The Crystal Structure of 1,4-Etheno-2-hydroxy-2,4a,6,9-tetramethyloctahydronaphthal-5-ene-3,7,8-trione

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The crystal structure of the title compound, $C_{16}H_{18}O_4$, has been determined from 2077 independent X-ray diffractometer reflexion data. The crystals are yellow and have monoclinic symmetry; the unit cell, with the dimensions $a = 13.067$ Å, $b = 8.463$ Å, $c = 13.950$ Å, $\beta = 116.23°$, contains four molecules. The structure was refined, in space group $P2_1/c$, to a final value of $R = 0.053$ by a full-matrix least-squares procedure.

The Diels-Alder product 1,4-etheno-2-hydroxy-2,4a,6,9-tetramethyloctahydronaphthal-5-ene-3,7,8-trione is an adduct of 2,4-dimethyl-o-quinol and 3,5-dimethyl-o-quinone, both formed upon periodate oxidation of 2,4-dimethylphenol. The structure is rather strained, having $C(sp^3) - C(sp^3)$ bond lengths of 1.564, 1.553 and 1.580 Å for the bonds $C(1) - C(8a)$, $C(8a) - C(4a)$ and $C(4) - C(4a)$, respectively.

Periodate oxidation of 2,4-dimethylphenol yields, among other compounds, the Diels-Alder product 1,4-etheno-2-hydroxy-2,4a,6,9-tetramethyloctahydronaphthal-5-ene-3,7,8-trione, which is a spontaneous adduct of the oxidation products 2,4-dimethyl-o-quinol (diene) and 3,5-dimethyl-o-quinone (philodiene).[1]

This investigation has been undertaken as part of a program concerned with the factors governing the highly stereospecific addition reactions of oxidized phenols. This matter has been discussed by, e.g., Holmberg.[2] The specific aim of the X-ray analysis of the title compound was to establish the steric arrangement around carbon atom C(2) and to confirm the structure of the adduct.

EXPERIMENTAL

Unit cell dimensions were obtained, in least-squares refinement, from angular positions of 25 accurately centered reflexions on a computer-controlled Philips PW1100 diffractometer. Crystal data are: Space group $P2_1/c$, $a = 13.067(2)$, $b = 8.463(1)$, $c = 13.950(1)$ Å, $\beta = 116.23(2)°$, $V = 1384$ Å^3, $Z = 4$, $\varrho_{calc} = 1.32$ g cm^{-3}, $\mu = 7.80$ cm^{-1}. Intensity data were collected with the $\theta - 2\theta$ technique for $\theta \leqslant 70°$, with graphite monochromatized CuKα radiation. Backgrounds were estimated by stationary counting at $\Delta\theta = \pm 0.75°$ from the reflexion maxima. The scan speed was 0.02° s^{-1}. Three monitor reflexions were measured every 60 min. No systematic intensity variation was noticed. Of the 2616 independent reflexions measured, 2077 were considered to be significantly above background, having $I_{net} \geqslant 4\sigma(I_{net})$, where $\sigma(I_{net})$ is based on counter statistics. Lorentz and polarisation factors were applied, but no correction for absorption.

STRUCTURE DETERMINATION AND REFINEMENT

The structure was solved by the automatic MULTAN direct phase determination procedure[3] using the 200 highest normalized structure factor magnitudes obtained from Wilson's method. The phase set having the highest reliability index revealed all non-hydrogen atoms.

Positional and thermal parameters were refined by the full-matrix least-squares method. A difference synthesis calculated at an R value of 0.09 displayed 16 of the 18 hydrogen atoms. The remaining two were positioned by chemical reasoning. Subsequent least squares refinements, using anisotropic temperature factors for the non-hydrogen atoms and fixed isotropic temperature factors for the hydrogens, gave a final R value of 0.053 for the 2077 reflexions.

Table 1. Positional and anisotropic thermal parameters ($\times 10^4$) of the non-hydrogen atoms. The B-values refer to the temperature factor expression $\exp[-(h^2B11 + k^2B22 + l^2B33 + hkB12 + hlB13 + klB23)]$. Estimated standard deviations are given in parentheses.

