Energy minimization calculations by using the molecular mechanics program *MM2* showed that the crystal conformation is close to the global energy minimum in the conformational space (Hossain, Du, Symersky, Ji, van der Helm & Magarian, 1991). It therefore appears that this unique non-propeller conformation for the triaryl rings in the present structure is very likely a consequence of the constraint imposed by the cyclopropane ring with *gem*-dichloro substituent at C(1). However, more triarylcyclopropane (with and without dichloro substituents) structural results, including a systematic calculation of steric energies of such systems, are required to make any definitive conclusion. Work in both of these areas is in progress.

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Structure of Asperketal B

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Abstract. 3,7,11-Trimethyl-13-oxabicyclo[8.3.0]trideca-2,6-diene-12-spiro-2′-(5′,5′-dimethyltetrahydrofuran), asperketal B, $C_{20}H_{30}O_2$, $M_r = 302.46$, orthorhombic, $P2_12_12_1$, $a = 10.064$ (1), $b = 22.214$ (2), $c = 8.330$ (1) Å, $V = 1862.3$ Å^3, $Z = 4$, $D_x = 1.08$ g cm^{-3}, Cu $K\bar{\alpha}$, $\lambda = 1.54178$ Å, $\mu = 4.55$ cm^{-1}, $F(000) = 664$, $T = 294$ (1) K, $R = 0.031$, $wR = 0.027$ for 953 data. The backbone of the molecule is composed of a cyclodecadiene ring which is *cis* fused to a bicyclic ketal system. The relative configurations at C(1), C(10), C(11) and C(12) are 1*S**, 10*R**, 11*R** and 12*R**.

Introduction. Asperketal B (I) is one of the six new diterpenoids isolated from the Caribbean sea whip *Eunicea asperula*, for which the structures and the relative configurations have been assigned on the basis of chemical and spectral studies (Shin &

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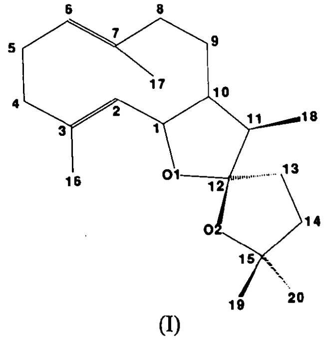
Fenical, 1988). The present X-ray study verifies the stereochemistry of asperketal B and firmly establishes that the O(1) five-membered ring *cis*-annelates to the ten-membered homocycle. Moreover, the conformational features of the two five-membered heterocycles and the cyclodecadiene system in the molecule of asperketal B are quantitatively described.



(I)

Experimental. Asperketal B was dissolved in a mixture of ethyl acetate and hexane (1:4 by volume) and crystallized at 277 K by slow evaporation of the solvent. A crystal of dimensions 0.07 × 0.17 × 0.47 mm was used. The X-ray diffraction data were collected at room temperature on an Enraf–Nonius CAD-4 diffractometer using Ni-filtered Cu $K\alpha$ radiation. 48 reflections ($23 > \theta > 20^\circ$) and Cu $K\alpha_1$ wavelength (1.54051 Å) were used for lattice constants. Systematic absences were $h00$ ($h = 2n + 1$), $0k0$ ($k = 2n + 1$) and $00l$ ($l = 2n + 1$). Two octants of data with $1.0 \leq 2\theta \leq 150.0^\circ$ in $0 \leq h \leq 12$, $0 \leq k \leq 27$ and $0 \leq l \leq 10$, and in $-21 \leq h \leq 0$, $-27 \leq k \leq 0$ and $0 \leq l \leq 10$ were collected using the ω–2θ scan technique and a variable scan width calculated as $(0.80 + 0.20\tan\theta)^\circ$. The maximum scan time for a single reflection was 60 s. The receiving aperture, located 173 mm from the data crystal, had a variable width which was calculated as $(2.40 + 0.86\tan\theta)$ mm, while the height of the aperture remained constant at 6 mm. Three orientational control monitors were checked every 200 reflections. Three intensity control monitors were measured every 7200 s of X-ray exposure time and they showed a maximum difference of 14% and an e.s.d. of 4%. A general decline of intensity for the monitors was observed as a result of decomposition of the compound by the X-rays. The data were scaled and merged ($R = 3.7\%$). The profiles of all the measured reflections were collected.

