Acta Cryst. (1993). **C49**, 1641–1643

Structure of 2-Methoxycarbonyl-1,4-dinitrocubane

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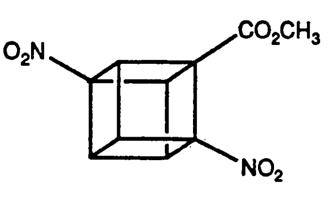
(*Received* 10 *September* 1992; *accepted* 9 *February* 1993)

Abstract

The title compound, methyl 2,7-dinitropentacyclo-[4.2.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]octane-1-carboxylate, is one of the few examples of cubanes with substituents on adjacent C atoms. There are two enantiomeric molecules per asymmetric unit in a structure with a noncentrosymmetric space group, $P2_12_12$. The molecules differ primarily in the conformations of the C—NO_2 groups adjacent to the methoxycarbonyl sustituents. The 1,2-disubstituted cubane C—C bonds average 1.564 Å, a typical value for an unsubstituted cubane bond.

Comment

Nitrocubanes are of interest as potential high energy density materials. Although several nitrocubanes are known, there are no examples of cubanes with nitro substituents on adjacent C atoms. The title compound, 2-methoxycarbonyl-1,4-dinitrocubane (I), was prepared as a possible precursor to a 1,2-dinitrocubane (Bashir-Hashemi, 1993).



(I)

There are two molecules per asymmetric unit. An *ORTEP* drawing of (I) is shown in Fig. 1. The molecules are enantiomers. There is an approximate local center of symmetry at 0.475, 0.133, 0.723. The structures differ primarily in the C1 and C1′ nitro-group conformations [*e.g.* C2—C1—N1—O1 = 65 (1), C2—C1—N1—O2 = −115.7 (8), C2′—C1′—N1′—O1′ = 30 (1), C2′—C1′—N1′—O2′ = −151.9 (7)°]. The 1.467 Å average of the four C—N distances is virtually identical to the 1.466 Å reported for 1,4-dinitrocubane (Eaton, Ravi Shankar, Price, Pluth, Gilbert, Alster & Sandus, 1984) and the average C—CO_2CH_3 distance of 1.476 Å is close to the 1.483 Å value in 1-methoxycarbonyl-4-phenylcubane (Moriarty, Khosrowshahi, Miller, Flippen-Anderson & Gilardi, 1989). The various ring C—C bond lengths, including C1—C2, are typical of cubanes. A recent summary (Ammon, Choi, Damavarapu, Iyer & Alster, 1990) of cubane C—C distances reported a range of 1.55–1.57 Å. The 1.564 Å average for C1—C2 is about midway between the 1.525 and 1.533 Å values for 1,2-disubstituted bonds found in cubanourea and *N*,*N*′-dinitrocubanourea (Eaton, Pramod & Gilardi, 1990), and the 1.598 and 1.607 Å distances found in 1-*tert*-butyl-2-cubylcubane (Gilardi, Maggini & Eaton, 1988) and 1,4-[bis(diisopropylamino)methyl]-2,7-diphenylcubane (Bashir-Hashemi, Ammon & Choi, 1990). This observation suggests that in cubanes with electron-withdrawing vicinal substituents, such as octanitrocubane, the cubane cage may not be stretched beyond normal values by the 1,2-non-bonded steric interactions.

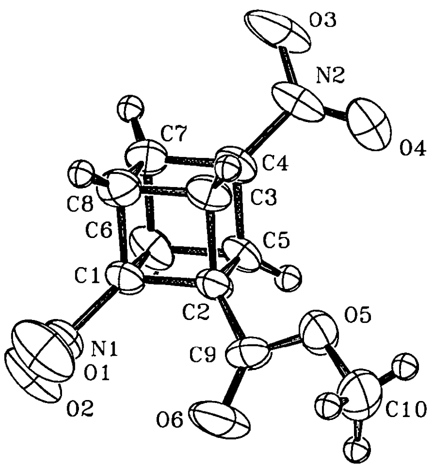


Fig. 1. An *ORTEP* drawing of (I). The C and N atoms are shown as 50% ellipsoids; H atoms as 0.1 Å spheres.

