shorter than 3·46 Å, the sum of the van der Waals radii of O and I (Bondi, 1964). They may be considered as secondary bonds (Alcock, 1972) so that the overall coordination geometry of iodine can be described as planar pentagonal. The T-shaped group, I, O(1), O(2), C(1), is planar to within 0·007 (7) Å with O(3) and O(4) at distances 0·158 (6) and 0·078 (7) Å from the mean plane. The dihedral angles between this plane and the planes of the acetoxy groups involving O(3) and O(4) are 4·3 (3) and 2·9 (3)°, respectively. The conformational details given so far are comparable with those for (phenyl)bis(trifluoroacetato)iodine(III) (FAIB hereafter) (Stergioudis, Kokkou, Bozopoulos & Rentzeperis, 1984; Alcock, Harrison & Howes, 1984) and those for bis(dichloroacetato)(phenyl)iodine(III) (PICA hereafter) (Alcock, Countryman, Esperas & Sawyer, 1979), and agree very well with those for diacetato(phenyl)iodine(III) (PID hereafter) (Alcock *et al.*, 1979). A comparison of FAIB and PICA with PID shows that secondary I···O bonding is very sensitive to the nature of the ligands. In going from PID to PICA or to FAIB considerable distortion of the overall planar-pentagonal coordination of the I atom occurs, *i.e.* deviations from planarity, appearance of a third weaker intermolecular I···O secondary bond and weakening of the existing intramolecular ones. In the present case the substitution of an *m*-tolyl for a phenyl group does not affect the I···O secondary bonding so that the planar-pentagonal coordination of I is preserved. However, the two I···O secondary bonds are essentially equal (difference 0·8σ) while those in PID [2·850 (5), 2·817 (6) Å] are unequal with a difference of 4·24σ. Also, the dihedral angles formed by the T group and the planar benzene ring [68·4 (2) in MTID, 74·43° in PID] differ significantly.

Fig. 2 shows the molecular packing of MTID in the unit cell. There are no intermolecular hydrogen bonds. The smallest intermolecular separations are: H(C4)···O(2) (at $\frac{1}{2}+x, y, \frac{1}{2}-z$) = 2·64 and H3(C10)···O(3) (at $-\frac{1}{2}+x, \frac{1}{2}-y, -z$) = 2·75 Å.

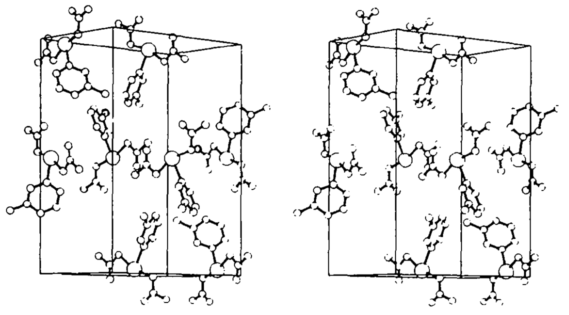

Fig. 2. Stereo plot of the unit cell viewed along [110]. The origin is in the upper front corner of the base of the outline, the *a* axis to the left and the *b* axis to the right. The *c* axis is vertical.

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3,3-Bis(methylnitraminomethyl)oxetane (I) and 3,3-Bis(nitratomethyl)oxetane (II)

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Abstract. (I): $C_7H_{14}N_4O_5$, $M_r = 234·21$, monoclinic, $P2_1/c$, $a = 14·106$ (4), $b = 6·472$ (2), $c = 11·963$ (3) Å, $\beta = 99·50$ (3)°, $V = 1077·2$ (6) Å^3, $Z = 4$, $D_x = 1·444$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0·115$ mm^{-1}, $F(000) = 496$, $T = 295$ K, final $R = 0·049$, $wR = 0·057$ for 1815 independent observed

