

several orientations referred to the C-atom plane, namely 26.5 (2), 76.4 (1), 29.8 (1), 79.7 (1) and 3.0 (2)° showing, alternately, low and high-angle values owing to steric hindrance and repulsion between O atoms. This molecular conformation is similar to the conformation found for benzenehexacarboxylic acid (Darlow, 1961) and differs from 1,2,4,5-benzenetetracarboxylic acid (Takusagawa, Hirotsu & Shimada, 1973) which shows a center of symmetry. The distances and angles are as expected for this type of compound.

Geometrical features of the hydrogen bonds are shown in Table 2. The molecules are associated through their carboxylic groups forming a network of hydrogen bonds. There are centrosymmetric hydrogen bonds connecting related molecules by a double hydrogen-bond link through the carboxylic group attached to C(3). The rest of the carboxyl groups are also doubly hydrogen bonded as donor and acceptor to different molecules, related by glide-plane symmetry. The effect of this hydrogen-bonding network on the packing seems to be too weak to protect the anhydrous material against the attack of water in the atmosphere, this probably being responsible for the observed instability of the crystal employed.

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Structures of a Spiro[3.3]heptane and a Related Dispiro[3.1.3.]decane Derivative

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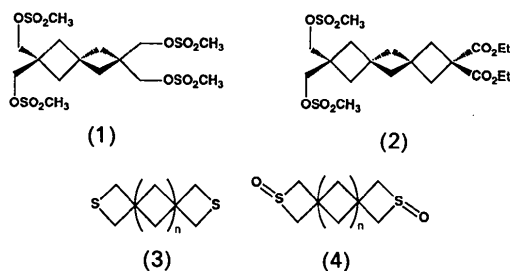
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Abstract. 2,2,6,6-Tetrakis(mesyloxymethyl)spiro[3.3]heptane (1), $C_{15}H_{28}O_{12}S_4$, $M_r = 528.64$, triclinic, $P\bar{1}$, $a = 10.319$ (1), $b = 14.233$ (2), $c = 8.5187$ (9) Å, $\alpha = 97.87$ (1), $\beta = 104.08$ (1), $\gamma = 98.86$ (1)°, $V = 1179.0$ (6) Å³, $Z = 2$, $D_m = 1.46$ (1), $D_x = 1.489$ Mg m⁻³, $\lambda(Mo K\alpha) = 0.71073$ Å, $\mu = 0.44$ mm⁻¹, $F(000) = 556$, $T = 298$ (1) K, $R = 0.036$ for 2411 reflections. Diethyl 8,8-bis(mesyloxymethyl)dispiro[3.1.3.]decane-2,2-dicarboxylate (2), $C_{20}H_{32}O_{10}S_2$, $M_r = 496.60$, triclinic, $P\bar{1}$, $a = 12.168$ (1), $b = 16.789$ (2), $c = 5.9411$ (6) Å, $\alpha =$

90.416 (8), $\beta = 94.294$ (9), $\gamma = 87.590$ (9)°, $V = 1209.2$ (4) Å³, $Z = 2$, $D_m = 1.35$ (1), $D_x = 1.364$ Mg m⁻³, $\lambda(Mo K\alpha) = 0.71073$ Å, $\mu = 0.26$ mm⁻¹, $F(000) = 528$, $T = 292$ (1) K, $R = 0.037$ for 2530 reflections. The cyclobutane rings in both structures are puckered. Dihedral angles of these rings in the spiroheptane derivative (1) [12.9 (7) and 21.2 (5)°], and in the end rings of the dispirodecane derivative (2) [18.9 (5) and -18.5 (4)°], are significantly smaller than that for the central cyclobutane ring in (2) [29.0 (3)°]. Ring puckering in (2) gives the

molecule a decided bow shape when viewed normal to the best plane of the central four-membered ring.