Experimental

Crystal data

$C_{10}H_8N_2O_6$
M_r = 252.18
Orthorhombic
$P2_12_12$
a = 13.484 (3) Å
b = 22.325 (3) Å
c = 6.987 (1) Å

λ = 1.5418 Å
Cell parameters from 25 reflections
θ = 7.9–25.4°
μ = 1.18 mm^{-1}
T = 293 K
Hexagonal plate

$V = 2103$ (1) Å^3
$Z = 8$
$D_x = 1.59$ Mg m^{-3}
Cu $K\alpha$ radiation
0.53 × 0.26 × 0.1 mm
Yellow–orange
Crystal source: Bashir-Hashemi

Data collection

Enraf-Nonius CAD-4 diffractometer
θ-2θ scans
Absorption correction: empirical
$T_{\min} = 0.779$, $T_{\max} = 1.00$
2732 measured reflections
2414 independent reflections
1570 observed reflections [$I > 3\sigma(I)$]
$R_{\rm int} = 0.007$
$\theta_{\max} = 72.05°$
h,k,l's generated to maintain $0 \leq \chi \leq 90°$
8 standard reflections
frequency: 60 min
intensity variation: ±1.5%

Refinement

Refinement on F
Final $R = 0.050$
$wR = 0.066$
$S = 1.50$
1570 reflections
381 parameters
All H-atom parameters refined
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} = 0.15$
$\Delta\rho_{\max} = 0.21$ e Å^{-3}
$\Delta\rho_{\min} = -0.23$ e Å^{-3}
Extinction correction: Zachariasen
Extinction coefficient: 1.82 (6) $\times 10^{-6}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O1	0.8636 (5)	0.0644 (2)	0.357 (1)	7.1 (3)
O2	0.9335 (4)	0.0815 (2)	0.619 (1)	6.4 (3)
O3	0.7206 (4)	0.3588 (2)	0.458 (1)	6.9 (3)
O4	0.5950 (5)	0.3122 (2)	0.578 (1)	7.3 (3)
O5	0.5489 (3)	0.1282 (2)	0.492 (1)	4.7 (2)
O6	0.6603 (4)	0.0590 (2)	0.569 (1)	6.0 (3)
N1	0.8783 (4)	0.0953 (2)	0.493 (1)	3.6 (2)
N2	0.6796 (5)	0.3137 (2)	0.517 (1)	4.4 (3)
C1	0.8265 (4)	0.1531 (2)	0.502 (1)	2.9 (2)
C2	0.7113 (4)	0.1595 (2)	0.519 (1)	2.9 (2)
C3	0.7161 (5)	0.2085 (3)	0.358 (1)	3.4 (3)
C4	0.7329 (4)	0.2564 (2)	0.513 (1)	3.2 (2)
C5	0.7287 (5)	0.2091 (3)	0.673 (1)	2.9 (3)
C6	0.8437 (6)	0.2014 (3)	0.655 (1)	3.5 (3)
C7	0.8473 (4)	0.2494 (2)	0.495 (1)	3.7 (3)
C8	0.8300 (6)	0.2002 (3)	0.340 (1)	3.8 (3)
C9	0.6401 (5)	0.1091 (2)	0.530 (1)	3.3 (3)
C10	0.4702 (6)	0.0830 (3)	0.495 (2)	6.0 (5)
O1′	0.1166 (5)	0.1934 (2)	0.903 (1)	8.2 (4)
O2′	−0.0043 (3)	0.1479 (2)	1.0286 (9)	5.6 (3)
O3′	0.3817 (4)	−0.0555 (3)	1.090 (1)	7.8 (4)
O4′	0.2625 (4)	−0.1078 (2)	0.981 (1)	6.3 (3)
O5′	0.4025 (3)	0.1371 (2)	0.9374 (8)	4.7 (2)
O6′	0.3060 (5)	0.1833 (2)	1.140 (1)	9.2 (4)
N1′	0.0792 (4)	0.1502 (2)	0.9727 (8)	3.6 (2)
N2′	0.2976 (4)	−0.0618 (2)	1.031 (1)	4.0 (3)
C1′	0.1383 (4)	0.0953 (2)	0.988 (1)	2.8 (2)
C2′	0.2535 (4)	0.0919 (2)	1.011 (1)	3.1 (3)
C3′	0.2364 (5)	0.0425 (2)	1.172 (1)	2.8 (2)
C4′	0.2385 (4)	−0.0070 (2)	1.015 (1)	2.8 (2)
C5′	0.2569 (5)	0.0411 (2)	0.856 (1)	3.0 (3)
C6′	0.1406 (5)	0.0455 (2)	0.831 (1)	2.8 (3)
C7′	0.1248 (4)	−0.0030 (2)	0.990 (1)	3.1 (2)
C8′	0.1216 (5)	0.0477 (3)	1.146 (1)	2.9 (2)
C9′	0.3221 (5)	0.1423 (2)	1.038 (1)	3.7 (3)
C10′	0.4780 (5)	0.1827 (3)	0.968 (2)	5.6 (4)

