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5,5-Bis(4-cyano-2-oxabutyl)-1,9-dicyano-3,7-dioxanonane

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Abstract

The pentaerythritol derivative, 5,5-bis(4-cyano-2-oxabutyl)-3,7-dioxanonane-1,9-dicarbonitrile, adopts a four-directional conformation in which each of the four appendages attached to the central C atom is extended with torsion angles within 30° of *anti*, except for that about the OC—CCN bond, which is *gauche*. One cyanomethyl group exhibits unresolved disorder.

Comment

The porosity of polyfunctionalized dendritic macromolecules is based, in part, on the microenvironment

instilled by the initial four-directional core (Newkome, Nayak, Behera, Moorefield & Baker, 1992; Newkome, Moorefield & Baker, 1992; Newkome & Lin, 1991; Newkome, Moorefield, Baker, Johnson & Behera, 1991). Treatment of pentaerythritol with acrylonitrile, using Burson's procedure (Burson, 1946), afforded one-step entry to the title compound (m.p. 312–313 K), which is an ideal polyfunctional core. In view of steric constraints in the carbon analogue, which has been reported (Newkome, Arai, Fronczek, Moorefield, Lin & Weis, 1993), the introduction of ethereal moieties in the inner lipophilic regions may circumvent part of these steric issues as well as instill new binding centers. Initial computational analysis of this compound indicated two nearly identical energetically equivalent conformers; thus a structural confirmation was deemed necessary prior to polymer construction.

This study confirms the four-directional conformation with extended chains, having *gauche*-oriented terminal cyano groups in the crystal structure. Torsion angles chemically equivalent to C1—C2—O1—C3 range 149.9 (2)–162.8 (2)° in magnitude, those equivalent to C2—O1—C3—C4 range 163.3 (6)–179.2 (2)° and those equivalent to O1—C3—C4—C5 range 35.5 (11)–57.7 (3)°, with the sign of O1—C3—C4—C5 being opposite to the other three. The value of the O4—C15—C16—C17 torsion angle, involving C16, as well as the values of the bond distances in that CH₂CN group, are uncertain as a result of the unresolved disorder. However, it is clear that the cyano groups alternate above and below the best plane of the remainder of the molecule.

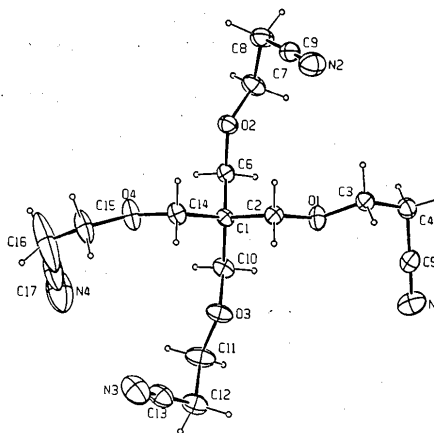


Fig. 1. The title molecule with thermal ellipsoids drawn at the 30% probability level and H atoms drawn as circles of arbitrary radii.

Experimental

Crystal data

C₁₇H₂₄N₄O₄
M_r = 348.4

Cu Kα radiation
λ = 1.54184 Å

Monoclinic
 $P2_1/c$
 $a = 21.693 (6) \text{ \AA}$
 $b = 5.762 (2) \text{ \AA}$
 $c = 16.404 (4) \text{ \AA}$
 $\beta = 107.05 (2)^\circ$
 $V = 1960 (2) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.180 \text{ Mg m}^{-3}$

Data collection

Enraf-Nonius CAD-4
 diffractometer
 ω - 2θ scans
 Absorption correction:
 empirical
 $T_{\min} = 0.8648$, $T_{\max} = 0.9973$
 4418 measured reflections
 3913 independent reflections
 2562 observed reflections
 $[I > 3\sigma(I)]$

Refinement

Refinement on F^2
 Final $R = 0.067$
 $wR = 0.081$
 $S = 3.504$
 2562 reflections
 227 parameters
 H-atom parameters not refined
 $w = 4F_o^2[\sigma^2(I) + (0.02F_o^2)^2]^{-1}$
 $(\Delta/\sigma)_{\max} = 0.07$

Cell parameters from 25
 reflections
 $\theta = 25-30^\circ$
 $\mu = 0.67 \text{ mm}^{-1}$
 $T = 301 \text{ K}$
 Needle
 $0.52 \times 0.18 \times 0.15 \text{ mm}$
 Colorless
 Crystal source: recrystallized
 from benzene/ethyl acetate

