les concernent sont comprises entre 3,23 et 3,30 Å et les angles C—H···O correspondants vont de 126 à 142°. Donohue (1968) rapporte des valeurs du même ordre de grandeur pour les liaisons C—H···O rencontrées dans l'acide tétraméthyl-1,3,7,9 urique et la L-thréonine. L'existence de ces liaisons hydrogène est subordonnée à la polarisation des liaisons C—H dans le sens $C^{(\delta-)}$ — $H^{(\delta+)}$. Cette polarisation est vraisemblable en raison de la présence dans le voisinage de chacune d'elles d'au moins un groupement ClO_4^-. La fixation d'un proton sur l'atome d'azote N(10) doit accentuer fortement la polarisation de C(9)—H(9).

L'atome H(5), signalé sur la Fig. 2 par une circonférence tracée en trait discontinu, est lié à deux atomes d'oxygène appartenant à deux groupements perchlorate qui se déduisent l'un de l'autre par la translation **a**.

Les principales interactions de van der Waals sont indiquées dans le Tableau 4. L'une d'entre elles est représentée sur les Figs. 1 et 2 par un trait en pointillés; elle s'établit entre les deux atomes d'oxygène O(3) et $O(3^{1}_{m})$ distants seulement de 3,00 Å.

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Structures of Three *cis*-Dioxoazacycloalkanes; 3,3,4,4-Tetramethyldiazetine 1,2-Dioxide, 2,3-Diazabicyclo[2.2.1]hept-2-ene 2,3-Dioxide and 6,7-Diazatetracyclo[3.2.1.1^{3,8}.0^{2,4}]non-6-ene 6,7-Dioxide

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The structures of $C_6H_{12}N_2O_2$ (1), $C_5H_8N_2O_2$ (2) and $C_7H_8N_2O_2$ (3) have been determined with counter data from Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å) and refined by a full-matrix least-squares method: (1) $a = 9{\cdot}95$ (1), $b = 6{\cdot}26$ (1), $c = 12{\cdot}62$ (1) Å, $\beta = 97{\cdot}54$ (1)°, $U = 779$ Å^3, $M_r = 144{\cdot}2$, $D_m = 1{\cdot}21$, $D_c = 1{\cdot}23$ g cm^{-3}, monoclinic $C2/c$, $Z = 4$, $R = 0{\cdot}066$; (2) $a = 8{\cdot}62$ (1), $b = 6{\cdot}72$ (1), $c = 10{\cdot}44$ (1) Å, $\beta = 99{\cdot}45$ (1)°, $U = 597$ Å^3, $M_r = 128{\cdot}2$, $D_c = 1{\cdot}42$ g cm^{-3}, monoclinic $P2_1/c$, $Z = 4$, $R = 0{\cdot}043$; (3) $a = 7{\cdot}66$ (1), $b = 9{\cdot}72$ (1), $c = 9{\cdot}10$ (1) Å, $\beta = 93{\cdot}55$ (1)°, $U = 676$ Å^3, $M_r = 152{\cdot}2$, $D_c = 1{\cdot}49$ g cm^{-3}, monoclinic $P2_1/n$, $Z = 4$, $R = 0{\cdot}047$.

Introduction

The tendency of *C*-nitroso compounds to dimerize to form *N*,*N*′-dioxides has led to the synthesis of *cis* and *trans*-azodioxides (Singh, 1975). The subjects of this investigation are of interest because of the influence of steric constraints on reactivity (Bünzli, Olsen & Snyder, 1977; Snyder, Heyman & Suciu, 1975).

Experimental

The experimental procedures were similar for all three compounds. The space groups were determined from photographs, and the unit-cell dimensions by a least-squares refinement from the setting angles of several reflexions measured at both positive and negative θ on a Hilger & Watts Y290 PDP8-controlled four-circle diffractometer. Intensity data were measured by an $\omega/2\theta$ scan with ordinate analysis (Watson, Shotton, Cox & Muirhead, 1970) using Mo $K\alpha$ radiation from a graphite monochromator. Reflexions with $\hat{I} < 3\sigma(\hat{I})$ or displaced by more than 0·15° from their predicted positions were eliminated from the data sets. Lorentz and polarization corrections were applied.

Structures (2) and (3) were easily solved with *MULTAN* (Woolfson, 1976) and (1) was solved from the Patterson function. Refinement was by a full-matrix least-squares method using isotropic temperature factors for the H atoms and anisotropic temperature factors for the others.

