

2,3,5-Trichloro-6-(2-diethylaminovinyl)-
1,4-benzoquinoneAlexander Krivokapic* and
Harry L. AndersonUniversity of Oxford, Department of Chemistry,
Dyson Perrins Laboratory, South Parks Road,
Oxford OX1 3QY, EnglandCorrespondence e-mail:
alexander.krivokapic@chem.ox.ac.uk

We report the structure of the title compound, $C_{12}H_{12}Cl_3NO_2$, which belongs to a group of compounds called blue quinones. It is a remarkable near-IR dye with interest for non-linear optics. It crystallized in monoclinic space group $P2_1/a$ with one molecule in the asymmetric unit. The molecular structure is approximately planar and exhibits little bond-length alternation, indicating a high degree of charge-transfer from the amine lone pair to the quinone.

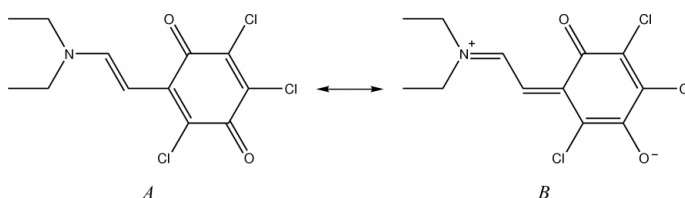
Received 4 February 2002
Accepted 5 February 2002
Online 8 February 2002

Key indicators

Single-crystal X-ray study
 $T = 150$ K
Mean $\sigma(C-C) = 0.002$ Å
 R factor = 0.026
 wR factor = 0.029
Data-to-parameter ratio = 10.3For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

Comment

Recently we isolated the title compound as a by-product during a porphyrin synthesis. Porphyrins are commonly prepared by the acid-catalysed reaction of aldehydes with pyrroles, followed by oxidation with *p*-chloranil (Lindsey *et al.*, 1987). If excess triethylamine is used to neutralize the acid prior to oxidation of the porphyrinogen with *p*-chloranil, the title compound is formed, as should have been expected from the known reaction of triethylamine with *p*-chloranil (Buckley, Dunstan & Henbest, 1957; Buckley, Henbest & Slade, 1957). This dye belongs to a class of compounds known as blue quinones. There has recently been renewed interest in these compounds in connection with non-linear optics, because of their remarkable long wavelength absorption (λ_{\max} at 680 nm in CH_2Cl_2) (Alnabari & Bittner, 2000). This absorption has been attributed to intramolecular charge-transfer of the type shown in the Scheme below.



The crystal structure presented here (Fig. 1) provides some insight into this resonance. The shortest bond length is N1—C8, which indicates that this bond has a substantial double-bond character, as in structure *B*, but the adjacent bond in the π -system, C8—C7, is also a partial double bond indicating a contribution from structure *A* (see bond lengths in Table 1). To the best of our knowledge, this is the first crystal structure of a blue quinone. Short intramolecular contacts occur between O1 and H81 and between Cl3 and H71 (Table 2), both of these are shorter than the sum of the van der Waals radii (2.68 and 2.86 Å, respectively) (Rowland & Taylor, 1996). These interactions cooperate to keep the amine coplanar with quinone, thus favouring π -conjugation.

Experimental

The title compound was synthesized as described by Buckley, Dunstan & Henbest (1957). Blue crystals were grown by layered addition of methanol to a toluene solution of the compound.

Crystal data

$C_{12}H_{12}Cl_3NO_2$
 $M_r = 308.59$
 Monoclinic, $P2_1/a$
 $a = 7.6548$ (2) Å
 $b = 15.7782$ (4) Å
 $c = 10.9114$ (4) Å
 $\beta = 95.299$ (1)°
 $V = 1312.23$ (7) Å³
 $Z = 4$

$D_x = 1.562$ Mg m⁻³
 Mo K α radiation
 Cell parameters from 3052 reflections
 $\theta = 1-27^\circ$
 $\mu = 0.69$ mm⁻¹
 $T = 150$ K
 Plate, blue
 $0.10 \times 0.05 \times 0.05$ mm

Data collection

Enraf-Nonius KappaCCD diffractometer
 ω scans
 Absorption correction: multi-scan (DENZO and SCALEPACK; Otwinowski & Minor, 1997)
 $T_{\min} = 0.959$, $T_{\max} = 0.966$
 5779 measured reflections

