C2—O2	1.237 (3)	C4′—O4′	1.431 (3)
N3—C4	1.331 (3)		
C6—C7—C8	115.6 (2)	C1′—C2′—C3′	103.1 (3)
N1—C1′—C2′	118.6 (3)	C2′—C3′—C4′	102.3 (2)
N1—C1′—O4′	108.6 (3)	C3′—C4′—O4′	103.4 (2)
C2′—C1′—O4′	107.8 (2)	C1′—O4′—C4′	106.9 (3)
C2—N1—C1′—O4′	73.9 (4)	C1′—C2′—C3′—C4′	25.7 (3)
O4′—C1′—C2′—C3′	−3.5 (2)	C2′—C3′—C4′—O4′	−39.6 (3)
C2′—C1′—O4′—C4′	−22.0 (3)	C3′—C4′—O4′—C1′	38.7 (3)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2′—HO2′···O5′$^{\rm i}$	0.95	1.78	2.707 (5)	162
O3′—HO3′···O2$^{\rm ii}$	1.00	1.75	2.674 (2)	152
O5′—HO5′···O3′$^{\rm iii}$	0.96	1.81	2.737 (3)	160
N4—H41···N3$^{\rm iv}$	0.95	2.03	2.974 (3)	174
N4—H42···O5′$^{\rm v}$	0.95	2.32	3.259 (3)	172

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

The structure was solved in the space-group *I*1 on the *NRCVAX* system (Gabe *et al.*, 1989) with the symbolic addition method. After a twofold axis was found, the space group was transformed to *C*2 and refined with full-matrix least-squares methods. A riding model was employed for the H atoms, those of the hydroxyl groups from a difference Fourier map and the remainder in calculated positions.

Data collection: *NRCCAD* (Le Page *et al.*, 1986). Cell refinement: *NRCCAD*. Data reduction: *NRCVAX*: *DATRD2*. Program(s) used to solve structure: *NRCVAX*: *SOLVER*. Program(s) used to refine structure: *NRCVAX*: *LSTSQ*. Software used to prepare material for publication: *NRCVAX*: *TABLES* (January 1994 version).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1416). Services for accessing these data are described at the back of the journal.

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1-*tert*-Butyl-9-methoxy-4-methyl-1,2,3,4-tetrahydro-2-azafluoren-3-one, a Novel Fluorenone

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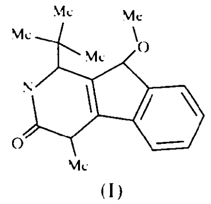
Abstract

The title compound, $C_{18}H_{23}NO_2$, is the final compound in the reaction between an ethynyl Fischer carbene and a 2-azadiene. The reaction proceeds to the stereoselective formation of a 2-azafluorenone. The structure determination reveals hydrogen bonding linking the carbonyl O atom and the H atom attached to the N atoms of symmetry-related molecules. As a result, the structure packing is composed of dimers connected by two hydrogen bonds. These hydrogen bonds show a similar geometry to those found between pairs of bases in DNA, and the structure itself resembles some synthetic inhibitors of DNA transcription.

Comment

Stabilized Fischer carbene complexes of group 6 metals have been recognized for their important role in the formation of a great variety of carbocyclic rings (Barluenga, Tomás, Ballesteros *et al.*, 1997), and as useful tools in the synthesis of natural products (Santiago-García *et al.*, 1997). In this particular synthesis, a tungsten–(phenylethynyl)carbene complex was used as a dienophile in a Diels–Alder reaction against a 2-azadiene, resulting in the stereoselective formation of a 2-azafluorenone, (I). Knowledge of the structure of this adduct is vital for determining the stereochemical assignment of the other adducts in the referenced work.



(I)

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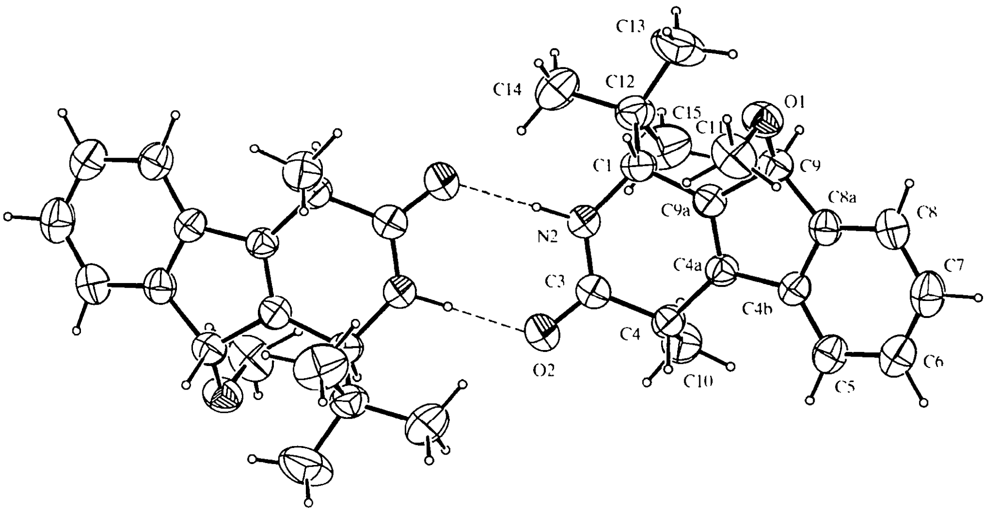

