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## Key indicators

Single-crystal X-ray study

T = 293 K

Mean  $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$ 

R factor = 0.052

wR factor = 0.134

Data-to-parameter ratio = 13.6

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

## Conformational chirality of chemically symmetric molecules and a superlattice through enantioselective self-assembly: 1,1,1-tris[(4-cyanophenoxy)methyl]-ethane

The title compound,  $\text{C}_{26}\text{H}_{21}\text{N}_3\text{O}_3$ , is a chemically symmetrical molecule with one methyl group and three (4-cyanophenoxy)-methyl groups bonded to a tetracoordinate C atom. It crystallizes in the centrosymmetric space group  $P\bar{1}$ . In the crystal structure, there are many non-covalent interactions, including  $\text{O} \cdots \text{N}$  short contacts and antiparallel dipole-dipole interactions. The tetracoordinate C atom of the molecule exhibits central chirality, while the three attached groups exhibit different axial chirality. The enantiomers form homochiral monolayers through enantioselective self-assembly, and the monolayers are packed in the formation of a superlattice based on alternating the two enantiomeric states. The physical image of molecular chirality as well as the concept of a superlattice with respect to chirality may provide a new insight into such a racemic crystal, which is very common in crystallography.

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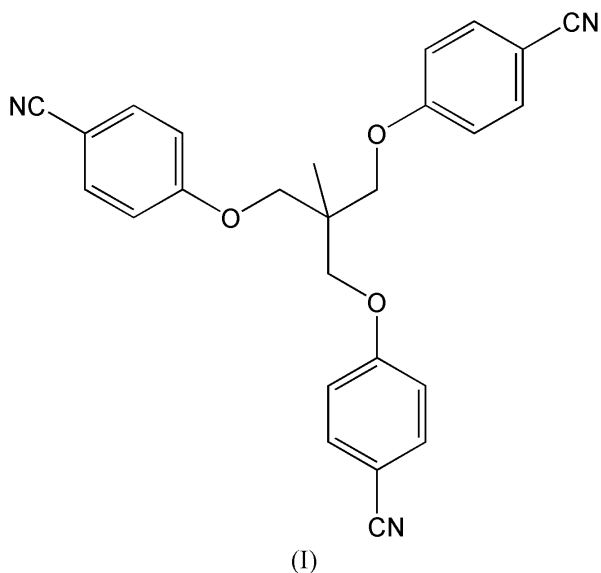
## Comment

Molecules usually will not maintain their ideal shapes upon adsorption on solid surfaces or being packed into condensed phases, since they are soft materials. In recent years, much attention has been devoted to the recognition and measurement of chirality in molecules and molecular assemblies (Fasel *et al.*, 2004; Lopinski *et al.*, 1998; Casarini *et al.*, 2001; Yuan & Liu, 2003; Borovkov *et al.*, 2003). However, the understanding of the molecular packing arrangement and particularly the knowledge of the molecular geometry remains incomplete (Anthony *et al.*, 1998; Pidcock & Motherwell, 2004). Very recently, we have shown that four chemically identical substituents attached to a central C atom have different conformations (Xu, Lu, Guo *et al.*, 2004; Xu, Lu, Liu *et al.*, 2004), indicating that the loss of ideal molecular symmetry does occur in the solid state. This paper continues our study of chemically symmetric molecules and focuses on the expression of molecular chirality and chiral structures in the solid state.