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reflections. (II): $C_5H_8N_2O_7$, M_r = 208·13, monoclinic, $C2/c$, a = 15·120 (4), b = 6·163 (1), c = 12·958 (4) Å, β = 132·76 (2)°, V = 886·5 (3) Å^3, Z = 4, D_x = 1·559 Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ = 0·139 mm^{-1}, F(000) = 432, T = 295 K, final R = 0·051, wR = 0·073 for 1039 independent observed reflections. The oxetane ring in (I) is puckered with a dihedral angle between the C—C—C and C—O—C oxetane ring planes of 20·6°. In molecule (II) the oxetane ring is planar and the molecule has crystallographic twofold (C_2) symmetry with respect to the cross ring C—O axis. The monomers of both (I) and (II) contain energetic side chains and may be polymerized to form stable energetic homo- or copolymers.

Introduction. Elastic energetic binders appropriate for use as a primary component of solid-state propellants can be made by polymerizing suitable small molecules with energetic substituents. Copolymerization using a variety of pairs of energetic monomers is a promising method for generating materials with specific physical properties (Manser, Fletcher & Knight, 1985); (I) and (II) are nitramino and nitrato substituted oxetane monomers which have been used to prepare new energetic polymers containing the polyether backbone.

Crystals of both (I) and (II) were provided by G. E. Manser of Morton Thiokol. Compound (I) was synthesized by the action of sodiomethylnitramine on 3,3-bis(iodomethyl)oxetane in refluxing ethanol, and (II) was prepared from acetyl nitrate and 3,3-bis(hydroxymethyl)oxetane (Manser *et al.*, 1985). Both (I) and (II) have been used to prepare new energetic copolymers. A nitramine polyether may be synthesized from (I) and 3-methylnitraminomethyl-3-methyloxetane, and a nitrate ester polyether may be synthesized from (II) and 3-nitratomethyl-3-methyloxetane. Both of these polymers exhibit high thermal stability despite the regular substitution with energetic groups.

Experimental. Clear crystals: 0·45 × 0·50 × 0·25 mm (I), 0·42 × 0·40 × 0·45 mm (II); m.p. 402–404 K (I), 363–365 K (II). Automated Nicolet *R3M* diffractometer with incident-beam graphite monochromator, λ = 0·71069 Å (Mo $K\alpha$), 24 centered reflections within $20 \leq 2\theta \leq 30$ (I), $25 \leq 2\theta \leq 35°$ (II) used for determining lattice parameters. $(\sin\theta/\lambda)_{\max}$ = 0·62 Å^{-1} (I), 0·70 Å^{-1} (II). Range of hkl: $-17 \leq h \leq 17$, $0 \leq k \leq 7$, $-14 \leq l \leq 14$ (I); $-16 \leq h \leq 21$, $0 \leq k \leq 7$, $-18 \leq l \leq 11$ (II). Standards 600, 040, 004 (I), 600, 040, 006 (II), monitored every 60 reflections with random variation 1·8% (I), 2·0% (II) over data collection; θ–2θ mode; scan width (1·8° + $\Delta_{\alpha1\alpha2}$) (I), (2·0° + $\Delta_{\alpha1\alpha2}$) (II); scan rate a function of count rate (4° min^{-1} minimum, 30° min^{-1} maximum) (I), (6° min^{-1} minimum, 30° min^{-1} maximum) (II). 5070 reflections measured, 2278 unique, $R_{\rm int}$ = 0·006, 1815 observed $F_o > 3\sigma(F_o)$ (I); 2165 measured, 1274 unique, $R_{\rm int}$ = 0·009, 1039 observed $F_o > 3\sigma(F_o)$ (II). Lorentz and polarization, but not absorption corrections applied. Structures solved by direct methods. The least-squares refinement used program *SHELXTL* (Sheldrick, 1980). $\sum w(|F_o| - |F_c|)^2$ minimized where $w = 1/[\sigma^2(|F_o|) + g(F_o)^2]$; g = 0·00030 (I), 0·00026 (II). The secondary-extinction value, x, in the expression $F_c^* = F_c/[1{\cdot}0 + 0{\cdot}002(x)F_o^2/\sin(2\theta)]^{0{\cdot}25}$ is 0·0067 (8) for (I) and 0·0051 (10) for (II). Refinement of (I): 202 parameters refined; atom coordinates, anisotropic temperature factors for all non-H atoms, isotropic temperature factors for H; R = 0·049, wR = 0·057, S = 1·934, $(\Delta/\sigma)_{\max}$ = 0·015. Refinement of (II): 66 parameters refined; all non-H atoms anisotropic, H atoms included using riding model, C—H = 0·96 Å, H—C—H = 109·5°, U(H) = 1·2$U_{\rm eq}$(C); R = 0·051, wR = 0·073, S = 2·700, $(\Delta/\sigma)_{\max}$ = 0·009. Final difference-Fourier excursions 0·23 and −0·26 e Å^{-3} (I), 0·20 and −0·18 e Å^{-3} (II). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Table 1 lists the refined coordinates and equivalent isotropic $U_{\rm eq}$ values.* Bond distances and angles are given in Table 2, with the numbering system for (I) and (II) following that given in Figs. 1 and 2, respectively.

