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Crystal Structure of 2,6-Di-*tert*-butyl-5,6-epoxy-2,4-dihydroxy-4-methyl-1,3-cyclohexanedione, an Oxidation Product of 2,6-Di-*tert*-butyl-4-methylphenol (BHT)*

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Abstract

2,6-Di-*tert*-butyl-5,6-epoxy-2,4-dihydroxy-4-methyl-1,3-cyclohexanedione, $C_{15}H_{24}O_5$ was isolated from the product mixture obtained by carefully controlled permanganate oxidation of 2,6-di-*tert*-butyl-4-methylphenol. Crystals are triclinic (space group $P\bar{1}$) with cell parameters (T = 297 K) a = 8·901 (13), b = 12·388 (8), c = 7·302 (6) Å, α = 100·79 (5), β = 94·02 (10), γ = 99·07 (10)°, Z = 2, and V = 776·78 Å^3 based on λ(Mo $K\alpha$) = 0·71069 Å. The structure was solved from X-ray diffraction data and refined by a least-squares procedure to an agreement index of 0·061 on F^2 for 3612 unique reflections. The cyclohexane ring is stabilized in the boat conformation by internal hydrogen bonds. The two *tert*-butyl substituents undergo internal torsional oscillation with amplitudes of 6·0 and 6·8° r.m.s. The epoxy group has a C—C distance of 1·472 (3) Å and C—O distances of 1·457 (2) and 1·433 (3) Å (1·479, 1·462, and 1·440 Å, respectively, when corrected for thermal motion) reflecting its conjugation with a neighboring carbonyl group.

Introduction

As part of a study of the structure of coal, one of us (VFR) has devised a novel method for controlled oxidation. In this procedure, finely ground coal is mixed intimately with diatomaceous earth (Celite‡) and the mixture placed in a chromatographic column. An oxidizing agent is then percolated down the column. In this way, oxidized fragments are removed from the reaction zone in order to minimize further reaction.

A test of this procedure, using potassium permanganate as the oxidant, was carried out (Benjamin, Raaen, Hagaman & Brown, 1978) on 2,6-di-*tert*-butyl-4-methylphenol (BHT), a model compound representative of hindered phenolic structural units in coal (Dryden, 1963). In addition to the principal acidic fraction, a small neutral fraction was isolated whose components proved to be monomeric. These are probably formed in preference to dimeric derivatives because of lack of mobility of the reactive intermediates which are absorbed on the Celite; dimeric derivatives are formed preferentially when BHT is subjected to batchwise oxidation with potassium permanganate in acetone solution (Musso, 1967).

The identities of the monomeric products were not immediately obvious from their elemental analyses and their ^{1}H and ^{13}C NMR and infrared spectral properties. One of the products was therefore chosen for X-ray crystallographic analysis and its structure is reported here. Knowledge of its unexpected epoxide structure aided in assignment of structures for the other products which will be reported elsewhere.

Crystal-data collection and reduction

In the analysis of the unknown crystal the initial cell parameters and the triclinic symmetry were determined from X-ray precession photographs. The observed and calculated densities (assuming an empirical formula of $C_{15}H_{24}O_5$ and two molecules per unit cell) were 1·20 and 1·21 Mg m^{-3} respectively, the observed density being determined by flotation in a mixture of heptane and carbon tetrachloride. An ellipsoidal crystal with diametral dimensions 0·47 × 0·38 × 0·34 mm was mounted on a computer-automated four-circle Picker X-ray diffractometer (Busing, Ellison, Levy, King & Roseberry, 1965). The radiation used, Mo $K\alpha$ (λ = 0·71069 Å), was filtered with niobium. The cell parameters, a = 8·901 (13), b = 12·388 (8), c = 7·302 (6) Å, α = 100·79 (5), β = 94·02 (10), γ = 99·07 (10)°, were refined by least-squares fitting to the observed Bragg angles for 100 strong reflections (T = 297 K) above 45° 2θ. Integrated intensities for 3612 unique reflections were collected out to 54° 2θ. The intensity statistics indicated the presence of a center of symmetry; the space group is therefore $P\bar{1}$ with Z = 2.

