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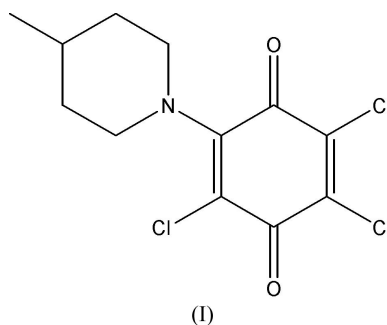
Key indicatorsSingle-crystal synchrotron study
 $T = 150$ K
Mean $\sigma(\text{C}-\text{C}) = 0.002$ Å
 R factor = 0.033
 wR factor = 0.092
Data-to-parameter ratio = 19.0For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.**2,3,5-Trichloro-6-(4-methylpiperidin-1-yl)-1,4-benzoquinone: a synchrotron study**

The title compound, $\text{C}_{12}\text{H}_{12}\text{Cl}_3\text{NO}_2$, 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 $\text{Cl}\cdots\text{Cl}$ 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 (Buhoi *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.



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

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(Fig. 2). The crystal packing is stabilized by close Cl \cdots Cl intermolecular contacts [Cl1ⁱ \cdots Cl1ⁱⁱ = 3.2333 (12) Å]. Another, albeit much weaker, Cl \cdots Cl intermolecular contact [Cl3ⁱⁱⁱ \cdots Cl3ⁱⁱⁱ = 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 C₁₂H₁₂Cl₃NO₂: C 46.71, N 4.54, H 3.92%; found: C 47.01, N 4.81, H 3.98%. ¹H NMR (400 Hz, CD₂Cl₂): δ 1.00 (doublet, 1 \times CH₃), 1.40 (quartet, 2 \times ¹H), 1.65 (multiplet, —CH—), 1.75 (doublet, 2 \times ¹H), 3.25 (triplet, 2 \times ¹H), 3.75 (doublet, 2 \times ¹H). ¹³C NMR (400 Hz, CD₂Cl₂): 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 ₃ NO ₂	Z = 2
<i>M</i> _r = 308.58	<i>D</i> _x = 1.573 Mg m ⁻³
Triclinic, <i>P</i> $\bar{1}$	Synchrotron radiation, λ = 0.6928 Å
<i>a</i> = 6.9577 (14) Å	Cell parameters from 3573 reflections
<i>b</i> = 9.3611 (19) Å	θ = 2.5–27.6°
<i>c</i> = 10.724 (2) Å	μ = 0.70 mm ⁻¹
α = 70.64 (3)°	<i>T</i> = 150 (2) K
β = 83.96 (3)°	Needle, deep purple
γ = 82.27 (3)°	0.09 \times 0.04 \times 0.02 mm
<i>V</i> = 651.6 (2) Å ³	

Data collection

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

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0527P)^2 + 0.1747P]$
$R[F^2 > 2\sigma(F^2)] = 0.033$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.092$	$(\Delta/\sigma)_{\max} = 0.001$
<i>S</i> = 1.05	$\Delta\rho_{\max} = 0.48 \text{ e \AA}^{-3}$
3099 reflections	$\Delta\rho_{\min} = -0.25 \text{ e \AA}^{-3}$
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) = 1.2*U*_{eq}(C), or 1.5*U*_{eq}(C) for methyl H atoms.

