# Crystal Structure of the Photoaddition Product of Iodoform and 3,4,5-Trimethylphenol

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A light yellow photoaddition compound is formed when dichloromethane solutions of iodoform and 3,4,5-trimethylphenol are irradiated with unfiltered light from a mercury vapour lamp. Three-dimensional *X*-ray diffraction analysis of crystals of this compound has shown them to be 4-di-iodomethyl-3,4,5-trimethylcyclohexa-2,5-dienone, indicating that the photoaddition has proceeded wholly by attack by photolytically generated $\cdot CHI_2$ radicals.

The structure was solved by direct methods and refined by full-matrix least-squares to *R* 0·047 for 1437 diffractometer measured intensities. Crystals are orthorhombic, space group *Pbca*, with $Z = 8$ in a cell of dimensions: $a = 17{\cdot}023 \pm 0{\cdot}009$, $b = 10{\cdot}559 \pm 0{\cdot}004$, and $c = 12{\cdot}889 \pm 0{\cdot}019$ Å. Bond distances and angles are all reasonable.

THE photodissociation of iodoform is known to proceed by two pathways, (1) and (2).[1] A variety of compounds (II)—(IV) could result from the attack of

$$\mathrm{CHI_3} \xrightarrow{h\nu} \begin{cases} \mathrm{I\cdot + \cdot CHI_2} & (1) \\ \mathrm{I_2 + {:}CHI} & (2) \end{cases}$$

radicals generated by reactions (1) or (2) on 3,4,5-trimethylphenol (I). These possible products all possess the empirical formula $C_{10}H_{12}I_2O$ suggested by the chemical analysis.[2] The correct structure could not be assigned from consideration of i.r. and u.v. spectra, which indicated only that the product was an α,β-unsaturated ketone. The 60 MHz $^1H$ n.m.r. spectrum consists of only four lines [$CHCl_3$, tetramethylsilane reference, δ 6·29 (5, 2), 5·65 (5, 1), 2·23 (5, 6), 1·50 (5, 3)] [2] which we initially assumed would not distinguish between the possible structures (II)—(IV). Because

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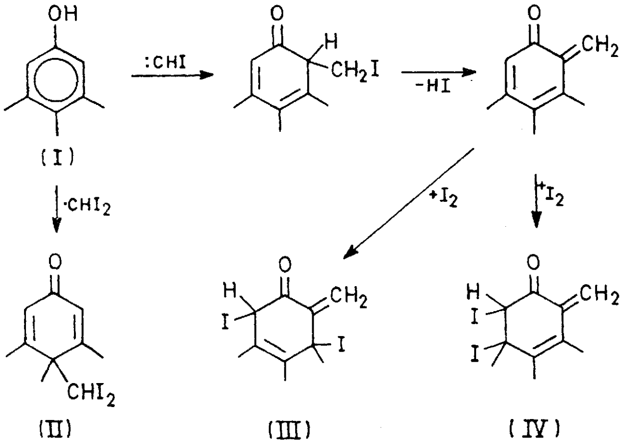
† Taken in part from G. G. Christoph, Ph.D. Thesis, University of Chicago, Chicago, Illinois, 1971.

[1] T. Marolewski and N. C. Yang, *Chem. Comm.*, 1967, 1225.

[2] K. Stiller, unpublished results.

of the biochemical interest in *o*-quinone methides as lignin constituents,[3] we undertook a three-dimensional crystal-structure analysis in order to settle unambiguously the identity of the photochemical product.



Subsequent to this analysis, a 220 MHz $^1H$ n.m.r. spectrum was taken, with results nearly identical to those of the 60 MHz experiment [δ 6·39 (5, 2), 5·73 (5, 1), 2·27 (5, 6), 1·52 (5, 3)], except that the vinyl proton resonance was much sharper than before. The equivalence of these protons argued against the *o*-quinone methide structures (III) and (IV) for the product, in full agreement with the results of the structural analysis reported here, which indicates that the product is (II) 4-di-iodomethyl-3,4,5-trimethylcyclohexa-2,5-dienone. The overall reaction consequently proceeds *via* attack of the $\cdot CHI_2$ radical generated by pathway (1) on (I).

*Description of the Structure.*—The structure of the photoaddition product is shown in Figure 1. Bond distances and angles are listed in Table 1 and final positional and thermal parameters in Table 2. The molecule is quite similar in form and structure to that of *p*-benzoquinone, except, of course, C(4) is saturated and bound to the di-iodomethyl and methyl groups. The C=O distance and the two C=C double bond distances are in quite good agreement with those found[4] in *p*-benzoquinone (1·222 and 1·322 Å). While the two C–C single-bonds adjacent to the keto-group are slightly shorter than the same bonds in *p*-benzoquinone, the differences are within the error of measurement.

