References

BORKAKOTI, N., LINDLEY, P. F., MOSS, D. S. & PALMER, R. A. (1978). *Acta Cryst.* B**34**, 3431–3433.

BRISSON, J. & BRISSE, F. (1984). *Acta Cryst.* C**40**, 1402–1404.

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

PINEAULT, C. & BRISSE, F. (1983). *Acta Cryst.* C**39**, 1437–1439.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1984). C**40**, 1407–1409

Structure of 1,1,1′,1′,3,3,3′,3′-Octamethyl-2,2′-biindanylidene, $C_{26}H_{32}$

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Abstract. $M_r = 344{\cdot}5$, orthorhombic, *Pbca*, $a = 21{\cdot}093\,(3)$, $b = 11{\cdot}495\,(2)$, $c = 8{\cdot}235\,(1)$ Å, $V = 1996{\cdot}7\,(4)$ Å^3, $Z = 4$, $D_m = 1{\cdot}131$, $D_x = 1{\cdot}146$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}06$ mm^{-1}, $F(000) = 752$, room temperature, $R = 0{\cdot}045$ for 1592 ($I > 1\sigma$) reflections. Steric hindrance reflects little on the ethylenic bond length [1·350 (2) Å], but more on the adjacent single bonds [mean 1·584 (1) Å] and on the angles involving methyl groups, which range between 105·6 (1) and 118·2 (1)°. The five-membered ring has an envelope conformation to minimize the steric hindrance of the methyl groups. There is no twisting around the central C–C bond which maintains its double-bond character. The molecule is at a crystallographic centre of symmetry, but has approximate $2/m$ symmetry.

Introduction. The conformation of overcrowded ethylenes has been a subject of interest in our laboratory for a long time, from both experimental and theoretical points of view (Favini, Simonetta, Sottocornola & Todeschini, 1982, and references therein). The present study is in line with our previous work. The interaction between the substituents can act on the ethylenic system in two ways: by twisting around the double bond or by distorting the geometry of the neighbouring groups.

The most evident example of the first type is diisopropyl 9,9′-bifluorenylidene-1,1′-dicarboxylate (Bayley & Hull, 1978). In this molecule the dihedral angle between the fluorene mean planes is 50–54°; the consequent π-overlap reduction that lengthens the double bond to 1·391 (11)–1·395 (11) Å is clear evidence of a partial diradical situation. On the other hand, the C(ethyl)–C(phenyl) bond lengths are unaffected or shortened: 1·458 (12)–1·489 (14) *versus* 1·483 (5)–1·488 (5) Å in fluorenone (Luss & Smith, 1972).

syn-2,2′-Bifenchylidene(*E*) (Pilati & Simonetta, 1977) is an example of the second type: here the distortion of the tetrasubstituted ethylenic plane is quite small [maximum deviation 0·106 (4) Å] and the double bond is only 1·347 (3) Å, but the mean value of the C_{sp^2}–C_{sp^3} bond distance is 1·565 (7) Å and the range of the C_{sp^2}–C_{sp^3}–C_{sp^3} angles is 99·4 (2)–122·4 (2)°.

Experimental. D_m by flotation in dilute K_2HgI_4 solution; colourless prism 0·25 × 0·20 × 0·18 mm; Enraf–Nonius CAD-4 diffractometer; graphite-monochromated Mo $K\alpha$ radiation; ω-scan technique. Cell constants from setting angles of 25 reflections with $9 < \theta < 14°$; correction for Lorentz and polarization but not for absorption. No significant variation of intensity in 3 standard reflections. 4540 reflections measured with $\theta < 27{\cdot}5°$, range of *hkl*: 0 to 27, 0 to 14, −10 to 10, 2273 independent, 1592 with $I > \sigma(I)$, agreement factor on observed intensity 0·026. All carbon atoms from *MULTAN* (Germain, Main & Woolfson, 1971), H atoms from Fourier synthesis. Anisotropic carbon, isotropic H atoms, final secondary extinction parameter $g = 3{\cdot}5\,(2) \times 10^{-5}$ (Larson, 1967, equation 3); full-matrix least-squares refinement on F, $w = 4F_o^2/\{\sigma^2(F_o^2) + 0{\cdot}0009(F_o^4)\}$; final $R = 0{\cdot}045$, $R_w = 0{\cdot}041$, $S = 1{\cdot}63$, $\Delta_{\max}/\sigma = 0{\cdot}05$, $\Delta\rho = 0{\cdot}15$ e Å^{-3}. Scattering factors from *International Tables for X-ray Crystallography* (1974). Programs used include Enraf–Nonius (1979) *SDP*, *ORTEP* (Johnson, 1965) and various in-house programs for data reduction and geometrical analysis running on a Gould SEL 32/7780 computer. The final positional parameters and their e.s.d.'s are given in Table 1.*

