Tableau 7. *Principaux contacts de van der Waals* (<3,8 Å)

Code de symétrie

(i) x,y,z; (ii) x, $1+y$, z; (iii) $2-x$, $\bar{y}$, $2-z$; (iv) $2-x$, $\frac{1}{2}+y$, $\frac{3}{2}-z$; (v) $1-x$; $\frac{1}{2}+y$, $\frac{3}{2}-z$; (vi) x, $\frac{1}{2}-y$, $\frac{1}{2}+z$; (vii) x, $-\frac{1}{2}-y$, $\frac{1}{2}+z$.

C(10^{i})–C(12^{ii})	3,778 (9)	C(12^{i})–C(18^{vi})	3,73 (1)
O(14^{i})–O(18^{ii})	3,202 (8)	C(9^{i})–C(4^{v})	3,715 (7)
C(2^{i})–O(17^{iii})	3,607 (6)	C(3^{i})–C(10^{vi})	3,769 (7)
C(7^{i})–O(17^{iii})	3,441 (5)	C(5^{i})–C(11^{vii})	3,788 (7)
O(17^{i})–C(15^{iii})	3,442 (6)		
C(10^{i})–C(18^{vi})	3,671 (9)	O(14^{i})–H(182^{ii})	2,26 (5)
C(11^{i})–C(18^{vi})	3,626 (9)	O(17^{i})–H(150^{iii})	2,77 (4)

Boucherle, 1977, 1979). Le signal de ces protons géminés est constitué par deux doublets centrés sur les positions $\delta_1 = 3{,}40$ p.p.m. et $\delta_2 = 4{,}12$ p.p.m. ($J = 14{,}5$ Hz).

Les résultats cristallographiques obtenus indiquent que dans le cristal, la libre rotation au niveau du groupement ($-CH_2-SO-$) est empêchée par les deux liaisons intramoléculaires N(13)···O(14) et S(16)···O(14) et par la liaison intermoléculaire O(17^{iii})···O(14^{i}). Ce résultat a également été montré en solution (Madesclaire & Boucherle, 1979).

Enfin, l'analyse par rayons X a permis d'attribuer à la molécule étudiée, la configuration relative (R^*,R^*) ce que les méthodes spectroscopiques n'avaient pas permis d'obtenir.

Les auteurs remercient M le Professeur M. Gadret pour l'intérêt qu'il a porté à ce travail.

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The Structures of *anti*-2,3;4,5-Diepoxy-12-oxa[4.4.3]propella-7,9-diene and *anti*-2,3;4,5-*syn*-7,8;9,10-Tetraepoxy-12-oxa[4.4.3]propellane

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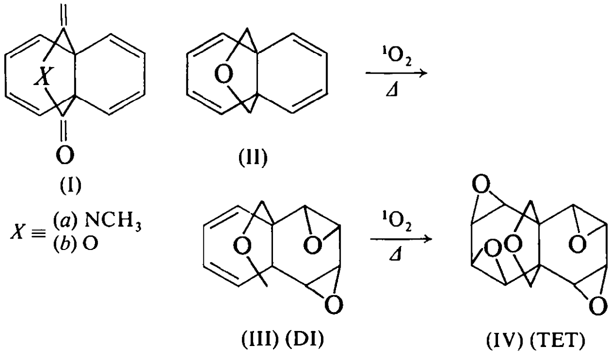
Abstract

anti-2,3;4,5-Diepoxy-12-oxa[4.4.3]propellane-7,9-diene (DI) ($C_{12}H_{12}O_3$, $M_r = 204{\cdot}22$) is orthorhombic, $P2_12_12_1$, $a = 12{\cdot}215$ (6), $b = 11{\cdot}811$ (5), $c = 6{\cdot}689$ (3) Å, $Z = 4$, $D_x = 1{\cdot}406$ Mg m^{-3}. The epoxy rings are *anti* with respect to the central hetero ring. The molecule deviates significantly from the mirror symmetry expected from its formula. *anti*-2,3;4,5-*syn*-7,8;9,10-Tetraepoxy-12-oxa[4.4.3]propellane (TET) ($C_{12}H_{12}O_5$, $M_r = 236{\cdot}22$) is monoclinic, $P2_1/n$, $a = 11{\cdot}932$ (6), $b = 21{\cdot}591$ (9), $c = 11{\cdot}846$ (6) Å, $\beta = 106{\cdot}15$ (2)°, $Z = 12$, $D_x = 1{\cdot}606$ Mg m^{-3}. There are three crystallographically independent molecules in the asymmetric unit. Two epoxy rings are *syn*, the other *anti*, with respect to the central hetero ring. In each of the molecules, the central hetero ring has an O atom flip towards the *syn* and *anti* epoxy rings with different degrees of disorder.