Weights used in the refinement were calculated from a modified Chebyshev polynomial (Rollett, 1965) $\{w = [\sum A_r T_r^*(x)]^{-1},\ x = F_o/F_o(\max)\}$ and a secondary-extinction parameter (Larson, 1970) was included for (2). The bond length and angle standard deviations were computed from the full variance–covariance matrix. All calculations were carried out on the Oxford University ICL 1906A computer with the Oxford *CRYSTALS* program (Carruthers, 1975) which incorporates *MULTAN*. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

(1) White needles from solution in ethanol/chloroform. Systematic absences hkl, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$, $(h = 2n + 1)$. Space group $C2/c$ or Cc. Crystal size 0·7 × 0·3 × 0·3 mm. $\mu = 1{\cdot}00$ cm^{-1}. 18 reflexions for cell-parameter determination, 335 for structure refinement. Weighting parameters 7·77, 8·46 and 2·25, final $R_w = 0{\cdot}084$ (Hamilton, 1964). There was no evidence to justify removing the crystallographic twofold axis.

(2) White prismatic crystals from solution in ethanol/chloroform. Systematic absences $0k0$, $k = 2n + 1$; $h0l$, $l = 2n + 1$. Space group $P2_1/c$. Crystal size 1·0 × 0·5 × 0·5 mm. $\mu = 1{\cdot}20$ cm^{-1}. 17 reflexions for cell-parameter determination, 1283 for structure refinement. Weighting parameters 676, 987, 378 and 63·2, final $R_w = 0{\cdot}062$.

(3) Thick white plates from solution in ethanol/chloroform. Systematic absences $h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$. Space group $P2_1/n$, $\pm(x,y,z;\ \frac{1}{2}+x,\ \frac{1}{2}-y,\ \frac{1}{2}+z)$. Crystal size 0·8 × 0·8 × 0·4 mm. $\mu = 1{\cdot}20$ cm^{-1}. 13 reflexions for cell-parameter determination, 2241 for structure refinement. Weighting parameters 1569, 2389, 1008 and 186·5, final $R_w = 0{\cdot}064$.

Tables 1–6 list the atomic and molecular parameters.*

Table 1. 3,3,4,4-*Tetramethyldiazetine* 1,2-*dioxide: final atomic coordinates* ($\times 10^4$; *for* H $\times 10^3$) *with standard deviations in parentheses*

	x	*y*	*z*
O(1)	100 (6)	6902 (8)	1375 (4)
N(1)	34 (6)	5355 (7)	1992 (4)
C(1)	68 (6)	2927 (9)	1882 (5)
C(2)	−1147 (8)	2182 (13)	1129 (6)
C(3)	1377 (8)	2194 (12)	1527 (7)
H(1)	702 (4)	220 (8)	878 (4)
H(2)	598 (6)	229 (10)	967 (6)
H(3)	129 (8)	56 (16)	376 (7)
H(4)	860 (5)	67 (10)	346 (4)
H(5)	368 (6)	223 (10)	924 (6)
H(6)	708 (7)	249 (10)	700 (6)

Table 2. 3,3,4,4-*Tetramethyldiazetine* 1,2-*dioxide: bond distances* (Å) *and angles* (°) *with standard deviations in parentheses*

O(1)–N(1)	1·250 (6)	C(2)–H(1)	0·97 (3)
N(1)–N(1′)	1·292 (10)	C(2)–H(2)	1·09 (7)
N(1)–C(1)	1·527 (7)	C(2)–H(3)	1·04 (10)
C(1)–C(1′)	1·582 (12)	C(3)–H(4)	0·95 (6)
C(1)–C(2)	1·511 (10)	C(3)–H(5)	1·02 (7)
C(1)–C(3)	1·503 (9)	C(3)–H(6)	0·88 (7)

O(1)–N(1)–N(1′)	129·2 (3)	O(1)–N(1)–C(1)	135·4 (5)
C(1)–N(1)–N(1′)	95·4 (3)	N(1)–C(1)–C(1′)	84·6 (3)
N(1)–C(1)–C(2)	109·8 (6)	N(1)–C(1)–C(3)	111·2 (6)
C(1′)–C(1)–C(2)	117·1 (7)	C(1′)–C(1)–C(3)	118·9 (7)
C(2)–C(1)–C(3)	111·8 (6)		
C–C–H (mean)	109·5	H–C–H (mean)	109·5