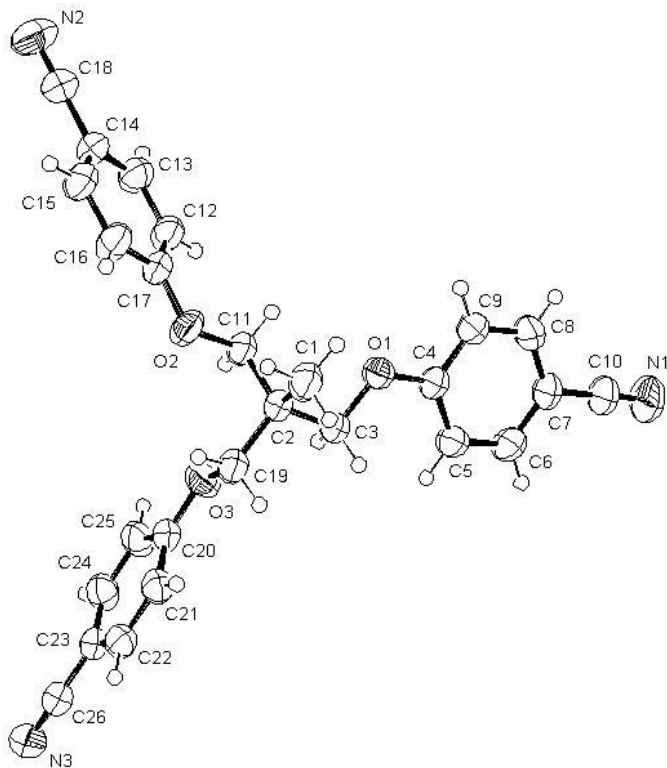
The title compound, (I), is a chemically symmetric molecule, with one methyl group and three (4-cyanophenoxy)methyl groups bonded to a tetracoordinate C atom. The molecular structure of (I), with the atom-labeling scheme, is shown in Fig. 1. Selected geometric parameters are given in Table 1.

In the crystal structure, there are  $\text{C}-\text{H} \cdots \text{N}$ ,  $\text{C}-\text{H} \cdots \text{O}$ ,  $\text{C}-\text{H} \cdots \text{C}$ ,  $\text{C}-\text{H} \cdots \pi(\text{C}\equiv\text{N})$  and edge-to-face aromatic interactions, similar to those observed in the crystal structure of tetrakis[(4-cyanophenoxy)methyl]methane (Xu *et al.*, 2004). The short  $\text{N} \cdots \text{O}^i$  separation [3.268 (3) Å; symmetry code: (i)  $-1 - x, 1 - y, 2 - z$ ] may partly be due to the dipole interaction between the N atom and the  $\text{O}^i$  atom, since (4-cyano-

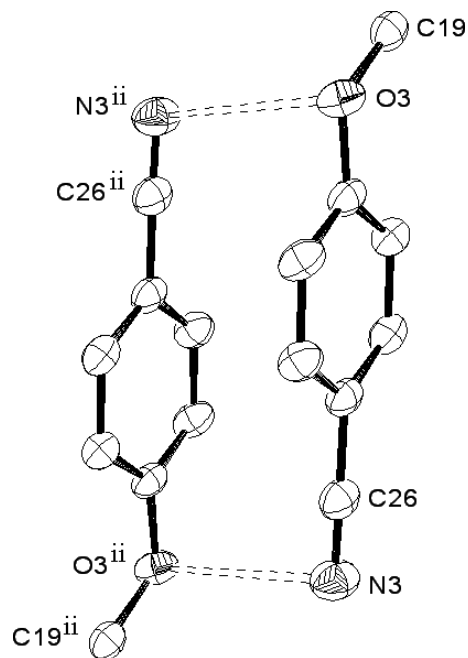
phenoxy)methyl groups are typical push–pull conjugated units.



In addition, the antiparallel dipole–dipole interactions between two push–pull conjugated units have been observed. For example, two conjugated units containing N3 are closely packed in the formation of a dimer, as shown in Fig. 2; the



**Figure 1**  
The molecular structure of the title compound. Displacement ellipsoids are drawn at the 30% probability level.



