

Table 4. *Intramolecular angles (°) with e.s.d.'s in parentheses*

	(a)	(b)		(a)	(b)		(a)	(b)
C(2)–C(1)–C(10)	113.0 (3)	112.8 (5)	C(1)–C(10)–C(5)	109.7 (2)	110.2 (5)	C(8)–C(14)–C(13)	113.5 (2)	113.4 (4)
C(1)–C(2)–C(3)	112.0 (3)	112.3 (5)	C(1)–C(10)–C(9)	108.9 (2)	109.3 (4)	C(8)–C(14)–C(15)	117.3 (3)	121.5 (5)
C(2)–C(3)–C(4)	117.4 (3)	115.0 (5)	C(1)–C(10)–C(19)	110.1 (3)	106.0 (4)	C(13)–C(14)–C(15)	106.9 (2)	105.0 (5)
C(2)–C(3)–O(3)	122.1 (3)	122.7 (5)	C(5)–C(10)–C(9)	107.2 (2)	106.8 (4)	C(14)–C(15)–C(16)	102.8 (3)	106.7 (5)
C(4)–C(3)–O(3)	120.5 (3)	122.3 (5)	C(5)–C(10)–C(19)	107.1 (2)	107.1 (4)	C(15)–C(16)–C(17)	106.5 (3)	104.5 (5)
C(3)–C(4)–C(5)	123.4 (3)	124.1 (5)	C(9)–C(10)–C(19)	113.8 (2)	117.4 (4)	C(13)–C(17)–C(16)	102.4 (3)	104.2 (5)
C(4)–C(5)–C(6)	120.4 (3)	119.8 (5)	C(9)–C(11)–C(12)	113.0 (2)	115.3 (4)	C(13)–C(17)–C(20)	113.7 (2)	115.7 (5)
C(4)–C(5)–C(10)	121.9 (3)	122.5 (5)	C(9)–C(11)–O(11)	110.2 (2)	109.5 (4)	C(13)–C(17)–O(17)	107.2 (2)	105.8 (4)
C(6)–C(5)–C(10)	117.4 (2)	117.4 (5)	C(12)–C(11)–O(11)	111.4 (2)	110.6 (5)	C(16)–C(17)–C(20)	113.2 (3)	114.2 (5)
C(5)–C(6)–C(7)	112.9 (3)	112.1 (5)	C(11)–C(12)–C(13)	112.9 (2)	113.6 (5)	C(16)–C(17)–O(17)	112.0 (2)	110.7 (4)
C(6)–C(7)–C(8)	112.5 (4)	111.1 (4)	C(12)–C(13)–C(14)	109.3 (2)	110.1 (5)	C(20)–C(17)–O(17)	108.1 (2)	105.9 (5)
C(7)–C(8)–C(9)	108.6 (2)	109.4 (4)	C(12)–C(13)–C(17)	116.1 (2)	117.2 (5)	C(17)–C(20)–C(21)	117.4 (3)	120.4 (6)
C(7)–C(8)–C(14)	110.5 (2)	108.4 (4)	C(12)–C(13)–C(18)	111.8 (3)	108.9 (4)	C(17)–C(20)–O(20)	121.7 (3)	119.2 (6)
C(9)–C(8)–C(14)	109.5 (2)	111.1 (4)	C(14)–C(13)–C(17)	98.7 (2)	99.6 (4)	C(21)–C(20)–O(20)	120.9 (3)	120.3 (6)
C(8)–C(9)–C(10)	112.7 (2)	113.3 (4)	C(14)–C(13)–C(18)	110.9 (3)	113.6 (5)	C(20)–C(21)–O(21)	108.9 (3)	
C(8)–C(9)–C(11)	115.3 (2)	111.9 (4)	C(17)–C(13)–C(18)	109.3 (2)	107.4 (5)	C(20)–C(21)–I		126.9 (6)
C(10)–C(9)–C(11)	113.9 (2)	115.7 (4)						

(a) Cortisol (Roberts *et al.*, 1973); (b) iodicortisol (this work).

