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Structure of 2-Bromo-2-nitroadamantane (I), $C_{10}H_{14}BrNO_2$, and 2,2-Dinitroadamantane (II), $C_{10}H_{14}N_2O_4$*

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Abstract. (I) $M_r = 260{\cdot}14$, orthorhombic, $P2_12_12_1$, $a = 6{\cdot}583\ (6)$, $b = 12{\cdot}095\ (7)$, $c = 13{\cdot}024\ (8)$ Å, $V = 1037{\cdot}0\ (15)$ Å^3, $Z = 4$, $D_x = 1{\cdot}67$ gcm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 41{\cdot}7$ cm^{-1}, $F(000) = 528$, $T = 300$ K, $R = 2{\cdot}7\%$ for 744 reflections, $S = 1{\cdot}54$. (II) $M_r = 226{\cdot}23$, monoclinic, $P2_1/n$, $a = 6{\cdot}586\ (2)$, $b = 12{\cdot}407\ (4)$, $c = 12{\cdot}916\ (5)$ Å, $\beta = 100{\cdot}88\ (3)°$, $V = 1036{\cdot}3\ (5)$ Å^3, $Z = 4$, $D_x = 1{\cdot}45$ gcm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 1{\cdot}2$ cm^{-1}, $F(000) = 480$, $T = 300$ K, $R = 5{\cdot}9\%$ for 1006 reflections, $S = 1{\cdot}25$. No significant distortion of the adamantane cage is apparent in either structure. Average C—C distances are 1·525 (9) (I) and 1·525 (5) Å (II).

Introduction. The investigation is part of a program to examine the structure of high-density poly-nitro organic compounds. Adamantanes with nitro substituents are potentially high-density energetic compounds and are a class of compounds for which little structural information is available.

Experimental. Crystals of both (I) and (II) were provided by Dr Kurt Baum of Fluorochem Inc. (Azusa, CA). Nearly clear crystals, 0·6 × 0·1 × 0·1 mm, coated with an acrylic polymer to inhibit degradation due to sublimation; Nicolet *P3F* diffractometer, incident-beam monochromator, $\theta/2\theta$ data collection, scan width 2°, scan rate a function of the count rate, $\sin\theta/\lambda_{\max} = 0{\cdot}54$ Å^{-1} for both (I) and (II), range of *hkl*, −7 to 7, 0 to 12, 0 to 13 (I), 0 to 7, 0 to 13, −13 to 12 (II); for (I), 1594 reflections measured, 820 unique, $R_{\rm int} = 0{\cdot}031$, 744 observed with $F_o > 3\sigma F_o$; for (II), 1662 reflections measured, 1368 unique, $R_{\rm int} = 0{\cdot}045$, 1006 observed with $F_o > 3\sigma F_o$; standard reflections 008, 0,10,0, $\bar{4}00$ (I) and 200, 060, 006 (II) monitored every 60 measurements, intensity variations 3·0% (I), and 2·0% (II); lattice parameters determined from 22 (I) and 16 (II) centered reflections; corrections for Lorentz and polarization, not for absorption.

Structure of (I) solved by routine application of the symbolic addition procedure (Karle & Karle, 1966), and (II) with *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); hydrogens initially positioned at computed idealized locations; initial refinements with a restrained-least-squares computer program using a sparse matrix, *RESLSQ* (Flippen-Anderson, Gilardi & Konnert, 1982); final refinement with full-matrix least-squares program *ORXFLS*3 (Busing, Martin, Levy, Ellison, Hamilton, Ibers, Johnson & Thiessen, 1975); standard deviation of the structure factors computed as

$$\sigma^2|F| = \frac{QI}{4\,\mathrm{Lp}}\left[\left(\frac{\sigma_I}{I}\right)^2 + \left(\frac{\sigma_Q}{Q}\right)^2\right].$$

Lp is the Lorentz–polarization factor and Q is the attenuator factor used when the source is attenuated with a metal-foil filter for measurement of intense diffraction peaks. σ_I includes counting statistics and a term for random errors (0·02 in this work) (Gilardi, 1973). The function minimized was $\sum w(|F_o| - |F_c|)^2$, $w = \sigma^{-2}(|F_o|)$. Parameters refined: atomic coordinates for all atoms, anisotropic temperature factors for nonhydrogen atoms; temperature factors for hydrogen atoms fixed equal to those of the atoms to which they are bonded; scattering factors from *International Tables for X-ray Crystallography* (1974), anomalous scattering factors for bromine from Cromer & Liberman (1970). (I): $R = 2{\cdot}7\%$, $R_w = 2{\cdot}7\%$ for 744 reflections, $R = 3{\cdot}3\%$ for the unique set; (II): $R = 5{\cdot}9\%$, $R_w = 4{\cdot}7\%$ for 1006 reflections, $R = 8{\cdot}9\%$ for the unique set; $\Delta_{\max}/\sigma$ and $\Delta_{\rm av}/\sigma$ 0·81 and 0·16 (I) and 0·08 and 0·02 (II), exclusive of hydrogen; final difference Fourier $\Delta\rho$ excursions 0·34 and −0·30 e Å^{-3} (I), 0·14 and −0·18 e Å^{-3} (II).†

