Table 2. *Selected torsional angles* (°)

Atoms	Designation*	Angle
N–Cα–C′–O″	ψ	60·2
C(8)–N–Cα–C′	φ	−96·3
C′–Cα–Cβ–Cγ		−175·7
N–Cα–Cβ–Cγ	χ^1	−51·5
Cα–Cβ–Cγ–C_1^δ	$\chi^{2.1}$	172·7
Cα–Cβ–Cγ–C_2^δ	$\chi^{2.2}$	−66·4
Cβ–Cγ–C_1^δ–$O_1^{\varepsilon1}$	$\chi^{3.1.1}$	14·8
Cβ–Cγ–C_1^δ–$O_1^{\varepsilon2}$	$\chi^{3.1.2}$	−165·1
Cβ–Cγ–C_2^δ–$O_2^{\varepsilon1}$	$\chi^{3.2.1}$	−37·4
Cβ–Cγ–C_2^δ–$O_2^{\varepsilon2}$	$\chi^{3.2.1}$	143·6

* IUPAC–IUB Commission on Biochemical Nomenclature (1970).

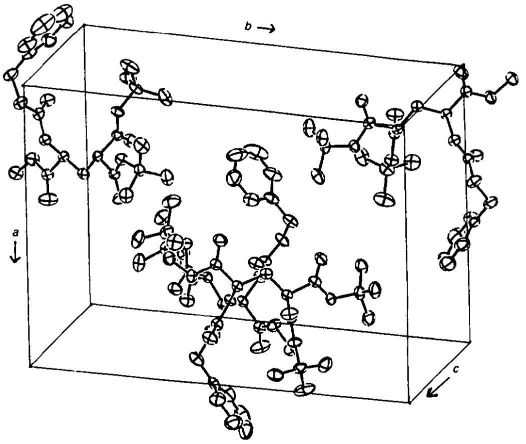

Fig. 2. The packing of the Z-Gla(O-^{t}Bu)$_2$OMe molecules in the cell. The crystallographic axial directions are shown on the figure.

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Structure of a Novel $C_{11}H_{12}N_2O_3$ Cage Molecule

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Abstract. *N*-Hydroxy-3-nitro-4-azahexacyclo[5.4.1.0^{2,6}.0^{3,10}.0^{5,9}.0^{8,11}]dodecane, $C_{11}H_{12}N_2O_3$, $M_r =$ 220·23, monoclinic, P_1/c, $a = 9{\cdot}924\,(7)$, $b = 9{\cdot}839\,(7)$, $c = 10{\cdot}287\,(7)$ Å, $\beta = 93{\cdot}40\,(6)°$, $V = 1003\,(1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}458$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}54178$ Å, $\mu = 9{\cdot}1$ cm^{-1}, $F(000) = 464$, $T = 300$ K,

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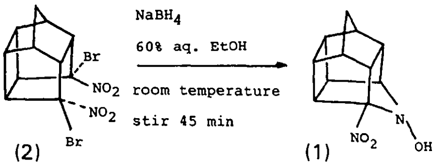
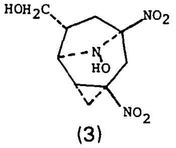
$R = 0{\cdot}093$ for 696 unique observed reflections. The cage is composed of one four-membered-ring face and six five-membered-ring faces. One five-membered ring contains an N (hydroxylamine moiety) adjacent to a bridgehead C bearing a nitro group. The crystals decompose rapidly upon exposure to air and X-rays.

Introduction. There is considerable current interest in the synthesis and chemistry of energetic polynitropolycyclic 'cage' compounds (*e.g.* Sollott & Gilbert, 1980; Eaton, Ravi Shankar, Price, Pluth, Gilbert, Alster & Sandus, 1984; Marchand & Suri, 1984; Marchand & Reddy, 1984; Paquette, Fischer & Engel, 1985). The title compound (1) was prepared as part of a continuing investigation of the structural features of this important class of energetic molecules (Ammon, Zhang, Choi, Sandus, Marchand & Suri, 1985; George, Gilardi, Flippen-Anderson, Choi, Marchand & Reddy, 1985). Compound (1) was synthesized *via* the sodium borohydride reduction of (2). It was isolated in 28% yield from the reaction mixture by column chromatography (silica gel, stationary phase, 1:2 ethyl acetate–hexane mixed solvent as eluent). Recrystallization from hexane afforded epimerically pure (1) as transparent colorless cubes, m.p. 407 K. Compound (1) is highly unusual in that it is a stable molecule of the type $R_2C(NO_2)(NHR')$ where $R' = OH$. Compounds of this type (*i.e.* those that contain a strongly electron-donating group and a strongly electron-withdrawing group bonded to the same sp^3-hybridized C atom) generally cannot be isolated. The unusual stability of (1) in this regard is most likely due to the fact that fragmentation of (1) requires concomitant formation of an anti-Bredt C=N double bond. A similar moiety exists in the dinitronortropane derivative (3) whose structure has been reported (Schenk & Benci, 1972). The structure of compound (1) is an important link in the development of new high-energy molecular systems.



