

Table 4. Selected intermolecular and intramolecular contacts

(a) Hydrogen bonds				A-C (Å)	B-C (Å)	ABC (°)
A	B	C				
N(4'α)	H(4'α2)	⋯O(1-3 ⁱ)	2.795 (4)	2.05 (5)	170 (5)	
N(4'α)	H(4'α1)	⋯O(W2 ⁱⁱ)	2.856 (4)	1.96 (5)	171 (4)	
N(1'')	H(1'')	⋯O(2-2 ⁱⁱⁱ)	2.672 (3)	1.73 (4)	176 (4)	
O(2-1)	H(2-1)	⋯O(2-3 ^{iv})	2.610 (3)	1.70 (7)	168 (6)	
O(W1)	H(W11)	⋯O(2-3 ⁱⁱⁱ)	2.910 (4)	2.22 (6)	168 (6)	
O(W1)	H(W12)	⋯O(2-2 ^v)	2.741 (4)	1.91 (10)	161 (10)	
O(W2)	H(W21)	⋯O(W1)	2.803 (4)	1.92 (6)	171 (6)	
O(W2)	H(W22)	⋯O(W3 ⁱ)	2.804 (4)	1.93 (6)	174 (6)	
O(W3)	H(W31)	⋯O(W1 ^v)	2.842 (4)	2.00 (7)	170 (7)	
O(W3)	H(W32)*	⋯O(W4)	2.780 (4)	—	—	
O(W4)	H(W41)	⋯O(2-3 ^{vii})	2.883 (4)	2.16 (6)	162 (6)	
O(W4)	H(W42)*	⋯O(W3 ^{viii})	2.848 (4)	—	—	
O(W5)	H(W51)*	⋯O(1-2)	2.843 (8)	—	—	
O(W5)	H(W52)*	⋯O(1-2 ^v)	2.960 (8)	—	—	
C(2)	H(2)	⋯O(1-3 ⁱⁱⁱ)	3.129 (4)	2.47 (3)	134 (3)	

(b) Close contacts around S						
C(2)	S(1)	⋯O(5 ^y)	—	2.892 (2)	156.7 (1)	
C(5)	S(1)	⋯O(5 ^y)	—	—	74.2 (1)	

(c) Symmetry code							
None	x	y	z	(iv)	-1-x	1-y	1-z
(i)	x	-1+y	z	(v)	-x	1-y	2-z
(ii)	-x	-y	1-z	(vi)	1-x	1-y	2-z
(iii)	-x	1-y	1-z	(vii)	1+x	y	z
				(viii)	1-x	2-y	1-z

* Not located.

inferences to be drawn from the current structure. However, it does provide added support for the conclusions drawn from the earlier structure.

The greater stability of the current polymorph (with respect to melting point and radiation sensitivity) is not readily explained by the respective crystal structures. The first polymorph gave indications that water was easily lost from the crystal, yet the hydrogen bonds

involving water molecules are the same or even slightly stronger in that structure. Also, in that structure, the water molecules form isolated clusters and do not form the continuous water column found in the current one.

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Acta Cryst. (1979). B35, 1637-1642

The Crystal Structure of syn-2,3;4,5-Diepoxy-12-oxa[4.4.3]propellane-11,13-dione [Forms (A) and (B)]

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Abstract

C₁₂H₁₂O₅, M_r = 237.30; two crystalline modifications were obtained: (A) monoclinic, P2₁/c, a = 17.782 (8), b = 8.221 (4), c = 16.252 (8) Å, β = 115.10 (2)°, Z =

8, D_x = 1.466 Mg m⁻³; (B) monoclinic, P2₁/c, a = 15.191 (8), b = 8.375 (4), c = 16.819 (8) Å, β = 94.98 (2)°, Z = 8, D_x = 1.479 Mg m⁻³. Each form contains two crystallographically independent molecules in the asymmetric unit. The configuration of