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The Structures of *cis*- and *trans*-4-*tert*-Butyl-1-phenyl-1,2-epoxycyclohexane

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Abstract

The crystal structures of the title compounds, (2) and (3), have been determined by three-dimensional diffrac-

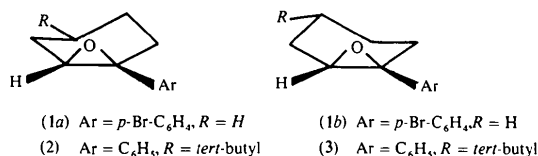
tion methods. Crystals of (3) are triclinic, space group $P\bar{1}$, with $Z = 2$, and $a = 10.802$ (1), $b = 8.362$ (1), $c = 8.297$ (1) Å, $\alpha = 75.0$ (1), $\beta = 103.9$ (1), $\gamma = 101.2$ (1)°. Crystals of (2) are monoclinic, space group $P2_1/c$, with $Z = 4$, and $a = 6.159$ (2), $b = 25.193$ (10), $c = 9.853$ (10) Å, $\beta = 115.8$ (1)°. The structures have

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been solved by direct methods and refined by least squares to $R = 0.076$ for (3) and $R = 0.096$ for (2). Owing to the high degree of decomposition of compound (2) during data collection, the discussion mainly concerns compound (3). Comparison is made with the analogous epoxide without the *tert*-butyl group.

Introduction

The unusual chemical behaviour of 1-aryl-substituted oxiranes is of particular interest (Buchanan & Sable, 1972; Battistini, Crotti & Macchia, 1975; Balsamo, Crotti, Macchia & Macchia, 1974) and the conjugative properties of the epoxide ring have been extensively documented (Cromwell & Hudson, 1953; Strait, Ketcham, Jambotkar & Shah, 1964; Strait, Jambotkar, Ketcham & Renoff, 1966; Merlino, Lami, Macchia, Macchia & Monti, 1972; Williams, Crotti, Macchia & Macchia, 1975) and theoretically justified (Barnett, 1967). An X-ray diffraction study of the *p*-bromo derivative of the conformationally mobile 1-phenyl-1,2-epoxycyclohexane (1*a*,*b*) showed that, at least in the solid state, ring conformation (1*a*) is the preferred one. This conformational preference was attributed to the pseudoconjugative interaction (Cromwell & Hudson, 1953; Strait, Ketcham, Jambotkar & Shah, 1964; Strait, Jambotkar, Ketcham & Renoff, 1966; Barnett, 1967) between the aryl and the three-membered ring which is at a maximum where the phenyl almost bisects the epoxide ring. Consequently, the conformation (1*a*) is adopted in order to lower the steric interactions between one of the *ortho* H atoms of the phenyl ring and the two H atoms in the 6-position of the cyclohexyl ring. The relative orientation of the two rings observed in (1) is very close to that found in a simple aryl-substituted oxirane, *p*-nitro- α,β -epoxystyrene (Williams, Crotti, Macchia & Macchia, 1975), and to the completely bisected one which theoretically should allow the maximum conjugation (Barnett, 1967).



We have now examined the X-ray crystal structures of the two diastereoisomeric epoxides *cis*-4-*tert*-butyl-1-phenyl-1,2-epoxycyclohexane (2) and *trans*-4-*tert*-butyl-1-phenyl-1,2-epoxycyclohexane (3) in which the *tert*-butyl group locks the mobile 1-phenyl-1,2-epoxycyclohexane system into half-chair conformations (Buchanan & Sable, 1972; Berti, Macchia & Macchia, 1968) that are equivalent to (1*a*) and (1*b*) respectively. The *tert*-butyl group has been widely used as an anchoring group in the cyclohexane ring (Eliel, Al-

linger, Angyal & Morrison, 1965; Jensen & Bushweller, 1971), even if it may cause some distortion in the cyclohexane system (Eliel, Allinger, Angyal & Morrison, 1965).

