The Crystal Structure of 1,4-Etheno-2,7-dihydroxy-2,4,6,8-tetramethyl-1,2,3,4-tetrahydronaphthalen-3-one

BENGT KARLSSON, ANNE-MARIE PILOTTI and ANNE-CHARLOTTE SÖDERHOLM

Department of Structural Chemistry, Arrhenius Laboratory, University of Stockholm, S-106 91 Stockholm, Sweden

X-Ray diffraction data from the title compound, $C_{16}H_{18}O_3$, were collected with a computer-controlled Philips PW1100 diffractometer. The unit cell is triclinic, space group $P\bar{1}$, having two independent molecules in the asymmetric unit. Cell dimensions are $a = 16.107$, $b = 10.649$, $c = 8.288$ Å, $\alpha = 107.13$, $\beta = 90.21$, $\gamma = 92.06°$. The structure was solved by the direct method and refined by the full-matrix least-squares technique to a final value of $R = 0.058$ for 3479 unique observed reflexions. Bond distances in the crystallographically independent molecules are identical within 3σ. The molecular packing is stabilized by a network of intermolecular hydrogen bonds involving all hydroxyl groups.

The title compound is obtained upon KOH/EtOH treatment of 1,4-etheno-2,8-diacetoxy-2,4,6,8-tetramethyloctahydronaphthal-5-ene-3,7-dione, a Diels-Alder dimer of 6-acetoxy-2,6-dimethyl-2,4-cyclohexadienone, which is formed upon lead tetraacetate oxidation of 2,6-dimethylphenol.

The formation of substituted 1,4-ethenonaphthalenes in Diels-Alder cycloaddition reactions involving oxidation products of methyl homologues of o-cresol has been discussed by, e.g., Adler et al,[1-6] Holmberg [7,8] and Lindgren et al.[9] Within a research program concerning the molecular geometry of this type of Diels-Alder adduct, we have earlier reported the crystal structures of adducts formed upon the action of different oxidation agents on 2,6-dimethylphenol [10-12] and 2,4-dimethylphenol.[13-15] The title compound is obtained upon KOH/EtOH treatment of 1,4-etheno-2,8-diacetoxy-2,4,6,8-tetramethyloctahydronaphthal-5-ene-3,7-dione,[3,7] a Diels-Alder dimer formed upon lead tetraacetate oxidation of 2,6-dimethylphenol.[6,12]

The UV spectrum [3] of the title compound might be interpreted to indicate an interaction between the aromatic system and the etheno part, reflected in an absorption maximum at 311 nm. This structure determination was, in part, performed to elucidate the geometry of molecular regions mentioned.

X-RAY EXPERIMENTAL

A crystal of the approximate volume 0.008 mm^3 was selected for the intensity measurements. Lattice parameters were obtained from least-squares treatment of the angular coordinates of 25 reflexions well centered on a Philips PW1100 diffractometer equipped with a graphite monochromator to reflect $CuK\alpha$ radiation. Crystal data are: space group $P\bar{1}$, $a = 16.107(1)$, $b = 10.649(4)$, $c = 8.228(3)$ Å, $\alpha = 107.13(4)$, $\beta = 90.21(3)$, $\gamma = 92.06(6)°$, $V = 1348$ $Å^3$, $Z = 4$, $D_{X-ray} = 1.27$ g cm^{-3}, $\mu(CuK\alpha) = 7.11$ cm^{-1}.

Diffraction intensities within the $+h$-hemisphere of the reciprocal space were collected out to $2\theta = 132°$ with the $\theta - 2\theta$ scan technique [scan width $1.5°(\theta)$, scan speed $1.32°(\theta)$ min^{-1}]. Background counts were measured half the total scan time at each scan limit.

In order to monitor alignment and possible deterioration of the crystal, three standard reflexions were measured every 90 min. No significant intensity variation was detected for these reflexions. Of the 4690 independent reflexions measured, 3479 were above the threshold value determined by the criterion $I_{net} > 4\sigma(I_{net})$, where $\sigma(I_{net})$ is based on counter statistics. Intensities were corrected for Lorentz and polarization effects, but not for absorption.