In compound (I) the oxetane ring common to both compounds is puckered with O(1) *trans* to C(5). The ring pucker, defined as the dihedral angle between planes C(4)—O(1)—C(2) and C(2)—C(3)—C(4), is 20·6 (1)°. In (II) the molecule has C_2 symmetry with O(1) and C(3) on a twofold axis through the planar oxetane ring. In the gas phase the oxetane rings in 3,3-bisazidomethyloxetane (George, Lowrey & Karle, 1985) and 2-methyloxacyclobutane (Schultz & Bartok, 1979) are planar, and crystallographic data on several oxetanes (Noordik & Cillissen, 1981; Holan, Kowala & Wunderlich, 1973; Hospital, LeRoy, Bats & Moulines, 1978) show a range of 0–16° for the ring pucker. Packing forces are expected to influence the ring conformation since the conformation of cyclic four-membered rings is determined by a sensitive balance between bond-angle strains and torsion-angle strains. The orientation of the methylnitraminomethyl groups in (I) may be defined by torsion angles C(4)—C(3)—C(5)—N(7) = 55·5 (2)° and C(4)—C(3)—C(6)—N(12) = 83·1 (2)°. The amino N atoms are pyramidal with the N—N vectors making angles of 22·2 and 13·4° with the three-atom planes C(5)—N(7)—C(8) and C(6)—N(12)—C(13), respectively, at

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42885 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

N(7) and N(12). In (II) the planar nitratomethyl group orientation may be defined by torsion angle C(2)—C(3)—C(4)—O(5) = 62·3 (2)°.

Bond distances and angles are normal in both molecules with the C—O bonds in the ring ranging from 1·431 (3) to 1·443 (3) Å, and averaging 1·437 Å for both (I) and (II). This is slightly larger than the average value for saturated heterocyclic C—O single bonds of 1·426 (5) Å (Sutton, 1965), but in keeping with the observation that the C—O bond is longer in four-membered rings than in other bonding environments (Mastryukov, Dorofeeva, Vilkov & Hargittai, 1975). The C—O bonds in the oxetanes from the previously cited crystallographic data average 1·46 (1) Å; those from the gas-phase data average 1·45 (1) Å. Intermolecular contacts are at normal van der Waals' separations. Nearest contacts in (I) are H(2*B*)···O(16)′ = 2·44 (3) Å (*x*, 0·5 − *y*, *z* − 0·5), and O(1)···H(5*b*)′ = 2·64 (3) Å (*x*, 1·0 + *y*, *z*). In (II) nearest contacts are O(8)···H(4a)′ = 2·68 Å (0·5 − *x*, *y* − 0·5, 0·5 − *z*).