A different orthorhombic unit cell (space group $C222_1$) was observed at low temperature (163 K), with $a = 16.5$, $b = 9.9$, $c = 43.9$ Å and $V = 7194$ Å^3. This observation indicated that a phase transition of the asperketal B crystal occurred with the change of temperature. However, the transition was not complete at this temperature, since several general reflections showed discrepancies in the intensities of their equivalent reflections governed by the Laue symmetry. Therefore, the structure solution was not pursued at low temperature.

The data set was processed using a profile analysis method (Blessing, 1987). Lorentz–polarization corrections were applied. No absorption correction was made. Among 2208 unique data, 953 were observed $[I \geq 2\theta(I)]$. The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1986). The best solution was used to calculate an E map from which a peak list was obtained. Then the peak list was subjected to four cycles of E-Fourier optimization. The R value for the 22 remaining atoms and 282 E values greater than 1.40 was 0.215. The 22 non-H atoms were refined anisotropically. The coordinates of the 30 H atoms were determined from successive difference Fourier syntheses and refined isotropically. *SHELX76* (Sheldrick, 1976) was employed to carry out the refinement and Fourier calculations. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, p. 71). A final R of 0.031 and wR of 0.027 were obtained by the full-matrix least-squares minimization of $\sum w(|F_o| - |kF_c|)^2$, where $w = 1/\sigma^2(F)$. The maximum shift/e.s.d. = 0.053 for non-H atoms and 0.060 for H atoms. The largest and the smallest peaks in the final difference Fourier map were 0.09 and -0.07 e Å^{-3}. The EOF = $[\sum w(F_o - F_c)^2/(N - NP)]^{1/2} = 1.2$, where N is the number of observed reflections used in the least-squares refinement and NP, the number of least-squares parameters, was 319. The absolute configuration for asperketal B was not determined.

Discussion. The final positional parameters and equivalent isotropic temperature factors for non-H atoms of asperketal B (I) are listed in Table 1.* Fig. 1 is a stereoview (Johnson, 1965) of a single molecule and shows the atomic numbering. Bond distances and bond angles are presented in Table 2. Selected torsional angles are shown in Table 3. The standard deviations are relatively high owing to the low ratio of the number of observations to the number of parameters.

The molecular skeleton of asperketal B deduced from high-resolution mass, ^{1}H NMR, ^{13}C NMR and COSY spectra (Shin & Fenical, 1988) has been confirmed by the X-ray diffraction study. As listed in

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* Lists of anisotropic thermal parameters, H-atom parameters, bond distances involving H atoms, and calculated and observed structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54683 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *for non-*H *atoms with e.s.d.'s in parentheses*

