O4	0.08850 (7)	0.7579 (2)	−0.1035 (2)	0.0450 (4)
N1	−0.29212 (7)	0.5195 (2)	−0.0857 (2)	0.0309 (3)
N2	−0.17380 (7)	0.5343 (2)	0.0374 (2)	0.0283 (3)
N3	−0.10575 (6)	0.58840 (14)	0.0473 (2)	0.0229 (2)
C	−0.23129 (7)	0.57975 (15)	−0.0869 (2)	0.0211 (2)

Table 2. *Selected geometric parameters (Å, °)*

P—O2	1.496 (1)	S—C	1.686 (2)
P—O1	1.516 (1)	N1—C	1.322 (2)
P—O4	1.566 (1)	N2—C	1.352 (2)
P—O3	1.567 (1)	N2—N3	1.409 (2)
O2—P—O1	115.96 (6)	O4—P—O3	106.61 (10)
O2—P—O4	107.28 (7)	C—N2—N3	120.51 (12)
O1—P—O4	109.47 (7)	N1—C—N2	115.25 (13)
O2—P—O3	107.85 (8)	N1—C—S	123.36 (11)
O1—P—O3	109.26 (6)	N2—C—S	121.36 (10)

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
N1—H3···O3$^{\rm i}$	0.82 (3)	2.12 (3)	2.943 (2)	176 (3)
N3—H6···O1	0.99 (3)	2.18 (3)	2.931 (2)	131 (2)
N3—H7···O2$^{\rm ii}$	0.99 (2)	1.74 (2)	2.725 (2)	170 (2)
N3—H8···O2$^{\rm iii}$	0.93 (2)	1.92 (3)	2.839 (2)	170 (2)
O3—H1···O1$^{\rm iv}$	0.76 (3)	1.83 (3)	2.578 (2)	166 (3)
O4—H2···O1$^{\rm v}$	0.78 (3)	1.84 (3)	2.623 (2)	172 (3)
N1—H4···S$^{\rm vi}$	0.82 (3)	2.80 (3)	3.535 (2)	152 (3)
N2—H5···S$^{\rm vi}$	0.87 (2)	2.44 (2)	3.282 (1)	161 (2)

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

The structure was solved by direct methods (*SHELXS*86; Sheldrick, 1990*a*) and refined by full-matrix least-squares techniques. All H atoms were located from difference maps and refined isotropically without any distance constraints.

Data collection: *KM*-4 *Software* (Kuma, 1998). Cell refinement: *KM*-4 *Software*. Data reduction: *KM*-4 *Software*. Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1990*b*). Software used to prepare material for publication: *SHELXL*93.

The author is grateful to Professor Z. Czapla (Wrocław University, Institute of Experimental Physics) for the crystal sample.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1366). Services for accessing these data are described at the back of the journal.

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

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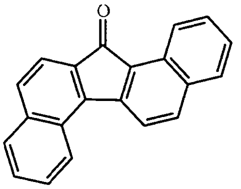
Abstract

The crystal structure determination of 13*H*-dibenzo[*a*,*g*]fluoren-13-one, $C_{21}H_{12}O$, has shown the molecule to be distorted from planarity as a consequence of the repulsive interaction between an $O_{\rm carbonyl}$ lone pair and the juxtaposed proton. These results substantiate an earlier indication of this interaction, suggested by a conspicuously low-field absorption in the ^{1}H NMR spectrum of this compound.

Comment

We report the crystal structure of the title compound, (I) (CAS Registry No. [63041-47-4]). This compound was of interest since its ^{1}H NMR spectrum (Harvey *et al.*, 1992) showed, in addition to a cluster of absorptions corresponding to seven protons in the range $\delta = 7.37$–7.76, single-proton absorptions at δ values of 7.78, 7.91, 8.07, 8.41 and 8.92 p.p.m. The lowest field absorption is assigned to H4 (Fig. 1) on account of its proximity to a lone pair on an O atom. This raises the question of whether the approach of H4 to the $O_{\rm carbonyl}$ lone pair is sufficiently close to make the molecule 'buckle' to any extent and thereby become non-planar.



(I)

In this context, the structure determination of (I) shows two interesting features. Firstly, the C atoms of the six-membered rings at each end of the molecule show small but significant displacements from the plane defined by atoms C21, C1 and C2, which comprises the carbonyl C atom and the adjacent C atoms of the five-membered ring [displacement values: C4 −0.116 (7), C5 −0.238 (9), C6 −0.305 (8), C7 −0.248 (8), C15 0.15 (2), C16 0.07 (2), C17 0.018 (12) and C18 0.023 (9) Å].

