2,6-Dimethyl-4-(α,α-diphenylmethylene)-1,4-benzoquinone* (γ Form)

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Abstract. $C_{21}H_{18}O$, $M_r = 286.4$, orthorhombic, $Pna2_1$, $a = 11.820$ (3), $b = 16.487$ (4), $c = 8.150$ (2) Å, $V = 1588.2$ Å^3, $Z = 4$, $D_c = 1.30$ Mg m^{-3}, μ(Mo $K\alpha$) = 0.08 mm^{-1}. While the molecular conformations are very similar in the crystalline polymorphs of the title compound (1), the packing of the molecules in the (1γ) form is very different from those determined previously for the (1α) and (1β) forms.

Introduction. 2,6-Dimethyl-4-(α,α-diphenylmethylene)-1,4-benzoquinone (2,6-dimethylfuchsone) (1) has been shown to crystallize in at least three forms. The structures of two of the forms (1α and 1β) have been described recently and some evidence was presented for a phase transition from the achiral ($P2_1/c$) form (1α), to the chiral ($P2_12_12_1$) form (1β) (Lewis, Paul & Curtin, 1979). A third form (1γ), obtainable as a few long, thin needles that grew in clusters from a saturated cyclohexane solution, was shown to belong to either the space group $Pna2_1$ or $Pnma$ (Lewis, 1977) and preliminary cell data were reported. The present paper describes the structure of the γ form. Cell data and intensity data out to $2\theta = 50°$ were obtained on a Syntex $P2_1$ diffractometer (Mo $K\alpha$, $\lambda = 0.70926$ Å) on the best available crystal cut to a size of $0.9 \times 0.15 \times 0.08$ mm. Out of a possible 1513 independent reflections, 680 were above zero at the 1.96σ significance level. The structure was determined by direct methods (Germain, Main & Woolfson, 1971). Most H atoms were located from difference maps, thus allowing the others to be positioned according to standard criteria. Refinement by full-matrix least squares on the positional and isotropic thermal parameters for the non-hydrogen atoms with the H atoms included in the calculations with fixed positions and thermal parameters ($B_{iso} = 5.0$ Å^2) gave values of 0.099 and 0.082 for R and R_w on the 680 non-zero reflections. The final value of $[\sum w||F_{obs}| - |F_{calc}||^2/(m - n)]^{1/2}$ was 1.95. The small number of reflections would not permit a meaningful refinement incorporating aniso-tropic thermal parameters. The atomic scattering factors were from *International Tables for X-ray*

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* IUPAC name: 2,6-dimethyl-4-(diphenylmethylene)-2,5-cyclo-hexadienone.

Crystallography (1974). The atomic coordinates are given in Table 1.†

(1)
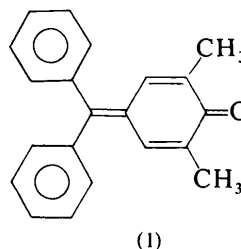
Discussion. Bond lengths and angles are given in Table 2. Within the large standard deviations, the values agree with those found for (1α) and (1β) (Lewis, Paul & Curtin, 1979). The molecular structure is shown in Fig. 1. The conformation is very similar to that found in the other two forms. The best plane through the ring C(2) – C(7) is inclined at an angle of 42.0° from the best plane through the four atoms C(1), C(2), C(8), and C(14); the values for the molecules in the α and β forms are 39.9 and 38.7°. The ring C(8) – C(13) is inclined at an angle of 55.6° to the four-atom plane; for (1α) and (1β), the values are 47.4 and 47.9°. The

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† Lists of structure factors and some intermolecular contacts have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34648 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallogrpahy, 5 Abbey Square, Chester CH1 2HU, England.
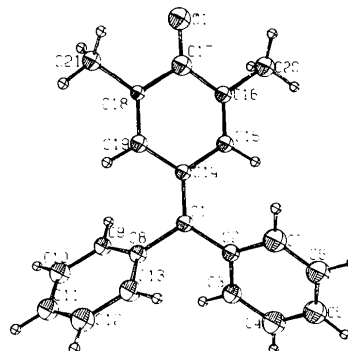

Fig. 1. A view of a single molecule of (1) in the γ crystalline form.