Introduction. Dithiaspiranes (3) and their disulfoxide analogues (4) have attracted considerable attention because they are relatively rigid and exhibit long-range, through-bond interactions. Electronic interactions between the functional groups of (4) ($n = 0, 1, 2$) have been studied theoretically (Rendell, Bacskay & Hush, 1988) and experimentally using photoelectron spectroscopy (Baker, Scharfman & Stein, 1983). The parent 2,6-dithiaspiro[3.3]heptane [(3), $n = 0$] has been used to link (NH₃)₅Ru^{II} and (NH₃)₅Ru^{III} units (Stein & Taube, 1981). The change in electronic coupling of the Ru^{II} and Ru^{III} centers with spacer length causes the intensity of the Ru^{II}/Ru^{III} metal-metal charge-transfer band to vary. As part of a project designed to probe the distance and orientation dependence of intramolecular electron transfer, we set out to prepare a series of porphyrin/quinone donor acceptors separated by oligospirocyclobutane spacers. We report here the structures of two synthetic intermediates, (1) and (2). These structural studies were undertaken to examine the flexibility of oligospirocyclobutane systems and to determine why the attempted double ring closure reaction of (1) with sodium malonate in benzene affords the diester (2) rather than the expected tetraester. While crystal structures of a few spiro[3.3]heptane derivatives have been reported (Hulshof, Vos & Wynberg, 1972; Hulshof, Wynberg, van Dijk & de Boer, 1976), we are unaware of any previous structural characterization of a dispiro[3.1.3.1]decane system.



Experimental. The tetramethanesulfonate (1), 2,2,6,6-tetrakis(mesyloxymethyl)spiro[3.3]heptane, was prepared in three steps from pentaerythritol tetratoluenesulfonate by modifying the procedure of Buchta & Merk (1966). When (1) was treated with excess diethyl malonate and sodium hydride in refluxing benzene containing hexamethylphosphoramide, the reaction stopped cleanly at the dimethanesulfonate (2), diethyl 8,8-bis(mesyloxymethyl)dispiro[3.1.3.1]decane-2,2-dicarboxylate. Significantly higher reaction temperatures were required to convert (2) to the tetraester. Diffraction quality

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters for (1)

	x	y	z	B _{eq} (Å ²)
S(1)	0.96394 (9)	0.75460 (6)	1.3557 (1)	4.43 (2)
S(2)	0.83571 (8)	0.60181 (6)	1.80574 (9)	3.48 (2)
S(3)	0.48607 (9)	0.16846 (7)	0.5309 (1)	4.39 (2)
S(4)	0.78327 (9)	0.04104 (6)	0.9987 (1)	4.16 (2)
O(1)	0.8601 (2)	0.6608 (2)	1.2616 (3)	4.04 (5)
O(2)	1.0038 (3)	0.7515 (2)	1.5260 (3)	6.82 (7)
O(3)	0.8998 (3)	0.8292 (2)	1.3027 (4)	8.26 (8)
O(4)	0.8463 (2)	0.5678 (2)	1.6263 (2)	3.43 (5)
O(5)	0.7093 (2)	0.5555 (2)	1.8203 (3)	5.01 (6)
O(6)	0.9575 (2)	0.5873 (2)	1.9099 (3)	5.52 (6)
O(7)	0.5504 (2)	0.1676 (2)	0.7156 (2)	4.38 (5)
O(8)	0.4509 (3)	0.2591 (2)	0.5116 (3)	6.77 (7)
O(9)	0.5819 (3)	0.1363 (2)	0.4513 (3)	6.16 (7)
O(10)	0.7529 (2)	0.1449 (2)	1.0030 (2)	4.04 (5)
O(11)	0.6604 (3)	-0.0278 (2)	0.9560 (4)	6.79 (8)
O(12)	0.8712 (2)	0.0358 (2)	0.8942 (3)	6.44 (7)
C(1)	0.7565 (3)	0.5162 (2)	1.3359 (3)	2.85 (6)
C(2)	0.6299 (3)	0.4931 (2)	1.1845 (4)	3.43 (7)
C(3)	0.6429 (3)	0.3872 (2)	1.1566 (3)	2.95 (7)
C(4)	0.6805 (3)	0.3399 (2)	1.0021 (3)	3.48 (7)
C(5)	0.5828 (3)	0.2452 (2)	0.9980 (3)	3.05 (7)
C(6)	0.5200 (3)	0.3031 (2)	1.1173 (3)	3.21 (7)
C(7)	0.7525 (3)	0.4059 (2)	1.3234 (4)	3.66 (7)
C(8)	0.8826 (3)	0.5663 (2)	1.3000 (3)	3.18 (7)
C(9)	1.1044 (4)	0.7496 (3)	1.2781 (4)	5.7 (1)
C(10)	0.7287 (3)	0.5662 (2)	1.4871 (4)	3.54 (7)
C(11)	0.8366 (4)	0.7245 (3)	1.8192 (4)	5.23 (9)
C(12)	0.4794 (3)	0.2008 (3)	0.8358 (4)	4.38 (8)
C(13)	0.3363 (4)	0.0816 (3)	0.4791 (5)	6.6 (1)
C(14)	0.6529 (3)	0.1741 (2)	1.0860 (4)	3.93 (7)
C(15)	0.8706 (4)	0.0421 (3)	1.2022 (4)	5.5 (1)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $\frac{1}{3}(a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23})$.

crystals of (1) and (2) were grown by vapor diffusion of petroleum ether into a solution of the compound in dichloromethane.

