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The Molecular Structure of a Photo-Oxidized Dimer of Plastoquinone-1, $C_{26}H_{30}O_4$*

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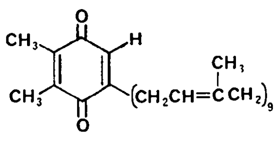
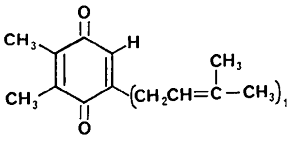
The compound 5,6,6a,7,7a,11b-hexahydro-2,3,5,7,7,9,10-octamethyl-6,11a,11c-metheno-1*H*-benzo[*c*]-fluorene-1,4,8,11(4a*H*)-tetrone was identified as one of the products formed by the ultraviolet irradiation of 2,3-dimethyl-5-(3-methylbut-2-enyl)-1,4-benzoquinone (plastoquinone-1). 2776 independent intensities were collected by counter methods, and the structure was solved through use of direct methods. The space group is *Pccn*, and the cell dimensions are $a=17\cdot849$ (5), $b=18\cdot820$ (10) and $c=12\cdot721$ (5) Å with 8 molecules per unit cell. The model was refined to an R value of 0·076 using 2259 reflections with intensities greater than $2\sigma(I)$. The parent quinone molecules are joined in three places in the photo-oxidized dimer yielding a highly strained set of fused rings. The dimer molecule contains a pseudo-twofold rotation axis.

Introduction

Electron-transport quinones are found in membranous cellular substructures such as mitochondria and chloroplast and are redox components of electron-transport chains. The loss or reduction of some biological functions have been attributed to the photochemical disruption of electron transport (Brodie, 1965). The photolabile electron-transport quinones are the most likely targets for this disruption. Plastoquinone-9 (I) is an essential transport quinone in photosynthetic processes, and far ultraviolet irradiation of autotropic cells which leads to the destruction of PQ-9 also results in the loss of several partial photosynthetic reactions (Mantai & Bishop, 1967). Since sunlight can modify PQ-9, the autotrophic cells must either have evolved mechanisms for protecting the plastoquinones from harmful radiation or they have evolved processes for their restoration. To answer these questions a study of the photochemistry of plastiquinones was initiated. Because of the limited availability of PQ-9, the quinone PQ-1 (II) was chosen as a model compound for initial studies.



(I)



(II)

After near-ultraviolet irradiation of PQ-1 in dry benzene under nitrogen, six photoproducts were discerned by t.l.c. (thin-layer chromatography) and the characterization of three of these has been reported (Creed, Werbin & Strom, 1971). A fourth melted at 285 °C and mass spectrometry gave a molecular weight of 406·2, $C_{26}H_{30}O_4$. The structure could not be determined from the n.m.r. spectrum or by other spectroscopic techniques, and the small quantity of sample precluded degradation studies. We report here the structure determination by direct methods and the identification of the compound as 5,6,6a,7,7a,11b-hexahydro-2,3,5,7,7,9,10-octamethyl-6,11a,11c-metheno-1*H*-benzo[*c*]fluorene-1,4,8,11(4a*H*)-tetrone. Hereafter the molecule is referred to as the dimer product of PQ-1. The interpretation of the n.m.r. spectrum has been reported (Watson, Whinnery, Creed, Werbin & Strom, 1972).

Experimental

A crystal of dimensions $0\cdot35\times0\cdot35\times0\cdot30$ mm was mounted with the b axis coincident with the rotation axis. The unit cell was found to be orthorhombic and room-temperature cell dimensions were determined from precession, b-axis oscillation and $h0l$ Weissenberg photographs. Sodium chloride lines, $a=5\cdot6402$ Å, were superimposed on the photographs, and the errors are standard deviations obtained from a calculation of cell edges for a number of reflections. The density, measured by the flotation technique, was the same as that of carbon disulfide.

$C_{26}H_{30}O_4$, molecular weight 406·5, $a=17\cdot849$ (5) $b=18\cdot820$ (10), $c=12\cdot721$ (5) Å. Systematic absences: $hk0$, $h+k=2n+1$; $0kl$, $l=2n+1$; $h0l$, $l=2n+1$. Space group: *Pccn* (No. 56). $Z=8$; $F(000)=1680$; $V=4273$ Å^3; $\mu=7\cdot10$ cm^{-1}; $D_{\rm exp}=1\cdot263$ g cm^{-3}; $D_{\rm cal}=1\cdot263$ g cm^{-3}; Cu $K\alpha$, $\lambda=1\cdot54178$ Å; graphite monochromator crystal $d_{200}=3\cdot354$ Å.