Introduction

The title compounds were obtained by Landheer & Ginsburg (1979) during an investigation of the possibility that singlet oxygen is capable of undergoing



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secondary orbital interaction with the π^* orbitals of the carbonyl groups in propellanes of type (I).

The crystal structures of the products obtained from (I*a*) and (I*b*) have been determined (Kaftory, 1978, 1979) and show that the dienophile reacts exclusively from the direction *syn* to the hetero ring. The crystal structures of DI and TET were undertaken in order to observe the preferred orientation of attack of singlet oxygen on propellanes of type (II) which lack carbonyl groups on the central hetero ring.

Experimental

Intensities from single crystals, colourless plates of DI, 0·2 × 0·4 × 0·4 mm, and colourless cubes of TET, 0·4 × 0·4 × 0·4 mm, were collected on a PW 1100 Philips four-circle computer-controlled diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ = 0·71069 Å). Crystallographic data and details of intensity measurements are given in Table 1.

Both crystal structures were solved with *MULTAN* 77 (Main, Woolfson, Lessinger, Germain & Declercq, 1977).

The structure of TET was solved after some unsuccessful trials. The *E* statistics indicated a hypercentric structure. Automatic use of *MULTAN* 77 with three origin-fixing reflexions and three other reflexions for the starting set revealed a crystal structure containing three molecules related by translations of $\frac{1}{3}$ along **b**. Careful checking of the *E* values indicated systematically high values of *E*'s with *k* divisible by three. The reflexions used for origin-fixing and for the starting set were of that kind, and therefore all the *E* values used for the phase determination were those with *k* divisible by three. Introduction of two more reflexions with k = 4 and 7 in the starting set revealed the correct structure.

The structures were refined by least-squares analysis with *SHELX* (Sheldrick, 1976). The structure of DI was refined in full matrix with anisotropic thermal parameters for C and O, isotropic for H atoms.

In the refinement of TET, each of the molecules was treated as a separate block. The ordered atoms and the disordered O atoms with the larger occupation factors were refined with anisotropic thermal parameters, H and disordered O atoms with smaller occupation factors with isotropic ones. (H atoms affected by the smaller disordered conformation were neglected.)

Scattering factors for C and O were taken from Cromer & Mann (1968), for H from Stewart, Davidson & Simpson (1965). The final agreement factors and weighting schemes are given in Table 1. Final positional parameters are listed in Tables 2 and 3.* Bond lengths

Table 1. *Crystallographic data and experimental details*

	DI	TET
Formula	$C_{12}H_{12}O_3$	$C_{12}H_{12}O_5$
a (Å)	12·215 (6)	11·932 (6)
b (Å)	11·811 (5)	21·591 (9)
c (Å)	6·689 (3)	11·846 (6)
β (°)	–	106·15 (2)
Z	4	12
Space group	$P2_12_12_1$	$P2_1/n$
D_x (Mg m^{-3})	1·406	1·606
Scan mode	$\omega/2\theta$	ω
$\Delta\omega$ (°)	1·4	1·2
Scan time (s)	28	24
Background time[a] (s)	28	20
$\theta_{\max}$ (°)	25	24
Reflexions measured	1024	4672
Significant [$F_o > 1{\cdot}5\sigma(F_o)$]	1024[b]	3044[c]
Weighting coefficient (k,g)[d]	0·4206, 0·0065	2·0065, 0·0010
R_ω	0·069	0·074
R	0·060	0·069

[a] Total background counting time.
[b] All reflexions have been used in the refinement.
[c] 11 reflexions have been suppressed due to error in measurement.
[d] $\omega = k/[\sigma^2(F_o) + gF_o^2]$.

