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The Synthesis and X-ray Structure of 2,6-Dimethyl-3,5-dipropynylcyclohexa-2,5-diene-1,4-dione ($C_{14}H_{12}O_2$): A Symmetrically Substituted *p*-Benzoquinone

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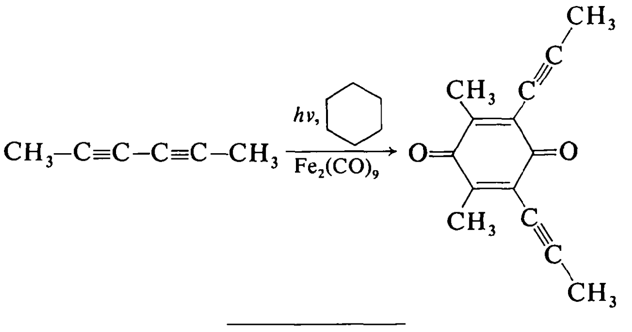
A derivative of *p*-benzoquinone has been isolated and structurally characterized as a reaction product from the photolysis of $Fe_2(CO)_9$ and dimethyldiacetylene (DMDA) in cyclohexane. The product is one of two possible isomers; this one contains propynyl groups on the 3,5 ring positions and methyl groups on the 2,6 ring positions. The molecule is considered to be formed from an intermediate symmetrically substituted cyclopentadienone iron tricarbonyl complex. The deep-yellow quinone crystallizes in space group $P\bar{1}$ with a = 9·722 (1), b = 4·812 (3), c = 12·812 (7) Å, α = 96·20 (6), β = 91·15 (7), γ = 81·92 (9)°, D_m = 1·17, D_c = 1·195 g cm^{-3}, μ(Mo $K\alpha$) = 0·85 cm^{-1}, crystal size 0·14 × 0·17 × 0·62 mm. The structure was solved by Patterson methods and refined by least-squares calculations to R = 0·045 and R_w = 0·048. There were 694 observed data.

Introduction

Reactions of metal carbonyls and acetylenes lead to a variety of organometallic complexes and organic compounds (Bowden & Lever, 1968; Hübel, 1968; Vollhardt, 1977; Yur'eva, 1974). Obviously the type and yield of product depend upon reaction conditions and the nature of the starting materials. The product molecules may consist of one or more acetylene units combined with carbon monoxide or fragments of metal carbonyls to form ring systems. The ring systems are frequently π-complexed to metal carbonyl groups such as $Fe(CO)_3$, $Mn(CO)_3$, *etc.* There are also situations where the products are devoid of any metal atoms, consisting solely of C, H and O plus whatever other atom types may be substituted on the acetylene units. The metal carbonyls can be viewed as catalysts in the formation of such organic products; the organometallic complexes are considered to be intermediates in the overall reaction sequence.

This study concerns the synthesis and structural elucidation of a substituted *p*-benzoquinone using $Fe_2(CO)_9$ and dimethyldiacetylene (DMDA) as starting materials. The reaction can be formulated as



The X-ray analysis was undertaken to resolve the ambiguity of isomer formation.

Experimental

Dimethyldiacetylene (DMDA) (7·8 g, 100 mmol) and $Fe_2(CO)_9$ (18·2 g, 50 mmol) were dissolved in 125 ml of dry, degassed cyclohexane and photolyzed under nitrogen for 2½ h (Hanovia high-pressure Hg lamp, Pyrex vessel). The reaction mixture was filtered, and the remaining solid washed with cyclohexane. The solid was then thoroughly extracted with benzene, and the benzene-soluble materials were chromatographed on a 25 × 230 mm silica gel column. Benzene eluted several bands, the second one of which was the title compound, 2,6-dimethyl-3,5-dipropynylcyclohexa-2,5-diene-1,3-dione. The yield was <1%. Elemental analysis: Found, 79·04%C, 5·66%H. Calculated for $C_{14}H_{12}O_2$, 79·22%C, 5·70%H. Infrared bands: C≡C(KBr), 2208*s*, 1776*m*; C=O(CHCl$_3$), 1657*s*, 1632*s*; C=C(KBr), 1580*s*; other bands (KBr) 2959*w*, 2915*w*, 1425*m*, 1368*m*, 1348*m*, ~1292*sb*, 1130*s*, 1060*w*, 1021*w*, 998*w*, 952*m*, 932*m*, 895*mb*, 768*w*, 749*m*, and 718*m*. PMR: 7·82 τ,*s* (CDCl$_3$); 7·94 τ,*s*(1) and 8·39 τ,*s*(1) (C_6H_6).

