Molecular Structure of a Unique Photoproduct of Plastoquinone-1 [2,3-Dimethyl-5-(3-methylbut-2-enyl)-1,4-benzoquinone]

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Summary Near-u.v. irradiation of plastoquinone-1, a model for the electron transport quinones in plants, gives rise to the unique dimer, 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.

In order to simplify the characterization of the photoproducts of plastoquinone-9, the electron-transport quinone found in algae and chloroplasts of plants, we examined the photochemistry of plastoquinone-1. After near-u.v. irradiation of the latter in dry benzene under nitrogen, six photoproducts were discerned by t.l.c. three of which have been characterized.[1] A fourth, following crystallization from hexane–benzene, had m.p. 285°; λ_{max} (EtOH) 252 nm (ϵ 14,100); ν_{max} (C=O) (Nujol) 1685 and 1665 cm^{-1}; M^+ 406·16, indicating an oxidized dimer. The structure could not be determined from the n.m.r. spectrum or by other spectroscopic techniques. The small amount of material precluded degradation studies, but sufficient was available for single-crystal X-ray diffraction analysis.

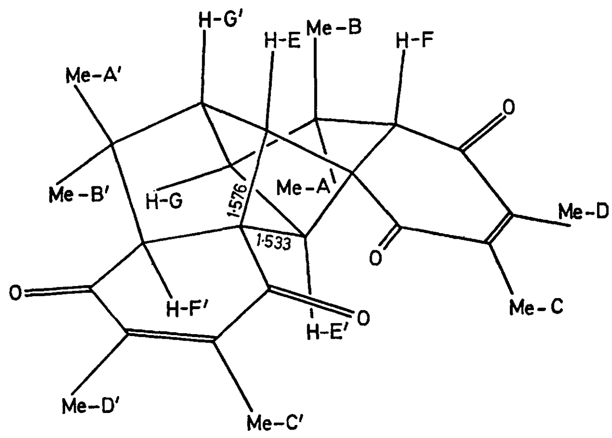

Figure. *Dimer photoproduct of plastoquinone*-1.

The photodimer crystallized in space group *Pccn*; a = 17·849(5), b = 18·820(10), and c = 12·721(5) Å; Z = 8. A total of 2259 counter-collected intensities were used to refine the model anisotropically to a conventional R index of 0·076. The structure (Figure) comprises two bicycloheptane rings which have four carbon atoms in common and incorporate a cyclobutane ring and two spiro-linkages. Space-group limitations do not require the molecule to possess any symmetry; however, within the statistical accuracy of the data, the molecule contains a two-fold axis which passes through the cyclobutane ring. The cyclobutane ring is highly puckered with a dihedral angle of 135° and bond lengths of 1·533(5) and 1·576(5) Å. The small dihedral angle and alternate bond lengths are unusual for cyclobutane systems[2] and this may be attributed to the fusion with the other ring systems. The cyclopentane rings also are strained and exhibit 3 bond lengths of 1·537(6) Å and 2 of 1·567(6) Å. Two carbonyl oxygen atoms are separated by 2·80 Å.

The proposed structure of the photodimer is consistent with its n.m.r. spectrum [δ ($CDCl_3$–C_6D_6, 50:50) 0·73 and 1·22 (each 6H, s), 1·72—1·82 (8H, complex m), 2·01 (6H, q, J 1·1 Hz, Me), 2·09 (2H, s), and 3·45 (2H, t, J 1·8 Hz) p.p.m.]. The multiplet at 1·72—1·82 p.p.m. includes a quartet at 1·76 p.p.m. (J 1·1 Hz) from at least 6 methyl protons and further methyl signals giving at least three lines. With expansion and increased resolution the triplet and the singlet at δ 0·73 p.p.m. formed doublets. A model shows that the Me-A,A′ protons are in the shielding cone[3,4] of the CO group in the opposite ring; the signals at 0·73 and 1·22 p.p.m. can be assigned to Me-A,A′ and

Me-B,B′ and similarly those at 1·76 and 2·01 p.p.m. to Me-C,C′ and Me-D,D′. The overlapping triplets at δ 3·45 are assigned to H-G,G′, since each is flanked by two protons with essentially equal dihedral angles. H-E,E′ should then appear as overlapping doublets (the multiplets overlapped with Me-C,C′). The singlet at δ 2·09 arises from H-F,F′ and the 0·26 p.p.m. upfield shift of this resonance upon dilution to 50% in C_6D_6 is consistent[5,6] with this assignment. The anomalous value for H-G,G′ is attributed to van der Waals deshielding[7] since a model shows steric interference between H-G′ and Me-B and H-G and Me-B′.

The biological importance of the photochemical modification of electron transport quinones is described elsewhere.[1]

We thank the National Science Foundation and The Robert A. Welch Foundation for financial support and Dr. Conrad Cone, University of Texas, Austin, for the mass analysis of the dimer.

(*Received, 28th February* 1972; *Com.* 325.)

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