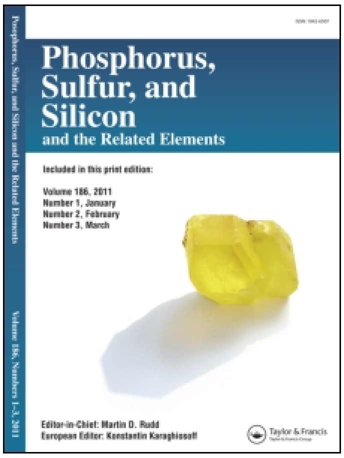

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THE CRYSTAL STRUCTURE OF 2,5-DICHLORO-3-METHOXY-6-(1'-TRIPHENYLPHOSPHONIO-CYCLOPENTADIEN-3-YL)-*p*-BENZOQUINONE

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THE CRYSTAL STRUCTURE OF 2,5-DICHLORO-3-METHOXY-6-(1′-TRIPHENYLPHOSPHONIO-CYCLOPENTADIEN-3-YL)-*p*-BENZOQUINONE

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A single crystal X-ray diffraction study confirms that the reaction of triphenylphosphonio cyclopentadienide **1** with 3-methoxy-2,5,6-trichloro-*p*-benzoquinone **4** gives a product **5** with the cyclopentadiene ring substituted in position 3 and the chlorine atoms of the quinone ring replaced at positions 3 and 6. This data confirms the prediction of earlier multinuclear 2D nmr data on the reaction of **1** with chloranil.

Key words: Triphenylphosphino cyclopentadienide; quinone derivative; X-ray crystallography; chloranil.

INTRODUCTION

The pioneering work of Ramirez *et al.*[1] showed that triphenylphosphonium cyclopentadienylide **1** behaves as a non-benzenoid aromatic compound in reacting with electrophiles which substitute in the cyclopentadiene ring. Most of these reactions[2–6] were alleged to proceed by substitution at position-2 of the cyclopentadiene ring and indeed, in the case of the azo-derivative **3** a chemical proof of substitution in this position was reported[2] and recently confirmed by X-ray crystallography.[7] This proof was used together with multinuclear 2D nmr data to show that in the case of the reaction of tetrahalo-quinones **6** with **1** the reaction proceeded by substitution in position-3 of the cyclopentadiene ring[8] to form **7**. The structure of **7** could not be determined crystallographically because, so far, it has been impossible to grow suitable crystals but, on reaction of **1** with **4**, a second chloride atom was displaced from the quinone ring to give **5** which could be isolated in a crystalline form suitable for X-ray crystallography. The results of this investigation are reported below.

RESULTS AND DISCUSSION

The nmr data of **5** shown in Table I are almost identical to those obtained with **7** especially with regard to the chemical shifts and coupling constants of the cyclopentadiene protons and, as expected, are entirely consistent with substitution in position-3 of the cyclopentadiene ring. The 2-D COSY spectrum of **5** displays one strong (3-bond) and two weak (4-bond) couplings between the three cpd protons as required by substitution in position-3 and on this basis all the observable carbon signals may be assigned (Table I) by a combination of DEPT and heteronuclear (C/H) correlation experiments. They strongly resemble the nmr data for **7**, a summary of which is also included in Table I. One cannot be absolutely certain of this

