organic compounds

2,3-Diethoxy-9,10-anthraquinone

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Anthraquinone derivatives form an important class of dyes and are also known for their medicinal properties. Recently, 2,3-disubstituted anthraquinones have been shown unexpectedly to jellify various organic solvents. No information on the packing mode of these derivatives was known. Here, the first X-ray structure of a 2,3-disubstituted anthraquinone is reported, namely 2,3-diethoxy-9,10-anthraquinone, $C_{18}H_{16}O_4$. The merit of this study lies in the observation of significant differences between the packing in 9,10-anthraquinone, which displays a herring-bone arrangement, and that in the title 2,3-diethoxy derivative, in which the molecules lie on parallel crystallographic morror planes separated by a distance of 3.4081 (1) Å, reminiscent of the graphite layer architecture.

Comment

In recent decades, the field of thermoreversible physical gels formed from low molar mass organogelators (LMOGs; Abdallah & Weiss, 2000) has been the subject of renewed interest (Terech & Weiss, 1997; Weiss & Terech, 2005). A number of new systems (Terech & Weiss, 1997) belonging to a variety of functionalities have been discovered. One class of organogelators, consisting of 2,3-dialkoxy-9,10-anthraquinones, (1_n) (see scheme; $8 \leq n \leq 12$), was found to form yellow gels readily in ethanol, heptane or acetonitrile (Clavier *et al.*, 1998). These gels are soft materials made of a self-assembled fibrillar network imprisoning a liquid. One of the main questions regarding the structure of these aggregates is best studied by X-ray crystallography (Ostuni *et al.*, 1996; Abdallah & Weiss, 2000). Usually, the gel-forming molecules do not yield good crystals, as was found to be the case for (1_n) ($8 \leq n \leq 12$). However, on shortening the chain length (*i.e.* for $n = 2$), we obtained single crystals suitable for X-ray analysis. No molecular and crystal structure of any 2,3-disubstituted 9,10-

anthraquinones has been determined so far. The first structure of a member of this important series, the title compound, 2,3-diethoxy-9,10-anthraquinone, (1_2), is reported here and is compared with that of the parent compound to examine how this substitution affects the packing arrangement.
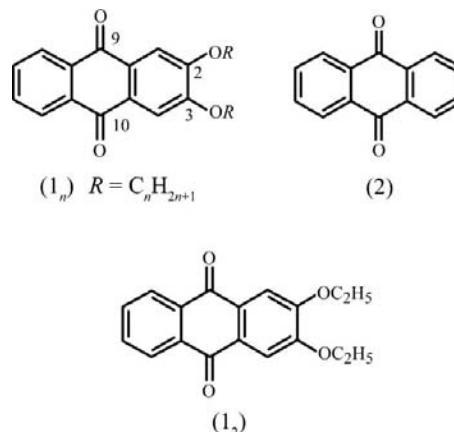

The presence of the two substituents induces a change of crystal space group, *viz.* from $P2_1/c$ in anthraquinone, (2) (Fu & Brock, 1998; Slouf, 2002, and references therein), to $C2/m$ in the present work. The molecule is perfectly planar, with all atoms except the H atoms of the methyl groups located on mirror planes (4*i*) (Fig. 1). It is noticeable that, despite their flexibility, the substituents lie in the anthraquinone substrate plane. Owing to their location on mirror planes parallel to the *b* axis, the molecules are stacked parallel to each other with an interplanar distance of 3.4081 (1) Å. Thus, the molecules form a monodirectional columnar packing, which is reminiscent of the packing of hexagonal graphite (3.40 Å; Pauling, 1945). Such packing results in π–π stacking occurring between the substituted benzene rings, whereas the nonsubstituted benzenes do not exhibit such an interaction (Table 1 and Fig. 2).

