1-(1-Amino-4-bromo-9,10-dioxo-9,10-dihydroanthracen-2-ylcarbonyl)-1,3-dicyclohexylurea

Li Wu, Hui-Min Liu, Wen-Tao Zhao* and Wen-Qin Zhang

Department of Chemistry, Tianjin University, Tianjin 300072, People's Republic of China

Correspondence e-mail: wqzhang@tju.edu.cn

In the title compound, $C_{28}H_{30}BrN_3O_4$, the molecules are linked by C—H···Br and N—H···O hydrogen bonds into one-dimensional chains, which are arranged into a three-dimensional network through a combination of C—H···O hydrogen bonds and two kinds of π–π interactions between the benzene rings of the anthraquinone units.

Comment

Anthraquinone compounds, as very stable basis dyestuffs, have been the subject of much technical and scientific interest. It has been reported that anthraquinone dichroic dyes dissolved in liquid crystals can strongly enhance photoinduced reorientational efficiency (Janossy *et al.*, 1990; Janossy & Lloyd, 1991; Yaegashi *et al.*, 2005). Recently, we have investigated a series of anthraquinone derivatives as highly efficient dyes for photoinduced reorientation. During the study, the crystal structure of the title *N*-substituted amidate, (I), was determined. Some chromophores with an acylureido substituent have been reported to exhibit unexpected strong solvatochromism, which provides important contributions to the development of sensitive tools (Cornelia *et al.*, 2005; Bonsignore *et al.*, 1999). We now present the title molecule, whose structure exhibits some interesting features regarding the way in which the *N*-acylureido group is attached to the anthraquinone group.

(I)
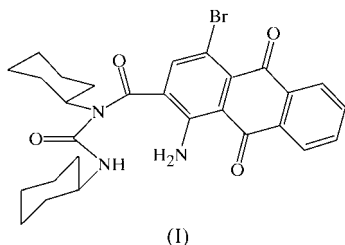
The molecular structure is presented in Fig. 1 and selected geometric parameters are given in Table 1. In contrast to the nearly planar arrangements observed in pyridinium 1-amino-4-bromo-9,10-anthraquinone-2-sulfonate (Skarżyński *et al.*, 1978) and 1-hydroxy-4-(4-methylphenylamino)-9,10-anthraquinone (Black *et al.*, 1992), the anthraquinone unit of (I) loses its planarity as a result of repulsion between atoms Br1 and O2. The two benzene rings *A* and *C* (see Fig. 1) form a 'V', intersecting at atoms C4 and C11 with a dihedral angle of 11.2 (2)°. This arrangement also forces the two carbonyl O atoms to lie out of the two mean planes *A* and *C*, and atoms O1 and O2 deviate from the central ring plane *B* by 0.3189 (5)
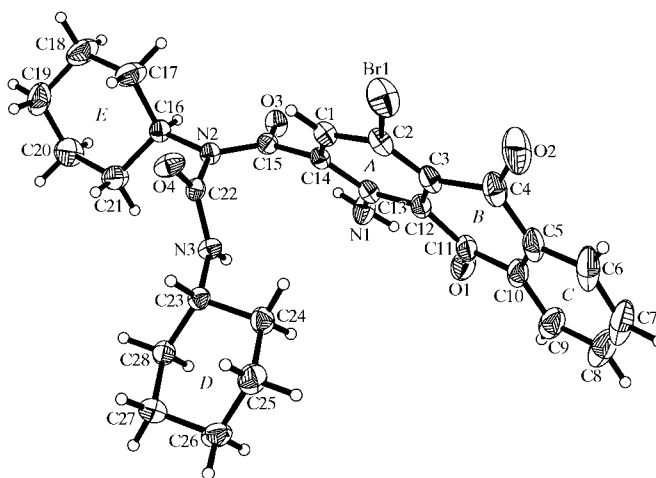

