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## 5-(2,4-Cyclopentadien-1-ylidene)cyclooctanone, a Bichromophoric Molecule

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**Abstract.**  $C_{13}H_{16}O$ ,  $M_r = 188.3$ , orthorhombic,  $P2_12_12_1$ ,  $a = 5.7499$  (12),  $b = 12.552$  (2),  $c = 15.021$  (3) Å,  $V = 1084.1$  (6) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.153$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 0.066$  mm<sup>-1</sup>,  $F(000) = 408$ ,  $T = 295$  K,  $R = 0.032$  for 1040 data having  $F_o^2 > 1\sigma(F_o^2)$ . The title molecule adopts a boat-chair conformation also found for 1,5-cyclooctadione [Miller & McPhail (1979). *J. Chem. Soc. Perkin Trans. 2*, pp. 1527–1531]. There are considerable bond-angle distortions observed for all the methylenes forming the eight-membered ring. These six bond angles range from 111.9 (2)–115.8 (2)°. The bond angle exocyclic to the cyclopentadienyldiene ring is 116.6 (2)°. The non-bonding distance between the O and the electrophilic fulvene C is 3.636 (2) Å. The cyclopentadienyldiene ring is planar, with maximum deviation of 0.002 (2) Å.

**Introduction.** The title molecule (Fig. 1) is being studied as part of an investigation of bichromophoric molecules. The two  $\pi$ -electronic systems of the title molecule are 'isolated' from each other by two trimethylene chains. Bichromophoric effects among flexible molecules are frequently most intense when the two chromophores are separated by this chain length (De Schryver, Boens & Put, 1977). This X-ray structure determination was undertaken to determine if any significant ground state–ground state interactions are detectable in this molecule.

**Experimental.** The title compound was prepared by condensation of 1,5-cyclooctadione with one equiv-

alent of freshly distilled 1,3-cyclopentadiene, catalyzed with pyrrolidine in methanol at room temperature (Stone & Little, 1985). Clear, yellow crystals, m.p. 358 K, were grown by sublimation at room temperature and 0.01 mm Hg. All standard spectroscopic measurements can be interpreted from the X-ray structure.

Intensity data were obtained from an irregular fragment of dimensions 0.18 × 0.35 × 0.40 mm mounted in a random orientation on an Enraf–Nonius CAD-4 diffractometer. Cell dimensions were determined at 295 K by a least-squares fit to setting angles of 25 reflections having  $10 < \theta < 12^\circ$ . Two octants of data having  $2 < 2\theta < 55^\circ$ ,  $0 \leq h \leq 7$ ,  $0 \leq k \leq 16$ ,  $-19 \leq l \leq 19$ , were measured using graphite-monochromated Mo  $K\alpha$  radiation.  $\omega$ – $2\theta$  scans were made at speeds ranging from 0.45 to 4.0° min<sup>-1</sup> to measure all significant data with approximately equal precision. Three standard reflections (200, 020, 004) declined in intensity by 2.7% during data collection, and a linear correction was applied. Data reduction also included corrections for background, Lorentz and polarization effects. Absorption was negligible. The two equivalent octants of data were averaged ( $R_{\text{int}} = 0.023$ ) to yield 1465 unique data of which 1040 had  $F_o^2 > 1\sigma(F_o^2)$  and were used in the refinement.

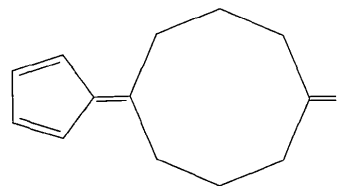


Fig. 1. 5-(2,4-Cyclopentadien-1-ylidene)cyclooctane.

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Table 1. Fractional coordinates and equivalent isotropic thermal parameters

$$B_{eq} = \frac{1}{3}(B_{11} + B_{22} + B_{33})$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
O	0.4330 (2)	0.10509 (9)	0.93462 (9)	5.37 (3)
C1	0.6356 (3)	0.0793 (1)	0.9365 (1)	3.62 (3)
C2	0.8229 (3)	0.1621 (1)	0.9458 (1)	3.95 (3)
C3	0.8682 (4)	0.2201 (1)	0.8583 (1)	4.30 (4)
C4	0.9834 (3)	0.1535 (1)	0.7847 (1)	4.18 (4)
C5	0.8350 (3)	0.0627 (1)	0.7512 (1)	3.74 (3)
C6	0.9019 (3)	-0.0474 (1)	0.7817 (1)	4.50 (4)
C7	0.9242 (3)	-0.0619 (1)	0.8821 (1)	4.15 (4)
C8	0.7033 (3)	-0.0369 (1)	0.9328 (1)	4.11 (4)
C9	0.6581 (4)	0.0794 (1)	0.6941 (1)	3.95 (3)
C10	0.4938 (4)	0.0014 (1)	0.6577 (1)	4.81 (4)
C11	0.3470 (4)	0.0509 (2)	0.6032 (1)	5.74 (4)
C12	0.4051 (4)	0.1634 (2)	0.6007 (1)	5.61 (5)
C13	0.5873 (4)	0.1807 (1)	0.6542 (1)	4.73 (4)