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39368 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Final coordinates and equivalent or isotropic thermal parameters*

$$B_{\mathrm{eq}} = 4(\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j)/3.$$

	x	y	z	B/B_{eq}(Å^2)
C(1)	0·43929 (6)	0·09333 (12)	0·14740 (15)	2·69 (3)
C(2)	0·46901 (6)	0·01117 (10)	0·01305 (14)	2·28 (3)
C(3)	0·41028 (6)	−0·04224 (12)	−0·08064 (16)	2·62 (3)
C(4)	0·29385 (7)	0·03584 (16)	−0·09387 (22)	4·08 (4)
C(5)	0·25014 (8)	0·11328 (17)	−0·03271 (21)	4·58 (4)
C(6)	0·26711 (8)	0·19047 (18)	0·08778 (23)	4·83 (5)
C(7)	0·32738 (8)	0·18977 (16)	0·15088 (22)	4·34 (4)
C(8)	0·37192 (6)	0·11220 (12)	0·08891 (17)	3·05 (3)
C(9)	0·35545 (6)	0·03656 (12)	−0·03226 (17)	3·01 (3)
C(10)	0·43316 (9)	0·02891 (17)	0·31247 (19)	3·68 (4)
C(11)	0·46811 (9)	0·21458 (13)	0·17061 (22)	3·51 (4)
C(12)	0·39297 (9)	−0·16541 (14)	−0·01569 (24)	3·86 (4)
C(13)	0·41220 (8)	−0·04080 (16)	−0·26689 (18)	3·29 (4)
H(4)	0·2835 (8)	−0·0195 (15)	−0·1754 (20)	5·0 (4)
H(5)	0·2068 (8)	0·1214 (14)	−0·0796 (19)	4·9 (4)
H(6)	0·2346 (9)	0·2421 (18)	0·1304 (23)	6·6 (5)
H(7)	0·3382 (9)	0·2410 (18)	0·2385 (23)	6·6 (5)
H(10*A*)	0·4094 (8)	0·0789 (16)	0·3939 (23)	5·5 (4)
H(10*B*)	0·4748 (10)	0·0230 (18)	0·3661 (25)	7·4 (5)
H(10*C*)	0·4102 (8)	−0·0458 (15)	0·3006 (19)	4·4 (4)
H(11*A*)	0·5136 (7)	0·2161 (13)	0·2168 (18)	4·5 (4)
H(11*B*)	0·4671 (7)	0·2608 (14)	0·0685 (18)	4·0 (3)
H(11*C*)	0·4434 (7)	0·2569 (16)	0·2405 (21)	4·5 (4)
H(12*A*)	0·4305 (11)	−0·2234 (20)	−0·0308 (26)	8·7 (6)
H(12*B*)	0·3784 (9)	−0·1629 (15)	0·0961 (25)	5·7 (4)
H(12*C*)	0·3624 (9)	−0·1964 (16)	−0·0820 (23)	6·3 (5)
H(13*A*)	0·4211 (7)	0·0370 (14)	−0·3071 (17)	3·6 (3)
H(13*B*)	0·4420 (7)	−0·0933 (13)	−0·3188 (18)	3·6 (3)
H(13*C*)	0·3689 (9)	−0·0634 (15)	−0·3138 (21)	5·6 (4)

Table 2. *Bond lengths* (Å) *and angles* (°)