Structure solution [values for (2) are given in parentheses]. D_m by flotation; colorless prism 0.05 × 0.13 × 0.48 mm (0.15 × 0.25 × 0.30 mm); Enraf-Nonius CAD-4 diffractometer; graphite-monochromated Mo $K\alpha$ radiation; θ - 2θ scan. No systematic absences. Cell constants from setting angles of 25 reflections with $11.60 < \theta < 19.50^\circ$ ($11.79 < \theta < 19.00^\circ$); data corrected for Lorentz, polarization and absorption [empirical correction, ψ scan; $0.98 < T < 1.00$ ($0.98 < T < 1.00$)] effects. Variation in intensity of three standard reflections $\pm 1.3\%$ (0.3%); 3066 (3153) unique reflections measured with $4 < 2\theta < 45^\circ$; 2411 (2530) with $I > 3\sigma(I)$ used in refinement; $R_{int} = 0.013$ (0.012) for observed data on I . Data collected: h 0 → 12(13); k -15(-17) → 15(17); l -9(-6) → 9(6). Structure solved by direct methods (MULTAN82; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and difference Fourier techniques; H atoms from difference maps; B_H set to $1.3B_N$ before final refinement cycles; H-atom coordinates refined. Full-matrix refinement on F ; all non-H atoms anisotropic; $w = 4F_o^2/[\sigma^2(F_o^2) + 0.0016F_o^4]$. Final $R = 0.036$ (0.037), $wR = 0.049$ (0.052), $S = 1.64$ (1.77), $(\Delta/\sigma)_{max} < 0.87$ (0.47) for H atoms, 0.28 (0.16) for non-H atoms, $\Delta\rho_{max} = 0.21$ (0.24) e Å⁻³. Scattering

Table 2. Fractional atomic coordinates and equivalent isotropic thermal parameters for (2)

	x	y	z	$B_{eq}(\text{\AA}^2)$
S(1)	0.56062 (6)	0.64904 (5)	1.0840 (1)	4.65 (2)
S(2)	0.82127 (6)	0.46675 (4)	0.5046 (1)	3.54 (1)
O(1)	0.6694 (2)	0.6252 (1)	0.9755 (3)	4.35 (4)
O(2)	0.5548 (3)	0.7326 (2)	1.1199 (5)	8.43 (7)
O(3)	0.5563 (2)	0.5960 (2)	1.2680 (4)	6.39 (6)
O(4)	0.8316 (2)	0.5573 (1)	0.5629 (3)	3.43 (4)
O(5)	0.8000 (2)	0.4635 (1)	0.2672 (3)	5.17 (5)
O(6)	0.9129 (2)	0.4221 (1)	0.6072 (4)	5.09 (5)
O(7)	1.1659 (2)	0.9432 (1)	1.5590 (3)	4.15 (4)
O(8)	1.1746 (2)	0.9863 (1)	1.2098 (4)	6.49 (6)
O(9)	1.3949 (2)	0.8800 (1)	1.4681 (5)	6.44 (6)
O(10)	1.3429 (2)	0.7578 (1)	1.5156 (4)	6.34 (6)
C(1)	0.8342 (2)	0.6664 (2)	0.8207 (4)	2.92 (5)
C(2)	0.8935 (2)	0.7053 (2)	1.0295 (4)	3.41 (6)
C(3)	0.9714 (2)	0.7451 (2)	0.8736 (4)	3.09 (6)
C(4)	1.0115 (2)	0.8299 (2)	0.9220 (5)	3.50 (6)
C(5)	1.1191 (2)	0.7918 (2)	1.0330 (4)	3.09 (6)
C(6)	1.1265 (2)	0.7908 (2)	1.2937 (4)	3.36 (6)
C(7)	1.2232 (2)	0.8490 (2)	1.2964 (4)	3.09 (6)
C(8)	1.2306 (2)	0.8314 (2)	1.0402 (4)	3.63 (6)
C(9)	1.0929 (2)	0.7148 (2)	0.9011 (4)	3.34 (6)
C(10)	0.8931 (2)	0.7232 (2)	0.6693 (4)	3.40 (6)
C(11)	0.7101 (2)	0.6760 (2)	0.8014 (5)	3.75 (6)
C(12)	0.4597 (3)	0.6243 (3)	0.8715 (7)	7.7 (1)
C(13)	0.8737 (2)	0.5804 (2)	0.7904 (4)	3.22 (6)
C(14)	0.7029 (3)	0.4429 (2)	0.6337 (6)	5.46 (8)
C(15)	1.1876 (2)	0.9341 (2)	1.3443 (4)	3.43 (6)
C(16)	1.1357 (3)	1.0231 (2)	1.6377 (5)	4.74 (7)
C(17)	1.2340 (3)	1.0680 (2)	1.6997 (7)	6.7 (1)
C(18)	1.3254 (2)	0.8229 (2)	1.4405 (5)	3.71 (6)
C(19)	1.5011 (3)	0.8591 (3)	1.596 (1)	10.0 (1)
C(20)	1.5224 (4)	0.9129 (3)	1.7700 (9)	9.8 (1)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $\frac{1}{3}(a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\beta)B_{12} + ac(\cos\alpha)B_{13} + bc(\cos\alpha)B_{23})$.

