

2,2,2',2',5,5,5',5'-Octamethyl-2,2',5,5'-tetrahydrofulvalene, C<sub>18</sub>H<sub>28</sub>

BY TULLIO PILATI AND MASSIMO SIMONETTA

Dipartimento di Chimica-Fisica ed Elettrochimica dell'Università e Centro del CNR, Via Golgi 19, 20133 Milano, Italy

(Received 30 July 1984; accepted 25 September 1984)

**Abstract.**  $M_r = 244.4$ , monoclinic,  $P2_1/n$ ,  $a = 9.735$  (3),  $b = 8.364$  (5),  $c = 9.985$  (4) Å,  $\beta = 108.61$  (3)°,  $V = 770.5$  (6) Å<sup>3</sup>,  $Z = 2$ ,  $D_m = 1.04$ ,  $D_x = 1.054$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 0.05$  mm<sup>-1</sup>,  $F(000) = 272$ , room temperature,  $R = 0.045$  for 1062 observed reflections. Steric hindrance reflects little on the ethylenic bond length [1.349 (4) Å], but more on the adjacent single bonds [mean 1.583 (2) Å] and on the angles involving methyl groups, which range between 105.8 (2) and 118.0 (2)°. The cyclopentene ring has an envelope conformation. The molecule is at a crystallographic centre of symmetry, but has approximate  $2/m$  symmetry. The tetrasubstituted ethylene is planar. The double bond of the cyclopentene ring is very compressed, being 1.289 (3) Å long.

**Introduction.** The crystal structure of 2,2,2',2',5,5,5',5'-octamethyl-2,2',5,5'-tetrahydrofulvalene (hereinafter OMFULV), is part of a study of overcrowded ethylenes (Pilati & Simonetta, 1984, and references therein). These compounds can be divided into two classes: those having a planar tetrasubstituted ethylene moiety and those with a more or less large rotation of the substituents around the double bond. OMFULV was expected to be of the first type, as is its parent compound 1,1,1',1',3,3,3',3'-octamethyl-2,2'-biindanylidene (Pilati & Simonetta, 1984), hereinafter called OMBIND.

**Experimental.**  $D_m$  by flotation in dilute K<sub>2</sub>HgI<sub>4</sub> solution; colourless prism 0.28 × 0.25 × 0.12 mm, sealed in a glass capillary to prevent sublimation; Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo  $K\alpha$  radiation,  $\omega$ -scan technique, variable rate 2–10° min<sup>-1</sup>. Cell constants from setting angles of 25 reflections with  $11 < \theta < 15^\circ$ ; correction for Lorentz and polarization but not for absorption. Three standard reflections, 3% intensity variation. 3519 reflections measured with  $\theta < 27.5^\circ$ , range of  $hkl$ : -12 to 12, 0 to 10, -13 to 13, 1762 independent, 1062 with  $I > 2\sigma(I)$ , agreement factor on observed intensity 0.018. C atoms from MULTAN (Germain, Main & Woolfson, 1971), H atoms from Fourier synthesis. Anisotropic C, isotropic H atoms, final secondary

extinction parameter  $g = 5.4$  (8) × 10<sup>-5</sup> (Larson, 1967, equation 3); full-matrix least-squares refinement on  $F_o$ ,  $w = 4F_o/[\sigma^2(F_o^2) + 0.0004(F_o^4)]$ ; final  $R = 0.045$ ,  $R_w = 0.045$ ,  $S = 1.69$ ,  $\Delta_{\text{max}}/\sigma = 0.07$ ,  $\Delta\rho = 0.2$  e Å<sup>-3</sup>. 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 refinement and geometrical analysis running on a Gould SEL 32/7780 computer.

