

contacts between the carbonyl and the benzodioxole ring oxygens [O(11'), O(3)] without compromising the delocalized bonding in the phenanthrenone-benzene rings. In GND, the cyclohexane ring system is sufficiently flexible to cope with these contacts.

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Structure of 4,4,5,5-Tetramethoxy-2,7-dimethylcyclohepta-2,6-dien-1-one

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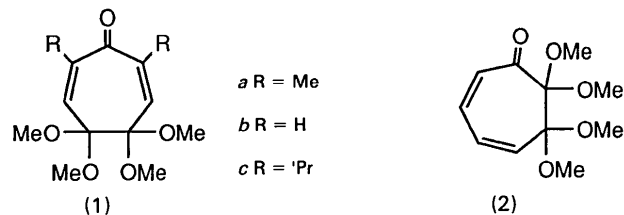
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Abstract. $C_{13}H_{20}O_5$, $M_r = 256.30$, triclinic, $P\bar{1}$, $a = 7.535$ (2), $b = 9.472$ (3), $c = 10.927$ (3) Å, $\alpha = 104.631$ (3), $\beta = 103.430$ (2), $\gamma = 109.130$ (3)°, $V = 669.34$ Å³, $Z = 2$, $D_x = 1.272$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu(\text{Mo } K\alpha) = 0.91$ cm⁻¹, $F(000) = 276$, $T = 293$ K, $R = 0.045$ for 2316 observed reflections. The crystal structure has a saddle-like C_1 symmetrical conformation: the angle of intersection between the two double bonds is 148.3° and the carbonyl oxygen atom is out of the two planes of the double bonds.

Introduction. Recently, we investigated the conformational exchanges of 4,4,5,5-tetramethoxycyclohepta-2,6-dienones (1) and 6,6,7,7-tetramethoxycyclohepta-2,4-dien-1-one (2) by variable-temperature NMR spectroscopy and found that the ground-state structure of (1) has C_1 symmetry

(Mori, Kubota & Takeshita, 1989). This conclusion is analogous to that for 10,11-dihydro-5H-dibenzo[*a,d*]cycloheptene derivatives (Weissensteiner, Hofer & Wagner, 1988). We report here the crystal structure of 4,4,5,5-tetramethoxy-2,7-dimethylcyclohepta-2,6-dien-1-one (1a), a monocyclic cyclohepta-2,6-dienone system.



Experimental. Crystalline (1a) was prepared as previously reported (Mori, Kubota & Takeshita, 1988)

Table 1. Final atomic coordinates and equivalent isotropic thermal parameters (\AA^2), with e.s.d.'s in parentheses

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

	x	y	z	$U_{\text{eq}}/U_{\text{iso}}$
O(1)	0.2974 (2)	0.2994 (1)	0.7391 (1)	0.1266
O(4)	0.7958 (2)	0.3102 (1)	0.8385 (1)	0.1803
O(2)	0.3574 (2)	0.0684 (1)	0.6884 (1)	0.0722
C(5)	0.6222 (2)	0.3319 (2)	0.8515 (2)	0.2138
O(3)	0.5675 (2)	0.2808 (1)	0.9522 (1)	0.1715
C(4)	0.4371 (2)	0.2359 (2)	0.7191 (2)	0.1528
C(8)	0.7936 (3)	0.7727 (2)	0.8614 (2)	0.1898
C(7)	0.7361 (3)	0.5950 (2)	0.8128 (2)	0.2452
C(6)	0.6771 (2)	0.5093 (2)	0.8861 (2)	0.2432
C(12)	0.7202 (3)	0.3512 (2)	1.0819 (2)	0.1652
C(13)	0.7869 (3)	0.1522 (2)	0.8128 (2)	0.1009
C(2)	0.6333 (2)	0.3655 (2)	0.5807 (2)	0.1736
C(10)	0.1264 (3)	0.2500 (3)	0.6228 (2)	0.0624
C(1)	0.7635 (3)	0.5290 (2)	0.6826 (2)	0.1920
C(3)	0.4957 (3)	0.2489 (2)	0.5968 (2)	0.1266
O(5)	0.8941 (3)	0.6163 (2)	0.6554 (2)	0.1057
C(11)	0.2414 (3)	0.0026 (2)	0.7628 (2)	0.0173
C(9)	0.6676 (3)	0.3405 (3)	0.4481 (2)	0.1099

Table 2. Bond lengths (\AA) and bond angles ($^\circ$), with e.s.d.'s in parentheses, and selected torsion angles ($^\circ$)