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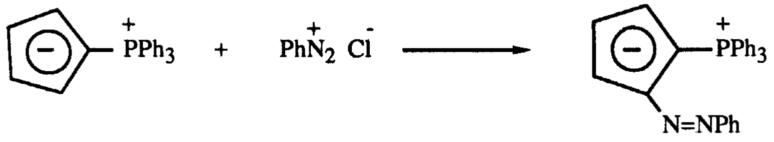
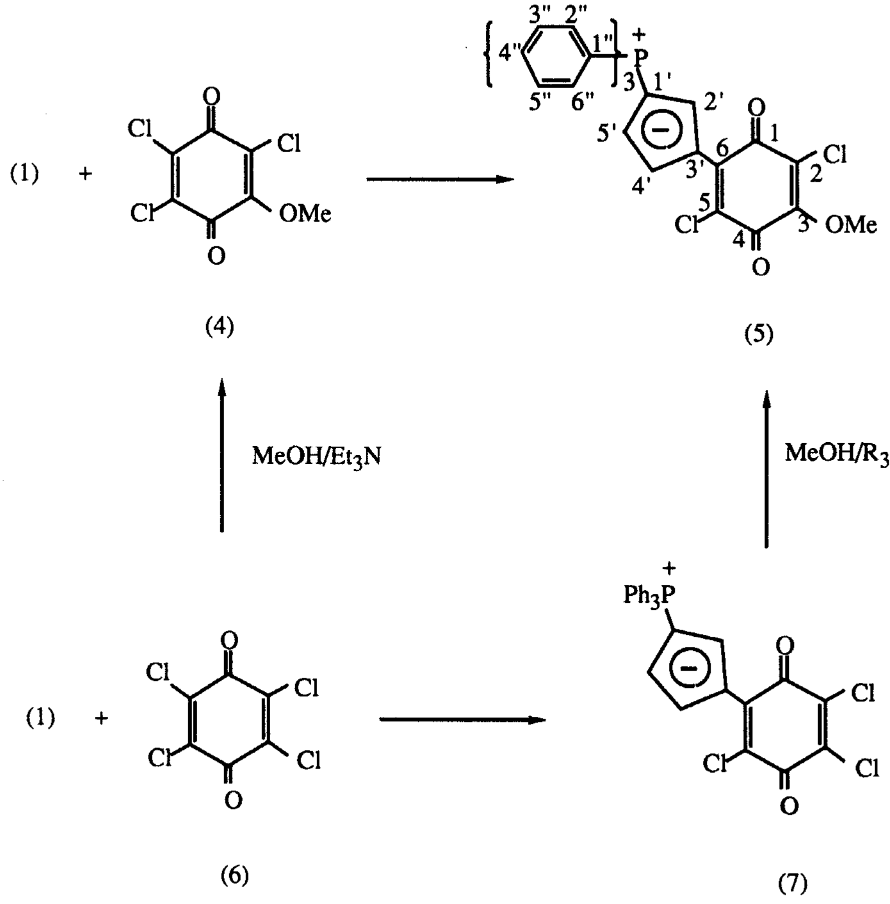


(1) (2) (3)



(4) (5) (6) (7)

assignment however on the basis of nmr data alone and there is no means by which nmr data can distinguish unambiguously between substitution in positions 3 and 6 of the quinone ring versus substitution in positions 5 and 6. Thus an X-ray crystallographic study of the structure of **5** was undertaken and the results of this work are reported below.

A perspective of the molecule is shown in Figure 1 and a selection of bond lengths and bond angles are given in Table II. It is immediately obvious from the Figure

TABLE I

The ^{1}H ^{13}C nmr data on compounds **5** and **7**. Solvent $CDCl_3$ and δ-values relative to TMS.

^{1}H nmr

δ (ppm)	Integration	Multiplicity	Assignment	Compound 7
7.5-7.75	15	m	Ph-H	7.6(m)
7.25	1	oct. (J_p=5.2; $J_{4'}$=4.8; $J_{2'}$=2.0)	H-5'	7.05(sex)
7.21	1	sex	H-2' (J_p=6.0; $J_{4'}$=2.0)	6.94(sex)
6.33	1	m(br)	H-4' (J_p=2.6)	6.36(quin)

^{13}C nmr

δ(ppm)	DEPT	Assignment	Jp (Hz)	Compound 7
181.5	0	C=O(C-1)	0	181.1
174.5	0	C=O(C-4)	0	172.7
155.0	0	C-3(quin)	0	--
139.3(x2)	0	C2,C5(quin)	0	(140-143)
133.8	+	C2",C6"	10.2	135.7(10.0)
133.6	+	C4"	2.9	135.7(0)
131.1	+	C2'	16.0	133.1(15.8)
129.5	+	C3",C5"	12.4	131.5(12.5)
123.8	0	C1"	90.7	124.7(90.6)
122.5	0	C6	0	123.9 (0)
122.3	0	C3'	20.0	124.0(20.3)
121.8	+	C5'	14.3	123.7(13.6)
119.3	+	C4'	13.9	121.4(13.6)
91.3	0	C1'	110.4	95.4(110.0)
61.7	+	OCH_3	0	—

that the bond connectivity is exactly as predicted with the cyclopentadiene ring substituted in positions 1 and 3 and the quinone ring substituted at positions 3- and 6- by a methoxy group and the cyclopentadienyl group respectively. Thus the analysis of the nmr data for this series of compounds is entirely justified and this offers the key to the structures of a whole series of compounds derived from **7**. There are, however, several other features of the crystal structure which are worthy of comment.