(2) (1)



(3)

Experimental. The clear colorless crystals become opaque upon exposure to air and give only a diffuse diffraction pattern. Freshly prepared crystals decomposed upon exposure to X-rays in the presence of air and a data set could not be collected. After three successive preparations of compound (1), a crystal of dimensions $0{\cdot}22 \times 0{\cdot}15 \times 0{\cdot}07$ mm was sealed in a quartz capillary containing a trace of hexane; Nicolet $R3m/\mu$ update of $P2_1$ diffractometer, data collected with Wyckoff scan (2θ fixed, ω varied), variable scan rate 10–29·3° min^{-1}, graphite-monochromated Cu $K\alpha$ radiation; diffraction spots on a rotation photograph were weak and lattice parameters obtained from a least-squares refinement of only nine reflections ($12{\cdot}44 < 2\theta < 21{\cdot}73°$), angles measured by a centering routine associated with the diffractometer; systematic absences ($h0l$, $l = 2n+1$; $0k0$, $k = 2n+1$) consistent with space group $P2_1/c$, Laue symmetry $2/m$, monitored reflections $\bar{1}1\bar{1}$ and 111 collected after every 48 reflections, the two reflections decreased in intensity by 40 and 45%, respectively; the unit-cell dimensions changed during data collection, automatic recentering, data scaled by an interpolation procedure; 1355 independent reflections measured ($0 \le h \le 12$, $0 \le k \le 12$, $-12 \le l \le 12$) with only 696 having intensities greater than $2{\cdot}5\sigma(I)$; Lorentz–polarization corrections applied, crystal deterioration did not permit a ψ-scan empirical absorption correction to be made nor more accurate measurement of unit-cell parameters; structure solved by direct methods, block-cascade refinement with riding model for H atoms (one isotropic temperature factor for all H atoms); final $R = 0{\cdot}093$, $wR = 0{\cdot}091$, 145 parameters, 696 reflections, $S = 1{\cdot}47$, $(\Delta/\sigma)_{\text{max}} = 0{\cdot}031$, $(\Delta/\sigma)_{\text{mean}} = 0{\cdot}006$, largest peaks in final difference Fourier map of $+0{\cdot}29$ and $-0{\cdot}27$ e Å^{-3}; $\sum w(|F_o| - |F_c|)^2$ minimized with $w = [\sigma^2(F_o) + 0{\cdot}0034F_o^2]^{-1}$, all computer programs supplied by Nicolet (1986) for Desktop 30 Microeclipse and Nova 4/C configuration; atomic scattering factors contained in the program package (*International Tables for X-ray Crystallography*, 1974). Table 1 lists atomic positional parameters while Table 2 contains distances and valence angles.*

Discussion. Fig. 1 is a thermal-ellipsoid drawing of compound (1). The cage consists of a four-membered-ring face and six five-membered-ring faces. The five-membered rings are in envelope conformations. One five-membered ring contains an N at the flap. Chemically similar bonds opposite the N substituent are internally consistent [*i.e.* C(2)—C(9) = 1·51 (2), C(3)—C(7) = 1·52 (2) Å; C(7)—C(8) = 1·51 (2), C(8)—C(9) = 1·54 (2) Å; C(6)—C(7) = 1·55 (1), C(9)—C(10) = 1·56 (1) Å]. In the dinitronortropane derivative (3) (Schenk & Benci, 1972) the C—N bond with the

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* Lists of structure factors, H-atom parameters and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43892 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

attached nitro group [1·451 (3) Å] is significantly shorter than the other C—N bond [1·471 (2) Å]. A peak consistent with the H of the hydroxylamine was found in a difference Fourier map, refined for several cycles and then held fixed. The H interacts with N(1) of an adjacent molecule [N(1)···H(O1) = 1·79 (7), O(1)···N(1) = 2·84 (1) Å]. The unique structure provides insight into a new class of high-energy compounds which may lead to the synthesis and characterization of useful materials. The structure also serves as a starting point for molecular and quantum mechanical investigations of these systems. With extrapolated values for the stretching, bending and torsional force constants of the unusual N-atom combination, the strain energy is calculated to be 414·5 kJ mol^{-1} (Allinger & Yuh, 1980).

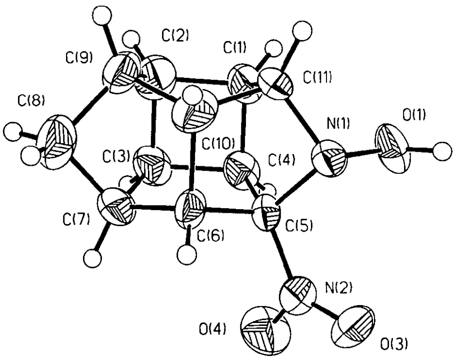

Fig. 1. Thermal-ellipsoid drawing of compound (1). Thermal ellipsoids are drawn at the 30% probability level. H atoms are represented by spheres of arbitrary size.

