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1,4-Bis(dinitromethyl)cubane

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Key indicators

Single-crystal X-ray study
T = 294 K
Mean σ(C–C) = 0.003 Å
R factor = 0.050
wR factor = 0.139
Data-to-parameter ratio = 8.9

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

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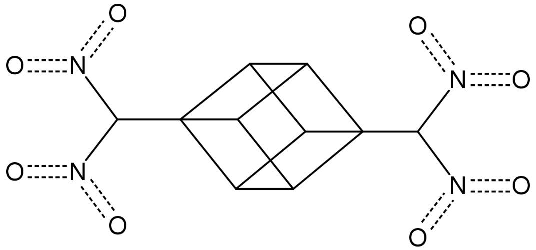
The title compound, 1,4-bis(dinitromethyl)pentacyclo[4.2.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]octane, $C_{10}H_8N_4O_8$, crystallizes in the monoclinic space group $P2_1/c$. The asymmetric unit consists of two half-molecules located about centers of inversion. There are no significant differences in chemically equivalent bond lengths and angles between the two half-molecules.

Comment

Cubane and its derivatives are highly strained stable molecules. Substituted cubanes are of interest because, with the proper number and type of energetic substituents, they have proved to be very high-energy high-density materials (Zhang *et al.*, 2000). The rigid framework of the cubane skeleton, in which multiple functional groups would possess unique arrangements, shows also potential applications for use in pharmaceutical and polymer chemistry (Butcher *et al.*, 1995). Functionalization of the cubane skeleton has involved displacement directly at the cubyl C atoms either *via* carbanions (Eaton *et al.*, 1987), radicals (Moriarty *et al.*, 1989) or hypervalent iodine methods (Eaton & Cunkle, 1986). In this study, we report on the next logical step in this synthetic area, exocyclic carbanionic functionalization involving the cubylcarbinyl carbanion, as in the conversion of 1,4-bis(nitromethyl)cubane to 1,4-bis(dinitromethyl)cubane, (I).



(I)

Fig. 1 shows the structure and labeling scheme for the title compound. Selected metrical parameters for the title compound are given in Table 1. The average C—C bond length (within the cube) of 21 disubstituted cubanes in the Cambridge Structural Database is 1.564 Å (n = 93; Allen & Kennard, 1993). Butcher *et al.* (1995) reported lengthening of the C—C bond when a π-donating or accepting group is oriented orthogonal to a cube edge and shortening of the C—C bond when such a substituent is nearly eclipsed with (*i.e.* parallel to) the cube edge. Based on the larger number of entries now in the Cambridge Structural Database, the average C—C bond length when a π-donating or accepting group is oriented orthogonal to a cube edge is 1.582 Å (n = 7), and 1.549 Å (n = 7) when such a group is parallel to the cube

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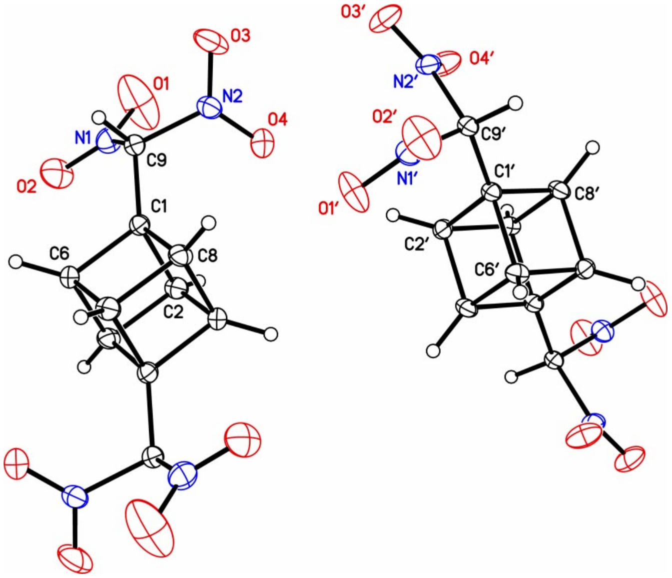

Figure 1
View of 1,4-bis(dinitromethyl)cubane showing the labeling of all non-H atoms. Displacement ellipsoids are at the 20% probability level. H atoms are drawn as small circles of arbitrary radii. Symmetry atoms required to complete the cubane structure are included but not labeled.

edge. When the nitro group is moved one carbon away from the cube this effect is absent, as the C—C bond lengths in (I) are 1.563 (3) or 1.565 (3) Å.

Experimental

The title compound, (I), was synthesized by nucleophilic displacement upon $C(NO_2)_4$ by the anion derived from 1,4-bis(nitromethyl)cubane, (I*a*). The dianion of (I*a*), generated at 273 K in methanol with 4.3 equivalents of KOH, was treated with 5.3 equivalents of tetranitromethane. The mixture was stirred for 10 min at 273 K, then was poured into chilled 1 *M* acetic acid. After work-up, chromatography and crystallization from CCl_4, the title compound was obtained in 18% yield. Clear pale yellow crystals of the title compound were grown from 2-butanone/*n*-octane.

Crystal data

$C_{10}H_8N_4O_8$
$M_r = 312.20$
Monoclinic, $P2_1/c$
$a = 11.2481$ (4) Å
$b = 7.1112$ (3) Å
$c = 16.1263$ (7) Å
$\beta = 99.043$ (5)°
$V = 1273.87$ (9) Å^3
$Z = 4$
$D_x = 1.628$ Mg m^{-3}

Cu *Kα* radiation
Cell parameters from 30 reflections
$\theta = 5.6$–31.4°
$\mu = 1.27$ mm^{-1}
$T = 294$ (2) K
Plate, pale yellow
0.60 × 0.46 × 0.06 mm

Data collection

Siemens *P*4 diffractometer
$2\theta/\omega$ scans
Absorption correction: analytical (*XPREP*; Siemens, 1994)
$T_{min} = 0.539$, $T_{max} = 0.927$
3788 measured reflections
1790 independent reflections
1636 reflections with $(I > 2\sigma(I)$

$R_{int} = 0.054$
$\theta_{max} = 58.2°$
$h = -12 \rightarrow 12$
$k = -7 \rightarrow 7$
$l = 0 \rightarrow 17$
3 standard reflections every 97 reflections intensity decay: 6.8%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.139$
$S = 1.03$
1790 reflections
200 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0782P)^2 + 0.7744P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.008$
$\Delta\rho_{max} = 0.42$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0091 (10)

Table 1
Selected geometric parameters (Å).

C1—C6	1.563 (3)	C1′—C8′	1.560 (3)
C1—C8	1.563 (3)	C1′—C2′	1.565 (3)
C1—C2	1.565 (3)	C1′—C6′	1.567 (3)

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS* (Siemens, 1994); data reduction: *XPREP* (Siemens, 1994); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXTL* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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