C(2)–C(2^{i})	1·350 (2)	C(2)–C(3)	1·583 (1)
C(1)–C(2)	1·584 (1)	C(3)–C(9)	1·522 (1)
C(1)–C(8)	1·516 (1)	C(3)–C(12)	1·557 (2)
C(1)–C(10)	1·553 (2)	C(3)–C(13)	1·534 (2)
C(1)–C(11)	1·533 (2)	C(6)–C(7)	1·373 (2)
C(4)–C(5)	1·377 (2)	C(7)–C(8)	1·392 (2)
C(4)–C(9)	1·395 (2)		
C(5)–C(6)	1·378 (2)		
C(8)–C(9)	1·368 (2)		
C_p–H	0·95–1·00		
C_m–H	0·92–1·04		
C(1)–C(2)–C(3)	105·2 (1)	C(3)–C(2)–C(2^{i})	127·3 (1)
C(1)–C(2)–C(2^{i})	127·5 (1)	C(2)–C(3)–C(9)	103·7 (1)
C(2)–C(1)–C(8)	103·6 (1)	C(2)–C(3)–C(12)	111·6 (1)
C(2)–C(1)–C(10)	111·1 (1)	C(2)–C(3)–C(13)	117·5 (1)
C(2)–C(1)–C(11)	118·2 (1)	C(9)–C(3)–C(12)	105·8 (1)
C(8)–C(1)–C(10)	105·6 (1)	C(9)–C(3)–C(13)	106·0 (1)
C(8)–C(1)–C(11)	106·3 (1)	C(6)–C(7)–C(8)	119·3 (1)
C(5)–C(4)–C(9)	119·1 (1)	C(5)–C(6)–C(7)	120·6 (1)
C(4)–C(5)–C(6)	120·4 (1)	C(12)–C(3)–C(13)	111·1 (1)
C(10)–C(1)–C(11)	110·9 (1)	C(3)–C(9)–C(4)	127·5 (1)
C(1)–C(8)–C(7)	127·4 (1)	C(3)–C(9)–C(8)	112·1 (1)
C(1)–C(8)–C(9)	112·3 (1)	C(4)–C(9)–C(8)	120·4 (1)
C(7)–C(8)–C(9)	120·2 (1)		
C_p–C_p–H	117–122		
C–C_m–H	108–117		
H–C–H	101–115		

Subscript: p = phenyl; m = methyl.
E.s.d.'s of bonds and angles involving H atoms are about 0·01 Å and 1°.
Symmetry code: (i) $1-x, -y, -z$.

Discussion. A view of the molecule with numbering scheme is given in Fig. 1. As can be easily seen from the figure, the molecule has approximate $2/m$ symmetry, with the mirror perpendicular to the indane moieties and passing through the C(2) and C(2′) atoms. Further evidence for this symmetry is given in Table 2 which shows bond distances and angles.

The conformation of the tetrasubstituted ethylene is similar but more strained than in *syn*-2,2′-bifenchylidene(*E*). The ethylene part of the molecule is planar (deviations in the range ±0·01 Å); the ethylenic bond is only a little more stressed [1·350 (2) *vs* 1·347 (3) Å], but the adjacent bonds are longer [1·584 (1) *vs* 1·565 (7) Å].

The strain due to the interaction between the methyl groups is also reflected by the deformation of the angles around C(1) and C(3) [103·6 (1) to 118·2 (1) and 103·7 (1) to 117·5 (1)°, respectively] and of the methyl groups [101 (1)–117 (1)°]. The puckering coordinates (Cremer & Pople, 1975) of the C(1), C(2), C(3), C(9), C(8) ring are $Q = 0{\cdot}184\,(1)$ Å and $\varphi = 29{\cdot}3\,(4)°$. Because of this conformation the distances of the methyl groups from the ethylenic plane range between 0·959 (2) and 1·447 (2) Å; this geometry allows a better engagement. In spite of all these adaptations of the molecular geometry, the interactions between the methyl groups are very strong: Table 3 reports some of the most significant non-bonded intramolecular contacts.

The molecular geometry is probably unaffected by the crystal field. In fact there are no intermolecular distances less than the sum of the van der Waals radii (1·7 and 1·2 Å for C and H atoms, respectively).

We are grateful to Professor F. S. Guziec Jr for the gift of the sample.

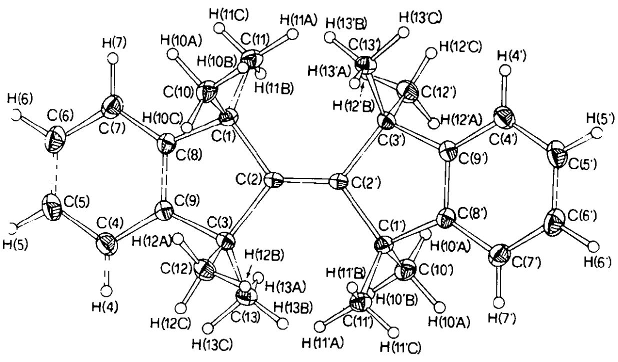

Fig. 1. A drawing of the molecule with the numbering scheme. Thermal ellipsoids for carbon atoms are at 20% of probability level; those of hydrogens are not to scale.

