Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

2,3,5-Trichloro-6-(4-methylpiperidin-1-yl)-1,4-benzoquinone: a synchrotron study

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Key indicators

Single-crystal synchrotron study
T = 150 K
Mean σ(C–C) = 0.002 Å
R factor = 0.033
wR factor = 0.092
Data-to-parameter ratio = 19.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

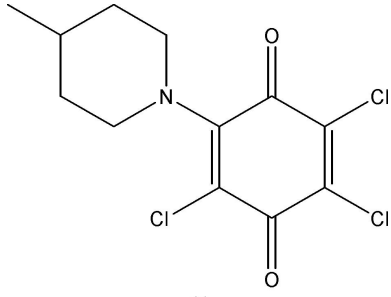
Received 19 January 2005
Accepted 4 February 2005
Online 19 February 2005

The title compound, $C_{12}H_{12}Cl_3NO_2$, is a purple chromophore with an absorption at 563 nm in acetone solution. The benzenoid ring in the structure exhibits strong quinoid-like character. In the crystal structure, the molecules pack in alternating layers that are stabilized by close Cl···Cl intermolecular contacts.

Comment

The reactions of primary, secondary and tertiary amines with 2,3,5,6-tetrachloro-1,4-benzoquinone (chloranil), which yield highly coloured products, are well documented (Sivadjian, 1935; Buckley *et al.*, 1957; Buckley & Henbest, 1956), and indeed the differently coloured products have been used as qualitative indicators of the degree of substitution on amines (Buuhoi *et al.*, 1954).

Recent interest has focused on the reactions of enamines derived from tertiary amines with chloranil (Krivokapic & Anderson, 2002; Alnabari & Bittner, 2000) and other symmetrical quinoidal (Szablewski, 1994) systems, yielding conjugated chromophores with long-wavelength absorptions which are of interest for non-linear optics.



(I)

The title compound, (I), is the result of a reaction between the secondary amine 4-methylpiperidine and chloranil. Although reactions between chloranil and heterocyclic secondary amines have been investigated (Smith & Davis, 1984; Muralikrishna & Krishnamurthy, 1984), as have been photo-induced reactions of the products (Kallmayer & Fritzen, 1992), we believe that no structure of such a compound has been reported to date.

The molecular structure of (I) is illustrated in Fig. 1. The benzenoid ring exhibits strong quinoidal character (see Table 1) due to the strong electronic influence of the two keto groups, substituted *para* to each other on the ring. The saturated ring displays a typical chair conformation.

In the crystal structure, the molecules pack in alternating *AB* layers; *A* and *B* being related by a center of symmetry

(Fig. 2). The crystal packing is stabilized by close Cl···Cl intermolecular contacts [$Cl1^{i}\cdots Cl1^{ii}$ = 3.2333 (12) Å]. Another, albeit much weaker, Cl···Cl intermolecular contact [$Cl3^{ii}\cdots Cl3^{iii}$ = 3.5450 (14) Å] is also present (see Fig. 2 for details).

Experimental

2,3,5,6-Tetrachloro-1,4-benzoquinone (1 g, 4 × 10^{-3} mol) was stirred in toluene (250 ml) with 4-methylpiperidine (0.8 g, 8 × 10^{-3} mol) at room temperature for 3 h. The solution very rapidly became dark purple in colour. Column chromatography of the reaction mixture performed on neutral silica gel with dichloromethane eluent was used to purify the product. After evaporating the solvent from the product-containing fraction *in vacuo*, the purified compound was recrystallized from hot dichloromethane, yielding purple microcrystals (0.260 g, 21%). Microanalysis calculated for $C_{12}H_{12}Cl_3NO_2$: C 46.71, N 4.54, H 3.92%; found: C 47.01, N 4.81, H 3.98%. ^{1}H NMR (400 Hz, CD_2Cl_2): δ 1.00 (doublet, 1 × CH_3), 1.40 (quartet, 2 × ^{1}H), 1.65 (multiplet, —CH—), 1.75 (doublet, 2 × ^{1}H), 3.25 (triplet, 2 × ^{1}H), 3.75 (doublet, 2 × ^{1}H). ^{13}C NMR (400 Hz, CD_2Cl_2): δ 22, 30, 35, 118, 138, 141, 171, 175. MS: *m*/*z*, M^+(EI+) 306.89. (100% molecular ion). The product displayed positive (bathochromic) solvatochromism (λ_{max} = 549 nm in hexane, 554 nm in diethyl ether, 556 nm in acetone, 571 nm in nitromethane and 576 nm in dichloromethane).