Table 2. *DI: coordinates for non-hydrogen atoms* (× 10^4) *and for* H *atoms* (× 10^3)

E.s.d.'s are in parentheses.

	x	*y*	*z*
O(1)	5048 (4)	2018 (3)	−1946 (5)
O(2)	6411 (3)	5201 (2)	332 (6)
O(3)	5935 (2)	4034 (2)	3821 (4)
C(1)	4938 (3)	3752 (3)	−248 (5)
C(2)	6068 (4)	4218 (3)	−759 (6)
C(3)	6969 (4)	4141 (4)	641 (8)
C(4)	6814 (4)	3598 (4)	2617 (7)
C(5)	5828 (3)	2937 (3)	2943 (6)
C(6)	4977 (3)	2795 (3)	1357 (5)
C(7)	3874 (3)	2674 (4)	2350 (6)
C(8)	3126 (3)	3482 (4)	2368 (7)
C(9)	3299 (3)	4546 (4)	1346 (8)
C(10)	4153 (3)	4697 (3)	202 (6)
C(11)	4511 (5)	3067 (4)	−2038 (7)
C(12)	5266 (4)	1745 (3)	76 (7)
H(2)	629 (4)	425 (5)	−224 (8)
H(3)	770 (3)	415 (3)	25 (7)
H(4)	752 (4)	344 (5)	339 (9)
H(5)	587 (5)	243 (6)	369 (11)
H(7)	387 (4)	195 (5)	303 (8)
H(8)	239 (3)	333 (3)	316 (6)
H(9)	276 (4)	515 (4)	154 (7)
H(10)	425 (3)	543 (4)	−41 (7)
H(111)	466 (5)	337 (6)	−337 (11)
H(112)	363 (5)	296 (5)	−197 (10)
H(121)	480 (4)	106 (4)	49 (8)
H(122)	608 (4)	160 (4)	15 (8)

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* List of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34526 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *TET: coordinates for non-hydrogen atoms* ($\times 10^4$), *for* O *atoms with low occupation factors and for* H *atoms* ($\times 10^3$)

E.s.d.'s are in parentheses.

