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## Structure of Cyclooctatetraene at 129 K

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**Abstract.**  $C_8H_8$ ,  $M_r = 104.2$ , orthorhombic,  $Aba2$ ,  $a = 7.664$  (6),  $b = 7.650$  (3),  $c = 10.688$  (6) Å,  $V = 627$  (1) Å<sup>3</sup>,  $T = 129$  K,  $Z = 4$ ,  $D_x = 1.10$  Mg m<sup>-3</sup>,  $F(000) = 224$ ,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 0.06$  mm<sup>-1</sup>, final  $R = 0.036$  ( $wR = 0.043$ ) for 529 observed reflections [ $I > 2\sigma(I)$ ] [4525 ( $\pm h, \pm k, \pm l$ ) measured, 597 averaged reflections ( $R_{\text{int}} 0.05$ ) and 52 refined parameters]. The molecular structure of COT in the solid state confirms earlier electron-diffraction results for the title compound suggesting a boat conformation. This is in accordance with recent structural investigations of COT derivatives.

**Introduction.** Cyclooctatetraene (COT) ring systems are capable of three structural changes, which involve ring inversion, bond shifting and valence isomerization (Paquette, 1975). Whereas the first process requires a planar transition state only, all bond-shifting mechanisms involve additionally an equalization of bond lengths, and consequently slightly higher energy barriers are found for the latter. As a ligand to transition metals, COT usually adopts a boat form or a twisted boat conformation (Brauer & Krüger, 1976); frequently the ligand shows fluxionality (Mann, 1982). As a dianionic ligand the COT skeleton is planar (Streitwieser *et al.*, 1973; Rösch & Streitwieser, 1978). For free, non-substituted COT a non-planar ring shape was found by electron diffraction (Bastiansen, Hedberg & Hedberg, 1957; Trætteberg, 1966); preliminary results of a crystal structure analysis of COT have been quoted in the literature (Bordener, Parker & Stanford, 1972). A low-temperature X-ray diffraction study of COT was undertaken to reveal basic structural data for this important compound in the solid state.

**Experimental.** Colourless single crystals of the title compound (m.p. 277.1 K by differential scanning calorimetry) were grown directly on the diffractometer at 248 K from polycrystalline material in capillaries (0.5 mm diameter, 0.01 mm wall thickness) using focused heat radiation techniques, as previously described (Brodalla & Mootz, 1981; Brodalla, 1983; Brodalla, Mootz, Boese & Osswald, 1985). Commercially available equipment was modified to operate under computer control on an Enraf–Nonius CAD-4 diffractometer. Crystal growth on the diffractometer was monitored by photographic techniques. After several attempts at crystallization a suitable crystal chosen for data collection had dimensions 0.14 × 0.29 × 0.36 mm. The crystal was subsequently cooled to 129 K and kept at this temperature for all further measurements. Several  $\Omega$  scans of low-order reflections along the three crystal axes showed that the crystal displayed acceptable mosaicity. Unit-cell parameters were obtained by a least-squares fit to the  $\theta$  values of 61 automatically centred reflections ( $12.6 < \theta < 19.7^\circ$ ). 4525 intensity data (before transformation:  $-13 < h < 13$ ,  $-19 < k < 19$ ,  $0 < l < 10$ ) were measured within the range  $1.9 < \theta < 39.9^\circ$  using graphite-monochromated Mo  $K\alpha$  X-radiation by a  $\theta$ - $2\theta$  scan technique in 48 steps, where the time spent measuring the background was half that taken to measure the peak. The intensity of a reflection and its e.s.d. were calculated from  $I = \text{INT} - 2(\text{BGL} + \text{BGR})/\text{Lp}$  and  $\sigma(I) = [\text{INT} + 4(\text{BGL} + \text{BGR})]^{1/2}/\text{Lp}$ , where INT, BGL and BGR are the peak intensity, left and right background counts, respectively. The horizontal detector aperture was  $(3.0 + 1.05 \tan \theta)$  mm and the vertical 4 mm;  $\omega$ -scan width =  $(0.8 + 0.35 \tan \theta)^\circ$ . The inten-

sities of three standard reflections, remeasured every 100 reflections, showed a variation of 8% during data collection. Data were corrected for Lorentz and polarization effects, but not for absorption.  $\sigma(F)$  was calculated from  $\sigma(F) = [\sigma(I)^2 + (IK)^2]^{1/2}/2F$ , where  $k = 0.02$ . The data set was transformed to yield the space group No. 41, *Aba2*. Of a total of 597 unique averaged intensities, 529 satisfied the criterion  $I > 2.0\sigma(I)$ , and only these were used in the solution and refinement of the structure.