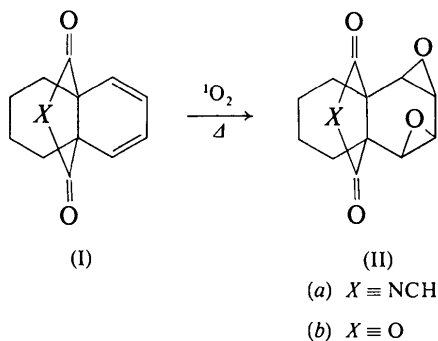
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the four independent molecules is the same; the unsubstituted six-membered ring is in a chair conformation, and the epoxy rings are *syn* with respect to the central hetero ring. The molecule deviates significantly from the mirror symmetry expected from its formula.

Introduction

The title compound was obtained by Landheer & Ginsburg (1979) during an investigation of the possibility that singlet oxygen is capable of undergoing secondary orbital interaction with the π^* orbitals of the carbonyl groups in propellanes of type (I).



The significant deviations from mirror symmetry observed in (IIa) (Kaftory, 1978) were attributed to an attractive intramolecular $\text{O} \cdots \text{C}=\text{O}$ interaction (Bürgi, Dunitz & Shefter, 1974). The carbonyl groups attached to an O atom [(IIb)] should be better electrophiles. The crystal structure of (IIb) was undertaken to check the existence of the same kind of distortions as observed in (IIa).

Experimental

The attainment of the two crystalline modifications is solvent dependent: modification (A) was obtained from CCl_4 , modification (B) from EtOAc.

Intensities from colourless needles, (A) $0.1 \times 0.15 \times 0.4$ mm, (B) $0.2 \times 0.2 \times 0.4$ mm, were collected on a Philips PW 1100 four-circle computer-controlled diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$). Crystallographic data and details of intensity measurements are given in Table 1.

The structures were solved with *MULTAN 77* (Main, Woolfson, Lessinger, Germain & Declercq, 1977) and refined with *SHELX* (Sheldrick, 1976). Each molecule was treated as a separate block with anisotropic thermal parameters for C and O, isotropic for H. Scattering factors for C and O were taken from Cromer & Mann (1968), for H from Stewart, Davidson & Simpson (1965). The final agreement factors and the weighting schemes are given in Table 1. Final posi-

Table 1. Crystallographic data and experimental details

	Form (A)	Form (B)
Formula	$\text{C}_{12}\text{H}_{12}\text{O}_5$	$\text{C}_{12}\text{H}_{12}\text{O}_5$
<i>a</i> (Å)	17.782 (8)	15.191 (8)
<i>b</i> (Å)	8.221 (4)	8.375 (4)
<i>c</i> (Å)	16.252 (8)	16.819 (8)
β (°)	115.10 (2)	94.98 (2)
Z	8	8
Space group	$P2_1/c$	$P2_1/c$
D_x (Mg m^{-3})	1.466	1.479
Scan mode	ω	ω
$\Delta\omega$ (°)	1.2	1.4
Scan time (s)	24	28
Background (s)*	20	20
θ_{max} (°)	24	24
Reflexions measured	3344	3428
Significant reflexions	2727	2658
	[$F_o > 1.5\sigma(F_o)$]	
Weighting coefficients	1.1733, 0.0076	0.6839, 0.0237
(<i>k, g</i>) [†]		
R_w	0.077	0.089
<i>R</i>	0.059	0.065

* Total background counting time.

[†] $w = k/[\sigma^2(F_o) + gF_o^2]$.

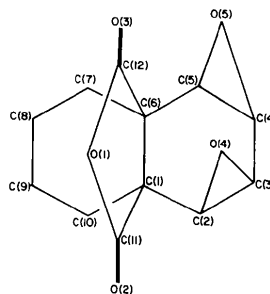


Fig. 1. Schematic representation of the compound showing atomic numbering.

tional parameters are listed in Tables 2 and 3.* Bond lengths, bond angles and torsion angles are given in Tables 4, 5 and 6 respectively, with atomic notation in Fig. 1.