factors from *International Tables for X-ray Crystallography* (1974, Vol. IV); programs from Enraf-Nonius (1985).

Discussion. Final positional parameters and their e.s.d.'s are given in Tables 1 and 2.* Views of (1) and (2) showing the atom-numbering schemes are given in Figs. 1 and 2, respectively. A packing diagram for (2) is given in Fig. 3. Selected bond distances and angles are listed in Tables 3 and 4.

The structures of (1) and (2) contain discrete molecules having no unusually short intermolecular contacts. The shortest intermolecular contacts of each type for (1) and (2) are listed in Tables 3 and 4, respectively. Bond distances and internal angles within the four-membered rings each span a small range and are similar to those reported for D-fecht acid, (5), and its barium salt (6) at 113 K [1.529 (5)–1.567 (6) Å, 86.8 (3)–89.3 (3)°; Hulshof, Vos & Wynberg, 1972; Hulshof, Wynberg, van Dijk & de Boer, 1976]. The average C(ring)—C(ring) bond distances also compare favorably with the value of

* Lists of structure factors, anisotropic thermal parameters H-atom bond angles and distances, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53093 (64 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

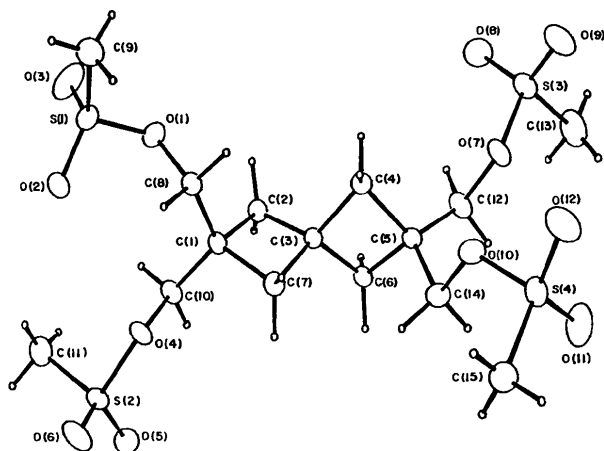


Fig. 1. View of the spiro[3.3]heptane derivative (1) showing the atom-numbering scheme.

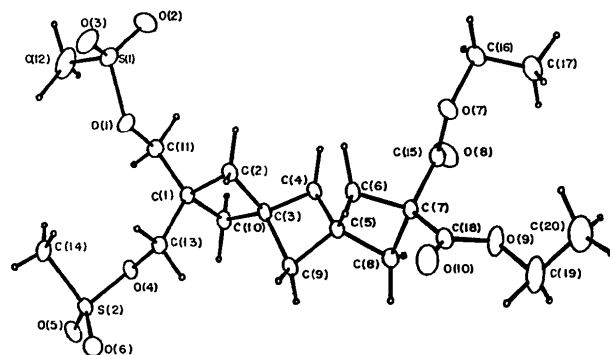


Fig. 2. View of the dispiro[3.1.3.1]decane derivative (2) showing the atom-numbering scheme.

