Acta Cryst. (1988). C**44**, 1747–1749

A Dipentafulvene with Head-to-Head Geometry

By Mark L. McLaughlin,* John M. Cronan Jr and Frank R. Fronczek

Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803, *USA*

(*Received* 8 *February* 1988; *accepted* 25 *April* 1988)

Abstract. 1,4-Bis(2,4-cyclopentadien-1-ylidene)cyclohexane, $C_{16}H_{16}$, $M_r = 208{\cdot}3$, monoclinic, $P2_1/n$, $a = 6{\cdot}150$ (2), $b = 7{\cdot}7033$ (13), $c = 12{\cdot}348$ (3) Å, $\beta = 94{\cdot}26$ (2)°, $V = 583{\cdot}4$ (4) Å^3, $T = 295$ K, $Z = 2$, $D_x = 1{\cdot}186$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 0{\cdot}062$ mm^{-1}, $F(000) = 224$, $R = 0{\cdot}063$ for 1209 data with $F_o^2 > 0$ [$R = 0{\cdot}039$ for 818 data having $F_o^2 > 3\sigma(F_o^2)$]. The six-membered ring of the molecule adopts a chair conformation; there are no bond-length distortions to support the contention for electronic interaction through the σ-bond framework. The bond angle C7—C6—C8 *endo*-cyclic to the six-membered ring and *exo*-cyclic to the fulvene is 112·71 (9)°; this bond-angle distortion partially contributes to the unusual spectroscopic properties of the title molecule. The cyclopentadienylidene ring is planar, with maximum deviation of 0·003 (1) Å.

Introduction. 6,6-Dialkylpentafulvenes exhibit predominantly cross-conjugated trienic character; bond-length alternation is observed within the five-membered ring and the *exo*-cyclic double-bond length is typical of a full double bond (Watts, 1981). The *exo*-cyclic double bond of fulvenes is polarized owing to stabilization derived from the aromatic character associated with the cyclopentadienyl anion. The dipolar nature of fulvenes imparts unusual reactivity to these hydrocarbons. Fulvenes undergo many reactions reminiscent of carbonyl groups; the electrophilic carbon readily undergoes nucleophilic addition with organolithium compounds (Yates, 1968) and deprotonation by strong base occurs α to the electrophilic carbon atom (Macomber, Hart, Rausch, Priester & Pittman, 1982). The polar *exo*-cyclic double bond is readily reduced by lithium tetrahydroaluminate (Sullivan & Little, 1967) and dissolving metal reduction (Schwemlein & Brintzinger, 1983). The cyclic diene system of fulvenes forms Diels–Alder adducts with powerful dienophiles (Yates & Kronis, 1984) and forms stable metal complexes with transition metals in low oxidation states (Bandy *et al.*, 1985).

Experimental. The title compound is prepared in one step by condensation of 1,4-cyclohexanedione with two molar equivalents of freshly distilled 1,3-cyclopentadiene catalyzed with one molar equivalent of pyrrolidine in methanol (Stone & Little, 1985). Clear yellow–orange crystals, DP = 478 K, of the title compound suitable for single-crystal X-ray structure determination collected on the air-stream-cooled condenser of a sublimation unit at 373 K, 0·1 mm Hg. All standard spectroscopic measurements support the X-ray structure, Figs. 1 and 2 (McLaughlin, Cronan, Garcia & Fronczek, 1988).

Intensity data were obtained from a parallelepiped of dimensions 0·25 × 0·30 × 0·50 mm mounted in a random orientation on an Enraf–Nonius CAD-4 diffractometer. Cell dimensions were determined at

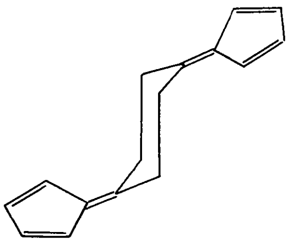

Fig. 1. 1,4-Bis(2,4-cyclopentadien-1-ylidene)cyclohexane.