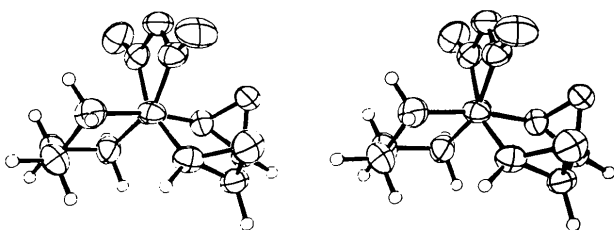
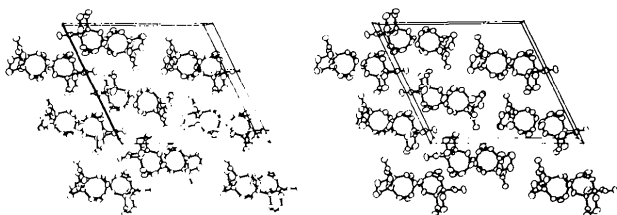
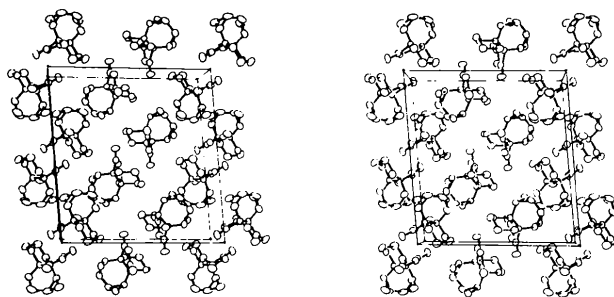
Description of the structure

The structure of the four molecules is the same and a stereodrawing of *A*(1) as a representative is shown in Fig. 2. The crystal structures of (A) and (B) are shown by stereodrawings in Figs. 3 and 4 respectively. The

* Lists of structure factors and thermal parameters for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34304 (34 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Form (A): coordinates for non-hydrogen ($\times 10^4$) and hydrogen atoms ($\times 10^3$) (e.s.d.'s in parentheses)*

