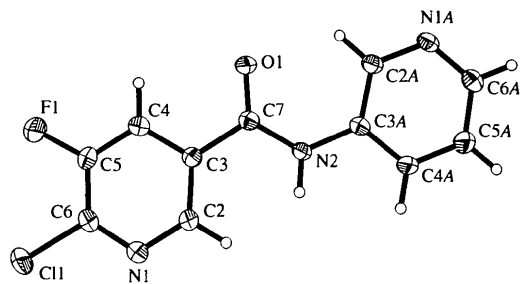


Fig. 2. View of 6-chloro-5-fluoro-*N*-(3-pyridyl)nicotinamide. Displacement ellipsoids are plotted at the 30% probability level for non-H atoms; H atoms are represented as spheres of arbitrary radii.

The carbon–halide distances of (I) appear influenced in some way by their positions on the aromatic ring relative to the amide linkage and the pyridine N atom. The planarity of the halogenated molecules suggests that the halide atoms participate in electron delocalization involving the entire molecule. However, there is no obvious pattern of shortening or electron localization in the lengths of other bonds of (I) or (II).

The packing of (I) shows an intermolecular distance of 2.57 Å between the H atom attached to N2 of the amide group and N1($-x, 2 - y, -\frac{1}{2} + z$) of the 5,6-dichloropyridyl ring. In (II), an intermolecular N2—H2B \cdots N1A($-\frac{1}{2} + x, -\frac{1}{2} - y, -\frac{1}{2} + z$) hydrogen bond [2.47 (2) Å] links the molecules together.

Experimental

For (I), *N*-(4-bromophenyl)-5,6-dichloronicotinamide (Setliff & Soman, 1992) (200 mg) was recrystallized from 5 ml of hot aqueous ethanol. On slow evaporation of the solution, colorless needles formed. For (II), the compound was crystallized from hot dichloromethane and methanol (3:1) to produce colorless cubic crystals.

Compound (I)

Crystal data

$C_{12}H_7BrCl_2N_2O$
 $M_r = 346.01$
 Orthorhombic
 $Pca2_1$
 $a = 22.076$ (3) Å
 $b = 8.722$ (1) Å
 $c = 6.552$ (1) Å

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 45 reflections
 $\theta = 5.258$ – 12.673°
 $\mu = 3.668$ mm $^{-1}$
 $T = 293$ (2) K

$V = 1261.6(3) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.822 \text{ Mg m}^{-3}$

Data collection

Siemens P4 four-circle
 diffractometer
 $\theta/2\theta$ scans
 Absorption correction:
 semi-empirical from six ψ
 scans (10° steps) (XEMP;
 Siemens, 1991)
 $T_{\min} = 0.31$, $T_{\max} = 0.50$
 1706 measured reflections
 1426 independent reflections
 509 observed reflections
 $[I > 4\sigma(I)]$

Refinement

Refinement on F^2
 $R(F) = 0.049$
 $wR(F^2) = 0.112$
 $S = 0.951$
 1417 reflections
 163 parameters
 H atoms refined using a
 riding model
 $w = 1/[\sigma^2(F_o^2) + (0.0347P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = -0.015$

Needle
 $0.15 \times 0.15 \times 0.15 \text{ mm}$
 Colorless

$R_{\text{int}} = 0.0782$
 $\theta_{\max} = 25.00^\circ$
 $h = 0 \rightarrow 26$
 $k = 0 \rightarrow 10$
 $l = -1 \rightarrow 7$
 3 standard reflections
 monitored every 97
 reflections
 intensity decay: 3.2%

$\Delta\rho_{\max} = 0.329 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.301 \text{ e \AA}^{-3}$
 Extinction correction:
 SHELXL93 (Sheldrick,
 1993)
 Extinction coefficient:
 0.0009 (9)
 Atomic scattering factors
 from *International Tables*
 for *Crystallography* (1992,
 Vol. C, Tables 4.2.6.8 and
 6.1.1.4)

