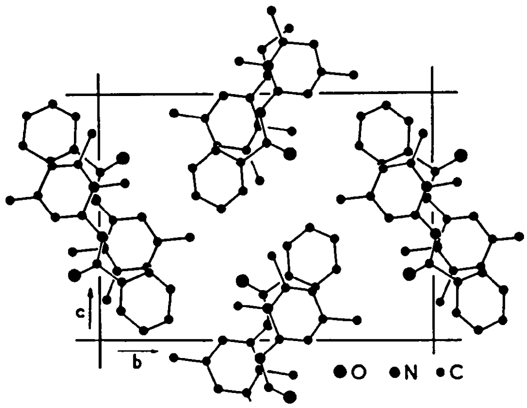

Fig. 2. Représentation de la structure vue parallèlement à l'axe *a*.

La Fig. 2 montre que la structure peut être considérée comme formée de colonnes de molécules édifiées le long de droites parallèles à l'axe *a* et passant par les points de coordonnées ($0 0 \frac{1}{2}$) et ($0 \frac{1}{2} 0$). Dans une même colonne, deux molécules voisines se correspondent par un centre de symétrie.

Si l'on admet pour rayons de van der Waals de l'atome de carbone les valeurs suivantes (Bondi, 1964): *r*(C aromatique) = 1,77 Å et *r*(C aliphatique) = 1,70 Å, on observe que les distances intermoléculaires C(3)—C(12^{i}), C(5)—C(13^{ii}), C(5)—C(14^{ii}), C(6)—C(14^{ii}), C(8)—C(15^{iii}) et C(10)—C(10^{iii}) diffèrent au plus de 0,12 Å de la somme des rayons de van der Waals des deux atomes concernés [(i) $1-x$, $-\frac{1}{2}+y$, $\frac{1}{2}-z$; (ii) $1-x$, $-y$, $1-z$; (iii) $1-x$, $-y$, $-z$].

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The Electrochemical Synthesis and Structure Determination of 3,3′,5,5′-Tetra-*tert*-butyl-1,1′-biphenylidene-4,4′-quinone

BY MASOOD A. KHAN, AKHTAR OSMAN AND DENNIS G. TUCK

Department of Chemistry, University of Windsor, Windsor, Ontario, Canada N9B 3P4

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Abstract. The title compound was obtained during unsuccessful attempts to synthesize $M(OR)_2$ compounds by the anodic oxidation of M (=Zn,Cd,Hg) in non-aqueous solutions of ROH (=2,6-di-*tert*-butylphenol). $C_{28}H_{40}O_2$, $M_r = 408{\cdot}6$, triclinic, $P\bar{1}$, $a = 6{\cdot}092\,(2)$, $b = 10{\cdot}522\,(4)$, $c = 10{\cdot}411\,(3)$ Å, $\alpha = 81{\cdot}51\,(3)$, $\beta = 81{\cdot}68\,(2)$, $\gamma = 75{\cdot}96\,(3)°$, $V = 636{\cdot}2\,(4)$ Å^3, $Z = 1$, $D_x = 1{\cdot}066$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}34$ cm^{-1}, $F(000) = 224$, $T = 295$ K, final $R = 0{\cdot}039$ for 1131 unique observed reflections. The molecules are planar and centrosymmetric with no short intermolecular contacts. The lengthening of the C(4)=C(4′) bond, and the shortening of the bonds from these atoms to the adjacent ring atoms, suggests partial delocalization over this system. This is supported by the bond angles at these atoms. A possible mode of formation of the product is discussed.

Introduction. Recent papers from this laboratory have described the direct electrochemical synthesis of inorganic and organometallic derivatives by the anodic oxidation of a metal in a non-aqueous cell containing the appropriate ligand or ligand precursor. Examples relevant to the present work include the preparation of derivatives of β-ketoenolates (Habeeb, Tuck & Walters, 1978; Kumar & Tuck, 1982; Bustos, Green, Khan & Tuck, 1983) and thiolates (Said & Tuck, 1982; Hencher, Khan, Said, Sieler & Tuck, 1982), where ML_n complexes are formed by electrolysis in solutions of the parent acid HL. Metal alkoxides and aryl oxides are

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also potentially accessible by this route, and the present results arose from the attempted synthesis of such $M(OR)_2$ compounds (M = Zn,Cd,Hg) by the electrochemical oxidation of the metal in solutions of ROH, where R is a phenyl ring with bulky groups *ortho* to OH. In the event, the electrochemical experiments did not yield the desired compounds, and in the case of ROH = 2,6-di-*tert*-butylphenol, the main product isolated from the cell was the title compound (1), whose molecular structure has been determined by X-ray crystallography.

