Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Dimethyl 2-(4-bromophenyl)-10,11-dimethoxy-2,3,7,8-tetrahydrospiro[azepino[2,1-*a*]isoquinoline-3,9′-fluorene]-4,5-dicarboxylate

Li Feng, Zhi-Ming Li, Zhen-Xia Chen, Yong-Sheng Tan, Lin-Hong Weng and Feng-Gang Tao*

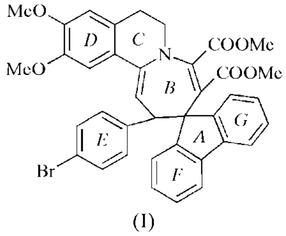
Department of Chemistry, Fudan University, Shanghai 200433, People's Republic of China
Correspondence e-mail: fgtao@fudan.edu.cn

Received 24 June 2004
Accepted 29 June 2004
Online 21 August 2004

The title compound, $C_{38}H_{32}BrNO_6$, is a new photochromic tetrahydroazepinoisoquinoline (THAI). The longest spiro bond [1.589 (4) Å] can be broken very easily by UV light, leading to ring opening. This explains the photochromic behaviour.

Comment

Photochromism has been the subject of extensive investigation, due to its wide range of applications (Dürr, 1998). Tan *et al.* (2001) found a new photochromic system, the aza-heptatriene tetrahydroazepinoisoquinoline (THAI), which constitutes a new class of molecules with interesting properties. In order to study the relationship between the substituting group and the structural and photophysical properties, we have synthesized several new THAI compounds using the method of Tan *et al.* (2001). The title compound, (I), is one of these and was investigated further with regard to its photochromic properties. The spectrum was also obtained (Feng, 2003).



(I)

The molecular structure of (I) and the atom-labelling scheme are shown in Fig. 1, which shows that compound (I) can be divided into three parts, namely fluorene, dihydroazepine and isoquinoline. The molecule can also be thought of as consisting of seven rings, *A* (the plane through C4/C21/C26/C27/C32), *B* (the plane through C1/C2/C5), *C* (the plane through C1/C7/C12/C13), *D* (atoms C7–C12), *E* (atoms C15–C20), *F* (atoms C21–C26) and *G* (atoms C27–C32) (Fig. 1).

Due to the rigid tetrahedral arrangement around the C4 spiro atom (Aldoshin, 1998), the fluorene part of the molecule of (I) is non-planar, with a dihedral angle between rings *F* and *G* of 5.20 (19)°. The dihedral angle between rings *E* and *F* is 37.02 (13)°, and that between rings *E* and *G* is 42.21 (12)°.

From the bond angles it follows that the seven-membered dihydroazepine ring exists in a slightly distorted boat shape. Taking plane *E* as the base, atom C4 deviates slightly from this plane, by −0.198 (6) Å. The dihedral angle between the plane passing through atoms C2, C3 and C5 and plane *E* is 32.2 (3)°, that between the plane through atoms C2, C4 and C5 and plane *E* is 9.1 (2)°, and that between the C6—N1 bond and plane *E* is 96.6°. The deviations of atoms N1, C3, C4 and C6 from plane *B* are 0.720 (5), 0.657 (6), −0.198 (6) and 0.564 (5) Å, respectively. While the C1—C2—C3 and C2—C1—N1 bond angles of 123.1 (3) and 119.3 (3)°, respectively, exhibit standard values, the N1—C6—C5 and C4—C5—C6 angles of 128.7 (3) and 127.5 (3)°, respectively, are distorted by about 8°. Atoms C2 and N1 are sp^2-hybridized, since the sums of the bond angles around them are about 360° (Dorweiler *et al.*, 1985), while the spiro-bonded atom C3, as well as atom C4, exhibit sp^3 configurations, with bond angles of 108.5 (2)° for C5—C4—C3 and 108.8 (2)° for C4—C3—C2.

The dihydroisoquinoline region is also non-planar, with the C1/C13/C14 plane 22.0 (4)° below and the C1/C13/N1 plane 13.3 (3)° above plane *C*. The vertical distance between atom N1 and plane *C* is −0.279 (6) Å and that between atom C14 and plane *C* is 0.465 (6) Å.