TABLE 1

Molecular geometry

| (*a*) Bond angles (°) | | (*b*) Bond distances (Å) | |
|---|---|---|---|
| I(1)–C(8)–I(2) | 110·8(4) | C(8)–I(1) | 2·14 |
| I(1)–C(8)–C(4) | 112·8(4) | C(8)–I(2) | 2·18 |
| I(2)–C(8)–C(4) | 117·0(7) | C(8)–C(4) | 1·56 |
| O(1)–C(1)–C(2) | 121·6(1·3) | C(4)–C(5) | 1·53 |
| O(1)–C(1)–C(6) | 132·1(1·3) | C(5)–C(6) | 1·34 |
| C(2)–C(1)–C(6) | 115·2(1·1) | C(5)–C(10) | 1·50 |
| C(1)–C(2)–C(3) | 125·2(1·1) | C(6)–C(1) | 1·44 |
| C(2)–C(3)–C(4) | 121·1(1·0) | C(1)–O(1) | 1·22 |
| C(2)–C(3)–C(7) | 121·4(1·0) | C(1)–C(2) | 1·45 |
| C(4)–C(3)–C(7) | 117·4(1·0) | C(2)–C(3) | 1·31 |
| C(3)–C(4)–C(5) | 122·9(0·9) | C(3)–C(4) | 1·54 |
| C(3)–C(4)–C(8) | 106·6(0·8) | C(3)–C(7) | 1·51 |
| C(3)–C(4)–C(9) | 106·7(0·8) | C(4)–C(9) | 1·56 |
| C(5)–C(4)–C(8) | 113·8(0·8) | C(8)–H(1) | 0·99 |
| C(5)–C(4)–C(9) | 108·1(0·8) | C(2)–H(2) | 1·11 |
| C(8)–C(4)–C(9) | 108·5(0·9) | C(6)–H(3) | 0·83 |
| C(4)–C(5)–C(6) | 120·5(1·0) | | |
| C(4)–C(5)–C(10) | 121·4(2·2) | | |
| C(6)–C(5)–C(10) | 118·0(1·2) | | |
| C(5)–C(6)–C(1) | 124·7(1·1) | | |

σ For distances involving C or O 0·02 Å, for C–I distances 0·01 Å

The tetrahedral carbon C(4) introduces some bond-angle strain into the cyclohexadiene ring. The distances from C(4) to C(3) and C(5) are quite normal and the bonds to the di-iodomethyl- and methyl-group carbon atoms, although slightly long, are still within error of being normal C–C single bonds. The methyl groups at the 3 and 5 positions both have high (*ca.* 0·3 Å root-mean-square) thermal vibration amplitudes perpendicular to the bonds connecting them to the rest of the molecule, and consequently would be expected to possess an apparent shortening of *ca.* 0·03 Å because of the librational motion.[5] The corrected values for the C(3)—C(7) and C(5)–C(10) bond lengths would then be *ca.* 1·54 and 1·53 Å, respectively. The bonds between C(8) and the two iodine atoms are both of normal length.

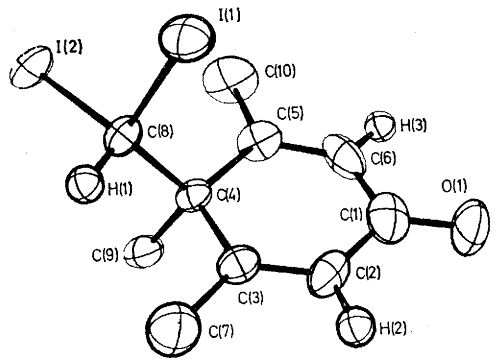


FIGURE 1 A drawing of the molecule: thermal ellipsoids enclose 50% probability

The inner angles around the cyclohexadiene ring are consistent with the strain caused by the tetrahedral nature of C(4). The inner angle at C(4) (1130) is *ca.* 4° greater than the tetrahedral value, and the adjacent single bonds of 1·54 Å result in the non-bonded C(3) · · · C(5) distance being 2·56 Å, *ca.* 0·1 Å greater than C(2) · · · C(6). The inner angles at C(2) and C(6) are slightly expanded to 125° to accommodate the larger spread. The inner angle at C(1), 115°, is somewhat less than the 118° found for *p*-benzoquinone, but the difference is barely 2σ.