	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
Molecule <i>A</i> (1)							
O(1)	3805 (1)	-397 (3)	2338 (2)	C(11)	3991 (2)	-446 (4)	3266 (2)
O(2)	4172 (2)	-1700 (3)	3665 (2)	C(12)	3577 (2)	1165 (4)	2008 (2)
O(3)	3499 (2)	1496 (4)	1269 (2)	H(2)	420 (4)	189 (9)	497 (5)
O(4)	3252 (2)	89 (3)	4494 (2)	H(3)	272 (5)	222 (9)	468 (5)
O(5)	2291 (1)	269 (3)	2638 (1)	H(4)	153 (5)	193 (9)	296 (5)
C(1)	3990 (2)	1264 (4)	3593 (2)	H(5)	205 (4)	238 (9)	180 (4)
C(2)	3720 (2)	1413 (4)	4357 (2)	H(71)	319 (4)	437 (8)	191 (4)
C(3)	2838 (2)	1617 (4)	4144 (2)	H(72)	333 (3)	453 (7)	303 (4)
C(4)	2226 (2)	1610 (4)	3183 (2)	H(81)	458 (4)	555 (9)	308 (5)
C(5)	2505 (2)	1884 (4)	2468 (2)	H(82)	469 (4)	403 (8)	257 (4)
C(6)	3417 (2)	2137 (4)	2699 (2)	H(91)	565 (4)	397 (8)	426 (4)
C(7)	3563 (2)	3963 (4)	2650 (3)	H(92)	481 (4)	414 (8)	444 (4)
C(8)	4478 (2)	4406 (5)	3002 (3)	H(101)	521 (3)	143 (7)	360 (4)
C(9)	4974 (2)	3693 (5)	3941 (3)	H(102)	529 (3)	135 (7)	460 (4)
C(10)	4901 (2)	1845 (5)	3914 (2)				
Molecule <i>A</i> (2)							
O(1)	146 (1)	10052 (3)	9089 (2)	C(11)	971 (2)	10406 (4)	9277 (2)
O(2)	1177 (2)	11768 (3)	9285 (2)	C(12)	16 (2)	8387 (4)	9042 (2)
O(3)	-618 (1)	7837 (4)	8979 (2)	H(2)	281 (4)	864 (9)	992 (4)
O(4)	2168 (2)	9889 (3)	8555 (2)	H(3)	247 (4)	768 (9)	821 (5)
O(5)	558 (2)	8868 (3)	7557 (2)	H(4)	112 (5)	717 (9)	703 (5)
C(1)	1456 (2)	8822 (3)	9506 (2)	H(5)	7 (4)	656 (9)	767 (5)
C(2)	2180 (2)	8783 (4)	9251 (2)	H(71)	132 (4)	532 (8)	927 (4)
C(3)	2049 (2)	8177 (4)	8352 (3)	H(72)	37 (4)	519 (9)	911 (4)
C(4)	1207 (3)	7695 (4)	7700 (2)	H(81)	88 (4)	608 (8)	1071 (4)
C(5)	563 (2)	7385 (4)	8017 (2)	H(82)	148 (4)	463 (9)	1075 (4)
C(6)	768 (2)	7550 (3)	9025 (2)	H(91)	253 (3)	655 (7)	1072 (4)
C(7)	940 (2)	5844 (4)	9439 (3)	H(92)	231 (3)	695 (7)	1159 (4)
C(8)	1284 (3)	5822 (5)	10455 (3)	H(101)	229 (4)	944 (8)	1084 (4)
C(9)	2029 (2)	6927 (5)	10867 (2)	H(102)	136 (4)	906 (7)	1078 (4)
C(10)	1772 (2)	8672 (4)	10549 (2)				

Fig. 2. Stereoscopic view of molecule *A*(1), down C(1)–C(6), showing vibration ellipsoids at the 50% probability level (Johnson, 1965).Fig. 3. Packing of molecules in the unit cell [modification (*A*)]. The origin is at the lower left-hand corner of the unit cell: *a* is horizontal, *b* is into the page and *c* is up the page.Fig. 4. Packing of molecules in the unit cell [modification (*B*)]. The origin is at the lower left-hand corner of the unit cell: *a* is horizontal, *b* is into the page and *c* is up the page.

packing in the two forms is very similar, layers of molecules running parallel to (102) in (*A*) and parallel to (10 $\bar{1}$) in (*B*).

The two epoxy rings are *syn* with respect to the hetero ring (with two carbonyl groups attached to it). The same configuration was found in *syn*-2,3,4,5-diepoxy-12-methyl-12-aza[4.4.3]propellane-11,13-dione (Kaftory, 1978).

Table 3. Form (B): coordinates for non-hydrogen ($\times 10^4$) and hydrogen atoms ($\times 10^3$) (e.s.d.'s in parentheses)