STRUCTURE DETERMINATION AND REFINEMENT

The overall temperature factor and scale factor were calculated from a least-squares fitted Wilson curve,[16] and normalized structure factors, $|E|$, were generated. Phases for the 353 $|E|$ values greater than 1.80 were computed for 128 sets by a modified version of the MULTAN [17] direct phase determination procedure. The E map computed with the set showing the second best reliability index, neglecting the trivial set, revealed all 38 non-hydrogen atoms. The structural parameters, assuming first isotropic and then anisotropic thermal vibrations, were refined according to the full-matrix least-squares technique. The positions of 26 hydrogen atoms were deduced from a difference Fourier synthesis, and of the remaining 10 from chemical reasoning. The hydrogens were included with fixed coordinates and isotropic temperature factors in the final refinement, involving one molecule at a time. The R-value converged to 0.058 for the 3479 unique observed reflexions. Hughes'[18] weighting scheme with $F_{o,min} = 2.75$ was used throughout the refinement. The

atomic scattering factors for carbon and oxygen were taken from the *International Tables for X-Ray Crystallography*,[19] and that of hydrogen from Stewart *et al.*[20] The final parameters for the non-hydrogen atoms are listed in Table 1, and those for the hydrogens in Table 2. A list of the observed and calculated structure factors is available from the authors on request.

RESULTS AND DISCUSSION

The molecular geometries of the two crystallographically independent molecules, henceforth called unprimed and primed, respectively, are shown in Fig. 1. Bond lengths and angles involving the non-hydrogen atoms are given in Fig. 2 and Table 3, respectively. The standard deviations are estimated to be ⩽0.004 and ⩽0.005 Å for the C−C and C−O bonds in the respective molecules. The esd's for the angles are ⩽0.3° in both molecules. The mean C−H bond lengths are 0.94 (range 0.75−1.04 Å) and 0.97 Å (range 0.82−1.10 Å), unprimed and primed respectively, in good agreement with the value of 0.94 Å given by Stewart *et al.*[20] The average bond distances for the $C(sp^2)-C(sp^3)$

Table 1. Positional and thermal parameters ($\times 10^4$) for the non-hydrogen atoms in the two molecules. Primed atoms belong to the primed molecule. The B_{ij} values refer to the temperature factor expression $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$. Estimated standard deviations are given in parentheses.