Table 1. *Atomic coordinates in fractions of the unit-cell edge and isotropic thermal parameters; standard deviations are in parentheses*

	x	y	z	B (Å²)
O(1)	0·2976 (8)	0·9209 (6)	0·500*	4·7 (3)
C(1)	0·7025 (11)	0·8656 (7)	0·808 (2)	2·7 (3)
C(2)	0·7134 (10)	0·8308 (8)	0·973 (2)	2·9 (3)
C(3)	0·7941 (11)	0·8605 (8)	1·084 (2)	3·8 (3)
C(4)	0·8093 (12)	0·8231 (9)	1·237 (2)	5·5 (4)
C(5)	0·7450 (12)	0·7582 (11)	1·277 (2)	5·2 (4)
C(6)	0·6655 (12)	0·7298 (8)	1·177 (2)	5·0 (4)
C(7)	0·6468 (12)	0·7655 (8)	1·022 (2)	4·9 (4)
C(8)	0·8125 (10)	0·8851 (8)	0·727 (2)	3·0 (3)
C(9)	0·8344 (9)	0·9615 (7)	0·668 (2)	3·2 (3)
C(10)	0·9364 (12)	0·9782 (8)	0·589 (2)	4·5 (4)
C(11)	1·0171 (11)	0·9196 (8)	0·566 (2)	4·5 (4)
C(12)	0·9953 (12)	0·8452 (9)	0·626 (2)	5·0 (3)
C(13)	0·8918 (12)	0·8239 (8)	0·706 (2)	4·1 (3)
C(14)	0·6009 (10)	0·8805 (7)	0·731 (2)	2·5 (3)
C(15)	0·4952 (11)	0·8838 (7)	0·822 (2)	2·8 (3)
C(16)	0·3955 (11)	0·9004 (7)	0·748 (2)	2·7 (3)
C(17)	0·3896 (12)	0·9072 (8)	0·573 (2)	3·9 (3)
C(18)	0·4945 (10)	0·9015 (6)	0·477 (2)	2·0 (3)
C(19)	0·5930 (10)	0·8916 (7)	0·555 (2)	2·8 (3)
C(20)	0·2866 (11)	0·9085 (9)	0·846 (2)	4·1 (4)
C(21)	0·4871 (10)	0·9037 (7)	0·293 (2)	3·2 (3)
H(3)†	0·8418	0·9080	1·053	5·0
H(4)	0·8667	0·8450	1·316	5·0
H(5)	0·7591	0·7302	1·384	5·0
H(6)	0·6166	0·6834	1·211	5·0
H(7)	0·5872	0·7439	0·946	5·0
H(9)	0·7766	1·0054	0·683	5·0
H(10)	0·9496	1·0346	0·547	5·0
H(11)	1·0897	0·9322	0·509	5·0
H(12)	1·0539	0·8020	0·610	5·0
H(13)	0·8776	0·7672	0·747	5·0
H(15)	0·4963	0·8730	0·942	5·0
H(19)	0·6643	0·8921	0·488	5·0
H(20a)	0·2870	0·9570	0·845	5·0
H(20b)	0·2202	0·8846	0·789	5·0
H(20c)	0·2937	0·8852	0·958	5·0
H(21a)	0·4646	0·9518	0·273	5·0
H(21b)	0·5625	0·8937	0·241	5·0
H(21c)	0·4313	0·8631	0·251	5·0

* The z coordinate of O(1) was held constant to define the origin in that direction.

† Hydrogen atoms are given the numbers of the atoms to which they are bonded; H-atom parameters were held constant.

quinone ring C(14) – C(19) is twisted by 19·5° from the four-atom plane; for (1α) and (1β), the values are 21·1 and 18·9°.