Experimental. *General.* Zinc and cadmium were the mossy granulated materials; mercury was triple distilled. Solvents were dried and stored over molecular sieves and/or calcium hydride; 2,6-di-*tert*-butylphenol was used as supplied (Aldrich). Metal analysis was by atomic absorption spectrophotometry.

Electrochemical. The attempted electrochemical preparation of $M(OR)_2$ followed the procedures described in the earlier publications quoted, with a zinc or cadmium plate suspended on a platinum wire; for mercury, a pool of the element was in contact with a platinum wire sealed through the wall of the vessel. A second platinum wire formed the cathode in each case. The solution phase consisted typically of 30 ml acetonitrile or methanol, 10 ml benzene, 1·0 g 2,6-di-*tert*-butylphenol (ROH) and 25 mg tetraethylammonium perchlorate. All experiments were carried out under dry nitrogen. An applied voltage of 30 V produced a current of 20 mA, and approximately 100–150 mg of metal dissolved during 10 h electrolysis. In each case, hydrogen was evolved at the cathode. In experiments with a zinc anode, precipitation of a light green solid, insoluble in all common organic solvents, was observed as the electrolysis proceeded. (Analysis Zn ~24%.) Cadmium also gave rise to a series of insoluble green compounds of undetermined structure (Cd ~ 30%), while in the case of mercury the solution became green-brown, with a grey compound depositing as the reaction proceeded. Following electrolysis, the final contents of the cell were filtered and the filtrate slowly evaporated to produce red-brown crystals of the title compound (1). Those used in the crystal-structure determination were derived from a mercury anode cell, but the product from a cadmium experiment was shown to be identical by field desorption mass spectrometry; the molecular ion was the predominant peak in both cases.

Crystallography. Crystals of (1) parallelepipeds. Crystal 0·50 × 0·19 × 0·010 mm, attached to glass fibre; Syntex $P2_1$ diffractometer, highly ordered graphite monochromator. Data collected and processed as described previously (Khan, Steevensz, Tuck, Noltes & Corfield, 1980). Intensities of three monitor reflections did not change significantly during data collection. Space group $P\bar{1}$ initially assumed, later taken to be correct because of successful refinement. 15 reflections used to measure lattice parameters. 2321 reflections measured ($\pm h, \pm k, l$, max. $h = 7$, $k = 12$, $l = 12$; $2\theta_{max} = 50°$), 1131 [$F_o^2 > 3\sigma(F_o)^2$] unique. Lorentz and polarization corrections applied. Structure solved by direct methods using *SHELX* (Sheldrick, 1977); refined by full-matrix least squares on F (*cf.* Khan & Tuck, 1982). All C and O atoms refined anisotropically, leading to $R = 0.096$. Difference map at this stage showed positions of all H atoms, included in subsequent cycles and refined isotropically. Final $R = 0.039$, $wR = 0.040$ for 1131 unique observed reflections; $w = [\sigma^2(F) + 0.01F^2]^{-1}$; $S = 0.58$. Largest shift/e.s.d. in final cycle of refinement 0·01. No features of chemical significance in final difference map; largest peak 0·2 e Å^{-3}. Atomic scattering factors from *SHELX*.