C6—N1—C2	118.4 (14)	O1—C7—C3	118.2 (16)
N1—C2—C3	124.0 (16)	N2—C7—C3	115.0 (15)
C2—C3—C4	116.1 (15)	C7—N2—C1A	128.1 (13)
C2—C3—C7	126.1 (14)	C6A—C1A—C2A	121.0 (17)
C4—C3—C7	117.7 (14)	C6A—C1A—N2	119.6 (15)
C5—C4—C3	121.1 (15)	C2A—C1A—N2	119.4 (15)
C4—C5—C6	118.6 (15)	C3A—C2A—C1A	117.3 (16)
C4—C5—C11	122.7 (13)	C4A—C3A—C2A	124.2 (17)
C6—C5—C11	118.6 (13)	C3A—C4A—C5A	116.5 (18)
N1—C6—C5	121.5 (16)	C3A—C4A—Br1	124.3 (16)
N1—C6—C12	117.0 (13)	C5A—C4A—Br1	119.1 (15)
C5—C6—C12	121.4 (13)	C6A—C5A—C4A	119.4 (17)
O1—C7—N2	126.8 (17)	C1A—C6A—C5A	121.4 (18)

Compound (II)*Crystal data*

C₁₁H₇ClFN₃O
 $M_r = 251.6$
 Monoclinic
 $P2_1/n$
 $a = 7.995(2) \text{ \AA}$
 $b = 12.483(2) \text{ \AA}$
 $c = 11.320(2) \text{ \AA}$
 $\beta = 108.37(1)^\circ$
 $V = 1072.1(3) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.559 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 45
 reflections
 $\theta = 5.5\text{--}12.32^\circ$
 $\mu = 0.355 \text{ mm}^{-1}$
 $T = 298 \text{ K}$
 Cube
 $0.3 \times 0.3 \times 0.3 \text{ mm}$
 Colorless

Data collection

Siemens P4 four-circle
 diffractometer
 $\theta/2\theta$ scans
 Absorption correction:
 none
 2031 measured reflections
 1889 independent reflections
 1416 observed reflections
 $[F > 7.0\sigma(F)]$

$R_{\text{int}} = 0.0162$
 $\theta_{\max} = 22.5^\circ$
 $h = -9 \rightarrow 8$
 $k = 0 \rightarrow 10$
 $l = 0 \rightarrow 13$
 3 standard reflections
 monitored every 97
 reflections
 intensity decay: 7.0%

Refinement

Refinement on F
 $R = 0.0398$
 $wR = 0.0588$
 $S = 1.57$
 1416 reflections
 155 parameters
 H atoms refined using a
 riding model
 $w = 1/[\sigma^2(F) + 0.0008F^2]$

$(\Delta/\sigma)_{\max} = 0.007$
 $\Delta\rho_{\max} = 0.25 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.21 \text{ e \AA}^{-3}$
 Extinction correction: none
 Atomic scattering factors
 from *International Tables*
 for *Crystallography* (1992,
 Vol. C, Tables 4.2.6.8 and
 6.1.1.4)

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for (II)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
Cl1	0.0675 (1)	0.2048 (1)	0.0240 (1)	0.062 (1)
F1	0.3674 (1)	0.2018 (1)	0.2482 (1)	0.086 (1)
N1	-0.0322 (1)	0.0538 (1)	0.1462 (1)	0.057 (1)
C2	-0.0102 (1)	-0.0094 (1)	0.2450 (1)	0.052 (1)
C3	0.1343 (1)	-0.0068 (1)	0.3500 (1)	0.033 (1)
C4	0.2652 (1)	0.0657 (1)	0.3524 (1)	0.045 (1)
C5	0.2436 (1)	0.1299 (1)	0.2506 (1)	0.044 (1)
C6	0.0942 (1)	0.1216 (1)	0.1503 (1)	0.041 (1)
C7	0.1605 (1)	-0.0756 (1)	0.4637 (1)	0.033 (1)
O1	0.2935 (1)	-0.0639 (1)	0.5527 (1)	0.046 (1)
N2	0.0352 (1)	-0.1490 (1)	0.4605 (1)	0.033 (1)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for (I)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
Cl1	0.1976 (2)	1.1827 (7)	0.8871	0.096 (2)
Cl2	0.0582 (2)	1.2477 (6)	0.9362 (13)	0.078 (1)
Br1	0.1351 (1)	0.4361 (2)	-0.6591 (11)	0.093 (1)
N1	0.0441 (6)	1.104 (1)	0.599 (2)	0.057 (4)
C2	0.0632 (7)	1.024 (2)	0.436 (3)	0.060 (5)
C3	0.1220 (6)	0.972 (2)	0.411 (2)	0.046 (5)
C4	0.1637 (9)	1.021 (2)	0.556 (3)	0.062 (5)
C5	0.1467 (6)	1.109 (2)	0.714 (3)	0.046 (4)
C6	0.0841 (8)	1.148 (2)	0.733 (3)	0.057 (5)
C7	0.1459 (9)	0.876 (2)	0.230 (3)	0.060 (5)
O1	0.2002 (4)	0.853 (1)	0.219 (2)	0.085 (4)
N2	0.1044 (5)	0.829 (2)	0.102 (2)	0.060 (4)
C1A	0.1121 (6)	0.735 (2)	-0.076 (3)	0.050 (4)
C2A	0.1703 (7)	0.705 (2)	-0.148 (3)	0.066 (5)
C3A	0.1755 (8)	0.612 (2)	-0.318 (3)	0.073 (6)
C4A	0.1282 (9)	0.557 (2)	-0.423 (3)	0.066 (5)
C5A	0.0691 (9)	0.590 (2)	-0.343 (3)	0.078 (6)
C6A	0.0637 (8)	0.678 (2)	-0.169 (4)	0.081 (6)