The molecule is only slightly puckered as a consequence of C(4) being tetrahedral. This deformation gives the molecule a somewhat chair-like form, although the dihedral angles are quite small. The angle between the least squares planes containing O(1), C(1), C(2), and C(6) [plane (*A*)] and C(2), C(3), C(5), and C(6)

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[3] J. M. Harkin, *Adv. in Chem.*, 1966, **59**, 65.
[4] J. Trotter, *Acta Cryst.*, 1960, **13**, 86.
[5] W. R. Busing and H. A. Levy, *Acta Cryst.*, 1964, **17**, 142.

TABLE 2

Final positional ($\times 10^4$; for iodine $\times 10^5$) and thermal parameters * (anisotropic $\times 10^4$, for iodine $\times 10^5$), with estimated standard deviations in parentheses

| | $x$ | $y$ | $z$ | $B$ | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| I(1) | 39166(5) | 3883(8) | 40670(5) | | 302(3) | 826(9) | 348(4) | 28(5) | −1(3) | −106(5) | |
| I(2) | 29402(4) | −25494(4) | 36506(6) | | 271(2) | 1061(10) | 507(5) | −129(6) | 72(3) | 106(7) | |
| O(1) | 4489(7) | 2246(9) | 374(7) | | 64(5) | 82(11) | 58(6) | −2(6) | 18(5) | 27(7) | |
| C(1) | 4340(9) | 1259(12) | 832(9) | | 46(6) | 62(12) | 45(7) | −5(8) | −3(6) | −10(9) | |
| C(2) | 4954(7) | 490(11) | 1293(8) | | 32(4) | 55(10) | 36(6) | −20(7) | 8(4) | −13(8) | |
| C(3) | 4839(6) | −536(11) | 1840(7) | | 20(3) | 63(11) | 29(5) | −2(6) | 2(4) | −5(7) | |
| C(4) | 4007(6) | −1083(10) | 1991(7) | | 20(3) | 61(10) | 21(5) | 0(6) | 1(3) | −1(6) | |
| C(5) | 3364(6) | −247(14) | 1522(8) | | 17(3) | 104(15) | 34(6) | −2(6) | −10(3) | 0(8) | |
| C(6) | 3554(8) | 783(13) | 962(10) | | 43(5) | 78(13) | 44(7) | 27(8) | −13(6) | −1(9) | |
| C(7) | 5515(7) | −1262(14) | 2305(11) | | 26(4) | 109(16) | 72(10) | 0(8) | 1(5) | 17(11) | |
| C(8) | 3907(6) | −1325(10) | 3177(8) | | 20(3) | 58(10) | 37(5) | −7(6) | 4(4) | 5(7) | |
| C(9) | 3991(6) | −2386(12) | 1420(8) | | 26(3) | 76(12) | 41(6) | 2(8) | 10(4) | −4(8) | |
| C(10) | 2513(7) | −597(19) | 1604(11) | | 20(4) | 160(22) | 84(10) | 4(9) | −13(5) | 1(13) | |
| H(1) | 4397 | −1792 | 3356 | 5·0 | | | | | | | |
| H(2) | 5515 | 748 | 1211 | 5·0 | | | | | | | |
| H(3) | 3137 | 1270 | 619 | 5·0 | | | | | | | |
| H(4) | 5968 | −1230 | 1821 | 7·7(1·3) | | | | | | | |
| H(5) | 5349 | −2155 | 2426 | 7·7(1·3) | | | | | | | rotational error 0·05 radians |
| H(6) | 5660 | − 857 | 2982 | 7·7(1·3) | | | | | | | |
| H(7) | 3454 | −2748 | 1460 | 5·4(1·1) | | | | | | | |
| H(8) | 4188 | −2301 | 729 | 5·4(1·1) | | | | | | | rotational error 0·04 radians |
| H(9) | 4358 | −2987 | 1843 | 5·4(1·1) | | | | | | | |
| H(10) | 2260 | −268 | 2292 | 2·6(0·6) | | | | | | | |
| H(11) | 2179 | −202 | 1030 | 2·6(0·6) | | | | | | | rotational error 0·03 radians |
| H(12) | 2405 | −1540 | 1594 | 2·6(0·6) | | | | | | | |

* The form of the anistropic thermal parameter is: exp $-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hl\beta_{13} + 2hk\beta_{12} + 2kl\beta_{23})$.

