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.

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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 (λ = 0·7107 Å, μ = 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*-phenylenediamine, 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 θ = 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

* This paper is dedicated to the memory of Professor Silvio Bezzi, an acknowledged pioneer of structural chemistry in Italy.

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structural solution was evident. The conventional R value was 0·41. Refinement of the structure parameters was carried out by a full-matrix least-squares analysis, allowing the atoms to vibrate anisotropically. The correction for the real and imaginary parts of the anomalous dispersion was applied to Cl only (*International Tables for X-ray Crystallography*, 1974). The final R value for the 1310 observed reflexions with $I \geq 2{\cdot}5\sigma(I)$ was 0·041 ($R_w = 0{\cdot}046$).

The quantity minimized was $\sum w(|F_o| - |F_c|)^2$, $w = 2{\cdot}05[\sigma^2(F_o) + 0{\cdot}001F_o^2]^{-1}$, to give average values of $w\Delta^2$ ($\Delta = |F_o| - |F_c|$) for groups of reflexions independent of the value of $|F_o|$.

The calculations were carried out on the Cyber 76 computer of the Centro di Calcolo Inter-Universitario Italia Nord Orientale, with the *SHELX* 76 system of crystallographic programs (Sheldrick, 1976). All atomic scattering factors were those of *International Tables for X-ray Crystallography* (1974).

Discussion. A view of the molecule with the numbering system is presented in Fig. 1. The final structural parameters of all atoms are reported in Table 1.* The molecule has essentially *mm*2 symmetry, although the only symmetry required by the space group is 1, as in the π-molecular compounds benzo[*c*]phenanthrene–DDQ, BPH–DDQ (Bernstein, Regev & Herbstein, 1977) and phenanthrene–DDQ, PH–DDQ (Herbstein, Kapon, Rzonzew & Rabinovich, 1978). The HNP 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 are given in Table 2. Small but significant deviations from planarity are observed in the molecule. The ring has therefore adopted a shallow twist-boat conformation and the substituents (Cl and CN) are bent towards the O atoms of the carbonyl groups. There is a further distortion in the DDQ molecule in that the O atoms are bent away from the Cl atoms towards the cyano groups.

The non-planarity of the DDQ molecule may presumably be ascribed to steric interactions between the substituents. The non-bonded distances [Cl(1)···Cl(2), 3·178; Cl(2)···O(1), 2·925; O(1)···C(7), 2·748; C(7)···C(8), 2·899; C(8)···O(2), 2·719; O(2)···Cl(1), 2·914 Å], which agree well with those observed in tetrachloro-*p*-benzoquinone (van Weperen & Visser, 1972) and in the π-molecular compounds BPH–DDQ and PH–DDQ, are appreciably shorter than the sums of the van der Waals radii (1·8, 1·4 and 1·7 Å for Cl, O and C respectively; Nyburg, 1961).

The bonding parameters of the DDQ molecule are in agreement with those found in analogous compounds (van Weperen & Visser, 1972; Tamura & Ogawa,

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34601 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

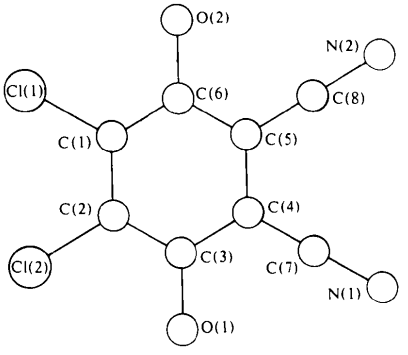

Fig. 1. The DDQ molecule with the atom numbering.

Table 1. *Atomic coordinates with their e.s.d.'s in parentheses*

	x	y	z
Cl(1)	0·50750 (5)	0·06909 (6)	−0·2642 (2)
Cl(2)	0·48441 (5)	0·17408 (6)	0·1782 (2)
O(1)	0·3251 (1)	0·2014 (1)	0·2662 (4)
O(2)	0·3656 (1)	0·0377 (1)	−0·4911 (4)
C(1)	0·4220 (2)	0·0999 (2)	−0·1748 (5)
C(2)	0·4121 (2)	0·1435 (2)	0·0128 (5)
C(3)	0·3361 (2)	0·1669 (2)	0·0904 (5)
C(4)	0·2716 (2)	0·1454 (2)	−0·0577 (5)
C(5)	0·2818 (2)	0·1023 (2)	−0·2468 (5)
C(6)	0·3584 (2)	0·0756 (2)	−0·3204 (5)
C(7)	0·1988 (2)	0·1733 (2)	0·0127 (5)
C(8)	0·2217 (2)	0·0781 (2)	−0·3910 (5)
N(1)	0·1416 (2)	0·1959 (2)	0·0666 (6)
N(2)	0·1756 (2)	0·0573 (2)	−0·5094 (5)

Table 2. *Deviations* (10^{-3} Å) *of the atoms from the least-squares plane of the* C_6 *ring*

The equation of the plane is $0{\cdot}0997X + 0{\cdot}8491Y - 0{\cdot}5187Z = 2{\cdot}7009$, 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 DDQ molecule in BPH–DDQ and PH–DDQ are reported for comparison.