Crystal data

$C_{12}H_{12}Cl_3NO_2$	Z = 2
M_r = 308.58	D_x = 1.573 Mg m^{-3}
Triclinic, $P\overline{1}$	Synchrotron radiation, λ = 0.6928 Å
a = 6.9577 (14) Å	Cell parameters from 3573 reflections
b = 9.3611 (19) Å	θ = 2.5–27.6°
c = 10.724 (2) Å	μ = 0.70 mm^{-1}
α = 70.64 (3)°	T = 150 (2) K
β = 83.96 (3)°	Needle, deep purple
γ = 82.27 (3)°	0.09 × 0.04 × 0.02 mm
V = 651.6 (2) Å^3	

Data collection

Bruker SMART CCD diffractometer	3099 independent reflections
ω scans	2932 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)	R_{int} = 0.024
T_{min} = 0.91, T_{max} = 0.99	θ_{max} = 28.3°
4339 measured reflections	$h = -9 \rightarrow 8$
	$k = -12 \rightarrow 10$
	$l = -13 \rightarrow 14$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0527P)^2 + 0.1747P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.033	$(\Delta/\sigma)_{max}$ = 0.001
$wR(F^2)$ = 0.092	$\Delta\rho_{max}$ = 0.48 e Å^{-3}
S = 1.05	$\Delta\rho_{min}$ = −0.25 e Å^{-3}
3099 reflections	
163 parameters	
H-atom parameters constrained	

Table 1
Selected bond lengths (Å).

C1—C6	1.3741 (18)	C2—C3	1.4914 (18)
C3—C4	1.3363 (18)	C4—C5	1.4979 (18)
C1—C2	1.5192 (17)	C5—C6	1.4564 (18)

The H atoms were included in calculated positions and treated as riding atoms, with C—H = 0.98–1.00 Å and U_{iso}(H) = 1.2U_{eq}(C), or 1.5U_{eq}(C) for methyl H atoms.

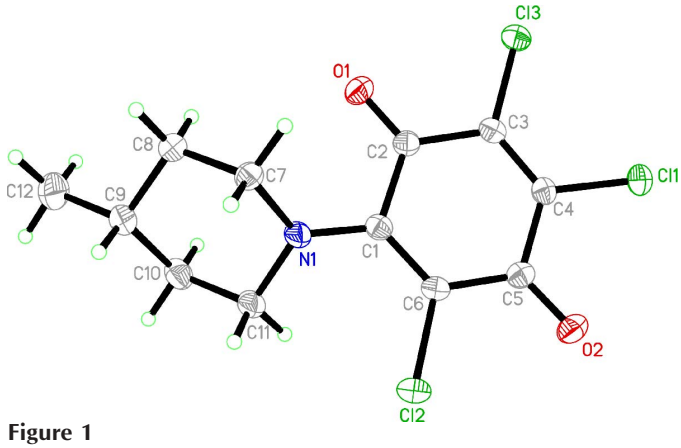


Figure 1
The molecular structure of compound (I). Anisotropic displacement parameters are displayed at the 50% probability level.