**Discussion.** The final positional parameters and their e.s.d.'s are given in Table 1.\*

Two views of OMFULV, one with the numbering scheme, are given in Fig. 1. As can be easily seen from the figure, the molecule has symmetry close to  $2/m$ , with the mirror perpendicular to the fulvalene mean-

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39769 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final coordinates and equivalent or isotropic thermal parameters

$$B_{\text{eq}} = \frac{1}{3}(\sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j)$$

	$x$	$y$	$z$	$B_{\text{eq}}/B(\text{Å}^2)$
C(1)	-0.0184 (2)	-0.0057 (2)	0.0595 (2)	2.60 (4)
C(2)	-0.1337 (2)	0.0978 (2)	0.1029 (2)	3.44 (5)
C(3)	-0.0947 (2)	0.0612 (3)	0.2585 (2)	4.92 (7)
C(4)	-0.0034 (2)	-0.0543 (3)	0.3006 (2)	4.90 (7)
C(5)	0.0443 (2)	-0.1279 (2)	0.1851 (2)	3.42 (5)
C(6)	-0.2905 (2)	0.0357 (3)	0.0349 (3)	4.71 (8)
C(7)	-0.1272 (3)	0.2790 (3)	0.0903 (3)	4.65 (8)
C(8)	-0.0296 (3)	-0.2929 (3)	0.1541 (3)	4.59 (7)
C(9)	0.2098 (2)	-0.1467 (3)	0.2445 (2)	4.32 (6)
H(3)	-0.143 (2)	0.125 (3)	0.313 (2)	6.0 (5)
H(4)	0.035 (2)	-0.102 (3)	0.395 (3)	6.5 (5)
H(61)	-0.355 (3)	0.087 (3)	0.073 (3)	9.0 (8)
H(62)	-0.331 (2)	0.061 (3)	-0.063 (3)	6.4 (6)
H(63)	-0.300 (3)	-0.083 (4)	0.052 (3)	9.9 (9)
H(71)	-0.184 (2)	0.322 (3)	0.141 (2)	6.3 (5)
H(72)	-0.167 (2)	0.325 (3)	-0.009 (2)	5.6 (5)
H(73)	-0.027 (2)	0.321 (2)	0.133 (2)	5.8 (5)
H(81)	-0.005 (2)	-0.358 (3)	0.241 (2)	6.5 (5)
H(82)	-0.003 (3)	-0.360 (3)	0.080 (3)	8.1 (7)
H(83)	-0.132 (3)	-0.279 (3)	0.126 (2)	6.5 (6)
H(91)	0.232 (2)	-0.202 (2)	0.335 (2)	5.6 (5)
H(92)	0.255 (2)	-0.215 (2)	0.180 (2)	4.7 (4)
H(93)	0.254 (2)	-0.042 (3)	0.267 (2)	5.1 (5)

square plane. Further evidence for this symmetry is given in Table 2 which shows bond distances and bond angles. The conformation of the tetrasubstituted ethylene is strictly planar (deviations  $\pm 0.003 \text{ \AA}$ ) and its geometry coincides (within  $1\sigma$ ) with the similar moiety in OMBIND. The C(1),C(2),C(3),C(4),C(5) ring has an envelope conformation, with puckering coordinates (Cremer & Pople, 1975)  $Q = 0.17(2) \text{ \AA}$  and  $\varphi = 179.8(9)^\circ$ .

The strain due to the interaction between the methyl groups is reflected by the length of the C(1)–C(1') double bond [ $1.349(4) \text{ \AA}$ ] and by the mean value of the

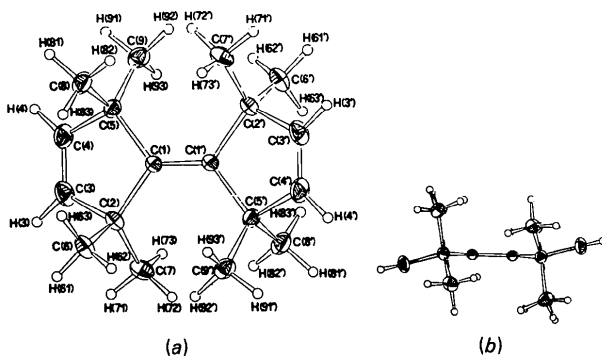


Fig. 1. Two views of the molecule. Thermal ellipsoids for C atoms are at 20% of probability level; those of H atoms are not to scale. (a) Frontal view with numbering scheme; (b) side view.