	x	y	z		x	y	z
Molecule B(1)							
O(1)	6013 (2)	393 (4)	409 (2)	C(11)	5982 (3)	575 (5)	1235 (3)
O(2)	5912 (2)	1854 (4)	1512 (2)	C(12)	6172 (3)	-1183 (6)	219 (3)
O(3)	6150 (2)	-1611 (5)	-453 (2)	H(2)	596 (3)	-157 (6)	288 (3)
O(4)	6985 (2)	4 (3)	2755 (2)	H(3)	750 (3)	-225 (6)	307 (3)
O(5)	7749 (2)	-405 (4)	1332 (2)	H(4)	848 (3)	-218 (6)	205 (3)
C(1)	5958 (2)	-1081 (4)	1601 (2)	H(5)	773 (3)	-261 (5)	74 (2)
C(2)	6376 (2)	-1217 (3)	2454 (4)	H(71)	634 (4)	-434 (6)	41 (3)
C(3)	7323 (3)	-1562 (5)	2599 (3)	H(72)	643 (3)	-430 (5)	139 (3)
C(4)	7854 (3)	-1700 (5)	1907 (3)	H(81)	503 (4)	-527 (7)	93 (3)
C(5)	7417 (3)	-1973 (5)	1111 (3)	H(82)	486 (4)	-373 (6)	46 (3)
C(6)	6419 (2)	-2097 (5)	985 (2)	H(91)	412 (4)	-346 (6)	168 (3)
C(7)	6164 (3)	-3861 (5)	941 (3)	H(92)	507 (3)	-374 (6)	210 (3)
C(8)	5181 (4)	-4160 (6)	939 (3)	H(101)	469 (4)	-112 (7)	105 (4)
C(9)	4809 (3)	-3287 (5)	1635 (3)	H(102)	470 (3)	-85 (5)	204 (3)
C(10)	4958 (3)	-1514 (5)	1578 (3)				
Molecule B(2)							
O(1)	9955 (2)	147 (3)	9082 (2)	C(11)	9118 (3)	-279 (5)	8760 (2)
O(2)	8954 (2)	-1643 (4)	8617 (2)	C(12)	10016 (3)	1786 (5)	9158 (3)
O(3)	10648 (2)	2390 (4)	9498 (2)	H(2)	725 (6)	131 (9)	827 (4)
O(4)	7943 (3)	143 (4)	7357 (2)	H(3)	756 (4)	233 (7)	693 (3)
O(5)	9635 (3)	1424 (4)	7422 (2)	H(4)	898 (4)	313 (8)	666 (4)
C(1)	8526 (2)	1175 (4)	8729 (2)	H(5)	994 (4)	358 (6)	786 (3)
C(2)	7829 (3)	1165 (5)	8023 (3)	H(71)	957 (5)	468 (8)	911 (4)
C(3)	8016 (4)	1840 (6)	7262 (3)	H(72)	853 (4)	474 (7)	865 (3)
C(4)	8911 (4)	2468 (6)	7164 (3)	H(81)	830 (5)	507 (8)	996 (4)
C(5)	9502 (3)	2832 (6)	7885 (3)	H(82)	894 (4)	358 (6)	1034 (3)
C(6)	9212 (2)	2547 (4)	8704 (2)	H(91)	746 (4)	279 (7)	1024 (3)
C(7)	8940 (3)	4157 (5)	9050 (3)	H(92)	729 (4)	327 (7)	932 (3)
C(8)	8512 (4)	3986 (7)	9836 (3)	H(101)	855 (4)	87 (6)	998 (3)
C(9)	7754 (4)	2805 (7)	9740 (4)	H(102)	766 (4)	30 (6)	949 (3)
C(10)	8098 (3)	1162 (6)	9527 (3)				

Table 4. Bond lengths (Å) in the four independent molecules (for atomic notation see Fig. 1)

The e.s.d.'s are typically:
for (A) 0.004–0.006 Å, for (B) 0.005–0.007 Å.