The space group was determined by systematic absences:  $h00$  with  $h$  odd,  $0k0$  with  $k$  odd, and  $00l$  with  $l$  odd. The structure was solved by direct methods and refined by full-matrix least squares based upon  $F_o$ , with weights  $w = 4F_o^2[\sigma^2(I) + (0.02F_o)^2]^{-1}$  using *Enraf-Nonius Structure Determination Package* (Frenz, 1985), scattering factors of Cromer & Waber (1974). C and O atoms were refined anisotropically; the H atoms were located by  $\Delta F$  synthesis and were refined isotropically. Final  $R = 0.032$  ( $R = 0.072$  for all 1465 unique reflections),  $wR = 0.028$ ,  $S = 1.196$  for 192 variables. Largest shift is  $< 0.01\sigma$  in the final cycle, maximum residual density is  $0.10$ , minimum  $-0.09 \text{ e \AA}^{-3}$ , and extinction coefficient  $g = 1.31(13) \times 10^{-6}$  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 bond lengths and angles about the carbonyl group are normal. There is considerable distortion observed for all the methylenes forming the eight-membered ring, *i.e.*  $C1-C2-C3 = 111.9(2)$ ,  $C2-C3-C4 = 115.7(2)$ ,  $C3-C4-C5 = 114.0(2)^\circ$ . Similar bond-angle distortions have been found in the single-crystal X-ray structure of 1,5-cyclooctadione (Miller & McPhail, 1979). The title molecule adopts a chair-boat conformation similar to that found for 1,5-cyclooctadione. A perspective drawing, Fig. 2,

\* Lists of H-atom coordinates and thermal parameters, distances and angles involving H atoms, torsion angles, least-squares planes, anisotropic thermal parameters and structure factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51754 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond distances ( $\text{\AA}$ ), angles ( $^\circ$ ) and selected torsion angles ( $^\circ$ )

O—C1	1.210 (2)	C6—C7	1.525 (3)
C1—C2	1.503 (3)	C7—C8	1.514 (3)
C1—C8	1.511 (3)	C9—C10	1.465 (3)
C2—C3	1.525 (3)	C9—C13	1.464 (3)
C3—C4	1.536 (3)	C10—C11	1.330 (3)
C4—C5	1.509 (3)	C11—C12	1.451 (3)
C5—C6	1.506 (3)	C12—C13	1.339 (3)
C5—C9	1.347 (3)		
O—C1—C2	120.5 (2)	C6—C7—C8	113.7 (2)
O—C1—C8	120.3 (2)	C1—C8—C7	115.8 (2)
C2—C1—C8	119.1 (2)	C9—C13—C12	108.8 (2)
C1—C2—C3	111.9 (2)	C5—C9—C10	128.4 (2)
C2—C3—C4	115.7 (2)	C5—C9—C13	127.2 (2)
C3—C4—C5	114.0 (2)	C10—C9—C13	104.4 (2)
C4—C5—C6	116.6 (2)	C9—C10—C11	109.1 (2)
C4—C5—C9	121.5 (2)	C10—C11—C12	108.9 (2)
C6—C5—C9	121.9 (2)	C11—C12—C13	108.8 (2)
C5—C6—C7	115.6 (2)		
O—C1—C2—C3	-77.5 (2)	O—C1—C8—C7	144.4 (2)
C8—C1—C2—C3	104.6 (2)	C2—C1—C8—C7	-37.7 (2)
C1—C2—C3—C4	-69.3 (2)	C2—C3—C4—C5	65.1 (2)
C3—C4—C5—C6	-104.8 (2)	C3—C4—C5—C9	77.9 (2)
C4—C5—C6—C7	53.5 (2)	C9—C5—C6—C7	-129.2 (2)
C5—C6—C7—C8	59.0 (2)	C6—C7—C8—C1	-70.5 (2)

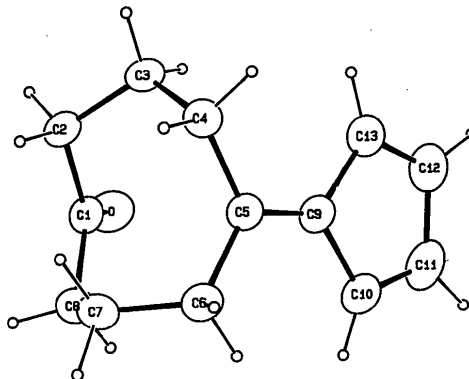


Fig. 2. ORTEP drawing (Johnson, 1965) of the title molecule, representing C and O by 40% probability ellipsoids and H by circles of arbitrary radius.

emphasizes the approach of the carbonyl O to the electrophilic C atom C5. This nonbonding distance is in fact quite long; O—C5 is  $3.636(2) \text{ \AA}$ . The O atom forms no intermolecular contacts, with other heavy atoms, closer than  $3.48 \text{ \AA}$ . However, the nonbonding distance C1—C5 of  $3.018(2) \text{ \AA}$  is within the sum of van der Waals radii for a C  $2p$  orbital.