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‡ Johns–Manville Products Corporation.

Electronic and crystal stabilities were monitored by periodic measurement (every 25 reflections) of the standard reflection 550 at 32° 2θ. The standard showed a systematic decrease in intensity with time. The reflections in the range 0–15° measured at the beginning and the end of the data collection reflected a similar trend, except that a 2θ dependence for the systematic decay also was evident. A correction for the decrease, assumed to result from radiation damage and sublimation effects, was made using a model with a linear dependence in time and an exponential temperature-factor-type dependence in 2θ.

The data were corrected for the Lorentz–polarization factor and for the absorption by the ellipsoidal crystal. The linear absorption coefficient used was 0·092 mm^{-1}.

Structure determination and refinement

The structure was solved by application of direct methods as implemented by the program *MULTAN* of Germain, Main & Woolfson (1970).* An E map for the most probable sign combination was calculated, and the 20 highest peaks in the three-dimensional E map gave correct trial positions for the 20 nonhydrogen atoms of the molecule. The H atom trial positions used were the difference Fourier peak positions closest to calculated positions assuming idealized geometry. The H atom positions for the two *tert*-butyl groups were located easily in the first difference Fourier map, as was the position of the H atom on C(5) of the ring. Successive difference Fourier calculations located the remaining H atoms.

* The computer programs used in this study were: *MULTAN* (Germain, Main & Woolfson, 1970); *ORESTES* (H. A. Levy & W. E. Thiessen); data-reduction programs (R. D. Ellison & H. A. Levy); *ORFLS* (Busing, Martin & Levy, 1962); *ORFFE* (Busing, Martin & Levy, 1964); *HYCOR* (G. M. Brown); *ORTEP* II (Johnson, 1965); *ORSBA* (Johnson, 1970*b*); *ORFFP* (H. A. Levy).

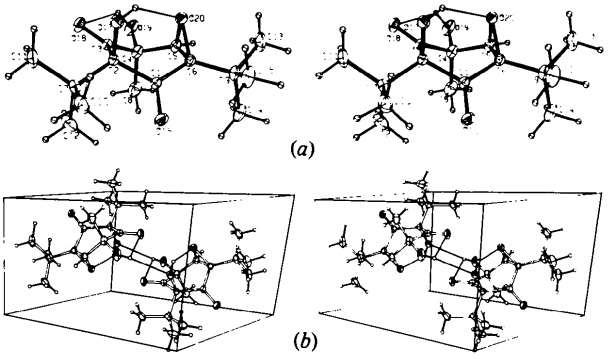

Fig. 1. Stereoscopic views of (*a*) a single molecule of 2,6-di-*tert*-butyl-5,6-epoxy-2,4-dihydroxy-4-methyl-1,3-cyclohexanedione, and (*b*) the molecular packing and hydrogen bonding. In (*b*) the *c* axis points towards the top of the page, and the *a* axis toward the left edge.

The H atom positional parameters and isotropic temperature factors were included in the unconstrained least-squares refinement. The nonhydrogen atoms were refined with anisotropic temperature factors. The function minimized was $\sum w(|F_o| - K^2|F_c|^2)^2$ where K is a scale factor and $w = 1/\sigma^2(|F_o|^2)$. The final agreement indices for the converged refinement of all parameters to the 3612 observations were: $R(F) = 0{\cdot}074$, $R(F^2) = 0{\cdot}061$, weighted $R(F^2) = 0{\cdot}097$, and 1·54 for the standard deviation of an observation of unit weight. No extinction correction was applied. The scattering factors used for O and C were those of Hanson, Herman, Lea & Skillman (1964). For H the scattering factors of Stewart, Davidson & Simpson (1965) were

Table 1. *Fractional coordinates* (10^4; *for* H $\times 10^3$)

The first two digits in the numbering system of the H atoms represent the parent atom to which the H atom is bonded.