The structure was solved by direct methods (Sheldrick, 1985). Refinement was by full-matrix least-squares methods, where the function minimized was  $\sum w(F_o - F_c)^2$  with  $w = 1/\sigma^2(F_o)$ . All hydrogen atoms were located in a difference Fourier map and included in the refinement with positional and isotropic thermal parameters. Refinement converged at  $R = 0.036$  ( $wR = 0.043$ ) for 52 variables and 529 reflections, and the value of the 'error of fit'  $S = 2.3$ . In the final refinement cycle the maximum shift to e.s.d. ratio was 0.02. Atomic scattering curves were taken from *International Tables for X-ray Crystallography* (1974). In the final difference Fourier synthesis, peaks of  $\pm 0.24 \text{ e } \text{Å}^{-3}$  were observed. Computer programs used in this investigation: *GFMLX* (Busing, Martin & Levy, 1962), *TRACER* (Lawton & Jacobson, 1965), *DATAP* (Coppens, Leiserowitz & Rabinovich, 1965), *DAESD* (Davis & Harris, 1970), *XANADU* (Roberts & Sheldrick, 1976), *ORTEP* (Johnson, 1976), *MOGLI* (Dearing, 1985).

**Discussion.** The results of the X-ray analysis are summarized in Tables 1 and 2, which give the final atomic coordinates and selected interatomic distances and angles.† Fig. 1 shows the molecular structure and Fig. 2 the packing of molecules in the unit cell. The geometry of the tub-shaped COT molecule in the solid state is characterized by crystallographic and molecular symmetry  $D_{2d}$ ; a twofold axis bisects the atom pairs C(1)–C(1\*) and C(4)–C(4\*) (see Fig. 1). Single- and double-bond distances are as expected for a non-planar compound with isolated double bonds and no significant  $\pi$ -orbital overlap. Both types of bonds are equal within the given standard deviations; the cyclic angles average to  $126.7(2)^\circ$ . Whereas adjacent C–H bonds at C–C double bonds are only slightly twisted out of the C–C bonding plane, the C–H bonds enclosing the C–C single bonds are twisted by  $46$  and  $41^\circ$ , respectively. The transannular distance between the centres of the opposite double bonds, characteristic

Table 1. Atomic fractional coordinates and equivalent isotropic thermal parameters ( $\text{Å}^2$ ) with standard deviations in parentheses

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}$
C(1)	0.0171 (2)	0.0945 (2)	0.0806	0.031
C(2)	0.1021 (2)	0.1845 (2)	−0.0069 (2)	0.030
C(3)	0.1771 (2)	0.1150 (2)	−0.1228 (2)	0.029
C(4)	0.0929 (2)	0.0245 (2)	−0.2105 (2)	0.029
H(1)	−0.017 (3)	0.154 (2)	0.157 (2)	0.034
H(2)	0.127 (2)	0.309 (3)	0.010 (2)	0.038
H(3)	0.303 (3)	0.148 (2)	−0.136 (3)	0.044
H(4)	0.156 (2)	−0.003 (3)	−0.293 (2)	0.038

Table 2. Selected interatomic distances ( $\text{Å}$ ), bond angles ( $^\circ$ ) and torsion angles ( $^\circ$ ) with e.s.d.'s in parentheses