The present study should give information on the influence of the *tert*-butyl group on the 1,2-epoxycyclohexane moiety. Furthermore, it should be able to indicate how the different conformation of the cyclohexane ring of the 1-phenyl-1,2-epoxycyclohexane system could modify the relative orientation of the phenyl and the epoxide ring.

X-ray data, structure determination and refinement

Epoxides (2) and (3) have been prepared as previously described (Berti, Macchia & Macchia, 1968), and crystals suitable for X-ray analysis were obtained [(2), m.p. 340–341 K; (3), m.p. 337–338.5 K] by slow evaporation of a 85:15 mixture of EtOH and H₂O; in (3) the crystallization was accomplished in the presence of trace amounts of K₂CO₃. Crystals of (2) and (3) are stable at room temperature.

Crystal data [from single-crystal diffractometry (Cu K α , λ 1.54178 Å); C₁₆H₂₂O, $M_r = 230.3$]

	(3)	(2)
<i>a</i> (Å)	10.802 (1)	6.159 (2)
<i>b</i> (Å)	8.362 (1)	25.193 (10)
<i>c</i> (Å)	8.297 (1)	9.853 (10)
α (°)	75.0 (1)	
β (°)	103.9 (1)	115.8 (1)
γ (°)	101.2 (1)	
<i>V</i> (Å ³)	695.7 (7)	1376.9 (2.0)
Space group	$P\bar{1}$	$P2_1/c$
<i>Z</i>	2	4
ρ_c (Mg m ⁻³)	1.10	1.12
μ (mm ⁻¹)	0.48	0.48
<i>F</i> (000)	252	504

Intensity data for both structures were collected on a Siemens AED diffractometer and measured by the moving-crystal moving-counter technique in the range $2 \leq \theta \leq 70^\circ$. 2376 from 2560 independent reflections for compound (3) and 648 for compound (2), with $F > 3\sigma(F)$, were used in the analysis. The structures were solved by direct methods using *MULTAN* (Germain, Main & Woolfson, 1971) and refined by full-matrix least squares, anisotropically for the non-hydrogen atoms, isotropically for the H atoms, on all non-zero reflections, by the *SHELX* program system (Sheldrick, 1976); final *R* values were 8.5% for (3) (7.6% not considering the 15 most intense reflections), and 9.6% for (2).*

* Lists of structure factors and anisotropic thermal parameters for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35464 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional coordinates ($\times 10^4$, for H $\times 10^3$), and equivalent isotropic thermal parameters for the non-hydrogen atoms

(a) Compound (3)

	x	y	z	B_{eq} (\AA^2)
O(1)	815 (1)	6724 (2)	3347 (2)	5.1
C(1)	2215 (2)	6893 (2)	3523 (2)	3.9
C(2)	1593 (2)	6103 (2)	4995 (3)	4.4
C(3)	1658 (2)	6982 (2)	6380 (3)	4.4
C(4)	2000 (1)	8884 (2)	5875 (2)	3.5
C(5)	3188 (2)	9283 (2)	5026 (2)	4.3
C(6)	2892 (2)	8688 (2)	3365 (2)	4.6
C(7)	2179 (2)	9777 (2)	7363 (2)	4.0
C(8)	2165 (3)	11657 (3)	6611 (3)	5.4
C(9)	1012 (2)	9139 (3)	8272 (3)	5.1
C(10)	3451 (2)	9497 (4)	8669 (3)	5.7
C(11)	2656 (2)	5790 (2)	2663 (2)	4.1
C(12)	1749 (2)	4811 (3)	1673 (3)	5.2
C(13)	2171 (3)	3755 (3)	925 (4)	6.8
C(14)	3491 (4)	3659 (3)	1184 (4)	7.2
C(15)	4394 (3)	4633 (4)	2151 (4)	6.9
C(16)	3985 (2)	5706 (3)	2890 (3)	5.6
H(2)	154 (3)	495 (4)	533 (4)	
H(31)	86 (3)	676 (4)	669 (4)	
H(32)	218 (3)	663 (4)	724 (5)	
H(4)	123 (3)	950 (3)	499 (3)	
H(51)	388 (3)	876 (4)	578 (4)	
H(52)	348 (3)	1032 (4)	469 (3)	
H(61)	371 (3)	863 (4)	316 (4)	
H(62)	231 (4)	949 (5)	243 (5)	
H(81)	292 (4)	1205 (5)	613 (5)	
H(82)	223 (4)	1238 (6)	765 (6)	
H(83)	127 (4)	1172 (5)	569 (5)	
H(91)	30 (4)	911 (4)	767 (4)	
H(92)	99 (4)	972 (4)	919 (5)	
H(93)	107 (2)	800 (3)	895 (3)	
H(101)	423 (4)	975 (5)	816 (5)	
H(102)	352 (3)	848 (4)	911 (5)	
H(103)	357 (2)	1003 (3)	962 (3)	
H(12)	75 (3)	502 (4)	148 (4)	
H(13)	135 (3)	313 (4)	12 (4)	
H(14)	375 (5)	297 (6)	65 (6)	
H(15)	531 (5)	470 (6)	217 (6)	
H(16)	471 (4)	647 (4)	361 (5)	

