Structure of Tetraethylammonium–2,3-Dichloro-5,6-dicyano-*p*-benzoquinone

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Abstract

Crystals of tetraethylammonium–2,3-dichloro-5,6-dicyano-*p*-benzoquinone (TEA$^+$–DDQ$^-$), $C_8H_{20}N^+.$-$C_8Cl_2N_2O_2^-$, $M_r = 357$, are monoclinic with $a = 12 \cdot 493$ (5), $b = 20 \cdot 114$ (7), $c = 6 \cdot 996$ (3) Å, $\beta = 98 \cdot 79$ (8)°, $V = 1737$ (1) Å^3, $Z = 4$, space group $P2_1/n$, $D_c = 1 \cdot 367$ g cm^{-3}. Intensity data were collected on a four-circle diffractometer with Mo $K\bar{\alpha}$ radiation. The structure was solved by direct methods and refined by full-matrix least squares to a final conventional R value of $0 \cdot 062$ ($R_w = 0 \cdot 064$) for the 2427 observed reflexions with $I \geq 2 \cdot 5\sigma(I)$. The quinoid ring is planar within the experimental error, with the substituents significantly displaced from its mean plane. The changes in the molecular dimensions of the DDQ$^-$ anion as compared with neutral DDQ correspond to a rearrangement of the π bonding upon addition of an unpaired electron. DDQ$^-$ anions are stacked with different intervals in the crystal, the interplanar spacing being $2 \cdot 906$ and $3 \cdot 626$ Å respectively. The shorter value suggests that the present structure could be represented as the packing of dimeric DDQ$^-$ units.

Introduction

2,3-Dichloro-5,6-dicyano-*p*-benzoquinone, DDQ, exhibits an electron affinity among the highest until now reported 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). DDQ forms stable (1:1) salts which, besides those of 7,7,8,8-tetracyanoquinodimethane and *N,N,N',N'*-tetramethyl-*p*-phenylenediamine, are the only organic radical crystals that exhibit triplet exciton behavior (Gordon & Hove, 1973; Pasimeni, Brustolon, Zanonato & Corvaja, 1980).

Furthermore, the recent finding (Mayerle & Torrance, 1981) of a new charge-transfer complex, dibenzotetrathiafulvalene–DDQ (DBTTF–DDQ), which exhibits a high room-temperature pellet electrical conductivity (8 Ω^{-1} cm^{-1}) makes DDQ one of the few molecules as yet known for which the attempt to synthesize highly conducting organic materials has been successful.

In a previous paper (Zanotti, Bardi & Del Pra, 1980) we reported 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. To our knowledge, no complete structural determination of systems containing the DDQ radical anion has until now been available. Only preliminary structural data have recently been reported (Mayerle & Torrance, 1981) on the charge-transfer complex tetrathiafulvalene–DDQ (TTF–DDQ) which, in the ground state, is composed of TTF cations and DDQ anions. We present in this paper the crystal and molecular structure of tetraethylammonium–DDQ (TEA$^+$–DDQ$^-$).

Experimental

Crystals of TEA$^+$–DDQ$^-$ were grown by slow evaporation of acetone solutions at room temperature.

Crystal data were obtained from single-crystal diffractometer measurements. Intensities were collected from a crystal of approximate dimensions $0 \cdot 20 \times 0 \cdot 25 \times 0 \cdot 12$ mm on a Philips PW 1100 four-circle diffractometer, operating in the θ–2θ scan mode (scan width $1 \cdot 4°$, scan speed $0 \cdot 025°$ s^{-1}), with Mo $K\bar{\alpha}$ radiation, monochromatized by a graphite crystal. 3768 independent reflections up to $\theta = 27°$ were measured, of which 2427 had $I > 2 \cdot 5\sigma(I)$, σ being calculated from counting statistics. During the data collection two standard reflections 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).

Structure determination and refinement

The positional parameters of non-hydrogen atoms were determined by direct methods. Normalized structure factors were calculated and the reflections with $|E(hkl)| \geq 1\cdot3$ were used in the phasing program SHELX 76 (Sheldrick, 1976). An E map was calculated and the structural solution was evident. The conventional R value was 0·30. The refinement of the structural parameters was carried out by full-matrix least-squares analysis, allowing Cl, O and N atoms to vibrate anisotropically, while the C atoms were assigned isotropic thermal parameters. H atoms were included in idealized calculated positions. The methyl H atoms were refined using the group-refinement procedure, whilst the methylene H atoms were not varied. Correction for the real and imaginary parts of the anomalous dispersion was applied (International Tables for X-ray Crystallography, 1974). The final R value for the 2427 observed reflections with $I \geq 2\cdot5\sigma(I)$ was 0·062 ($R_w = 0\cdot064$).

