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A new photochromic tetrahydroindolizine

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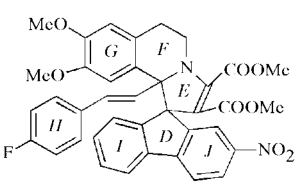
The title compound, dimethyl 10b′-(4-fluorostyryl)-8′,9′-dimethoxy-4-nitro-5′,6′-dihydrospiro[9*H*-fluorene-9,1′(10*b*′*H*)-pyrrolo[2,1-*a*]isoquinoline]-2′,3′-dicarboxylate, $C_{38}H_{31}FN_2O_8$, is a new photochromic tetrahydroindolizine. One of the C—C bonds at the spiro C atom is very long [1.630 (2) Å], thus explaining the photochromic behaviour.

Comment

Photochromism, one of the most noticeable phenomena of photochemistry, involves light-induced reversible transformation of a molecule between two states with different absorption spectra. This phenomenon has attracted increasing interest in recent years. Amongst the many known photochromic systems, photochromic tetrahydroindolizines (THIs; Dürr *et al.*, 1983) have received particular attention owing to their remarkable photofatigue resistance and the range of photochromic properties that they possess (Tan *et al.*, 2001).

We report here the structure of the title compound, (I) (Fig. 1) (Tan *et al.*, 2001). The photochromic properties of (I) have been studied by laser flash photolysis [308 nm; the Full Width at Half-Maximum (FWHM) is 20 ns (Jian *et al.*, 1991)], and these studies show that there are three transients.



(I)

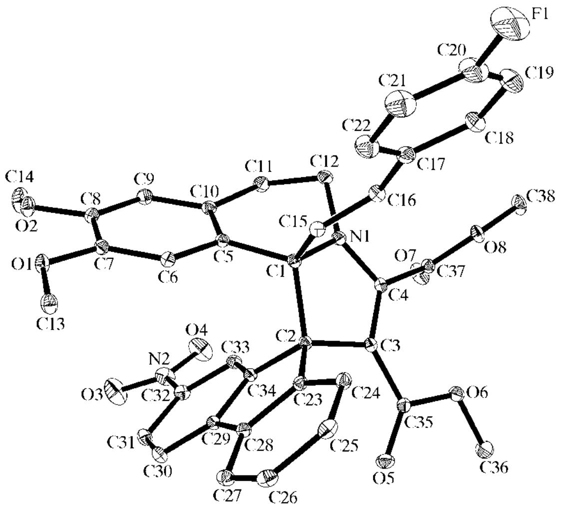


Figure 1
A view of (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 10% probability level.

All the THI regions [*i.e.* the fluorene, ester and dihydroisoquinoline groups, denoted *A*, *B* and *C* (Dürr *et al.*, 1983)] are clearly present in (I). The molecule comprises seven rings, denoted *D*, *E*, *F*, *G*, *H*, *I* and *J* (see scheme). The dihedral angles between these planes are 80.11 (14) [between *D* and *E* (plane through C2, C3 and C4)], 42.31 (16) [between *E* (plane through C2, C3 and C4) and *F* (plane through C1, C5, C10 and C11), 79.48 (14) [*E* (plane through C2, C3 and C4) and *H*], 40.52 (7) (*H* and *I*), 37.72 (7) (*H* and *J*) and 2.85 (3)° (*I* and *J*).

The bonds and dihedral angles of the C3—C2—C1—N1 fragment show clearly that the dihydroisoquinoline region is not planar, the C1/N1/C12 and N1/C12/C11 planes making angles of, respectively, 11.56 (13)° below and 47.76 (13)° above the C1/C5/C10/C11 plane. The vertical distances between atom N1 and the C1/C5/C10/C11 plane and between atom C12 and the C1/C5/C10/C11 plane are 0.096 (3) and 0.600 (3) Å, respectively. The pyrroline ring is also non-planar, the C1/N1/C4 plane and the plane through N1, *sp*^{3}-hybridized C1 and C2 making angles of 11.56 (13) and 21.91 (10)°, respectively, above the C2/C3/C4 plane. The vertical distances between atom N1 and the C2/C3/C4 plane and between atom C1 and the C2/C3/C4 plane are 0.168 (4) and 0.449 (5) Å, respectively. Atoms N1, C3 and C4 exhibit a planar coordination.

The bond lengths (Table 1) in the non-aromatic portion of the molecule show clear evidence of bond fixation, most of the single- and double-bond distances being typical of their types (Dorweiler *et al.*, 1985). However, the C1—C2 bond is significantly longer than a typical single bond between four-connected C atoms. This lengthening may be due to the spiro-concatenation on atom C2. This effect is also shown by a MINDO/3 calculation in the spiro-azanonatriene system (Dorweiler *et al.*, 1988). This long bond is relatively weak and is easily cleaved by UV light, leading to ring opening (Dorweiler *et al.*, 1988).

The C2—C23 and C2—C34 bonds are ~0.06 Å longer than the corresponding bonds in the unsubstituted fluorene molecule (Burns & Hall, 1954). They are, however, in good agreement with those in bisfluorene systems (Neupert-Laes & Dobler, 1981). The C23—C2—C34 angle is almost identical to those found in bisfluorenes and spiro-linked systems (Ege *et al.*, 1981).

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Experimental

The title compound, (I), was synthesized as described by Tan *et al.* (2001). Recrystallization from a dichloromethane–ether solution gave yellow prisms of (I) (m.p. 448–450 K).

Crystal data

$C_{38}H_{31}FN_2O_8$
$M_r = 662.65$
Monoclinic, $P2_1/n$
$a = 12.2895\ (16)$ Å
$b = 20.015\ (3)$ Å
$c = 13.4042\ (18)$ Å
$\beta = 98.739\ (2)°$
$V = 3258.8\ (8)$ Å^3
$Z = 4$
$D_x = 1.351$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6208 reflections
$\theta = 2.3$–$26.8°$
$\mu = 0.10$ mm^{-1}
$T = 298\ (2)$ K
Prism, yellow
0.40 × 0.30 × 0.20 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.962$, $T_{\max} = 0.981$
14 831 measured reflections
6400 independent reflections
4837 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.035$
$\theta_{\max} = 26.0°$
$h = -15 \rightarrow 10$
$k = -24 \rightarrow 24$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.143$
$S = 1.01$
6400 reflections
447 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0831P)^2 + 0.2767P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.014$
$\Delta\rho_{\max} = 0.48$ e Å^{-3}
$\Delta\rho_{\min} = -0.25$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0088 (9)

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1999); software used to prepare material for publication: *SHELXTL*.

Table 1
Selected geometric parameters (Å, °).

N1—C1	1.468 (2)	C2—C23	1.529 (2)
N1—C4	1.347 (2)	C2—C34	1.525 (2)
N1—C12	1.456 (2)	C10—C11	1.511 (2)
C1—C2	1.630 (2)	C11—C12	1.509 (3)
C1—C5	1.525 (2)	C15—C16	1.321 (2)
C1—C15	1.518 (2)	C16—C17	1.463 (3)
C2—C3	1.525 (2)	C28—C29	1.459 (2)
C1—C2—C3	100.79 (12)	C3—C2—C23	118.26 (13)
C1—C2—C23	114.50 (13)	C3—C2—C34	110.82 (13)
C1—C2—C34	111.68 (13)	C23—C2—C34	101.17 (12)

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1322). Services for accessing these data are described at the back of the journal.

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