Table 3. 2,3-*Diazabicyclo*[2.2.1]*hept*-2-*ene* 2,3-*dioxide: final atomic coordinates* ($\times 10^4$; *for* H $\times 10^3$) *with standard deviations in parentheses*

	x	*y*	*z*
O(1)	7356 (2)	1824 (2)	484 (1)
O(2)	8103 (1)	16 (2)	4098 (1)
N(1)	7742 (1)	3495 (2)	973 (1)
N(2)	8113 (1)	5015 (1)	310 (1)
C(1)	7592 (2)	4235 (2)	2299 (1)
C(2)	3922 (2)	512 (3)	2897 (2)
C(3)	3460 (2)	2305 (2)	3678 (1)
C(4)	1768 (2)	1793 (2)	3828 (1)
C(5)	1119 (2)	814 (2)	2538 (1)
H(1)	764 (2)	311 (3)	294 (2)
H(2)	414 (3)	94 (4)	204 (2)
H(3)	521 (3)	471 (3)	162 (2)
H(4)	413 (3)	255 (3)	446 (2)
H(5)	348 (3)	358 (3)	323 (2)
H(6)	117 (2)	289 (3)	418 (2)
H(7)	1005 (3)	33 (3)	250 (2)
H(8)	115 (2)	170 (3)	179 (2)

Table 4. 2,3-*Diazabicyclo*[2.2.1]*hept*-2-*ene* 2,3-*dioxide: bond distances* (Å) *and angles* (°) *with standard deviations in parentheses*

O(1)–N(1)	1·256 (1)	C(1)–H(1)	1·01 (2)
O(2)–N(2)	1·264 (1)	C(2)–H(2)	0·98 (2)
N(1)–N(2)	1·303 (1)	C(2)–H(3)	0·99 (2)
N(1)–C(1)	1·496 (2)	C(3)–H(4)	0·94 (2)
N(2)–C(4)	1·490 (2)	C(3)–H(5)	0·98 (2)
C(1)–C(2)	1·547 (2)	C(4)–H(6)	1·00 (2)
C(2)–C(3)	1·544 (2)	C(5)–H(7)	0·98 (3)
C(3)–C(4)	1·532 (2)	C(5)–H(8)	0·98 (2)
C(4)–C(5)	1·521 (2)		
C(5)–C(1)	1·526 (2)		

O(1)–N(1)–N(2)	123·8 (1)	O(2)–N(2)–N(1)	123·8 (1)
O(1)–N(1)–C(1)	128·0 (1)	O(2)–N(2)–C(4)	127·4 (1)
N(2)–N(1)–C(1)	107·3 (1)	N(1)–N(2)–C(4)	107·8 (1)
N(1)–C(1)–C(2)	105·1 (1)	N(2)–C(4)–C(3)	105·6 (1)
N(1)–C(1)–C(5)	99·4 (1)	N(2)–C(4)–C(5)	99·6 (1)
C(2)–C(1)–C(5)	102·3 (1)	C(3)–C(4)–C(5)	103·0 (1)
C(1)–C(2)–C(3)	102·6 (1)	C(2)–C(3)–C(4)	102·2 (1)
C(1)–C(5)–C(4)	92·7 (1)		

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33533 (35 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 5. 6,7-*Diazetetracyclo*[3.2.1.1^{3,8}.0^{2,4}]*non*-6-*ene* 6,7-*dioxide: final atomic coordinates* (×10^4; *for* H, ×10^3) *with standard deviations in parentheses*

	x	y	z
O(1)	3155 (1)	5787 (1)	4952 (2)
O(2)	1977 (2)	4579 (1)	2387 (1)
N(1)	2924 (1)	4511 (1)	4799 (1)
N(2)	2365 (1)	3928 (1)	3565 (1)
C(1)	2973 (2)	3438 (1)	5963 (1)
C(2)	1081 (2)	3056 (1)	6227 (1)
C(3)	443 (2)	2385 (1)	4788 (1)
C(4)	2035 (2)	2452 (1)	3860 (1)
C(5)	3447 (2)	2147 (1)	5093 (1)
C(6)	2748 (2)	946 (1)	5941 (2)
C(7)	938 (2)	1507 (1)	6119 (2)
H(1)	376 (2)	375 (2)	676 (2)
H(2)	34 (2)	364 (2)	684 (2)
H(3)	−73 (3)	250 (2)	439 (2)
H(4)	205 (2)	196 (2)	296 (2)
H(5)	463 (2)	214 (2)	478 (2)
H(6)	341 (3)	88 (2)	692 (2)
H(7)	272 (3)	8 (2)	538 (2)
H(8)	0 (3)	105 (2)	662 (2)

Table 6. 6,7-*Diazatetracyclo*[3.2.1.1^{3,8}.0^{2,4}]*non*-6-*ene* 6,7-*dioxide: bond distances* (Å) *and angles* (°) *with standard deviations in parentheses*