| ATOM	X	Y	Z	B11	B22	B33	B12	B13	B23
C(1)	1613(2)	3299(3)	7124(4)	23(1)	73(3)	115(5)	13(3)	3(3)	63(6)
C(2)	716(2)	2871(3)	7436(4)	20(1)	65(3)	133(5)	12(3)	-7(3)	24(6)
C(3)	668(2)	2927(3)	9338(4)	23(1)	71(3)	148(5)	13(3)	14(4)	41(6)
C(4)	1488(2)	3364(3)	10335(4)	22(1)	74(3)	108(5)	15(3)	9(3)	22(6)
C(4A)	2130(2)	2413(3)	9332(3)	18(1)	63(3)	107(5)	4(3)	5(3)	33(5)
C(5)	2644(2)	1684(3)	10010(4)	25(1)	84(3)	102(4)	8(3)	3(4)	64(6)
C(6)	3248(2)	921(3)	9019(4)	21(1)	71(3)	138(5)	6(3)	0(4)	72(6)
C(7)	3302(2)	884(3)	7317(3)	17(1)	61(3)	118(5)	6(3)	8(3)	27(5)
C(8)	2784(2)	1602(3)	6571(3)	18(1)	66(3)	106(4)	-5(3)	2(3)	37(5)
C(8A)	2197(2)	2372(3)	7627(3)	17(1)	64(3)	113(5)	5(3)	0(3)	51(5)
C(9)	1751(2)	4654(3)	8399(4)	25(1)	65(3)	182(6)	6(3)	-2(4)	73(6)
C(10)	1679(2)	4691(3)	10004(4)	24(1)	62(3)	164(6)	6(3)	-8(4)	6(6)
C(11)	75(2)	3743(3)	7026(4)	29(1)	100(4)	184(6)	35(3)	-24(4)	36(7)
O(12)	557(1)	1538(2)	6443(3)	21(1)	79(2)	176(4)	15(2)	-10(3)	-17(5)
O(13)	39(2)	2663(3)	9958(3)	28(1)	195(4)	209(5)	-27(3)	30(3)	123(7)
C(14)	1412(2)	3429(4)	12192(4)	33(2)	122(4)	123(5)	43(4)	27(4)	42(7)
C(15)	3850(2)	199(4)	9774(4)	30(1)	117(4)	193(6)	38(4)	2(5)	130(8)
O(16)	3939(1)	168(2)	6424(3)	24(1)	81(2)	146(4)	22(2)	13(3)	16(4)
C(17)	2885(2)	1553(3)	4737(4)	26(1)	99(3)	116(5)	12(3)	14(4)	66(6)
C'(1)	6463(2)	3319(3)	7974(4)	21(1)	79(3)	112(5)	9(3)	10(3)	32(6)
C'(2)	5617(2)	2682(3)	7207(4)	19(1)	63(3)	129(5)	5(3)	17(4)	25(6)
C'(3)	5518(2)	2959(3)	5477(4)	19(1)	76(3)	158(5)	19(3)	7(4)	56(6)
C'(4)	6249(2)	3776(3)	5043(4)	23(1)	84(3)	178(6)	21(3)	16(4)	113(7)
C'(4A)	7003(2)	2947(3)	5108(4)	19(1)	67(3)	142(5)	3(3)	-2(4)	78(6)
C'(5)	7535(2)	2447(3)	3791(4)	23(1)	79(3)	127(5)	-1(3)	5(4)	86(6)
C'(6)	8198(2)	1692(3)	3997(4)	21(1)	70(3)	115(5)	0(3)	11(3)	49(6)
C'(7)	8280(2)	1427(3)	5543(3)	17(1)	59(3)	113(4)	1(3)	-8(3)	26(5)
C'(8)	7758(2)	1942(3)	6927(3)	19(1)	60(3)	104(4)	-6(3)	-3(3)	30(5)
C'(8A)	7117(2)	2709(3)	6679(3)	16(1)	63(3)	110(4)	-3(3)	1(3)	31(5)
C'(9)	6424(2)	4763(3)	8061(5)	21(1)	68(3)	213(7)	2(3)	12(4)	-8(7)
C'(10)	6305(2)	4988(3)	6588(5)	24(1)	71(3)	251(8)	12(3)	17(5)	81(8)
C'(11)	4898(2)	3220(3)	8375(4)	23(1)	94(3)	152(6)	8(3)	28(4)	12(7)
O'(12)	5648(1)	1287(2)	6907(3)	26(1)	70(2)	152(4)	-1(2)	10(3)	50(4)
O'(13)	4916(2)	2585(3)	4577(3)	30(1)	152(3)	209(5)	-11(3)	-38(4)	137(6)
C'(14)	6111(2)	4064(4)	3364(5)	33(2)	148(5)	252(8)	40(4)	17(5)	261(10)
C'(15)	8800(2)	1186(3)	2571(4)	33(2)	109(4)	140(5)	33(4)	44(4)	82(7)
O'(16)	8906(1)	652(2)	5817(3)	24(1)	73(2)	135(4)	22(2)	-6(3)	24(4)
C'(17)	7916(2)	1656(3)	8587(4)	27(1)	90(3)	116(5)	10(3)	-2(4)	65(6)
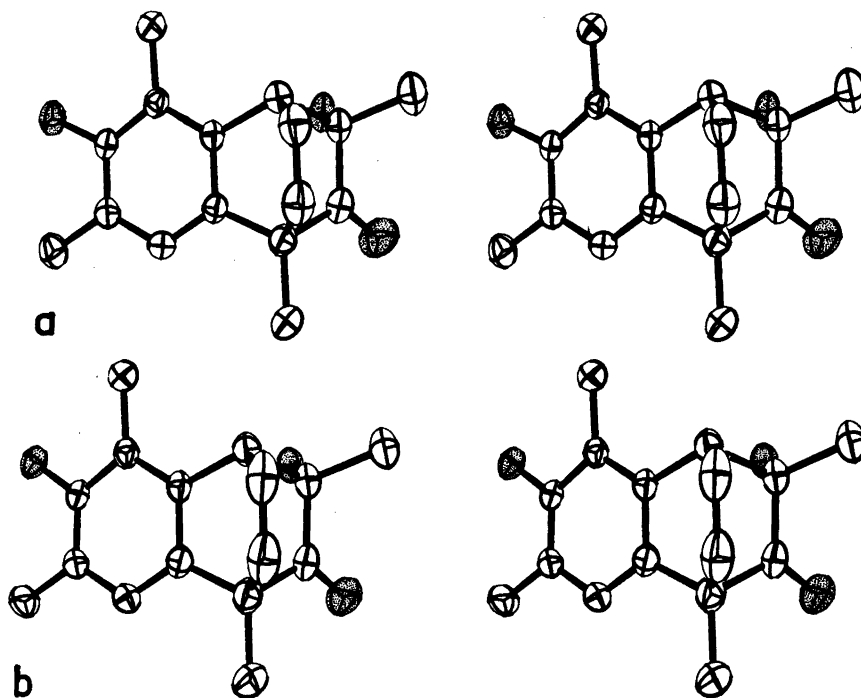
Fig. 1. Stereoscopic views of the two molecules in the asymmetric unit. *a*, Unprimed and *b*, primed molecule. The oxygen atoms are represented with shaded ellipsoids.
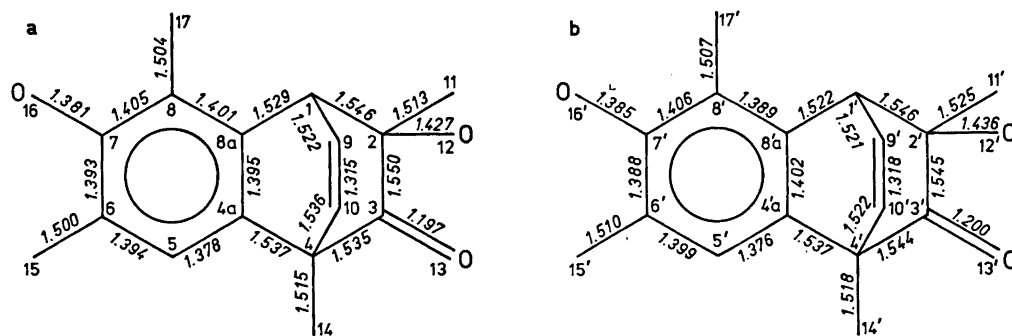