	x	*y*	*z*
C(1)	1144 (2)	2129 (1)	2697 (2)
C(2)	−48 (2)	2910 (1)	2597 (2)
C(3)	836 (2)	4126 (1)	2896 (2)
C(4)	2586 (2)	4367 (1)	3269 (2)
C(5)	3076 (2)	3650 (1)	4577 (2)
C(6)	2361 (2)	2471 (1)	4348 (2)
C(7)	−1210 (2)	2562 (1)	802 (2)
C(8)	3352 (3)	4141 (2)	1476 (4)
C(9)	3231 (2)	1600 (1)	4945 (2)
C(10)	−2059 (3)	1366 (2)	655 (3)
C(11)	−2426 (3)	3320 (2)	930 (4)
C(12)	−389 (3)	2655 (3)	−944 (3)
C(13)	4161 (3)	2072 (2)	6842 (4)
C(14)	4310 (3)	1287 (2)	3465 (4)
C(15)	2088 (3)	567 (2)	5101 (5)
O(16)	1187 (1)	1337 (1)	1488 (2)
O(17)	−922 (1)	2853 (1)	4160 (2)
O(18)	167 (1)	4904 (1)	2988 (2)
O(19)	3083 (2)	5505 (1)	4129 (2)
O(20)	2002 (1)	3325 (1)	5831 (1)
H(101)	−252 (2)	127 (2)	188 (3)
H(102)	−283 (2)	120 (2)	−31 (3)
H(103)	−141 (2)	81 (2)	40 (3)
H(111)	−202 (2)	410 (2)	99 (3)
H(112)	−309 (2)	307 (2)	−17 (3)
H(113)	−302 (3)	326 (2)	211 (3)
H(121)	44 (3)	214 (2)	−113 (3)
H(122)	−117 (2)	242 (2)	−198 (3)
H(123)	12 (3)	344 (2)	−93 (3)
H(131)	343 (4)	221 (3)	780 (4)
H(132)	470 (2)	150 (2)	716 (3)
H(133)	495 (3)	277 (2)	680 (3)
H(141)	509 (3)	197 (2)	346 (3)
H(142)	486 (2)	74 (2)	382 (2)
H(143)	373 (3)	99 (2)	211 (3)
H(151)	149 (3)	16 (2)	383 (3)
H(152)	265 (2)	1 (2)	553 (3)
H(153)	144 (3)	78 (2)	603 (3)
H(051)	410 (2)	389 (1)	513 (2)
H(081)	311 (2)	459 (2)	63 (3)
H(082)	445 (3)	431 (2)	183 (3)
H(083)	306 (2)	336 (2)	74 (3)
H(171)	−31 (2)	310 (2)	508 (3)
H(191)	240 (3)	577 (2)	446 (3)

used. The final positional parameters are listed in Table 1.* The crystal contains the racemic mixture of molecules of 2,6-di-*tert*-butyl-5,6-epoxy-2,4-dihydroxy-4-methyl-1,3-cyclohexanedione (I). Stereoscopic views of the molecule and its packing in the crystal are shown in Fig. 1.

Results and discussion

Chemistry

A plausible sequence of reactions which ultimately give rise to (I) can be formulated (see Fig. 2). The intermediate first produced is probably the radical (II) (Musso, 1967), which, after some shuffling of the electrons, rearranges to (III). Hydroxylation of one of the double bonds, by permanganate, can occur to give (V). Alternatively, an unspecified oxidant can react with (IV), resulting in the epoxy derivative (VI) (Nishinaga, Itahara & Matsuura, 1974). Hydroxylation of (VI) or epoxidation of (V) will give the same compound (VII). Finally, one more stage of oxidation, involving the secondary alcohol group of (VII), will produce (I). The properties of compounds (V) and (VII), which have been isolated, will be reported elsewhere.

* Lists of structure factors, thermal parameters and distances and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34419 (72 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

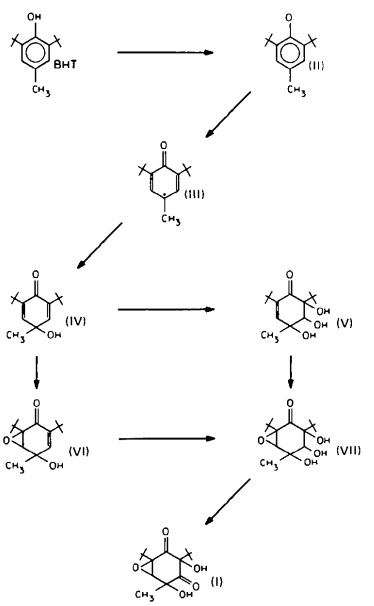

Fig. 2. Proposed mechanism for oxidation reaction.

