syn-1,6:8,13-Bismethano[14]annulene

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Abstract. $C_{16}H_{14}$, $M_r = 206.3$, monoclinic, $C2/c$, $a = 18.779$ (4), $b = 6.246$ (1), $c = 19.399$ (4) Å, $\beta = 100.27$ (2)°, $V = 2239$ Å^3; $D_o = 1.22$ (1) (flotation in dilute K_2HgI_4 solution), $D_c = 1.224$ g cm^{-3}, $Z = 8$. Computer-controlled four-circle diffractometer data (Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, graphite monochromator), $F(000) = 880$, μ(Mo $K\alpha$) = 0.75 cm^{-1}, $t = 18 \pm 2$ °C. Final $R = 0.042$ for 1390 reflexions with $I > 2\sigma(I)$ (counting statistics). The aromatic character of the molecule is achieved at the expense of a relevant steric compression of the two inner bridge H atoms, the distance between them amounting to 1.78 (2) Å.

Introduction. The title compound (here onwards SBM) is the first bridged annulene with two methano groups in the *syn* position to be synthetized (Vogel, Sombroek & Wagemann, 1975). Spectral data have stressed the necessity of an accurate molecular-geometry determination to evaluate the degree of steric compression of the two inner bridge H atoms and the consequence of this interference on the conformation of the annulene ring. In order to answer this problem the study of the crystal structure of this compound was undertaken.

Accurate cell dimensions were obtained by the fitting of sin$^2 \theta$ values of 58 reflexions. Systematic absences hkl, $h + k \neq 2n$ and $h0l$, $l \neq 2n$ indicate the space groups $C2/c$ or Cc; intensity statistics and successful structure determination confirm $C2/c$. Intensities were collected on a Syntex P1̄ diffractometer to a maximum 2θ value of 50° using a variable rate $\theta–2\theta$ scan technique. Background measurements were taken at both ends of the scan range, each for a time equal to one-half of the scan time. Three standard reflexions were checked after each 40 intensity measurements; they showed no appreciable trend.

Intensity measurements were obtained for 1991 unique reflexions of which 1390 were treated as observed with $I > 2\sigma(I)$ (counting statistics). Each reflexion was assigned a variance of $\sigma^2(I) = \sigma^2(I)_{c.s.} + (0.03S)^2$, where S is the scan count. Lorentz and polarization effects were corrected for, but no correction for absorption was deemed necessary.

The structure was solved by direct methods; the positions of all C atoms were recovered from an E map and those of the H atoms from a difference syn-

thesis. Refinement was by full-matrix least-squares minimization of the quantity $\Sigma w(|F_o| - |F_c|)^2$, with weights w equal to $4F_o^2/\sigma^2(F_o^2)$. In the final cycles, 201 parameters were simultaneously adjusted: coordinates and anisotropic temperature coefficients b_{ij} for the 16 C atoms, coordinates and isotropic B's for the 14 H atoms, and a scale factor. The resulting atomic parameters are given in Table 1.* The final R, $\Sigma ||F_o| - |F_c||/\Sigma |F_o|$, was 0.042; the weighted $R \{R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}\}$ was 0.035; and the goodness-of-fit. based on 1390 weighted reflexions and 201 parameters, was 1.27. Atomic form factors for C were from Cromer & Waber (1965), and for H from Stewart, Davidson & Simpson (1965).

Discussion. The atom numbering is shown in Fig. 1. Bond distances and angles are reported in Tables 2 and

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32324 (10 pp.). Copies may be obtained through The Executive Secretary. International Union of Crystallography. 13 White Friars. Chester CH1 1NZ. England.
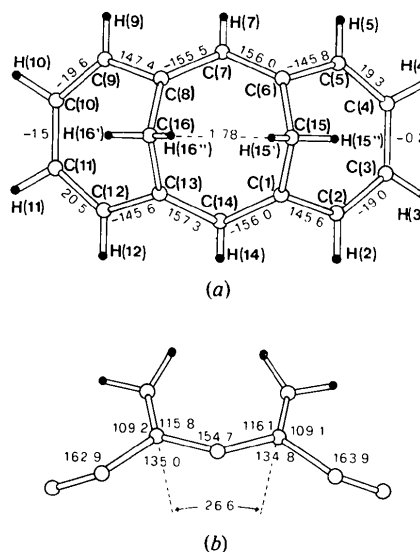

Fig. 1. The molecule of SBM viewed along two principal axes of inertia. (*a*) Numbering scheme, torsional angles along the annulene perimeter, and the distance H(15′)···H(16″). (*b*) Dihedral angles.