The bond distances in (I), especially those in the azepine ring (Table 1), are of interest. The four bonds C2—C3, C3—C4, C4—C5 and C1—N1 in the seven-membered ring are incorporated as single bonds, with bond lengths of 1.499 (4), 1.589 (4), 1.530 (4) and 1.433 (4) Å, respectively. Due to the tension in the region of the dihydroazepine ring, the C3—C4 bond [1.589 (4) Å], almost 0.05 Å greater than the corresponding normal bond length (1.540 Å), is the weakest and most elongated single bond in the azepine ring. The length of

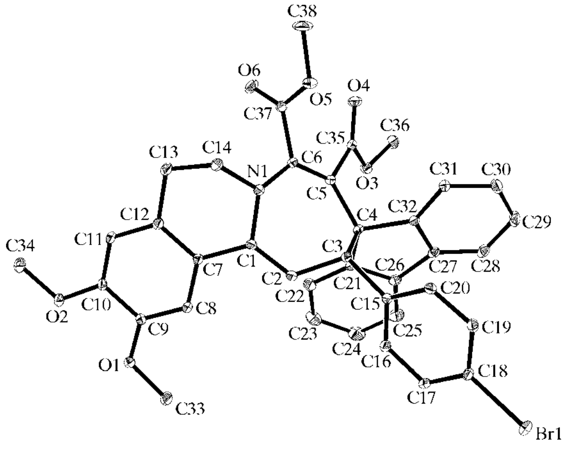


Figure 1
A view of the molecule of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 10% probability level and H atoms have been omitted for clarity.

DOI: 10.1107/S0108270104015860

this C3—C4 bond means it is easily broken during the photochromic process (Dorweiler *et al.*, 1988). The C5—C6 and C1—C2 bonds of 1.360 (4) and 1.320 (4) Å, respectively, have double-bond character, in agreement with the NMR data (Feng, 2003). The short N1—C6 bond of 1.369 (4) Å probably results from a partially delocalized imine–enamine structure.

Experimental

The title compound, (I), was synthesized according to the method of Tan *et al.* (2001). Recrystallization from a solution in dichloromethane–ether (5:1) gave colourless prisms of (I) (m.p. 423–425 K).

Crystal data

$C_{38}H_{32}BrNO_6$
$M_r = 678.56$
Monoclinic, $C2/c$
$a = 21.137$ (4) Å
$b = 9.1906$ (16) Å
$c = 32.459$ (6) Å
$\beta = 95.746$ (3)°
$V = 6273.7$ (19) Å^3
$Z = 8$
$D_x = 1.437$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2541 reflections
$\theta = 2.4$–21.9°
$\mu = 1.36$ mm^{-1}
$T = 298$ (2) K
Prism, colourless
0.45 × 0.30 × 0.05 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.580$, $T_{\max} = 0.935$
14 103 measured reflections
6150 independent reflections
3325 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.067$
$\theta_{\max} = 26.0°$
$h = -24 \rightarrow 26$
$k = -11 \rightarrow 10$
$l = -37 \rightarrow 40$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.092$
$S = 0.83$
6150 reflections
419 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0292P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.53$ e Å^{-3}
$\Delta\rho_{\min} = -0.50$ e Å^{-3}

H atoms were added geometrically and treated as riding, with C—H distances in the range 0.93–0.98 Å, and with $U_{\rm iso}(\rm H) = 1.5U_{\rm eq}(\rm C)$ for methyl H atoms and $1.2U_{\rm eq}(\rm C)$ for the other H atoms.

Table 1
Selected geometric parameters (Å, °).

Br1—C18	1.899 (3)	C2—C3	1.499 (4)
N1—C6	1.369 (4)	C3—C4	1.589 (4)
N1—C1	1.433 (4)	C4—C5	1.530 (4)
C1—C2	1.320 (4)	C5—C6	1.360 (4)
C2—C1—N1	119.3 (3)	C3—C4—C5	108.5 (2)
C1—C2—C3	123.1 (3)	C4—C5—C6	127.5 (3)
C2—C3—C4	108.8 (2)	C5—C6—N1	128.7 (3)

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

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1741). Services for accessing these data are described at the back of the journal.

References

Aldoshin, S. (1998). *Organic Photochromic and Thermochromic Compounds*, Vol. 2, edited by J. C. Crano & R. J. Guglielmetli, pp. 297–355. New York: Kluwer Academic/Plenum.

Bruker (2001). *SMART*. Version 5.625. Bruker AXS Inc., Madison, Wisconsin, USA.

Dorweiler, C., Holdebaum, M., Münzmay, T., Spang, P., Dürr, H., Krueger, C. & Raabe, E. (1988). *Chem. Ber.* **121**, 843–851.

Dorweiler, C., Spang, P., Dürr, H., Peters, K. & von Schnering, H. G. (1985). *Isr. J. Chem.* **25**, 246–251.

Dürr, H. (1998). *Organic Photochromic and Thermochromic Compounds*, Vol. 1, edited by J. C. Crano & R. J. Guglielmetli, pp. 223–266. New York: Kluwer Academic/Plenum.

Feng, L. (2003). PhD thesis, Fudan University, People's Republic of China.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Sheldrick, G. M. (1999). *SHELXTL*. University of Göttingen, Germany.

Tan, Y. S., Hartmann, T., Huch, V., Dürr, H., Valat, P., Wintgens, V. & Kossanyl, J. (2001). *J. Org. Chem.* **66**, 1130–1137.