The molecular packing in the form (1α) consists of stacked two-dimensional layers which are alternately mirror images of each other while that in form (1β) has successive layers that differ only by rotation and translation (Lewis, Paul & Curtin, 1979). The assembly of molecules in the (1γ) form is rather different. A stereoscopic view of the contents of a unit cell is shown in Fig. 2. While the relationship of molecules along the **c** direction (the polar axis) corresponds generally to those in the **a** directions of the layers in the α and β forms, no

Table 2. *Bond lengths (Å) and angles (°) for the molecule in the (1γ) form*

O(1)–C(17)	1·26 (2)	C(9)–C(10)	1·39 (2)
C(1)–C(2)	1·46 (2)	C(10)–C(11)	1·37 (2)
C(1)–C(8)	1·49 (2)	C(11)–C(12)	1·35 (2)
C(1)–C(14)	1·38 (2)	C(12)–C(13)	1·43 (2)
C(2)–C(3)	1·40 (2)	C(14)–C(15)	1·46 (2)
C(2)–C(7)	1·39 (2)	C(14)–C(19)	1·45 (2)
C(3)–C(4)	1·40 (2)	C(15)–C(16)	1·35 (2)
C(4)–C(5)	1·35 (2)	C(16)–C(17)	1·43 (2)
C(5)–C(6)	1·33 (2)	C(16)–C(20)	1·52 (2)
C(6)–C(7)	1·41 (2)	C(17)–C(18)	1·47 (2)
C(8)–C(9)	1·37 (2)	C(18)–C(19)	1·33 (2)
C(8)–C(13)	1·39 (2)	C(18)–C(21)	1·50 (2)
C(2)–C(1)–C(8)	114·4 (11)	C(12)–C(11)–C(10)	117·4 (14)
C(2)–C(1)–C(14)	124·6 (12)	C(13)–C(12)–C(11)	123·6 (14)
C(8)–C(1)–C(14)	120·9 (12)	C(8)–C(13)–C(12)	117·1 (13)
C(3)–C(2)–C(7)	118·0 (13)	C(15)–C(14)–C(19)	116·5 (12)
C(3)–C(2)–C(1)	121·0 (12)	C(15)–C(14)–C(1)	121·2 (12)
C(7)–C(2)–C(1)	121·0 (13)	C(19)–C(14)–C(1)	122·3 (12)
C(4)–C(3)–C(2)	120·5 (14)	C(16)–C(15)–C(14)	121·8 (12)
C(5)–C(4)–C(3)	119·3 (15)	C(17)–C(16)–C(20)	118·4 (13)
C(6)–C(5)–C(4)	121·9 (16)	C(17)–C(16)–C(15)	120·2 (13)
C(7)–C(6)–C(5)	120·8 (15)	C(20)–C(16)–C(15)	121·3 (13)
C(2)–C(7)–C(6)	119·4 (14)	C(18)–C(17)–O(1)	119·1 (13)
C(9)–C(8)–C(13)	119·8 (13)	C(18)–C(17)–C(16)	119·0 (13)
C(9)–C(8)–C(1)	121·1 (12)	O(1)–C(17)–C(16)	121·8 (13)
C(13)–C(8)–C(1)	119·1 (12)	C(19)–C(18)–C(21)	121·9 (12)
C(10)–C(9)–C(8)	120·3 (13)	C(19)–C(18)–C(17)	119·3 (12)
C(11)–C(10)–C(9)	121·7 (14)	C(21)–C(18)–C(17)	118·7 (12)
		C(14)–C(19)–C(18)	122·8 (12)
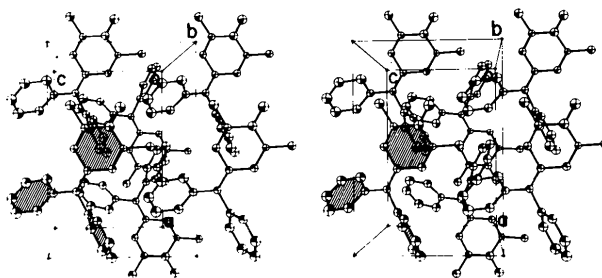
Fig. 2. A stereoscopic view of the packing in the crystal of (1γ).

two-dimensional layered arrangement corresponding to those in the α and β forms can be discerned in the structure of the γ form. In view of the quite different packing found in the crystals of (1γ), it is not surprising that there is no evidence for the presence of microcrystalline (1γ) when microcrystals of (1α) are heated to give (1β) (Lewis, Paul & Curtin, 1979) nor when crystals of the carbinol (2) are dehydrated to give

(2)
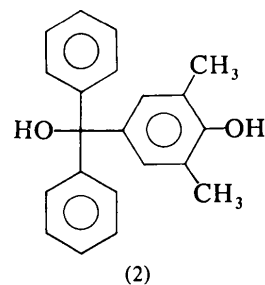
microcrystalline (1β) (Lewis, Curtin & Paul, 1979).