O(1)–N(1)	1·259 (1)	C(2)–C(7)	1·513 (2)
O(2)–N(2)	1·265 (1)	C(3)–C(4)	1·527 (2)
N(1)–N(2)	1·307 (2)	C(3)–C(7)	1·511 (2)
N(1)–C(1)	1·486 (2)	C(4)–C(5)	1·538 (2)
N(2)–C(4)	1·485 (1)	C(5)–C(1)	1·539 (2)
C(1)–C(2)	1·529 (2)	C(5)–C(6)	1·516 (2)
C(2)–C(3)	1·516 (2)	C(6)–C(7)	1·508 (2)
O(1)–N(1)–N(2)	124·0 (1)	O(2)–N(2)–N(1)	124·0 (1)
O(1)–N(1)–C(1)	128·0 (1)	O(2)–N(2)–C(4)	127·2 (1)
N(2)–N(1)–C(1)	107·5 (1)	N(1)–N(2)–C(4)	108·3 (1)
N(1)–C(1)–C(2)	107·5 (1)	N(2)–C(4)–C(3)	107·0 (1)
N(1)–C(1)–C(5)	101·6 (1)	N(2)–C(4)–C(5)	101·4 (1)
C(2)–C(1)–C(5)	98·0 (1)	C(3)–C(4)–C(5)	97·9 (1)
C(1)–C(2)–C(3)	103·1 (1)	C(2)–C(3)–C(4)	103·5 (1)
C(1)–C(2)–C(7)	107·3 (1)	C(4)–C(3)–C(7)	107·4 (1)
C(3)–C(2)–C(7)	59·9 (1)	C(2)–C(3)–C(7)	60·0 (1)
C(1)–C(5)–C(6)	105·3 (1)	C(4)–C(5)–C(6)	105·3 (1)
C(2)–C(7)–C(6)	107·7 (1)	C(3)–C(7)–C(6)	107·7 (1)
C(1)–C(5)–C(4)	92·3 (1)	C(5)–C(6)–C(7)	97·6 (1)
C(2)–C(7)–C(3)	60·2 (1)		

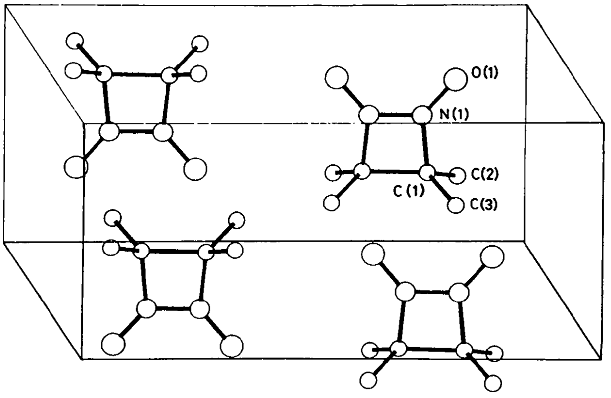


Fig. 1. 3,3,4,4-Tetramethyldiazetine 1,2-dioxide projected parallel to (1·0, 0·5, 0·15).

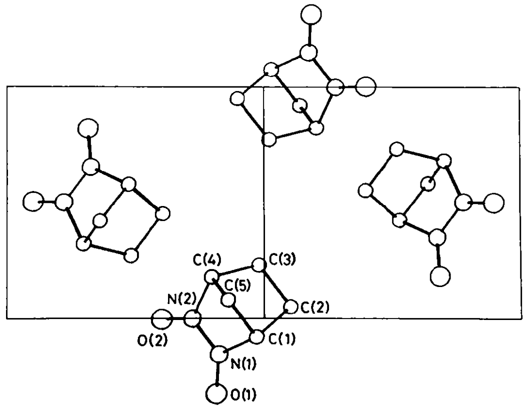


Fig. 2. 2,3-Diazabicyclo[2.2.1]hept-2-ene 2,3-dioxide projected parallel to (101).

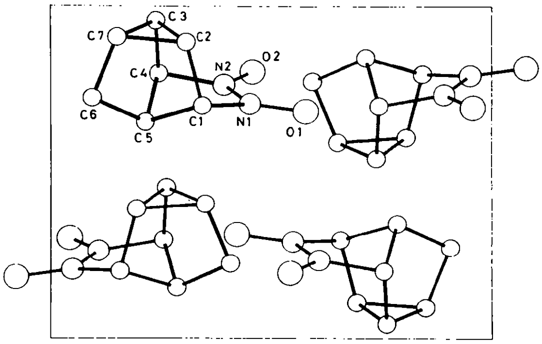


Fig. 3. 6,7-Diazatetracyclo[3.2.1.1^{3,8}.0^{2,4}]non-6-ene 6,7-dioxide, projected parallel to the c axis.