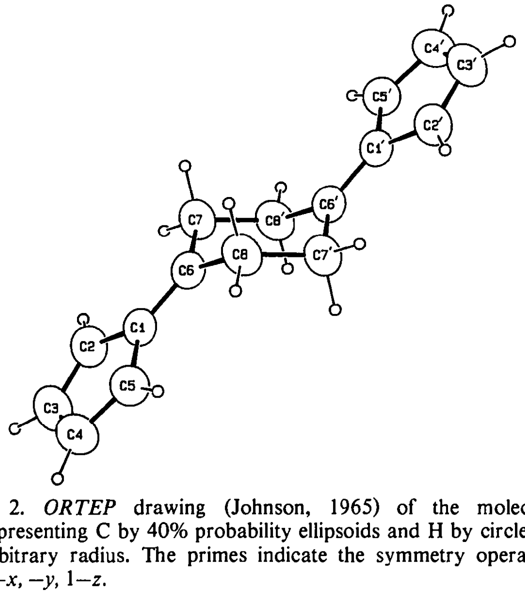

Fig. 2. *ORTEP* drawing (Johnson, 1965) of the molecule, representing C by 40% probability ellipsoids and H by circles of arbitrary radius. The primes indicate the symmetry operation 1−*x*, −*y*, 1−*z*.

---

* To whom correspondence should be addressed.

0108-2701/88/101747-03$03.00

295 K by a least-squares fit to setting angles of 25 reflections having $12 < \theta < 13°$. A hemisphere of data with $2 < 2\theta < 60°$, $0 \le h \le 8$, $-10 \le k \le 10$, $-17 \le l \le 17$ was measured using graphite-monochromated Mo $K\alpha$ radiation. ω–2θ scans were made at speeds ranging from 0·31 to 4·0° min^{-1} to measure all significant data with approximately equal precision. Three standard reflections (111, 020, 002) increased in intensity by 2·0% during data collection, and a linear correction was applied. Data were corrected for background, Lorentz and polarization. Absorption effects were insignificant. Two equivalent quadrants of data from the monoclinic crystals were averaged ($R_{\text{int}} = 0{\cdot}022$) to yield 1699 unique data, of which 1209 had $F_o^2 > 0$, and were used in the refinement. The coordinates tabulated are based upon this refinement.

Systematic absences $h0l$ with $h+l$ odd and $0k0$ with k odd uniquely determine the space group, $P2_1/n$. The structure was solved by direct methods and refined by full-matrix least squares based upon F, with weights $w = 4F_o^2[\sigma^2(I) + (0{\cdot}02F_o^2)^2]^{-1}$, using the *Enraf–Nonius Structure Determination Package* (Frenz, 1985), scattering factors of Cromer & Waber (1974) and anomalous coefficients of Cromer (1974). Non-H atoms were refined anisotropically; the H atoms were located by ΔF synthesis and were refined isotropically. Final $R = 0{\cdot}063$ for 1209 reflections having $F_o^2 > 0$ [$R = 0{\cdot}039$ for 818 reflections having $F_o^2 > 3\sigma(F_o^2)$ and $R = 0{\cdot}114$ for all data], $wR = 0{\cdot}043$, $S = 1{\cdot}504$ for 106 variables. Largest shift $< 0{\cdot}01\sigma$ in the final cycle, maximum residual density 0·16, minimum $-0{\cdot}15$ e Å^{-3}, extinction coefficient $g = 1{\cdot}6\,(3) \times 10^{-6}$, where the correction factor $(1 + gI_c)^{-1}$ was applied to F_c.

Discussion. The fractional coordinates of the title compound are given in Table 1. Fig. 2 is a perspective drawing showing the atom numbering. Selected distances, angles and torsion angles are presented in Table 2.*

The single-crystal X-ray structure determination was undertaken to probe the molecule for evidence of an interaction through the carbon σ bonds that allows a significant degree of cooperation between the two 'isolated' π-electronic systems. If the two ground-state fulvene moieties interact through the σ-bond framework, then the bonds C6—C7, C6—C8, C6′—C7′ and C6′—C8′ should be shorter than normal sp^2—sp^3 bond lengths and the bonds C7—C8′ and C8—C7′ should be longer than normal sp^3—sp^3 bond lengths (Fig. 2). In fact, there is no indication of this phenomenon; average bond lengths for sp^2—sp^3 and sp^3—sp^3 hybridized carbons are 1·50 and 1·54 Å, respectively (March, 1985). Thus, if there is an interaction between the fulvenes it must be either a through-space interaction or more likely an interaction between the first excited state of one fulvene with the ground state of the other. Similar bichromophoric absorption mechanisms have been proposed for simpler chromophores (Chandross & Dempster, 1970).