Fig. 2. Bond distances (Å) involving the non-hydrogen atoms. *a*, Unprimed and *b*, primed molecule.
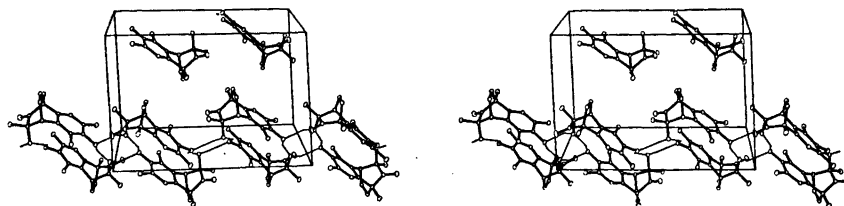

Fig. 3. A stereoscopic view of the molecular packing. O − H and O···H interactions in the hydrogen bonds are indicated with weak lines. The origin is at the bottom left corner, *a* is directed to the right, *b* upwards and *c* towards the reader.

Table 2. Positional ($\times 10^3$) and thermal ($\times 10^2$) parameters for the hydrogen atoms. Primed atoms belong to the primed molecule.

ATOM	X	Y	Z	B
H(C1)	164	313	594	254
H(C5)	262	176	1114	235
H(C9)	183	546	810	281
H(C10)	179	549	1091	289
H1(C11)	19	461	754	374
H2(C11)	10	358	608	374
H3(C11)	-44	351	690	374
H(O12)	2	149	617	309
H1(C14)	129	250	1227	352
H2(C14)	197	377	1276	352
H3(C14)	104	399	1256	352
H1(C15)	384	-70	910	389
H2(C15)	434	64	1017	389
H3(C15)	357	16	1086	389
H(O16)	375	-35	547	291
H1(C17)	238	100	406	284
H2(C17)	285	240	452	284
H3(C17)	342	114	430	284
H(C'1)	649	313	902	251
H(C'5)	752	267	267	253
H(C'9)	655	555	902	323
H(C'10)	619	585	645	341
H1(C'11)	439	290	786	321
H2(C'11)	486	417	877	321
H3(C'11)	500	309	929	321
H(O'12)	511	98	672	275
H1(C'14)	557	443	330	431
H2(C'14)	598	313	238	431
H3(C'14)	655	463	308	431
H1(C'15)	938	112	302	342
H2(C'15)	878	30	199	342
H3(C'15)	880	180	180	342
H(O'16)	890	-11	499	263
H1(C'17)	845	207	908	272
H2(C'17)	800	77	835	272
H3(C'17)	737	175	913	272