2985 independent reflections
 2055 reflections with $I > 3\sigma(I)$
 $R_{\text{int}} = 0.01$
 $\theta_{\text{max}} = 27.4^\circ$
 $h = -9 \rightarrow 9$
 $k = -20 \rightarrow 20$
 $l = -14 \rightarrow 14$

Refinement

Refinement on F
 $R = 0.026$
 $wR = 0.029$
 $S = 1.02$
 2055 reflections
 199 parameters
 All H-atom parameters refined

Weighting scheme: Chebyshev polynomial with 3 parameters, 0.365, 0.183, 0.148 (Carruthers & Watkin, 1979)
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.23$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.26$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

C12—C3	1.7135 (17)	C1—C2	1.489 (2)
C3—C4	1.500 (2)	C1—O1	1.219 (2)
C3—C2	1.335 (3)	C2—C11	1.7198 (17)
C4—O2	1.234 (2)	C7—C8	1.387 (2)
C4—C5	1.432 (2)	C8—N1	1.320 (2)
C5—Cl3	1.7380 (16)	N1—C9	1.472 (2)
C5—C6	1.391 (2)	N1—C11	1.470 (2)
C6—C1	1.511 (2)	C9—C10	1.513 (3)
C6—C7	1.409 (2)	C11—C12	1.513 (3)
C12—C3—C4	115.53 (13)	C5—C6—C7	122.08 (15)
C12—C3—C2	122.57 (14)	C1—C6—C7	121.20 (15)
C4—C3—C2	121.90 (16)	C6—C1—C2	117.79 (14)
C3—C4—O2	119.45 (15)	C6—C1—O1	122.83 (15)
C3—C4—C5	115.56 (15)	C2—C1—O1	119.35 (15)
O2—C4—C5	124.98 (15)	C3—C2—C11	122.47 (14)
C4—C5—Cl3	114.54 (12)	C1—C2—C11	115.63 (13)
C4—C5—C6	125.86 (15)	C6—C7—C8	127.73 (16)
Cl3—C5—C6	119.31 (13)	C7—C8—N1	124.61 (16)
C5—C6—C1	116.68 (14)		

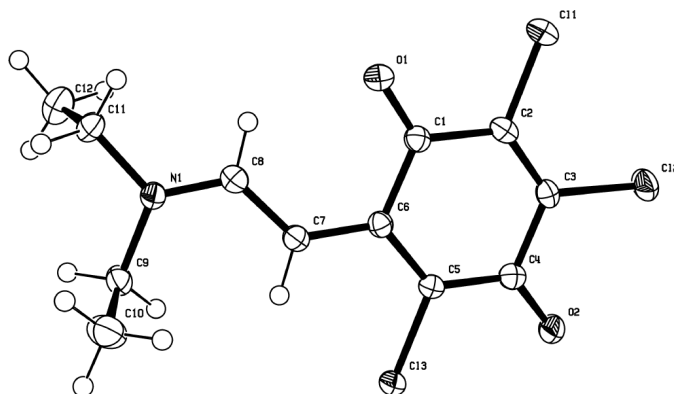


Figure 1

The molecular structure of the title compound, showing 50% probability displacement ellipsoids.

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C7—H71 \cdots Cl3	0.96 (2)	2.51 (2)	3.008 (2)	112 (1)
C8—H81 \cdots O1	0.94 (2)	2.22 (2)	2.832 (2)	122 (2)
C9—H91 \cdots Cl3 ⁱ	0.97 (2)	2.81 (2)	3.662 (2)	147 (2)

Symmetry code: (i) $\frac{3}{2} - x, y - \frac{1}{2}, 1 - z$.

H atoms were refined isotropically.

Data collection: COLLECT (Nonius, 1997–2001); cell refinement: DENZO and SCALEPACK (Otwinowski & Minor, 1997); data reduction: DENZO and SCALEPACK; program(s) used to solve structure: SIR92 (Altomare *et al.*, 1994); program(s) used to refine structure: CRYSTALS (Watkin *et al.*, 2001); molecular graphics: ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: CRYSTALS (Watkin *et al.*, 2001).

We thank DSTL (Defence Science and Technology Laboratory, Malvern) for financial support.

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