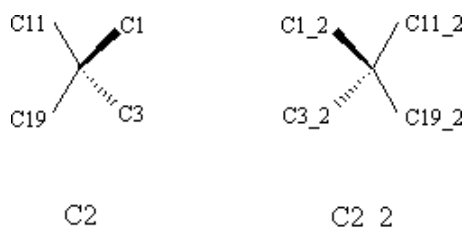
**Figure 2**  
The antiparallel dipole–dipole interactions (broken lines) between two push–pull conjugated units. [Symmetry code: (ii)  $1 - x, 2 - y, 1 - z$ ]

$N3 \cdots O3^{ii}$  separation is 3.478 (3) Å and the  $C26-N3 \cdots O3^{ii}$  angle is 97.80 (15)° [symmetry code: (ii)  $1 - x, 2 - y, 1 - z$ ]. A relatively weak antiparallel dipole–dipole interaction exists between two conjugated units containing N2; the  $N2 \cdots O2^i$  separation is 4.242 (4) Å and the  $C18-N2 \cdots O2^i$  angle is 97.48 (19)°. However, as for the conjugated units containing N1, the antiparallel dipole–dipole interaction can be neglected, since the separation between the two antiparallel units is larger than 5 Å. This discrimination suggests that the three (4-cyanophenoxy)methyl groups of the same molecule participate in different dipole interactions, and it also implies that such chemically identical groups are situated in different interaction environments.

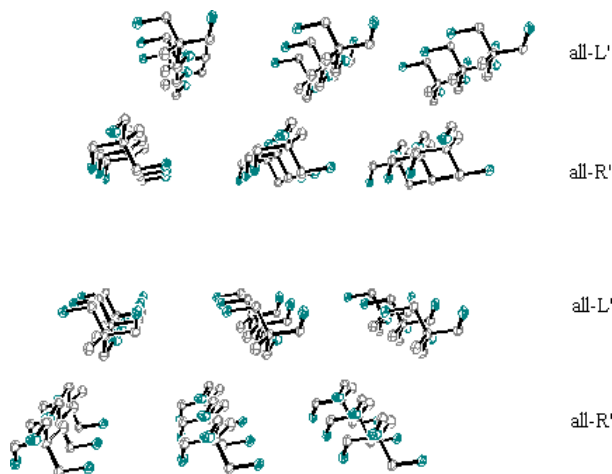
As can be seen in Table 1, the bond length C2–C3 is larger than C2–C11 and C2–C19. Although C2–C11 and C2–C19 are the same, C11–O2 and C19–O3 are different. Such differences are further confirmed by the torsion angles (see Table 1). For example, the torsion angles C2–C3–O1–C4, C2–C11–O2–C17 and C2–C19–O3–C20 are different, and the differences are far larger than their uncertainties [174.6 (2), 163.7 (2) and 172.8 (2)°, respectively]. This indicates that the three chemically identical groups are different, and accordingly the tetracoordinated C2 can be regarded as an asymmetric center.

Considering each molecule in the unit cell, the spatial arrangement of the central C2 and the four neighboring atoms (C1, C3, C11 and C19) can be displayed by using ORTEP-3 (Farrugia, 1999). The configurations ( $Z = 2$ ) are depicted in Fig. 3 and show that the tetracoordinate C2 is the mirror image of  $C2^{iii}$  [symmetry code: (iii)  $1 - x, -y, 1 - z$ ].

Furthermore, the corresponding torsion angles from one attached group are found to be different. For example, the



**Figure 3**  
The configurations of the two tetracoordinate centers ( $Z = 2$ ).



**Figure 4**  
The superlattice with respect to chirality shows an ... $L'R'L'R'$ ... stacking sequence, along  $b$  axis. 4-Cyanophenyl groups and H atoms have been omitted for clarity.

torsion angles C11–O2–C17–C12 and C11–O2–C17–C16 are  $14.6(3)$  and  $-166.65(18)^\circ$ , respectively, suggesting that the arrangement of the bond C11–O2 and the benzene ring exhibits axial chirality. According to the space group, if one (4-cyanophenoxy)methyl group of the C2-molecule has a right-handed twist, the corresponding group of the C2<sup>iii</sup>-molecule has a left-handed one, or *vice-versa*.