Discussion. Table 1 lists the refined coordinates and $B_{\rm eq}$ values for the nonhydrogen atoms.

Bond distances and angles for (I) and (II) are listed in Table 2, and their conformations are illustrated in Figs. 1

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* Adamantane is tricyclo[3.3.1.1^{3,7}] decane.

† Lists of structure factors, anisotropic thermal parameters and hydrogen coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38686 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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and 2, which were prepared with the aid of *ORTEP* (Johnson, 1965). No significant distortion of the adamantane cage is apparent in either structure. Average C–C distances are 1·525 (9) (I) and 1·525 (5) Å (II), while the average $\angle C_tC_sC_t =$ 110·3 (6) (I) and 110·5 (3)° (II) and $\angle C_sC_tC_s =$ 109·1 (6) (I) and 108·9 (3)° (II), where the subscripts denote the secondary and tertiary atoms. The C–Br distance is 1·979 (6) Å, which is longer than that usually observed for paraffinic monobromides, 1·937 (3) Å (Sutton, 1965). The C–NO_2 bond lengths of 1·538 (7) Å (I), 1·560 (5) and 1·555 (5) Å (II) are also long compared to C–N bonds involving nitrogen in other types of bonding environments (1·4–1·5 Å, Sutton, 1965). They are similar to those observed for the halopicrins (CX_3NO_2), where the C–NO_2 distances range from 1·56 (2) to 1·59 (2) Å (Karle & Karle, 1962; Knudsen, George & Karle, 1966), and to those observed for nitro groups bonded to tetrahedral carbon, *e.g.* 1·531–1·561 Å in 1,4-difluoro-1,1,4,4-tetranitro-2,3-dinitrooxybutane (Ammon & Bhattacharjee, 1982), 1·535–1·570 Å in 1,4-difluoro-1,1,4,4-tetranitro-2,3-butanediol (Dickerson & Holden, 1979), and 1·517–1·530 Å in 4,7-bis(fluorodinitromethyl)-1,3-dioxepane (Gilardi, 1983). The nitro groups are essentially planar, with the nitrogen atoms deviating from the least-squares planes passing through the CNO_2 groups by 0·008 (12) Å (I), 0·013 (10) and 0·011 (10) Å (II). Torsion angles for O(1)–N(1)–C(2)–Br and O(2)–N(1)–C(2)–Br are −91·1 (6) and 87·2 (6)°, respectively, for (I). Torsion angles for nitro groups on (II) are O(1)–N(1)–C(2)–N(2) 82·6 (3), O(2)–N(1)–C(2)–N(2) −94·5 (3), O(3)–N(2)–C(2)–N(1) −95·4 (3), and O(4)–N(2)–C(2)–N(1) 82·5 (3)°. Intermolecular contacts in both (I) and (II) are normal van der Waals interactions. The nearest H···H′ approaches are 2·36 (1)–2·52 (1) Å, H(3)···H(9′) and H(7)···H(4′) (I), H(1)···H(1′) and H(4)···H(7′) (II). No close O···O or O···Br contacts are observed.

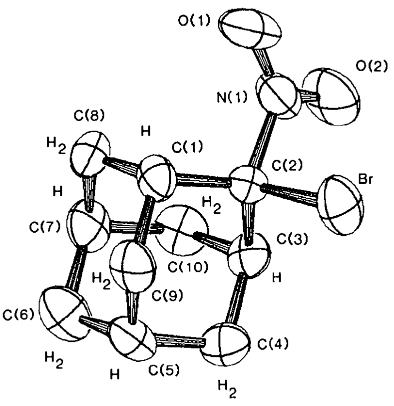

Fig. 1. A representation of the molecular structure and thermal motion of 2-bromo-2-nitroadamantane (I). Thermal ellipsoids are at the 50% probability level.