The dihedral angle between the planes of the cyclopentadiene and quinone rings is 33° which contrasts with the almost perfect planarity of the cyclopentadiene-phenylazo system.[7] The angle is probably generated by steric interactions between the chlorine atom on C16 and the hydrogen atom on C4 (calculated distance, 2.74Å)

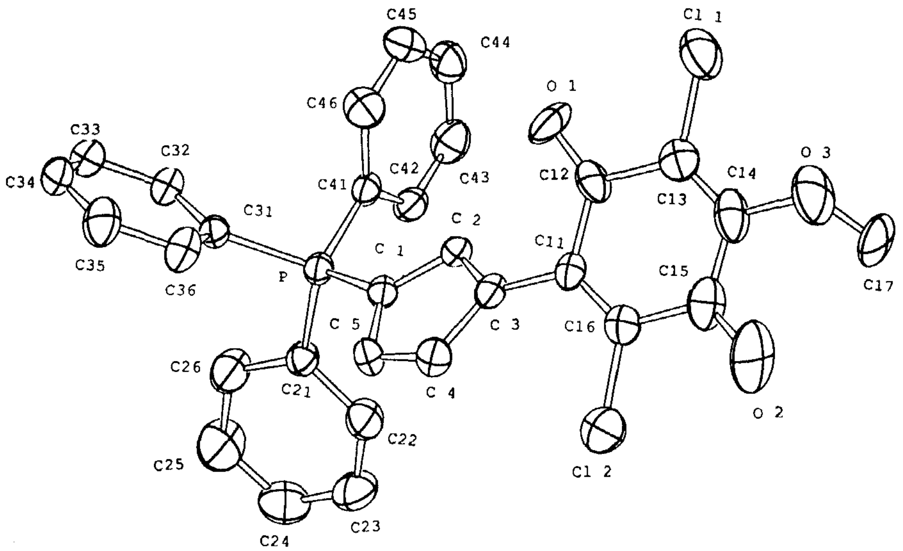


FIGURE 1 The X-ray crystallographic structure of **5** showing the bond connectivity with the dihedral angle between the planes of the cyclopentadiene and quinone rings.

TABLE II

Selected bond lengths (Å) and bond angles from the crystal structure of **5**.

P-C(1)	1.748(6)	C(14)-C(15)	1.500(15)
P-C(21)	1.800(6)	C(15)-C(16)	1.473(10)
P-C(31)	1.8134(6)	C(12)-C(22)	1.368(10)
P-C(41)	1.793(7)	C(21)-C(26)	1.378(10)
Cl(1)-C(13)	1.729(8)	C(22)-C(23)	1.374(12)
Cl(2)-C(16)	1.715(8)	C(23)-C(24)	1.327(16)
O(1)-C(12)	1.228(10)	C(24)-C(25)	1.357(17)
0(2)-C(15)	1.254(12)	C(25)-C(26)	1.393(12)
0(3)-C(14)	1.409(9)	C(31)-C(32)	1.369(11)
0(3)-C(17)	1.275(12)	C(31)-C(36)	1.354(13)
C(1)-C(2)	1.394(9)	C(32)-C(33)	1.378(12)
C(1)-C(5)	1.404(11)	C(33)-C(34)	1.352(20)
C(2)-C(3)	1.410(10)	C(34)-C(35)	1.342(18)
C(3)-C(4)	1.425(11)	C(35)-C(36)	1.402(12)
C(3)-C(11)	1.458(9)	C(41)-C(42)	1.366(10)
C(4)-C(5)	1.362(11)	C(41)-C(46)	1.393(10)
C(11)-C(12)	1.506(10)	C(42)-C(43)	1.372(14)
C(11)-C(16)	1.357(10)	C(43)-C(44)	1.354(15)
C(12)-C(13)	1.493(10)	C(44)-C(45)	1.354(16)
C(13)-C(14)	1.304(14)	C(45)-C(46)	1.372(14)