	DDQ	BPH–DDQ	PH–DDQ
C(1)	−2 (3)	2	8
C(2)	19 (3)	11	−15
C(3)	−24 (3)	6	19
C(4)	13 (3)	−6	6
C(5)	4 (3)	−19	−14
C(6)	−10 (3)	0	−4
C(7)*	61 (3)	12	1
C(8)*	−1 (3)	−40	−4
N(1)*	113 (3)	Not given	−9
N(2)*	−12 (3)	Not given	11
O(1)*	−97 (2)	7	98
O(2)*	−8 (2)	15	−41
Cl(1)*	−10 (1)	−8	12
Cl(2)*	71 (1)	−10	−89

Table 3. *Comparison of the bond lengths* (Å) *and angles* (°) *in the DDQ molecule as found in DDQ, BPH–DDQ and PH–DDQ*

E.s.d.'s of BPH–DDQ and PH–DDQ are ~0·007 Å for C–C, ~0·006 Å for C–O and ~0·005 Å for C–Cl bonds and for angles ~0·5°.

	DDQ	BPH–DDQ	PH–DDQ
Cl(1)–C(1)	1·695 (3)	1·732	1·715
Cl(2)–C(2)	1·698 (3)	1·741	1·707
O(1)–C(3)	1·206 (3)	1·203	1·206
O(2)–C(6)	1·199 (3)	1·214	1·222
N(1)–C(7)	1·133 (4)	Not given	1·127
N(2)–C(8)	1·135 (4)	Not given	1·144
C(7)–C(4)	1·442 (4)	1·503	1·460
C(8)–C(5)	1·429 (4)	1·455	1·439
C(1)–C(2)	1·339 (4)	1·344	1·350
C(2)–C(3)	1·483 (4)	1·490	1·499
C(3)–C(4)	1·491 (4)	1·477	1·502
C(4)–C(5)	1·343 (4)	1·345	1·334
C(5)–C(6)	1·502 (4)	1·502	1·499
C(6)–C(1)	1·481 (4)	1·458	1·484
Cl(1)–C(1)–C(2)	122·8 (2)	120·9	122·2
Cl(1)–C(1)–C(6)	115·1 (2)	116·5	115·8
C(2)–C(1)–C(6)	122·1 (2)	122·5	121·9
Cl(2)–C(2)–C(1)	122·8 (2)	122·9	123·0
Cl(2)–C(2)–C(3)	115·9 (2)	115·9	115·6
C(1)–C(2)–C(3)	121·3 (2)	121·2	121·5
O(1)–C(3)–C(4)	119·8 (3)	120·8	121·3
O(1)–C(3)–C(2)	122·8 (2)	122·5	122·7
C(2)–C(3)–C(4)	117·4 (2)	116·7	116·0
N(1)–C(7)–C(4)	179·3 (3)	Not given	178·4
C(7)–C(4)–C(3)	116·6 (2)	117·1	115·5
C(7)–C(4)–C(5)	122·4 (2)	121·0	122·2
C(3)–C(4)–C(5)	121·0 (2)	121·8	122·3
N(2)–C(8)–C(5)	177·6 (3)	Not given	177·5
C(8)–C(5)–C(6)	115·2 (2)	116·6	116·4
C(8)–C(5)–C(4)	123·2 (2)	122·3	122·1
C(4)–C(5)–C(6)	121·6 (2)	121·1	121·5
O(2)–C(6)–C(5)	119·8 (2)	119·4	120·4
O(2)–C(6)–C(1)	123·7 (2)	124·0	122·8
C(5)–C(6)–C(1)	116·5 (2)	116·7	116·8

1977; Chu, Jeffrey & Sakurai, 1962; Long, Sparks & Trueblood, 1965; Yakushi, Ikemoto & Kuroda, 1974; Prout & Tickle, 1973).

Finally, the present X-ray analysis of DDQ provides a standard geometry for comparison with those found in the previously quoted π-molecular compounds. In Tables 2 and 3, therefore, the geometry of the DDQ molecule is compared with those of DDQ in BPH–DDQ and PH–DDQ. As in other charge-transfer molecular compounds, no significant differences between bond lengths and angles in the molecules in the DDQ crystals and in BPH–DDQ and PH–DDQ are found. This is not surprising since the forces required to alter these geometrical features are larger than those involved in molecular-compound formation. In addition there seems little doubt that the ground state of the π-molecular compounds is non-ionic. The DDQ molecule, however, appears to be slightly less distorted from planarity in BPH–DDQ and PH–DDQ than in DDQ itself. The reduction in the deformation of the DDQ molecules that occurs on their incorporation in the molecular compounds may be due to the donor–acceptor interaction.