The stereochemistry of (I) is unique in that all of the oxy substituents are on one side of the molecule, that is, in an all-*cis* relationship (see Fig. 2). A mechanism has been proposed (Nishinaga, Itahara & Matsuura, 1974) in which epoxidation occurs at positions 2 and 3 in a *cis* relationship to the OH group at position 4 in substituted phenols. It is possible that the remainder of the highly stereospecific *cis* hydroxylation is a result of permanganate-ion coordination with the oxygen moieties prior to reaction with the double bond.

Molecular geometry

The bond lengths and angles with standard deviations are given in Tables 2 and 3 respectively. Corrected distances between pairs of nonhydrogen atoms assuming segmented-body motion (see *Thermal motion* below) are included in Fig. 3.

There are seven methyl groups in the compound. The mean distance between the methyl C atoms and those

Table 2. *Bond lengths* (Å) *not involving hydrogen atoms with standard deviations in parentheses*

Distances are not corrected for thermal motion.

C(1)–O(16)	1·198 (2)	C(5)–O(20)	1·433 (3)
C(1)–C(6)	1·513 (3)	C(5)–C(6)	1·472 (3)
C(1)–C(2)	1·551 (3)	C(6)–O(20)	1·457 (2)
C(2)–O(17)	1·432 (2)	C(6)–C(9)	1·532 (3)
C(2)–C(3)	1·554 (3)	C(7)–C(10)	1·534 (3)
C(2)–C(7)	1·559 (3)	C(7)–C(11)	1·537 (3)
C(3)–O(18)	1·204 (2)	C(7)–C(12)	1·527 (3)
C(3)–C(4)	1·535 (3)	C(9)–C(13)	1·526 (3)
C(4)–O(19)	1·418 (2)	C(9)–C(14)	1·532 (3)
C(4)–C(5)	1·507 (3)	C(9)–C(15)	1·532 (3)
C(4)–C(8)	1·518 (3)		

Table 3. *Angles* (°) *not involving hydrogen atoms with standard deviations in parentheses*

O(16)–C(1)–C(6)	120·4 (2)	C(6)–C(5)–C(4)	121·3 (2)
O(16)–C(1)–C(2)	123·1 (2)	O(20)–C(6)–C(5)	58·6 (1)
C(6)–C(1)–C(2)	116·3 (1)	O(20)–C(6)–C(1)	113·2 (1)
O(17)–C(2)–C(1)	107·1 (1)	O(20)–C(6)–C(9)	117·1 (1)
O(17)–C(2)–C(3)	106·9 (1)	C(5)–C(6)–C(1)	111·3 (2)
O(17)–C(2)–C(7)	106·6 (1)	C(5)–C(6)–C(9)	122·0 (2)
C(1)–C(2)–C(3)	107·9 (1)	C(1)–C(6)–C(9)	119·8 (1)
C(1)–C(2)–C(7)	114·2 (1)	C(12)–C(7)–C(10)	110·4 (2)
C(3)–C(2)–C(7)	113·7 (1)	C(12)–C(7)–C(11)	109·1 (2)
O(18)–C(3)–C(4)	118·4 (2)	C(12)–C(7)–C(2)	110·5 (2)
O(18)–C(3)–C(2)	121·1 (2)	C(10)–C(7)–C(11)	106·8 (2)
C(4)–C(3)–C(2)	120·2 (1)	C(10)–C(7)–C(2)	110·0 (2)
O(19)–C(4)–C(5)	108·9 (2)	C(11)–C(7)–C(2)	109·9 (2)
O(19)–C(4)–C(8)	107·8 (2)	C(13)–C(9)–C(14)	109·5 (2)
O(19)–C(4)–C(3)	109·6 (2)	C(13)–C(9)–C(15)	109·0 (2)
C(5)–C(4)–C(8)	109·5 (2)	C(13)–C(9)–C(6)	110·4 (2)
C(5)–C(4)–C(3)	109·0 (2)	C(14)–C(9)–C(15)	110·1 (2)
C(8)–C(4)–C(3)	112·1 (2)	C(14)–C(9)–C(6)	108·5 (2)
O(20)–C(5)–C(6)	60·2 (1)	C(15)–C(9)–C(6)	109·4 (2)
O(20)–C(5)–C(4)	116·7 (1)	C(5)–O(20)–C(6)	61·2 (1)