Table 2. *Bond lengths* (Å), *angles* (°) *and selected torsion angles* (°)

O1—N1	1.191 (7)	O1′—N1′	1.193 (6)
O2—N1	1.196 (7)	O2′—N1′	1.193 (6)
O3—N2	1.222 (7)	O3′—N2′	1.216 (7)
O4—N2	1.216 (8)	O4′—N2′	1.182 (7)
O5—C9	1.329 (7)	O5′—C9′	1.298 (7)
O5—C10	1.464 (8)	O5′—C10′	1.455 (7)
O6—C9	1.183 (6)	O6′—C9′	1.180 (7)
N1—C1	1.468 (6)	N1′—C1′	1.467 (6)
N2—C4	1.469 (6)	N2′—C4′	1.465 (6)
C1—C6	1.533 (8)	C1′—C8′	1.548 (8)
C1—C8	1.547 (9)	C1′—C6′	1.562 (8)
C1—C2	1.565 (7)	C1′—C2′	1.563 (7)
C2—C9	1.482 (7)	C2′—C9′	1.470 (7)
C2—C5	1.559 (8)	C2′—C5′	1.569 (8)
C2—C3	1.571 (8)	C2′—C3′	1.590 (9)
C3—C4	1.538 (9)	C3′—C4′	1.555 (8)
C3—C8	1.55 (1)	C3′—C8′	1.563 (9)
C4—C5	1.54 (1)	C4′—C5′	1.567 (8)
C4—C7	1.556 (8)	C4′—C7′	1.545 (7)
C5—C6	1.57 (1)	C5′—C6′	1.58 (1)
C6—C7	1.55 (1)	C6′—C7′	1.567 (8)
C7—C8	1.56 (1)	C7′—C8′	1.570 (8)
C9—O5—C10	116.5 (5)	C1—C8—C3	89.6 (5)
O1—N1—O2	123.0 (5)	C1—C8—C7	88.6 (5)
O1—N1—C1	117.7 (6)	C3—C8—C7	90.4 (5)
O2—N1—C1	119.3 (5)	O6—C9—O5	124.2 (5)
O4—N2—O3	124.4 (5)	O6—C9—C2	125.5 (6)
O4—N2—C4	116.3 (6)	O5—C9—C2	110.3 (4)
O3—N2—C4	119.3 (6)	C9′—O5′—C10′	116.2 (5)
N1—C1—C6	125.3 (5)	O1′—N1′—O2′	124.6 (5)
N1—C1—C8	123.4 (6)	O1′—N1′—C1′	118.5 (5)
N1—C1—C2	123.8 (4)	O2′—N1′—C1′	116.9 (5)
C6—C1—C8	91.4 (4)	O4′—N2′—O3′	125.0 (6)
C6—C1—C2	91.9 (5)	O4′—N2′—C4′	119.1 (6)
C8—C1—C2	91.3 (5)	O3′—N2′—C4′	115.9 (5)
C9—C2—C5	127.1 (6)	N1′—C1′—C8′	123.2 (5)
C9—C2—C1	125.3 (4)	N1′—C1′—C6′	123.6 (6)
C9—C2—C3	126.2 (6)	C4′—C7′—C8′	89.5 (4)
C5—C2—C1	88.2 (4)	C6′—C7′—C8′	89.9 (4)