The chiral feature of such a symmetric molecule is actually a combination of central and axial chirality: the tetracoordinate center exhibits central chirality, whereas the attached groups have axial chirality with left-handed or right-handed twist. For its convenience, if the molecule of C2 is defined as left-handed ( $L'$ ), the molecule of C2<sup>iii</sup> is right-handed ( $R'$ ).

Inspection of the molecular packing arrangement of (I) reveals that the two enantiomers self-assemble into homochiral monolayers (all- $L'$  or all- $R'$ ) parallel to (001). Each monolayer contains just one type of enantiomer. The monolayers repeat in an ... $L'R'L'R'$ ... stacking sequence, forming a superlattice based on alternating the two enantiomeric layers, as shown in Fig. 4. Such a superlattice is very different from any ordinary superlattice (Noh *et al.*, 1995; Gido, 1999), since the latter usually is based on alternating two different entities such as  $A$ -layer and  $B$ -layer.

Similar features have been seen in the crystal structures of tetrakis[(4-cyanophenoxy)methyl]methane (Xu *et al.*, 2004).

In that case, the tetracoordinate C1 and C1<sup>iv</sup> have the same configuration, while C1<sup>v</sup> and C1<sup>vi</sup> exist in the enantiomeric state of C1 and C1<sup>iv</sup> [symmetry codes: (iv)  $1 - x, y - \frac{1}{2}, \frac{1}{2} + z$ ; (v)  $1 - x, 1 - y, 1 - z$ ; (vi)  $x, \frac{3}{2} - y, \frac{1}{2} + z$ ]. It has also been seen that the enantiomers self-assemble into homochiral monolayers, and further form a superlattice with respect to chirality.

The alternate packing of enantiomeric layers may be very common in many crystal structures; however, the concept of such a superlattice has never been mentioned. It may be helpful in the study of the physical and functional properties of a crystal, if we have a clear concept that the crystal is actually a low-dimensional system with respect to chirality. The fact that symmetric molecules exist in enantiomeric states may be the reason why high molecular symmetry does not necessarily lead to high crystal symmetry (Anthony *et al.*, 1998). It also suggests that enantioselective self-organization should be taken into consideration in the description of the crystal packing of symmetric molecules (Pidcock & Motherwell, 2004).

## Experimental

Compound (I) was synthesized by reacting 1,1,1-tris(bromomethyl)ethane and potassium 4-cyanophenoxide, analogous to the procedure for the preparation of tetrakis[(4-cyanophenoxy)methyl]methane (Xu *et al.*, 2004). Work-up gave the desired product (yield 76.8%), which was purified by recrystallization from dimethylformamide and ethanol (m.p. 387–389 K); IR (KBr):  $\nu$  2944, 2877, 2223, 1605, 1509, 1470, 1302, 1254, 1172, 1021, 829, 713  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  1.36 (s, 3H), 4.14 (s, 6H), 6.97 (d,  $J = 8.85$  Hz, 6H), 7.58 (d,  $J = 8.82$  Hz, 6H).

### Crystal data

$\text{C}_{26}\text{H}_{21}\text{N}_3\text{O}_3$	$Z = 2$
$M_r = 423.46$	$D_x = 1.237 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 8.248(3) \text{ \AA}$	Cell parameters from 828 reflections
$b = 10.097(3) \text{ \AA}$	$\theta = 2.7\text{--}27.1^\circ$
$c = 14.786(5) \text{ \AA}$	$\mu = 0.08 \text{ mm}^{-1}$
$\alpha = 79.404(5)^\circ$	$T = 293(2) \text{ K}$
$\beta = 74.292(5)^\circ$	Parallelepiped, colorless
$\gamma = 75.089(4)^\circ$	$0.45 \times 0.40 \times 0.35 \text{ mm}$
$V = 1136.8(6) \text{ \AA}^3$	