$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
O(1)	0.3044 (3)	0.6104 (1)	−0.1896 (4)	0.105 (2)
O(2)	0.2826 (2)	0.7123 (1)	−0.1257 (3)	0.072 (1)
C(1)	0.1663 (4)	0.5980 (2)	−0.2185 (7)	0.076 (2)
C(2)	0.1456 (5)	0.5312 (2)	−0.2320 (9)	0.090 (2)
C(3)	0.0753 (5)	0.4963 (2)	−0.1386 (8)	0.091 (2)
C(4)	0.0353 (8)	0.4356 (3)	−0.200 (1)	0.122 (3)
C(5)	−0.0965 (7)	0.4417 (3)	−0.301 (1)	0.123 (3)
C(6)	−0.0793 (5)	0.4853 (3)	−0.4313 (8)	0.099 (2)
C(7)	−0.1100 (5)	0.5434 (2)	−0.4257 (6)	0.086 (2)
C(8)	−0.0576 (6)	0.5863 (3)	−0.5496 (8)	0.107 (3)
C(9)	0.0885 (7)	0.6045 (3)	−0.5272 (8)	0.103 (3)
C(10)	0.1280 (5)	0.6362 (2)	−0.3697 (6)	0.076 (2)
C(11)	0.2517 (5)	0.6752 (3)	−0.3955 (8)	0.099 (3)
C(12)	0.3289 (4)	0.6700 (2)	−0.2405 (7)	0.093 (2)
C(13)	0.4761 (6)	0.6798 (3)	−0.241 (1)	0.160 (4)
C(14)	0.5077 (5)	0.7194 (3)	−0.135 (1)	0.141 (3)
C(15)	0.3927 (4)	0.7415 (2)	−0.0465 (6)	0.082 (2)
C(16)	0.0172 (8)	0.5148 (4)	0.019 (1)	0.117 (3)
C(17)	−0.1917 (7)	0.5707 (4)	−0.296 (1)	0.106 (3)
C(18)	0.229 (1)	0.7385 (4)	−0.447 (1)	0.155 (5)
C(19)	0.3742 (8)	0.8094 (3)	−0.064 (1)	0.115 (3)
C(20)	0.390 (1)	0.7268 (4)	0.132 (1)	0.142 (4)

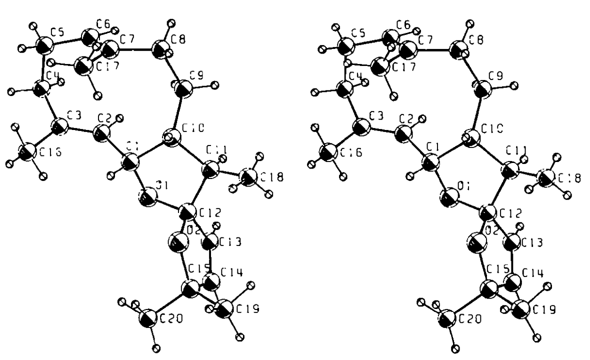

Fig. 1. Stereoview of a single molecule of asperketal B showing the atomic numbering system.

Table 2. *Bond distances* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

O(1)—C(1)	1.438 (5)	O(1)—C(12)	1.411 (6)
O(2)—C(12)	1.420 (6)	O(2)—C(15)	1.443 (5)
C(1)—C(2)	1.503 (7)	C(1)—C(10)	1.566 (7)
C(2)—C(3)	1.307 (8)	C(3)—C(4)	1.496 (8)
C(3)—C(16)	1.49 (1)	C(4)—C(5)	1.58 (1)
C(5)—C(6)	1.47 (1)	C(6)—C(7)	1.330 (8)
C(7)—C(8)	1.499 (9)	C(7)—C(17)	1.487 (9)
C(8)—C(9)	1.537 (9)	C(9)—C(10)	1.541 (8)
C(10)—C(11)	1.533 (7)	C(11)—C(12)	1.511 (8)
C(11)—C(18)	1.49 (1)	C(12)—C(13)	1.497 (7)
C(13)—C(14)	1.29 (1)	C(14)—C(15)	1.458 (8)
C(15)—C(19)	1.526 (7)	C(15)—C(20)	1.52 (1)