	Form (A)		Form (B)	
	A(1)	A(2)	B(1)	B(2)
C(1)–C(2)	1.513	1.511	1.522	1.521
C(1)–C(6)	1.553	1.546	1.554	1.554
C(1)–C(10)	1.553	1.548	1.559	1.541
C(1)–C(11)	1.504	1.519	1.520	1.512
C(2)–C(3)	1.466	1.466	1.466	1.449
C(2)–O(4)	1.445	1.445	1.441	1.432
C(3)–O(4)	1.446	1.441	1.442	1.435
C(3)–C(4)	1.478	1.475	1.477	1.480
C(4)–C(5)	1.462	1.463	1.460	1.478
C(4)–O(5)	1.449	1.446	1.453	1.442
C(5)–O(5)	1.440	1.428	1.444	1.437
C(5)–C(6)	1.515	1.525	1.517	1.501
C(6)–C(7)	1.531	1.529	1.527	1.539
C(6)–C(12)	1.500	1.515	1.517	1.523
C(7)–C(8)	1.523	1.498	1.514	1.530
C(8)–C(9)	1.519	1.509	1.530	1.516
C(9)–C(10)	1.524	1.528	1.506	1.526
C(11)–O(1)	1.401	1.396	1.402	1.385
C(11)–O(2)	1.187	1.176	1.177	1.189
C(12)–O(1)	1.385	1.385	1.384	1.381
C(12)–O(3)	1.181	1.179	1.183	1.188

The unsubstituted six-membered ring adopts the chair conformation. Torsion angles (Table 6) are related by approximate mirror symmetry passing through C(6) and C(9).

Discussion

The mean C(3)–C(4) length (1.478 Å) is shorter than a single sp^3 – sp^3 bond and close to an sp^2 – sp^2 single bond (1.480 Å). The same shortening was found in syn-2,3;4,5-diepoxy-12-methyl-12-aza[4.4.3]propellane-11,13-dione (1.478 Å; Kaftory, 1978) and in 9-cyano-anti-dioxatris(σ -homobenzene) (1.480 Å; Kabuto, Yagihara, Asao & Kitahara, 1973). A somewhat smaller shortening was observed in cis-trioxatris(σ -homobenzene) (1.487 Å; Littke & Drück, 1974) and in syn,syn,syn,syn-1,2;3,4;5,6;7,8-anti-9,10-naphthalene pentoxide (1.495 Å; Vogel, Breuer, Sommerfeld, Davis & Liu, 1977). The shortening indicates that multi-conjugated interactions occur between three-membered rings, as assumed between cyclopropane rings and double bonds (Fritchie, 1966; Heller, Dreiding, Grieb & Niggli, 1972; Hwang, Donohue & Tsai, 1972).

Table 5. Bond angles ($^{\circ}$) in the four independent molecules (for atomic notation see Fig. 1)The e.s.d.'s are typically: for (A) 0.2–0.4 $^{\circ}$, for (B) 0.3–0.5 $^{\circ}$.

	Form (A)		Form (B)	
	A(1)	A(2)	B(1)	B(2)
C(12)–O(1)–C(11)	109.9	110.7	110.8	110.1
C(3)–O(4)–C(2)	61.0	61.1	61.2	60.7
C(5)–O(5)–C(4)	60.8	61.2	60.5	61.8
C(6)–C(1)–C(2)	114.9	115.5	114.4	113.9
C(10)–C(1)–C(2)	110.4	110.0	109.4	111.2
C(10)–C(1)–C(6)	110.4	110.0	110.5	111.3
C(11)–C(1)–C(2)	114.5	114.4	115.4	113.3
C(11)–C(1)–C(6)	101.5	102.2	101.6	101.5
C(11)–C(1)–C(10)	104.4	104.0	105.1	105.0
C(1)–C(2)–O(4)	118.0	118.0	118.7	119.3
C(3)–C(2)–O(4)	59.5	59.3	59.4	59.8
C(3)–C(2)–C(1)	119.7	119.1	119.6	120.7
C(2)–C(3)–O(4)	59.5	59.6	59.4	59.5
C(4)–C(3)–O(4)	115.9	115.7	116.3	116.4
C(4)–C(3)–C(2)	118.9	119.4	118.7	119.4
C(3)–C(4)–O(5)	115.8	115.7	115.5	115.7
C(5)–C(4)–O(5)	59.3	58.8	59.4	59.0
C(5)–C(4)–C(3)	119.6	120.2	119.9	118.7
C(4)–C(5)–O(5)	59.9	60.0	60.0	59.3
C(6)–C(5)–O(5)	114.9	115.5	114.9	115.7
C(6)–C(5)–C(4)	120.9	119.7	120.6	121.0
C(5)–C(6)–C(1)	112.1	112.4	111.8	113.2
C(7)–C(6)–C(1)	116.4	115.5	115.8	115.8
C(7)–C(6)–C(5)	108.0	107.7	108.5	108.5
C(12)–C(6)–C(1)	101.3	101.4	101.5	100.8
C(12)–C(6)–C(5)	105.3	104.4	104.7	103.9
C(12)–C(6)–C(7)	113.2	114.9	113.9	114.0
C(8)–C(7)–C(6)	113.1	114.1	113.9	113.2
C(9)–C(8)–C(7)	110.9	110.6	110.5	110.1
C(10)–C(9)–C(8)	110.5	109.6	110.7	109.9
C(9)–C(10)–C(1)	112.3	111.2	112.3	112.2
O(2)–C(11)–O(1)	119.9	119.6	120.3	119.7
C(1)–C(11)–O(1)	108.6	108.0	107.9	109.3
C(1)–C(11)–O(2)	131.2	132.2	131.5	130.7
O(3)–C(12)–O(1)	119.8	121.0	121.2	120.8
C(6)–C(12)–O(1)	108.8	108.8	108.6	109.0
C(6)–C(12)–O(3)	131.3	130.1	130.0	130.0