Table 1. *Final atomic parameters and standard deviations* (*in parentheses*)

The anisotropic temperature coefficients are in the form: $T = \exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl)]$. Fractional coordinates are $\times 10^5$ for C, $\times 10^4$ for H. Anisotropic temperature coefficients are $\times 10^4$, isotropic B's $\times 10$.

	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(1)	14705 (12)	46804 (30)	6071 (8)	43 (1)	251 (6)	20 (1)	1 (2)	0 (1)	−4 (1)
C(2)	9052 (15)	32035 (41)	6456 (11)	52 (1)	283 (7)	32 (1)	−12 (3)	−3 (1)	−3 (2)
C(3)	3069 (14)	36143 (44)	9333 (12)	37 (1)	422 (9)	39 (1)	−25 (3)	−5 (1)	19 (2)
C(4)	2144 (13)	52580 (44)	14057 (13)	31 (1)	463 (9)	44 (1)	8 (3)	3 (1)	19 (2)
C(5)	7000 (11)	67989 (39)	16828 (13)	31 (1)	394 (8)	38 (1)	25 (2)	4 (1)	−3 (2)
C(6)	13085 (11)	74208 (27)	14018 (9)	33 (1)	223 (5)	32 (1)	23 (2)	4 (1)	0 (1)
C(7)	19484 (11)	80445 (28)	18351 (10)	39 (1)	213 (5)	26 (1)	14 (2)	7 (1)	−12 (1)
C(8)	26430 (10)	79847 (26)	16785 (9)	36 (1)	181 (5)	27 (1)	−1 (2)	7 (1)	−8 (1)
C(9)	32612 (11)	78599 (32)	22117 (11)	38 (1)	290 (6)	29 (1)	−22 (2)	6 (1)	−12 (2)
C(10)	38903 (12)	68160 (37)	21438 (12)	32 (1)	391 (8)	37 (1)	−15 (2)	5 (1)	13 (2)
C(11)	39916 (13)	52382 (38)	16590 (12)	34 (1)	384 (8)	42 (1)	17 (2)	14 (1)	26 (2)
C(12)	34845 (13)	43303 (39)	11473 (11)	46 (1)	295 (7)	36 (1)	28 (2)	19 (1)	9 (2)
C(13)	28086 (12)	52718 (28)	8748 (8)	44 (1)	234 (6)	21 (1)	14 (2)	13 (1)	1 (1)
C(14)	21885 (13)	40389 (33)	6648 (9)	53 (1)	199 (6)	22 (1)	10 (2)	10 (1)	−6 (1)
C(15)	12379 (14)	69671 (33)	6292 (10)	37 (1)	274 (6)	30 (1)	9 (2)	−1 (1)	17 (2)
C(16)	28005 (13)	76533 (31)	9580 (10)	39 (1)	238 (6)	27 (1)	3 (2)	8 (1)	14 (1)

	x	y	z	B		x	y	z	B
H(2)	984 (11)	1856 (34)	494 (10)	70 (5)	H(11)	4463 (12)	4460 (33)	1754 (10)	80 (6)
H(3)	−52 (12)	2531 (34)	874 (11)	80 (6)	H(12)	3582 (11)	2964 (33)	974 (10)	69 (5)
H(4)	−206 (12)	5068 (35)	1634 (11)	81 (6)	H(14)	2257 (10)	2540 (30)	657 (9)	57 (5)
H(5)	651 (10)	7443 (28)	2138 (10)	64 (5)	H(15')	1516 (10)	7959 (29)	376 (9)	57 (4)
H(7)	1908 (9)	8205 (25)	2339 (9)	50 (4)	H(15")	739 (11)	7089 (29)	430 (10)	64 (5)
H(9)	3223 (10)	8443 (29)	2661 (10)	67 (5)	H(16')	3277 (10)	8240 (27)	943 (9)	53 (4)
H(10)	4285 (11)	6996 (33)	2543 (11)	77 (6)	H(16")	2463 (9)	8387 (25)	611 (8)	46 (4)