(b) Compound (2)

	x	y	z	B_{eq} (\AA^2)
O(1)	4154 (18)	2542 (6)	5902 (17)	9.6
C(1)	6594 (28)	2384 (10)	6975 (22)	8.0
C(2)	5107 (32)	2719 (9)	7572 (29)	8.8
C(3)	5363 (30)	3309 (8)	7794 (24)	8.1
C(4)	7699 (27)	3507 (8)	7756 (22)	6.9
C(5)	8000 (31)	3261 (9)	6393 (24)	7.9
C(6)	8630 (29)	2679 (8)	6688 (24)	8.1
C(7)	7731 (35)	4104 (9)	7749 (30)	7.6
C(8)	10197 (43)	4318 (10)	7872 (31)	10.4
C(9)	7557 (46)	4341 (12)	9181 (34)	10.0
C(10)	5749 (50)	4383 (12)	6394 (37)	9.6
C(11)	6903 (37)	1795 (9)	7314 (24)	6.4
C(12)	4849 (38)	1481 (10)	6887 (25)	7.8
C(13)	5168 (50)	951 (12)	7218 (30)	9.1
C(14)	7401 (58)	717 (10)	7910 (29)	9.0
C(15)	9371 (51)	1039 (12)	8263 (30)	9.3
C(16)	9181 (39)	1575 (11)	7991 (27)	7.8

Table 1 (cont.)

	x	y	z
H(81)	1020 (24)	477 (6)	804 (17)
H(82)	1107 (28)	409 (6)	864 (20)
H(91)	605 (27)	426 (6)	892 (19)
H(92)	739 (24)	484 (7)	909 (18)
H(93)	924 (26)	419 (6)	1021 (18)
H(101)	583 (27)	484 (7)	648 (19)
H(102)	605 (28)	424 (7)	564 (21)
H(103)	416 (25)	425 (6)	624 (18)
H(12)	322 (23)	170 (6)	643 (16)
H(13)	362 (24)	69 (5)	674 (16)
H(14)	750 (23)	21 (6)	808 (16)
H(15)	1070 (30)	81 (7)	895 (20)
H(16)	1059 (22)	182 (5)	847 (16)

The difference Fourier maps showed most of the H atoms; those missing were placed in calculated positions. Considerable decomposition occurred during data collection, the intensity of the standard reflection falling about 14% during the measurement period for compound (3); another data collection did not give better results. Compound (2) suffered a greater degree of decomposition, so that only 648 from 2024 collected reflections were used in the analysis; since the results of this last structural determination are not reliable, they are reported only for comparison.

Table 1(a) gives the final fractional coordinates and isotropic thermal parameters for compound (3), Table 1(b) those for compound (2).