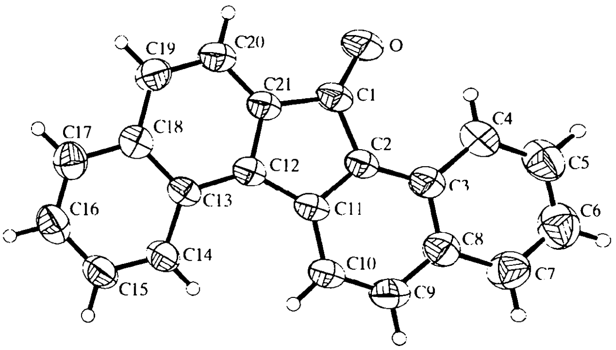


Fig. 1. The molecular diagram of (I), showing 40% probability ellipsoids. H atoms are shown as spheres of arbitrary radii.

These data reveal a slight buckle, with the greater out-of-plane deviation found on the C4 side of the molecule. Additionally, the $O_{carbonyl}$ atom experiences a significant deviation away from H4, as evidenced by the bond angles O—C1—C2 [128.3 (2)°] and O—C1—C21 [126.0 (2)°], although it remains in the plane defined by atoms C21, C1 and C2.

We considered our results in relation to a previous structure determination of fluorenone (Luss & Smith, 1972) which shows two unique molecules, both of which are essentially planar, within the asymmetric unit. The atomic displacements from a plane defined by the carbonyl C atom and the two adjacent C atoms are an order of magnitude smaller for fluorenone than the analogous values determined for (I).

In contrast to (I), the O—C—C bond angles about the carbonyl groups of the fluorenone structures are effectively equivalent: 127.1, 127.2, 126.8 and 127.4° [crystal structure data for fluorenone were accessed using appropriate software (Allen & Kennard, 1993; Fletcher *et al.*, 1996) at the Chemical Database Service, Daresbury].

Our structure determination of (I) confirms the indications of the ^{1}H NMR data (Harvey *et al.*, 1992) and demonstrates small but significant molecular distortions due to the repulsive interaction between H4 and an $O_{carbonyl}$ lone pair.

We are not aware of any other deviation from planarity induced in this manner in a multiple-fused-ring aromatic system. However, cases are known in which H···H non-bonded interactions cause deviations from planarity in aromatic molecules, exemplified by bifluorenylidene (Bailey & Hull, 1978) and tetrabenzonaphthalene (Herbstein, 1979). In the light of the present findings, we will search for other and larger deviations from planarity brought about by non-bonded interactions involving an $O_{carbonyl}$ lone pair.

Experimental

The title compound was prepared according to the method published by Harvey *et al.* (1992).

Crystal data

$C_{21}H_{12}O$
$M_r = 280.31$
Monoclinic
$C2/c$
$a = 13.002 (9)$ Å
$b = 9.329 (6)$ Å
$c = 22.798 (14)$ Å
$\beta = 95.21 (5)°$
$V = 2754 (3)$ Å^3
$Z = 8$
$D_x = 1.352$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 14 reflections
$\theta = 7.9–12.0°$
$\mu = 0.082$ mm^{-1}
$T = 298 (2)$ K
Plate
1.20 × 0.60 × 0.06 mm
Dark red

Data collection

Nicolet $P3$ diffractometer
ω scan
Absorption correction: none
2534 measured reflections
2431 independent reflections
1439 reflections with $I > 2\sigma(I)$
$R_{int} = 0.039$

$\theta_{max} = 25.01°$
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 11$
$l = -27 \rightarrow 26$
2 standard reflections every 50 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.136$
$S = 1.010$
2431 reflections
200 parameters
H atoms riding, with common U_{iso}

$w = 1/[\sigma^2(F_o^2) + (0.0586P)^2 + 0.5228P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.119$ e Å^{-3}
$\Delta\rho_{min} = -0.155$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O—C1	1.223 (3)	C1—C21	1.484 (4)
C1—C2	1.483 (3)		
O—C1—C2	128.3 (2)	C3—C2—C1	128.9 (2)
O—C1—C21	126.0 (2)	C2—C3—C4	123.9 (2)
C2—C1—C21	105.72 (19)	C20—C21—C1	128.0 (2)

We have, for convenience, numbered the C atoms of the title molecule such 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. Azimuthal scans showed no significant intensity variation, so no absorption correction was applied. The refined U^{ij} values are normal.