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Table 1. *Fractional coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

$$B_{\rm eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$(Å^2)
2-Bromo-2-nitroadamantane				
C(1)	0·0362 (11)	0·3958 (5)	0·0227 (5)	3·6 (2)
C(2)	0·0773 (8)	0·4086 (5)	0·1375 (5)	3·1 (1)
C(3)	0·0797 (9)	0·5294 (4)	0·1676 (5)	3·5 (2)
C(4)	0·2440 (12)	0·5901 (5)	0·1071 (5)	4·2 (2)
C(5)	0·2001 (11)	0·5784 (5)	−0·0092 (5)	4·2 (2)
C(6)	−0·0075 (14)	0·6269 (6)	−0·0335 (6)	5·3 (2)
C(7)	−0·1724 (12)	0·5688 (5)	0·0275 (5)	4·5 (2)
C(8)	−0·1702 (13)	0·4463 (6)	−0·0012 (5)	4·5 (2)
C(9)	0·1995 (11)	0·4561 (6)	−0·0376 (5)	4·4 (2)
C(10)	−0·1288 (11)	0·5778 (6)	0·1427 (5)	4·4 (2)
N(1)	−0·0750 (8)	0·3425 (5)	0·2029 (4)	4·5 (2)
O(1)	−0·1531 (9)	0·2622 (4)	0·1650 (4)	6·9 (2)
O(2)	−0·1041 (8)	0·3737 (4)	0·2887 (3)	6·4 (2)
Br	0·3339 (1)	0·3344 (1)	0·1767 (1)	5·2 (1)
2,2-Dinitroadamantane				
C(1)	0·5579 (5)	0·0521 (2)	0·3619 (3)	3·7 (1)
C(2)	0·6078 (5)	0·1708 (3)	0·3656 (2)	3·4 (1)
C(3)	0·5597 (5)	0·2226 (3)	0·2578 (3)	4·0 (1)
C(4)	0·6850 (6)	0·1657 (4)	0·1851 (3)	5·0 (1)
C(5)	0·6345 (6)	0·0467 (3)	0·1782 (3)	5·0 (1)
C(6)	0·4049 (6)	0·0312 (4)	0·1326 (3)	5·5 (1)
C(7)	0·2765 (6)	0·0868 (3)	0·2047 (3)	4·6 (1)
C(8)	0·3281 (6)	0·0375 (3)	0·3154 (3)	4·8 (1)
C(9)	0·6846 (6)	−0·0026 (3)	0·2882 (3)	4·6 (1)
C(10)	0·3280 (6)	0·2066 (3)	0·2146 (3)	4·4 (1)
N(1)	0·5017 (4)	0·2320 (3)	0·4461 (3)	4·2 (1)
O(1)	0·4461 (4)	0·1807 (2)	0·5149 (2)	6·8 (1)
O(2)	0·4867 (4)	0·3285 (2)	0·4363 (2)	7·3 (1)
N(2)	0·8378 (5)	0·1893 (3)	0·4195 (3)	4·4 (1)
O(3)	0·9091 (4)	0·1292 (3)	0·4902 (2)	6·1 (1)
O(4)	0·9289 (4)	0·2646 (3)	0·3907 (3)	7·3 (1)

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

The e.s.d.'s are listed for distances; all angle e.s.d.'s are 0·6° (I) and 0·3° (II).

	(I)	(II)		(I)	(II)
C(1)–C(2)	1·528 (8)	1·508 (3)	C(7)–C(8)	1·528 (9)	1·534 (6)
C(1)–C(8)	1·521 (11)	1·530 (5)	C(7)–C(10)	1·532 (9)	1·526 (6)
C(1)–C(9)	1·517 (10)	1·537 (5)	C(2)–N(1)	1·538 (7)	1·555 (5)
C(2)–C(3)	1·512 (8)	1·511 (5)	N(1)–O(1)	1·205 (7)	1·206 (4)
C(3)–C(4)	1·527 (9)	1·535 (5)	N(1)–O(2)	1·195 (6)	1·206 (4)
C(3)–C(10)	1·527 (9)	1·536 (5)	C(2)–Br	1·979 (6)	
C(4)–C(5)	1·548 (10)	1·511 (6)	C(2)–N(2)		1·560 (5)
C(5)–C(6)	1·520 (11)	1·528 (6)	N(2)–O(3)		1·205 (4)
C(5)–C(9)	1·525 (9)	1·526 (6)	N(2)–O(4)		1·206 (4)
C(6)–C(7)	1·517 (11)	1·533 (6)			