Table 1. *Atomic coordinates* (× 10^4) *and equivalent isotropic thermal parameters* (Å^2 × 10^3)

	x	*y*	*z*	U_{eq}*
C(1)	6290 (10)	1090 (11)	1731 (8)	74 (4)
C(2)	7226 (11)	495 (12)	718 (10)	91 (5)
C(3)	8449 (9)	841 (10)	1662 (9)	73 (4)
C(4)	7487 (9)	1423 (10)	2670 (9)	62 (4)
C(5)	7402 (8)	383 (8)	3702 (7)	45 (3)
C(6)	7901 (8)	−950 (9)	3127 (7)	56 (3)
C(7)	8947 (9)	−540 (13)	2142 (9)	75 (4)
C(8)	8644 (10)	−1468 (12)	995 (9)	96 (5)
C(9)	7159 (10)	−1036 (13)	798 (10)	79 (5)
C(10)	6649 (10)	−1321 (12)	2179 (9)	81 (4)
C(11)	5672 (8)	−143 (10)	2442 (8)	64 (4)
N(1)	5942 (7)	81 (8)	3837 (6)	57 (3)
N(2)	8061 (9)	686 (9)	4984 (8)	67 (3)
O(1)	5315 (6)	1353 (7)	4171 (7)	78 (3)
O(3)	7614 (7)	289 (9)	5971 (6)	102 (4)
O(4)	9108 (8)	1337 (8)	4956 (8)	105 (4)

* U_{eq} defined as one third of the trace of the orthogonalized U_{ij} tensor.

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

C(1)—C(2)	1·551 (14)	C(1)—C(4)	1·521 (13)
C(1)—C(11)	1·561 (14)	C(2)—C(3)	1·547 (14)
C(2)—C(9)	1·510 (17)	C(3)—C(4)	1·560 (13)
C(3)—C(7)	1·519 (16)	C(4)—C(5)	1·479 (12)
C(5)—C(6)	1·533 (12)	C(5)—N(1)	1·494 (10)
C(5)—N(2)	1·468 (11)	C(6)—C(7)	1·546 (13)
C(6)—C(10)	1·576 (12)	C(7)—C(8)	1·508 (15)
C(8)—C(9)	1·536 (15)	C(9)—C(10)	1·561 (14)
C(10)—C(11)	1·545 (14)	C(11)—N(1)	1·461 (11)
N(1)—O(1)	1·448 (10)	N(2)—O(3)	1·197 (11)
N(2)—O(4)	1·222 (12)		

C(2)—C(1)—C(4)	91·8 (7)	C(2)—C(1)—C(11)	106·8 (8)
C(4)—C(1)—C(11)	100·6 (7)	C(1)—C(2)—C(3)	88·5 (7)
C(1)—C(2)—C(9)	108·0 (9)	C(3)—C(2)—C(9)	102·7 (8)
C(2)—C(3)—C(4)	90·5 (7)	C(2)—C(3)—C(7)	103·6 (8)
C(4)—C(3)—C(7)	108·2 (8)	C(1)—C(4)—C(3)	89·1 (7)
C(1)—C(4)—C(5)	103·4 (7)	C(3)—C(4)—C(5)	106·6 (8)
C(4)—C(5)—C(6)	106·4 (7)	C(4)—C(5)—N(1)	107·5 (6)
C(6)—C(5)—N(1)	101·7 (6)	C(4)—C(5)—N(2)	117·6 (7)
C(6)—C(5)—N(2)	112·6 (7)	N(1)—C(5)—N(2)	109·8 (6)
C(5)—C(6)—C(7)	105·9 (8)	C(5)—C(6)—C(10)	100·2 (7)
C(7)—C(6)—C(10)	101·0 (7)	C(3)—C(7)—C(6)	103·2 (8)
C(3)—C(7)—C(8)	104·0 (8)	C(6)—C(7)—C(8)	104·1 (8)
C(7)—C(8)—C(9)	94·6 (8)	C(2)—C(9)—C(8)	103·8 (9)
C(2)—C(9)—C(10)	104·3 (9)	C(8)—C(9)—C(10)	101·0 (8)
C(6)—C(10)—C(9)	103·6 (7)	C(6)—C(10)—C(11)	101·4 (8)
C(9)—C(10)—C(11)	105·4 (8)	C(1)—C(11)—C(10)	103·4 (7)
C(1)—C(11)—N(1)	106·8 (7)	C(10)—C(11)—N(1)	101·8 (7)
C(5)—N(1)—C(11)	93·5 (6)	C(5)—N(1)—O(1)	106·4 (6)
C(11)—N(1)—O(1)	107·9 (6)	C(5)—N(2)—O(3)	121·9 (8)
C(5)—N(2)—O(4)	114·8 (8)	O(3)—N(2)—O(4)	123·3 (8)

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