O(1)—C(4)	1.405 (2)	O(3)—C(12)	1.428 (2)
O(1)—C(10)	1.427 (2)	C(4)—C(3)	1.523 (3)
O(4)—C(5)	1.421 (2)	C(8)—C(7)	1.505 (3)
O(4)—C(13)	1.428 (3)	C(7)—C(6)	1.326 (3)
O(2)—C(4)	1.415 (2)	C(7)—C(1)	1.493 (3)
O(2)—C(11)	1.429 (3)	C(2)—C(1)	1.493 (2)
C(5)—O(3)	1.401 (2)	C(2)—C(3)	1.326 (3)
C(5)—C(4)	1.560 (2)	C(2)—C(9)	1.504 (3)
C(5)—C(6)	1.512 (2)	C(1)—O(5)	1.211 (3)
C(4)—O(1)—C(10)	115.5 (1)	O(2)—C(4)—C(3)	101.7 (1)
C(5)—O(4)—C(13)	116.7 (1)	C(5)—C(4)—C(3)	110.9 (1)
C(4)—O(2)—C(11)	119.1 (2)	C(8)—C(7)—C(6)	121.1 (2)
O(4)—C(5)—O(3)	111.3 (2)	C(8)—C(7)—C(1)	114.7 (2)
O(4)—C(5)—C(4)	112.5 (1)	C(6)—C(7)—C(1)	124.2 (2)
O(4)—C(5)—C(6)	105.4 (1)	C(5)—C(6)—C(7)	126.4 (2)
O(3)—C(5)—C(4)	106.6 (1)	C(1)—C(2)—C(3)	126.6 (2)
O(3)—C(5)—C(6)	111.2 (1)	C(1)—C(2)—C(9)	113.2 (2)
C(4)—C(5)—C(6)	109.8 (2)	C(3)—C(2)—C(9)	120.1 (1)
C(5)—O(3)—C(12)	115.6 (1)	C(7)—C(1)—C(2)	124.1 (2)
O(1)—C(4)—O(2)	111.8 (1)	C(7)—C(1)—O(5)	117.8 (1)
O(1)—C(4)—C(5)	104.6 (1)	C(2)—C(1)—O(5)	117.9 (2)
O(1)—C(4)—C(3)	114.2 (2)	C(4)—C(3)—C(2)	131.8 (1)
O(2)—C(4)—C(5)	114.0 (2)		
C(7)—C(1)—C(2)—C(3)	9.9	C(3)—C(4)—C(5)—C(6)	74.3
C(2)—C(1)—C(7)—C(6)	36.4		

and recrystallized from benzene-hexane. Crystal dimensions 0.2 mm. X-ray measurements were made using an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated $\text{Mo K}\alpha$ radiation. Lattice parameters were from the settings of 22 reflections with $9.68 < \theta < 13.12^\circ$. ω - 2θ scan technique was used to collect the intensities of 4167 reflections with $1 \leq \theta \leq 30^\circ$ ($0 \leq h \leq 10$, $-13 \leq k \leq 13$, $-15 \leq l \leq 15$), and 2316 reflections were considered as observed [$I > 3\sigma(I)$]. Two standard reflections were monitored every 3600 s and a 0.11% decrease in intensity per hour was noted. No absorption correction was applied. The structure was solved by direct methods

and positions of hydrogen atoms were determined by difference Fourier syntheses. Refinement was accomplished by full-matrix least squares. The function minimized was $[\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2}$. C and O were anisotropic and H was isotropic with B fixed at 4.0\AA^2 . The final conventional R is 0.045; $wR = 0.070$ was obtained for $w = 4(F_o)^2 / [(F_o)^2]^2$. $(\Delta/\sigma)_{\text{max}}$ in final least-squares cycle 0.64; no peaks $> 0.299 \text{ e \AA}^{-3}$ in last difference Fourier map; refined secondary-extinction value $g = 6.72 \times 10^{-8}$, which was defined by $|F_c| = |F_o|(1 + gI_o)$. Atomic scattering factors were from *International Tables for X-ray Crystallography* (1974, Vol. IV). Computation on a PDP 11/23 computer was performed by using Enraf-Nonius *SDP-Plus* (Frenz, 1985) and *ORTEPII* (Johnson, 1976) programs.