Table 2. *Bond lengths* (Å)

C(1)–C(2)	1·418 (3)	C(10)–C(11)	1·398 (3)
C(2)–C(3)	1·365 (4)	C(11)–C(12)	1·370 (3)
C(3)–C(4)	1·407 (4)	C(12)–C(13)	1·413 (3)
C(4)–C(5)	1·368 (4)	C(13)–C(14)	1·395 (3)
C(5)–C(6)	1·406 (3)	C(14)–C(1)	1·392 (3)
C(6)–C(7)	1·394 (3)	C(1)–C(15)	1·496 (3)
C(7)–C(8)	1·392 (3)	C(15)–C(6)	1·508 (3)
C(8)–C(9)	1·413 (3)	C(8)–C(16)	1·494 (3)
C(9)–C(10)	1·376 (3)	C(16)–C(13)	1·497 (3)
C(2)–H(2)	0·91 (2)	C(11)–H(11)	1·00 (2)
C(3)–H(3)	0·95 (2)	C(12)–H(12)	0·95 (2)
C(4)–H(4)	0·98 (2)	C(14)–H(14)	0·95 (2)
C(5)–H(5)	0·99 (2)	C(15)–H(15')	1·00 (2)
C(7)–H(7)	1·00 (2)	C(15)–H(15")	0·95 (2)
C(9)–H(9)	0·96 (2)	C(16)–H(16')	0·97 (2)
C(10)–H(10)	0·98 (2)	C(16)–H(16")	0·95 (2)

Table 3. *Bond angles* (°)

C(1)–C(2)–C(3)	125·3 (2)	C(14)–C(1)–C(2)	122·1 (2)
C(2)–C(3)–C(4)	127·6 (2)	C(14)–C(1)–C(15)	123·8 (2)
C(3)–C(4)–C(5)	128·2 (2)	C(2)–C(1)–C(15)	113·2 (2)
C(4)–C(5)–C(6)	125·0 (2)	C(5)–C(6)–C(7)	121·1 (2)
C(6)–C(7)–C(8)	127·0 (2)	C(7)–C(6)–C(15)	124·5 (2)
C(8)–C(9)–C(10)	124·3 (2)	C(5)–C(6)–C(15)	113·6 (2)
C(9)–C(10)–C(11)	128·3 (2)	C(7)–C(8)–C(9)	121·4 (2)
C(10)–C(11)–C(12)	128·2 (2)	C(9)–C(8)–C(16)	123·9 (2)
C(11)–C(12)–C(13)	124·1 (2)	C(7)–C(8)–C(16)	113·8 (2)
C(13)–C(14)–C(1)	127·7 (2)	C(12)–C(13)–C(14)	121·8 (2)
C(1)–C(15)–C(6)	103·5 (2)	C(14)–C(13)–C(16)	123·8 (2)
C(8)–C(16)–C(13)	104·3 (2)	C(12)–C(13)–C(16)	113·5 (2)
C(1)–C(2)–H(2)	115 (1)	C(12)–C(11)–H(11)	114 (1)
C(3)–C(2)–H(2)	120 (1)	C(11)–C(12)–H(12)	118 (1)
C(2)–C(3)–H(3)	116 (1)	C(13)–C(12)–H(12)	117 (1)
C(4)–C(3)–H(3)	116 (1)	C(13)–C(14)–H(14)	116 (1)
C(3)–C(4)–H(4)	114 (1)	C(1)–C(14)–H(14)	115 (1)
C(5)–C(4)–H(4)	116 (1)	C(1)–C(15)–H(15')	113 (1)
C(4)–C(5)–H(5)	118 (1)	C(1)–C(15)–H(15")	110 (1)
C(6)–C(5)–H(5)	116 (1)	C(6)–C(15)–H(15')	114 (1)
C(6)–C(7)–H(7)	114 (1)	C(6)–C(15)–H(15")	107 (1)
C(8)–C(7)–H(7)	117 (1)	C(8)–C(16)–H(16')	108 (1)
C(8)–C(9)–H(9)	117 (1)	C(8)–C(16)–H(16")	112 (1)
C(10)–C(9)–H(9)	118 (1)	C(13)–C(16)–H(16')	110 (1)
C(9)–C(10)–H(10)	114 (1)	C(13)–C(16)–H(16")	115 (1)
C(11)–C(10)–H(10)	116 (1)	H(15')–C(15)–H(15")	108 (2)
C(10)–C(11)–H(11)	116 (1)	H(16')–C(16)–H(16")	107 (1)