bonds are 1.526 Å in both molecules, which is $\geqslant 5\sigma$ longer than the standard value of 1.501 Å given by Lide;[11] this is presumably due to the fact that many of the long bonds involve highly substituted atoms.

The two independent molecules are quite similar; all individual bonds differ $< 3\sigma$ and most angles $\leqslant 1°$. Corresponding angles involving O(16) and O'(16) differ by about 5°, however, indicating that these hydroxyl groups have slightly differing orientations, possibly due to their participation in the hydrogen bonding system.

The aromatic rings, C(4a)−C(8a), *cf.* Fig. 2, and C'(4a)−C'(8a), show mean values for the C−C bond lengths of 1.394 and 1.395 Å, respectively; the bonds C(4a)−C(5), 1.378 and 1.376 Å, unprimed and primed respectively, and C(7)−C(8), 1.405 and 1.406 Å, likewise, are the ones that differ most from these means. The distances of the ring atoms from the L.S. planes for the aromatic rings, A and A', are

given in Table 4. It can be seen that A is somewhat more planar (± 0.009 Å) than A' (± 0.017 Å). Table 4 also summarizes the deviations from planarity for the L.S. planes in ring system B and B', each of which consists of the three boat-shaped rings. The dihedral angle between the A plane and the plane defined by the atoms C(4a), C(8a), C(9) and C(10) is 148.6°. The corresponding angle in the primed molecule is 154.1°. The torsion angles C(1)−C(8a)−C(4a)−C(5) are −177 and −179°, primed and unprimed respectively; and those of C(4)−C(4a)−C(8a)−C(8) are 177 and 178°, likewise. These conformation angles exclude the above mentioned possibility of an interac-

Table 3. Bond angles (°) involving the non-hydrogen atoms.

	Unprimed molecule	Primed molecule
C(2)−C(1)−C(8a)	107.4	106.4
C(2)−C(1)−C(9)	104.6	105.5
C(8a)−C(1)−C(9)	107.4	107.8
C(1)−C(2)−C(3)	107.0	106.8
C(1)−C(2)−C(11)	112.5	112.0
C(1)−C(2)−O(12)	109.1	108.3
C(3)−C(2)−C(11)	110.1	111.1
C(3)−C(2)−O(12)	107.8	108.5
C(11)−C(2)−O(12)	110.1	110.0
C(2)−C(3)−C(4)	114.1	114.0
C(2)−C(3)−O(13)	122.1	122.3
C(4)−C(3)−O(13)	123.8	123.7
C(3)−C(4)−C(4a)	104.9	103.0
C(3)−C(4)−C(10)	101.4	102.9
C(3)−C(4)−C(14)	112.5	112.2
C(4a)−C(4)−C(10)	106.4	107.7
C(4a)−C(4)−C(14)	115.4	115.2
C(10)−C(4)−C(14)	115.0	114.6
C(4)−C(4a)−C(5)	125.2	125.7
C(4)−C(4a)−C(8a)	114.7	113.8
C(5)−C(4a)−C(8a)	120.1	120.5
C(4a)−C(5)−C(6)	120.7	120.6
C(5)−C(6)−C(7)	118.4	117.9
C(5)−C(6)−C(15)	121.1	120.5
C(7)−C(6)−C(15)	120.4	121.7
C(6)−C(7)−C(8)	122.7	123.1
C(6)−C(7)−O(16)	115.7	120.9
C(8)−C(7)−O(16)	121.5	116.0
C(7)−C(8)−C(8a)	116.8	117.2
C(7)−C(8)−C(17)	120.4	119.6
C(8a)−C(8)−C(17)	122.8	123.3
C(1)−C(8a)−C(4a)	112.9	113.2
C(1)−C(8a)−C(8)	125.7	126.0
C(4a)−C(8a)−C(8)	121.3	120.8
C(1)−C(9)−C(10)	115.1	115.0
C(4)−C(10)−C(9)	115.9	115.7

Table 4. Least-squares planes and deviations. The planes are described in terms of normalized equations in the orthogonal coordinate system (m,n,p), having $p||c$, n in the bc plane and m in the abc octant. The primed planes belong to the primed molecule. Atoms marked with asterisks were omitted from the calculations of the least-squares planes.