Discussion

The structures of molecules (2) and (3) are shown in Figs. 1 and 2 (*PLUTO*, Motherwell, 1976) and relevant structural parameters (bond distances, bond angles, torsion angles, and puckering parameters) are collected in Tables 2–5.

The bond distances and e.s.d.'s involving H atoms in the *trans* compound (3) are in the range 0.82–1.15 Å and 0.03–0.06 Å respectively.

Unfortunately the unreliable data on epoxide (2) do not allow a sound comparison of the structure of the non-rigid epoxide (1) with that of the rigid analogues (2) and (3). Furthermore, the preferred conformation found for (1) in the solid state (Merlino, Lami, Macchia, Macchia & Monti, 1972) (1a) corresponds to the conformation of compound (2) whose structural data are not trustworthy.

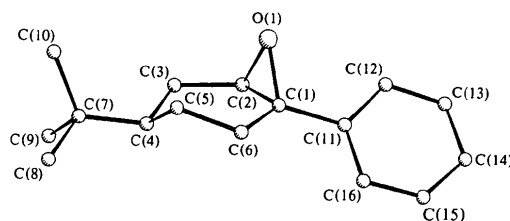


Fig. 1. Perspective view of the molecular structure of compound (2).

Table 2. Bond distances (Å) with their e.s.d.'s in parentheses

	(3)	(2)		(3)	(2)		(3)	(2)
O(1)—C(1)	1.466 (2)	1.47 (2)	C(4)—C(5)	1.549 (3)	1.56 (3)	C(11)—C(12)	1.398 (3)	1.39 (3)
O(1)—C(2)	1.448 (3)	1.55 (3)	C(4)—C(7)	1.557 (3)	1.50 (3)	C(11)—C(16)	1.416 (3)	1.38 (3)
C(1)—C(2)	1.478 (3)	1.54 (4)	C(5)—C(6)	1.527 (3)	1.51 (3)	C(12)—C(13)	1.396 (5)	1.37 (4)
C(1)—C(6)	1.524 (3)	1.58 (3)	C(7)—C(8)	1.535 (3)	1.56 (4)	C(13)—C(14)	1.405 (5)	1.37 (4)
C(1)—C(11)	1.504 (3)	1.51 (3)	C(7)—C(9)	1.559 (3)	1.58 (5)	C(14)—C(15)	1.383 (5)	1.37 (4)
C(2)—C(3)	1.498 (4)	1.50 (3)	C(7)—C(10)	1.548 (3)	1.53 (3)	C(15)—C(16)	1.395 (5)	1.37 (4)
C(3)—C(4)	1.531 (2)	1.54 (3)						

Table 3. Bond angles (°) with their e.s.d.'s in parentheses

	(3)	(2)		(3)	(2)		(3)	(2)
C(1)—O(1)—C(2)	60.9 (2)	61 (1)	C(2)—C(3)—C(4)	114.1 (2)	111 (2)	C(8)—C(7)—C(10)	109.6 (3)	107 (2)
O(1)—C(1)—C(11)	114.8 (3)	115 (2)	C(3)—C(4)—C(7)	113.9 (2)	110 (2)	C(8)—C(7)—C(9)	107.0 (3)	104 (2)
O(1)—C(1)—C(6)	114.1 (3)	113 (2)	C(3)—C(4)—C(5)	108.3 (3)	111 (2)	C(1)—C(11)—C(16)	120.2 (3)	120 (2)
O(1)—C(1)—C(2)	58.9 (2)	62 (1)	C(5)—C(4)—C(7)	113.1 (3)	113 (2)	C(1)—C(11)—C(12)	119.9 (4)	119 (2)
C(6)—C(1)—C(11)	117.4 (3)	118 (2)	C(4)—C(5)—C(6)	111.9 (3)	110 (2)	C(12)—C(11)—C(16)	119.9 (3)	121 (2)
C(2)—C(1)—C(11)	118.7 (3)	119 (2)	C(1)—C(6)—C(5)	113.4 (2)	109 (2)	C(11)—C(12)—C(13)	119.3 (4)	118 (2)
C(2)—C(1)—C(6)	119.0 (2)	117 (2)	C(4)—C(7)—C(10)	112.3 (3)	117 (2)	C(12)—C(13)—C(14)	120.4 (4)	123 (3)
O(1)—C(2)—C(1)	60.2 (2)	57 (1)	C(4)—C(7)—C(9)	109.4 (3)	112 (2)	C(13)—C(14)—C(15)	120.7 (5)	117 (3)
C(1)—C(2)—C(3)	122.1 (3)	124 (2)	C(4)—C(7)—C(8)	108.5 (2)	111 (2)	C(14)—C(15)—C(16)	119.5 (4)	123 (3)
O(1)—C(2)—C(3)	117.1 (3)	114 (2)	C(9)—C(7)—C(10)	109.9 (2)	106 (2)	C(11)—C(16)—C(15)	120.3 (3)	118 (3)