Crystal data

Deep-yellow square needles. M.p. 106–107°C (decomposition). Triclinic, $P\bar{1}$; a = 9·722 (1), b = 4·812 (3), c = 12·812 (7) Å, α = 96·20 (6), β = 91·15 (7), γ = 81·92 (9)°, U = 589·9 (8) Å^3, Z = 2, D_c = 1·195, D_m = 1·17 g cm^{-3}. Mo $K\alpha$ radiation (λ = 0·71069 Å). Crystal size: 0·14 × 0·17 × 0·62 mm. μ(Mo $K\alpha$) = 0·85 cm^{-1}.

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Suitable crystals for an X-ray analysis were grown from a diethyl ether/isopentane solution. Unit-cell dimensions were determined from a least-squares refinement of carefully measured 2θ angles for 40 independent reflections. Intensity data were collected on a manual General Electric XRD 700 diffractometer equipped with balanced Zr/Y filters. The stationary crystal/stationary counter method of data collection was employed with 10 s counts being recorded for each filter. The diffractometer take-off angle from the X-ray tube was set at 5·0°. Of 1542 measurements, 694 were considered observed having $[I_{\rm Zr} - 2\sigma(I)_{\rm Zr}] - [I_{\rm Y} + 2\sigma(I)_{\rm Y}] \geq 100$ counts, where $I_{\rm Zr}$ and $I_{\rm Y}$ are the counts for the zirconium and yttrium filters respectively, and $\sigma(I)_{\rm Zr}$ and $\sigma(I)_{\rm Y}$ are the usual standard errors from counting statistics. A weight w was assigned to each reflection where $w = 1/\sigma^2_{F_o}$ and $\sigma(F_o) = \frac{1}{2}\{({\rm LP}^{-1}).[I_{\rm Zr} + I_{\rm Y}]/(I_{\rm Zr} - I_{\rm Y})\}^{1/2}$, and LP is the Lorentz–polarization factor. $2\theta_{\rm max}$ was 50·00° or $(\sin\theta/\lambda)_{\rm max} = 0{\cdot}5385$ Å^{-1}. No corrections were made for absorption or for crystal decay.

The structure was solved by Patterson methods assuming the molecular configuration to be that of a *p*-benzoquinone with $-{\rm CH_3}$ groups bonded to the 2,6 ring positions and $-{\rm C{\equiv}CCH_3}$ groups bonded to the 3,5 ring positions. This isomer has $2mm$ point-group symmetry. The other possible isomer would have $2/m$ point-group symmetry with $-{\rm CH_3}$ groups at the 2,5 positions and $-{\rm C{\equiv}CCH_3}$ groups at the 3,6 positions. Both isomers are consistent with the spectroscopic data, but the former was chosen since the compound was thought to be formed from the intermediate 3,4-bis(1-propynyl)-2,5-dimethylcyclopentadienonetricarbonyliron(0), a molecule with m point group symmetry (Cash & Pettersen, 1978). The plane and orientation of the quinone molecule were determined from a consistent set of six vector peaks near the origin of the Patterson map. One of these vectors (magnitude 1·20 Å) defined the position of the O atoms on the ring. The molecular center was defined by a seventh vector of magnitude 7·78 Å. Simple packing considerations eliminated one of the two possible molecular orientations.