Discussion. The final atomic coordinates and isotropic temperature factors of (1a) are given in Table 1. Bond lengths and angles and some relevant

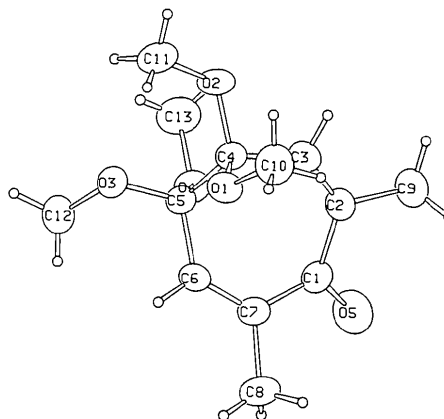


Fig. 1. Crystal structure of (1a).

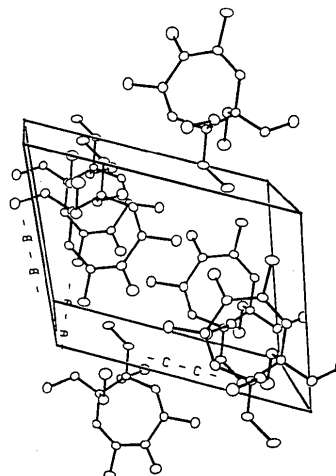


Fig. 2. Stereoview of the packing in the unit cell.

torsion angles are shown in Table 2.* Fig. 1 shows the crystal structure and the numbering of the atoms and Fig. 2 the crystal packing. The angle of intersection between plane *A*, defined by C(1), C(2) and C(3) and plane *B*, defined by C(1), C(7) and C(6), is 148.3° (α_1), whereas the angle of intersection between plane *A* and plane *C*, defined by C(2), C(1) and C(7), is 9.9° (α_2) and that between planes *B* and *C* is 36.4° (α_3). These values are close to those ($\alpha_1 = 145.2$, $\alpha_2 = 14.1$ and $\alpha_3 = 39.6^\circ$) of 10,11-dihydro-dibenzo[*a,d*]cyclohepten-5-one (3) (Weissensteiner, Hofer & Wagner, 1988). The dihedral angle between bonds C(3)—C(4) and C(5)—C(6) is 74.3°, whereas the corresponding angle for (3) is reported to be 81.8° (Weissensteiner, Hofer & Wagner, 1988). Thus, the molecule is saddle-like in shape with C_1 symmetry.

In solution, the carbonyl group of (1) flips freely via a C_2 symmetrical transition state and the bond twisting at the sp^3 carbons occurs between two half-

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond distances and angles involving H atoms, and r.m.s. amplitudes of thermal vibration have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53084 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

boat forms via a C_3 symmetrical transition state. The Gibbs energy of this bond twisting is 63–65 kJ mol⁻¹ at 298 K (Mori, Kubota & Takeshita, 1989), whereas the interconversion barriers for 10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene derivatives were calculated to be smaller than 29 kJ mol⁻¹ (Weissensteiner, Hofer & Wagner, 1988). The conformation of (1) in the solid state seems to be similar to that observed in solution.

The X-ray diffraction measurements were made using a CAD-4 diffractometer at the Center of Advanced Instrumental Analysis, Kyushu University.

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Structure of *trans*-1,6-Diphenyl-3-hexene-1,5-diyne

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Abstract. $C_{18}H_{12}$, $M_r = 228.29$, monoclinic, $C2/c$, $a = 24.246$ (3), $b = 14.214$ (1), $c = 11.536$ (6) Å, $\beta = 101.19$ (3)°, $V = 3899.92$ (3) Å³, $Z = 12$, $D_m = 1.14$, $D_x = 1.17$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.54177$ Å, $\mu = 4.682$ cm⁻¹, $F(000) = 1440$, $T = 293$ K, $R = 0.052$ for 1807 observed reflections. The asymmetric unit contains one molecule in a general position and a half molecule at a centre of symmetry. The phenyl rings are planar, and for the molecule in a general position, inclined with respect to each other by a dihedral angle of 9.1 (1)°. The C—C bonds in the chain

connecting the two phenyl rings have single-, double- and triple-bond character.

Introduction. Conjugated polymers such as polydiacetylene, polyacetylene and poly(*p*-phenylene) have interesting properties resembling those of photoconductors, semiconductors or even metals (Whangbo, Hoffman & Woodward, 1979).

Among these polymers the polydiacetylenes (I) are especially important as they may be obtained as pure single crystals with interesting optical properties. Thus, they change colour under the influence of heat, light or solvents (Chance, Washabaugh & Hupe,

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