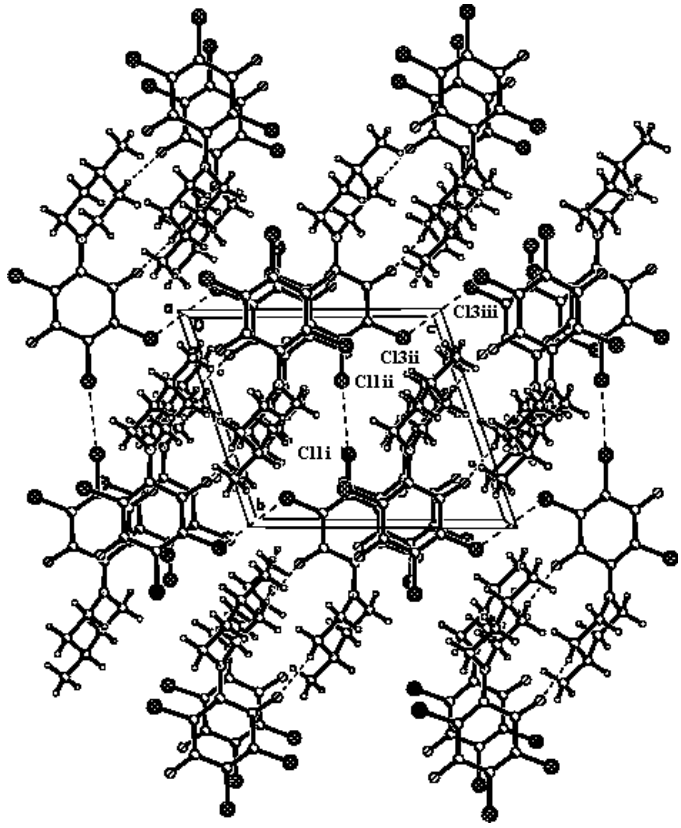


Figure 2
The crystal packing of compound (I), viewed down the *a* axis. The Cl···Cl contacts are illustrated by dashed lines [Symmetry codes: (i) *x*, *y*, *z*; (ii) 1 − *x*, 1 − *y*, 1 − *z*; (iii) *x* + 1, *y* − 1, *z* + 1.]

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXL97*.

The authors acknowledge Simon J. Teat (CCLRC Daresbury Laboratory) for local synchrotron support and the Synchrotron Radiation Source, CCLRC Daresbury Labora-

tory, England, for access to scientific facilities. JMC also thanks the Royal Society for a University Research Fellowship and St Catharine's College, Cambridge, for a Bibby Research Fellowship. KFB is grateful to the EPSRC for a PhD studentship (0280020X) and the Centre of Molecular Structure and Dynamics (CMSD), CCLRC, for a CASE sponsorship.

References

Alnabari, M. & Bittner, S. (2000). *Synthesis*, pp. 1087–1090.
Bruker (1998). *SADABS*, *SMART*, *SAINT* and *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
Buckley, D., Dunstan, S. & Henbest, H. B. (1957). *J. Chem. Soc.* pp. 4880–4891.
Buckley, D. & Henbest, H. B. (1956). *Chem. Ind.* pp. 1096–1096.
Buuhoi, N. P., Royer, R. & Huberthabart, M. (1954). *Recl Trav. Chim. Pays-Bas* **73**, 188–192.
Kallmayer, H. J. & Fritzen, W (1992). *Pharm. Acta Helv.* **67**, 210–213.
Krivokapic, A. & Anderson, H. L. (2002). *Acta Cryst.* E**58**, o259–o260.
Muralikrishna, U. & Krishnamurthy, M. (1984). *Spectrochim. Acta A*, **40**, 65–68.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Sivadjian, J. (1935). *Bull. Soc. Chim. Fr.* **2**, 623–625.
Smith, R. E. & Davis, W. R. (1984). *Anal. Chem.* **56**, 2345–2349.
Szablewski, M. (1994). *J. Org. Chem.* **59**, 954–956.