[plane ($B$)] is only 3·1°, while that between plane ($B$) and the plane containing C(3), C(4), and C(5) [plane ($C$)] is 3·7°. The atoms comprising plane ($A$) are coplanar, as are the atoms comprising plane ($B$).

Figure 1 illustrates the thermal motion in the molecule. The wagging motion of the methyl groups and the small vibration amplitudes of the massive iodine atoms and of the atoms linked to them are as expected. The unusual thermal motion of the ring carbons, in particular the large amplitudes of C(2) and C(6) along the bonds linking them to C(1), indicate a rigid-body libration in the plane of the ring about C(4). The iodine amplitudes also appear to be a consequence of this torsional oscillation about the C(4)–C(8) bond.

TABLE 3

Close intermolecular approaches (Å)

| | | | |
|---|---|---|---|
| I(1) · · · H($11^{VI}$) | 3·15 | I(2) · · · H($10^{II}$) | 3·38 |
| I(1) · · · O($1^{III}$) | 3·17 | O(1) · · · H($8^{I}$) | 2·66 |
| I(2) · · · H($2^{IV}$) | 3·19 | O(1) · · · H($1^{V}$) | 2·70 |

Roman numerals refer to the equivalent positions relative to the reference molecule at $x, y, z$:

I $-x, -y, -z$
II $\frac{1}{2} - x, \frac{1}{2} + y, z$
III $x, \frac{1}{2} - y, \frac{1}{2} + z$
IV $-x, \frac{1}{2} + y, \frac{1}{2} - z$
V $\frac{1}{2} - x, -y, \frac{1}{2} + z$

All intermolecular close approaches (Table 3) appear to be normal van der Waals contacts. The packing is illustrated in Figure 2. Pairs of molecules related by centres of symmetry have the ring moiety planes parallel to one another. The closest approach between such pairs is C(2) · · · C(2′) on the related molecule (3·5 Å). The perpendicular distance between the planes of the two related molecules (3·3 Å) is essentially the van der Waals stacking distance between aromatic molecules.

EXPERIMENTAL

*Preparation of* (II).[3]—A dichloromethane solution of iodoform and (I) was irradiated with unfiltered light from a 450 W Hanovia mercury vapour lamp in a quartz immersion well. The product was chromatographically isolated from unreacted starting materials, and recrystallized (× 2) from benzene as fine pale yellow polyhedral crystals. The spacegroup was determined from precession photographs. The crystal used for the measurement of cell constants and for

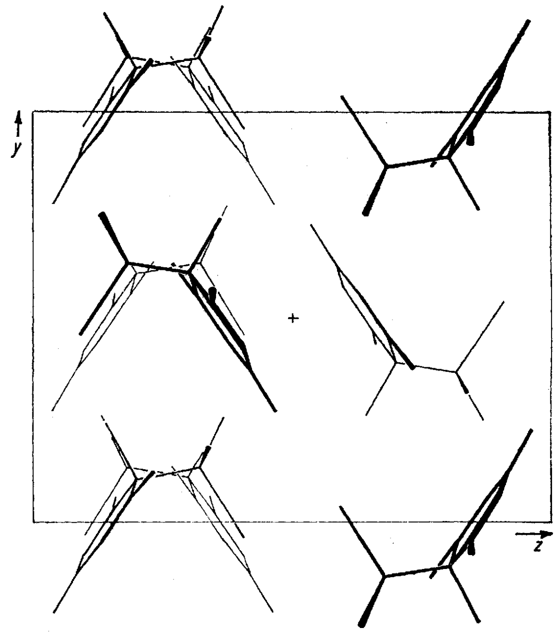

FIGURE 2 Molecular packing in the crystal: the origin is at the centre. Half the molecules related by the $a$ glide have been omitted for clarity

data collection was a truncated rhombohedral pyramid with prominent faces (100), (111), (11$\bar{1}$), (1$\bar{1}$1), and (1$\bar{1}\bar{1}$), and maximum dimensions along the *a*, *b*, and *c* axes of 0·15, 0·40, and 0·50 mm. Accurate cell constants were determined by Ladell's ω-method for the PAILRED diffractometer,[6] using quartz-monochromatized Mo-$K_\alpha$ radiation.

