Synthesis and *X*-Ray Structure of 6-Acetoxy-7,9-Diphenylcyclohepta[*cd*]-isobenzofuran-2,8-dione

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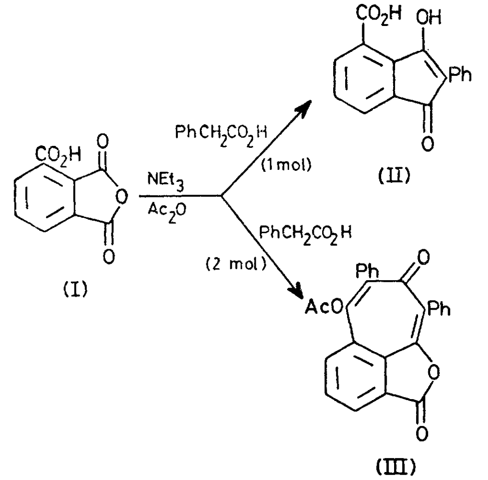
Summary The title compound (III) arose as a by-product during the base-catalysed condensation of hemimellitic anhydride (I) and phenylacetic acid; its *X*-ray crystal structure has been solved by a novel application of direct methods in space group *P*1.

4-Carboxy-2-phenylindane-1,3-dione (II) was synthesised in 10% yield by condensation of phenylacetic acid with hemimellitic anhydride (I) in a mixture of acetic anhydride and triethylamine in an analogous manner to that described by Oskaja and Vanags[1] for the preparation of 4-nitro-2-phenylindane-1,3-dione. A second product (m.p. 202—203 °C) was isolated from the neutral fraction by dry column chromatography in almost the same yield. High resolution mass spectroscopy indicated a molecular formula of $C_{26}H_{16}O_5$, confirmed by elemental analysis. The n.m.r. spectrum showed the presence of one methyl group, probably in an acetyl group, and 13 aromatic protons. The i.r. spectrum showed bands at 1795, 1750, 1600, and 1565 cm^{-1} but no band above 3000 cm^{-1}. It seemed likely that the product contained an enol acetate and that it had arisen from the condensation of two moles of phenylacetic acid and one of hemimellitic anhydride but we were unable to provide a structure which would accommodate the i.r. spectrum. The product was finally shown to be a representative of the new ring system cyclohepta[*cd*]isobenzofuran (III) by *X*-ray crystallography.

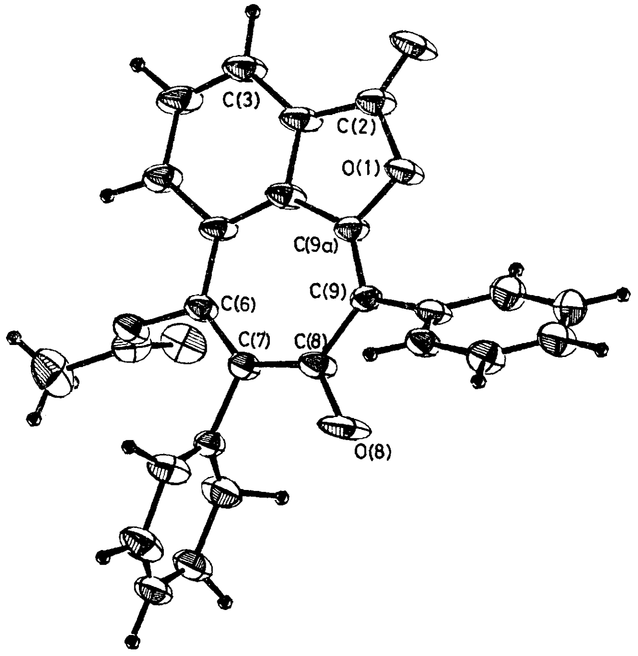
The solution of the crystal structure defied initial attempts using direct methods and vector search techniques. The structure was finally solved *via* a least-squares analysis of quartet invariants. Cosines were estimated for 8668 quartets using the 7-magnitude formula of Hauptman.[2]

The 4000 most reliable were subjected to a least-squares analysis conceptually similar to that employed by Hauptman for triple-phase invariants.[3] Details will be published elsewhere.[4] 24 possible solutions were generated, one of which yielded an E-map in which the positions of 21 of the 31 non-hydrogen atoms were indicated. The structure was completed by Fourier methods and refined to a current R factor of 0·11 for 1771 independent reflections $[I > 3\sigma(I)]$.



The Figure gives a perspective view of the molecule. The bond lengths (mean σ 0·015 Å) of the tropone unit show alternation in good agreement with those found in tropone,[5] heptafulvalene,[6] and in particular the benzotropones investigated by Shimanouchi *et al.*[7] Bond angles differ slightly from published values, probably owing to the fusion of the extra lactone ring into the system.

The fused five-, six-, and seven-membered rings are essentially planar (maximum torsion angle 10°). The two phenyl groups are twisted out of the polycyclic ring plane and the angle between the planes of C(6), C(7), and C(8) and the attached phenyl ring is 86·7°, and C(8), C(9), and C(9a) and its attached phenyl ring is 55·3°. The shortest intermolecular contact (3·2 Å) occurs between O(8) and C(3) of neighbouring molecules.



FIGURE

Crystal data: $C_{26}H_{16}O_5$, $M = 408{\cdot}4$, triclinic, $a = 5{\cdot}067(1)$, $b = 11{\cdot}644(3)$, $c = 8{\cdot}824(2)$ Å, $\alpha = 77{\cdot}74(4)$, $\beta = 85{\cdot}92(3)$, $\gamma = 91{\cdot}06(3)°$, $U = 507{\cdot}2$ Å^3, $F(000) = 212$, $D_c = 1{\cdot}34$ g cm^{-3}, $Z = 1$, space group $P1$, μ (Mo-K_α) = 1·0 cm^{-1}.†

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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