### Data collection

Bruker SMART CCD area-detector diffractometer	3936 independent reflections
$\varphi$ and $\omega$ scans	3350 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan ( <i>SADABS</i> ; Sheldrick, 1996)	$R_{\text{int}} = 0.015$
$T_{\text{min}} = 0.964$ , $T_{\text{max}} = 0.972$	$\theta_{\text{max}} = 25.0^\circ$
4780 measured reflections	$h = -9 \rightarrow 9$
	$k = -11 \rightarrow 11$
	$l = -12 \rightarrow 17$

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0533P)^2 + 0.3456P]$
$R[F^2 > 2\sigma(F^2)] = 0.052$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.134$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.05$	$\Delta\rho_{\text{max}} = 0.22 \text{ e \AA}^{-3}$
3936 reflections	$\Delta\rho_{\text{min}} = -0.16 \text{ e \AA}^{-3}$
289 parameters	
H-atom parameters constrained	

**Table 1**

Selected geometric parameters (Å, °).

O1—C3	1.428 (2)	C2—C11	1.519 (3)
O2—C11	1.437 (2)	C2—C19	1.519 (3)
O3—C19	1.426 (2)	C2—C3	1.532 (3)
C1—C2—C3—O1	−59.9 (2)	C3—O1—C4—C5	−0.6 (3)
C1—C2—C11—O2	−59.3 (2)	C3—O1—C4—C9	−179.73 (18)
C1—C2—C19—O3	172.34 (15)	C11—O2—C17—C12	14.6 (3)
C2—C3—O1—C4	174.57 (16)	C11—O2—C17—C16	−166.65 (18)
C2—C11—O2—C17	163.67 (16)	C19—O3—C20—C21	−4.9 (3)
C2—C19—O3—C20	172.76 (15)	C19—O3—C20—C25	175.73 (17)

H atoms were included using a riding model, with C—H = 0.95 Å and  $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C})$ .

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINTE* (Bruker, 1999); data reduction: *SAINTE* (Bruker, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a); molecular graphics: *SHELXTL* (Sheldrick, 1997b); software used to prepare material for publication: *SHELXTL*.

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## References

- Anthony, A., Desiraju, G. R., Jetti, R. K. R., Kuduva, S. S., Madhavi, N. N. L., Nangia, A., Thaimattam, R. & Thalladi, V. R. (1998). *Mater. Res. Bull.* **1**, 1–18.
- Borovkov, V. V., Harada, T., Hembury, G. A., Inoue, Y. & Kuroda, R. (2003). *Angew. Chem. Int. Ed.* **42**, 1746–1749.
- Bruker (1999). *SMART* and *SAINTE*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Casarini, D., Lunazzi, L. & Mazzanti, A. (2001). *Angew. Chem. Int. Ed.* **40**, 2536–2540.
- Farrugia, L. J. (1999). *ORTEP-3* for Windows. Version 1.05. University of Glasgow, Scotland.
- Fasel, R., Wider, J., Quitmann, C., Ernst, K.-H. & Greber, T. (2004). *Angew. Chem. Int. Ed.* **43**, 2853–2856.
- Gido, S. P. (1999). *Nature (London)*, **398**, 107–108.
- Lopinski, G. P., Moffatt, D. J., Wayner, D. D. & Wolkow, R. A. (1998). *Nature (London)*, **392**, 909–911.
- Noh, M., Thiel, J. & Johnson, D. C. (1995). *Science*, **270**, 1181–1184.
- Pidcock, E. & Motherwell, W. D. S. (2004). *Cryst. Growth Des.* **4**, 611–620.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997a). *SHELXS97* & *SHELXL97*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997b). *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Xu, W., Lu, Y.-X., Guo, P., Zhou, H. & Lan, B.-J. (2004). *Acta Cryst. E* **60**, o428–o430.
- Xu, W., Lu, Y.-X., Liu, C.-M., Guo, P., Lan, B.-J. & Zhou, H. (2004). *Acta Cryst. E* **60**, o1049–o1050.
- Yuan, J. & Liu, M.-H. (2003). *J. Am. Chem. Soc.* **125**, 5051–5056.