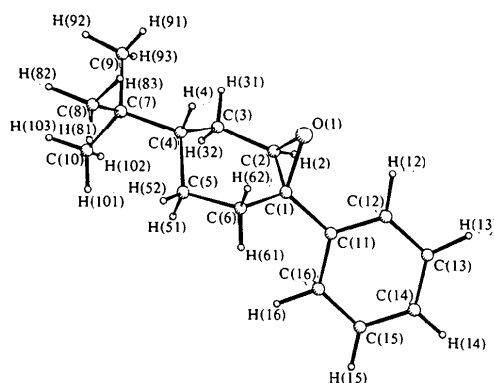


Fig. 2. Perspective view of the molecular structure of compound (3).

Table 4. Selected torsion angles (°) with their e.s.d.'s in parentheses

The sign convention is as defined by Klyne & Prelog (1960).

Cyclohexane ring	(3)	(2)
C(6)—C(1)—C(2)—C(3)	-2.9 (5)	4 (3)
C(1)—C(2)—C(3)—C(4)	19.5 (5)	-15 (3)
C(2)—C(3)—C(4)—C(5)	-48.3 (4)	47 (2)
C(3)—C(4)—C(5)—C(6)	64.3 (4)	-72 (2)
C(4)—C(5)—C(6)—C(1)	-48.3 (4)	57 (2)
C(5)—C(6)—C(1)—C(2)	17.3 (4)	-25 (2)
tert-Butyl group		
C(3)—C(4)—C(7)—C(8)	-165.5 (3)	174 (2)
C(3)—C(4)—C(7)—C(9)	-49.0 (4)	59 (2)
C(3)—C(4)—C(7)—C(10)	73.3 (4)	-63 (3)
C(5)—C(4)—C(7)—C(8)	70.3 (4)	-62 (2)
C(5)—C(4)—C(7)—C(9)	-173.3 (3)	-177 (2)
C(5)—C(4)—C(7)—C(10)	-51.0 (4)	61 (3)

Table 5. Puckering parameters (Cremer & Pople, 1975) for the cyclohexane ring and distances of C(4) and C(5) from the mean plane through C(1)C(2)C(3)C(6)

For linear values e.s.d.'s are one unit in the last reported digit; for angles e.s.d.'s are 0.2–0.5° for (a) and (b), and 1.0–2.0° for (c).

References	q_2 (Å)	q_3 (Å)	Q (Å)	θ_2 (°)	ϕ_2 (°)	C(4) (Å)	C(5) (Å)
(a)	0.38	0.34	0.51	48.4	208.0	0.41	-0.37
(b)	0.41	-0.34	0.54	129.4	41.3	-0.26	0.54
(c)	0.4	-0.4	0.6	132	41	-0.3	0.6

References: (a) compound (3); present work, *trans* form; (b) compound (1); Merlino, Lami, Macchia, Macchia & Monti (1972); (c) compound (2); present work, *cis* form.

