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Dispiro[indene-2,5′-indeno[2,1-*a*]fluorene-6′,2″-indene]-1,1″,3,3″,11′,12′-hexaone: a three-dimensional hydrogen-bonded framework

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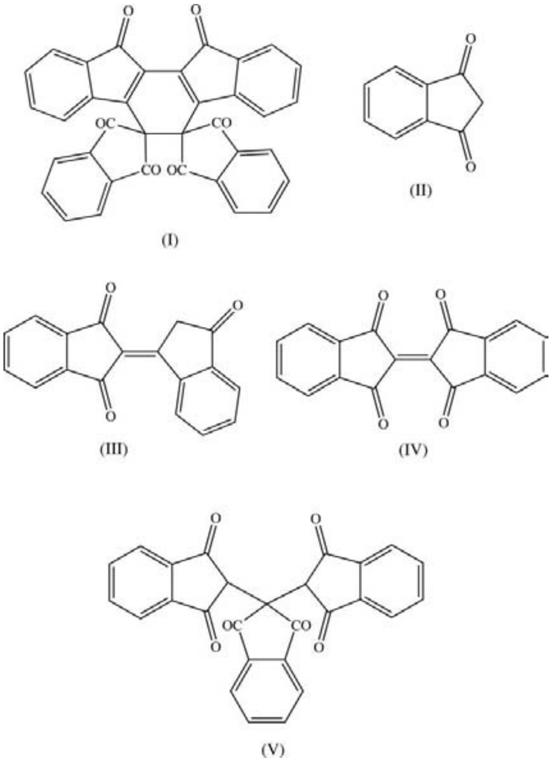
The title compound, $C_{36}H_{16}O_6$, (I), was obtained as a new and unexpected oxidation product of 1,2′-biindene-1′,3,3′(2*H*)-trione. The molecules of (I) exhibit approximate, but noncrystallographic, twofold rotation symmetry and the central ring of the fused pentacyclic portion is distinctly puckered, with a conformation intermediate between half-chair and screw-boat. Six independent C—H···O hydrogen bonds link the molecules into a three-dimensional framework structure of considerable complexity. Comparisons are drawn between the crystal structure of (I) and those of several simpler analogues, which show wide variation in their patterns of supramolecular aggregation.

Comment

Benzodiazepines, a class of psychoactive drugs, have found extensive use as minor tranquilizers with a broad range of applications (Pozharskii *et al.*, 1997; Lueddens & Korpi, 2007). Pyrimidobenzodiazepines and their fused derivatives also display similar properties and have extended the range of pharmaceutical applications (Długosz, 1995). In order to explore synthetic routes to new pyrimido[4,5-*b*][1,4]diazepine derivatives incorporating fused and/or spiro units linked to the diazepine moiety, we have utilized the chalcone reagent 1,2′-biindene-1′,3,3′(2*H*)-trione, (III), prepared by autocondensation of indane-1,3-dione, (II), in reactions with 4,5-diaminopyrimidines. Instead of the expected fused derivative, the reaction between 2,5,6-triaminopyrimidin-4(3*H*)-one and 1,2′-biindene-1′,3,3′(2*H*)-trione produced 3-[(2,4-diamino-6-oxo-1,6-dihydropyrimidin-5-yl)amino]-1,2′-biindene-1′,3′-dione in 90% yield, together with a small quantity of the unexpected dispiro[indene-2,5′-indeno[2,1-*a*]fluorene-6′,2″-indene]-1,1″,3,3″,11′,12′-hexaone, (I) (Fig. 1). Subsequently, we found that heating compound (III) in refluxing dilute aqueous hydrochloric acid gave compound (I) in a modest, but still useful, yield. The formation of (I) from indanetrione (III) must involve an oxidative process; the identity of the oxidant has not yet been investigated but plausible mechanisms for the conversion of (III) to (I) in aqueous or ethanolic solutions are not easy to envisage. We report here the molecular and supramolecular structure of (I) and briefly compare its supramolecular aggregation with that in some simpler analogues, *i.e.* (II)–(V) (see scheme).