to which they are bound is 1·529 Å with a standard deviation of the mean of 0·007 Å. The corresponding mean separation corrected for thermal motion is 1·546 Å ± 0·007 Å. The mean C—H distance and standard deviation of the mean are 0·99 ± 0·04 Å. These values for the methyl groups compare favorably with previously published values. The conformations of the *tert*-butyl groups are such that the bond to one H atom of each methyl group is roughly antiparallel to the bond joining the quaternary C atom to the ring (see Fig. 1). The *tert*-butyl groups are staggered with respect to the ring bonds and achieve minimum steric interaction with carbonyl O(16) atom. The H atoms of the methyl group C(8) attached to the ring are staggered relative to the two adjacent C—C bonds of the ring and the hydroxyl bond C(4)—O(19).

The C—C bonds springing from the epoxide carbon show the expected shortening (Szabo, Betkouski, Deyrup, Mathew & Palenik, 1973). The fact that the epoxide ring is nearly bisected by the projection on it of the C—O vector of the carbonyl group [C(1)—O(16)] bonded to it suggests that conjugation between the two groups should be important and the observed geometry of the epoxide ring bears this out: The C_α—O [C(6)—O(20)] distance is significantly longer than the C_β—O [C(5)—O(20)] distance. An analogous effect is found in cyclopropyl ketones (Thiessen, 1977).

It is of interest that when the relationship between the epoxide ring and the neighboring carbonyl group is such that conjugation is effectively precluded (Watkins, Fischer & Bernal, 1973) the opposite pattern of bond lengths appears. Their C_α—O bond length of 1·410 Å is distinctly shorter than C_β—O (1·448 Å) and their C_α—C_β bond distance of 1·455 Å is appreciably shorter than our 1·472 Å (1·479 Å when corrected for thermal motion). We submit that their pattern is the one to be expected in cases of *inductive* electron withdrawal as found, for instance, in bromocyclopropane (Lam & Dailey, 1968). The displacement of bonding electron density toward the electron-withdrawing group 'leaves more room' for the other bonds to that C atom, widening the angle between them (*i.e.*, decreasing their *p* character) and shortening them. The opposite effect in the case of *conjugative* electron withdrawal reflects an increase in *p* character in these same bonds because of the conjugation with the π-system of the carbonyl group.

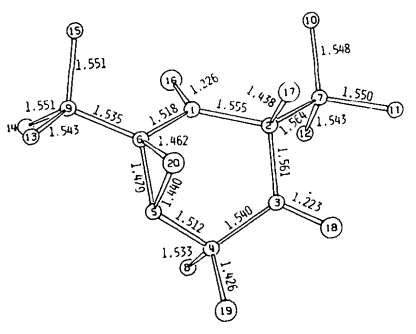

Fig. 3. Bond distances (Å) after correction for thermal motion. The H atoms are omitted for clarity.

Within the molecule, the H atom of the O(17) hydroxyl group forms a normal hydrogen bond to the epoxy O(20) atom, to produce six- and seven-membered rings: O(17)—H(171)···O(20)—C(6)—C(1)—C(2) and O(17)—H(171)···O(20)—C(5)—C(4)—C(3)—C(2). The O(17)···O(20) distance is 2·723 (4) Å, and the O(17)—H(171)···O(20) distances and angle are 0·81 (2), 2·06 (2) Å, and 138 (2)°, respectively.