$R_{\text{int}} = 0.014$
 $\theta_{\text{max}} = 75^\circ$
 $h = 0 \rightarrow 27$
 $k = 0 \rightarrow 6$
 $l = -19 \rightarrow 19$
 3 standard reflections
 frequency: 166.67 min
 (10 000 s)
 intensity variation: random

$\Delta\rho_{\text{max}} = 0.56 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.11 \text{ e \AA}^{-3}$
 Extinction correction:
 $(1 + gI_c)^{-1}$ applied to I_c
 Extinction coefficient: $g = 1.4 (2) \times 10^{-6}$
 Atomic scattering factors
 from *International Tables*
 for *X-ray Crystallography*
 (1974, Vol. IV)

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

	$B_{\text{eq}} = \frac{8\pi^2}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$		
	x	y	z
O1	0.63660 (9)	0.0797 (4)	-0.0513 (1)
O2	0.71139 (9)	0.2447 (4)	0.1484 (1)
O3	0.7829 (1)	0.0821 (4)	-0.0962 (1)
O4	0.8515 (1)	0.3098 (4)	0.0964 (2)
N1	0.5644 (2)	-0.3401 (6)	-0.2077 (2)
N2	0.5759 (2)	0.5998 (6)	0.0969 (2)
N3	0.8798 (2)	0.4569 (6)	-0.1799 (2)
N4	0.9869 (2)	-0.0412 (8)	0.1091 (4)
C1	0.7447 (1)	0.1808 (5)	0.0228 (2)
C2	0.6801 (1)	0.2691 (5)	-0.0325 (2)
C3	0.5715 (1)	0.1436 (6)	-0.0807 (2)
C4	0.5324 (1)	-0.0781 (6)	-0.0988 (2)
C5	0.5502 (2)	-0.2250 (6)	-0.1602 (2)
C6	0.7371 (1)	0.0746 (5)	0.1047 (2)
C7	0.6732 (2)	0.1544 (7)	0.1973 (2)
C8	0.6399 (2)	0.3566 (7)	0.2253 (2)
C9	0.6037 (1)	0.4948 (6)	0.1537 (2)
C10	0.7712 (1)	-0.0077 (5)	-0.0221 (2)
C11	0.8272 (2)	-0.0614 (7)	-0.1221 (2)
C12	0.8401 (2)	0.0366 (7)	-0.1982 (2)
C13	0.8638 (2)	0.2743 (7)	-0.1864 (2)
C14	0.7909 (1)	0.3847 (6)	0.0435 (2)
C15	0.9021 (2)	0.4623 (8)	0.0985 (3)
C16	0.9602 (2)	0.368 (1)	0.1290 (7)
C17	0.9755 (2)	0.1411 (9)	0.1163 (4)

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

O1—C2	1.416 (4)	C1—C2	1.517 (3)
O1—C3	1.400 (3)	C1—C6	1.528 (4)
O2—C6	1.421 (4)	C1—C10	1.517 (4)
O2—C7	1.410 (4)	C1—C14	1.514 (4)
O3—C10	1.411 (4)	C3—C4	1.514 (5)
O3—C11	1.423 (5)	C4—C5	1.452 (5)
O4—C14	1.414 (3)	C7—C8	1.512 (5)
O4—C15	1.399 (5)	C8—C9	1.446 (4)
N1—C5	1.133 (5)	C11—C12	1.471 (6)
N2—C9	1.126 (4)	C12—C13	1.455 (5)
N3—C13	1.103 (5)	C15—C16	1.328 (6)
N4—C17	1.094 (7)	C16—C17	1.379 (8)
C2—O1—C3	114.3 (2)	N1—C5—C4	179.6 (3)
C6—O2—C7	114.5 (3)	O2—C6—C1	109.1 (2)
C10—O3—C11	110.6 (2)	O2—C7—C8	107.5 (3)
C14—O4—C15	113.9 (3)	C7—C8—C9	111.8 (3)
C2—C1—C6	110.0 (2)	N2—C9—C8	178.6 (4)
C2—C1—C10	111.4 (2)	O3—C10—C1	110.2 (2)
C2—C1—C14	108.0 (2)	O3—C11—C12	110.1 (3)
C6—C1—C10	107.1 (2)	C11—C12—C13	113.3 (3)
C6—C1—C14	110.4 (2)	N3—C13—C12	177.4 (3)
C10—C1—C14	110.1 (2)	O4—C14—C1	109.6 (2)
O1—C2—C1	108.1 (2)	O4—C15—C16	113.8 (4)
O1—C3—C4	107.2 (3)	C15—C16—C17	125.1 (5)
C3—C4—C5	112.3 (3)	N4—C17—C16	177.1 (8)

Programs used were *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982), *SDP* (Frenz, 1978) and *ORTEP* (Johnson, 1965). The cyanomethyl group C16—C17—N4 exhibits apparent unresolved disorder. The refinement model, which was most successful in accounting for the electron density in this region, used single anisotropic sites, which necessarily leads to unrealistic bond distances and angles.