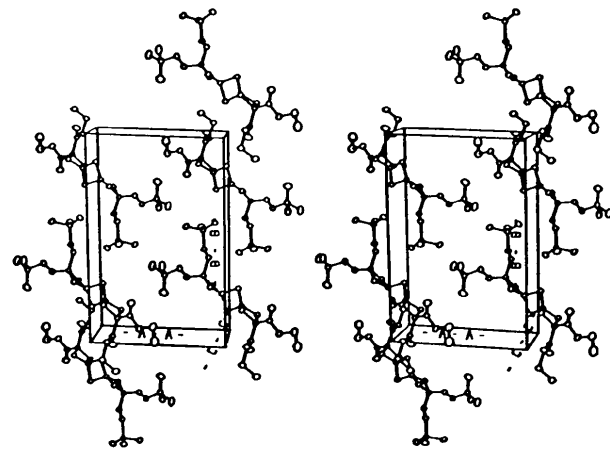


Fig. 3. Packing diagram of the dispiro[3.1.3.1]decane derivative (2).

Table 3. Selected bond lengths (Å), angles (°) and dihedral angles (°) for (1)

S(1)—O(1)	1.555 (3)	O(1)—C(8)	1.467 (4)
S(1)—O(2)	1.417 (2)	O(4)—C(10)	1.471 (3)
S(1)—O(3)	1.404 (3)	O(7)—C(12)	1.467 (3)
S(1)—C(9)	1.739 (4)	O(10)—C(14)	1.464 (3)
S(2)—O(4)	1.574 (2)	C(1)—C(2)	1.552 (3)
S(2)—O(5)	1.409 (2)	C(1)—C(7)	1.552 (4)
S(2)—O(6)	1.413 (3)	C(1)—C(8)	1.504 (3)
S(2)—C(11)	1.733 (4)	C(1)—C(10)	1.496 (4)
S(3)—O(7)	1.554 (2)	C(2)—C(3)	1.525 (4)
S(3)—O(8)	1.413 (2)	C(3)—C(4)	1.556 (4)
S(3)—O(9)	1.425 (2)	C(3)—C(6)	1.538 (4)
S(3)—C(13)	1.744 (4)	C(3)—C(7)	1.546 (4)
S(4)—O(10)	1.555 (2)	C(4)—C(5)	1.544 (4)
S(4)—O(11)	1.412 (2)	C(5)—C(6)	1.544 (4)
S(4)—O(12)	1.420 (2)	C(5)—C(12)	1.511 (4)
S(4)—C(15)	1.746 (4)	C(5)—C(14)	1.509 (4)
O(1)—S(1)—O(2)	109.8 (1)	S(4)—O(10)—C(14)	120.0 (2)
O(1)—S(1)—O(3)	103.8 (1)	C(2)—C(1)—C(7)	88.5 (2)
O(1)—S(1)—C(9)	104.1 (2)	C(2)—C(1)—C(8)	112.9 (2)
O(2)—S(1)—O(3)	119.5 (2)	C(2)—C(1)—C(10)	112.5 (3)
O(2)—S(1)—C(9)	108.5 (2)	C(7)—C(1)—C(8)	111.2 (3)
O(3)—S(1)—C(9)	110.1 (2)	C(7)—C(1)—C(10)	115.9 (2)
O(4)—S(2)—O(5)	108.9 (1)	C(8)—C(1)—C(10)	113.5 (2)
O(4)—S(2)—O(6)	104.7 (2)	C(1)—C(2)—C(3)	90.6 (2)
O(4)—S(2)—C(11)	104.3 (1)	C(2)—C(3)—C(4)	121.9 (2)
O(5)—S(2)—O(6)	119.4 (1)	C(2)—C(3)—C(6)	122.9 (2)
O(5)—S(2)—C(11)	108.6 (2)	C(2)—C(3)—C(7)	89.8 (2)
O(6)—S(2)—C(11)	109.8 (2)	C(4)—C(3)—C(6)	88.2 (2)
O(7)—S(3)—O(8)	110.3 (1)	C(4)—C(3)—C(7)	117.2 (2)
O(7)—S(3)—O(9)	103.8 (1)	C(6)—C(3)—C(7)	120.2 (2)
O(7)—S(3)—C(13)	103.9 (2)	C(3)—C(4)—C(5)	89.3 (2)
O(8)—S(3)—O(9)	118.8 (1)	C(4)—C(5)—C(6)	88.5 (2)
O(8)—S(3)—C(13)	108.3 (2)	C(4)—C(5)—C(12)	116.7 (2)
O(9)—S(3)—C(13)	110.6 (2)	C(4)—C(5)—C(14)	113.4 (2)
O(10)—S(4)—O(11)	110.2 (1)	C(6)—C(5)—C(12)	111.9 (2)
O(10)—S(4)—O(12)	103.9 (1)	C(6)—C(5)—C(14)	108.5 (2)
O(10)—S(4)—C(15)	103.4 (2)	C(12)—C(5)—C(14)	114.7 (2)
O(11)—S(4)—O(12)	118.2 (2)	C(3)—C(6)—C(5)	90.0 (2)
O(11)—S(4)—C(15)	109.0 (2)	C(1)—C(7)—C(3)	89.7 (2)
O(12)—S(4)—C(15)	111.0 (2)	O(1)—C(8)—C(1)	108.2 (3)
S(1)—O(1)—C(8)	120.5 (2)	O(4)—C(10)—C(1)	107.1 (3)
S(2)—O(4)—C(10)	118.4 (1)	O(7)—C(12)—C(5)	109.2 (2)
S(3)—O(7)—C(12)	118.4 (2)	O(10)—C(14)—C(5)	109.2 (3)