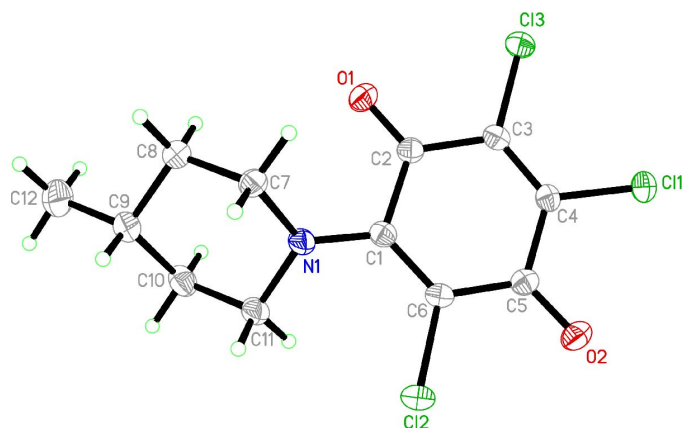


Figure 1

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

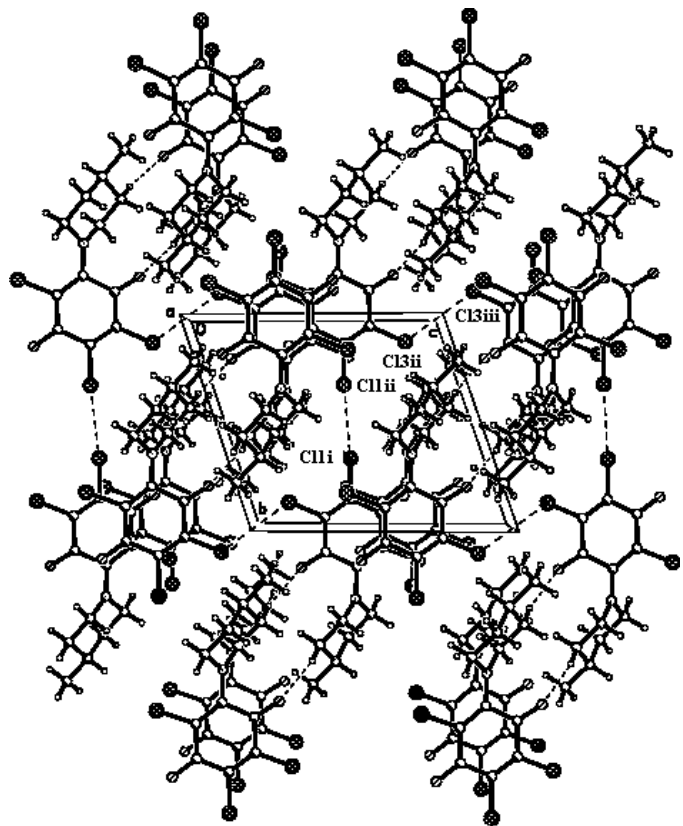


Figure 2

The crystal packing of compound (I), viewed down the *a* axis. The Cl \cdots 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*.

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supporting information

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Crystal data

$C_{12}H_{12}Cl_3NO_2$

$M_r = 308.58$

Triclinic, $P\bar{1}$

Hall symbol: -P 1

$a = 6.9577$ (14) Å

$b = 9.3611$ (19) Å

$c = 10.724$ (2) Å

$\alpha = 70.64$ (3)°

$\beta = 83.96$ (3)°

$\gamma = 82.27$ (3)°

$V = 651.6$ (2) Å³

$Z = 2$

$F(000) = 316$

$D_x = 1.573$ Mg m⁻³

Synchrotron radiation, $\lambda = 0.6928$ Å

Cell parameters from 3573 reflections

$\theta = 2.5$ – 27.6 °

$\mu = 0.70$ mm⁻¹

$T = 150$ K

Needle, deep purple

$0.09 \times 0.04 \times 0.02$ mm

Data collection

Bruker SMART

diffractometer

Radiation source: Station 9.8, SRS, Daresbury

labs, UK

Si (111) monochromator

CCD scans

Absorption correction: multi-scan

(SADABS; Bruker, 1998)

$T_{\min} = 0.91$, $T_{\max} = 0.99$

4339 measured reflections

3099 independent reflections

2932 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.024$

$\theta_{\max} = 28.3$ °, $\theta_{\min} = 2.0$ °

$h = -9 \rightarrow 8$

$k = -12 \rightarrow 10$

$l = -13 \rightarrow 14$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.033$

$wR(F^2) = 0.092$

$S = 1.05$

3099 reflections

163 parameters

0 restraints

Primary atom site location: heavy-atom method

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0527P)^2 + 0.1747P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.48$ e Å⁻³

$\Delta\rho_{\min} = -0.25$ e Å⁻³

Special details

Experimental. H atoms were positioned according to idealized geometries and treated as riding atoms [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for non-methyl H atoms; $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl H atoms].