Coordinates were calculated for all the C and O atoms based on the model described above. The structure was refined by full-matrix least-squares calculations to a final R index of 0·045 where $R = (\sum|F_o - |F_c||)/\sum F_o$ and a final $R_w = 0{\cdot}048$, where $R_w = [(\sum w|F_o - |F_c||^2)/\sum wF_o^2]^{1/2}$ and w is the weight of each reflection equal to $1/\sigma^2_{F_o}$. The final cycles of refinement included anisotropic temperature factors for the C and O atoms. All the H atoms (12) were included in the structure factor calculations, but their parameters were not allowed to refine. Each was assigned a fixed isotropic temperature factor of $U = 0{\cdot}05$ Å^2. Coordinates for the six H atoms attached to C(12) and C(13) were determined from a difference Fourier map calculated before the final cycles of refinement. A disordered model was used for the remaining H atoms and effectively places twelve half-atoms at geometrically idealized positions; six of these half-atoms bond to C(11) and six bond to C(16). The largest shift/error in the final refinement cycle was 0·30 and for most parameters it was 0·10 or less. A final difference map had a maximum residual peak of 0·13 e Å^{-3}. Atomic fractional coordinates are listed in Table 1. Scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974). Most of the crystallographic computations were done using the *SHELX* 76 program system (Sheldrick, 1976).

At the suggestion of a referee, all the measured data were included in the structure factor calculations. In this case F was computed in the usual way for all measurements with $[I_{\rm Zr} - 2\sigma(I)_{\rm Zr}] - [I_{\rm Y} + 2\sigma(I)_{\rm Y}] > 0$ counts. As in the previous computation for F_o, $I_{\rm Zr}$ had a scattering background correction subtracted from it. There were 998 reflections with a net positive count. Those reflections with zero or negative counts (544)

Table 1. *Fractional coordinates for* $\rm C_{14}H_{12}O_2$

Estimated standard errors are given in parentheses.

	x	y	z
C(1)	0·3365 (7)	0·1960 (10)	0·2058 (4)
C(2)	0·3042 (6)	0·4234 (10)	0·2950 (4)
C(3)	0·1749 (6)	0·4853 (10)	0·3342 (4)
C(4)	0·0631 (7)	0·3341 (11)	0·2881 (4)
C(5)	0·0921 (6)	0·1077 (10)	0·2003 (4)
C(6)	0·2225 (6)	0·0419 (10)	0·1622 (4)
O(7)	0·4533 (4)	0·1381 (7)	0·1705 (3)
O(8)	−0·0548 (4)	0·3927 (8)	0·3225 (3)
C(9)	0·4164 (7)	0·5646 (12)	0·3316 (5)
C(10)	0·5101 (7)	0·6837 (12)	0·3589 (4)
C(11)	0·6296 (6)	0·8318 (14)	0·3896 (5)
C(12)	0·1386 (6)	0·7058 (12)	0·4201 (4)
C(13)	−0·0239 (6)	−0·0358 (12)	0·1590 (5)
C(14)	0·2593 (5)	−0·1779 (12)	0·0786 (4)
C(15)	0·2915 (5)	−0·3556 (12)	0·0096 (4)
C(16)	0·3337 (6)	−0·5719 (11)	−0·0752 (4)

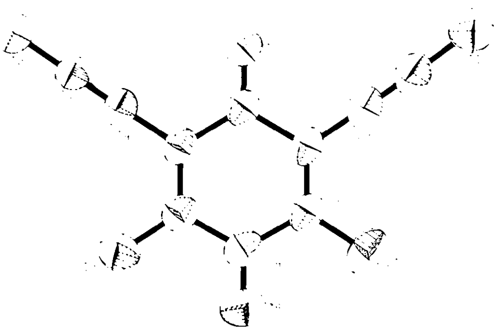

Fig. 1. The molecular structure of $\rm C_{14}H_{12}O_2$. Ellipsoids are at 50% probability.

were assigned a value of $F_o = 1{\cdot}13$, or half the value of the minimum F_o calculated. σ for these reflections was set at 0·40. The structural parameters were refined to convergence using all the data in the least-squares calculations. The final R index is 0·095 and R_w = 0·107. There were no significant structural changes and the coordinates reported are those using the limited data set.*

Rapid solution of this structure was prevented by the early observation of a single sharp PMR peak at 7·82τ in $CDCl_3$ solution. A structure model was proposed which contained six NMR equivalent H atoms. A suggestion to use benzene as a solvent resolved the sharp singlet into a doublet at 7·94τ(1) and 8·39τ(1). Evidently solvent effects of the $CDCl_3$ equalized the electronic shielding of all six H nuclei.