Fig. 1. *EUCLID* (Spek, 1982) plot showing 50% probability displacement ellipsoids of the two molecules in the unit cell, together with the hydrogen bonding and the atomic numbering scheme.

Although distances and angles in (I) are within normal ranges, some features deserve comment. The N atom is in an almost planar environment [sum of angles is 358 (4)°] and the N2—C3 bond distance is 1.334 (4) Å, shorter than the N2—C1 distance of 1.478 (4) Å. The torsion angle H2—N2—C3—O2 is 12 (2)°. The flattening and the differences in the bond distances are due to conjugation with the carbonyl group; compare this with C=O distances in similar compounds, but without conjugation, where the distances are 1.216 (4) and 1.209 (4) Å (García-Granda, Santiago-García *et al.*, 1997). An example of a similar (long) conjugated C=O distance of 1.244 (9) Å is found in Barluenga, Tomás, Bieger *et al.* (1997). The C3—O2 distance of 1.237 (4) Å is slightly long for a carbonyl group. The bonds C4a—C4b at 1.479 (4) and C9a—C4a at 1.335 (4) Å are evidence of conjugation of the double bond with the phenyl group. This can be confirmed by examination of the torsion angles. The C8a—C4b—C4a—C9a and C5—C4b—C4a—C9a torsion angles are 0.5 (4) and 178.8 (3)°, respectively, both of which are very close to planarity. The bond distances and the geometry confirm the conjugation of the double bond C4a=C9a and the phenyl group.

The conformations of the rings in the compound have been examined. The six-membered N2-containing ring adopts a boat conformation, ${}^{3,6}B$ (Boeyens, 1978). The Cremer & Pople (1975) ring puckering parameters are q_2 = 0.254 (4), q_3 = 0.037 (3), Q = 0.257 (4) Å, φ = 115.8 (7) and θ = 81.7 (7)°. The torsion angles involved are shown in Table 1. The five-membered ring is in an envelope conformation, with atoms C8a, C4b, C4a and C9a almost in a plane [maximum deviation from the least-squares plane is 0.003 (3) Å for C4b] and atom C9 is out of the ideal least-squares plane [0.087 (3) Å]. The ring puckering parameters are q_2 = 0.052 (3) Å and φ = 66 (3)°. The other six-membered ring (C4b, C5–C8 and C8a) is planar within experimental limits, the maximum deviation from the least-squares plane being 0.008 (3) Å for the C5 atom.

An interesting feature in the crystal structure is the formation of two hydrogen bonds. Both O2 and H2 (bonded to N2) in the same molecule are involved in the formation of two hydrogen bonds with a symmetry-related molecule (Fig. 1). A careful inspection of the geometry of the hydrogen bonds [H2···O2 1.90 (3) Å and N2—H2···O2 178 (3)°] shows a geometry very close to ideal. A similar hydrogen-bonding network is found in the DNA structure. The geometry found in H2—N2—C3=O2 is also found in well known heterocyclic compounds such as cytosine, thymine and guanine (formers of DNA), uracil (present in RNA) and theobromine (present in tea). Several different compounds are known to inhibit DNA transcription. We can find two different types of inhibitors of DNA transcription, *i.e.* those which bind to RNA-polymerase and those which bind in a non-covalent way to DNA, voiding their function as a pattern. Among the latter, synthetic 2-acetylaminofluorene is well known to be carcinogenic. We can conclude that the title compound could be a carcinogenic compound as well, and could be a useful tool in molecular recognition because of similarities in the structure and the hydrogen-bond network.

Experimental

A (phenylethynyl) tungsten carbene complex (1 mmol) was allowed to react with 1-*tert*-butyl-4-methyl-2-azadiene (1 mmol) in THF at 333 K and stirred for 18 h. Then the solvent was evaporated under reduced pressure and the crude product purified by column chromatography (hexane/ethyl acetate 3:1) to give the final compound (2-azafluorenone). The whole transformation most likely involves two intermediates. The former represents the expected [4+2] cycloadduct, which would undergo further selective electrocyclic ring closure, and last a suprafacial [1,5]-hydrogen shift and reductive elimination (Barluengam, Tomás, Ballesteros *et al.*, 1997).

