angle of 24° with the normal to the plane. The hybridization at the N atom is. not far from sp^2, with an unshared electron pair in a p orbital directed toward one of the sp^2 orbitals on O(1), which is occupied by an unshared pair on that atom. Study of molecular models suggests that the methylanilino group could comfortably occupy a pseudo-axial position, which would place the phenyl ring above the diene–dione system. Apparently, however, that conformation is not favored even in solution; NMR evidence (Bugner, 1982) indicates that the conformation found in the crystal (Fig. 1) is also present in CDCl₃ solution.

There are no unusual intermolecular distances; the shortest intermolecular distance not involving hydrogen is 3·35 Å, from O(8) to C(17)($\frac{1}{2}$ + x, $\frac{1}{2}$ − y, 1 − z).

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(C₆H₃OCH₃)₆(CH₂)₂S, An Expanded Hemispherand

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Abstract. 34,35,36,37,38,39-Hexamethoxy-28-thiahepta-cyclo[28.3.1.1²,⁶.1⁷,¹¹.1¹²,¹⁶.1¹⁷,²¹.1²²,²⁶]nonatriaconta-1-(34),2,4,6(39),7,9,11(38),12,14,16(37),17,19,21(36),22,-24,26(35),30,32-octadecaene, C₄₄H₄₀O₆S, M_r = 696·87, monoclinic, Cc, a = 12·693 (4), b = 18·382 (9), c = 16·009 (7) Å, β = 99·50 (3)°, V = 3684 (3) Å³, Z = 4, D_x = 1·26 g cm⁻³, λ(Mo $K\alpha$) = 0·7107 Å, μ = 1·26 cm⁻¹, $F(000)$ = 1472, T = 295 K, R = 0·092 for 3155 unique nonzero reflections. The molecule has an approximate (non-crystallographic) twofold axis. The methoxy methyl groups nearest to the −CH₂−S−CH₂− unit turn inward, occupying the cavity of this uncomplexed host molecule. The remaining four methoxy methyl groups are directed outward, in an alternating up-down-up-down arrangement. The −CH₂−S−CH₂− linkage provides conformational flexibility relative to the prototype spherand, (CH₃OC₆H₂CH₃)₆.

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Introduction. Hemispherands have been defined as hosts for which at least half of the cavity has been preorganized during synthesis, but which must undergo partial conformational reorganization during complexation (Cram & Trueblood, 1981). The title compound (1) was designed, with the help of CPK molecular models, to have a cavity complementary to larger monatomic cations, such as K⁺ and Rb⁺, and in fact does complex these two cations more strongly than it does either Na⁺ or Cs⁺ (Cram, deGrandpre, Knobler & Trueblood, 1984).

Experimental. (1) prepared as described (Cram *et al.*, 1984) and recrystallized from CH₂Cl₂/benzene. Colorless parallelepiped, 0·35 × 0·36 × 0·50 mm, Syntex $P\bar{1}$ diffractometer, graphite monochromator, orientation matrix and unit-cell dimensions from 15 carefully centered reflections with 2θ < 24°; intensities measured for 2θ < 50° (h_{max} = 15, k_{max} = 20, l = −18 to 18), θ–2θ scan, 4° min⁻¹ in 2θ, from 1° below $K\alpha_1$ to 1° above $K\alpha_2$; intensities of three standard reflections

measured every 97 reflections showed no significant change during data collection;* total of 3271 independent reflections, 3155 reflections with $I > 0$ used in structure solution and refinement; absorption corrections not made; no correction for extinction; structure determined by direct methods with *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and refined by least squares on F (Busing, Martin & Levy, 1962), scattering factors and anomalous-dispersion terms from *International Tables for X-ray Crystallography* (1974); H atoms (with the exception of some H's on methyl groups) located approximately and fixed in position (C—H = 1·0 Å; for H on ring C, C—H directed along outward bisector of C—C—C angle; for H on methyl group, H—C—H angle = 109·5°); refinement completed for positional and anisotropic displacement parameters† for non-H atoms, and isotropic displacement parameters for H atoms (a single displacement parameter was refined for the three H atoms of each methyl group). In all, 458 parameters refined, $R = 0.092$, $wR = 0.093$ for all unique nonzero reflections, weighted on $1/\sigma^2(F_o)$, g.o.f. = 2·48. Largest positional-parameter and displacement-parameter shift/e.s.d. ratios in final cycle of refinement for non-H atoms 0·02 and 0·03 respectively; largest peak in final difference map 0·4 e Å^{-3} (within 1·2 Å of S), lowest -0.8 e Å^{-3}. All calculations on a VAX 11/780 and a VAX 11/750, using the *UCLA Crystallographic Package* (1984) (locally edited versions of *CARESS, PROFILE, MULTAN, ORFLS, ORFFE, ABSORB, ORTEP, PLUTO, SHELX*, and a local molecular-geometry program, *MG84*).