Table 1. *Atom coordinates and equivalent isotropic thermal parameters*

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

	x	*y*	*z*	U_{eq}(Å^2)
(I) 3,3-Bis(methylnitraminomethyl)oxetane				
O(1)	0·3012 (1)	0·2147 (2)	0·3583 (2)	0·101 (1)
C(2)	0·2672 (2)	0·3480 (4)	0·2636 (3)	0·074 (1)
C(3)	0·2486 (1)	0·5222 (2)	0·3438 (1)	0·038 (1)
C(4)	0·3107 (1)	0·3876 (3)	0·4340 (2)	0·062 (1)
C(5)	0·2822 (1)	0·7397 (2)	0·3246 (1)	0·036 (1)
C(6)	0·1424 (1)	0·5238 (3)	0·3547 (1)	0·042 (1)
N(7)	0·3792 (1)	0·7545 (2)	0·2972 (1)	0·037 (1)
C(8)	0·4589 (1)	0·8264 (3)	0·3801 (2)	0·051 (1)
N(9)	0·3872 (1)	0·7783 (3)	0·1882 (1)	0·049 (1)
O(10)	0·3171 (1)	0·7359 (3)	0·1161 (1)	0·079 (1)
O(11)	0·4649 (1)	0·8355 (2)	0·1660 (1)	0·068 (1)
N(12)	0·1168 (1)	0·6698 (2)	0·4374 (1)	0·045 (1)
C(13)	0·0820 (2)	0·8764 (4)	0·4060 (2)	0·071 (1)
N(14)	0·1034 (1)	0·6041 (3)	0·5395 (1)	0·060 (1)
O(15)	0·0726 (1)	0·7294 (3)	0·6026 (1)	0·086 (1)
O(16)	0·1229 (1)	0·4240 (3)	0·5647 (1)	0·088 (1)
(II) 3,3-Bis(nitratomethyl)oxetane				
O(1)	0·0000	0·5429 (3)	0·2500	0·074 (2)
C(2)	0·0869 (2)	0·3806 (3)	0·3470 (2)	0·056 (1)
C(3)	0·0000	0·1964 (3)	0·2500	0·038 (1)
C(4)	0·0361 (1)	0·0595 (3)	0·1868 (2)	0·043 (1)
O(5)	0·1491 (1)	−0·0401 (2)	0·3073 (1)	0·048 (1)
N(6)	0·1910 (2)	−0·1947 (3)	0·2717 (2)	0·062 (1)
O(7)	0·1349 (2)	−0·2334 (4)	0·1519 (2)	0·090 (2)
O(8)	0·2846 (1)	−0·2705 (3)	0·3741 (2)	0·095 (1)