Results and discussion

Fig. 1 is an *ORTEP* plot (Johnson, 1965) of the molecular structure. Table 2 presents the bond distances and valence angles with estimated standard deviations. The results clearly show the synthesis of the molecule from starting materials. The C(2)—C(3) and C(5)—C(6) triple bonds of what were two separate DMDA molecules have been reduced to double bonds and bridge to one another *via* CO units obtained from the $Fe_2(CO)_9$. The resulting quinone is planar as expected, although the propynyl groups deviate from the least-squares plane containing atoms C(1) through C(6). Deviations (Å) were calculated to be: C(9) −0·04, C(10) −0·10, C(11) −0·21, C(14) 0·04, C(15) 0·05, and C(16) 0·06.

Table 2. *Bond distances* (Å) *and valence angles* (°) *for* $C_{14}H_{12}O_2$

C(1)—C(2)	1·500 (7)	C(2)—C(9)	1·411 (8)
C(2)—C(3)	1·345 (6)	C(9)—C(10)	1·171 (7)
C(3)—C(4)	1·471 (7)	C(10)—C(11)	1·472 (8)
C(4)—C(5)	1·481 (7)	C(6)—C(14)	1·434 (7)
C(5)—C(6)	1·352 (6)	C(14)—C(15)	1·176 (7)
C(6)—C(1)	1·486 (7)	C(15)—C(16)	1·444 (7)
C(3)—C(12)	1·456 (7)	C(1)—O(7)	1·214 (5)
C(5)—C(13)	1·464 (7)	C(4)—O(8)	1·220 (6)

C(2)—C(1)—C(6)	118·4 (6)	C(3)—C(4)—C(5)	120·6 (5)
C(2)—C(1)—O(7)	120·8 (5)	C(3)—C(4)—O(8)	120·2 (5)
C(6)—C(1)—O(7)	120·8 (5)	C(5)—C(4)—O(8)	119·2 (6)
C(1)—C(2)—C(3)	120·5 (5)	C(4)—C(5)—C(6)	119·3 (5)
C(1)—C(2)—C(9)	115·6 (6)	C(4)—C(5)—C(13)	117·6 (6)
C(3)—C(2)—C(9)	123·9 (5)	C(6)—C(5)—C(13)	123·0 (5)
C(2)—C(9)—C(10)	177·9 (7)	C(5)—C(6)—C(1)	121·0 (5)
C(9)—C(10)—C(11)	178·1 (7)	C(5)—C(6)—C(14)	122·6 (5)
C(2)—C(3)—C(4)	120·1 (5)	C(1)—C(6)—C(14)	116·3 (5)
C(2)—C(3)—C(12)	122·4 (5)	C(6)—C(14)—C(15)	178·8 (6)
C(4)—C(3)—C(12)	117·5 (6)	C(14)—C(15)—C(16)	178·8 (6)

A discussion of isomer formation has been presented in connection with the structure determination of 3,4-bis(1-propynyl)-2,5-dimethylcyclopentadienonetricarbonyliron(0) $[(DMDA)_2COFe(CO)_3]$ (Cash & Pettersen, 1978). This product is a symmetric isomer obtained from the photo-reaction of $Fe(CO)_5$ and DMDA. It was also observed as a product of the reaction reported here and appeared in the cyclohexane after extraction of the solid reaction product. This compound is assumed to be an intermediate to the formation of the quinone.

A number of other quinone syntheses *via* metal carbonyl catalysts have been reported. The reaction of dimethylacetylene (DMA) and $Mn(CO)_5$ in sunlight yields duroquinone as a product $[(DMA)_2(CO)_2]$ (Markby, Sternberg & Wender, 1959). UV irradiation of a DMA/$Fe(CO)_5$ solution also leads to duroquinone as a product (Sternberg, Markby & Wender, 1958). The reaction of 3-hexyne (diethylacetylene) and $[Rh(CO)_2Cl]_2$ in refluxing benzene yields tetraethylcyclopentadienone rhodium chloride (40%) and 2,3,5,6-tetraethyl-*p*-benzoquinone (8%) (Maitlis & McVey, 1965). Both possible substituted *p*-benzoquinone isomers are observed as products from the photolysis of $Fe(CO)_5$ and the asymmetric cyclopropylacetylene in either hexane or CH_2Cl_2 (Victor, Ben-Shoshan & Sarel, 1973). It is interesting that the triple bond participates in compound formation, while the cyclopropyl group remains intact as a substituent group on the quinone ring. The isomers were distinguished by their melting points. The yield of individual isomers was not reported, but the total overall yield was 70%.