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C11	0.40844 (5)	0.67593 (3)	0.46314 (3)	0.02639 (10)
C12	0.12225 (5)	1.17185 (4)	0.59392 (3)	0.02531 (10)
C13	0.52239 (5)	0.88092 (4)	0.16632 (3)	0.02700 (11)
O2	0.23842 (15)	0.85730 (12)	0.62530 (10)	0.0287 (2)
O1	0.38847 (15)	1.19610 (11)	0.12496 (9)	0.0279 (2)
C5	0.26794 (17)	0.93849 (14)	0.51072 (12)	0.0202 (2)
N1	0.23548 (16)	1.35048 (12)	0.29519 (11)	0.0223 (2)
C2	0.36597 (18)	1.12306 (14)	0.24144 (12)	0.0201 (2)
C1	0.27294 (17)	1.19709 (14)	0.34266 (12)	0.0192 (2)
C6	0.22229 (17)	1.10331 (15)	0.46732 (12)	0.0197 (2)
C4	0.36487 (17)	0.86981 (14)	0.40931 (12)	0.0198 (2)
C7	0.38420 (18)	1.44789 (14)	0.21613 (12)	0.0219 (2)
H7A	0.4948	1.3836	0.1894	0.026*
H7B	0.4335	1.4999	0.2711	0.026*
C11	0.05998 (19)	1.43523 (15)	0.33421 (14)	0.0261 (3)
H11A	0.0924	1.4867	0.3952	0.031*
H11B	-0.0372	1.3642	0.3811	0.031*
C8	0.3023 (2)	1.56646 (15)	0.09304 (13)	0.0249 (3)
H8A	0.2685	1.5149	0.0325	0.030*
H8B	0.4024	1.6347	0.0461	0.030*
C3	0.41441 (17)	0.95444 (14)	0.28565 (12)	0.0201 (2)
C9	0.1219 (2)	1.66056 (15)	0.12904 (14)	0.0270 (3)
H9A	0.1611	1.7167	0.1854	0.032*
C10	-0.0247 (2)	1.55350 (15)	0.21080 (15)	0.0279 (3)
H10A	-0.0696	1.5003	0.1551	0.033*
H10B	-0.1390	1.6140	0.2382	0.033*
C12	0.0382 (3)	1.77758 (19)	0.00529 (17)	0.0406 (4)
H12A	-0.0777	1.8362	0.0309	0.061*
H12B	0.0029	1.7251	-0.0530	0.061*
H12C	0.1356	1.8466	-0.0415	0.061*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	0.03073 (19)	0.01802 (16)	0.02813 (18)	-0.00103 (12)	-0.00157 (13)	-0.00509 (12)
C12	0.02420 (17)	0.03121 (18)	0.02312 (17)	-0.00301 (12)	0.00309 (12)	-0.01355 (13)
C13	0.03295 (19)	0.02597 (18)	0.02271 (17)	0.00095 (13)	0.00197 (12)	-0.01137 (13)
O2	0.0344 (5)	0.0274 (5)	0.0209 (5)	-0.0057 (4)	0.0029 (4)	-0.0037 (4)
O1	0.0370 (5)	0.0247 (5)	0.0194 (4)	-0.0033 (4)	0.0020 (4)	-0.0046 (4)
C5	0.0167 (6)	0.0235 (6)	0.0205 (6)	-0.0045 (4)	-0.0007 (4)	-0.0065 (5)
N1	0.0195 (5)	0.0195 (5)	0.0261 (5)	-0.0018 (4)	0.0045 (4)	-0.0069 (4)
C2	0.0186 (5)	0.0214 (6)	0.0203 (6)	-0.0025 (4)	-0.0004 (4)	-0.0071 (5)
C1	0.0163 (5)	0.0206 (6)	0.0215 (6)	-0.0024 (4)	-0.0004 (4)	-0.0080 (5)
C6	0.0174 (5)	0.0237 (6)	0.0198 (6)	-0.0027 (4)	0.0004 (4)	-0.0098 (5)
C4	0.0182 (5)	0.0183 (5)	0.0230 (6)	-0.0018 (4)	-0.0025 (4)	-0.0065 (4)
C7	0.0209 (6)	0.0214 (6)	0.0229 (6)	-0.0054 (4)	0.0021 (4)	-0.0062 (5)
C11	0.0233 (6)	0.0222 (6)	0.0306 (7)	-0.0013 (5)	0.0065 (5)	-0.0086 (5)
C8	0.0274 (6)	0.0226 (6)	0.0227 (6)	-0.0023 (5)	0.0017 (5)	-0.0058 (5)
C3	0.0186 (6)	0.0221 (6)	0.0211 (6)	-0.0006 (4)	-0.0014 (4)	-0.0096 (5)
C9	0.0285 (7)	0.0221 (6)	0.0291 (7)	0.0002 (5)	0.0001 (5)	-0.0083 (5)
C10	0.0236 (6)	0.0238 (6)	0.0362 (7)	0.0004 (5)	-0.0004 (5)	-0.0112 (5)
C12	0.0421 (9)	0.0309 (8)	0.0392 (8)	0.0074 (6)	-0.0042 (7)	-0.0022 (6)