Figure 1
The molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.
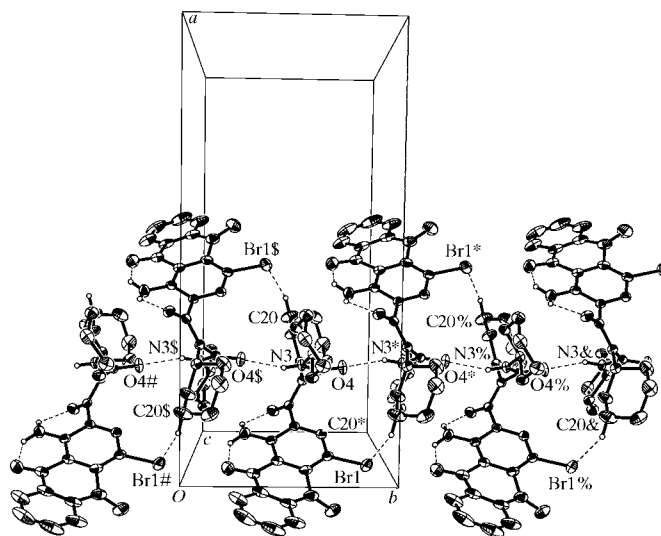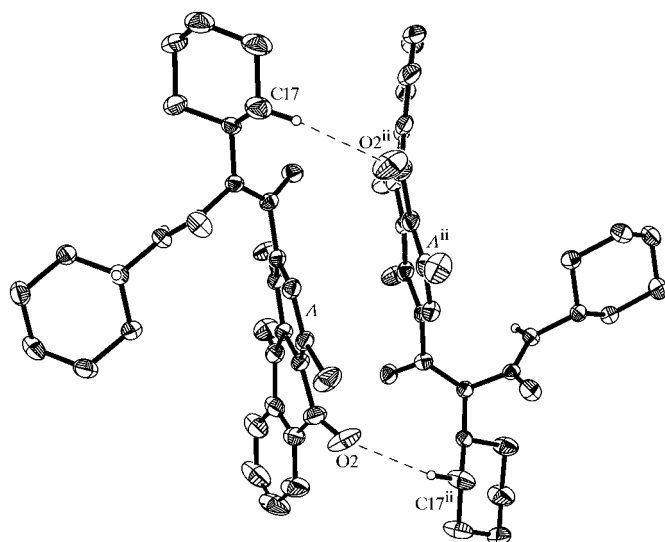
Figure 2
Part of the crystal structure of (I), showing the formation of a one-dimensional chain along the *b* axis *via* N—H···O and C—H···Br hydrogen bonds (dashed lines). For the sake of clarity, H atoms not involved in the motif have been omitted. [Symmetry codes: (#) x, $y - 1$, z; (%) x, $y + 1$, z; ($) $\frac{1}{2} - x$, $y - \frac{1}{2}$, $\frac{1}{2} - z$; (*) $\frac{1}{2} - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$; (@) $\frac{1}{2} - x$, $\frac{3}{2} + y$, $\frac{1}{2} - z$.]

and 0.4973 (5) Å, respectively. In addition, the dihedral angles between plane B and planes A and C are 20.1 (2) and 9.2 (2)°, respectively.
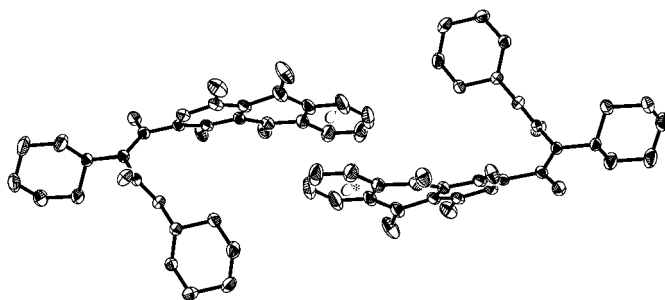
In the N-acylureido unit, the two carbonyl groups are twisted substantially at the central atom N2, with a dihedral angle of 77.3 (1)° between the O3/C15/N2 and N2/C22/O4 planes, which increases the distance between atoms O3 and N3. Therefore, as expected, no intramolecular N3—H3···O3 hydrogen bond is formed. Moreover, carbonyl atom O3 deviates from the anthraquinone plane by 0.6200 (6) Å, which weakens the conjugation between the carbonyl and anthraquinone groups.