Dihedral angles

C(8)—C(1)—C(10)/C(2)—C(1)—C(7)	88.0 (2)
C(2)—C(3)—C(7)/C(4)—C(3)—C(6)	89.0 (2)
C(4)—C(5)—C(6)/C(12)—C(5)—C(14)	89.6 (2)
C(2)—C(1)—C(7)/C(2)—C(3)—C(7)	12.9 (7)
C(4)—C(3)—C(6)/C(4)—C(5)—C(6)	21.2 (5)

Intermolecular contacts

S(2)···O(1 ^b)	3.797 (2)	O(12)···C(15 ^b)	3.276 (5)
O(12)···O(12 ^b)	3.220 (4)	C(2)···C(2 ^b)	3.652 (4)

Symmetry transformations (i) $x, y, 1+z$; (ii) $2-x, -y, 2-z$; (iii) $1-x, 1-y, 2-z$.

1.548 (3) Å determined for cyclobutane by electron diffraction (Almenningen, Bastiansen & Skancke, 1961). The external C(ring)—C(ring)—C(ring) angles at each spiro carbon center connecting two cyclobutyl groups [e.g. C(2)—C(3)—C(6) and C(4)—C(3)—C(7) in (1)] show much larger differences than do the internal angles, an observation noted previously for (5). Overall, as judged by comparisons of simple angles and bond distances, the geometries of the four-membered ring systems in these spiroheptane and dispirodecane derivatives are remarkably similar.

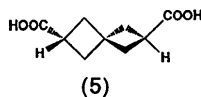


Table 4. Selected bond lengths (Å), angles (°) and dihedral angles (°) for (2)