Discussion. The molecule is chiral and contains an approximate non-crystallographic twofold (C_2) axis (see Fig. 1), which makes angles of 50 to 60° with all three crystal axes. Two of the six methyl groups (those adjacent to methylene groups) point into the cavity in the molecule (Figs. 1 and 2); the remaining four methyl groups turn away from the cavity, in an alternating up-down-up-down arrangement, similar to that of the methoxy methyl groups in the prototype spherand, $(CH_3OC_6H_2CH_3)_6$ (Trueblood, Knobler, Maverick, Helgeson, Brown & Cram, 1981). There are no unusually short distances between molecules: the nearest approach to S is from H(25)$(x-1,-y,z-\frac{1}{2})$, 3·02 Å; to O, from H(33)$(x-\frac{1}{2},y-\frac{1}{2},z)$ to O(45), 2·61 Å; to C, from H(49)$(\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z)$ to C(31), 2·68 Å, and the shortest intermolecular distance not involving H is from O(45)$(\frac{1}{2}+x,\frac{1}{2}+y,z)$ to C(33), 3·34 Å.

* We discovered, long after collecting the data and solving the structure, that one of the angle encoders was occasionally behaving erratically and apparently had been doing so for some time. This may have introduced errors into some measured intensities, although we did not attempt to remeasure any as a check.

† Heretofore commonly called 'vibration parameters' or 'temperature-factor parameters'.

Final atomic parameters for all refined atoms are given in Table 1.* The atom-numbering scheme is illustrated in Fig. 1. Some average features of the molecular geometry are summarized in Table 2. Many individual bond distances deviate by 3 e.s.d. or more from standard values [*e.g.* C(2)—C(3), 1·541 (12) Å, with an expected value of 1·50–1·51 Å; C(28)—O(29), 1·336 (9) Å, with an expected value of about 1·38 Å; and five short aromatic C—C distances of 1·333–1·352 Å, with e.s.d.'s of 0·011–0·014 Å]. There is comparatively little rigid-body motion (Schomaker & Trueblood, 1968), and although there may be small wagging motions of the phenyl groups that could give rise to small foreshortenings of some of these bonds, we believe that the positional-parameter e.s.d.'s are too low by a factor of at least two as estimates of the actual population standard deviations. Underestimates of derived standard deviations are thought to be quite common in crystal-structure refinements (Abrahams & Keve, 1969). The fact that the *average* values of the

* Lists of anisotropic displacement parameters, bond lengths, bond angles and torsion angles, H-atom parameters, and observed and calculated structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42226 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
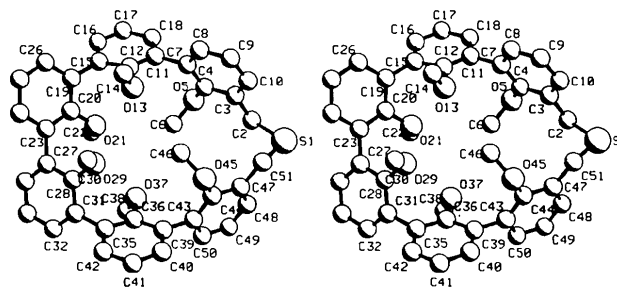