Plane				
A	0.6614 m	+0.7496 n	+0.0265 p =	4.1883
B1	0.2501 m	+0.9680 n	−0.0194 p =	2.9769
B2	−0.7222 m	+0.6879 n	−0.0722 p =	0.7638
B3	0.9526 m	+0.2961 n	+0.0695 p =	4.4300
A'	0.5963 m	+0.7989 n	+0.0787 p =	9.0310
B1'	0.0630 m	+0.9823 n	+0.1762 p =	3.8006
B2'	0.8365 m	−0.5102 n	−0.1999 p =	5.3484
B3'	0.8804 m	+0.4727 n	−0.0379 p =	11.0076

Planes A,A'

Atom	Deviation	
	(A)	(A')
C(4a)	0.003 Å	−0.009 Å
C(5)	−0.009	−0.004
C(6)	0.008	0.017
C(7)	−0.002	−0.017
C(8)	−0.004	0.004
C(8a)	0.004	0.009

Planes B1,B1'

Atom	Deviation	
	(B1)	(B1')
C(1)*	0.732 Å	0.742 Å
C(2)	−0.005	−0.003
C(3)	0.005	0.003
C(4)*	0.702	0.741
C(4a)	−0.005	−0.004
C(8a)	0.005	0.004

Planes B2,B2'

Atom	Deviation	
	(B2)	(B2')
C(1)*	−0.746 Å	0.740 Å
C(2)	0.007	−0.010
C(3)	−0.008	0.010
C(4)*	−0.739	0.717
C(9)	−0.009	0.012
C(10)	0.009	−0.012

Planes B3,B3'

Atom	Deviation	
	(B3)	(B3')
C(1)*	−0.657 Å	−0.651 Å
C(4)*	−0.645	−0.632
C(4a)	0.003	0.004
C(8a)	−0.003	−0.004
C(9)	0.003	0.004
C(10)	−0.003	−0.004

Table 5. Distances (Å), angles (°) and symmetry codes for the atoms involved in the hydrogen bonds.

	$X^i−H^i\cdots Y^{ii}$	$X\cdots Y$	$X−H$	$H\cdots Y$	$\angle X−H\cdots Y$	i	ii
I:	O(12)−H(O12)$\cdots$O'(16)	2.784	0.881	1.962	154.5	$x+1,y,z$	x,y,z
II:	O'(16)−H(O'16)$\cdots$O(12)	2.692	0.889	1.874	152.1	x,y,z	$1−x,−y,1−z$
III:	O(16)−H(O16)$\cdots$O'(12)	2.819	0.860	2.171	131.9	x,y,z	$1−x,−y,1−z$
IV:	O'(12)−H(O'12)$\cdots$O(16)	2.939	0.907	2.034	174.9	x,y,z	x,y,z

tion between the aromatic system and the etheno bridge.

The molecular packing pattern is illustrated in Fig. 3. It consists of strings, parallel to the a axis, of hydrogen bonded molecules. Distances, angles and symmetry codes for the atoms involved are listed in Table 5. Two pairs of independent molecules are connected through octagons consisting of one O−H group from each molecule. Two different octagons exist: the bonds I and II, *cf.* Table 5, and their centric equivalents across $1,0,\frac{1}{2}$ form one; the bonds III and IV and their equivalents across the center of symmetry $\frac{1}{2},0,\frac{1}{2}$, the other. Each string binds neighbouring strings by van der Waals forces. There is, however, one such contact shorter than 3.5 Å; C(10)^i−C'(9)^{ii} = 3.39 Å (i≡x,y,z; ii≡$1−x$, $1−y$, $2−z$).

A further discussion of this structure and of related ones will be given in a forthcoming article.

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