Table 1. *Coordinates and equivalent isotropic thermal parameters*

$$B_{\text{eq}} = (8\pi^2/3)\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
C1	0·4118 (2)	0·3191 (1)	0·41215 (8)	3·58 (2)
C2	0·5292 (2)	0·4067 (2)	0·32906 (9)	4·48 (3)
C3	0·4000 (2)	0·5321 (2)	0·2843 (1)	5·46 (3)
C4	0·1961 (2)	0·5324 (2)	0·3346 (1)	5·35 (3)
C5	0·2008 (2)	0·4075 (2)	0·4111 (1)	4·33 (3)
C6	0·4788 (2)	0·1835 (2)	0·47498 (8)	3·54 (2)
C7	0·6926 (2)	0·0931 (2)	0·46680 (9)	4·20 (3)
C8	0·3427 (2)	0·1014 (2)	0·55718 (8)	4·11 (3)

Table 2. *Bond distances* (Å), *bond angles* (°) *and selected torsion angles* (°)

C1—C2	1·463 (1)	C4—C5	1·346 (2)
C1—C5	1·464 (1)	C6—C7	1·498 (1)
C1—C6	1·348 (1)	C6—C8	1·503 (1)
C2—C3	1·343 (2)	C7—C8′	1·540 (2)
C3—C4	1·440 (2)		

C2—C1—C5	105·2 (1)	C1—C5—C4	108·1 (1)
C2—C1—C6	128·0 (1)	C1—C6—C7	123·65 (9)
C5—C1—C6	126·77 (9)	C1—C6—C8	123·59 (9)
C1—C2—C3	108·2 (1)	C7—C6—C8	112·71 (9)
C2—C3—C4	109·3 (1)	C6—C7—C8′	110·68 (9)
C3—C4—C5	109·1 (1)	C6—C8—C7′	110·95 (9)

C5—C1—C6—C8	−0·8 (2)	C2—C1—C6—C7	−2·0 (2)
C7—C6—C8—C7′	−55·2 (2)	C8—C6—C7—C8′	55·1 (2)
C6—C8—C7′—C6′	54·1 (2)		

The six-membered ring adopts a chair conformation. There is considerable distortion from ideal sp^2 hybridization at the carbon fusing the cyclopentadienylidene unit with the six-membered ring; the bond angle C7—C6—C8 is 112·71 (9)°. The degree of distortion caused by ring strain partially contributes to the unusual electronic properties of the molecule. Two monofulvenes which model the effect of ring strain in the title molecule are 5-cyclopentylidene-1,3-cyclopentadiene and 5-cyclohexylidene-1,3-cyclopentadiene; both exhibit moderate batho- and hyperchromic shifts in the electronic spectrum *versus* 6,6-dimethylfulvene, but do not shift proportionately as much as the difulvene (McLaughlin, Cronan, Garcia & Fronczek, 1988).

Acknowledgement is made to the Donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

---

* Lists of H-atom coordinates and thermal parameters, distances and angles involving H, anisotropic thermal parameters, and structure-factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51032 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Bandy, J. A., Mtetwa, V. S., Prout, K., Green, J. C., Davies, C. E., Green, M. L. H., Hazel, N. J., Izquierdo, A. & Martin-Polo, J. J. (1985). *J. Chem. Soc. Dalton Trans.* pp. 2037–2049.

Chandross, E. A. & Dempster, C. J. (1970). *J. Am. Chem. Soc.* **92**, 3568–3593.

Cromer, D. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.3.1. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.B. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Frenz, B. A. (1985). *Enraf–Nonius Structure Determination Package*. Enraf–Nonius, Delft, The Netherlands.

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

McLaughlin, M. L., Cronan, J. M. Jr, Garcia, J. G. & Fronczek, F. R. (1988). *J. Org. Chem.* Submitted.

Macomber, D. W., Hart, W. P., Rausch, M. D., Priester, R. D. & Pittman, C. W. Jr (1982). *J. Am. Chem. Soc.* **104**, 884–886.

March, J. (1985). *Advanced Organic Chemistry*, 3rd ed., p. 19. New York: McGraw-Hill.

Schwemlein, H. & Brintzinger, H. H. (1983). *J. Organomet. Chem.* **254**, 69–73.

Stone, K. J. & Little, R. D. (1985). *J. Org. Chem.* **49**, 1849–1853.

Sullivan, M. F. & Little, W. F. (1967). *J. Organomet. Chem.* **8**, 277–285.