	(I)	(II)		(I)	(II)
C(2)–C(1)–C(8)	108·5	108·7	C(1)–C(8)–C(7)	110·3	110·3
C(2)–C(1)–C(9)	109·4	108·0	C(1)–C(9)–C(5)	110·1	110·7
C(8)–C(1)–C(9)	109·5	108·5	C(3)–C(10)–C(7)	110·4	110·2
C(1)–C(2)–C(3)	110·6	112·3	C(1)–C(2)–N(1)	112·0	112·0
C(2)–C(3)–C(4)	109·8	108·9	C(3)–C(2)–N(1)	111·4	111·4
C(2)–C(3)–C(10)	107·9	107·5	C(1)–C(2)–Br.N(2)	110·9	110·2
C(4)–C(3)–C(10)	110·0	109·3	C(3)–C(2)–Br.N(2)	111·2	111·4
C(3)–C(4)–C(5)	109·2	110·4	C(2)–N(1)–O(1)	118·0	118·2
C(4)–C(5)–C(6)	109·6	109·7	C(2)–N(1)–O(2)	117·2	116·9
C(4)–C(5)–C(9)	109·0	109·2	O(1)–N(1)–O(2)	124·7	124·8
C(6)–C(5)–C(9)	108·8	109·4	N(1)–C(2)–Br.N(2)	100·3	98·7
C(5)–C(6)–C(7)	110·8	109·2	C(2)–N(2)–O(3)		117·0
C(6)–C(7)–C(8)	108·3	109·7	C(2)–N(2)–O(4)		118·3
C(6)–C(7)–C(10)	110·2	110·5	O(3)–N(2)–O(4)		124·6
C(8)–C(7)–C(10)	107·9	107·6			

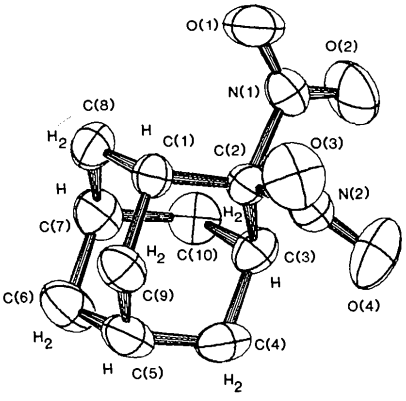

Fig. 2. A representation of the molecular structure and thermal motion of 2,2-dinitroadamantane (II). Thermal ellipsoids are at the 50% probability level.

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Structure of (±)-Methyl 7,7-Ethylenedioxy-*cis*-4a,5,6,7,8,8a-hexahydro-4a-coumarincarboxylate, $C_{13}H_{16}O_6$, and the Configuration of the 1,3-Dioxolane Ring

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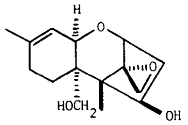
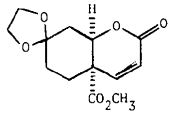
Abstract. $M_r = 268{\cdot}27$, monoclinic, $P2_1/n$, $a = 13{\cdot}296\,(6)$, $b = 15{\cdot}143\,(5)$, $c = 6{\cdot}288\,(2)$ Å, $\beta = 98{\cdot}89\,(3)°$, $V = 1250{\cdot}8\,(9)$ Å^3, $Z = 4$, $D_m = 1{\cdot}405$, $D_x = 1{\cdot}425$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 1{\cdot}06$ cm^{-1}, $F(000) = 568$, $T = 293\,(2)$ K. Final $R = 0{\cdot}052$ for 2052 observed reflections. The compound is a precursor to the anti-tumor agent verrucarol and related verrucarins (antibiotic substances isolated from a soil fungus). The X-ray study confirmed the *cis* configuration of the H atom at C(8a) and the methoxycarbonyl group at C(4a). The configuration of the ethylenedioxy (1,3-dioxolane) group is between an envelope and a twist, but closer to a twist; comparisons with the configurations of this group in other structures are presented.

Introduction. The verrucarins, a family of antibiotic substances isolated from the soil fungus *Myrothecium verrucaria* are among the most active cytostatic agents known (Tamm, 1974). A common unit found in the structures of these complex metabolites is the sesquiterpene verrucarol (I).



(I)



(II)

Approaches to the synthesis of (I) are in progress in the laboratory of J. D. White of this University (White, Matsui & Thomas, 1981; White, Carter & Kezar, 1982). In the course of these studies, it became important to establish that a key intermediate, lactone (II), possesses the *cis* ring fusion shown. Since this configuration will ultimately appear in (I) and since the

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