The mean values of bond lengths in the oxirane ring (C–O 1.442 Å, C–C 1.472 Å) agree well with the mean values of 1.435, 1.465 Å (Kaftory, 1978), and 1.437, 1.470 Å (Littke & Drück, 1974) and with 1.439 Å (C–O), but not with 1.458 Å (C–C) (Vogel *et al.*, 1977). The major difference in the geometrical parameters is the non-planarity of the substituted six-membered ring in the present work and in Kaftory (1978) (torsion angles in Table 6) while in the other structures mentioned it is planar.

The four molecules are appreciably distorted from mirror symmetry (Fig. 2 and Table 6). The distortion can be described as a twist of the molecule around C(1)–C(6) (the torsion angles at this bond are $-41 \rightarrow -44^{\circ}$). As a result of the distortion there is a significant shear of the two epoxy rings with respect to the ideal position of the mirror plane: O(5) is shifted towards the midpoint of C(11) and C(12). The average

Table 6. Comparison of torsion angles ($^{\circ}$) (for atomic notation see Fig. 1)The e.s.d.'s are typically: 0.5–0.7 $^{\circ}$ in (A), 0.6–0.8 $^{\circ}$ in (B).

	Form (A)		Form (B)	
	A(1)	A(2)	B(1)	B(2)
C(1)–C(2)–C(3)–C(4)	2	3	3	3
C(2)–C(3)–C(4)–C(5)	-18	-17	-18	-18
C(3)–C(4)–C(5)–C(6)	1	1	1	1
C(4)–C(5)–C(6)–C(1)	29	30	30	28
C(5)–C(6)–C(1)–C(2)	-42	-42	-44	-41
C(6)–C(1)–C(2)–C(3)	28	27	29	27
C(1)–C(6)–C(7)–C(8)	45	44	45	44
C(6)–C(7)–C(8)–C(9)	-52	-52	-52	-53
C(7)–C(8)–C(9)–C(10)	60	61	60	62
C(8)–C(9)–C(10)–C(1)	-60	-63	-60	-62
C(9)–C(10)–C(1)–C(6)	50	53	51	50
C(10)–C(1)–C(6)–C(7)	-43	-44	-43	-41
C(2)–C(1)–C(6)–C(7)	83	82	81	85
C(5)–C(6)–C(1)–C(10)	-168	-168	-168	-168
C(2)–C(1)–C(11)–O(1)	149	149	150	147
C(10)–C(1)–C(11)–O(1)	-91	-91	-89	-91
C(5)–C(6)–C(12)–O(1)	-89	-92	-91	-91
C(7)–C(6)–C(12)–O(1)	153	151	151	151
C(1)–C(6)–C(12)–O(1)	28	25	26	26
C(6)–C(12)–O(1)–C(11)	-13	-11	-10	-12
C(12)–O(1)–C(11)–C(1)	-8	-9	-11	-9
O(1)–C(11)–C(1)–C(6)	24	24	26	25
C(11)–C(1)–C(6)–C(12)	-30	-29	-30	-29