S(1)—O(1)	1.551 (2)	C(1)—C(10)	1.549 (3)
S(1)—O(2)	1.417 (2)	C(1)—C(11)	1.508 (4)
S(1)—O(3)	1.420 (3)	C(1)—C(13)	1.515 (3)
S(1)—C(12)	1.755 (4)	C(2)—C(3)	1.548 (4)
S(2)—O(4)	1.564 (1)	C(3)—C(4)	1.543 (3)
S(2)—O(5)	1.416 (2)	C(3)—C(9)	1.541 (3)
S(2)—O(6)	1.418 (2)	C(3)—C(10)	1.538 (3)
S(2)—C(14)	1.744 (3)	C(4)—C(5)	1.538 (3)
O(1)—C(11)	1.472 (3)	C(5)—C(6)	1.546 (3)
O(4)—C(13)	1.465 (3)	C(5)—C(8)	1.532 (3)
O(7)—C(15)	1.328 (3)	C(5)—C(9)	1.540 (3)
O(7)—C(16)	1.458 (3)	C(6)—C(7)	1.561 (4)
O(8)—C(15)	1.189 (2)	C(7)—C(8)	1.557 (3)
O(9)—C(18)	1.306 (3)	C(7)—C(15)	1.506 (4)
O(9)—C(19)	1.481 (4)	C(7)—C(17)	1.508 (3)
O(10)—C(18)	1.188 (3)	C(16)—C(17)	1.464 (4)
C(1)—C(2)	1.542 (4)	C(19)—C(20)	1.385 (7)
O(1)—S(1)—O(2)	109.5 (1)	C(9)—C(3)—C(10)	122.7 (2)
O(1)—S(1)—O(3)	105.2 (2)	C(3)—C(4)—C(5)	88.3 (2)
O(1)—S(1)—C(12)	102.5 (2)	C(4)—C(5)—C(6)	114.8 (2)
O(2)—S(1)—O(3)	120.3 (1)	C(4)—C(5)—C(8)	123.7 (2)
O(2)—S(1)—C(12)	109.1 (2)	C(4)—C(5)—C(9)	88.2 (2)
O(3)—S(1)—C(12)	108.9 (2)	C(6)—C(5)—C(8)	89.8 (2)
O(4)—S(2)—O(5)	105.34 (9)	C(6)—C(5)—C(9)	119.4 (2)
O(4)—S(2)—O(6)	110.0 (1)	C(8)—C(5)—C(9)	124.1 (2)
O(4)—S(2)—C(14)	102.7 (1)	C(5)—C(6)—C(7)	89.2 (2)
O(5)—S(2)—O(6)	119.2 (2)	C(6)—C(7)—C(8)	88.8 (2)
O(5)—S(2)—C(14)	109.4 (1)	C(6)—C(7)—C(15)	113.0 (2)
O(6)—S(2)—C(14)	109.0 (1)	C(6)—C(7)—C(18)	115.1 (2)
S(1)—O(1)—C(11)	120.2 (1)	C(8)—C(7)—C(15)	113.1 (2)
S(2)—O(4)—C(13)	119.2 (1)	C(8)—C(7)—C(18)	113.7 (2)
C(15)—O(7)—C(16)	118.1 (2)	C(15)—C(7)—C(18)	111.9 (2)
C(18)—O(9)—C(19)	116.1 (2)	C(5)—C(8)—C(7)	89.8 (2)
C(2)—C(1)—C(10)	88.8 (2)	C(3)—C(9)—C(5)	88.2 (2)
C(2)—C(1)—C(11)	115.9 (2)	C(1)—C(10)—C(3)	89.6 (1)
C(2)—C(1)—C(13)	111.8 (2)	O(1)—C(11)—C(11)	107.1 (2)
C(10)—C(1)—C(11)	114.7 (2)	O(4)—C(13)—C(11)	106.0 (2)
C(10)—C(1)—C(13)	111.5 (2)	O(7)—C(15)—O(8)	123.2 (2)
C(11)—C(1)—C(13)	112.1 (2)	O(7)—C(15)—C(7)	110.8 (2)
C(1)—C(2)—C(3)	89.5 (2)	O(8)—C(15)—C(7)	126.0 (3)
C(2)—C(3)—C(4)	123.3 (2)	O(7)—C(16)—C(17)	110.9 (2)
C(2)—C(3)—C(9)	115.2 (2)	O(9)—C(18)—O(10)	123.5 (2)
C(2)—C(3)—C(10)	89.0 (2)	O(9)—C(18)—C(7)	111.8 (2)
C(4)—C(3)—C(9)	88.1 (2)	O(10)—C(18)—C(7)	124.7 (2)
C(4)—C(3)—C(10)	123.9 (2)	O(9)—C(19)—C(20)	111.0 (4)

Dihedral angles

C(11)—C(1)—C(13)/C(2)—C(1)—C(10)	89.7 (2)
C(2)—C(3)—C(10)/C(4)—C(3)—C(9)	87.6 (2)
C(6)—C(5)—C(8)/C(4)—C(5)—C(9)	87.9 (2)
C(6)—C(7)—C(8)/C(15)—C(7)—C(18)	89.5 (2)
C(2)—C(1)—C(10)/C(2)—C(3)—C(10)	18.9 (5)
C(4)—C(3)—C(9)/C(4)—C(5)—C(9)	29.0 (3)
C(6)—C(5)—C(8)/C(6)—C(7)—C(8)	-18.5 (4)

Intermolecular contacts

S(2)···O(6)	3.903 (2)	O(10)···C(12 ^b)	3.296 (5)
O(4)···O(6)	3.372 (3)	C(12)···C(14 ^b)	3.667 (5)

Symmetry transformations: (i) $2-x, 1-y, 1-z$; (ii) $1+x, y, 1+z$; (iii) $1-x, 1-y, 1-z$.