The molecules pack in layers, but are staggered in a way that avoids nearly all overlap between layers. The equation describing the least-squares plane containing atoms C(1) through C(6) is:

$$1{\cdot}047x - 3{\cdot}498y + 9{\cdot}311z = 1{\cdot}588\ \text{Å},$$

Table 3. *Intermolecular contacts less than* 3·55 Å *for* $C_{14}H_{12}O_2$

Contact	Distance (Å)	Symmetry operation to generate second atom
O(7)···C(16)	3·32 (2)	$1-x, -1-y, -z$
O(7)···C(10)	3·41 (2)	$x, -1+y, z$
O(7)···C(16)	3·46 (2)	$1-x, -y, -z$
O(1)···C(15)	3·47 (2)	$x, 1+y, z$
O(8)···C(12)	3·51 (2)	$-x, 1-y, 1-z$
O(14)···C(2)	3·52 (2)	$x, -1+y, z$
O(8)···C(11)	3·54 (2)	$-1+x, y, z$
C(10)···C(1)	3·54 (2)	$x, 1+y, z$
C(15)···C(7)	3·54 (2)	$x, -1+y, z$

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* Lists of structure factors, anisotropic thermal parameters and H-atom positional parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33838 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

where x, y, and z are fractional coordinates and the coefficients are in Å. This plane is nearly parallel to the $(0\bar{1}3)$ crystallographic plane. The spacing between the molecular planes related by the inversion at 0,0,0 is 3·176 Å and that related by the inversion at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ is 3·684 Å. However, there are only a few intermolecular contacts less than 3·55 Å. These are listed in Table 3.

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Structure of a Photo-addition Product of an α,β-Unsaturated Ketone and Allene, $C_{14}H_{22}O$†

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$C_{14}H_{22}O$ is triclinic, $P\bar{1}$, $a = 13·173$ (5), $b = 13·460$ (5), $c = 13·038$ (6) Å, $\alpha = 104·76$ (6), $\beta = 105·33$ (4), $\gamma = 113·59$ (5)°, $Z = 6$. The structure has been refined to $R = 0·060$ and $R_w = 0·061$ for the 4591 observed reflexions. The molecule contains a central six-membered ring which is *cis*-fused to a four-membered ring on one side and to a six-membered ring on the other. The central ring is a distorted chair, with substituents OH equatorial and CH_3 axial, and the other six-membered ring is a regular chair. The valency and torsion angles of the central ring appear to be susceptible to small but significant changes depending on the position of OH. The three independent molecules of the unit cell and their centrosymmetric equivalents are linked by O–H···O hydrogen bonds into hexamers. No links are present between the molecules of different hexamers.

Introduction

In order to study the geometry and conformational preferences of the $n.\pi^*$ excited states of α,β-unsaturated ketones, Wiesner (1977) and his collaborators prepared a number of photochemical addition compounds. Through addition of allene to the α,β-unsaturated ketone (I), the adduct (II) was produced, and this was subsequently reduced by sodium borohydride to compound (III) whose structure is reported here. The crystals were obtained from a solution of methanol and H_2O as colourless prisms which lose diffracting power fairly fast and turn opaque upon exposure to X-rays. This necessitated the use of four crystals for the collection of the full data set. A comparison of the intensities of all the reflexions within one octant of reciprocal space, measured with a fresh crystal and again with another after it had lost 30% of its diffracting power, showed that the intensity drop was systematic for all reflexions. The crystal system was determined from precession photographs as triclinic with $Z = 6$, and a careful examination of the interplanar spacings and intensity distribution of the reflexions within $2\theta = 20°$ did not reveal a higher symmetry. Also, the E distribution statistics were consistent with those of a centrosymmetric structure, and the analysis was therefore carried out in space group $P\bar{1}$ with three independent molecules in the asymmetric unit.

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