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

(I) 3,3-Bis(methylnitraminomethyl)oxetane			
O(1)—C(2)	1·443 (3)	O(1)—C(4)	1·431 (3)
C(2)—C(3)	1·531 (3)	C(3)—C(4)	1·542 (3)
C(3)—C(5)	1·515 (2)	C(3)—C(6)	1·525 (2)
C(5)—N(7)	1·462 (2)	C(6)—N(12)	1·456 (2)
N(7)—C(8)	1·447 (2)	N(7)—N(9)	1·336 (2)
N(9)—O(10)	1·231 (2)	N(9)—O(11)	1·228 (2)
N(12)—C(13)	1·452 (3)	N(12)—N(14)	1·336 (2)
N(14)—O(15)	1·235 (3)	N(14)—O(16)	1·223 (3)
C(2)—O(1)—C(4)	90·8 (2)	O(1)—C(2)—C(3)	91·0 (2)
C(2)—C(3)—C(4)	83·5 (1)	C(2)—C(3)—C(5)	119·9 (2)
C(4)—C(3)—C(5)	118·3 (1)	C(2)—C(3)—C(6)	109·3 (1)
C(4)—C(3)—C(6)	113·4 (1)	C(5)—C(3)—C(6)	110·1 (1)
O(1)—C(4)—C(3)	90·9 (2)	C(3)—C(5)—N(7)	115·0 (1)
C(3)—C(6)—N(12)	114·8 (1)	C(5)—N(7)—C(8)	121·2 (1)
C(5)—N(7)—N(9)	117·3 (1)	C(8)—N(7)—N(9)	116·8 (1)
N(7)—N(9)—O(10)	118·1 (2)	N(7)—N(9)—O(11)	117·9 (1)
O(10)—N(9)—O(11)	123·9 (2)	C(6)—N(12)—C(13)	122·2 (2)
C(6)—N(12)—N(14)	120·2 (2)	C(13)—N(12)—N(14)	115·9 (2)
N(12)—N(14)—O(15)	117·8 (2)	N(12)—N(14)—O(16)	117·9 (2)
O(15)—N(14)—O(16)	124·3 (2)		
(II) 3,3-Bis(nitratomethyl)oxetane			
O(1)—C(2)	1·437 (2)	C(2)—C(3)	1·533 (2)
C(3)—C(4)	1·512 (3)	C(4)—O(5)	1·453 (2)
O(5)—N(6)	1·385 (3)	N(6)—O(7)	1·182 (3)
N(6)—O(8)	1·196 (2)		
C(2)—O(1)—C(2)′	91·7 (2)	O(1)—C(2)—C(3)	91·9 (1)
C(2)—C(3)—C(2)′	84·5 (2)	C(2)—C(3)—C(4)	115·7 (1)
C(4)—C(3)—C(4)′	112·2 (2)	C(3)—C(4)—O(5)	104·3 (1)
C(2)—C(3)—C(4)′	113·0 (2)	O(5)—N(6)—O(7)	119·6 (2)
C(4)—O(5)—N(6)	113·7 (1)	O(7)—N(6)—O(8)	129·1 (3)
O(5)—N(6)—O(8)	111·3 (2)		

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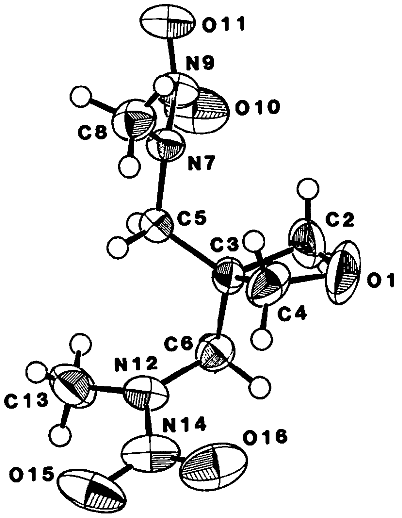

Fig. 1. *ORTEP* (Johnson, 1965) drawing of (I) with thermal ellipsoids drawn at 50% probability level.

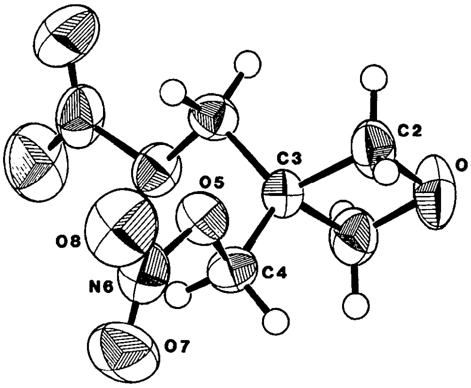

Fig. 2. *ORTEP* (Johnson, 1965) drawing of (II) with thermal ellipsoids drawn at 50% probability level.