The quantity minimized was $\sum w(|F_o| - |F_c|)^2$ $\{w = [\sigma^2(F_o) - 0\cdot0001F_c^2]^{-1}\}$ to give average values of $w\varDelta^2$ ($\varDelta = |F_o| - |F_c|$), for groups of reflections, independent of the value of $|F_o|$.

The calculations were carried out on the Cyber 76 computer of CINECA with the SHELX 76 program for crystal structure determination (Sheldrick, 1976). All atomic scattering factors were those of International Tables for X-ray Crystallography (1974).*

Results and discussion

The final coordinates of non-hydrogen atoms, with their e.s.d.'s, are reported in Table 1. Bond lengths and valence angles for TEA+ are listed in Table 2. A view of the DDQ− anion with bond lengths and valence angles is presented in Fig. 1.

DDQ− has essentially $mm2$ symmetry although that required by the space group is $\bar{1}$, as in the π-molecular compounds benzo[c]phenanthrene–DDQ, BPH–DDQ

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36495 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
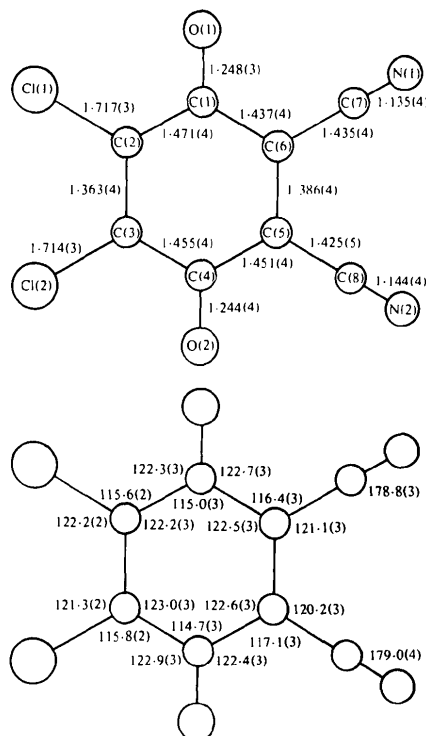
Table 1. Atomic coordinates ($\times 10^4$) with their e.s.d.'s in parentheses and isotropic temperature factors ($\times 10^4$)

U_{eq} = one third the trace of $\bar{\mathbf{U}}$.

	x	y	z	U_{eq} (Å^2)
DDQ−				
Cl(1)	6133 (1)	3998 (1)	3584 (1)	549
Cl(2)	3666 (1)	3631 (1)	3567 (2)	675
O(1)	6417 (2)	5320 (1)	2000 (4)	490
O(2)	2198 (2)	4719 (2)	2208 (4)	634
C(1)	5448 (3)	5186 (2)	2062 (5)	364
C(2)	5105 (3)	4540 (2)	2747 (5)	376
C(3)	4043 (3)	4387 (2)	2758 (5)	410
C(4)	3164 (3)	4851 (2)	2138 (5)	437
C(5)	3506 (3)	5491 (2)	1484 (5)	393
C(6)	4585 (3)	5651 (2)	1488 (5)	358
C(7)	4901 (3)	6309 (2)	1016 (5)	409
C(8)	2681 (3)	5968 (2)	884 (6)	514
N(1)	5144 (3)	6835 (2)	670 (5)	577
N(2)	2025 (3)	6353 (2)	377 (6)	801
TEA+				
C(11)	5312 (3)	2074 (2)	3505 (6)	482
C(12)	5877 (5)	2206 (3)	5558 (7)	827
C(13)	6992 (3)	1582 (2)	2548 (6)	483
C(14)	7325 (4)	2244 (2)	1746 (7)	640
C(15)	5588 (4)	862 (2)	3547 (6)	543
C(16)	5877 (4)	232 (2)	2577 (7)	641
C(17)	5247 (3)	1488 (2)	412 (6)	506
C(18)	4032 (4)	1359 (3)	118 (8)	730
N(3)	5777 (2)	1501 (1)	2504 (4)	402

Table 2. Bond lengths (Å) and angles (°), with e.s.d.'s in parentheses for the cation TEA+

