Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

2a,8a-Dichloro-1-(2-ethynylphenyl)-2a,8a-dihydrocyclobuta[*b*]naphthalene-3,8-dione

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Received 18 January 2007
Accepted 22 January 2007

Key indicators

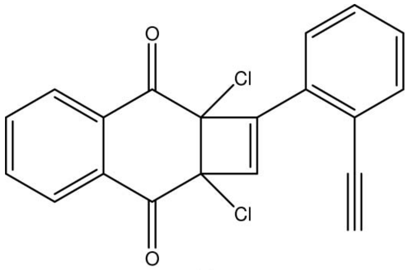
Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.002 Å
R factor = 0.032
wR factor = 0.086
Data-to-parameter ratio = 37.8

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

The title compound, $C_{20}H_{10}Cl_2O_2$, crystallizes with two crystallographically independent molecules in the asymmetric unit. In both molecules, the cyclohexene ring adopts a boat conformation. The molecules are linked into a sheet parallel to the *ab* plane by C—H···Cl hydrogen bonds and C—H···π interactions.

Comment

In continuation of our recent investigation on photoinduced reactions of quinones with alkynes (Wang *et al.*, 2005), we have studied the photoreaction of 2,3-dichloro-1,4-naphthoquinone with 1,2-diethynylbenzene and found that this proceeded *via* the ππ* excited triplet state of the quinone to give the title compound, (I), as a [2 + 2]-cycloaddition product. An X-ray crystallographic analysis was undertaken to establish its structure and conformation.



(I)

The asymmetric unit of (I) contains two molecules, *A* and *B* (Fig. 1). The bond lengths and angles of these two molecules agree with each other and have normal values (Allen *et al.*, 1987), and are comparable to those in a related structure [(II); Shi *et al.*, 2003]. In both molecules, the cyclohexene ring adopts a boat conformation, with atoms C2 and C9 deviating from the C1/C3/C8/C10 plane by 0.238 (1) and 0.187 (1) Å, respectively, in molecule *A* and by 0.224 (1) and 0.174 (1) Å, respectively, in *B*. The Cremer & Pople (1975) puckering parameters *Q*, θ and φ are 0.380 (1) Å, 99.5 (2) and 229.2 (2)°, respectively, in molecule *A*, and 0.355 (1)Å, 100.0 (2) and 229.9 (2)° in *B*. In both *A* and *B*, the C13–C18 benzene ring is twisted slightly away from the cyclobutene ring (C1/C10–C12), with a dihedral angle of 13.33 (7)° in molecule *A* and 19.77 (7)° in *B*; the corresponding dihedral angle in (II) is 2.9 (2)°. The dihedral angle between the cyclobutene ring and the C3–C8 benzene ring is 88.81 (6)° in molecule *A* and 89.50 (6)° in *B*, comparable to 87.9 (2)° in (II).

In the crystal structure, C5*A*—H5*AA*···Cl1*A*^{i} and C7*A*—H7*AA*···Cl1*A*^{ii} hydrogen bonds link *A*-type molecules into a

doi:10.1107/S160053680700342X

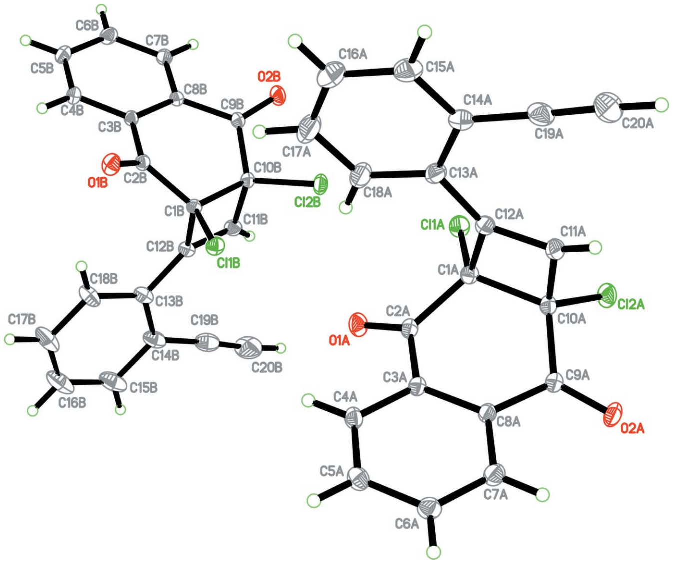


Figure 1
The asymmetric unit of (I), showing 50% probability displacement ellipsoids and the atomic numbering.