Table 3. *Some intramolecular non-bonded short distances* (Å)

C(10)–C(13^{i})	3·286 (2)	C(11)–C(12^{i})	3·246 (2)
C(11)–C(13^{i})	3·316 (2)	C(10)–H(13^{i}*B*)	2·74 (1)
C(11)–H(12^{i}*A*)	2·43 (1)	C(11)–H(13^{i}*B*)	2·65 (1)
C(12)–H(11^{i}*A*)	2·64 (1)	C(13)–H(10^{i}*B*)	2·53 (2)
C(13)–H(11^{i}*A*)	2·59 (1)	H(10*B*)–H(13^{i}*A*)	2·35 (2)
H(10*B*)–H(13^{i}*B*)	1·97 (2)	H(11*A*)–H(12^{i}*A*)	1·94 (2)
H(11*A*)–H(13^{i}*B*)	1·89 (2)	H(11*B*)–H(12^{i}*A*)	2·22 (2)

Symmetry code: (i) $1-x, -y, -z$.

References

BAYLEY, N. A. & HULL, S. E. (1978). *Acta Cryst.* B**34**, 3289–3295.

CREMER, D. & POPLE, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

Enraf–Nonius (1979). *Structure Determination Package*. Enraf–Nonius, Delft.

FAVINI, G., SIMONETTA, M., SOTTOCORNOLA, M. & TODESCHINI, R. (1982). *J. Comput. Chem.* **3**, 178–184.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 149–150. Birmingham: Kynoch Press.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

LARSON, A. C. (1967). *Acta Cryst.* **23**, 664–665.

LUSS, H. R. & SMITH, D. L. (1972). *Acta Cryst.* B**28**, 884–889.

PILATI, T. & SIMONETTA, M. (1977). *J. Chem. Soc. Perkin Trans.* 2, pp. 1435–1437.

Acta Cryst. (1984). C**40**, 1409–1412

The Structure of 1-Methylisoguanine Dihydrate, $C_6H_7N_5O.2H_2O$

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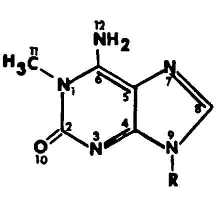
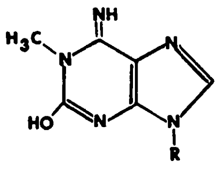
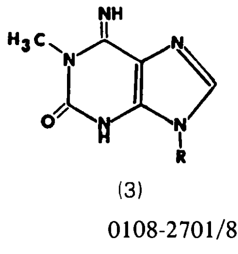
Abstract. $M_r = 201\cdot2$, triclinic, $P\bar{1}$, $a = 4\cdot110\,(2)$, $b = 9\cdot454\,(5)$, $c = 12\cdot303\,(7)$ Å, $\alpha = 74\cdot09\,(5)$, $\beta = 84\cdot52\,(5)$, $\gamma = 79\cdot96\,(4)°$, $V = 452\cdot1\,(4)$ Å^3, $Z = 2$, $D_x = 1\cdot48$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1\cdot5418$ Å, $\mu = 9\cdot8$ cm^{-1}, $F(000) = 212$, $T = 295$ K, $R(R_w) = 0\cdot045$ ($0\cdot046$) for 1043 unique observed reflections. 1-Methylisoguanine crystallizes from aqueous solution as the dihydrate. In the crystal structure, the 1-methylisoguanine molecules are linked together in an infinite chain by N—H···N hydrogen bonds. Each of these molecules is hydrogen bonded further to two different water molecules through its carbonyl and amino substituents on the pyrimidine ring. The pair of water molecules enhances the formation of a more complete system of hydrogen bonds. The 1-methylisoguanine molecule occurs in the N(12) amino rather than imino tautomeric form.



(1)



(2)



(3)

a: R=H

b: R= Ribose

Introduction. 1-Methylisoguanine (1*a*) (Pratt & Kraus, 1981) is the base component of the nucleoside dorisdosine (1-methylisoguanosine) (1*b*), a potent cardioactive natural product (Kim, Nachman, Pavelka, Mosher, Fuhrman & Fuhrman, 1981; Fuhrman, Fuhrman, Kim, Pavelka & Mosher, 1980; Cook, Bartlett, Gregson & Quinn, 1980). Like doridosine, 1-methylisoguanine can potentially exist as one of three tautomers represented by structures (1*a*), (2*a*), and (3*a*). This is complicated further by an additional possible tautomeric equilibrium between N(7) and N(9) in (1*a*). Therefore, we chose to determine the tautomeric preference of the base (1*a*) in the hydrated crystal by means of X-ray crystallography. While the results of the X-ray analysis cannot be directly extrapolated to describe aqueous solution behavior, it nevertheless determines absolutely the most stable tautomer of this base in the *hydrated* crystalline form. Such information may be of interest to those investigating the mode of action of the parent nucleoside, doridosine. Evidence compiled by Davies, Quinn and co-workers (Davies, Taylor, Gregson & Quinn, 1980; Norton, Gregson & Quinn, 1980) from analysis of ^{13}C NMR spin-lattice

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