Discussion

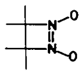
Figs. 1–3 show, in projection, the crystal and molecular structures of (1), (2) and (3). In spite of the high melting points (190–2, 153–4, 184–5 °C) there are no unusually short intermolecular contacts. The most significant features are the *cis*-dioxoazacycloalkane systems, which can also be regarded as internal nitroso dimers. Table 7 lists some relevant dimensions of related nitroso dimers. The N–O bonds are all similar, and though the N–N lengths fall within a narrow range, those associated with aromatic systems are noticeably longer. Since the shortest N–N bond is in the strained four-membered ring in (1) and the longest in the less strained five-membered ring in (4), the lengthening might be attributed to conjugation with the aromatic system rather than to ring strain. In (5) and (6) the aromatic rings are not coplanar with the dioxoaza system so that the lengthening is not so marked. C–N bonds in (2), (3) and (8) are similar, and noticeably longer than those in the aromatic dimers (4), (5) and (6). The long C–N bonds in (1) are probably

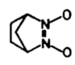
Table 7. *Selected dimensions of some nitroso dimers*

	(1)	(2)	(3)	(4)	(5)	(6)	(8)
N—O (Å)	1·250	1·260	1·263	1·264	1·264	1·267	1·262
N—N (Å)	1·292	1·303	1·307	1·376	1·323	1·324	1·300
C—N (Å)	1·527	1·493	1·486	1·434	1·454	1·439	1·470
O—N—N (°)	129·2	123·8	124·1	122·4	~120	119·4	121·1
O—N—C (°)	135·4	127·7	127·6	129·0	~120	120·7	121·4
N—N—C (°)	95·4	107·6	107·9	108·8	~120	119·9	117·4

(1), (2) and (3) this work, (4) Prout, Cameron, Dunn, Hodder & Viterbo (1971), (5) Dieterich, Paul & Curtin (1970), (6) Prout, Coda, Forder & Kamenar (1974), (8) Boer & Turley (1969).

due to steric repulsion between O(1) and the methyl groups. The stereochemistry of the cyclic systems (1)–(4) requires the N—N—C angles to be less than 120°, though in the unconstrained systems (5), (6) and (8) this value is approached. The N—N—C angles in (2) and (3) are similar to the angles at C(5) (107·3°) and C(6) (108·0°) in (9) (Pfluger, Harlow & Simonsen, 1973). The highly constrained N—N—C angle in (1) is what would be expected by analogy with (10) (Bellůs, Mez & Rihs, 1974). The largest O—N—C angle is found in (1), presumably again the result of steric repulsion between O and the methyl groups.


(1)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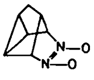
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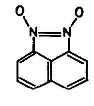
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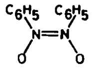
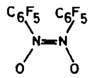
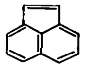


(5)



(6)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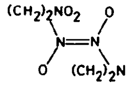

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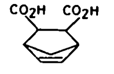
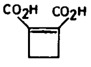


(9)



(10)

The C—N—N—C systems in (2) and (3) are planar (r.m.s. deviation 0·001 Å), in contrast with the open chain (5) and (6), where the torsion angles are 7·5 and 17·9°. (1) is not quite planar (r.m.s. deviation 0·01 Å), with a C—N—N—C torsion angle of 2°. In (2) and (3) the O atoms lie out of the C—N—N—C mean plane (0·17, 0·20 Å and 0·14, 0·16 Å), with both O atoms on the same side of the plane. Surprisingly, in (1) the O atom lies on the mean plane (0·004 Å) perhaps again due to the symmetric steric constraints imposed by the methyl groups.

The C atom skeleton of (2) is similar to that found in (9) and the anhydride of (9) (Filippini, Gramaccioli, Rovere & Simonetta, 1972), and (3) is similar to 5-*exo*-iodo-2,3-*endo*-dimethoxycarbonyl-7-isopropylidenenortricyclene (Nelson & Calabrese, 1973). The C(1)—C(1′) bond in (1) is very long (1·582 Å), even longer than the corresponding bond in (10) (1·568 Å). In (1) however, the two methyl substituents are eclipsed, [C(2)—C(1)—C(1′)—C(3′) 0·1°], and this overcrowding may be the cause of the anomaly. A similar lengthening of C—C single bonds is found in *cis,trans,-cis*-1,2,3,4-cyclobutanetetracarboxylic acid tetramethyl ester (Margulis, 1971).

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