The overlap between closest molecules occurs by symmetry around a twofold screw axis. Two consecutive molecules in the same plane exhibit a head-to-tail orientation. This is also the case for closest molecules in the stacking direction. This feature appears clearly in Fig. 2, where four molecules in the unit cell are represented. A salient feature is that the quinoid ring is superimposable on the ethoxy substituents of a neigh-
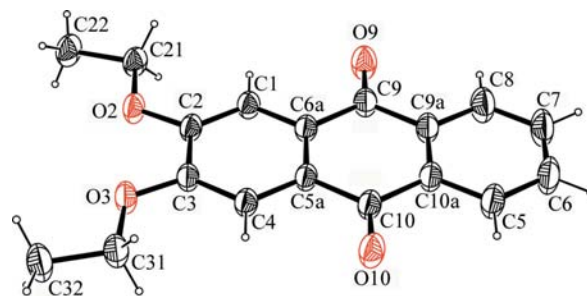
Figure 1
The molecular structure of (1_2), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are represented as small spheres of arbitrary radii.
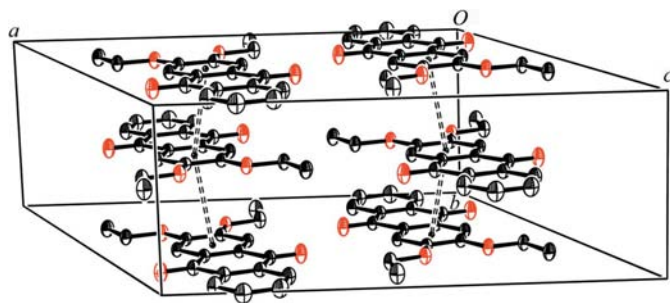
Figure 2
A partial packing view of (1$_2$), showing the head-to-tail arrangement of the molecules and the π–π interactions which develop along the *b* axis. H atoms have been omitted for clarity.
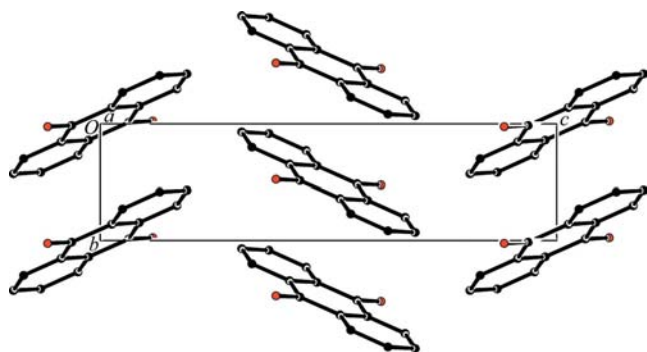
Figure 3
A partial packing view of 9,10-anthraquinone, (2) (Fu & Brock, 1998; Slouf, 2002), showing the herring-bone arrangement. H atoms have been omitted for clarity.

ouring molecule. The intermolecular distances between the carbonyl O atom and the ethoxy CH$_2$ C atom on the same side of the molecule are O9$\cdots$C31 = 3.4764 (4) Å and O10$\cdots$C21 = 3.4831 (4) Å, whereas the distances between the carbonyl and ethoxy O atoms are O9$\cdots$O3 = 3.6254 (5) Å and O10$\cdots$O2 = 3.9034 (8) Å. For comparison, the intermolecular distance between the carbonyl O atom of one molecule and the ethoxy CH$_2$ C atom of another molecule in the same plane was 3.554 (2) Å. Finally, the O$\cdots$O distance between the two closest carbonyl groups from molecules in the same plane was 3.752 (3) Å. This value is smaller than the shortest equivalent distance in the anthraquinone lattice.

The crystal structure of anthraquinone, (2), has been determined a number of times in order to carry out different analyses, and better refinements have been obtained recently (Fu & Brock, 1998; Slouf, 2002). It was found to crystallize in the monoclinic system (296 K, space group $P2_1/c$) with two molecules per unit cell. Each molecule is arranged around an inversion centre located in the middle of the quinone ring. As seen in Fig. 3, the packing shows a herring-bone arrangement where the two closest molecules are slightly staggered relative to each other and overlap at a perpendicular distance of 3.4930 (7) Å, which is completely different from the title compound. In (2), one observes a mutual overlap between the quinoid (central) ring of one molecule and the benzenoid (lateral) ring of the other which results in the formation of a slipped π–π stacking arrangement (Table 1). In the unit cell,

the distances between the closest O atoms are 3.963 (2), 5.083 (2) and 5.278 (2) Å.

Thus, our work has shown that the presence of two ethoxy substituents along the long axis of the 9,10-anthraquinone substrate induces a fundamental change in the molecular arrangement in the crystal, significantly affecting the intermolecular parameters. It seems to be worth examining the influence of chain lengthening on these properties and the possible analogy of (1$_2$) with graphite.

Experimental

The preparation of (1$_2$) (m.p. 445 K) has been described by Desvergne *et al.* (2005). Single crystals were obtained by slow evaporation of a solution of (1$_2$) in a mixture of ethanol and dichloromethane (2:10 *v/v*).

Table 1
Comparison of π–π stacking parameters (Å) in the title compound, (1$_2$), and in anthraquinone, (2).

Data for (2) are from Fu & Brock (1998) and Slouf (2002).

	Centroid-to-centroid distance	Interplanar distance	Slippage
Compound (1$_2$)			
$Cg1\cdots Cg1^i$ (substituted benzene rings)	3.4879 (2)	3.408	0.747
Compound (2)			
$Cg1\cdots Cg1^{ii}$ (quinone rings)	3.8961 (6)	3.476	1.761
$Cg1\cdots Cg2^{iii}$ (quinone–benzene rings)	3.5616 (6)	3.481	0.876

Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$; (ii) $2 - x, 1 - y, 2 - z$; (iii) $x, y - 1, z$. Symmetry codes (ii) and (iii) are for compound (2) in the space group $P2_1/c$.

H atoms were generated geometrically and treated as riding on their parent atoms, with C—H = 0.93 (aromatic), 0.96 (methyl) or 0.97 Å (methylene) and with U_{iso}(H) values of 1.2U_{eq}(C) or 1.5U_{eq}(methyl C). The methyl H atoms are disordered about the mirror plane.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN3097). Services for accessing these data are described at the back of the journal.

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