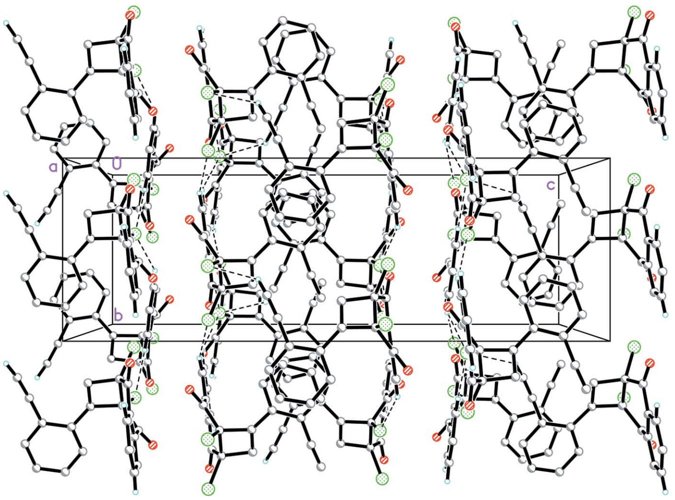


Figure 2
The crystal packing of (I), viewed down the *a* axis, showing the sheets. Dashed lines indicate hydrogen bonds. H atoms not involved in the interactions have been omitted.

layer parallel to the *ab* plane. Similarly, *B*-type molecules are linked into another layer parallel to the *ab* plane by C4*B*—H4*BA*···Cl2*B*^{iii}, C5*B*—H5*BA*···Cl1*B*^{iv} and C7*B*—H7*BA*···Cl1*B*^{v} hydrogen bonds (symmetry codes are given in Table 1). C20*A*—H20*A*···Cl1*B*^{vi} hydrogen bonds cross-link adjacent *A*- and *B*-type layers into a sheet-like structure (Fig. 2 and Table 1). A C—H···π interaction involving the C3*B*–C8*B* benzene ring (Table 1) is also observed within a sheet.

Experimental

Compound (I) was prepared by the photolysis of a benzene solution (60ml) of 2,3-dichloro-1,4-naphthoquinone (3 mmol) in the presence of an excess amount (1.5 equiv.) of 1,2-diethynylbenzene. The photoreaction yielded (I) as the main product after column chromatographic separation of the reaction mixture with petroleum ether–ethyl acetate as eluents. Single crystals suitable for X-ray crystallographic analysis were grown by slow evaporation of solvents from a solution of (I) in petroleum ether–ethyl acetate (2:1 *v*/*v*).

Crystal data

$C_{20}H_{10}Cl_2O_2$
$M_r = 353.18$
Orthorhombic, $Pna2_1$
$a = 16.0627$ (2) Å
$b = 8.0482$ (1) Å
$c = 24.0821$ (3) Å
$V = 3113.23$ (7) Å^3
$Z = 8$
$D_x = 1.507$ Mg m^{-3}
Mo *Kα* radiation
$\mu = 0.43$ mm^{-1}
$T = 100.0$ (1) K
Block, orange
0.47 × 0.41 × 0.30 mm

Data collection

Bruker SMART APEX2 CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
$T_{min} = 0.822$, $T_{max} = 0.883$
127742 measured reflections
16384 independent reflections
15176 reflections with $I > 2\sigma(I)$
$R_{int} = 0.034$
$\theta_{max} = 37.5°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.086$
$S = 1.04$
16384 reflections
434 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0511P)^2 + 0.4718P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.55$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}
Absolute structure: Flack (1983), 8036 Friedel pairs
Flack parameter: 0.54 (2)

Table 1
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5*A*—H5*AA*···Cl1*A*^{i}	0.93	2.78	3.603 (1)	148
C7*A*—H7*AA*···Cl1*A*^{ii}	0.93	2.72	3.651 (1)	177
C4*B*—H4*BA*···Cl2*B*^{iii}	0.93	2.83	3.715 (1)	160
C5*B*—H5*BA*···Cl1*B*^{iv}	0.93	2.77	3.584 (1)	147
C7*B*—H7*BA*···Cl1*B*^{v}	0.93	2.75	3.682 (1)	176
C20*A*—H20*A*···Cl1*B*^{vi}	0.97	2.80	3.607 (1)	142
C15*A*—H15*A*···*Cg*1^{vii}	0.93	2.55	3.479 (1)	175

Symmetry codes: (i) $x+\frac{1}{2}, -y+\frac{3}{2}, z$; (ii) $x+\frac{1}{2}, -y+\frac{1}{2}, z$; (iii) $x, y+1, z$; (iv) $x-\frac{1}{2}, -y+\frac{5}{2}, z$; (v) $x-\frac{1}{2}, -y+\frac{3}{2}, z$; (vi) $-x+1, -y+1, z-\frac{1}{2}$; (vii) $-x+\frac{1}{2}, y-\frac{1}{2}, z-\frac{1}{2}$. *Cg*1 is the centroid of the C3*B*–C8*B* benzene ring.

H atoms were placed in calculated positions and constrained to ride on their carrier atoms, with C—H = 0.93–1.01 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. The structure is an inversion twin with almost equal contributions of the two components.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2005); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

The authors thank the Malaysian Government and Universiti Sains Malaysia for the Scientific Advancement Grant Allocation (SAGA) grant No. 304/PFIZIK/653003/A118.

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