Discussion. Positional coordinates for non-H atoms are given in Table 1, and interatomic distances and angles in Table 2. The molecule with the numbering scheme is shown in Fig. 1.* The crystal structure of (1) consists of discrete planar centrosymmetric molecules which are separated by distances equal to or larger than the appropriate van der Waals radii; the shortest contact is O···C(73), at a distance of 3·413 Å. The bond distances and angles within the molecule identify it immediately as a substituted biphenylidenequinone. There are apparently no structural data on biphenylidenequinones to allow any direct comparison, but the relevant C=O, C=C and C–C distances are in good agreement with the reported values in *p*-benzoquinone (as its addition compound with resorcinol) (Ito, Minobe & Sakurai, 1970), in quinhydrone [1,4-benzediol–*p*-benzoquinone (1/1)] and phenoquinone [*p*-benzoquinone–phenol (1/2)] (Sakurai, 1968), and in a symmetrically substituted *p*-benzoquinone (Cash & Pettersen, 1978). One interesting feature of the present structure is the significant shortening of the C(4)–C(3) and C(4)–C(5) bonds compared to C(1)–C(2) and C(1)–C(6), and this, taken with the relatively long C(4)=C(4′) distance of 1·402 (4) Å, suggests partial electron delocalization in the C(5)/C(3) >C(4)=C(4′) system. The bond angles are in good general agreement with the idealized value of 120°, with the exception of C(3)–C(4)–C(5) 116·0 (2), C(4)–C(5)–C(6) 124·2 (2) and C(2)–C(3)–C(4) 124·2 (2)°, these angles being compatible with the delocalization at C(5)–C(4)–C(3).

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42988 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

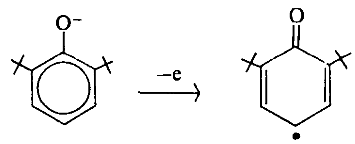
The formation of (1) is in keeping with the known electrochemical behaviour of substituted phenols (Parker, 1973; Nyberg, 1973; Weinberg, 1974). Although much of the published work refers to aqueous, or mixed aqueous–non-aqueous media, the results are transferable to the present work. The cathode reaction

$$R\mathrm{OH} + \mathrm{e} \rightarrow \mathrm{RO}^- + 1/2\mathrm{H}_2\,(g) \qquad (1)$$

is followed by diffusion of $R\mathrm{O}^-$ to the anode, so that the products observed are the results of reactions going on at or near the anode surface. These reactions must include

$$M + nR\mathrm{O}^- \rightarrow \text{‘products’} \qquad (2)$$

where ‘products’ refers to the insoluble metal-containing solids which precipitated during the electrolysis, but discharge must lead to the radical $R\mathrm{O}^{\bullet}$ (2)



(3)

(2)

Table 1. *Positional coordinates for non-*H *atoms; e.s.d.'s are in parentheses*

	x	y	z	U_{eq}(Å^2)*
O	0·4540 (4)	0·4190 (2)	0·3544 (2)	0·102
C(1)	0·3420 (4)	0·4408 (2)	0·2613 (2)	0·044
C(2)	0·3441 (4)	0·3335 (2)	0·1836 (2)	0·036
C(3)	0·2129 (4)	0·3616 (2)	0·0851 (2)	0·039
C(4)	0·0683 (4)	0·4887 (2)	0·0511 (2)	0·036
C(5)	0·0738 (4)	0·5912 (2)	0·1276 (2)	0·039
C(6)	0·2022 (4)	0·5741 (2)	0·2261 (2)	0·036
C(7)	0·4947 (4)	0·1966 (2)	0·2173 (2)	0·040
C(8)	0·2073 (4)	0·6864 (2)	0·3031 (2)	0·039
C(71)	0·4765 (7)	0·1004 (3)	0·1248 (4)	0·062
C(72)	0·4212 (8)	0·1399 (3)	0·3563 (3)	0·068
C(73)	0·7437 (5)	0·2067 (4)	0·2029 (4)	0·068
C(81)	0·0587 (7)	0·8166 (3)	0·2502 (4)	0·060
C(82)	0·4515 (6)	0·7046 (4)	0·2924 (4)	0·061
C(83)	0·1206 (7)	0·6547 (4)	0·4480 (3)	0·061

* $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*(\mathbf{a}_i.\mathbf{a}_j)$.

Table 2. *Interatomic distances* (Å) *and angles* (°) *for* (1)

The mean value is reported for the distances and angles involving H atoms; e.s.d.'s of mean values are calculated from $\sigma=[\sum(d_i-\bar{d})^2/(N-1)]^{1/2}$, where d_i is the ith and $\bar{d}$ is the mean of N equal measurements.