O(1)—C(12)—O(2)	111.1 (4)	O(1)—C(1)—C(2)	109.6 (4)
O(1)—C(1)—C(10)	105.6 (4)	O(1)—C(12)—C(11)	103.9 (4)
O(1)—C(12)—C(13)	108.1 (4)	O(2)—C(12)—C(11)	110.8 (4)
O(2)—C(12)—C(13)	103.3 (5)	O(2)—C(15)—C(14)	103.1 (4)
O(2)—C(15)—C(19)	107.9 (4)	O(2)—C(15)—C(20)	109.7 (5)
C(1)—O(1)—C(12)	107.3 (3)	C(1)—C(2)—C(3)	128.1 (6)
C(1)—C(10)—C(9)	120.1 (4)	C(1)—C(10)—C(11)	102.6 (4)
C(2)—C(1)—C(10)	116.1 (5)	C(2)—C(3)—C(4)	118.6 (7)
C(2)—C(3)—C(16)	124.8 (6)	C(3)—C(4)—C(5)	109.3 (5)
C(4)—C(3)—C(16)	116.2 (6)	C(4)—C(5)—C(6)	110.7 (6)
C(5)—C(6)—C(7)	126.1 (6)	C(6)—C(7)—C(8)	120.7 (5)
C(6)—C(7)—C(17)	123.3 (5)	C(7)—C(8)—C(9)	114.9 (5)
C(8)—C(7)—C(17)	115.9 (5)	C(8)—C(9)—C(10)	118.1 (5)
C(9)—C(10)—C(11)	110.4 (5)	C(10)—C(11)—C(12)	104.7 (5)
C(10)—C(11)—C(18)	117.0 (6)	C(11)—C(12)—C(13)	119.7 (6)
C(12)—O(2)—C(15)	110.8 (3)	C(12)—C(11)—C(18)	113.4 (6)
C(12)—C(13)—C(14)	110.0 (6)	C(13)—C(14)—C(15)	112.4 (5)
C(14)—C(15)—C(19)	112.3 (5)	C(14)—C(15)—C(20)	115.8 (6)
C(19)—C(15)—C(20)	107.8 (5)		

Table 3. *Endocyclic torsion angles* (°) *with e.s.d.'s in parentheses*

	Asperketal B	Calculated values*
C(10)—C(1)—C(2)=C(3)	−124.0 (7)	83
C(1)—C(2)=C(3)—C(4)	162.1 (6)	−172
C(2)=C(3)—C(4)—C(5)	−85.0 (8)	92
C(3)—C(4)—C(5)—C(6)	56.1 (9)	−40
C(4)—C(5)—C(6)=C(7)	−93.9 (8)	106
C(5)—C(6)=C(7)—C(8)	164.7 (6)	−172
C(6)=C(7)—C(8)—C(9)	−77.0 (7)	61
C(7)—C(8)—C(9)—C(10)	−59.7 (8)	57
C(8)—C(9)—C(10)—C(1)	86.5 (7)	−118
C(9)—C(10)—C(1)—C(2)	−7.3 (6)	50
O(1)—C(1)—C(10)—C(11)	−8.5 (5)	
C(1)—C(10)—C(11)—C(12)	−15.1 (5)	
C(10)—C(11)—C(12)—O(1)	34.3 (5)	
C(11)—C(12)—O(1)—C(1)	−41.2 (5)	
C(12)—O(1)—C(1)—C(10)	31.2 (5)	
O(2)—C(12)—C(13)—C(14)	3.2 (8)	
C(12)—C(13)=C(14)—C(15)	1 (1)	
C(13)=C(14)—C(15)—C(16)	−4.7 (8)	
C(14)—C(15)—O(2)—C(12)	6.7 (5)	
C(15)—O(2)—C(12)—C(13)	−6.2 (6)	

* Calculated values for one of the two minimum energy conformations of dimethylcyclodeca-1,5-diene (Guy, Sim & White, 1976).

Table 2, bond distances C(2)—C(3), C(6)—C(7) and C(13)—C(14) range from 1.29 to 1.33 Å which are the typical lengths of C_{sp^2}=C_{sp^2} double bonds. The four C_{sp^3}—O single bonds show normal lengths of about 1.43 Å. Also, all other bond distances are close to the expected values.

The ten-membered ring is *cis* fused at C(1) and C(10) to the five-membered ring containing O(1), with H(1) and H(10) *cis* oriented (Fig. 1). This can also be seen from the torsional angles C(2)—C(1)—C(10)—C(9) and O(1)—C(1)—C(10)—C(11) (Table 3). The relative configurations at C(1), C(10), C(11) and C(12) are 1*S**, 10*R**, 11*R** and 12*R**, the same as those proposed by Shin & Fenical (1988).