Dihedral angles at the spiro centers are all within 3° of the ideal value (90°), as expected. The cyclobutane rings in both structures are puckered. Dihedral angles of these rings (Tables 3 and 4) in the spiroheptane derivative (1) and in the end rings of the dispirodecane derivative (2) are significantly smaller than that for the central cyclobutane ring in (2) [(29.0 (3))°]. These angles are all smaller than the value of 35° in cyclobutane (Almenningen, Bastiansen & Skancke, 1961) and show a larger range than the values reported for the fecht acid derivatives (5) and (6) (148.5—157.0°; Hulshof, Vos & Wynberg, 1972; Hulshof, Wynberg, van Dijk & de Boer, 1976). The relatively large dihedral angle in the central ring of (2) gives the molecule a decided bow

shape when viewed normal to the best plane of the central four-membered ring.

Derived parameters for the methanesulfonyl (mesyl) groups are similar to each other and to those reported previously for other compounds (Harms, Sheldrick, Reichert & Tietze, 1986; Schlemper & Clark, 1985). Comparison of the structural parameters of (1) and the dimesyl portion of (2) offers no clue as to why the subsequent reaction of (2) with sodium malonate requires a temperature increase of approximately 50 K.

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A 1,20-Cyclo Derivative from Atisine*

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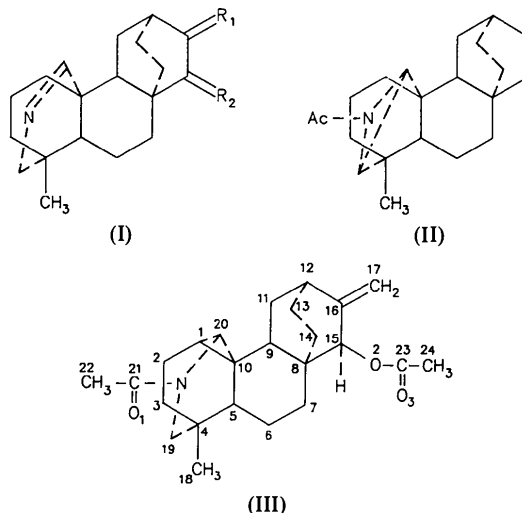
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Abstract. *N*-Acetyl-1,20-cyclo-16,17-didehydroatidan-15 β -yl acetate, C₂₄H₃₃NO₃, *M_r* = 383.53, orthorhombic, *P*2₁2₁2₁, *a* = 12.555 (2), *b* = 22.301 (4), *c* = 7.387 (2) Å, *V* = 2068.3 Å³, *Z* = 4, *D_m* = 1.219, *D_x* = 1.231 Mg m⁻³, λ(Cu Kα₁) = 1.54056 Å, μ = 0.597 mm⁻¹, *F*(000) = 832, *T* = 293 K, *R* = 0.060 for 1625 observed reflexions with *I* ≥ 2.0σ(*I*). The presence of a three-membered ring leads to considerable distortion of two adjoining six-membered rings. Weak hydrogen bonds of the type C—H⋯O=C link the molecules into chains parallel to *c*.

Introduction. An unusual reaction of a series of azomethines derived from atisine and ajaonine was discovered some time ago (Edwards, 1961). Those observations were confirmed later by Pelletier & Parthasarathy (1965). The azomethine with the least substituents, (I): *R*₁ = *R*₂ = H₂, when heated with an acetic acid–acetic anhydride mixture gave a saturated *N*-acetyl derivative. It was suggested (Edwards, 1961) that this had structure (II); however, the ¹³C NMR spectrum of this product did not fit this structure. An alternative formula, (III): *R*₁ = CH₂; *R*₂ = β-OAc,

α-H, was later suggested by R. J. Kolt in these laboratories for the acetylation product of the more-substituted azomethine, (I): *R*₁ = CH₂; *R*₂ = OH, H. Confirmation of (III) came from this X-ray analysis. A full account of the chemical and spectroscopic work carried out recently will be published (Edwards, Dvornik & Kolt, 1990).



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