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13*H*-Dibenzo[*a*,*i*]fluoren-13-one

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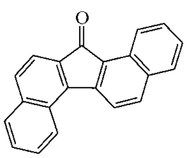
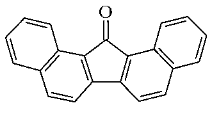
Molecules of 13*H*-dibenzo[*a*,*i*]fluoren-13-one, $C_{21}H_{12}O$, straddle a crystallographic mirror plane and are essentially planar, with a dihedral angle of only 1.9 (1)° between the two naphthalene ring systems. Repulsive intramolecular C=O···H interactions therefore do not explain the larger distortions found in isomeric ketones.

Comment

In a recent publication (Morris *et al.*, 1998) we described the crystal structure of 13*H*-dibenzo[*a*,*g*]fluoren-13-one (CAS Registry No. [63041-47-4]), (I), which had previously been shown by Harvey *et al.* (1992) to exhibit an anomolously low field resonance in the ^{1}H NMR spectrum for the H atom (H4) closest to the carbonyl O.

Molecules of (I) show small but significant distortions from planarity: the two naphthalene ring systems define a dihedral angle of 6.0 (1)° and are themselves slightly ruffled (r.m.s. deviations for the two C_{10} planes are 0.019 and 0.012 Å). Repulsive intramolecular C=O···H interactions (O···H 2.48 Å and O···C—H 124°) were considered to be the most likely cause of these distortions (Morris *et al.*, 1998). However, the geometry of the C=O···H sub-unit in (I) falls in the region where it is difficult to discriminate between 'repulsive forced interactions' and weak C—H···O hydrogen bonds (Jeffrey, 1997). The bay region of (I) also contains a short intramolecular C10—H···H—C14 contact of 2.07 Å, which is indicative of overcrowding. In order to investigate this point we have determined the structure of the isomeric compound 13*H*-dibenzo[*a*,*i*]fluoren-13-one, (II) (CAS Registry No. [86854-01-5]), in which there are no short H···H contacts but two C=O···H interactions of the type found in (I).


(I)


(II)

Molecules of (II) straddle a crystallographic mirror plane which is normal to the five-membered ring, passing through C1, O and the midpoint of the C11—C11(x, $\frac{1}{2} - y$, z). Bond lengths and angles in (II) are unexceptional (Table 1) and agree with comparable values in (I). The single independent naphthalene ring system in (II), defined by C2–C11, has an r.m.s. deviation from planarity of only 0.007 Å and the angle between the two mirror-related ring systems within the same molecule is only 1.9 (1)°. Compound (II) is therefore planar almost to within experimental error; only one skeletal torsion angle deviates from 0 or 180° by more than 1° [C3—C2—C1—O −1.4 (3)°]. However, the C=O···H contact in (II) [O···H4 2.47 (5) Å and O···H4—C4 125 (2)°] is very similar to the corresponding contact in (I). This is consistent with the observation of low field signals in the ^{1}H NMR spectra of both molecules. Taken together, the structural and NMR results for (I) and (II) suggest that the C=O···H interactions in both molecules are not strongly repulsive and indeed may be indicative of weak intramolecular hydrogen bonding. The slight distortion observed in (I) probably helps to relieve H···H steric crowding.

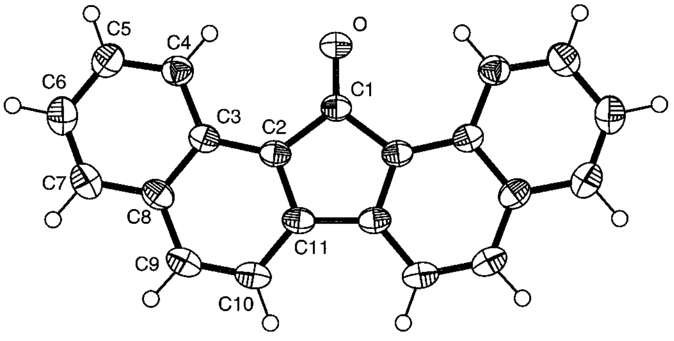


Figure 1
The molecular structure of (II) showing 50% probability displacement ellipsoids and with H atoms drawn as arbitrary spheres.

Experimental

Compound (II) was made by coupling the Grignard reagent from 1-bromonaphthalene (Blicke, 1927) with ethyl formate to give 1,1-dinaphthylmethanol. This was converted to 13*H*-dibenzo[*a*,*i*]fluorene (m.p. 505–506 K; literature value 504–506 K; Harvey *et al.*, 1991) by the action of *meta*-phosphoric acid at 448 K (other dehydrating agents were unsuccessful). Reaction of the hydrocarbon with potassium methoxide and acetone gave compound (II) (m.p. 544–545 K; literature value 542–543 K; Harvey *et al.*, 1991). The ^{1}H NMR spectrum of compound (II) in $CDCl_3$ was determined with a Bruker DPX 400 spectrometer at 9.4 T, and chemical shifts in p.p.m. were referenced to chloroform at 7.25. Spectroscopic analysis, ^{1}H NMR: 8.89 (*d*, J = 8.44 Hz), 2.89 (*d*, J = 8.16 Hz), 7.70 (*d*, J = 8.32 Hz), 7.59 (*d*, J = 8.20 Hz), 7.50 (*d*, J = 7.60 Hz), 7.33 (*d*, J = 7.56 Hz). All absorptions were equally intense. The low-field absorption is assigned to the protons closest to the lone pairs of the carbonyl-O atom. We have, for convenience, numbered the C atoms of (II) so that the oxygen-bearing C atom is defined as C1 (Fig. 1). However, this is at variance with IUPAC nomenclature, which defines C4 in Fig. 1 as C1, with the other C atoms numbered in sequence around the ring away from the carbonyl-C atom.

Crystal data

$C_{21}H_{12}O$
M_r = 280.31
Orthorhombic, *Pnma*
a = 13.2543 (9) Å
b = 25.7694 (18) Å
c = 3.8521 (2) Å
V = 1315.71 (15) Å^3
Z = 4
D_x = 1.415 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 19.0–23.4°
μ = 0.086 mm^{-1}
T = 293 (2) K
Plate, red
0.63 × 0.34 × 0.13 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
3713 measured reflections
2502 independent reflections
1371 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.018
$\theta_{\rm max}$ = 32.9°
$h = -20 \rightarrow 2$
$k = -3 \rightarrow 39$
$l = -5 \rightarrow 1$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.054
$wR(F^2)$ = 0.167
S = 1.004
2502 reflections
127 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0846P)^2 + 0.1556P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max}$ = 0.36 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.24 e Å^{-3}

The C—H distances are in the range 0.96 (2)–0.99 (2) Å.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1992); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

Table 1
Selected geometric parameters (Å, °).

O—C1	1.223 (2)	C11—C2	1.386 (2)
C1—C2	1.495 (2)	C11—C11$^{\rm i}$	1.483 (3)
O—C1—C2	127.04 (8)	C11—C2—C1	108.03 (12)
C2$^{\rm i}$—C1—C2	105.92 (15)	C3—C2—C1	130.51 (12)
C2—C3—C4	123.87 (12)		
C4—C3—C2—C1	0.4 (3)	O—C1—C2—C3	−1.4 (3)

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

We wish to acknowledge the use of the EPSRC Chemical Database Service at Daresbury.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1115). Services for accessing these data are described at the back of the journal.

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