The molecule of (I) exhibits approximate but noncrystallographic twofold rotation symmetry about the line joining the mid-points of the C11—C21 and C31—C41 bonds, as illustrated by the leading torsion angles (Table 1). Within the central ring, the C11—C17 and C21—C27 bonds are both clearly double bonds, while the C31—C41 bond is long, presumably as a consequence of the steric congestion around atoms C31 and C41. Unlike all the other rings in the molecule, the central ring is not planar, as exemplified by the C17—C31—C41—C27 torsion angle. The ring-puckering angles (Cremer & Pople, 1975) for the atom-sequence C11—C17—C31—C41—C27—C21 are θ = 119.3 (3)° and φ = 330.2 (4)°, with Q = 0.315 (2) Å, indicating a ring conformation intermediate between half-chair and screw-boat. The ring puckering may be ascribed to the substitution at atoms C31 and C41. The remaining bond distances and interbond angles show no unusual features.

There are six independent C—H···O hydrogen bonds in the crystal structure of (I), such that each molecule acts as both a sixfold donor and a sixfold acceptor of hydrogen bonds. The resulting aggregation is three-dimensional but it can

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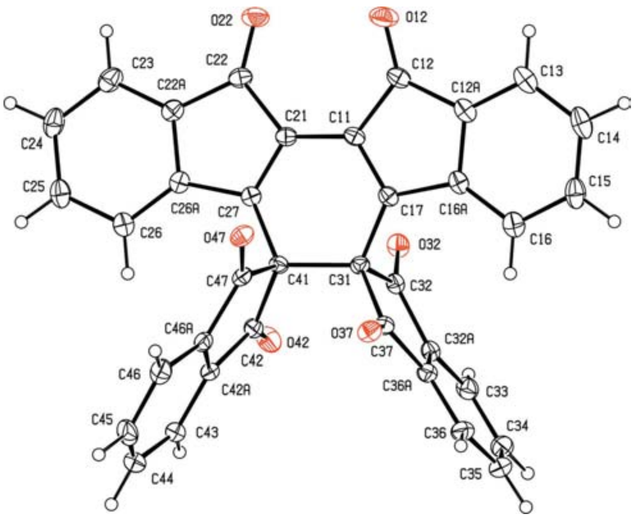

Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

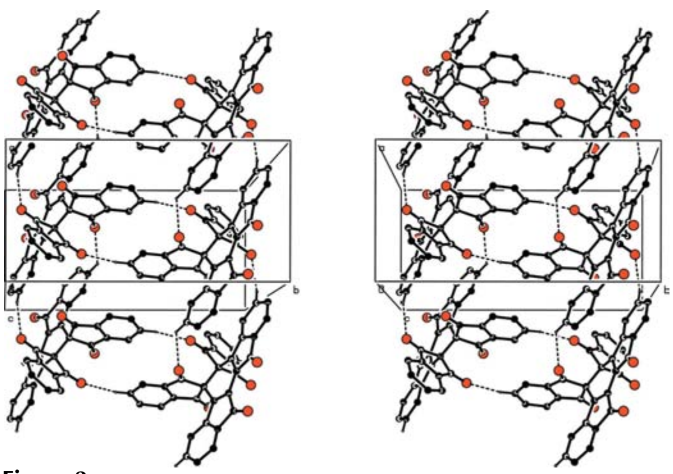

Figure 2
A stereoview of part of the crystal structure of (I), showing the formation of a complex chain of rings along [100]. For the sake of clarity, H atoms not involved in the motifs shown have been omitted.

readily be analyzed in terms of four independent one-dimensional substructures. Three of these are very simple, involving only a single hydrogen bond in each substructure, while the fourth substructure is more complex, with three hydrogen bonds involved in its formation.

Atoms C35 and C43 in the molecule at (x, y, z) act as hydrogen-bond donors to, respectively, atom O47 at ($-\frac{1}{2} + x$, $\frac{1}{2} - y$, $-\frac{1}{2} + z$) and atom O12 at ($\frac{1}{2} + x$, $\frac{1}{2} - y$, $-\frac{1}{2} + z$), thereby forming a $C(9)$ (Bernstein *et al.*, 1995) chain parallel to the [101] direction and a $C(10)$ chain parallel to the $[10\overline{1}]$ direction, both built from molecules related by the *n*-glide plane at $y = \frac{1}{4}$. In addition, atom C46 in the molecule at (x, y, z) acts as hydrogen-bond donor to atom O22 in the molecule at ($\frac{3}{2} - x$, $\frac{1}{2} + y$, $\frac{3}{2} - z$), so forming a second $C(9)$ chain, this time running parallel to the [010] direction and comprising molecules related by the 2_1 screw axis along ($\frac{3}{4}$, y, $\frac{3}{4}$). These three chains, along [010], [101] and $[10\overline{1}]$, respectively, would in fact suffice to generate a continuous three-dimensional framework.