Each of the cyclohexyl groups in (I) (D and E) adopts a common chair conformation, as is required for the minimum energy. Moreover, for each ring the bond distances are similar to those in 1,3-dicyclohexylurea (Govindasamy & Subramanian, 1997).
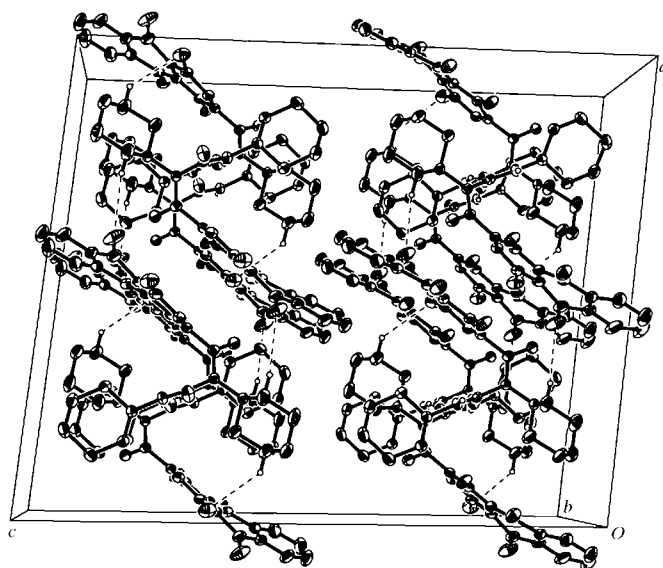
The molecules of (I) are stacked into a three-dimensional framework *via* a variety of weak but direction-specific inter-

Figure 5
A stereoview of part of the crystal structure of (I), viewed down the b axis, showing the formation of the three-dimensional framework by a combination of hydrogen bonds (dashed lines) and π–π stacking interactions. For the sake of clarity, H atoms not involved in the motifs shown have been omitted.

molecular forces, and the formation of this framework is readily analysed by means of the substructure approach.

Atoms N3 and C20 at (x, y, z) acts as hydrogen-bond donors to, respectively, atom O4 in the molecule at $(-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2})$ and atom Br1 in the molecule at $(-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2})$ (Table 2). In this manner, a one-dimensional polymer chain is generated along the b direction (Fig. 2).

Probably as a result of a π–π stacking interaction bringing atoms C17 and O2 into close proximity, atom C17 in the molecule at (x, y, z) acts as a hydrogen-bond donor to atom O2 in the molecule at $(-x, y, -z + \frac{1}{2})$, producing a centro-symmetric motif. Adjacent one-dimensional chains are strongly linked into segments by a combination of these hydrogen-bond pairs and π–π stacking interactions, with a centre-to-centre distance of 3.573 (6) Å between benzene rings A at (x, y, z) and $(-x, y, -z + \frac{1}{2})$ (Fig. 3).

These segments are strongly linked by π–π stacking interactions between rings C at (x, y, z) and $(-x, -y + 1, -z)$, which are parallel to each other, with an interplanar spacing of 3.387 (6) Å and a ring-centroid separation of 3.641 (6) Å (Fig. 4). Propagation by the space group of this interaction is sufficient to link all of these segments into a three-dimensional framework (Fig. 5).

Figure 3
Part of the crystal structure of (I), showing the π–π stacking interaction and pairs of C17—H17A···O2 hydrogen bonds (dashed lines). For clarity, the unit-cell box and H atoms not involved in the motif have been omitted. [Symmetry code: (ii) $-x, y, -z + \frac{1}{2}$.]

Figure 4
Part of the crystal structure of (I), showing the π–π stacking interaction that links these segments together. For clarity, all H atoms and the unit-cell box have been omitted. The asterisk (*) denotes the symmetry code $(-x, -y + 1, -z)$.