The intensity data, $h0l$ through $h15l$, were collected with a Philips PAILRED diffractometer using equi-inclination geometry and the continuous ω-scan technique. A scan range of 3·4 to 7·2° at 2·5° per min was used. The larger scan range was used for lower angles and upper levels. A background count of 20 sec was taken on either side of the ω-scan range. The intensities of four reflections were monitored during data collection, and only statistical variations in their intensities were observed. A total of 2776 independent reflections were measured and 2259 were greater than $2\sigma(I)$. No absorption corrections were made. The data

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were adjusted to an absolute scale with a Wilson plot, and standard deviations in the structure factor amplitudes were assigned on the basis of counting statistics (Ting & Watson, 1972). In addition to the structure factor magnitudes $|F_o|$, the normalized structure factors $|E_h|$ were computed. The scattering factors of Cromer & Waber (1965) were used for the carbon and oxygen atoms while those of Stewart, Davidson & Simpson (1965) were used for the hydrogen atoms.

Structure determination and refinement

A direct-method program package, developed by Stemple (1970) for the IBM 1800 computer, was used in the structure analysis. The package contains a modified version of the program by Long (1965) for centrosymmetric structures. Application of Long's program to the set of 150 E's > 1·87 followed by tangent refinement of the 373 largest E's resulted in signs of 318 reflections being accepted. An E map calculated with these reflections showed 31 large peaks. 30 of these could be connected by reasonable bond distances and angles. The parameters from these peak positions were used in three cycles of isotropic least-squares refinement with 524 reflections and all atoms assigned carbon scattering factors. The R value dropped to 0·19 where $R=[\sum\Delta F_{\text{meas}}/\sum|F_{\text{meas}}|]$. A difference Fourier map indicated one atom was placed incorrectly. The correct atomic position was located and the four oxygen atoms per molecule were identified. Two cycles of block-diagonal refinement lowered R to 0·098. An error-analysis program indicated secondary extinction was important. The data were corrected by applying the equation $F^2_{\text{corr}}=F^2_{\text{ob}}(1+2gI_{\text{cal}})$. The value $2g=0{\cdot}32\times10^{-5}$ was obtained by a least-squares fit. Two cycles of refinement with the corrected data lowered R to 0·080. Two cycles of block-diagonal least-squares anisotropic refinement with 1661 reflections gave an R of 0·089. A three-dimensional difference Fourier map was calculated and all 30 hydrogen atoms were located. Peaks consistent with methyl hydrogen atoms were prominent in the difference map. The contributions of the hydrogen atoms to the structure factors were calculated, but the parameters were not refined. Two cycles of full-matrix refinement with 2259 reflections gave a final R value of 0·076.

The function minimized was $\sum w(\Delta F_{\text{meas}})^2$ where $w=[1/\sigma(F_o)]^2$. A final three-dimensional Fourier map contained no peak larger than 0·3 e Å^{-3}. The estimated standard deviations of the parameters were calculated from the inverse of the normal-equations matrix of the last least-squares cycle. All shifts of the parameters during the final cycle were less than 0·1 of the estimated standard deviation. The atomic and thermal parameters along with the estimated standard deviations, are given in Table 1. A list of structure factors has been deposited.*

Table 1. *Atomic and thermal parameters for plastoquinone-*1 *dimer*

Thermal parameters are of the form $\exp[-0{\cdot}25(B_{11}h^2a^{*2}+B_{22}k^2b^{*2}+B_{33}l^2c^{*2}+2B_{12}hka^*b^*+2B_{13}hla^*c^*+2B_{23}klb^*c^*)]$.