ATOM	X	Y	Z	B11	B22	B33	B12	B13	B23
C(1)	2847(2)	1995(3)	7642(2)	51(2)	101(3)	34(1)	-7(3)	39(2)	8(3)
C(2)	2943(2)	2732(3)	8692(2)	56(2)	111(3)	38(1)	-7(3)	40(2)	-10(3)
C(3)	3016(2)	1342(3)	9435(2)	41(2)	145(3)	34(1)	-9(3)	29(2)	2(3)
C(4)	2884(2)	-259(3)	8915(2)	57(2)	115(3)	36(1)	-1(3)	42(2)	25(3)
C(4A)	1713(2)	-309(3)	7871(2)	52(2)	120(3)	35(1)	-22(3)	44(2)	-2(3)
C(5)	1645(2)	-1927(3)	7409(2)	66(2)	119(3)	45(2)	-29(4)	54(3)	3(3)
C(6)	1688(2)	-2341(3)	6501(2)	68(2)	125(3)	50(2)	-12(4)	60(3)	-15(3)
C(7)	1765(2)	-1103(3)	5808(2)	91(2)	154(4)	45(2)	-31(4)	75(3)	-24(4)
C(8)	1498(2)	573(3)	6013(2)	64(2)	137(4)	34(1)	-37(4)	33(2)	14(3)
C(8A)	1699(2)	1058(3)	7122(2)	48(2)	112(3)	37(1)	3(3)	36(2)	5(3)
C(9)	3839(2)	851(3)	7942(2)	47(2)	129(3)	44(2)	0(3)	44(2)	1(3)
C(10)	3845(2)	-295(3)	8591(2)	48(2)	127(3)	45(2)	21(4)	34(2)	10(3)
C(11)	3975(2)	3806(4)	9212(2)	89(2)	146(4)	55(2)	-75(5)	60(3)	-34(4)
O(12)	1926(2)	3591(2)	8460(2)	83(2)	165(3)	45(1)	67(3)	55(2)	-12(3)
O(13)	3194(2)	1548(2)	10356(1)	86(2)	183(3)	38(1)	-34(3)	54(2)	-14(3)
C(14)	720(2)	-126(4)	8173(2)	53(2)	190(5)	53(2)	-38(4)	58(3)	-19(4)
C(15)	1641(3)	-4022(3)	6154(3)	126(3)	132(4)	74(2)	-5(5)	120(4)	-25(5)
O(16)	1991(3)	-1336(3)	5057(2)	240(4)	207(4)	97(4)	-20(6)	251(4)	-22(4)
O(17)	1123(2)	1482(2)	5270(2)	154(3)	172(3)	43(1)	-28(4)	55(3)	30(3)
C(18)	4708(2)	1084(4)	7529(3)	66(2)	207(5)	70(2)	35(5)	87(3)	47(5)

Table 2. Positional parameters ($\times 10^3$) and isotropic temperature factors ($\times 10^2$) for the hydrogen atoms. Estimated standard deviations for the positional parameters are given in parentheses.

ATOM	X	Y	Z	B
H(C1)	285(2)	283(3)	715(2)	243
H(C4)	293(2)	-110(3)	937(2)	275
H(C5)	161(2)	-283(3)	786(2)	304
H(C8A)	109(2)	180(3)	702(2)	253
H(C10)	439(2)	-112(3)	883(2)	284
H1(C11)	388(3)	465(4)	878(2)	407
H2(C11)	397(3)	428(3)	985(2)	407
H3(C11)	462(3)	323(3)	935(2)	407
H(O12)	195(2)	392(3)	904(3)	364
H1(C14)	9(3)	-19(3)	761(2)	373
H2(C14)	73(2)	-109(3)	863(2)	373
H3(C14)	74(2)	92(4)	849(2)	373
H1(C15)	93(3)	-423(3)	549(2)	403
H2(C15)	229(3)	-423(3)	601(2)	403
H3(C15)	160(2)	-471(3)	665(2)	403
H1(C18)	505(3)	213(4)	774(2)	397
H2(C18)	445(3)	122(3)	686(3)	397
H3(C18)	527(3)	34(4)	779(2)	397

Hughes' weighting procedure [4] with $F_{o,min} = 2.0$ was applied. Scattering factors for the non-hydrogen atoms were taken from the *International Tables for X-Ray Crystallography* [5] and that for hydrogen from Stewart, Davidson and Simpson.[6] The final positional and thermal parameters for the non-hydrogen atoms are given in Table 1, and those for the hydrogen atoms in Table 2. A list of the observed and calculated structure factors is available from the authors on request.

RESULTS AND DISCUSSION

A stereoscopic view of the molecule is given in Fig. 1, which shows that the addition has followed the *endo*-rule. The configuration around carbon atom C(2) is in harmony with that found in our X-ray investigations of related compounds. [7–10] The more polarizable hydroxyl substituent is oriented *anti* to the etheno bridge, in accordance with the results from Williamson *et al.*,[11] concomitantly leaving the bulkier methyl group to be directed away from the reaction center.