N(3)–C(11)	1·510 (4)	C(11)–N(3)–C(13)	111·2 (2)
N(3)–C(13)	1·522 (4)	C(11)–N(3)–C(15)	109·0 (2)
N(3)–C(15)	1·513 (4)	C(11)–N(3)–C(17)	108·6 (2)
N(3)–C(17)	1·512 (4)	C(13)–N(3)–C(15)	108·0 (2)
C(11)–C(12)	1·524 (5)	C(13)–N(3)–C(17)	108·0 (2)
C(13)–C(14)	1·528 (5)	C(15)–N(3)–C(17)	112·0 (3)
C(15)–C(16)	1·509 (5)	N(3)–C(11)–C(12)	114·5 (3)
C(17)–C(18)	1·523 (5)	N(3)–C(13)–C(14)	114·4 (3)
		N(3)–C(15)–C(16)	115·5 (3)
		N(3)–C(17)–C(18)	114·4 (3)

(Bernstein, Regev & Herbstein, 1977) and phenanthrene–DDQ, PH–DDQ (Herbstein, Kapon, Rzonzew & Rabinovich, 1978). The half-normal probability test (Abrahams & Keve, 1971) indicates that there is no significant difference in the bond lengths and angles, which are chemically but not crystallographically equivalent. The equation of the best least-squares plane through the ring atoms with the deviations of the substituents out of the plane is shown in Table 4. The ring is planar within experimental error, with the substituents significantly displaced from its mean plane. In addition Cl and CN are bent towards the O atoms of the carbonyl groups.

The non-planarity of the DDQ− anion may presumably be ascribed to steric interaction between the

Fig. 1. The DDQ⁻ anion with atom numbering, bond distances (Å) and valence angles (°).

Table 3. *Comparison of the bond lengths (Å) and angles (°) in the DDQ molecule as found in TEA⁺–DDQ⁻ and in DDQ*

	TEA⁺–DDQ⁻	DDQ
Cl–C	1·717–1·714 (3)	1·698–1·695 (3)
O–C	1·244–1·248 (4)	1·199–1·206 (3)
N–C	1·135–1·144 (4)	1·133–1·135 (4)
C(6)–C(7) C(5)–C(8)	1·425–1·435 (5)	1·429–1·442 (4)
C(1)–C(2) C(3)–C(4)	1·455–1·471 (4)	1·481–1·483 (4)
C(1)–C(6) C(4)–C(5)	1·437–1·451 (4)	1·491–1·502 (4)
C(2)–C(3) C(5)–C(6)	1·363–1·386 (4)	1·339–1·343 (4)

substituents. The non-bonded distances [Cl(1)···Cl(2) 3·167 (4), Cl(2)···O(2) 2·919 (5), O(1)···C(7) 2·760 (6), C(7)···C(8) 2·845 (6), C(8)···O(2) 2·776 (6), O(1)···Cl(1) 2·923 (5) Å], which agree well with those observed in neutral DDQ (Zanotti, Bardi & Del Pra, 1980), in tetrachloro-*p*-benzoquinone (van Weperen & Visser, 1972), and in the π-molecular compounds BPH–DDQ and PH–DDQ, are appreciably shorter than the sum of the van der Waals radii (1·8, 1·4 and 1·7 Å for Cl, O and C respectively; Nyburg, 1961).

Table 4. *Deviations (10⁻³ Å) of the atoms from the least-squares plane of the C₆ ring*

The equation of the plane is $0·0734X + 0·3506Y + 0·9336Z = 4·5413$ in orthogonal Å space with X parallel to a, Z perpendicular to a in the *ac* plane and Y perpendicular to the *ac* plane. An asterisk denotes an atom not used in the plane calculation. The corresponding values for the neutral DDQ molecule are reported for comparison.

	TEA⁺–DDQ⁻	DDQ
C(1)	−14 (5)	−24 (3)
C(2)	8 (5)	19 (3)
C(3)	0 (5)	−2 (3)
C(4)	−1 (5)	−10 (3)
C(5)	−7 (5)	4 (3)
C(6)	14 (5)	13 (3)
C(7)*	142 (5)	61 (3)
C(8)*	10 (5)	−1 (3)
N(1)*	266 (5)	113 (3)
N(2)*	8 (5)	−12 (3)
O(1)*	−45 (3)	−97 (2)
O(2)*	36 (3)	−8 (2)
Cl(1)*	82 (2)	71 (1)
Cl(2)*	28 (2)	−10 (1)

Finally, the present X-ray analysis of TEA⁺–DDQ⁻ provides bonding parameters for comparison with those found in the neutral DDQ molecule. In Tables 3 and 4, therefore, the geometry of the DDQ molecule is compared with that of DDQ in TEA⁺–DDQ⁻. There are significant differences in the C=O, C=C and =C–C= bonds. The first and the second are longer whilst the third is shorter in TEA⁺–DDQ⁻ than in DDQ. These changes are comparable to those found in other *p*-benzoquinoid structures in going from the neutral molecule to the radical anion (Herbstein, 1971; Zanotti & Del Pra, 1980). The bond-length variations correspond to a rearrangement of the π bonding upon addition of the unpaired electron causing a weaker carbonyl bond and a more benzenoid character of the ring. In addition the DDQ molecule appears to be slightly less distorted from planarity in TEA⁺–DDQ⁻ than in DDQ itself. The reduction in the deformation of the DDQ molecules, that occurs also on their incorporation in the π-molecular compounds, may be due to the donor–acceptor interaction.