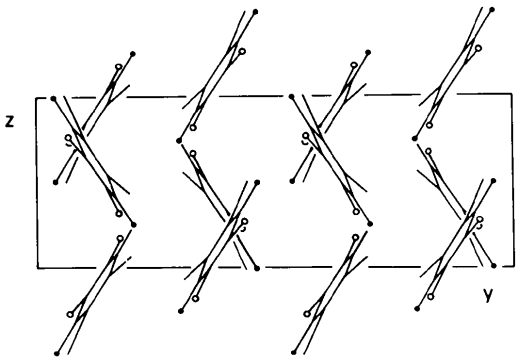

Fig. 2. Crystal structure viewed down *a*.

The molecules are involved in the conventional herring-bone packing of planar rings, which is mainly due to van der Waals forces. The DDQ crystal structure viewed down *a* is presented in Fig. 2. Apart from a rather short intermolecular distance, 2·94 Å, between a cyano N atom and a C of the quinoid ring, the remaining contact distances are as expected for standard van der Waals values.

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trans-(2*R*,5*R*)-2,5-Dimethylpyrrolidinium (*S*)-Mandelate at 238 K

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Abstract. $C_6H_{14}N^+.C_8H_7O_3^-$, $M_r = 251{\cdot}33$, triclinic, $P1$, $Z = 1$, $F(000) = 272$, at 238 K, $a = 7{\cdot}610\,(4)$, $b = 8{\cdot}325\,(4)$, $c = 5{\cdot}863\,(4)$ Å, $\alpha = 96{\cdot}58\,(5)$, $\beta = 102{\cdot}58\,(5)$, $\gamma = 78{\cdot}90\,(5)°$, $V = 354{\cdot}7\,(8)$ Å^3, $D_x = 1{\cdot}18$, $D_m = 1{\cdot}15$ Mg m^{-3} (measured at 296 K, by flotation in a carbon tetrachloride/cyclohexane mixture). Full-matrix least-squares refinement of 795 reflections resulted in a final conventional R index of 0·038. The absolute configuration of the (−)-*trans*-2,5-dimethylpyrrolidine moiety is 2*R*,5*R*.

Introduction. Single crystals of $C_{14}H_{21}NO_3$ formed as clear tablets from a dichloromethane solution upon standing at room temperature. The specimen crystal used to collect the intensity data was of dimensions 0·3 × 0·1 × 0·1 mm. Intensity data were collected using a Syntex $P2_1$ automated four-circle diffractometer and graphite-monochromatized Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å. The data crystal was kept at 238 K with a Syntex LT-1 low-temperature inert-gas flow system (N_2). Intensity data were measured by the ω-scan technique, with ω-scan rate variable from 1·5 to 5·0° min^{-1}. Each reflection was scanned symmetrically over 1·0° in ω about the $K\bar{\alpha}$ maximum and background offset ±1·0° in ω from the $K\bar{\alpha}$ maximum. Four check reflections were remeasured after every 96 reflections. An analysis of check reflections (Henslee & Davis, 1975) indicated no significant change from the initial intensities during the 22·5 h data-collection period. Usual corrections and standard-deviation assignments to the data were as detailed elsewhere (Riley & Davis, 1975); absorption corrections ($\mu = 0{\cdot}088$ mm^{-1}) were not applied; the p factor was set at 0·05. Of 925 reflections measured in the range $4° \leq 2\theta \leq 45°$, only 795 with $I_o \geq 1{\cdot}5\sigma(I_o)$ were used in the ensuing solution and refinement of the structure.

The structure was solved by direct phasing methods, using the *MULTAN* program package (Main, Woolfson, Declercq & Germain, 1974). Full-matrix least-squares refinement of all non-hydrogen atoms, initially isotropic and then anisotropic, resulted in convergence. A difference map at this stage yielded the locations of all H atoms, which were included isotropically in later cycles of refinement. At full convergence, $R = \sum ||F_o| - |F_c||/\sum |F_o| = 0{\cdot}038$ and $R_w = (\sum w||F_o| - |F_c||^2/\sum w|F_o|^2)^{1/2} = 0{\cdot}039$. The function minimized was $(\sum w||F_o| - |F_c||^2)$, where the weights w are $1/\sigma(|F_o|)^2$, the reciprocal square of the standard deviation of each observation $|F_o|$. Neutral-atom scattering factors for O, N, C (*International Tables for X-ray Crystallography*, 1974) and H (Stewart, Davidson & Simpson, 1965) were used. In the final cycle of least-squares refinement, no non-hydrogen parameter shifted by more than 0·12 of its e.s.d., and no H parameter by more than 0·25 of its e.s.d. The largest peaks on a final difference map were about 0·15 e Å^{-3}.

Final atomic fractional coordinates, with estimated standard deviations as obtained from the inverse matrix, are presented in Table 1.†

Discussion. *trans*-2,5-Dimethylpyrrolidine, prepared by catalytic reduction (Overberger, Palmer, Marks & Byrd, 1955) of the *N*-aminopyrrolidine (Dervan & Uyehara, 1976) and resolved *via* the salts of mandelic acid, has been studied extensively. The present work has been undertaken to determine the absolute configuration of (−)-*trans*-2,5-dimethylpyrrolidine, which

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† Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34746 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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