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Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55838 (27 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH1014]

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Structure of a Hexasubstituted 1,3-Dioxane Compound Derived from Meldrum's Acid: $C_4O_4(CH_3)_2(CH_2CO_2C_2H_5)_2$

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Abstract

The species $C_4O_4(CH_3)_2(CH_2CO_2C_2H_5)_2$ (diethyl 2,2-dimethyl-4,6-dioxo-1,3-dioxane-5,5-diacetate) was synthesized from Meldrum's acid and ethyl bromoacetate and subjected to an X-ray diffraction study. The molecule has approximate C_{2v} symmetry. The 1,3-dioxane system is essentially planar and has neither the boat nor the chair conformation typical of saturated six-membered 1,3-dioxane rings.

Comment

'Meldrum's acid', $C_6H_8O_4$, was first reported more than 80 years ago as the product of the condensation of malonic acid with acetone. It was originally misformulated (Meldrum, 1908) as the carboxylic acid $C(O)=O-CMe_2-CHCO_2H$. This product was correctly identified as isopropylidene malonate or 2,2-dimethyl-1,3-dioxane-4,6-dione by Davidson & Bernhard (1948). This compound has been used extensively as an organic reagent (Fieser & Fieser, 1967; McNab, 1978). Most 1,3-dioxane derivatives have a boat conformation, although 2,2,5,5-tetrasubstituted compounds favor the chair conformation (Jones & Kennard, 1977). In contrast to this, the present structure is based upon a planar (± 0.007 Å) hexasubstituted 1,3-dioxane ring. Deviations of atoms from the least-squares plane of the 1,3-dioxane ring are -0.003 for C(1), -0.007 for C(12), 0.014 for O(13), -0.012 for C(14), 0.003 for O(15) and 0.005 Å for C(16). The two O atoms linked by $C=O$

double bonds [C(12)—O(12) = 1.197 (3) and C(16)—O(16) = 1.199 (3) Å] to the ring are also essentially coplanar with the dioxane ring with deviations of -0.039 for O(12) and 0.014 Å for O(16). The remaining substituents are located symmetrically above and below the 1,3-dioxane plane with deviations of -1.276 for C(17), 1.215 for C(18), -1.235 for C(22) and 1.221 Å for C(32).

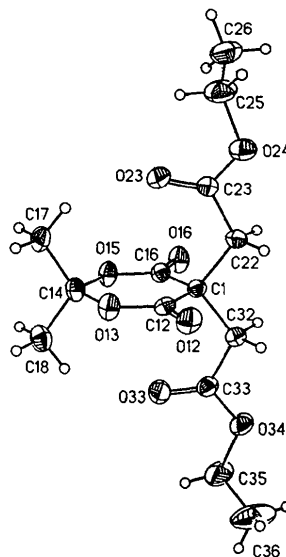


Fig. 1. Labelling of atoms in $C_4O_4(CH_3)_2(CH_2CO_2C_2H_5)_2$; ORTEPII (Johnson, 1976) diagram with 50% probability ellipsoids and H atoms artificially reduced.

Experimental

Crystal data

$C_{14}H_{20}O_8$
 $M_r = 316.3$
 Monoclinic
 $P2_1/c$
 $a = 17.696$ (4) Å
 $b = 10.360$ (2) Å
 $c = 8.733$ (1) Å
 $\beta = 93.47$ (2)°
 $V = 1598.0$ (5) Å³
 $Z = 4$

$D_x = 1.315$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 50 reflections
 $\theta = 12.5$ – 15.0 °
 $\mu = 0.102$ mm⁻¹
 $T = 295$ K
 Plate
 $0.6 \times 0.5 \times 0.3$ mm
 Colorless

Data collection

Siemens R3m/V diffractometer
 2θ (counter)— θ (crystal) scans
 Absorption correction: none
 4488 measured reflections
 2103 independent reflections
 2103 observed reflections
 $[F > 0.5\sigma(F)]$
 $R_{int} = 0.0127$

$\theta_{max} = 22.5$ °
 $h = -19 \rightarrow 19$
 $k = -11 \rightarrow 0$
 $l = -9 \rightarrow 9$
 3 standard reflections monitored every 97 reflections
 intensity variation: not significant

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