Watts, W. E. (1981). *J. Organomet. Chem.* **220**, 165–172.

Yates, P. (1968). *Adv. Alicyclic Chem.* **2**, 59–181.

Yates, P. & Kronis, J. D. (1984). *Can. J. Chem.* **62**, 1751–1764.

Acta Cryst. (1988). C**44**, 1749–1751

Structure of Tetraethylammonium Thiosulfate Dihydrate

By Wayne Leyten*

Ballard Technologies Corporation, 1164 West 15th Street, North Vancouver, BC, Canada V7P 1M9

and Steven J. Rettig and James Trotter

Department of Chemistry, University of British Columbia, Vancouver, BC, Canada V6T 1Y6

(*Received* 7 *March* 1988; *accepted* 16 *May* 1988)

Abstract. $[(C_2H_5)_4N]_2S_2O_3.2H_2O$, $C_{16}H_{44}N_2O_5S_2$, $M_r = 408\cdot67$, monoclinic, $P2_1$, $a = 7\cdot2356\,(5)$, $b = 16\cdot5216\,(6)$, $c = 9\cdot5964\,(7)$ Å, $\beta = 94\cdot596\,(4)^\circ$, $V = 1143\cdot50\,(13)$ Å^3, $Z = 2$, $D_x = 1\cdot187$ g cm^{-3}, $\lambda(\mathrm{Mo}\ K\alpha_1) = 0\cdot70930$ Å, $\mu = 2\cdot5$ cm^{-1}, $F(000) = 452$, $T = 295$ K, $R = 0\cdot030$ for 2855 reflections. The structure contains tetrahedral cations with approximate D_{2d} symmetry, tetrahedral anions with approximate C_{3v} symmetry, and water molecules which link the anions into chains along **a** *via* O—H···S and O—H···O hydrogen bonds. Mean N—C = 1·527 (2), C—C = 1·515 (2), S—S = 2·028 (1), S—O = 1·481 (2) Å (corrected for libration); O—(H)···S = 3·349 (3), 3·458 (2), O—(H)···O = 2·817 (3), and bifurcated 3·121 (4) and 3·154 (4) Å.

Introduction. The title compound was synthesized as part of a project to produce non-aqueous electrolytes, but proved unsuitable, since the present X-ray study showed that it contained water of crystallization.

Experimental. Colourless blocks, (001), $(\bar{2}21)$, $\pm(120)$, $\pm(01\bar{1})$ developed, uniform dimensions ~0·4 mm, Enraf–Nonius CAD-4F diffractometer, lattice parameters from 25 reflections with $\theta = 20$–23°. Intensities for $\theta \le 32\cdot5^\circ$, *hkl*: 0 to 10, 0 to 24, −14 to 14, ω–2θ scan, ω scan width $(0\cdot65 + 0\cdot35\tan\theta)^\circ$ at 1·2–10° min^{-1}, extended 25% on each side for background measurement, three standard reflections showed negligible variations in intensity, Lp but no absorption corrections, 4236 independent reflections measured, 2855 with $I \ge 3\sigma(I)$, where $\sigma^2(I) = S + 4(B_1 + B_2) + (0\cdot04I)^2$, S = scan, B_1 and B_2 = background counts. Structure by Patterson and Fourier methods, refined by full-matrix least squares on F, H atoms from a difference map, weights used $w = 1/\sigma^2(F)$, scattering factors and anomalous-dispersion corrections for S ($f'' = 0\cdot124$) from *International Tables for X-ray Crystallography* (1974), locally written, or locally modified versions of standard computer programs, final $R = 0\cdot030$, $wR = 0\cdot036$ for 2855 reflections (the enantiomorph for the crystal used had R and wR ratios of 1·015, and could be rejected), $S = 1\cdot4$, 225 parameters (non-hydrogen atoms, plus 176 H parameters), $R = 0\cdot058$ for all 4236 reflections, $\Delta/\sigma = 0\cdot10$ (mean), 1·8 [maximum, for B of H(11*c*)], maximum final difference density $\pm 0\cdot18$ e Å^{-3}.

The thermal motions of the anion and of the two independent cations were analysed separately in terms

---

* Present address: Canadian Scientific Trading Service, 2604 SW Marine Drive, Vancouver, BC, Canada V6P 6C2.

0108-2701/88/101749-03$03.00