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	4053 (2)	5556 (2)	4160 (3)	3·0 (2)	3·0 (2)	2·7 (2)	−0·5 (2)	−0·5 (2)	−0·1 (1)
C(2)	3489 (2)	6075 (2)	4565 (3)	3·6 (2)	2·2 (2)	3·7 (2)	0·2 (2)	−0·6 (2)	−0·3 (2)
C(3)	3120 (2)	5931 (2)	5454 (4)	3·2 (2)	2·7 (2)	4·1 (2)	0·3 (2)	−0·2 (2)	−1·1 (2)
C(4)	3262 (1)	5262 (2)	6029 (3)	3·0 (2)	3·6 (2)	3·1 (2)	0·0 (2)	−0·1 (2)	−0·7 (2)
C(5)	3606 (2)	4643 (2)	5467 (3)	2·7 (2)	2·9 (2)	2·4 (2)	0·3 (1)	0·0 (1)	0·3 (2)
C(6)	3045 (2)	4014 (2)	5295 (3)	3·1 (2)	2·6 (2)	3·3 (2)	−0·2 (2)	0·2 (2)	0·5 (2)
C(7)	3337 (2)	3725 (2)	4245 (3)	2·9 (2)	1·9 (2)	3·1 (2)	−0·4 (1)	−0·3 (1)	0·1 (2)
C(8)	4190 (2)	3536 (2)	4295 (3)	3·3 (2)	2·1 (2)	2·5 (2)	−0·1 (1)	−0·1 (1)	0·3 (1)
C(9)	4422 (2)	3029 (2)	3407 (3)	4·3 (2)	1·9 (2)	3·0 (2)	0·3 (2)	−0·5 (2)	−0·1 (2)
C(10)	4206 (2)	3485 (2)	2421 (3)	3·3 (2)	2·9 (2)	2·5 (2)	−0·3 (2)	−0·5 (1)	−0·4 (2)
C(11)	4775 (3)	3421 (2)	1549 (3)	4·9 (2)	3·6 (2)	2·6 (2)	0·3 (2)	−0·3 (2)	−0·2 (2)
C(12)	5281 (3)	4028 (3)	1339 (4)	4·1 (2)	3·6 (3)	3·2 (2)	0·1 (2)	0·3 (2)	0·4 (2)
C(13)	5059 (2)	4683 (3)	1580 (3)	3·7 (2)	3·4 (2)	2·6 (2)	−0·2 (2)	0·1 (2)	0·6 (2)
C(14)	4319 (2)	4794 (2)	2079 (3)	3·4 (2)	2·9 (2)	2·1 (2)	−0·3 (2)	−0·7 (1)	−0·2 (1)
C(15)	4110 (2)	4239 (2)	2865 (3)	2·8 (2)	2·3 (2)	2·2 (2)	−0·1 (1)	−0·7 (1)	0·2 (2)
C(16)	4497 (2)	4268 (2)	3975 (3)	2·2 (1)	2·7 (2)	2·1 (2)	0·4 (1)	−0·0 (1)	−0·1 (1)
C(17)	3901 (2)	4792 (2)	4357 (3)	2·4 (2)	2·2 (2)	2·4 (2)	−0·1 (1)	−0·2 (1)	0·1 (1)
C(18)	3404 (2)	4381 (2)	3524 (3)	2·5 (2)	2·6 (2)	2·5 (2)	−0·2 (1)	−0·5 (1)	0·0 (2)
O(19)	4614 (2)	5770 (1)	3720 (2)	3·7 (1)	3·1 (1)	4·0 (1)	−0·6 (1)	0·1 (1)	0·1 (1)
C(20)	3438 (3)	6748 (3)	3963 (5)	6·0 (3)	2·8 (2)	6·2 (3)	0·4 (2)	0·1 (2)	0·5 (2)
C(21)	2603 (3)	6442 (3)	6001 (4)	5·1 (3)	4·0 (2)	6·0 (3)	0·6 (2)	0·8 (2)	−1·4 (2)
O(22)	3101 (2)	5209 (2)	6963 (3)	5·9 (2)	5·6 (2)	3·2 (2)	0·9 (2)	0·8 (1)	−0·5 (1)
C(23)	2245 (2)	4274 (3)	5166 (4)	2·7 (2)	4·3 (3)	5·2 (2)	−0·5 (2)	0·4 (2)	−0·3 (2)
C(24)	3074 (2)	3477 (2)	6190 (2)	5·2 (3)	4·0 (3)	4·2 (2)	−0·2 (2)	1·2 (2)	1·0 (2)
C(25)	4030 (3)	2321 (2)	3446 (4)	6·7 (3)	2·5 (2)	3·9 (2)	−0·1 (2)	0·2 (2)	−0·4 (2)
C(26)	5264 (3)	2901 (2)	3476 (4)	5·0 (2)	3·6 (2)	3·4 (2)	1·7 (2)	0·0 (2)	−0·4 (2)
O(27)	4822 (2)	2871 (2)	1050 (3)	7·8 (2)	4·1 (2)	3·9 (2)	0·1 (2)	1·0 (2)	−1·8 (1)
C(28)	5998 (3)	3861 (3)	0780 (4)	5·8 (3)	5·2 (3)	5·5 (3)	0·8 (2)	2·1 (2)	0·2 (2)
C(29)	5487 (3)	5345 (3)	1305 (4)	4·5 (3)	4·5 (3)	4·5 (2)	−0·5 (2)	0·5 (2)	0·6 (2)
O(30)	3915 (2)	5285 (2)	1839 (2)	4·1 (1)	3·6 (2)	3·8 (1)	0·4 (1)	−0·4 (1)	1·0 (2)

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* This table has been deposited with the National Lending Library, England (Supplementary Publication No. 30107). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1 NZ, England.