C(1)–C(1*)	1.470 (2)	C(1*)–C(1)–C(2)	126.6 (1)
C(1)–C(2)	1.333 (2)	C(3)–C(2)–C(1)	126.7 (1)
C(2)–C(3)	1.465 (3)	C(4)–C(3)–C(2)	126.4 (1)
C(3)–C(4)	1.333 (2)	C(4*)–C(4)–C(3)	126.9 (2)
C(4)–C(4*)	1.473 (2)		
C(1)–C(2)–C(3)–C(4)	55.4 (3)	H(1)–C(1)–C(1*)–H(1*)	−45.5 (2.1)
C(2)–C(3)–C(4)–C(4*)	0.3 (5)	H(2)–C(2)–C(3)–H(3)	46.4 (1.7)
C(1*)–C(1)–C(2)–C(3)	1.1 (3)	H(1)–C(1)–C(2)–H(2)	0.2 (1.9)
C(2*)–C(1*)–C(1)–C(2)	−57.9 (3)	H(3)–C(3)–C(4)–H(4)	−4.3 (1.9)
C(3)–C(4)–C(4*)–C(3*)	−56.6 (3)	H(4)–C(4)–C(4*)–H(4*)	−40.6 (2.0)

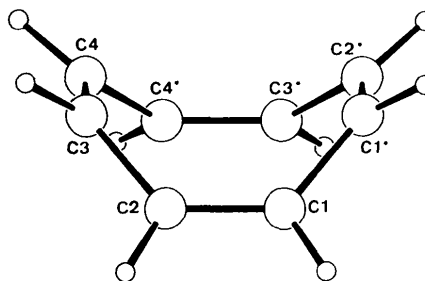


Fig. 1. The molecular structure of the title compound.

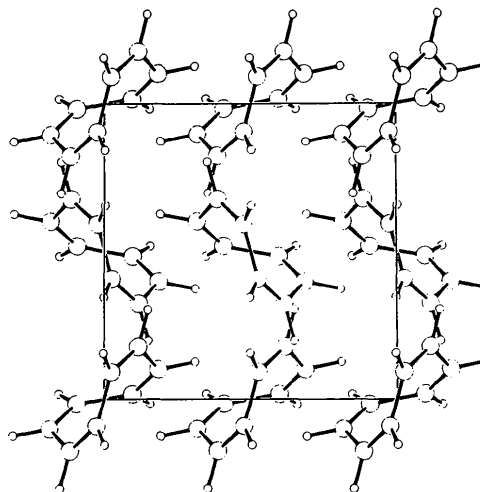


Fig. 2. The packing of the title compound in the unit cell, viewed down  $e$  towards the origin.

† Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and a table of bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51028 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

for the tub conformation, is 3.085 Å. The observed geometry is in striking accordance with the results of earlier electron-diffraction work and force-field computations (Ermer, 1981). Addition of substituents results in differences of the ring geometry. Thus steric repulsion of the methyl groups causes significant flattening of the ring of octamethyl-COT (Bordener, Parker & Stanford, 1972).

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## Structures of Two Bufadienolides: Bufotalin (3 $\beta$ ,14-Dihydroxy-16 $\beta$ -acetoxy-5 $\beta$ ,14 $\beta$ -bufa-20,22-dienolide) and Cinobufotalin (3 $\beta$ ,5 $\beta$ -Dihydroxy-14,15 $\beta$ -epoxy-16 $\beta$ -acetoxy-5 $\beta$ ,14 $\beta$ -bufa-20,22-dienolide)

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**Abstract.** Bufotalin (16-Acetoxybufalin) (1), C<sub>26</sub>H<sub>36</sub>O<sub>6</sub>,  $M_r = 444.57$ , orthorhombic,  $P2_12_12_1$ ,  $a = 11.247(1)$ ,  $b = 12.334(1)$ ,  $c = 17.031(1)$  Å,  $V = 2362.6(5)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.25$  Mg m<sup>-3</sup>,  $\lambda(\text{Cu K}\alpha) = 1.54184$  Å,  $\mu = 0.67$  mm<sup>-1</sup>,  $F(000) =$

960,  $T = 296(1)$  K,  $R = 0.045$  for 2479 unique observed reflections. The presence of a 16 $\beta$ -acetoxy group does not change the  $E^{14}$  conformation of ring D observed in the parent compound bufalin, but the rotation of the  $\delta$ -lactone ring about C(17)–C(20) is

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