Experimental

For the synthesis of (I), a solution of 1-amino-4-bromo-9,10-dioxo-anthracene-2-carboxylic acid (1.0 g), 1,3-dicyclohexylcarbodiimide (0.7 g), 4-(dimethylamino)pyridine (0.03 g) and cyclohexanol (0.5 g) in dry dimethylformamide (DMF, 30 ml) was stirred at 373 K for 4 h. The hot solution was cooled to room temperature and poured into methanol (50 ml) with stirring. The resulting precipitate was collected by filtration, washed with methanol and dried in a vacuum. The product was obtained as a yellow powder in 82% yield. The yellow

crystal used for the X-ray analysis was grown by slow evaporation of a DMF solution at room temperature (m.p. 558–560 K). ^{1}H NMR (500 MHz, DMSO): δ 8.14–8.17 (m, 2H), 8.08–8.10 (d, 2H), 7.84–7.91 (m, 2H), 7.76 (s, 1H), 4.0–4.12 (m, 1H), 3.24–3.26 (m, 1H), 1.91 (d, J = 11.6 Hz, 2H), 1.78 (d, J = 13.2 Hz, 2H), 1.57–1.62 (m, 3H), 1.47–1.50 (m, 4H), 1.38–1.42 (m, 1H), 1.25–1.34 (m, 2H), 1.07–1.13 (m, 3H), 0.94–1.00 (m, 3H).

Crystal data

$C_{28}H_{30}BrN_3O_4$	$Z = 8$
$M_r = 552.45$	$D_x = 1.447$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 20.725$ (6) Å	$\mu = 1.66$ mm^{-1}
$b = 9.727$ (3) Å	$T = 293$ (2) K
$c = 25.306$ (7) Å	Lamellar, yelllow
$\beta = 96.095$ (4)°	$0.26 \times 0.14 \times 0.08$ mm
$V = 5073$ (2) Å^3	

Data collection

Bruker APEX-II CCD area-detector diffractometer	13483 measured reflections
	4495 independent reflections
φ and ω scans	2936 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan ($SADABS$; Bruker, 1997)	$R_{int} = 0.041$
$T_{min} = 0.757$, $T_{max} = 0.880$	$\theta_{max} = 25.0°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0411P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.042$	$+ 5.4394P]$
$wR(F^2) = 0.108$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.01$	$(\Delta/\sigma)_{max} < 0.001$
4495 reflections	$\Delta\rho_{max} = 0.42$ e Å^{-3}
325 parameters	$\Delta\rho_{min} = -0.40$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

O3—C15	1.222 (3)	C18—C19	1.481 (6)
O4—C22	1.212 (3)	C19—C20	1.471 (6)
N2—C15	1.363 (4)	C20—C21	1.539 (5)
N2—C22	1.447 (4)	C23—C28	1.516 (4)
N2—C16	1.483 (4)	C23—C24	1.517 (4)
N3—C22	1.315 (4)	C24—C25	1.521 (5)
C16—C21	1.495 (5)	C25—C26	1.515 (5)
C16—C17	1.503 (5)	C26—C27	1.512 (5)
C17—C18	1.529 (5)	C27—C28	1.518 (4)
C22—N2—C15—O3	168.7 (3)	C16—N2—C15—C14	170.3 (3)
C16—N2—C15—O3	−8.0 (4)	C16—N2—C22—O4	−68.0 (4)
C22—N2—C15—C14	−12.9 (4)	C15—N2—C22—N3	−66.7 (3)

Table 2
Hydrogen-bond geometry (Å, °)..

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
C20—H20$B\cdots$Br1^i	0.97	2.91	3.711 (5)	140
C17—H17$A\cdots$O2^{ii}	0.97	2.67	3.617 (5)	166
N3—H3$A\cdots$O4^i	0.86	2.08	2.907 (5)	161

Symmetry codes: (i) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x, y, -z + \frac{1}{2}$.

Amide H atoms were found in a difference map and refined with $U_{iso}(H)$ values of $1.2U_{eq}(N)$; N—H bond lengths were constrained to 0.86–0.89 Å. All other H atoms were positioned geometrically (C—H = 0.93–0.98 Å) and refined as riding, with $U_{iso}(H)$ values of $1.2U_{eq}(C)$. In the absence of significant anomalous scattering effects, Friedel pairs were merged in the final refinement cycles.

Data collection: $APEX-II$ (Bruker, 1997); cell refinement: $APEX-II$; data reduction: $SAINT$ (Bruker, 1997); program(s) used to solve structure: $SHELXTL$ (Bruker, 1997); program(s) used to refine structure: $SHELXTL$; molecular graphics: $SHELXTL$ and $MERCURY$ (Version 1.4; Bruno et $al.$, 2002); software used to prepare material for publication: $SHELXTL$ and local programs.

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