O–C(1)	1·228 (2)	C(1)–C(2)	1·479 (3)
C(1)–C(6)	1·478 (3)	C(2)–C(3)	1·346 (3)
C(2)–C(7)	1·530 (3)	C(3)–C(4)	1·439 (3)
C(4)–C(4^i)	1·402 (4)	C(4)–C(5)	1·441 (3)
C(5)–C(6)	1·343 (3)	C(6)–C(8)	1·532 (3)
C(7)–C(71)	1·529 (4)	C(7)–C(72)	1·529 (4)
C(7)–C(73)	1·530 (4)	C(8)–C(81)	1·523 (3)
C(8)–C(82)	1·532 (4)	C(8)–C(83)	1·540 (4)
C–H(ring)	0·92 (2)	C–H(methyl)	0·99 (4)
O–C(1)–C(2)	120·3 (2)	O–C(1)–C(6)	120·5 (2)
C(2)–C(1)–C(6)	119·2 (2)	C(1)–C(2)–C(3)	118·0 (2)
C(1)–C(2)–C(7)	119·2 (2)	C(3)–C(2)–C(7)	122·8 (2)
C(2)–C(3)–C(4)	124·4 (2)	C(3)–C(4)–C(4^i)	121·8 (2)
C(3)–C(4)–C(5)	116·0 (2)	C(4^i)–C(4)–C(5)	122·2 (2)
C(4)–C(5)–C(6)	124·2 (2)	C(1)–C(6)–C(5)	118·2 (2)
C(1)–C(6)–C(8)	119·2 (2)	C(5)–C(6)–C(8)	122·6 (2)
C(2)–C(7)–C(71)	111·4 (2)	C(2)–C(7)–C(72)	110·2 (2)
C(2)–C(7)–C(73)	109·3 (2)	C(71)–C(7)–C(72)	107·6 (3)
C(71)–C(7)–C(72)	107·6 (3)	C(72)–C(7)–C(73)	110·7 (3)
C(6)–C(8)–C(81)	111·6 (2)	C(6)–C(8)–C(82)	109·6 (2)
C(6)–C(8)–C(83)	110·2 (2)	C(81)–C(8)–C(82)	107·8 (3)
C(81)–C(8)–C(83)	108·3 (3)	C(82)–C(8)–C(83)	109·3 (3)
C–C–H(ring)	117·8 (8)	C–C–H(methyl)	110 (2)
H–C–H	109 (3)		

Symmetry code: (i) $-x$, $1-y$, $-z$.

Dimerization of (2), or reaction at the *para* position of a molecule of ROH, followed by elimination of H_2, then leads to (1). The oxidation of 2,6-di-*tert*-butylphenol by molecular oxygen is known to be catalysed by transition-metal complexes (Bedell & Martell, 1983; Wang, Motekaitis & Martell, 1984), but given the electrochemical evidence there seems to be no need to invoke the participation of the metal itself or metal-containing products in the above reaction scheme. Finally, we note that the electrochemical efficiency, E_F, defined as moles of metal dissolved per Faraday of electricity for the Zn and Cd systems, was of the order of 0·2 mol F^{-1}. (1 Faraday = $9{\cdot}6487 \times 10^4$ C.) In comparable experiments with these metals and other weak acids, E_F was 0·5 mol F^{-1}, corresponding to the anode reaction

$$M + 2A^- \rightarrow MA_2 + 2\mathrm{e}. \qquad (4)$$

The lower E_F values recorded in the present work clearly imply that reaction (4) is here of minor importance, which is in keeping with the formation of the major product (1). The relative lack of reaction with the anode may be due to the stability of the radical (2) against formation of a metal–carbon bonded species.