	Molecule *A*				Molecule *B*				Molecule *C*		
	x	*y*	*z*		*x*	*y*	*z*		*x*	*y*	*z*
O(1)	4398 (4)	1169 (2)	4011 (4)	O(1)	882 (6)	−469 (3)	980 (6)	O(1)	6798 (5)	2391 (2)	6561 (5)
O(2)	2581 (3)	2610 (2)	5425 (3)	O(2)	2625 (3)	954 (2)	−572 (3)	O(2)	7571 (3)	1829 (2)	2912 (3)
O(3)	2782 (3)	1634 (2)	6947 (3)	O(3)	2530 (3)	−49 (2)	−1996 (3)	O(3)	8036 (3)	809 (1)	4319 (3)
O(4)	1469 (3)	359 (2)	3974 (3)	O(4)	3744 (3)	−1289 (2)	1069 (3)	O(4)	9491 (3)	1947 (2)	7390 (3)
O(5)	841 (3)	1397 (2)	2638 (3)	O(5)	4394 (3)	−202 (2)	2276 (3)	O(5)	9132 (3)	2971 (1)	5975 (3)
C(1)	2715 (4)	1666 (2)	4221 (4)	C(1)	2525 (4)	15 (2)	675 (4)	C(1)	7531 (4)	2236 (2)	4913 (4)
C(2)	3206 (4)	2288 (2)	4729 (5)	C(2)	2005 (4)	620 (2)	124 (4)	C(2)	6927 (4)	2121 (2)	3612 (4)
C(3)	3741 (5)	2397 (2)	5986 (5)	C(3)	1481 (4)	713 (2)	−1123 (4)	C(3)	6580 (4)	1519 (3)	3108 (4)
C(4)	3852 (4)	1886 (3)	6811 (5)	C(4)	1421 (4)	190 (3)	−1936 (4)	C(4)	6818 (4)	956 (2)	3843 (4)
C(5)	3488 (4)	1276 (3)	6407 (4)	C(5)	1810 (4)	−425 (2)	−1469 (4)	C(5)	7376 (4)	1024 (2)	5100 (4)
C(6)	2994 (4)	1107 (2)	5109 (4)	C(6)	2256 (4)	−561 (2)	−172 (4)	C(6)	7744 (3)	1635 (2)	5720 (3)
C(7)	1990 (4)	671 (2)	5063 (4)	C(7)	3248 (4)	−1012 (2)	−58 (4)	C(7)	8986 (4)	1525 (3)	6458 (5)
C(8)	785 (4)	801 (2)	4406 (4)	C(8)	4450 (5)	−882 (2)	606 (4)	C(8)	9960 (5)	1924 (3)	6408 (5)
C(9)	497 (4)	1377 (3)	3708 (5)	C(9)	4743 (4)	−281 (3)	1219 (5)	C(9)	9763 (5)	2474 (3)	5635 (5)
C(10)	1425 (4)	1792 (2)	3608 (4)	C(10)	3807 (4)	149 (2)	1267 (4)	C(10)	8593 (5)	2621 (2)	4940 (4)
C(11)	3386 (5)	1482 (3)	3334 (5)	C(11)	1884 (6)	−157 (3)	1587 (5)	C(11)	6671 (6)	2606 (3)	5421 (6)
C(12)	3975 (5)	756 (3)	4716 (6)	C(12)	1244 (5)	−876 (3)	198 (6)	C(12)	6936 (6)	1756 (3)	6508 (6)
O(*1)	371 (5)	96 (2)	351 (4)	O(*1)	143 (2)	−76 (1)	139 (1)	O(*1)	607 (1)	216 (1)	596 (1)
H(2)	346 (4)	251 (2)	407 (4)	H(2)	182 (4)	86 (2)	80 (4)	H(2)	650 (3)	244 (2)	329 (3)
H(3)	431 (5)	277 (3)	627 (5)	H(3)	89 (4)	101 (2)	−145 (4)	H(3)	598 (4)	145 (2)	259 (5)
H(4)	440 (3)	199 (2)	749 (4)	H(4)	90 (6)	27 (3)	−263 (6)	H(4)	617 (3)	62 (2)	341 (3)
H(5)	382 (4)	93 (2)	685 (4)	H(5)	143 (4)	−75 (2)	−199 (4)	H(5)	725 (4)	67 (2)	576 (4)
H(7)	219 (5)	40 (3)	583 (5)	H(7)	310 (4)	−133 (2)	−79 (4)	H(7)	919 (6)	110 (3)	673 (6)
H(8)	15 (5)	61 (2)	470 (5)	H(8)	513 (6)	−107 (3)	40 (5)	H(8)	1073 (8)	180 (4)	652 (8)
H(9)	−26 (6)	156 (3)	380 (6)	H(9)	550 (5)	−9 (3)	114 (5)	H(9)	1039 (4)	262 (2)	536 (4)
H(10)	133 (4)	224 (2)	337 (4)	H(10)	397 (3)	55 (2)	147 (3)	H(10)	846 (3)	284 (2)	424 (3)
H(111)	298 (4)	111 (2)	276 (4)	H(111)	232 (6)	−50 (3)	207 (6)	H(111)	683 (5)	302 (3)	546 (5)
H(112)	369 (6)	181 (3)	294 (6)	H(112)	154 (6)	13 (3)	183 (6)	H(112)	587 (5)	262 (3)	500 (5)
H(121)	475 (6)	66 (3)	551 (5)	H(121)	53 (5)	−93 (3)	−36 (5)	H(121)	616 (5)	155 (3)	610 (5)
H(122)	376 (5)	38 (2)	439 (5)	H(122)	140 (5)	−131 (3)	56 (5)	H(122)	717 (6)	166 (3)	717 (6)

bond angles and torsion angles of atoms C and O are given in Tables 4, 5 and 6 respectively, with atomic notation in Fig. 1.

Description of the structures

DI

The molecule deviates from the mirror symmetry expected from its formula. The two epoxy rings are *anti* to the central hetero ring, *syn* to the unsubstituted six-membered ring (Fig. 2). The packing in the cell is shown in Fig. 3.

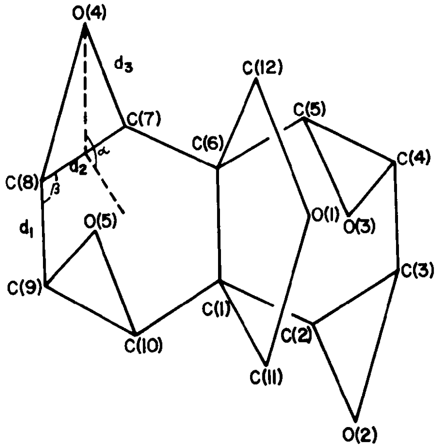

Fig. 1. Schematic drawing of TET showing atomic numbering and other symbols used. For DI replace O(4) and O(5) by double bonds.