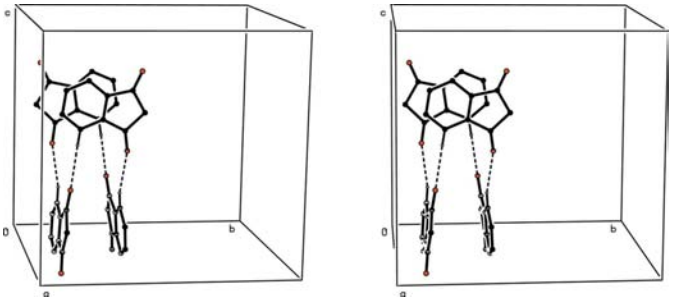

Figure 3
A stereoview of part of the crystal structure of (II), showing the formation of an $R^4_4(20)$ tetramer around a $\overline{4}$ axis. For the sake of clarity, H atoms not involved in the motifs shown have been omitted.

The more complex motif involves three hydrogen bonds. Atoms C15 and C25 in the molecule at (x, y, z) act as hydrogen-bond donors to, respectively, atom O32 in the molecule at ($-1 + x$, y, z) and atom O47 in the molecule at ($1 + x$, y, z). The resulting pair of antiparallel chains generated by translation along [100] combine to form a $C(8)C(8)[R^2_2(18)]$ chain of rings. The final hydrogen bond links pairs of these chains into a complex tubular substructure. Atom C45 in the molecule at (x, y, z) acts as hydrogen-bond donor to atom O37 in the molecule at ($1 - x$, $1 - y$, $1 - z$), so forming a complex chain containing three types of ring. In addition to the $R^2_2(18)$ rings generated by translation, there are two types of ring generated by inversion, such that $R^2_2(18)$ rings centred at ($n + \frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$), where n represents zero or an integer, alternate with $R^4_4(30)$ rings centred at (n, $\frac{1}{2}$, $\frac{1}{2}$), where n represents zero or an integer (Fig. 2).

It is of interest to compare briefly the supramolecular aggregation in the crystal structure of (I) with that of some close analogues, namely compounds (II) and (III)–(V), which are all notionally derived from (II) by condensation and/or oxidation. The original reports of compounds (II)–(V) were all concerned with proof of constitution, without discussion of any hydrogen bonding.

The crystal structure of compound (III) [Cambridge Structural Database (CSD; Allen, 2002) refcode BIINDO; Bravic, Bravic *et al.*, 1976], which is a condensation product from the dione, (I), contains a single intermolecular C—H$\cdots$O hydrogen bond which links molecules related by a 2_1 screw axis into simple $C(4)$ chains.

Compound (IV) (CSD refcode WEVSUL; Khodorkovsky *et al.*, 1994) is formally an oxidation product of (II) (Kaufmann, 1897), although most reported preparations involving the oxidation of (II) are not readily reproducible (Khodorkovsky *et al.*, 1994). The crystal structure of (IV) again contains a single intermolecular C—H$\cdots$O hydrogen bond, which links molecules related by a glide plane into $C(6)$ chains.

By contrast, a single C—H$\cdots$O hydrogen bond in compound (II) (CSD refcode INDDON; Bravic, Bechtel *et al.*, 1976) links molecules related by a $\overline{4}$ axis into $R^4_4(20)$ tetramers (Fig. 3).

In compound (V) (CSD refcode KETROR; Ji *et al.*, 2006), which was obtained as an unexpected oxidation product during the attempted nitration of (IV), the molecules lie

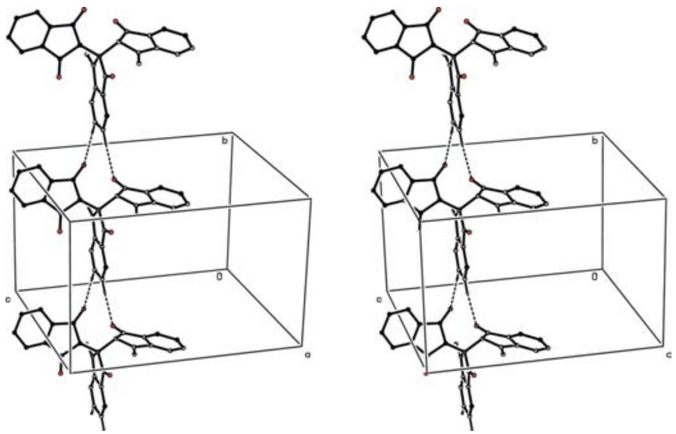

Figure 4
A stereoview of part of the crystal structure of (V), showing the formation of a column of $R_2^2(11)$ rings along a twofold rotation axis. For the sake of clarity, H atoms not involved in the motifs shown have been omitted.