The cyclodecadiene system displays a pseudo-twofold axis through the midpoints of the bonds C(4)—C(5) and C(9)—C(10). This is illustrated by the endocyclic torsion angle sequence along the ring (Table 3). The spatial arrangement of the two *trans* double bonds, C(2)=C(3) and C(6)=C(7), can be referred to as $[_{15}D^5,\ {}^1D_{14}]$ (Samek & Harmatha, 1978). The overall conformation of the ten-membered ring is of the chair–boat type, with the allylic methyl groups *syn* oriented on the *α* face of the molecule. As expected, the values of some torsion angles differ considerably from those calculated for the chair–boat conformation of dimethylcyclodeca-1,5-diene (Guy, Sim & White, 1976), especially those for C(1) and C(10) involved in the *cis* fusion of the ten-membered ring with the O(1) five-membered ring.

The two five-membered rings which form a spiro-[4.4] system *via* C(12) show different conformations. The one containing O(1) can be described as a distorted C(10) half-chair with the asymmetry parameter $\Delta C_2 = 5.2$, and the other a distorted O(2) envelope with $\Delta C_s = 1.1$ [O(2) deviates from the plane through C(12), C(13), C(14) and C(15) by 0.10 Å] (Duax & Norton, 1975). For the ideal envelope conformation, $\Delta C_s = 0$, while for the ideal half-chair, $\Delta C_2 = 0$.

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Structures of 2,2′-Polymethylene-1,1′-biisoquinolinium Dibromides

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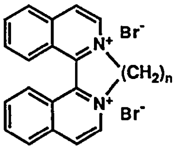
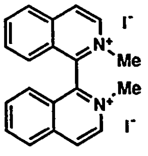
Abstract. 2,2′-Dimethylene-1,1′-biisoquinolinium dibromide (I), $C_{20}H_{16}N_2^{2+}.2Br^-$, $M_r = 444.15$, tetragonal, $I4_1/a$ (origin is located on $\bar{1}$), $a = 14.696$ (3), $c = 15.853$ (3) Å, $V = 3423.6$ (12) Å^3, $Z = 8$, $D_x = 1.72$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71068 Å, $\mu = 46.9$ cm^{-1}, $F(000) = 1760$, $T = 294$ K, $R = 0.041$ for 1201 unique observed reflections. 2,2′-Trimethylene-1,1′-biisoquinolinium dibromide monohydrate (II), $C_{21}H_{18}N_2^{2+}.2Br^-.H_2O$, $M_r = 476.17$, triclinic, $P\bar{1}$, $a = 9.934$ (2), $b = 13.285$ (3), $c = 7.969$ (1) Å, $\alpha = 95.32$ (1), $\beta = 92.64$ (2), $\gamma = 114.70$ (2)°, $V = 947.1$ (3) Å^3, $Z = 2$, $D_x = 1.67$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71068 Å, $\mu = 42.5$ cm^{-1}, $F(000) = 476$, $T = 294$ K, $R = 0.051$ for 3337 unique observed reflections. (I) shows C_2 symmetry and the molecular axis coincides with the crystallographic twofold axis, while the dication of (II) adopts a nearly C_2 symmetrical conformation. The dihedral angles between the two isoquinoline rings of (I) and (II) are 49.1 (1) and 61.9 (1)°, respectively.

Introduction. Bridged bisquaternary salts of 1,1′-biisoquinolines (I)–(IV) are known to produce a blue chemiluminescence in hydroxylic solvents by addition of base, and the efficiency of the chemiluminescence falls in the series of (I) > (II) > (III) > (IV) (Mason & Roberts, 1967). It was reported that (I) was reduced electrochemically or chemically to the radical cation and further to the neutral olefin, which was oxidized to biisoquinolone accompanying light emission (Heller, Henry & Fritsch, 1973). Redox properties and the chemiluminescence efficiency of these biisoquinolinium salts are expected to be greatly influenced by the degree of conjugation between the two heteroaromatic rings and the conformational flexibility. It was reported that reduction potentials of bisquaternary salts of 2,2′-biimidazoles are related to the dihedral angles between the two imidazole rings (Thummel, Goulle & Chen, 1989). In this study we have determined the crystal structures



(I) n=2
(II) n=3
(III) n=4



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