Fig. 1. A stereoview of the molecule, illustrating the numbering system employed. For clarity, H atoms have been omitted.
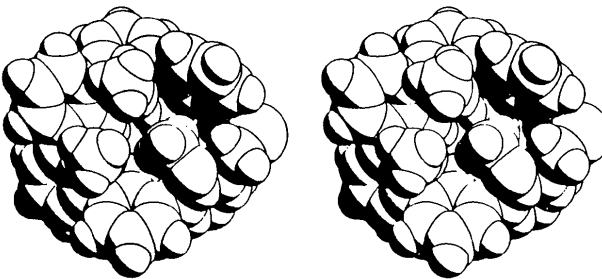

Fig. 2. A stereoview of the molecule, drawn with van der Waals radii, showing the cavity.

bond distances (Table 2*a*) are quite reasonable is consistent with this; the encoder problems alluded to earlier may have contributed to the difficulty by introducing errors in the intensities of uncertain magnitude. If indeed the e.s.d.'s are underestimated, the geometry is quite normal.

Although the structure determination has not been as precise or accurate as it might have been, the general conformational features of particular interest are well defined. This molecule differs from the prototype spherand (Trueblood *et al.*, 1981) because of the inserted $-CH_2-S-CH_2-$ linkage. Although the cavity in the prototype molecule is defined by the six octahedrally arranged O atoms, the added conformational flexibility provided by the expansion of the macroring in the present structure makes it more

Table 1. Positional and displacement parameters for an expanded hemispherand, $C_{44}H_{40}O_6S$

$$\langle u^2 \rangle = [1/(8\pi^2)]B_{eq}(\text{as defined by Hamilton, 1959}).$$

	x	y	z	$\langle u^2\rangle(\text{Å}^2)$
S(1)	0·65500	−0·09898 (13)	−0·11900	0·060
C(2)	0·7855 (7)	−0·0684 (6)	−0·1398 (6)	0·065
C(3)	0·8793 (6)	−0·0927 (5)	−0·0718 (5)	0·055
C(4)	0·9751 (6)	−0·0519 (4)	−0·0653 (5)	0·049
O(5)	0·9802 (5)	0·0032 (4)	−0·1208 (4)	0·062
C(6)	0·9683 (10)	0·0729 (7)	−0·0890 (8)	0·096
C(7)	1·0633 (6)	−0·0711 (4)	−0·0048 (5)	0·049
C(8)	1·0558 (7)	−0·1285 (5)	0·0487 (6)	0·065
C(9)	0·9625 (8)	−0·1678 (5)	0·0416 (8)	0·077
C(10)	0·8755 (7)	−0·1506 (5)	−0·0191 (7)	0·067
C(11)	1·1654 (6)	−0·0286 (5)	0·0045 (5)	0·048
C(12)	1·1914 (6)	0·0189 (5)	0·0677 (5)	0·051
O(13)	1·1209 (5)	0·0286 (3)	0·1268 (4)	0·061
C(14)	1·1561 (10)	−0·0002 (7)	0·2080 (8)	0·094
C(15)	1·2829 (6)	0·0650 (5)	0·0768 (5)	0·050
C(16)	1·3519 (7)	0·0534 (6)	0·0169 (6)	0·066
C(17)	1·3286 (7)	0·0042 (5)	−0·0456 (7)	0·072
C(18)	1·2327 (7)	−0·0370 (6)	−0·0554 (6)	0·068
C(19)	1·2989 (6)	0·1251 (5)	0·1383 (5)	0·053
C(20)	1·2244 (6)	0·1805 (4)	0·1316 (5)	0·044
O(21)	1·1387 (4)	0·1788 (3)	0·0659 (4)	0·052
C(22)	1·1489 (10)	0·2212 (7)	0·0032 (8)	0·107
C(23)	1·2313 (6)	0·2363 (4)	0·1906 (5)	0·046
C(24)	1·3198 (6)	0·2387 (5)	0·2547 (5)	0·055
C(25)	1·3970 (6)	0·1840 (6)	0·2610 (6)	0·066
C(26)	1·3871 (6)	0·1284 (5)	0·2041 (6)	0·057
C(27)	1·1441 (6)	0·2924 (5)	0·1882 (5)	0·049
C(28)	1·0392 (6)	0·2649 (4)	0·1888 (5)	0·043
O(29)	1·0220 (4)	0·1941 (3)	0·1997 (4)	0·048
C(30)	1·0293 (8)	0·1713 (5)	0·2836 (7)	0·076
C(31)	0·9534 (6)	0·3161 (4)	0·1810 (5)	0·045
C(32)	0·9715 (7)	0·3872 (4)	0·1751 (5)	0·052
C(33)	1·0758 (7)	0·4150 (5)	0·1787 (6)	0·057
C(34)	1·1592 (7)	0·3660 (4)	0·1826 (5)	0·054
C(35)	0·8434 (6)	0·2828 (4)	0·1773 (5)	0·044
C(36)	0·8042 (6)	0·2361 (4)	0·1133 (5)	0·043
O(37)	0·8585 (4)	0·2230 (3)	0·0460 (4)	0·060
C(38)	0·8585 (10)	0·2831 (7)	−0·0108 (7)	0·094
C(39)	0·7092 (6)	0·1972 (4)	0·1125 (5)	0·047
C(40)	0·6560 (6)	0·2082 (5)	0·1817 (5)	0·053
C(41)	0·6913 (6)	0·2563 (5)	0·2440 (6)	0·056
C(42)	0·7857 (6)	0·2948 (5)	0·2441 (5)	0·053
C(43)	0·6677 (6)	0·1478 (4)	0·0392 (5)	0·045
C(44)	0·6812 (5)	0·0751 (4)	0·0422 (5)	0·044
O(45)	0·7331 (4)	0·0417 (3)	0·1145 (4)	0·055
C(46)	0·8487 (7)	0·0426 (6)	0·1247 (6)	0·071
C(47)	0·6393 (6)	0·0297 (4)	−0·0266 (5)	0·047
C(48)	0·5846 (6)	0·0646 (5)	−0·0985 (5)	0·053
C(49)	0·5711 (7)	0·1374 (6)	−0·1025 (6)	0·068
C(50)	0·6103 (7)	0·1813 (5)	−0·0340 (6)	0·062
C(51)	0·6485 (7)	−0·0503 (5)	−0·0213 (6)	0·056