across twofold rotation axes in the *C*2/*c* space group, and a single C—H···O hydrogen bond links molecules related by translation along this axis into columns of $R_2^2(11)$ rings (Fig. 4).

Experimental

A mixture of 2,5,6-triaminopyrimidin-4(3*H*)-one (1.1 mmol) and 1,2′-biindene-1′,3,3′(2*H*)-trione (1.1 mmol) in dry ethanol (10 ml) was heated under reflux with magnetic stirring for 5 h, while the progress of the reaction was monitored by thin-layer chromatography. The reaction mixture was cooled to ambient temperature, and the resulting precipitate collected by filtration and washed with ethanol, yielding 3-[(2,4-diamino-6-oxo-1,6-dihydropyrimidin-5-yl)amino]-1,2′-biindene-1′,3′-dione as a violet solid (m.p. 561–563 K, yield 90%), from which crystals suitable for single-crystal X-ray diffraction have not yet been obtained. The resulting filtrate was evaporated to dryness and the solid residue was crystallized from a mixture of dimethylformamide and ethanol (1:10 *v*/*v*) to yield violet crystals of the title compound, (I) (m.p. 616 K), which proved to be suitable for single-crystal X-ray diffraction. When a solution of (III) in an excess of dilute (10%) aqueous hydrochloric acid was heated under reflux for 18 h, compound (I) was produced in 22% yield.

Table 1
Selected geometric parameters (Å, °).

C11—C21	1.440 (2)	C31—C41	1.573 (2)
C11—C17	1.352 (2)	C21—C27	1.352 (2)
C17—C31	1.498 (2)	C27—C41	1.504 (2)
C17—C11—C21—C27	8.3 (2)	C17—C31—C41—C27	35.27 (18)
C11—C21—C27—C41	4.4 (2)	C21—C11—C17—C31	4.4 (2)
C21—C27—C41—C31	−26.4 (2)	C11—C17—C31—C41	−26.4 (2)
C11—C17—C31—C32	97.2 (2)	C21—C27—C41—C47	97.0 (2)
C11—C17—C31—C37	−151.6 (2)	C21—C27—C41—C42	−152.19 (15)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C15—H15···O32^{i}	0.95	2.40	3.247 (2)	148
C25—H25···O47^{ii}	0.95	2.40	3.096 (2)	130
C35—H35···O47^{iii}	0.95	2.28	3.136 (2)	150
C43—H43···O12^{iv}	0.95	2.48	3.215 (2)	134
C45—H45···O37^{v}	0.95	2.33	3.253 (2)	163
C46—H46···O22^{vi}	0.95	2.42	3.291 (2)	152

Symmetry codes: (i) $x-1, y, z$; (ii) $x+1, y, z$; (iii) $x-\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; (iv) $x+\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; (v) $-x+1, -y+1, -z+1$; (vi) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$.

Crystal data

$C_{36}H_{16}O_6$
$M_r = 544.49$
Monoclinic, $P2_1/n$
$a = 8.2209$ (11) Å
$b = 16.552$ (3) Å
$c = 18.423$ (3) Å
$\beta = 97.775$ (19)°
$V = 2483.8$ (7) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.10$ mm^{-1}
$T = 120$ (2) K
0.51 × 0.28 × 0.10 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.958$, $T_{max} = 0.990$
55752 measured reflections
5702 independent reflections
4483 reflections with $I > 2\sigma(I)$
$R_{int} = 0.036$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.103$
$S = 1.07$
5702 reflections
379 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.31$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ e Å^{-3}

The space group $P2_1/n$ was uniquely assigned from the systematic absences. All H atoms were located in a difference map and then treated as riding atoms in geometrically idealized positions, with C—H = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DIRAX*/*LSQ* (Duisenberg *et al.*, 2000); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *OSCAIL* (McArdle, 2003) and *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3204). Services for accessing these data are described at the back of the journal.

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