Table 2. Geometric parameters (\AA , $^\circ$) for (I)

Cl1—C5	1.725 (15)	C7—O1	1.22 (2)
Cl2—C6	1.69 (2)	C7—N2	1.31 (2)
Br1—C4A	1.88 (2)	N2—C1A	1.43 (2)
N1—C6	1.31 (2)	C1A—C6A	1.33 (2)
N1—C2	1.34 (2)	C1A—C2A	1.39 (2)
C2—C3	1.38 (2)	C2A—C3A	1.38 (2)
C3—C4	1.39 (2)	C3A—C4A	1.34 (2)
C3—C7	1.55 (2)	C4A—C5A	1.43 (2)
C4—C5	1.34 (2)	C5A—C6A	1.38 (2)
C5—C6	1.43 (2)		

N1A	0.1767 (1)	-0.3136 (1)	0.7473 (1)	0.042 (1)
C2A	0.1743 (1)	-0.2358 (1)	0.6650 (1)	0.037 (1)
C3A	0.0415 (1)	-0.2274 (1)	0.5512 (1)	0.032 (1)
C4A	-0.0918 (1)	-0.3025 (1)	0.5247 (1)	0.051 (1)
C5A	-0.0896 (1)	-0.3808 (1)	0.6103 (1)	0.063 (1)
C6A	0.0466 (1)	-0.3836 (1)	0.7208 (1)	0.051 (1)

Table 4. Geometric parameters (\AA , $^\circ$) for (II)

C11—C6	1.725 (1)	O1—C7	1.222 (1)
C5—F1	1.342 (1)	N2—C7	1.349 (1)
N1—C2	1.335 (1)	N2—C3A	1.408 (1)
N1—C6	1.308 (1)	N1A—C2A	1.341 (1)
C2—C3	1.372 (1)	N1A—C6A	1.318 (1)
C3—C4	1.377 (1)	C2A—C3A	1.391 (1)
C3—C7	1.506 (1)	C3A—C4A	1.379 (1)
C4—C5	1.369 (1)	C4A—C5A	1.373 (1)
C6—C5	1.368 (1)	C5A—C6A	1.376 (1)
C2—N1—C6	117.2 (1)	O1—C7—C3	119.1 (1)
C3—C2—N1	124.4 (1)	C3—C7—N2	117.5 (1)
C2—C3—C4	117.4 (1)	O1—C7—N2	123.3 (1)
C2—C3—C7	125.4 (1)	C7—N2—C3A	126.6 (1)
C4—C3—C7	117.3 (1)	C2A—N1A—C6A	119.0 (1)
C3—C4—C5	118.3 (1)	N1A—C2A—C3A	122.5 (1)
F1—C5—C4	120.7 (1)	N2—C3A—C2A	124.7 (1)
F1—C5—C6	119.3 (1)	C4A—C3A—N2	117.8 (1)
C4—C5—C6	120.0 (1)	C2A—C3A—C4A	117.5 (1)
N1—C6—C11	117.9 (1)	C3A—C4A—C5A	119.6 (1)
C11—C6—C5	119.4 (1)	C4A—C5A—C6A	119.3 (1)
C5—C6—N1	122.8 (1)	N1A—C6A—C5A	122.1 (1)

Dispersion corrections and absorption coefficients were taken from *International Tables for Crystallography*, 1992, Vol. C, Tables 6.1.1.4 and 4.2.6.8, and 4.2.4.2, respectively.