TET

Three different molecules are present in the asymmetric unit. The main difference between them is the degree of disorder observed in the conformation of the hetero five-membered ring with respect to the epoxy rings. The occupancy factors of the O atom in molecule *A* (Fig. 4) flipping towards the epoxy rings in position *anti* and position *syn* are 0·91 (2) and 0·09 (2), respectively, in *B* 0·69 (2) and 0·31 (2), respectively, in *C* 0·29 (1) and 0·71 (1), respectively. The packing in the cell is shown in Fig. 5.

Table 4. *Bond lengths* (Å)

(For atomic notation see Fig. 1.)

The e.s.d.'s of bond lengths are typically: for TET 0·005–0·008 Å, for DI 0·004–0·007 Å, for those involving O(*1) 0·05 Å (*A*), 0·02 Å (*B*,*C*).

	TET			DI
	A	*B*	*C*	
C(1)–C(2)	1·521	1·516	1·529	1·525
C(1)–C(6)	1·575	1·574	1·590	1·560
C(1)–C(10)	1·533	1·523	1·508	1·501
C(1)–C(11)	1·539	1·532	1·548	1·536
C(2)–C(3)	1·467	1·449	1·442	1·448
C(3)–C(4)	1·455	1·472	1·475	1·481
C(4)–C(5)	1·428	1·463	1·460	1·453
C(5)–C(6)	1·530	1·508	1·514	1·495
C(6)–C(7)	1·512	1·509	1·515	1·509
C(6)–C(12)	1·570	1·551	1·540	1·547
C(7)–C(8)	1·460	1·459	1·461	1·321
C(8)–C(9)	1·480	1·479	1·478	1·446
C(9)–C(10)	1·455	1·466	1·444	1·305
O(1)–C(11)	1·422	1·386	1·396	1·403
O(1)–C(12)	1·408	1·428	1·384	1·416
O(2)–C(2)	1·436	1·444	1·425	1·433
O(2)–C(3)	1·435	1·437	1·433	1·440
O(3)–C(4)	1·439	1·440	1·441	1·438
O(3)–C(5)	1·420	1·443	1·448	1·429
O(4)–C(7)	1·435	1·432	1·429	–
O(4)–C(8)	1·439	1·429	1·425	–
O(5)–C(9)	1·438	1·434	1·432	–
O(5)–C(10)	1·445	1·424	1·432	–
O(*1)–C(11)	1·20	1·41	1·45	–
O(*1)–C(12)	1·44	1·39	1·38	–

Discussion

DI can be regarded as an intermediate of TET. The first dienophile reacts on (II) exclusively from the direction *anti* to the hetero ring while the second dienophile reacts on (III) (DI) from the direction *syn* to the hetero ring.

The distortions observed in the structure of DI are similar to those observed by Kaftory (1978, 1979) for (I). The distortions in the latter were attributed to the attractive intramolecular O···C=O interaction. The same distortion, although to a lesser extent [the torsion angle C(5)–C(6)–C(1)–C(2) is 36° compared with 41–44° in the latter], in the vicinity of carbonyl groups raises some doubts about the assumption previously made. There is still a possibility that the lone-pair electrons of the O atoms of the epoxy rings will tend to interact with the π orbitals of the double bonds C(7)–C(8), C(9)–C(10). The intramolecular non-bonded distance O(2)···C(10) of 2·823 Å is shorter than the sum of the van der Waals radii (3·15 Å). The other distances are: O(2)···C(7) 3·326, O(3)···C(7) 3·144 and O(3)···C(10) 3·348 Å. Although the explanation for the distortion given before might also hold here, it seems necessary to determine the crystal structure of the saturated DI compound, which lacks any attractive groups for the epoxy lone-pair electrons, to see whether the distortion is due to real attractive forces or to other effects. The deviation from mirror

Table 5. *Bond angles* (°)

(For atomic notation see Fig. 1.)

The e.s.d.'s of bond angles are typically: for TET 0·3–0·5°, for DI 0·3–0·4°, for those involving O(*1) 2–4° (*A*), 0·9–1·0° (*B*), 0·7–1·0° (*C*).