C(1)-P-C(21)	110.5(3)	O(2)-C(15)-C(16)	121.3(9)
C(1)-P-C(31)	113.3(3)	C(14)-C(15)-C(16)	115.2(8)
C(1)-P-C(41)	109.5(3)	Cl(2)-C(16)-C(11)	124.5(5)
C(21)-P-C(31)	107.1(3)	Cl(2)-C(16)-C(15)	111.0(6)
C(21)-P-C(41)	109.4(3)	C(11)-C(16)-C(15)	124.5(7)
C(31)-P-C(41)	107.0(3)	P-C(21)-C(22)	119.2(5)
C(14)-O(3)-C(17)	119.2(7)	P-C(21)-C(26)	122.6(5)
P-C(1)-C(2)	126.2(6)	C(22)-C(21)-C(26)	118.3(7)
P-C(1)-C(5)	125.9(5)	C(21)-C(22)-C(23)	121.2(8)
C(2)-C(1)-C(5)	107.9(6)	C(22)-C(23)-C(24)	120.1(9)
C(1)-C(2)-C(3)	108.2(7)	C(23)-C(24)C(25)	120.9(9)
C(2)-C(3)-C(4)	106.3(6)	C(24)-C(25)-C(26)	119.8(9)
C(2)-C(3)-C(11)	125.8(7)	C(21)-C(26)-C(25)	119.6(8)

TABLE II (*Continued*)

C(4)-C(3)-C(11)	127.8(7)	P-C(31)-C(32)	120.2(6)
C(3)-C(4)-C(5)	108.9(7)	P-C(31)-C(36)	120.0(6)
C(1)-C(5)-C(4)	108.6(7)	C(32)-C(31)-C(36)	119.7(7)
C(3)-C(11)-C(12)	115.9(6)	C(31)-C(32)-C(33)	120.1(10)
C(3)-C(11)-C(16)	126.2(7)	C(32)-C(33)-C(34)	119.5(10)
C(12)-C(11)-C(16)	117.8(6)	C(33)-C(34)-C(35)	121.7(9)
O(1)-C(12)-C(11)	127.0(6)	C(34)-C(35)-C(36)	118.9(11)
O(1)-C(12)-C(13)	115.7(7)	C(31)-C(36)-C(35)	120.1(10)
C(11)-C(12)-C(13)	117.2(7)	P-C(41)-C(42)	122.9(6)
Cl(1)-C(13)-C(12)	114.0(6)	P-C(41)-C(46)	119.3(6)
Cl(1)-C(13)-C(14)	123.7(7)	C(42)-C(41)-C(46)	117.7(7)
C(12)-C(13)-C(14)	122.3(8)	C(41)-C(42)-C(43)	120.7(8)
O(3)-C(14)-C(13)	121.6(9)	C(42)-C(43)-C(44)	120.5(9)
O(3)-C(13)-C(15)	116.1(8)	C(43)-C(44)-C(45)	120.4(9)
C(13)-C(14)-(15)	122.0(7)	C(44)-C(45)-C(46)	119.5(9)
O(2)-C(15)-C(14)	123.6(8)	C(41)-C(46)-C(45)	121.1(9)

and steric interactions between O1 and the hydrogen on C2 of the cyclopentadiene ring (calculated distance 2.56Å). These distances would be 2.30Å and 2.15Å respectively if the rings were coplanar. Thus the conjugation between the cyclopentadiene and quinone rings is limited. There is a difference in the two short bonds C(13)—C(14) and C(11)—C(16) in the quinone ring at 1.304(14) and 1.357(10)Å respectively compared with chloranil at 1.344(2)Å,[9] but both clearly have double bond character. So also does the inter-ring bond C(3)—C(11) at 1.458(9)Å, indicating some fulvene character in the five-membered ring with C(1)—C(2) and C(4)—C(5) at 1.394(9) in 1.362(11)Å compared with an average of 1.413(11)Å for the remaining ring bonds. The extent of delocalisation in solution, as estimated by electronic spectroscopy, appears to be very similar for compounds of type **5** and **7** with $\lambda_{max}(CH_2Cl_2)$ = 672nm (ε = 10,200) for **5** and $\lambda_{max}(CH_2Cl_2)$ = 694 nm (ε = 7,200) for **7**.

SUPPLEMENTARY MATERIAL

A Table of atomic coordinates (Table S1) has been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW.