Table 2. Some features of the molecular geometry

A complete list of bond distances, bond angles and torsion angles has been deposited.

	Average value	Range of values	Typical e.s.d. of an individual value
(a) Bond distances			
C_{arom}–O	1·377 Å	1·336–1·416 Å	0·008 Å
O–CH_3	1·409	1·378–1·449	0·006
C_{arom}–C_{arom}	1·388	1·333–1·429	0·009
Inter-ring C–C	1·501	1·471–1·516	0·008
S–C	1·824	1·816–1·831	0·003
C_{arom}–CH_2	1·508	1·475–1·541	0·009
(b) Bond angles			
CH_2–S–CH_2	100·2 (4)°		
S–CH_2–C_{arom}	115·3	113·5–117·1°	0·7°
C_{arom}–O–CH_3	115·2	114·2–115·7	0·7
(c) Torsion angles and dihedral angles*			
CH_2–S–CH_2–C_{arom}	66°	64–68°	1°

Angles between normals to aromatic rings:

A–B	104°	B–C	63°	C–D	56°
E–F	98	D–E	64		

Angles between normals to aromatic rings and normal to median plane:

A	69°	B	39°	C	32°
F	60	E	43	D	33

* Ring *A* comprises C(3), C(4), C(7), C(8), C(9) and C(10); rings *B, C, D, E* and *F* comprise, respectively, atoms with these numbers increased successively by eight. The median plane comprises the twelve aromatic C atoms immediately adjacent to the atoms attached to OCH_3 groups *i.e.* C(3), C(7), C(11), C(15), ... The e.s.d.'s of the dihedral angles are about 0·3°.