C5—C2—C3	89.6 (4)	C1′—C8′—C3′	89.4 (4)
C1—C2—C3	88.2 (5)	C1′—C8′—C7′	89.8 (5)
C4—C3—C8	89.7 (5)	C3′—C8′—C7′	90.0 (4)
C4—C3—C2	89.2 (5)	O6′—C9′—O5′	123.5 (6)
C8—C3—C2	90.9 (5)	C9′—C2′—C3′	122.2 (6)
N2—C4—C5	124.4 (6)	C1′—C2′—C5′	89.6 (5)
N2—C4—C3	123.3 (6)	C1′—C2′—C3′	87.8 (4)
N2—C4—C7	125.0 (5)	C5′—C2′—C3′	89.5 (4)
C5—C4—C3	91.6 (4)	C4′—C3′—C8′	89.4 (4)
N1′—C1′—C2′	126.0 (4)	C4′—C3′—C2′	89.6 (5)
C8′—C1′—C6′	90.9 (4)	C8′—C3′—C2′	90.6 (5)
C8′—C1′—C2′	92.2 (4)	N2′—C4′—C7′	126.7 (4)
C6′—C1′—C2′	91.0 (4)	N2′—C4′—C3′	123.5 (6)
C9′—C2′—C1′	127.0 (4)	N2′—C4′—C5′	122.6 (5)
C9′—C2′—C5′	128.6 (6)	C7′—C4′—C3′	91.2 (4)
C5—C4—C7	91.6 (5)	C7′—C4′—C5′	92.1 (5)
C3—C4—C7	91.1 (5)	C3′—C4′—C5′	90.9 (4)
C4—C5—C2	89.6 (5)	C4′—C5′—C2′	90.0 (5)
C4—C5—C6	88.9 (5)	C4′—C5′—C6′	87.9 (5)
C2—C5—C6	90.9 (5)	C2′—C5′—C6′	90.1 (4)
C1—C6—C7	89.5 (5)	C1′—C6′—C7′	89.4 (5)
C1—C6—C5	89.1 (5)	C1′—C6′—C5′	89.2 (4)
C7—C6—C5	90.8 (5)	C7′—C6′—C5′	90.8 (4)
C6—C7—C4	88.8 (5)	C4′—C7′—C6′	89.2 (4)
C6—C7—C8	90.4 (4)	O6′—C9′—C2′	123.7 (6)
C4—C7—C8	88.8 (5)	O5′—C9′—C2′	112.8 (5)
O1—N1—C1—C6	−173.5 (7)	O1′—N1′—C1′—C6′	−91.1 (8)
O1—N1—C1—C8	−53.3 (9)	O1′—N1′—C1′—C8′	151.7 (7)
O1—N1—C1—C2	65 (1)	O1′—N1′—C1′—C2′	30 (1)
O2—N1—C1—C6	6 (1)	O2′—N1′—C1′—C6′	87.5 (8)
O2—N1—C1—C8	126.1 (7)	O2′—N1′—C1′—C8′	−30 (1)
O2—N1—C1—C2	−115.7 (8)	O2′—N1′—C1′—C2′	−151.9 (7)
O3—N2—C4—C5	140.4 (7)	O3′—N2′—C4′—C5′	73.3 (9)
O3—N2—C4—C3	−100.2 (8)	O3′—N2′—C4′—C3′	−43 (1)
O3—N2—C4—C7	19 (1)	O3′—N2′—C4′—C7′	−164.7 (8)