The TEA⁺ cation assumes a distorted tetrahedral configuration with valence angles ranging from 108·0 to 112·1° [mean 109·5 (2)°]. The N⁺–C(sp^3) bonds range from 1·510 to 1·522 Å and average 1·514 (4) Å. This value agrees with the standard value (Pauling, 1960) and with those reported for several quaternary ammonium salts (Zanotti, Valle & Del Pra, 1978). The C(sp^3)–C(sp^3) bonds are slightly shorter than the standard value, but the difference does not appear to be chemically significant. Finally, the departure of the N⁺–C–C angles [114·4–115·5°; mean 114·7 (3)°] from the tetrahedral value could be explained by the steric hindrance within the bulky TEA⁺ cation.
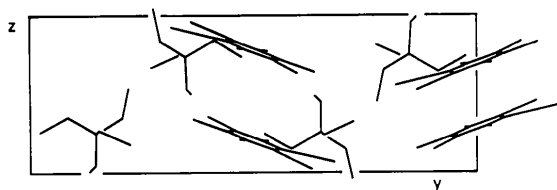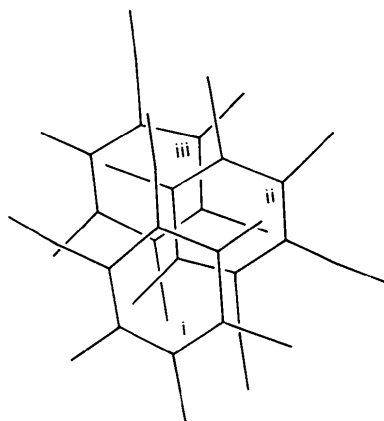
Fig. 2. Crystal structure viewed down **a**.

Fig. 3. Nearest-neighbor packing within the column of DDQ⁻. Direction of view is perpendicular to the molecular plane. (i) is related to (ii) by a centre of symmetry and to (iii) by the c translation.

Table 5. *Shortest intermolecular contacts* (Å) *within a dimeric unit, with e.s.d.'s in parentheses*

Primed atoms are related to unprimed ones by a crystallographic center of symmetry at $\frac{1}{2},\frac{1}{2},0$. (The equivalent position of the primed atoms is $1 - x, 1 - y, -z$).

C(5)···O(1')	2·947 (6)	C(2)···C(6')	3·070 (6)
C(6)···C(1')	2·995 (6)	C(2)···C(7')	3·137 (6)
C(1)···C(1')	3·025 (6)	C(5)···C(1')	3·272 (6)

The TEA⁺–DDQ⁻ crystal structure viewed down **a** is presented in Fig. 2. DDQ⁻ anions are stacked face-to-face along the c axis forming columns which are held together through TEA⁺ cations. Within a DDQ⁻ column two markedly different interplanar separations alternate: 2·906 (6) and 3·626 (6) Å. In addition DDQ⁻ anions are tilted at an angle of 21·0° with respect to the c axis and the molecular overlaps, as viewed perpendicularly to the molecular plane, are shown in Fig. 3. The shortest intermolecular contacts within a closely spaced DDQ⁻ pair (indicated as i–ii in Fig. 3) are listed in Table 5. No interatomic distances appreciably shorter than the sums of the van der Waals radii have been found between DDQ⁻ columns and TEA⁺ cations.

TEA⁺–DDQ⁻ is thus a quasi one-dimensional structure which, with respect to charge-transfer and exchange interactions, may be viewed as made up of dimeric (DDQ⁻)₂ units arranged in columns, the interaction between dimers being relatively weak. Such a view is confirmed by recent optical (Bozio, Ragazzon, Girlando, Zanon & Pecile, 1981) and ESR measurements (Pasimeni, Brustolon, Zanonato & Corvaja, 1980).

