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1,1,1-Tris[(pyrrol-1-yl)methyl]ethane: herring-bone packing of supramolecular assemblies in a homochiral crystal from chemically symmetric molecules

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Key indicators

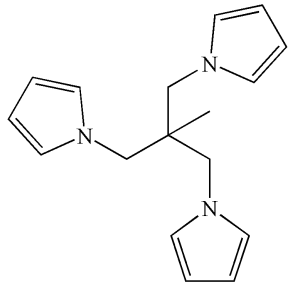
Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.005 Å
R factor = 0.057
wR factor = 0.138
Data-to-parameter ratio = 9.5

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

The title compound, $C_{17}H_{21}N_3$, is a chemically symmetric molecule with one methyl group and three (pyrrol-1-yl)methyl groups bonded to a central C atom. It crystallizes in the non-centrosymmetric space group $P2_12_12_1$. The three (pyrrol-1-yl)methyl groups are orientated differently with respect to one another and to the central C—CH_3 bond; hence, the molecule exhibits conformational chirality. The crystal structure is homochiral and contains just one type of enantiomer. In the crystal structure, a herring-bone packing of the supramolecular assemblies is revealed.

Comment

In general, a central C atom bearing four different groups is chiral; if any two of the four groups are identical, the central C atom is achiral. 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 molecular symmetry breaking may occur in the solid state (Anthony *et al.*, 1998). This paper reports the structure of a homochiral crystal that consists of chemically symmetric molecules.



(I)

The title compound, (I), is a chemically symmetric molecule, with one methyl group and three (pyrrol-1-yl)methyl groups bonded to a central 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.

As can be seen in Table 1, the corresponding bond lengths and angles amongst the three (pyrrol-1-yl)methyl groups are not strictly equal. Such subtle differences are further indicated by the torsion angles about bonds C2—N1, C7—N2 and C12—N3, where the differences between any two corresponding torsion angles are far larger than their uncertainties (see Table 1). The different torsion angles C17—C1—C2—N1, C17—C1—C7—N2 and C17—C1—C12—N3 [51.4 (3), 64.1 (3) and 48.2 (3)°, respectively] indicate that the orientations of the three (pyrrol-1-yl)methyl groups about the C1—C17 bond are

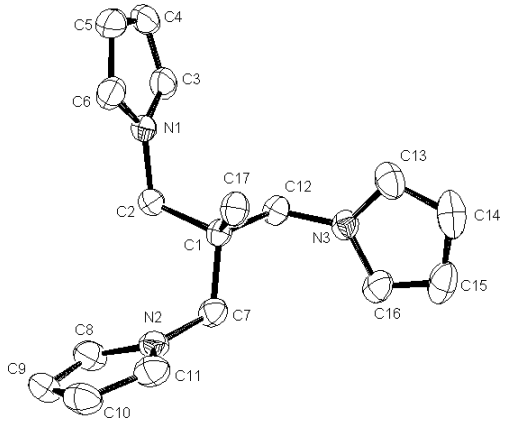


Figure 1
The molecular structure of the title compound, (I). Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity.

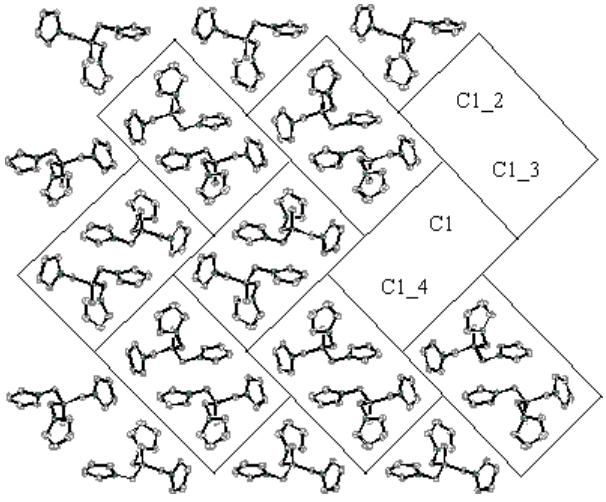


Figure 2
The molecular packing arrangement of (I), viewed normal to (100), showing the herring-bone packing of the supramolecular assembly units. H atoms have been omitted.

also different. There is one significantly short intramolecular C—H···N hydrogen bond involving atoms N2 and H2*B*, with a H···*A* distance (H2*B*···C2) of 2.52 Å and a *D*···*A* distance (C2···N2) of 2.95 Å. The molecular shape is therefore distorted from an ideal triangular pyramid and, in fact, lacks any improper rotation symmetry; hence, the molecular geometry is chiral (Raval, 2003).