	TET			DI
	A	*B*	*C*	
C(11)–O(1)–C(12)	104·4	105·2	105·5	109·3
C(11)–O(*1)–C(12)	115	106	103	–
C(3)–O(2)–C(2)	61·5	60·4	60·6	60·5
C(5)–O(3)–C(4)	59·9	61·0	60·7	60·9
C(8)–O(4)–C(7)	61·1	61·3	61·6	–
C(10)–O(5)–C(9)	60·6	61·7	60·6	
C(6)–C(1)–C(2)	115·2	114·9	115·2	112·8
C(10)–C(1)–C(2)	104·8	105·8	105·6	110·8
C(10)–C(1)–C(6)	116·8	116·4	116·4	114·8
C(11)–C(1)–C(2)	106·3	106·7	107·3	108·8
C(11)–C(1)–C(6)	101·9	101·9	101·5	99·5
C(11)–C(1)–C(10)	111·5	110·9	110·6	109·3
C(1)–C(2)–O(2)	116·8	117·5	118·6	116·3
C(3)–C(2)–O(2)	59·2	59·5	60·0	60·0
C(3)–C(2)–C(1)	123·8	124·5	124·3	121·4
C(2)–C(3)–O(2)	59·3	60·1	59·4	59·5
C(4)–C(3)–O(2)	116·8	116·2	116·6	116·4
C(4)–C(3)–C(2)	119·5	119·4	120·8	120·5
C(3)–C(4)–O(3)	116·5	115·4	114·9	116·1
C(5)–C(4)–O(3)	59·4	59·6	59·9	59·3
C(5)–C(4)–C(3)	120·8	119·7	118·6	118·2
C(4)–C(5)–O(3)	60·7	59·4	59·4	59·9
C(6)–C(5)–O(3)	118·1	117·8	117·0	117·2

	TET			DI
	A	*B*	*C*	
C(6)–C(5)–C(4)	123·7	123·2	124·8	122·0
C(5)–C(6)–C(1)	116·0	116·5	116·3	115·4
C(7)–C(6)–C(1)	115·8	115·9	116·2	110·1
C(7)–C(6)–C(5)	105·4	105·3	104·4	108·6
C(12)–C(6)–C(1)	102·0	101·7	101·7	101·9
C(12)–C(6)–C(5)	107·6	107·0	107·3	108·9
C(12)–C(6)–C(7)	109·7	110·1	110·7	111·8
C(6)–C(7)–O(4)	117·8	117·6	118·7	–
C(8)–C(7)–O(4)	59·6	59·2	59·1	–
C(8)–C(7)–C(6)	123·5	123·5	123·1	123·6
C(7)–C(8)–O(4)	59·3	59·5	59·4	–
C(9)–C(8)–O(4)	115·2	115·8	116·6	–
C(9)–C(8)–C(7)	120·1	119·8	120·5	121·4
C(8)–C(9)–O(5)	116·0	116·6	115·6	–
C(10)–C(9)–O(5)	59·9	58·8	59·7	–
C(10)–C(9)–C(8)	120·0	119·8	119·4	120·9
C(1)–C(10)–O(5)	118·0	118·8	118·9	–
C(9)–C(10)–O(5)	59·5	59·5	59·7	–
C(9)–C(10)–C(1)	122·6	122·6	124·4	121·7
C(1)–C(11)–O(1)	105·0	106·2	107·4	105·8
C(1)–C(11)–O(*1)	109	110·6	107·3	–
C(6)–C(12)–O(1)	106·8	108·2	107·4	107·7
C(6)–C(12)–O(*1)	100	107·1	110·0	–

Table 6. *Torsion angles* (°)

(For atomic notation see Fig. 1.) Torsion angles involving the disordered atoms with low occupancies are not given. E.s.d.'s are typically 0·6–0·8°.