Geometric parameters (\AA , $^\circ$)

C11—C4	1.7069 (13)	C7—H7B	0.9900
C12—C6	1.7315 (13)	C11—C10	1.530 (2)
C13—C3	1.7083 (13)	C11—H11A	0.9900
O2—C5	1.2245 (16)	C11—H11B	0.9900
O1—C2	1.2139 (16)	C8—C9	1.5254 (19)
N1—C1	1.3534 (16)	C8—H8A	0.9900
N1—C11	1.4653 (16)	C8—H8B	0.9900
N1—C7	1.4757 (17)	C9—C10	1.522 (2)
C1—C6	1.3741 (18)	C9—C12	1.526 (2)
C3—C4	1.3363 (18)	C9—H9A	1.0000
C1—C2	1.5192 (17)	C10—H10A	0.9900
C2—C3	1.4914 (18)	C10—H10B	0.9900
C4—C5	1.4979 (18)	C12—H12A	0.9800
C5—C6	1.4564 (18)	C12—H12B	0.9800
C7—C8	1.5219 (19)	C12—H12C	0.9800
C7—H7A	0.9900		
O2—C5—C6	123.14 (12)	H11A—C11—H11B	108.2
O2—C5—C4	119.91 (12)	C7—C8—C9	111.12 (11)
C6—C5—C4	116.88 (11)	C7—C8—H8A	109.4
C1—N1—C11	123.69 (11)	C9—C8—H8A	109.4
C1—N1—C7	121.70 (11)	C7—C8—H8B	109.4
C11—N1—C7	113.90 (10)	C9—C8—H8B	109.4
O1—C2—C3	119.68 (12)	H8A—C8—H8B	108.0

O1—C2—C1	121.60 (11)	C4—C3—C2	120.51 (11)
C3—C2—C1	118.51 (11)	C4—C3—C13	123.93 (10)
N1—C1—C6	127.03 (12)	C2—C3—C13	115.47 (9)
N1—C1—C2	114.93 (11)	C10—C9—C8	108.97 (11)
C6—C1—C2	117.83 (11)	C10—C9—C12	112.57 (13)
C1—C6—C5	123.64 (11)	C8—C9—C12	111.00 (12)
C1—C6—C12	122.83 (10)	C10—C9—H9A	108.1
C5—C6—C12	113.15 (9)	C8—C9—H9A	108.1
C3—C4—C5	122.34 (11)	C12—C9—H9A	108.1
C3—C4—C11	122.41 (10)	C9—C10—C11	112.52 (12)
C5—C4—C11	115.24 (9)	C9—C10—H10A	109.1
N1—C7—C8	111.48 (11)	C11—C10—H10A	109.1
N1—C7—H7A	109.3	C9—C10—H10B	109.1
C8—C7—H7A	109.3	C11—C10—H10B	109.1
N1—C7—H7B	109.3	H10A—C10—H10B	107.8
C8—C7—H7B	109.3	C9—C12—H12A	109.5
H7A—C7—H7B	108.0	C9—C12—H12B	109.5
N1—C11—C10	109.52 (11)	H12A—C12—H12B	109.5
N1—C11—H11A	109.8	C9—C12—H12C	109.5
C10—C11—H11A	109.8	H12A—C12—H12C	109.5
N1—C11—H11B	109.8	H12B—C12—H12C	109.5
C10—C11—H11B	109.8		