*Crystal Data.*—$C_{10}H_{12}I_2O$, $M = 402{\cdot}02$. Orthorhombic, $a = 17{\cdot}023 \pm 0{\cdot}009$, $b = 10{\cdot}559 \pm 0{\cdot}004$, $c = 12{\cdot}889 \pm 0{\cdot}019$ Å, $U = 2318{\cdot}5$ Å$^3$, $D_m = 2{\cdot}27 \pm 0{\cdot}05$ g cm$^{-3}$, $Z = 8$, $D_c = 2{\cdot}297 \pm 0{\cdot}03$ g cm$^{-3}$. Space group *Pbca* (No. 81, $D_{2h}^{15}$) from systematic absences: $h0l$, $l = 2n + 1$; $hk0$, $h = 2n + 1$; and $0kl$, $k = 2n + 1$. Mo-$K_\alpha$ radiation, $\lambda = 0{\cdot}7107$ Å; $\mu$(Mo-$K_\alpha$) = 54·49 cm$^{-1}$.

Intensity measurements were carried out on a PAILRED automated diffractometer with graphite-monochromatized Mo-$K_\alpha$ radiation. The *b* axis of the crystal was aligned collinear with the ω axis of the diffractometer. Data was collected by the ω-scan technique with scan ranges of 3·0° and scan rate of 2·5° min$^{-1}$ and background counts of 10 s at each end of the scans. Only reflections with $2\theta < 60°$ were measured. Although the crystal finally became deep red-purple, remeasurement of several $hll$ reflections indicated that there had been no measureable decay during data collection.

The intensities were reduced to $F$ values in the usual way and multiply measured reflections averaged. Normalized structure factors were calculated and the symbolic-addition procedure [7] as coded in Dewar's program MAGIC [8] was used to solve the phase problem. Iodine atoms were located on an $E$ map generated by use of the phases thus determined. Remaining atoms were located in successive cycles of structure-factor Fourier calculations: $R$ based on 1691 reflections for all non-hydrogen atoms, was then 0·21. Full-matrix least-squares refinement of the positional and thermal parameters (iodine atoms anisotropic) reduced $R$ to 0·12. Further refinement was hindered, owing to systematic errors from the neglect of absorption effects. Accordingly, absorption corrections were calculated by the gaussian integration method [9] using a 6 × 6 × 6 grid.

Hydrogen atoms were successfully located on subsequently calculated difference Fourier maps. Methyl groups were given fixed tetrahedral geometry (assuming C–H 1·0 Å) and only the degree of rotation about the C–C bond was varied as a least-squares parameter. In addition, the thermal parameters for the oxygen atom and the carbon atoms were refined anisotropically. Inclusion of the hydrogen positional parameters and an empirical weighting scheme in the refinement led to a final $R$ of 0·047 for the 1437 independent, most intense $F_o$ values ($>13$ e$^-$, *ca.* 1σ above background). The quantity minimized was $[\Sigma w(|F_o| - |F_c|)^2/wF_o^2]^{\frac{1}{2}}$ (= $R'$, which was 0·054 at the conclusion of the refinement); weights $w$ are defined by $w = \sigma^{-2}$, where:

$$\sigma = \begin{cases} 2{\cdot}8 + (60\text{-}F_o) \times 0{\cdot}0325 & F_o < 60 \\ 2{\cdot}8 & 60 \leqslant F_o \leqslant 100 \\ 2{\cdot}8 + (F_o\text{-}100) \times 0{\cdot}025 & F_o > 100 \end{cases}$$

with the $F_o$ and σ in units of electrons. Observed and calculated structure factors and thermal amplitude parameters are listed in Supplementary Publication No. SUP 21232 (3 pp., 1 microfiche).* Atomic scattering factors for neutral atoms used in the refinement were taken from ref. 10. The shifts in the parameters in the final least squares cycle were all $<0{\cdot}5\sigma$ obtained from the elements of the inverted matrix from the last cycle. The 'goodness of fit,' or standard deviation of an observation of unit weight was 1·31, which would indicate that the sigmas of the $F$ values had been chosen too large and/or that there was some residual systematic error in the data, probably from inaccuracies in the absorption correction. Although such inaccuracies presumably could have been removed by a more extensive, more expensive treatment, we did not feel the value to be gained justified the expenditure. The final difference map reflected these errors: there were four peaks and several holes of *ca.* 1·1—0·9 eA$^{-3}$, all associated with the iodine atoms. The remaining peaks ranged downward from *ca.* 0·5 eA$^{-3}$ and were randomly distributed in the cell.

As is common in structures containing one or two very heavy atoms, the light-atom parameters in this molecule have been determined with substantially lower precision than those for the heavy atoms (Table 1). The estimated error in the C–I distances (0·01 Å) is due wholly to the uncertainty in the position of C(8). It is reassuring that chemically equivalent bond distances and angles in this structure are equal, within the limits of our measurements.

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

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