	TET			DI
	A	*B*	*C*	
C(1)–C(2)–C(3)–C(4)	2	1	−1	0
C(2)–C(3)–C(4)–C(5)	2	5	2	13
C(3)–C(4)–C(5)–C(6)	2	1	0	0
C(4)–C(5)–C(6)–C(1)	−9	−12	−2	−25
C(5)–C(6)–C(1)–C(2)	12	16	3	36
C(6)–C(1)–C(2)–C(3)	−9	−11	−1	−25
C(1)–C(6)–C(7)–C(8)	−11	−12	−3	−21
C(6)–C(7)–C(8)–C(9)	2	1	1	3
C(7)–C(8)–C(9)–C(10)	5	7	1	7
C(8)–C(9)–C(10)–C(1)	−1	−2	−2	5
C(9)–C(10)–C(1)–C(6)	−8	−10	1	−25
C(10)–C(1)–C(6)–C(7)	13	16	2	31
C(2)–C(1)–C(6)–C(7)	137	140	126	159
C(5)–C(6)–C(1)–C(10)	−111	−109	−121	−93
C(2)–C(1)–C(11)–O(1)	87	85	143	78
C(10)–C(1)–C(11)–O(1)	−159	−160	−102	−160
C(5)–C(6)–C(12)–O(1)	−106	−114	−148	−139
C(7)–C(6)–C(12)–O(1)	140	133	99	101
C(1)–C(6)–C(12)–O(1)	16	9	−26	−17
C(6)–C(12)–O(1)–C(11)	−40	−32	41	−8
C(12)–O(1)–C(11)–C(1)	46	43	−40	31
O(1)–C(11)–C(1)–C(6)	−34	−35	22	−40
C(11)–C(1)–C(6)–C(12)	10	15	2	33

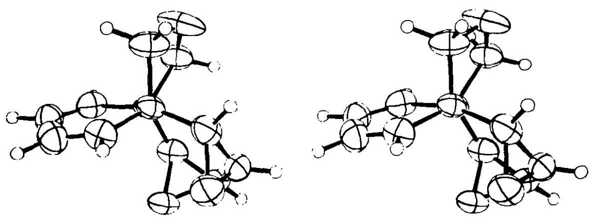

Fig. 2. Stereoscopic view of DI down C(1)–C(6), showing vibration ellipsoids at the 50% probability level (Johnson, 1965).

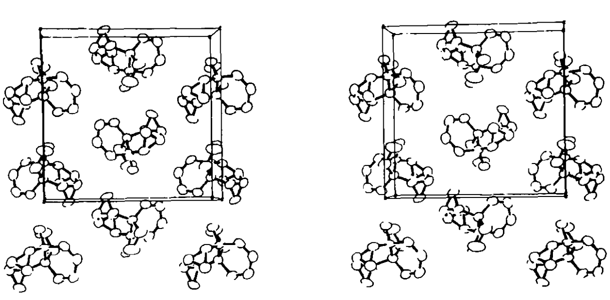

Fig. 3. Packing of DI molecules in the cell. The origin is at the lower left-hand corner; **a** is horizontal, **b** is up the page and **c** towards the reader.

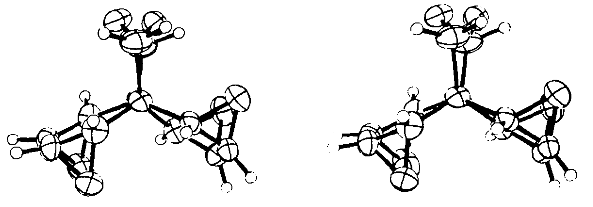

Fig. 4. Stereoscopic view of TET down C(6)–C(1), showing vibration ellipsoids at the 50% probability level (Johnson, 1965). Molecule *A*.

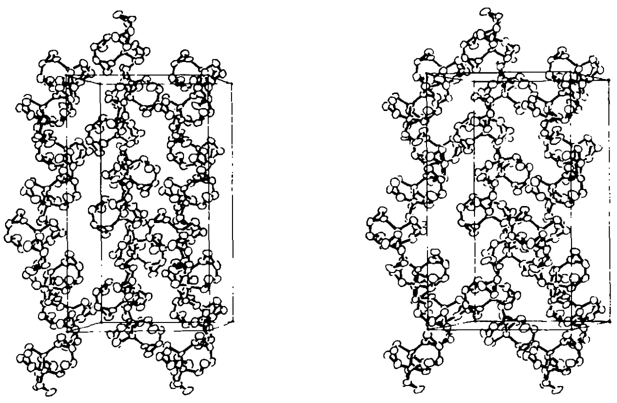

Fig. 5. Packing of TET molecules in the cell. The origin is at the lower left-hand corner; **a** is horizontal, **b** is up the page and **c** towards the reader.

symmetry is much smaller in the more strained molecules of TET. The torsion angles C(5)–C(6)–C(1)–C(2) are 12, 16 and 3° in *A*, *B* and *C*, respectively. Comparison of torsion angles in TET and DI is given in Table 6.

The hetero five-membered ring in DI has an envelope shape; the best mean plane passes through C(6), C(11), C(12), O(1) (–0·03 – 0·04 Å); C(1) lies 0·60 Å out of this plane towards the epoxy rings.