Intramolecular distances and bond angles involving the non-hydrogen atoms are given
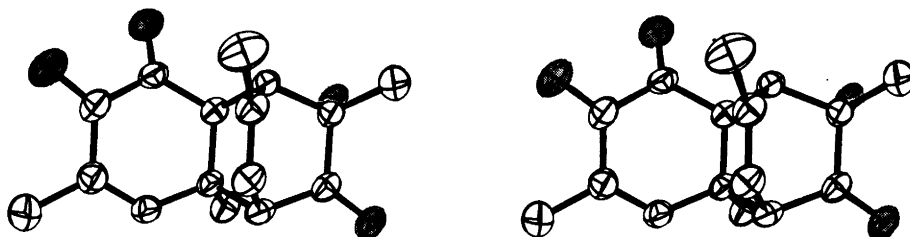

Fig. 1. A stereoscopic view of the molecule. Hydrogen atoms have been omitted. The oxygen atoms are represented by shaded ellipsoids.
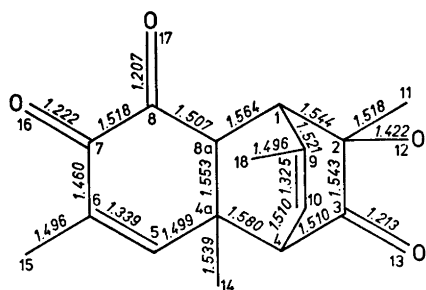
Fig. 2. Bond distances in the molecule. Standard deviations are estimated to be ≤ 0.003 Å.

Table 3. Bond angles (°) involving non-hydrogen atoms. Standard deviations are estimated to be ≤ 0.3°.

C(2)	− C(1)	− C(8a)	107.7
C(2)	− C(1)	− C(9)	107.1
C(8a)	− C(1)	− C(9)	109.4
C(1)	− C(2)	− C(3)	106.5
C(1)	− C(2)	− C(11)	112.2
C(1)	− C(2)	− O(12)	108.4
C(3)	− C(2)	− C(11)	110.9
C(3)	− C(2)	− O(12)	108.4
C(11)	− C(2)	− O(12)	110.2
C(2)	− C(3)	− C(4)	113.6
C(2)	− C(3)	− O(13)	121.9
C(4)	− C(3)	− O(13)	124.4
C(3)	− C(4)	− C(4a)	109.0
C(3)	− C(4)	− C(10)	103.2
C(4a)	− C(4)	− C(10)	108.5
C(4)	− C(4a)	− C(5)	105.7
C(4)	− C(4a)	− C(8a)	108.6
C(4)	− C(4a)	− C(14)	109.6
C(5)	− C(4a)	− C(8a)	114.3
C(5)	− C(4a)	− C(14)	108.2
C(8a)	− C(4a)	− C(14)	110.4
C(4a)	− C(5)	− C(6)	128.8
C(5)	− C(6)	− C(7)	118.9
C(5)	− C(6)	− C(15)	122.8
C(7)	− C(6)	− C(15)	118.2
C(6)	− C(7)	− C(8)	117.2
C(6)	− C(7)	− O(16)	124.4
C(8)	− C(7)	− O(16)	118.3
C(7)	− C(8)	− C(8a)	120.0
C(7)	− C(8)	− O(17)	118.3
C(8a)	− C(8)	− O(17)	121.9
C(1)	− C(8a)	− C(4a)	110.0
C(1)	− C(8a)	− C(8)	108.1
C(4a)	− C(8a)	− C(8)	115.6
C(1)	− C(9)	− C(10)	113.6
C(1)	− C(9)	− C(18)	120.7
C(10)	− C(9)	− C(18)	125.7
C(4)	− C(10)	− C(9)	115.8

in Fig. 2 and Table 3, respectively. The hydrogen atoms lie in chemically reasonable positions, with a mean C−H distance of 0.95 Å, in good agreement with values found by Stewart, Davidson and Simpson.[6] No correction of the measured distances for riding thermal motion has been applied. The lengthened bonds around C(4a) and C(8a) are consonant with observations in similar structures.[7-10] This effect is probably due to internal strain in the molecule.

The arrangement of molecules in the unit cell is given in Fig. 3. All intermolecular contacts are normal van der Waals distances.

Some general structural features found in molecules of this type will be given in a forthcoming article.

Fig. 3. A stereoscopic view of the molecular packing.

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