Data collection: *P*3 *Software* (Nicolet, 1980). Cell refinement: *P*3 *Software*. Data reduction: *RDNIC* (Howie, 1980). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ORTEX* (McArdle, 1994). Software used to prepare material for publication: *SHELXL*97.

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

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1248). Services for accessing these data are described at the back of the journal.

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3-(*o*-Carboxyphenyl)-1-ethyltriazene 1-Oxide†

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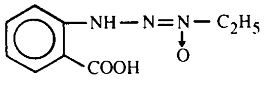
Abstract

The structure determination of the title compound, $C_9H_{11}N_3O_3$, establishes the *N*-oxide form of triazene. The two independent molecules in the asymmetric unit are hydrogen bonded and have different conformations. One molecule is essentially planar, while in the other molecule, the terminal ethyl and carboxy groups deviate considerably from the corresponding molecular plane. The planar phenyl ring and the trigonal-planar geometry about the triazene N atom bonded to the phenyl ring suggest a resonance interaction extending over adjacent atoms. Intermolecular hydrogen bonds link the molecules into infinite chains.

Comment

Substituted triazenes (*R*N=N—NH—) find wide-ranging applications as initiators of radical polymerization (Rapta *et al.*, 1996), as efficient chelating agents (Leman *et al.*, 1992; Cotton *et al.*, 1992) and as anti-tumor drugs (Wilman, 1988). As part of our systematic studies on the synthesis and characterization of triazene 1-oxide derivatives (Samanta *et al.*, 1985, 1997) and to build up a hierarchy for such systems, the structure determination of 3-(*o*-carboxyphenyl)-1-ethyltriazene 1-oxide, (I), was undertaken.



(I)

The results of the present X-ray analysis are in agreement with those of the structure analyses of similar substituted triazenes (Samanta *et al.*, 1997; Anulewicz, 1997; Neidle & Wilman, 1992) and establish the tautomeric *N*-oxide form of triazene (Smith *et al.*, 1992). The asymmetric unit of (I) (Fig. 1) consists of two independent molecules (*A* and *B*) which are approximately orthogonal to each other; the dihedral angle between the essentially planar molecule *A* (r.m.s. deviation 0.032 Å) and the planar part of molecule *B* through atoms C11–C17, N4–N6 and O6 (r.m.s. deviation 0.034 Å) is 85.11 (5)°. In molecule *B*, but not in *A*, the carboxy and ethyl groups are significantly out of the molecular plane (see torsion angles in Table 1). The N1 and N4 atoms, with bond angles summing to 360.0°, are sp^2 hybridized. Each displays trigonal-planar bonding geometry and coplanarity with the phenyl group, strongly suggesting a resonance interaction extending

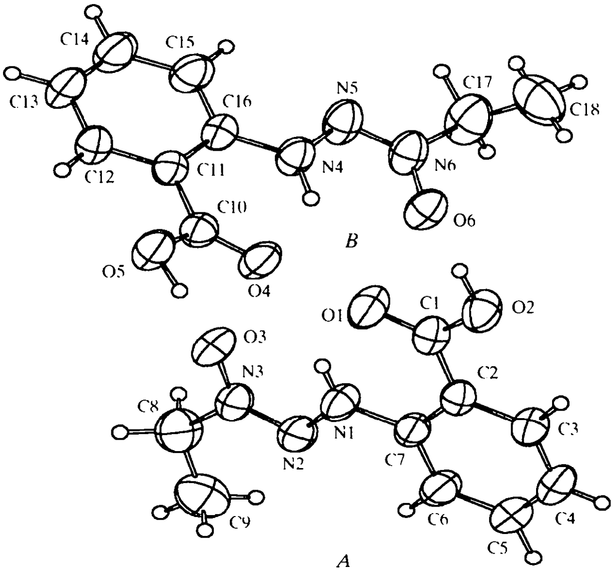


Fig. 1. View (50% probability level) of the two molecules in the asymmetric unit showing the atom-labelling scheme.

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† Alternative name: *o*-(3-ethyl-2-triazeno)benzoic acid N^3-oxide.