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Structure of 7-(2,4-Dinitrophenylthio)-5-*exo*-nitrobicyclo[2.2.1]hept-2-*exo*-yl Acetate

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Abstract. $C_{15}H_{15}N_3O_8S$, M_r=397·4, monoclinic, $P2_1/c$, $a = 12{\cdot}132$ (2), $b = 15{\cdot}430$ (2), $c = 10{\cdot}033$ (2) Å, $\beta = 111{\cdot}04$ (1)°, $V = 1752{\cdot}9$ (2) Å^3, $Z = 4$, $D_x = 1{\cdot}506$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 20{\cdot}764$ cm^{-1}, $F(000) = 824$, room temperature, $R = 0{\cdot}055$ for 2489 observed reflections. The conformation of the bicyclo[2.2.1]heptane framework is synchro-twist to relieve the steric strain imposed by the presence of the substituents. The molecule contains two short S···O non-bonded distances of 2·788 (2) and 2·987 (2) Å whose directions are close to the C—S bond vectors [C—S···O angles 162·1 (1) and 172·8 (1)°, respectively].

Introduction. 8,9,10-Trinorbornane is a traditional model for studying electrophilic addition to the C—C double bond. Disubstituted 8,9,10-trinorbornanes formed in these reactions can be identified unambiguously on the basis of their ^{1}H NMR spectra and some reliable criteria exist (Start, 1958; Zefirov *et al.*, 1980) for assignment of the NMR signals in these systems. However, analogous criteria for trisubstituted 8,9,10-trinorbornanes, adducts of electrophiles to monosubstituted 8,9,10-trinorbornenes, are as yet lacking.

The reaction of 5-*endo*-nitro-8,9,10-trinorbornene (I) with 2,4-dinitrophenylsulfenyl chloride under the 'doping addition' conditions (CH_3COOH + $LiClO_4$) (Zefirov, Sadovaya, Maggerramov, Bodrikov & Kartachov, 1975; Zefirov, Sadovaya, Novgorodtseva & Bodrikov, 1978), proceeds to give the trisubstituted 8,9,10-trinorbornane, $C_{15}H_{15}N_3O_8S$ (IV) (Fig. 1), whose structure is proved unambiguously by X-ray diffraction in this paper.

Experimental. Prismatic crystal of dimensions 0·2 × 0·3 × 0·2 mm used for measurement of unit-cell parameters (from 24 reflections with θ between 35 and 37°) and intensities of 3182 reflections ($h = 0$ to 14, $k = 0$ to 18, $l = 10$ to 10) using a Hilger & Watts four-circle automatic diffractometer (293 K, Cu $K\alpha$, graphite monochromator, $\theta/2\theta$ scan, $\theta_{max} = 66°$). Two standard reflections (170 and $\bar{3}04$) measured after every 98 reflections showed no noticeable intensity variations. No absorption or secondary-extinction

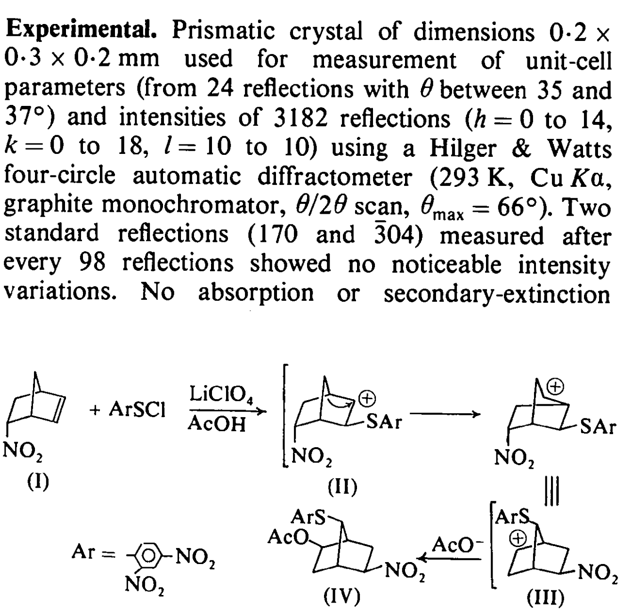

Fig. 1. The scheme of the reaction.

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