For similar free-radical salts, such as the alkali TCNQ salts, two crystal phases are known: the high-temperature one contains regularly spaced anion columns, that at low temperature contains alternating or dimerized columns (Terauchi, 1978). The transition between the two phases has been interpreted as a spin–Peierls transition which occurs because of the instability of the one-dimensional system towards a periodic lattice distortion. The strong dimerization of the anion columns found at room temperature in TEA⁺–DDQ⁻ as well as in TTF–DDQ (Mayerle & Torrance, 1981) (intra- and interdimer spacings: 3·0 and 3·56 Å) suggests that the distorted dimeric structure is strongly stabilized in DDQ systems as compared with other free-radical salts. It is tempting to think that the attractive interaction between permanent dipole moments of the DDQ⁻ anions may play a role in this stabilization and, together with the strong electronic exchange interaction, may determine the unusually short interplanar separation in the (DDQ⁻)₂ dimers.

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The Structure of 2,3,6,7-Tetramethyl-4aβ,5,8,8aβ-tetrahydro-1-naphthoquin-4α-ol*

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Abstract

Crystals of the title compound, $C_{14}H_{20}O_2$, $M_r = 220 \cdot 31$, are monoclinic, $C2/c$, with $a = 13 \cdot 898$ (3), $b = 5 \cdot 228$ (1), $c = 17 \cdot 316$ (3) Å, $\beta = 97 \cdot 442$ (7)°, $V = 1247 \cdot 7$ (5) Å^3, $Z = 4$, $D_c = 1 \cdot 1728$, $D_o = 1 \cdot 174$ g cm^{-3}, μ(Mo $K\alpha$) $= 0 \cdot 714$ cm^{-1}, λ(Mo $K\alpha$) $= 0 \cdot 71073$ Å. Data were collected on a CAD-4 single-crystal X-ray diffractometer using Mo $K\alpha$ radiation. The structure was determined by direct methods and refined to $R = 0 \cdot 058$ for 888 independent observed reflections. The structure contains molecules lying on twofold axes as a result of disorder within the lattice. Two types of hydrogen bonding, $O(4) \cdots O(1)$ and $O(4) \cdots O(4)$, join molecules into a network within slabs parallel to (001). Molecules adopt a conformation where the hydroxyl group occupies a position pseudo-equatorial to the cyclohexenone ring. On the basis of the molecular conformation and the relatively short $C(3) \cdots H(5)$ distance, the photochemical reaction involving hydrogen abstraction is rationalized.

Introduction

Several structural analyses on tetrahydronaphthoquinols have been reported (Greenhough & Trotter, 1980*a,b,c*) in conjunction with photochemical studies on their solid-state reactions. As part of these continuing studies, a structural determination of the present compound was undertaken to verify the molecular conformation in the solid state and to elucidate the geometric parameters in the photoreaction involving hydrogen abstraction by the β-enone carbon.

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* IUPAC name: 4α-hydroxy-2,3,6,7-tetramethyl-4aβ,5,8,8aβ-tetrahydro-1(4*H*)-naphthalenone.

Experimental

The title compound was synthesized *via* sodium borohydride reduction of the 2,3-dimethyl-*p*-benzoquinone/2,3-dimethyl-1,3-butadiene Diels–Alder adduct (Fig. 1) and was subsequently recrystallized from an ethanol/petroleum ether solution. The crystal used for photographs and data collection measured approximately $0 \cdot 3 \times 0 \cdot 6 \times 0 \cdot 4$ mm, having seven well defined faces.

Preliminary precession and Weissenberg photographs revealed the following absence conditions: *h0l*, $l = 2n + 1$, and *hkl*, $h + k = 2n + 1$, characteristic of the space groups Cc and $C2/c$.

The crystal was mounted in a general orientation on an Enraf–Nonius CAD-4 diffractometer. Cell constants and an orientation matrix were determined from a least-squares refinement of the setting angles for 25
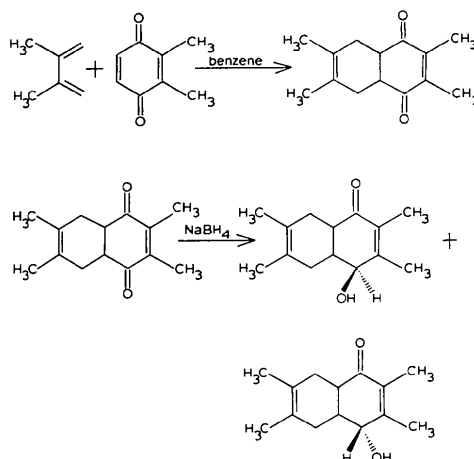

Fig. 1. Preparative reaction scheme leading to 2,3,6,7-tetramethyl-4aβ,5,8,8aβ-tetrahydro-1-naphthoquin-4α-ol.