The range of symmetries exhibited by the three structures (1α), (1β), and (1γ) deserves mention. (1α), in crystal class 2/m, is centrosymmetric and thus achiral and non-polar. (1β), in class 222, is chiral with non-polar crystallographic axes. (1γ), in class mm2, is achiral but with the polar crystallographic axis c.

References

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). Acta Cryst. A27, 368–376.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 71–147. Birmingham: Kynoch Press.

LEWIS, T. W. (1977). PhD Thesis, Univ. of Illinois, Urbana, Illinois.

LEWIS, T. W., CURTIN, D. Y. & PAUL, I. C. (1979). J. Am. Chem. Soc. In the press.

LEWIS, T. W., PAUL, I. C. & CURTIN, D. Y. (1979). Acta Cryst. B35, 70–77.

Structure of 2,3-Dichloro-5,6-dicyano-p-benzoquinone (DDQ)*

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Abstract. $C_8Cl_2N_2O_2$, $M_r = 227.0$, orthorhombic, Pbca, $a = 17.839$ (8), $b = 16.632$ (7), $c = 5.930$ (4) Å, $Z = 8$, $V = 1759.4$ Å^3, $D_c = 1.713$ Mg m^{-3}. Intensity data were collected on a four-circle diffractometer with Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å, $\mu = 0.705$ mm^{-1}). The structure was solved by direct methods and refined by full-matrix least squares to a final conventional R value of 0.041 ($R_w = 0.046$). The quinoid ring is slightly non-planar and adopts a shallow boat conformation with the substituents significantly displaced from its mean plane. The molecular dimensions are in agreement with those found in p-benzoquinone, in the π-molecular compounds phenanthrene–DDQ and benzo[c]phenanthrene–DDQ, and other analogous compounds. The crystal packing is mainly determined by van der Waals forces and none of the intermolecular contacts are shorter than the sum of the van der Waals radii.

Introduction. The title compound exhibits an electron affinity which is among the highest reported to date for organic molecules associated with a permanent molecular dipole moment. These features offer an almost unique opportunity to study the role of polarity in determining the crystal packing in electron donor–acceptor compounds and in organic free-radical salts (Herbstein, 1971). In addition, DDQ forms stable (1:1) salts which, besides those of 7,7,8,8-tetracyanoquinodimethane and N,N,N',N'-tetramethyl-p-phenylene-

diamine, are the only organic radical crystals that exhibit triplet exciton behaviour (Gordon & Hove, 1973).

The present paper reports the crystal and molecular structure of neutral DDQ as the starting point in the investigation of crystal structures in which DDQ or its radical anion are involved in charge-transfer compounds.

Crystals of DDQ were grown from a solution in chloroform. Crystal data were obtained by single-crystal diffractometry. Intensities were collected from a crystal of approximate dimensions 0.4 × 0.3 × 0.07 mm on a Philips PW 1100 four-circle diffractometer, operating in the $\theta/2\theta$ scan mode (scan width = 1.1°, scan speed = 0.02° s^{-1}), with Mo $K\alpha$ radiation, monochromatized by a graphite crystal. 2113 independent reflexions up to $\theta = 28°$ were measured, of which 1310 had intensities greater than 2.5 times their standard deviations (σ), σ being calculated from the counting statistics of the measurements. During the data collection three standard reflexions were measured every 180 min to check the stability of the crystal and electronics. Intensities were corrected for Lorentz and polarization effects and were converted to an absolute scale by Wilson's method. An experimental absorption correction was applied (North, Phillips & Mathews, 1968).

The positional parameters of all atoms were determined by direct methods. Normalized structure factors were calculated and the 159 reflexions with $|E(hkl)| \geq 1.2$ were used in the phasing program SHELX 76 (Sheldrick, 1976). An E map was calculated and the