EXPERIMENTAL

The chloranil derivative, **7**, of **1** was prepared as described previously,[8] purified by flash chromatography on silica with dichloromethane/1% methanol as eluent and isolated as dark blue crystalline needles by recrystallisation from dichloromethane/pentane. As reported earlier,[8] the ^1H, ^{13}C and 2D nmr data are consistent with, but do not afford conclusive proof of, substitution in position 3 of the cyclopentadiene ring. Compound **5** was prepared by the reaction of **6** with methanol to form **4** followed by reaction of **4** with **1** to form **5** as described below.[10]

A suspension of **6** (1g, 4.10 × 10^{-3} mol) in methanol (15 ml) containing triethylamine (0.3 ml, 4 × 10^{-3} mol) was heated at 60°C for 15 min. The mixture was filtered, and the filtrate washed with water, dried and evaporated. The residue was extracted with pentane and the residue from the combined pentane extracts was recrystallised from ether/pentane to give yellow crystals of **4** (0.62 g, 60%), m.p. 95°C (m.p. of ethoxychloranil = 98-9°C),[10] ^1H nmr, δ ($CDCl_3$) 4.25 (OMe) and ^{13}Cnmr, δ = 62.2 ppm (OCH_3). A solution of the methoxy-trichloroquinone (0.46 g, 1.8 × 10^{-3} mole) in dichloromethane (20 ml) was added to a solution of the ylid, **1** (0.58 g, 1.8 × 10^{-3} mole) and quinuclidine (0.20 g, 1.8 × 10^{-3} mole) in dichloromethane (30 ml) and the mixture was stirred for 1h at room temperature.

The resultant dark blue solution was then evaporated and the blue product was purified by flash chromatography on Silica 60H using mixtures of dichloromethane (99–90%) and methanol (1–10%) as eluant. The residual solid was recrystallised from dichloromethane/pentane to give 0.5 g (55%) of dark blue, lustrous crystals, m.p. > 250°C, $\lambda_{max}(CH_2Cl_2)$ 672 nm, ε = 10,200. Found: C = 67.7, H = 3.74, Cl = 13.4, P = 6.07%; calc for $C_{30}H_{21}Cl_2O_3P$, C = 67.74, H = 3.95, Cl = 13.36, P = 5.83%. Compound **5** could also be prepared by the reaction of **7** with excess methanol in the presence of quinuclidine but the rate of displacement of the second chlorine atom by methanol was very slow. The ^1H and ^{13}C nmr data of **5** (Bruker AM360) are shown in Table I together with a summary of the comparable data for **7**.

A very thin, dark blue, rhomb (0.65 × 0.38 × 0.03 mm) of **5** was X-ray photographed to establish its quality. The cell dimensions were obtained from 20 centered reflections ($45° < 2\theta < 75°$) using an automated Picker four-circle diffractometer with Ni-filtered CuKα radiation. Data were collected using $\theta/2\theta$ scans with pulse height analysis. A standard reflection was measured every 25 reflections and showed no significant change during the data collection.

The structure was solved by direct methods using the NRCVAX programme.[11] Positions for all the hydrogen atoms were identified on the difference map, but the hydrogen atoms of the methyl group on C17 did not give reasonable bond angles on refinement. Accordingly, the experimentally observed position of H17C was used to place H17A and H17B in calculated positions and all three were subsequently fixed in the refinement. The positions of all the other atoms were refined by full least squares with unit weighting of the F values. The non-hydrogen atoms were refined with anisotropic temperature factors and the hydrogen atoms with isotropic temperature factors. An absorption correction was made according to the NRCVAX procedure, and caused an improvement of about 0.01 in the final value of R which was 0.061. The minimum and maximum values of the transmission factor were 0.49 and 0.92.

Crystal data. $C_{30}H_{21}Cl_2O_3P$. M_r = 531.37, monoclinic, C2/c. a = 25.302(8), b = 9.969(1), c = 23.674(8)Å. β = 120.2(2). V = 5160Å^3. Z = 8, D_c = 1.37, D_{obs} = 1.34 g cm^{-3}. λ(CuKα) = 1.5418Å, μ = 31.4 cm^{-1}. F(000) = 2192. Temperature = 298K; R = 0.061, R_w = 0.058, GoF = 5.16 for 2069 reflections with $I_{net} > 2.5\sigma(I)$ out of the total of 2643 with $5° < 2\theta < 100°$.

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