Crystal data

$C_{18}H_{23}NO_2$
$M_r = 285.37$
Monoclinic
$P2_1/n$
$a = 10.571\ (3)$ Å
$b = 6.3565\ (15)$ Å
$c = 24.36\ (1)$ Å
$\beta = 100.37\ (4)°$
$V = 1610.2\ (9)$ Å^3
$Z = 4$
$D_x = 1.177$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 13–15°$
$\mu = 0.076$ mm^{-1}
$T = 293\ (2)$ K
Prismatic
0.26 × 0.20 × 0.13 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega–2\theta$ scans
Absorption correction: refined from ΔF (Parkin *et al.*, 1995)
$T_{\min} = 0.981$, $T_{\max} = 0.990$
6400 measured reflections
2836 independent reflections

1163 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.085$
$\theta_{\max} = 25°$
$h = -12 \rightarrow 12$
$k = -7 \rightarrow 7$
$l = -28 \rightarrow 28$
3 standard reflections every 200 reflections intensity decay: 5.32%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.145$
$S = 0.979$
2836 reflections
282 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0619P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.190$ e Å^{-3}
$\Delta\rho_{\min} = -0.193$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

O1—C9	1.422 (4)	C4a—C9a	1.335 (4)
O1—C11	1.436 (4)	C4a—C4b	1.479 (4)
O2—C3	1.237 (4)	C4b—C5	1.380 (4)
C1—N2	1.478 (4)	C4b—C8a	1.383 (4)
C1—C9a	1.501 (4)	C5—C6	1.402 (5)
C1—C12	1.556 (5)	C6—C7	1.383 (5)
C1—H1	1.03 (3)	C7—C8	1.382 (5)
N2—C3	1.334 (4)	C8—C8a	1.383 (4)
N2—H2	0.97 (4)	C8a—C9	1.513 (4)
C3—C4	1.511 (4)	C9—C9a	1.527 (4)
C4—C4a	1.489 (4)		
C3—N2—C1	128.5 (3)	C5—C4b—C4a	130.1 (3)
C3—N2—H2	115 (2)	C8a—C4b—C4a	108.2 (3)
C1—N2—H2	114 (2)	C4b—C8a—C8	120.9 (3)
O2—C3—N2	121.0 (3)	C4b—C8a—C9	109.5 (3)
O2—C3—C4	119.3 (3)	C8—C8a—C9	129.5 (3)
N2—C3—C4	119.7 (3)	C8a—C9—C9a	101.9 (3)
C9a—C4a—C4b	109.6 (3)	C4a—C9a—C1	123.9 (3)
C9a—C4a—C4	124.2 (3)	C4a—C9a—C9	110.4 (3)
C4b—C4a—C4	126.1 (3)	C1—C9a—C9	125.6 (3)
C5—C4b—C8a	121.6 (3)		
C9a—C1—N2—C3	−13.3 (5)	C5—C4b—C8a—C8	−1.0 (5)
C1—N2—C3—C4	−5.3 (5)	C4a—C4b—C8a—C9	−3.9 (3)
N2—C3—C4—C4a	22.0 (4)	C7—C8—C8a—C4b	0.1 (5)
C3—C4—C4a—C9a	−21.2 (5)	C4b—C8a—C9—C9a	5.4 (3)
C8a—C4b—C5—C6	1.6 (5)	C4—C4a—C9a—C1	2.8 (5)
C4b—C5—C6—C7	−1.4 (5)	C4b—C4a—C9a—C9	3.1 (4)
C5—C6—C7—C8	0.6 (6)	N2—C1—C9a—C4a	14.5 (5)
C6—C7—C8—C8a	0.1 (6)	C8a—C9—C9a—C4a	−5.1 (4)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O2$^{\rm i}$	0.97 (3)	1.90 (3)	2.873 (4)	178 (3)

Symmetry code: (i) $1 - x, -y, -z$.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989), with profile analysis over all reflections (Lehmann & Larsen, 1974; Grant & Gabe, 1978). Cell refinement: *CRYSDA* (*DIRDIF*; Beurskens *et al.*, 1992). Data reduction: *THE REFLEX* (García-Granda, Aguirre-Pérez *et al.*, 1997). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *EUCLID* (Spek, 1982). Software used to prepare material for publication: *SHELXL*97. Geometrical calculations: *PARST* (Nardelli, 1983). All calculations were made at the University of Oviedo on the Scientific Computer Center and X-ray group VAX/AXP computers.

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