Table 1 (*cont.*)

Isotropic temperature factor of 2·0 assigned to all hydrogen atoms.

	x/a	y/b	z/c
H(1)	321	713	439
H(2)	315	669	331
H(3)	393	693	376
H(4)	290	678	642
H(5)	225	618	644
H(6)	232	671	550
H(7)	402	447	591
H(8)	221	464	461
H(9)	193	391	482
H(10)	204	445	582
H(11)	357	329	628
H(12)	287	369	683
H(13)	274	307	602
H(14)	305	330	406
H(15)	430	331	498
H(16)	440	193	350
H(17)	360	232	389
H(18)	381	220	276
H(19)	555	334	340
H(20)	544	256	295
H(21)	540	271	417
H(22)	371	333	215
H(23)	644	402	120
H(24)	604	337	059
H(25)	603	414	011
H(26)	585	524	076
H(27)	581	549	189
H(28)	516	573	108
H(29)	505	423	389
H(30)	297	441	306

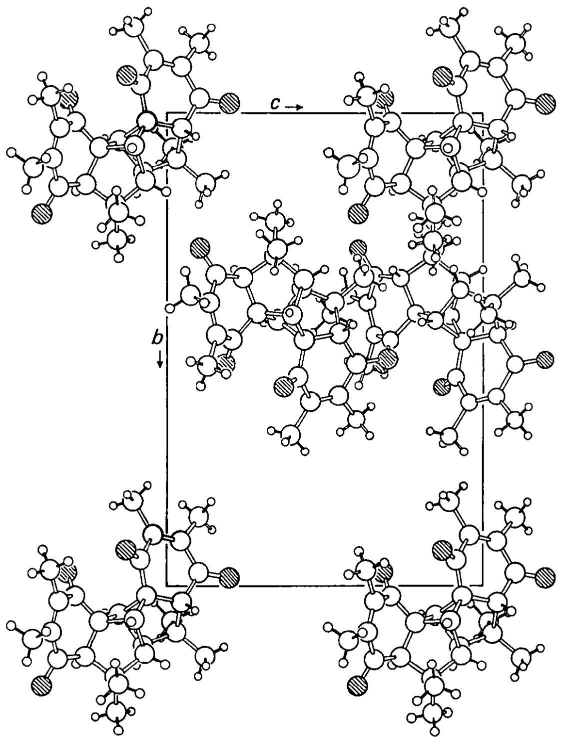
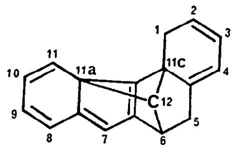


Fig. 1. Projection of the unit-cell contents onto the *bc* plane.

Discussion

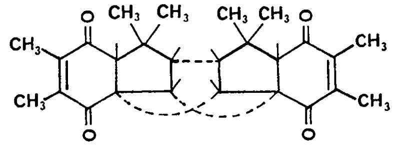
Fig. 1 shows a projection of the unit cell contents onto the *bc* plane. Fig. 2 indicates the numbering system used in all Tables and gives bond lengths and angles within the molecule. This is not the numbering system used in the systematic naming of the compound. The systematic name is derived from the fundamental ring system 6,11a,11c-metheno-1*H*-benzo[*c*]fluorene (III). (Loening, 1971).



(III)

The standard deviations of the bond lengths range from 0·005 Å for oxygen and skeletal carbon atoms to 0·007 Å for methyl groups while the standard deviations of the bond angles are 0·4°.

The fusion points of the monomer units may be visualized by first considering the cyclization of plastoquinone-1 into an indenoquinone derivative followed by oxidative dimerization in which monomers are joined in three positions (IV).



(IV)

The product undoubtedly is formed by a complex step-wise mechanism since fusion at three points is unusual.

The molecule has a pseudo-twofold axis passing through the center of a four-membered ring and bisecting the bond between carbon atoms 7 and 8. All bond lengths related by the twofold axis are equivalent within three standard deviations, and only six equivalent bond angles differ by more than three standard deviations. The n.m.r. spectrum of the molecule reflects the equivalence generated by the pseudo-twofold axis (Watson, Whinnery, Creed, Werbin & Strom 1972).