In epoxide (3), in which (as pointed out) the 1-phenyl-1,2-epoxycyclohexane system is constrained in a conformation corresponding to (1*b*), the rotameric disposition of the phenyl with respect to the epoxide ring markedly differs from that found in (1*a*) and from the bisected conformation [the dihedral angle is 69.7 (5)° in (3); *cf* 82.6 (1.6)° for 1(*a*) (Merlino, Lami, Macchia, Macchia & Monti, 1972) and 90° for the completely bisected conformation]. The conformational arrangement of the phenyl in (3) is shown in the Newman diagram (Fig. 3) where the plane of the aromatic ring lies just outside the epoxide ring but very close to the O itself. The steric interaction between the aromatic protons H(16) and H(61) must push away the phenyl from the geometry (bisected) for the maximum pseudoconjugative interaction. However, the conformation observed is different from what may be

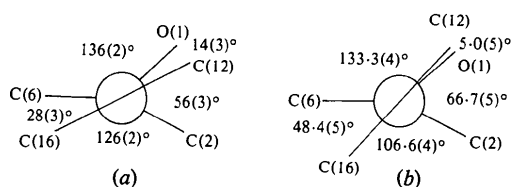


Fig. 3. Newman projections down the bond [C(11)—C(1)] linking the phenyl and oxirane rings (a) for compound (2), (b) for compound (3).

expected in order to minimize the steric interaction [H(16)···H(61) and H(12)···O(1)]. The actual geometry evidently derives from a compromise between pseudoconjugative and steric effects.

The corresponding bond angles of (1) and (3) are comparable, whereas small differences in the corresponding torsion angles can be observed. As for the bond lengths in the oxirane ring, whereas in (1) the C(1)—O(1) is shorter than C(2)—O(1), in compound (3) the situation is just the opposite [in *p*-nitro- α,β -epoxystyrene the two bond lengths are equal (Williams, Crotti, Macchia & Macchia, 1975)]. This difference can be attributed to the different strain in the molecules.

Finally, the *tert*-butyl group in compound (3) assumes a conformation twisted away from the staggered position by a mean value of -12.0° . The deviation from the staggered position, not often observed in simple *tert*-butylcyclohexane derivatives* (Ohrt & Parthasarathy, 1972; Faber & Altona, 1971, 1974; Parthasarathy, Ohrt, Kagan & Fiaud, 1972; Johnson, Cheer, Schaefer, James & Moore, 1972; Johnson, Schaefer, James & McConnell, 1972; Bellucci, Berti, Colapietro, Spagna & Zambonelli, 1976; Bellucci, Colapietro, Ingrosso, Spagna & Zambonelli, 1978), must be attributed in the present case to the minimization of the steric interactions of the H atoms of the *tert*-butyl group with those at C(3) and C(4). This results from the distortion of the cyclohexane chair caused by the presence of the oxirane ring.

The puckering parameters (Table 5) appear, even though the data of compound (2) are not completely reliable, to be roughly equivalent in the three epoxides [practically equal in epoxides (2) and (1), which have similar conformations]. In all cases a more or less distorted half chair is observed. Whereas the distances of C(4) and C(5) from the mean plane through C(1)C(2)C(3)C(6) are roughly equivalent in compound (3), they differ significantly in (1) and (2).

* Recalculation of the torsion angles of the *tert*-butyl group in *cis*-1-*p*-bromophenyl-4-*tert*-butylcyclohexane showed that in this case also a small deviation from the perfectly staggered conformation, previously reported by Berti, Macchia, Macchia, Merlino & Muccini (1971), is observed.

Packing of the molecules in the crystal is determined by the following van der Waals interactions (Å) less than 3.9 Å:

C(8)—C(2) ($x, 1 + y, z$)	3.722 (3)
C(2)—O(1) ($x, 1 + y, 1 + z$)	3.447 (2)
C(3)—O(1) ($x, 1 + y, 1 + z$)	3.674 (2)
C(2)—C(2) ($x, 1 + y, 1 + z$)	3.575 (3)
C(8)—O(1) ($x, 2 + y, 1 + z$)	3.739 (2)
C(16)—C(16) ($1 + x, 1 + y, 1 + z$)	3.690 (3)
C(10)—C(10) ($1 + x, 2 + y, 2 + z$)	3.619 (3)
C(5)—C(5) ($1 + x, 2 + y, 1 + z$)	3.872 (4);

C(5)···C(5) and C(10)···C(10) are less than the sum of the methyl and methylene radii.