The hetero five-membered ring in TET has an envelope shape with the O atom as flap. Mean-plane calculations, with the O atom having the largest occupation factor in each of the three independent molecules, show that in *A* and *B* the O atom lies 0·58 and 0·53 Å from the plane through C(1), C(6), C(11), C(12), towards the epoxy rings in position *anti* while in *C* it is 0·50 Å towards those in position *syn*. In the crystal structure of 12-oxa[4.4.3]propella-2,4,7,9-tetraenebis(tricarbonyliron) (Birnbaum, 1972), the five-membered ring is planar but the O atom has rather high thermal vibration parameters which might indicate the presence of disorder too; the five-membered ring occurs in the envelope conformation with O bent to both sides with equal probability.

Some geometrical data observed in compounds with more than a single epoxy ring bonded to a cyclohexane skeleton are given in Table 7 (explanation of symbols is given in Fig. 1).

Table 7. *Comparison of geometrical data in some multi oxacyclohexanes*

(For explanation of the symbols see Fig. 1.)

	(*a*)	(*b*)	(*c*)	(*d*)	(*e*)	(*f*)	(*g*)
α	104·8	104·8	104·9	104·8	105·6	106·9	104·9
β	119·9	119·4	119·3	119·3	120·0	120·0	119·9
d_1	1·473	1·481	1·478	1·478	1·495	1·487	1·480
d_2	1·455	1·450	1·464	1·465	1·458	1·470	1·463
d_3	1·435	1·435	1·442	1·435	1·439	1·437	1·447

(*a*) *anti*-2,3;4,5-*syn*-7,8;9,10-Tetraepoxy-12-oxa[4.4.3]propellane (Kaftory, present work).
(*b*) *anti*-2,3;4,5-Diepoxy-12-oxa[4.4.3]propella-7,9-diene (Kaftory, present work).
(*c*) *syn*-2,3;4,5-Diepoxy-12-oxa[4.4.3]propellane-11,13-dione (Kaftory, 1979). [The values given here are the mean values of form (*A*) and form (*B*).]
(*d*) *syn*-2,3;4,5-Diepoxy-12-methyl-12-aza[4.4.3]propellane-11,13-dione (Kaftory, 1978).
(*e*) *syn,syn,syn,syn*-1,2;3,4;5,6;7,8-*anti*-9,10-Naphthalene pentoxide (Vogel, Breuer, Sommerfeld, Davis & Liu, 1977). (The geometrical parameters involving the central ring were eliminated.)
(*f*) *cis*-Trioxatris-σ-homobenzene (Littke & Drück, 1974).
(*g*) 9-Cyano-*anti*-dioxatris-σ-homobenzene (Kabuto, Yagihara, Asao & Kitahara, 1973).

There is good agreement between the dihedral angles (α) (104·8 ~ 106·9°). (In *e*, *f* and *g* the cyclohexane ring is planar and the dihedral angle is defined by the angle between this plane and the plane of the epoxy ring; in *a*, *b*, *c* and *d* it is the angle between the epoxy ring plane and the plane through the two C atoms bonded to the O atom and the next bonded atoms on both sides.)

The shortening of the C—C single-bond distances (d_1 = 1·473–1·495; d_2 = 1·450–1·470 Å) corresponds to an sp^2–sp^2 single bond, although the C atoms are in sp^3 hybridization, and is an indication for multi-conjugated interactions which occur between three-membered rings, as assumed between cyclopropane rings and double bonds. The values observed for the angle β (119·3–120·0°) are similar to those observed in conjugated systems and suggest that the ring is an intermediate of cyclohexane with sp^3 C atoms and benzene with sp^2 C atoms.

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The Crystal and Molecular Structure of 6,6′-Dibromo-6,6′-dideoxy-α,α-trehalose Hexaacetate Chloroform Adduct, $C_{24}H_{32}Br_2O_{15}.CHCl_3$

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Abstract

The crystal structure of $C_{24}H_{32}Br_2O_{15}.CHCl_3$ has been solved by direct methods from 3658 independent reflections and refined by a least-squares block-diagonal approximation to a final R value of 0·084. The crystal data are: a = 11·532 (7), b = 18·340 (8), c = 16·810 (10) Å, β = 91·35 (10)°, space group $P2_1$. There are two molecules of each 6,6′-dibromo-trehalose hexaacetate and chloroform per asymmetric

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