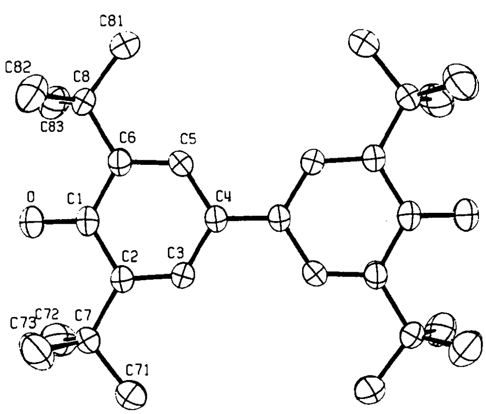


Fig. 1. The molecular structure of 3,3′,5,5′-tetra-*tert*-butyl-1,1′-biphenylene-4,4′-quinone, showing the numbering system. H atoms are omitted for clarity.

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Novel Protein Kinase C Inhibitor K-252a

BY NORIAKI HIRAYAMA,† TAKAO IIDA AND KUNIKATSU SHIRAHATA

Tokyo Research Laboratories, Kyowa Hakko Kogyo Co. Ltd, 3-6-6 *Asahimachi, Machida, Tokyo* 194, *Japan*

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Abstract. Methyl (8*R**,9*S**,11*S**)-2,3,8,9,10,11-hexahydro-9-hydroxy-8-methyl-8,11-epoxy-1-oxo-1*H*-2,7*b*,-11*a*-triazadibenzo[*a*,*g*]cycloocta[*c*,*d*,*e*]trindene-9-carboxylate,‡ $C_{27}H_{21}N_3O_5.2CH_3OH$, $M_r = 531\cdot57$, monoclinic, $P2_1$, $a = 14\cdot040$ (1), $b = 7\cdot005$ (1), $c = 13\cdot283$ (1) Å, $\beta = 106\cdot38$ (1)°, $V = 1253\cdot4$ Å^3, $Z = 2$, $D_x = 1\cdot408$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1\cdot5418$ Å, $\mu = 6\cdot780$ cm^{-1}, $F(000) = 560$, $T = 295$ K, $R = 0\cdot052$ for 2613 unique significant reflections. The molecule, which is a novel strong inhibitor of protein kinase C, adopts a unique skeletal structure composed of eight rings.

Introduction. The novel compound K-252a was isolated from *Nocardiopsis* sp. K252 and found to be a strong inhibitor of protein kinase C (Kase, Iwahashi & Matsuda, 1986). As the activity of K252a is stronger than that of chlorpromazine we were prompted to establish the structure of the molecule.

Experimental. Pale-yellow prismatic crystals [m.p. 535–546 K (dec)] were obtained from acetone–methanol solution. Single crystal with dimensions of $0\cdot3 \times 0\cdot3 \times 0\cdot4$ mm was sealed in a glass capillary for the data collection. Cell dimensions by least-squares refinement of 25 θ values measured on an Enraf–Nonius CAD-4 diffractometer. Intensity measurements with ω–2θ scan mode up to $\theta = 75\cdot0°$ ($-17 \le h \le 17$, $0 \le k \le 8$, $0 \le l \le 16$), max. scan time 100 s, no significant changes in three standard reflections monitored every 3600 s; 2909 unique reflections, 2613 with $I > 3\sigma(I)$ used for refinement. No corrections for absorption or secondary extinction. Lorentz and polarization corrections; structure solved by *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982), full-matrix least-squares refinement on *F*. All hydrogen atoms except those of solvent molecules located in difference Fourier map and refined, anisotropic and isotropic temperature factors for non-hydrogen and hydrogen atoms, respectively. Final $R = 0\cdot052$, $wR = 0\cdot052$, unit weights, number of variables 469, max. $\Delta/\sigma = 0\cdot02$ for non-H atoms, highest peak in a final difference synthesis $0\cdot22$ e Å^{-3}. The absolute configuration $\{[\alpha]_D = -23\cdot2°$ (c 0·5, $CHCl_3$)$\}$ was not determined. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974), calculations carried out on a PDP 11/34A with *SDP-Plus* V.1·0 (Frenz, 1982).§

† To whom correspondence should be addressed.

‡ Methyl (2'*R**,3'*S**,5'*S**)-*N*,*N*'-(3-hydroxy-2-methyltetrahydro-2,5-furandiyl)-5-oxo-5,7-dihydroisoindolo[5,4-*b*:6,7-*b*']diindole-3'-carboxylate.

§ Lists of structure factors, anisotropic thermal parameters, and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 43026 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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