For both compounds, data collection: XSCANS (Siemens, 1991); cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve structures: SHELXS86 (Sheldrick, 1985). Program(s) used to refine structures: SHELXL93 (Sheldrick, 1993) for (I); SHELXS86 for (II). Molecular graphics: SHELXTL-Plus (Sheldrick, 1992) for (I); XP (Siemens, 1990) for (II). Software used to prepare material for publication: SHELXTL-Plus for (I); SHELXS86 for (II).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1196). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Boer, F. P., Turley, J. W. & van Remoortere, F. P. (1972). *J. Chem. Soc. Chem. Commun.* pp. 573–574.
- Carter, D. R. & Boer, F. P. (1974). *Acta Cryst.* **B30**, 2762–2763.
- Gdaniec, M., Jaskolski, M. & Kosturkiewicz, Z. (1979). *Pol. J. Chem.* **53**, 2563–2569.
- Ham, D. M. W. van den & van Hummel, G. J. (1977). *Acta Cryst.* **B33**, 3866–3868.
- Heaney, S. P., Shephard, M. C., Crowley, P. J. & Shearing, S. J. (1988). *Brighton Crop Protection Conference – Pests and Diseases*, Vol. 2, p. 551. Jealott's Hill Research Station, ICI Agrochemicals, Bracknell, Berkshire RG12 6EY, England.
- Redhouse, A. D. (1974). *J. Chem. Soc. Perkin Trans. 2*, pp. 1925–1927.
- Setliff, F. L. & Caldwell, J. Z. (1991). *Proc. Ark. Acad. Sci.* **45**, 92–94.
- Setliff, F. L. & Huie, W. R. (1981). *J. Chem. Eng. Data*, **26**, 332–333.
- Setliff, F. L. & Palmer, H. E. (1987). *J. Chem. Eng. Data*, **32**, 393–394.
- Setliff, F. L. & Rankin, S. H. (1988). *J. Chem. Eng. Data*, **33**, 223–224.

- Setliff, F. L. & Soman, N. G. (1992). *Proc. Ark. Acad. Sci.* **46**, 69–71.
- Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
- Sheldrick, G. M. (1992). *SHELXTL-Plus. Release 4.21/V*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1993). *SHELXL93. Program for Crystal Structure Refinement*. University of Göttingen, Germany.
- Siemens (1990). *XP. Interactive Molecular Graphics Program. Version 4.1*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1991). *XSCANS User's Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Soman, N. G. (1992). Masters thesis, University of Arkansas at Little Rock, USA.
- Yamaguchi, K., Matsumura, G., Haga, N. & Shudo, K. (1992). *Acta Cryst.* **C48**, 559–561.

Acta Cryst. (1996). **C52**, 441–444

A Chiral Mesogenic Compound

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Abstract

Single-crystal X-ray analysis has been carried out for 4-(1-methylheptyloxycarbonyl)phenyl 4-heptyloxytolane-4'-carboxylate [C₇-tolane, C₃₇H₄₄O₅, tolane = 1,1'-(1,2-ethylenediyl)bisbenzene]. The crystal has a smectic C-like layer structure composed of largely bent molecules; the chain of the chiral group is quasi-perpendicular (86°) to the core moiety. The molecular arrangement is similar to that of 4-[(S)-1-methylheptyloxycarbonyl]phenyl 4'-octyloxybiphenyl-4-carboxylate and agrees with the data of the *n* = 8 homologue (C8-tolane) antiferroelectric mesophase.

Comment

In a number of crystal structures of mesogenic materials, good correlations have been established between the crystal organization and the mesomorphic smectic arrangement. In the case of ferroelectric materials it has been shown (Hori & Ohashi, 1991, 1993; Hori & Endo, 1993) that the molecular packing in the smectic-like solid layers is controlled by the arrangement of the polar groups. In a recent paper, Hori, Kawahara & Ito (1993) described the crystalline structure of several antiferroelectric materials. The most striking behaviour in the molecular structure is that the chain of the chiral groups is almost perpendicular to the core moiety; moreover,