The $P2_12_12_1$ space group indicates that the crystal is homochiral and contains just one type of enantiomer. Inspection of the molecular packing arrangement reveals that the single-handed molecules self-assemble into one-dimensional stacks along the *a* axis, and these stacks are packed in the formation of dimeric stacks. Such dimers can be described as supramolecular assembly units, and each has a rectangular cross-section on (100) and an unlimited length along the *a* axis. Fig. 2 shows the herring-bone packing of the supramolecular assembly units in the crystal.

This paper further emphasizes the need to consider the structural parameters of molecules when discussing molecular symmetry and molecular chirality (Berger *et al.*, 2001; Casarini *et al.*, 2001). It also suggests that chiral shapes of chemically symmetric molecules should be taken into consideration in the description of crystal packing (Pidcock & Motherwell, 2004; Anthony *et al.*, 1998), since spontaneous chiral symmetry breaking occurs in the solid state.

Experimental

The title compound was synthesized by reacting 1,1,1-tris(bromomethyl)ethane (3.09 g, 0.01 mol) and the sodium salt of pyrrole (2.94 g, 0.033 mol) in dry dimethylformamide (50 ml) at room temperature for 6 h, then at 333 K for 6 h. The mixture was then cooled to room temperature and poured into ice water (100 ml). The precipitate was filtered off, washed with water and ethanol, and purified by recrystallization from hot ethanol and dimethylformamide (1:1) to yield colorless crystals (yield 72.6%; m.p. 453–455 K). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.95 (*s*, 3H), 3.84 (*s*, 6H), 6.17(*t*, *J* = 2.0 Hz, 6H), 6.57 (*t*, *J* = 1.98 Hz, 6H); IR (KBr) ν: 3099, 2979, 2874, 1578, 1498, 1454, 1353, 1282, 1088, 966, 735, 622 cm^{-1}.

Crystal data

$C_{17}H_{21}N_3$
M_r = 267.37
Orthorhombic, $P2_12_12_1$
a = 7.7625 (14) Å
b = 11.2496 (19) Å
c = 17.542 (3) Å
V = 1531.8 (5) Å^3
Z = 4
D_x = 1.159 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2807 reflections
θ = 2.2–22.4°
μ = 0.07 mm^{-1}
T = 298 (2) K
Prism, colorless
0.70 × 0.55 × 0.40 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.953, T_{max} = 0.973
7054 measured reflections
1746 independent reflections
1594 reflections with $I > 2\sigma(I)$
R_{int} = 0.045
θ_{max} = 26.0°
h = −9 → 9
k = −13 → 12
l = −12 → 21

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.057
$wR(F^2)$ = 0.138
S = 1.17
1746 reflections
183 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0751P)^2 + 0.0401P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.033 (5)

Table 1
Selected geometric parameters (Å, °).

N1—C2	1.451 (3)	C4—C5	1.386 (6)
N2—C7	1.457 (3)	C9—C10	1.409 (5)
N3—C12	1.442 (3)	C14—C15	1.406 (5)
C3—N1—C6	108.7 (3)	N1—C2—C1	115.8 (2)
C11—N2—C8	108.3 (2)	N2—C7—C1	114.6 (2)
C13—N3—C16	107.6 (3)	N3—C12—C1	115.5 (2)
C3—N1—C2—C1	90.1 (3)	C16—N3—C12—C1	80.4 (3)
C6—N1—C2—C1	−91.8 (3)	C17—C1—C2—N1	51.4 (3)
C8—N2—C7—C1	92.3 (3)	C17—C1—C7—N2	64.1 (3)
C11—N2—C7—C1	−87.8 (3)	C17—C1—C12—N3	48.2 (3)
C13—N3—C12—C1	−94.5 (3)		

H atoms were included in calculated positions and treated as riding atoms, with C—H = 0.95 Å and $U_{iso} = 1.2U_{eq}$(C). In the absence of significant anomalous dispersion effects, Friedel pairs were merged.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); 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). *Cryst. Eng.* **1**, 1–18.
Berger, R., Gottselig, M., Quack, M. & Willeke, M. (2001). *Angew. Chem. Int. Ed.* **40**, 4195–4198.
Bruker. (1999). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Casarini, D., Lunazzi, L. & Mazzanti, A. (2001). *Angew. Chem. Int. Ed.* **40**, 2536–2540.
Pidcock, E. & Motherwell, W. D. S. (2004). *Cryst. Growth Des*. **4**, 611–620.
Raval, R. (2003). *Nature (London)*, **425**, 463–464.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1997*a*). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Sheldrick, G. M. (1997*b*). *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.