3 respectively. As already found in other *syn*-bridged annulene derivatives (Ganis & Dunitz, 1967; Casalone, Gavezzotti, Mugnoli & Simonetta, 1970), the symmetry of the molecule is nearly *mm*2. In contrast to its *anti*-isomer, which is a cyclopolyolefin (Barrow & Mills, 1971; Gramaccioli, Mimun, Mugnoli & Simonetta, 1973), SBM has aromatic character, as demonstrated by the values of the bond lengths along the annulene perimeter.

Bond distances and angles of SBM along the ring, as well as dihedral and torsional angles, are virtually identical with the corresponding ones in 1,6 : 8,13-butane-1,4-diylidene[14]annulene (here onwards BUT) (Gramaccioli, Mugnoli, Pilati, Raimondi & Simonetta, 1972), the greatest differences being 0·015 Å, 1·4, 1·3

and 1·5° respectively. The four H atoms of the methano groups and the two C atoms to which they are bonded are coplanar within experimental uncertainty [maximum deviation 0·03 (2) Å]. The contact between the two inner bridge H atoms [H(15′)···H(16″) distance = 1·78 Å] is partly relieved by slight rotation and deformation of the —CH₂— groups: the bisectors of the HĈH angles deviate by about 5° from the bisectors of the related bridgehead CĈC angles, and the HĈH angles are both less than the tetrahedral angle, notwithstanding the small values of the CĈC bridgehead angles (104°). The dihedral angle between the two bridges is increased from the 0·6° value found in 1,6:8,13-propane-1,3-diylidene[14]annulene (Gavezzotti *et al.*, 1972) to 26·6° (to be compared with 26·0° in the butane analogue BUT).

The *mm*2-averaged C—C bond distance involving the bridge C atoms is 1·498 Å in SBM, only slightly less than the corresponding length in BUT (1·505 Å); the CĈC angles at the bridge C atoms are 103·9° (average value) in SBM and 102·9° in BUT; and the distances between these two C atoms are 2·921 and 2·914 Å respectively. It can therefore be stated that the two internal H atoms affect the position of the bridge C atoms, and hence the conformation of the annulene perimeter, in much the same way as the —CH₂—CH₂— group does in BUT.

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4-(*p*-Chlorophenyl)-4-hydroxy-*N,N*-dimethyl-α,α-diphenylpiperidine-1-butyramide (Loperamide) Hydrate

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Abstract. $C_{29}H_{33}N_2O_2Cl.H_2O$, F.W. 495·0; orthorhombic, *Pbca*; $a = 15·160$ (3), $b = 20·715$ (5), $c = 16·803$ (3) Å; $t = 25\,°C$; $Z = 8$. The molecules are connected by direct hydrogen bonds and through the water molecules.

Introduction. Loperamide is a specific, long-acting antidiarrhoeal drug. Slow evaporation of a solution in etha-

nol yielded transparent colourless crystals. The space group was determined from Weissenberg photographs; final cell dimensions and intensities were measured on a Picker four-circle diffractometer. The experimental conditions are given in Table 1. The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971) and refined by block-diagonal least squares (Ahmed, Hall, Pippy & Huber, 1966). The final $R = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$ is 0·09 for all observed reflexions. The scattering factors used are those given in