non-bonded distances are: O(5)···C(11) 2.827 Å (2.797 \rightarrow 2.865 Å); O(5)···C(12) 2.968 Å (2.942 \rightarrow 2.981 Å); O(4)···C(11) 2.868 Å (2.852 \rightarrow 2.900 Å); and O(4)···C(12) 4.413 Å (4.396 \rightarrow 4.449 Å). The values in the structure with N as the hetero-atom (Kaftory, 1978) are 2.929, 2.943, 2.884 and 4.383 Å respectively. The possibility of an attractive intramolecular O(5)···C(11)=O(2) interaction (Bürgi, Dunitz & Shefter, 1974) cannot be eliminated. The shortening of O(5)···C(11) (2.827 Å) in the present work (O as hetero-atom attached to the carbonyl groups) compared with 2.929 Å (N as hetero-atom; Kaftory, 1978) might support the assumption of the better electrophilicity of a carbonyl C atom bonded to an O rather than to an N atom. The hetero-ring has an envelope shape. O(1), C(6), C(11) and C(12) are planar (out of plane displacement range $-0.06 \rightarrow 0.06$ Å) while C(1) lies 0.45 \rightarrow 0.48 Å from that plane away from the epoxy rings ($-0.03 \rightarrow 0.03$ Å and 0.42 Å; Kaftory, 1978). O(2) is displaced by 0.10 \rightarrow 0.13 Å towards, O(3) by 0.10 \rightarrow 0.17 Å away from the epoxy rings (0.11, 0.11 Å; Kaftory, 1978).

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Structural Studies of the Interaction between Indole Derivatives and Biologically Important Aromatic Compounds.

III. The Crystal and Molecular Structure of Tryptamine : 1-Thyminylacetic Acid (1 : 1) Complex

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Abstract

The crystal structure of a 1:1 complex of tryptamine and 1-thyminylacetic acid, $C_{10}H_{13}N_2^+ \cdot C_7H_7N_2O_4^-$, has been determined by the X-ray method. The crystal is monoclinic, space group $P2_1/c$ with unit-cell dimensions: $a = 9.793$ (2), $b = 6.122$ (1), $c = 28.160$ (3) Å and $\beta = 95.46$ (2)°. The structure was solved using *MULTAN* and refined by a block-diagonal least-squares method to give a final R value of 0.058. As for the interaction between the acid and the amine, an ion pair (salt bridge) is formed between the positive charge at the terminal amino N atom of tryptamine and the negative charge at the carboxyl O atom of 1-thyminylacetic acid. No prominent interaction between the pyrimidine and indole rings is observed in the crystal. Both component molecules are held together by three-dimensional frameworks of hydrogen bonds around the twofold screw axis to form an infinite helical array in the b direction.

Introduction

In order to understand the role of the tryptophan residue in protein–nucleic acid interaction, the interactions between tryptophan and nucleic acids have been widely investigated by kinetics, chemical modification, UV, CD and NMR spectroscopies or X-ray structure analysis.

It is of interest to identify which of the four nucleic bases could interact most specifically with the indole ring of the tryptophan residue.

In the present paper, we report the crystal structure of the title complex by the X-ray diffraction method, which is a model for the study of the indole–thymine interaction.

Experimental

The synthesis of potassium 1-thyminyacetate (I) was carried out according to the method previously