Table 2. Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) and mean values assuming  $2/m$  symmetry

		Mean	
C(1)–C(1')	1.349 (4)	—	
C(1)–C(2)	1.584 (3)	C(1)–C(5)	1.582 (2)
C(2)–C(3)	1.509 (3)	C(4)–C(5)	1.505 (3)
C(2)–C(6)	1.549 (3)	C(5)–C(8)	1.541 (3)
C(2)–C(7)	1.523 (3)	C(5)–C(9)	1.537 (3)
C(3)–C(4)	1.289 (3)		—
C(3)–H(3)	0.99 (2)	C(4)–H(4)	0.98 (2)
$C_m$ –H	0.93–1.05		0.98
C(2)–C(1)–C(5)	105.3 (1)	—	
C(2)–C(1)–C(1')	127.8 (2)	C(5)–C(1)–C(1')	126.9 (2)
C(1)–C(2)–C(3)	101.7 (2)	C(1)–C(5)–C(4)	102.0 (2)
C(1)–C(2)–C(6)	112.5 (2)	C(1)–C(5)–C(8)	112.5 (2)
C(1)–C(2)–C(7)	118.0 (2)	C(1)–C(5)–C(9)	117.6 (2)
C(3)–C(2)–C(6)	105.8 (2)	C(4)–C(5)–C(8)	106.3 (2)
C(3)–C(2)–C(7)	106.5 (2)	C(4)–C(5)–C(9)	106.7 (2)
C(6)–C(2)–C(7)	111.0 (2)	C(8)–C(5)–C(9)	110.5 (2)
C(2)–C(3)–C(4)	114.1 (2)	C(3)–C(4)–C(5)	113.9 (2)
C(2)–C(3)–H(3)	117 (1)	C(5)–C(4)–H(4)	117 (1)
C(4)–C(3)–H(3)	129 (1)	C(3)–C(4)–H(4)	129 (1)
C– $C_m$ –H	107–116		
H– $C_m$ –H	102–113		

Subscript:  $m$  = methyl.

E.s.d.'s of bonds and angles involving H atoms are 0.02–0.03  $\text{\AA}$  and  $1-2^\circ$ .

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

Table 3. Some intramolecular non-bonded short distances ( $\text{\AA}$ )

C(6)–C(9)	3.265 (4)	C(7)–C(8)	3.268 (4)
C(6)–H(92)	2.73 (2)	C(7)–H(82')	2.51 (3)
C(8)–H(72)	2.76 (2)	C(9)–H(62')	2.56 (3)
C(9)–H(72)	2.70 (2)	H(62)–H(92')	2.03 (3)
H(62)–H(93)	2.39 (4)	H(72)–H(82)	2.02 (4)
H(72)–H(92')	1.89 (3)	H(73)–H(82')	2.25 (4)

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

adjacent bonds [ $1.583(2) \text{ \AA}$ ]. The spread of the angles involving methyl groups ( $105.8-118.0^\circ$ ) is also a consequence of this interaction.

The greater thermal libration of OMFULV with respect to OMBIND is only partially responsible for the apparent reduction of the  $C_{sp^3}-C_{sp^3}$  bond, together with a small but significant reduction of the molecular strain due to the shorter [ $1.289(2) \text{ \AA}$ ] C(3)–C(4) ethylenic bond in OMFULV with respect to the corresponding aromatic bond [ $1.365(2) \text{ \AA}$ ] in OMBIND, that allows a better arrangement of the methyl groups. In fact the short non-bonded interactions reported in Table 3 are up to  $0.06 \text{ \AA}$  longer than the equivalent distances in OMBIND.

A surprising aspect of the strain in OMFULV (and in OMBIND) is the great compression of the C(3)–C(4) bond. This is not an artefact due to a particularly high thermal libration. In fact the correction of this bond length, following the rigid-body procedure of Schomaker & Trueblood (1967), is only  $0.005 \text{ \AA}$ .

Another interesting feature of this ethylenic part of OMFULV is the very large value of the angles C(4)–C(3)–H(3) and C(3)–C(4)–H(4) [ $129(1)^\circ$ ] with respect to C(2)–C(3)–H(3) and C(5)–C(4)–H(4) [ $117(1)^\circ$ ]. This geometry is probably uncorrelated with the compression of this double bond, but is due to electrostatic interaction among H(3), H(4), C(2) and C(5).

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

## References

- CREMER, D. & POPLER, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
- Enraf–Nonius (1979). *Structure Determination Package*. Enraf–Nonius, Delft.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 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.
- PILATI, T. & SIMONETTA, M. (1984). *Acta Cryst.* **C40**, 1407–1409.
- SCHOMAKER, V. & TRUEBLOOD, K. N. (1967). *Acta Cryst.* **B24**, 63–76.