All calculations were carried out on the Cyber 76 computer of the Centro di Calcolo Elettronico dell'Italia Nord-Orientale, Casalecchio (Bologna), with financial support from the University of Parma.

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The Structure of Sodium 1-Pyrrolidinecarbodithioate Dihydrate at 295, 150 and 27 K: A Study of Conformational Reorientation

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Abstract

The structure of $\text{Na}[\text{S}_2\text{CN}(\text{CH}_2)_4] \cdot 2\text{H}_2\text{O}$ has been determined at 295, 150 and 27 K. The crystals are monoclinic, space group $P2_1/a$, $Z = 4$ with: 295 K, $a = 12.121$ (4), $b = 5.789$ (1), $c = 14.008$ (2) Å, $\beta = 98.58$ (2)°; 150 K, $a = 12.050$ (4), $b = 5.767$ (2), $c = 13.937$ (5) Å, $\beta = 98.41$ (3)°; 27 K, $a = 11.938$ (22), $b = 5.716$ (6), $c = 13.893$ (48) Å, $\beta = 98.56$ (25)°. Final $R = 0.031$, 0.050 and 0.056 at 295, 150 and 27 K, respectively. Only minor changes in the crystal and molecular geometry are observed between the three temperatures. Conformational reorientation of the pyrrolidiny ring in the room-temperature solid persists down to 150 K, but at 27 K the molecules are ordered in only one of the orientations. As a result an apparent C–C distance of 1.39 Å at 295 K increases to 1.51 Å at 27 K. Each Na^+ ion is surrounded by four water O atoms and two S atoms forming a distorted octahedron. The coordination polyhedra share edges and corners in layers parallel to the ab plane. Along c the structure is held together by van der Waals forces between the pyrrolidiny rings. The carbodithioate ion acts as a unidentate ligand and each S atom is an acceptor of two hydrogen bonds.

Introduction

Substituted dithiocarbamate ligands, $-\text{S}_2\text{CN}(\text{RR}')$, form complexes with a variety of metals. The importance of this ligand in coordination chemistry stems partly from its ability to stabilize high formal oxidation states on

the metal. The dithiocarbamate ligand has a delocalized π -orbital system, in which electron density can be transferred from N to S. The net effect is a high electron density in the metal–sulphur bond, which is not reflected in the formal oxidation number.

It has been suggested that the anomalous magnetic behaviour of Fe^{III} dithiocarbamates is due to such an electronic rearrangement (Eley, Myers & Duffy, 1972; Gregson & Doddrell, 1975). One of our research projects aims to correlate magnetic behaviour with geometrical and bonding features for Fe^{III} dithiocarbamates (Albertsson, Elding & Oskarsson, 1979). Knowledge of the precise geometry of a dithiocarbamate ligand in a structure with small metal–ligand interaction would facilitate such a comparison. A sodium dithiocarbamate hydrate is suitable for the investigation since Na^+ does not interact with the delocalized π -orbital system of the ligand and forms weaker complexes with the S atoms than with water O atoms. Only one alkali-metal dithiocarbamate hydrate structure has so far been determined by X-ray crystallography (Colapietro, Domenicano & Vaciago, 1968).

Atomic parameters derived from room-temperature X-ray crystallographic experiments have systematic errors due to the thermal motion of the atoms. Bond distances and angles calculated from such parameters will thus also be in error. Corrections for libration and/or riding motion, when applicable, can improve the accuracy of bond distances and angles, but the problem is to find a good model for the correlation of atomic motion. Furthermore, these corrections are based on the usually inaccurate thermal parameters.