appropriate to define the cavity (Fig. 1 or Fig. 2) by the two methoxy methyl groups nearest S(1) and the other four O atoms. The cross-cavity C···O and O···O distances are 4·67, 5·08 and 4·91 Å, indicating that in this conformation the cavity could accommodate an atom or ion of radius 0·8 to 1·0 Å (*e.g.* Na$^+$), although if in fact a cation were in the cavity, a more stable molecular conformation would be that with all methyl groups directed outward and all O atoms directed inward. If the two inward-turning methoxy methyl groups rotated so that they were directed outward, like the other four, the cavity could accommodate a larger guest, *e.g.* K$^+$ (Cram *et al.*, 1984). Changes in the tilt of the aromatic rings, especially the two nearest the S atom, would doubtless also accompany such a conformational reorganization, as is apparent from models. The tilt of these rings in the present host conformation, as measured by the angles between the planes of the aromatic rings and between these planes and the median plane of the molecule (Table 2*c*), varies systematically in different regions of the molecule, being smaller in the 'closed end', with values comparable to those in the prototypical hexaanisyl spherands (Trueblood *et al.*, 1981), and larger in the more flexible part of the molecule, with values quite comparable with those in the larger and more flexible octaanisyl analogs of the prototype spherands (Trueblood, deGrandpre, Carmack & Cram, 1984, unpublished work).

$(C_6H_3OCH_3)_6(CH_2)_2S$

This work was supported by grant CHE82-05803 from the National Science Foundation.

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Structure of a Triterpene Derivative from *Hebeloma* Species: 2α,3β-*O*-Isopropylideneanhydrocrustulinol,* C₃₃H₅₂O₅

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Abstract. $M_r = 528.77$, triclinic, $P1$, $a = 17.237$ (8), $b = 7.287$ (5), $c = 6.275$ (2) Å, $\alpha = 109.52$ (2), $\beta = 89.92$ (3), $\gamma = 99.15$ (2)°, $V = 732.3$ (7) Å³, $Z = 1$, $D_x = 1.20$ g cm⁻³, $\lambda(Mo\ K\alpha) = 0.7107$ Å, $\mu = 0.73$ cm⁻¹, $F(000) = 269.00$, $T = 295$ K, $R = 0.081$ for 1609 observed reflections. The title compound was obtained from a lanostane triterpene isolated from two *Hebeloma* species (Basidiomycetes). The overall stereochemistry of the lanostane nucleus was confirmed and the oxygenation pattern of the molecule shown. The five-, six- and seven-membered rings constituting the bicyclo[3.2.1]octane system adopt the half-chair, chair and boat conformations, respectively.

Introduction. The structure of a new cytotoxic triterpene (I) which was first isolated from *Hebeloma crustuliniforme* (Bull. ex Fr.) Quélét and *Hebeloma sinapizans* Fr. (Basidiomycetes) has already been proposed as 3β-acetyl-2α-(3-hydroxy-3-methyl)-glutarylcrustulinol on the basis of chemical and NMR, IR and mass-spectral evidence (De Bernardi, Fronza, Gianotti, Mellerio, Vidari & Vita Finzi, 1983).

As a part of the chemical work carried out to establish the oxygenation pattern of the molecule, particularly of ring *A* and of the side chain, including the characteristic hemiacetal ring, we prepared the title

compound (II) by hydrolysis of (I) followed by treatment with acetone and a catalytic amount of *p*-toluenesulfonic acid. X-ray diffraction analysis of (II) was undertaken to confirm the configuration of the C(24) centre and the structure of the 4,7,7-trisubstituted 6,8-dioxabicyclo[3.2.1]octane system.

(I)

(II)
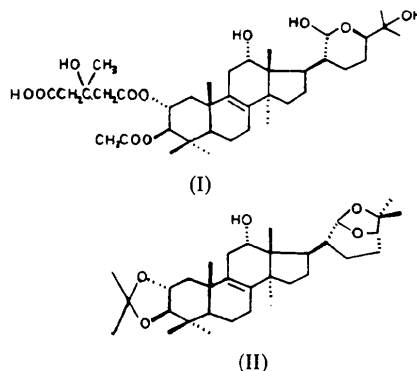
Experimental. Transparent colourless flat prisms grown from methanol–dichloromethane, single crystal 0·48 × 0·29 × 0·10 mm, Philips PW 1100 four-circle diffractometer, graphite-monochromatized Mo *K*α. Cell parameters by least squares based on 24 reflections in range $9.2 \leq \theta \leq 18.7°$. Intensities measured up to $2\theta = 44°$ (index range: $-18 \leq h \leq 18$, $-7 \leq k \leq 7$,

* (21*R*,24*R*)-21,24:21,25-Diepoxy-2α,3β-isopropylidenedioxyl-anost-8-en-12α-ol.