H(191) forms a bifurcated hydrogen bond from O(19) to O(18) of the same molecule and to O(17) of another molecule across a center of symmetry [O(17)′]. The intermolecular hydrogen bond produces a dimer (see Fig. 2). These hydrogen bonds are asymmetrical, with the donor H atom closer to O(18) [at a distance of 2·20 (2) Å], than it is to O(17)′ [at a distance of 2·44 (2) Å]. The O(19)···O(*X*) distances (*X* = 18,17′) are 2·614 (4) Å and 3·162 (4) Å respectively. The O(19)···O(18) hydrogen bond is nonlinear, with an O(19)—H(191)···O(18) angle of 115 (2)°, and creates an unusual five-membered ring [O(19)—H(191)···O(18)—C(3)—C(4)]. The existence of this intramolecular hydrogen bond, although strained, is a partial explanation for the fact that the cyclohexane ring exists in the boat conformation. The long intermolecular hydrogen bond H(191)···O(17)′ is more nearly linear, with an O(19)—H(191)···O(17)′ angle of 160 (2)°. A least-squares fitting of the best plane through the four atoms [O(19), H(191), O(18), and O(17)′] involved in the bifurcated hydrogen bond showed the atoms to be approximately coplanar, the H atom having the largest deviation from the plane (−0·036 Å).

In a perfect boat conformation with ideal valence angles, the groups C(4)—C(5)—C(6)—C(1) and C(1)—C(2)—C(3)—C(4) would both be expected to be planar. The best planes listed in Table 4 attest how nearly this expectation is realized. Further, the conformation angles C(7)—C(2)—C(3)—O(18) and O(17)—C(2)—C(3)—O(18) should be equal in magnitude and opposite in sign. Their observed values of 56·5 and −60·8° reflect the fact that the valence angles about C(2) are not tetrahedral; four of the six angles have values smaller than the ideal 109·47° while C(1)—C(2)—C(7) and C(3)—C(2)—C(7) are much larger (Table 3). If this

Table 4. *Distances* (Å) *of atoms from least-squares planes fitted to the four atoms in each column*

C(1)	−0·0001 (5)	C(1)	−0·0044 (5)
C(4)	0·0001 (6)	C(2)	0·0083 (9)
C(5)	−0·0002 (11)	C(3)	−0·0088 (10)
C(6)	0·0002 (10)	C(4)	0·0049 (6)

were not the case, an unacceptably short contact between H(083) and H(121) would result. If the molecule had adopted the half-chair conformation with C(3) on the opposite side of the C(4)—C(5)—C(6)—C(1) plane from O(20) there would be no unacceptable alkyl—alkyl contacts, but the O(19)—H(191)···O(18) intramolecular hydrogen bond would have been disrupted and both carbonyl groups would be eclipsed by flanking alkyl groups on both sides. No conformation with C(2) on the opposite side of the C(4)—C(5)—C(6)—C(1) plane from O(20) could be adopted because of alkyl—alkyl contacts and disruption of the O(17)—O(171)···O(20) hydrogen bond. In short, intramolecular hydrogen bonding seems to be important in determining the conformation actually adopted.

Thermal motion

Since the *tert*-butyl groups have considerable freedom for internal motion, a rigid-body approximation for thermal motion of the complete molecule is not appropriate. The segmented-body model (Johnson, 1970*a*) permits one to study a system of coupled rigid bodies (segments). In this model, a terminal segment 'rides' on a parent segment; that is, the terminal segment has all the motion of the parent segment plus a component of uncorrelated motion constrained to conform to large-amplitude internal modes of molecular vibration. The segmented-body model used permitted internal rotational motion of the *tert*-butyl groups about their points of attachment to the cyclohexane ring. The resulting major components of internal libration (*i.e.*, mean-square rotational vibration) are about the bonds between the quaternary and ring C atoms with 6·0° r.m.s. amplitude for the group at C(7) and 6·8° r.m.s. for the group at C(9). The principal values of libration and translation for the parent segment are 4·7, 3·2, 2·1°, and 0·19, 0·18, 0·16 Å r.m.s. respectively. The carbonyl and hydroxyl O atoms and the methyl group attached to the cyclohexane ring were omitted from the calculation because of their large internal motion. The thermal-motion correction for these C—O and C—C distances is based on the 'rigid motion plus riding' model (Johnson, 1970*b*). The corrected distances are given in Fig. 3.

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