The fusion produces a strained four-membered ring, two six-membered rings and two additional five-membered rings. These ring systems share a number of common atoms. The four-membered ring has a dihedral angle of 135° along a line through C(16)–C(18). This is less than that found in most substituted cyclobutanes (Schaefer & Walthers, 1971); however, it is close to the value of 137° reported for bycyclo[3·1·1]-heptane (Dallinga & Toneman, 1969). The nonequivalent bond lengths of 1·533 and 1·577 Å are within the reported range of 1·537 to 1·600 Å (Schaefer & Walthers, 1971).

The quinone rings are bent into a boat-like conformation. The four atom systems C(13)C(14)C(15)O(30), C(12)C(11)C(10)O(27), C(17)C(1)C(2)O(19) and C(3)C(4)C(5)O(22) are planar within 0·01 Å; however, the conjugated systems O(30) through O(27) and O(19) through O(22) are not planar. The torsion angle C(29)–C(13)–C(14)–O(30) is 41° while the C(28)–C(12)–C(11)–O(27) angle is 21°. The equivalent angles in the other quinone ring are comparable. The largest deviation is due to a steric interaction between O(19) and O(30) created by the ring fusion, and even with distortion they are separated only by 2·85 Å. Atoms within the quinone rings deviate by more than 0·2 Å from least-squares-fitted planes. Bond lengths in the quinone portions of the molecule are normal.

The average torsion angles around the five-membered rings are given in Table 2 (Edsall, Flory, Kendrew, Liquori, Némethy, Ramachandran & Scheraga, 1966). The five-membered rings C(8)C(9)C(10)C(15)C(16), C(7)C(8)C(16)C(15)C(18) and those related by the twofold axis deviate considerably from planarity. The angle between the least-squares planes fitted to C(8)C(9)C(10)C(15) and C(8)C(16)C(15) is 47° while that fitted to C(7)C(8)C(16)C(18) and C(15)C(16)C(18) is 68°. The strains within the fused-ring systems are reflected in the bond lengths and angles.

Table 2. *Average torsion angles around five-membered rings*

φ 8– 9	−48°	φ 8–16	−62°
φ 9–10	+19	φ16–15	+74
φ10–15	+15	φ15–18	−63
φ15–16	−40	φ18– 7	+28
φ16– 8	+53	φ 7– 8	+21
Δ* = −7°,	φ = 54	Δ = 3°,	φ = 73

* Parameters defined by Altona, Geise & Romers (1968).

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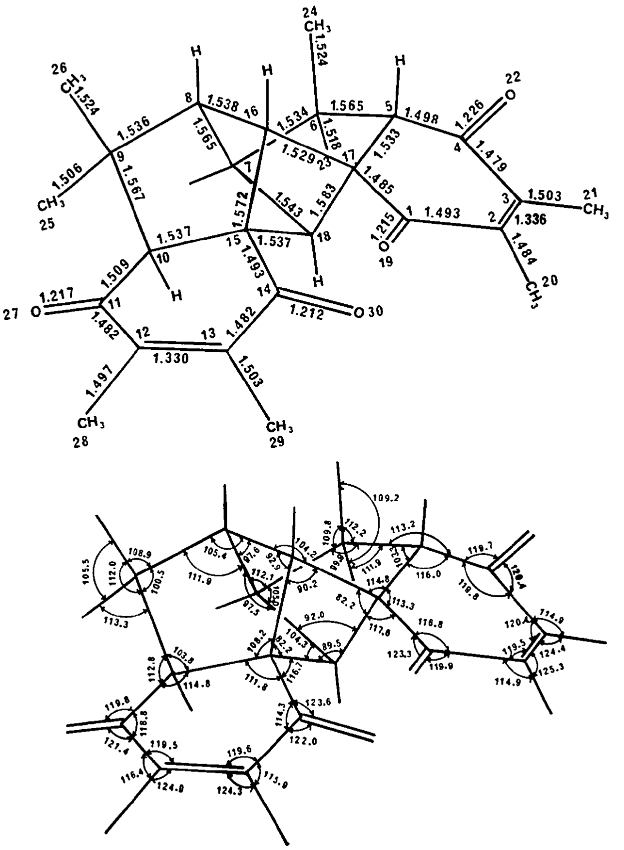

Fig. 2. Bond lengths and angles for the photodimer of plastoquinone-1.

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