O4—N2—C4—C5	−41 (1)	O4′—N2′—C4′—C5′	−105.0 (8)
O4—N2—C4—C3	78 (1)	O4′—N2′—C4′—C3′	138.6 (7)
O4—N2—C4—C7	−162.8 (8)	O4′—N2′—C4′—C7′	17 (1)
O5—C9—C2—C5	77.6 (8)	O5′—C9′—C2′—C5′	−12 (1)
O5—C9—C2—C1	−163.3 (7)	O5′—C9′—C2′—C1′	−137.8 (7)
O5—C9—C2—C3	−45 (1)	O5′—C9′—C2′—C3′	107.5 (7)
O6—C9—O5—C10	−2 (1)	O6′—C9′—O5′—C10′	5 (1)
O6—C9—C2—C5	−101.5 (9)	O6′—C9′—C2′—C5′	168.4 (7)
O6—C9—C2—C1	18 (1)	O6′—C9′—C2′—C1′	42 (1)
O6—C9—C2—C3	135.7 (8)	O6′—C9′—C2′—C3′	−72 (1)

Data collection: Enraf–Nonius CAD-4 diffractometer software (Version 5.0). θ-scan width of $1.5(1.05 + \tan\theta)^\circ$. Scan recorded as 96 steps with two outermost 16-step blocks for background determination, θ scan speed = 8.24–1.10° min^{-1}. All crystallographic calculations performed with the *TEXSAN* system (Molecular Structure Corporation, 1987) on Digital Equipment Corporation MicroVAX II and VAXStation II computers. Structure solution with *MITHRIL* (Gilmore, 1983). The figures were drawn with *ORTEP* (Johnson, 1976) inlaid in the *TEXSAN* system. *PLOTMD* (Luo, Ammon & Gilliland, 1989) was used to display the drawings on a VAXStation monitor, add labels and prepare files for a Hewlett-Packard Laserjet II printer.

The instrumentation used in this work was obtained in part with grants from the National Science Foundation (CHE-84-02155) and the National Institutes of Health (RR-03354).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71081 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR1046]

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Acta Cryst. (1993). C**49**, 1643–1646

Phosphor(V)-Hydrazin-Sauerstoff-Achtring mit Boot-Sessel-Konformation

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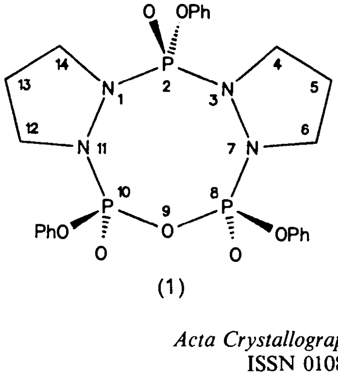
(*Eingegangen am* 8. *September* 1992; *angenommen am* 3. *Februar* 1993)

Abstract

The compound 2,8,10-triphenoxy-9-oxa-1,3,7,11-tetraaza-2λ^5,8λ^5,10λ^5-triphosphatricyclo[9.3.0.0^{3,7}]-tetradecane 2,8,10-trioxide was formed by hydrolysis as a byproduct during the synthesis of phosphoric acid–pyrazolidine ring compounds in our laboratory. The central inorganic eight-membered ring has a boat–chair conformation (approximate *m* symmetry) with a *cis*/*trans*/*trans* substituent pattern (O and O-phenyl) at the three $\mathrm{P^V}$ atoms. The C atoms of the pyrazolidine rings not bonded to N are disordered as a result of the high flexibility of these organic five-membered rings. The bond angle at the ring O atom in the P—O—P moiety is rather large [131.3 (7)°]. Bond distances and the other bond angles are in the expected ranges with mean values: N—N 1.437 (9), P—N 1.654 (9), P—O(ring) 1.595 (6), P—O(exocyclic) 1.58 (1), P═O 1.451 (8) Å.

Bemerkungen

Da nur sehr wenige Strukturen anorganischer, nichtalternierender Heterocyclen mittlerer Ringgröße bekannt sind und in der neuen, in unserem Laboratorium erstmals erhaltenen Verbindung aus spektroskopischen Daten eine Achtringstruktur (1) erwartet werden konnte, deren Daten im Vergleich mit verwandten Phosphor(V)-Hydrazin-Sechsringen interessant erschienen, haben wir die Strukturuntersuchung durchgeführt. Die Verfeinerung der



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Acta Crystallographica Section C
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