The bond angle exocyclic to the cyclopentadienylidene ring, C4—C5—C6, is  $116.6(2)^\circ$ , significantly greater than the analogous bond angle for 1,4-bis(2,4-cyclopentadien-1-ylidene)cyclohexane which is  $112.71(9)^\circ$  (McLaughlin, Cronan & Fronczek, 1988). The fulvene shows the normal bond-length alternation and is planar with maximum deviation of  $0.002(2) \text{ \AA}$ .

There is no indication of any through-bond ground state-ground state interactions; all the  $\sigma$  bonds that connect the two  $\pi$ -electronic systems are normal.

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## Structure of 7-Ethylamino-4,6-dimethylcoumarin

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**Abstract.**  $C_{13}H_{15}NO_2$ ,  $M_r = 217.2$ , monoclinic,  $P2_1/c$ ,  $a = 7.343$  (1),  $b = 7.800$  (2),  $c = 19.589$  (4) Å,  $\beta = 91.45^\circ$ ,  $V = 1121.6$  (4) Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.29$  (2) (floatation),  $D_x = 1.286$  g cm<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.5418$  Å,  $\mu = 6.618$  cm<sup>-1</sup>,  $F(000) = 464$ ,  $T = 298$  K. Final  $R$  value is 0.051 for 1451 observed reflections. The coumarin moiety is planar and the ethylamino group is coplanar with the ring system. The crystal structure is stabilized by intermolecular N–H...O hydrogen bonds between glide-related molecules with N...O = 3.119 (3) Å and N–H...O = 173 (4)°.

**Introduction.** Coumarin dyes are widely used in the field of lasers owing to tunability and high gain. Some, in weakly polar solvents, give dual fluorescence (Masilamani, Chandrasekar, Sivaram, Sivashankar & Natarajan, 1986). The title compound has been found to give two bands, one around 415 nm and the other around 435 nm under nitrogen laser pumping (Masilamani, Sastikumar, Natarajan & Natarajan, 1987). This dual fluorescence is attributed to the Twisted Intramolecular Charge Transfer (TICT) effect in the excited state (Grabowski, Rotkiewicz, Siemiarczuk, Cowley & Baumann, 1979; Rettig, 1986). The crystal and molecular structure of this compound has been determined in order to study the conformation of the molecule in the ground state.

**Experimental.** Compound obtained from Exiton, New York; colourless rectangular crystals from a mixture of aqueous ethanol and chloroform, crystal size 0.7 × 0.5 × 0.1 mm, Enraf-Nonius CAD-4 diffractometer, graphite-monochromated Cu  $K\alpha$  radiation, cell parameters from the least-squares treatment of the setting

angles of 25 reflections with  $30 \leq \theta \leq 45^\circ$ ;  $\omega/2\theta$  scan technique, intensity variation of the two standard reflections monitored every 100 reflections is less than 3%, 2028 unique reflections measured with  $2\theta \leq 120^\circ$ ; 1451 reflections are observed [ $I \geq 3\sigma(I)$ ],  $h - 8$  to 8,  $k 0$  to 9,  $l 0$  to 23. Data were corrected for Lp but not for absorption, structure solution by direct methods using *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), no immediate solution was obtained. The coumarin molecule was then given as the input to calculate a spherically averaged molecular scattering factor and statistically weighted tangent refinement was used to obtain the structure. Full-matrix least-squares refinement on  $F$  using *SHELX76* (Sheldrick, 1976): H atoms from difference Fourier map, anisotropic thermal parameters for non-H and isotropic for H atoms,  $w = 1/[\sigma^2(F_o) + 0.0013F_o^2]$ , final  $R = 0.051$ ,  $wR = 0.056$ ,  $S = 1.69$ ,  $(\Delta/\sigma)_{\max} = 0.027$ , final difference map is featureless with max. and min. peak heights 0.20 and  $-0.30$  e Å<sup>-3</sup>; no correction for secondary extinction, atomic scattering factors for all atoms as in *SHELX76* (Sheldrick, 1976), other geometrical calculations using *PARST* (Nardelli, 1983). An IBM 360/44 computer was used.

**Discussion.** Final atomic parameters are listed in Table 1.\* Atom numbering and bond lengths and angles are

\* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, distances and angles involving H atoms, torsion angles and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51741 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.