Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, bond distances and angles involving H atoms and non-bonded contact distances have been deposited with the IUCr (Reference: HA1098). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Photochromic Pyrido-Annulated 2,2-Diphenylchromene

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Abstract

A photochromic pyrido-annulated chromene, 3,3-diphenylpyrano[5,6-*f*]quinoline, $C_{24}H_{17}NO$, has been studied. The photoreactive C_{sp^3}—O bond length is longer than the standard values observed for oxygen-containing heterocycles as a result of steric interactions between the two phenyl groups.

Comment

Previous X-ray studies of spiropyrans containing nitrogen, oxygen and sulfur as additional heteroatoms (Hoff-

man *et al.*, 1972; Shustov, Zolotoy & Kostyanovskii, 1982; Aldoshin, Kholmanskij & Atovmian, 1986; Aldoshin *et al.*, 1987) have showed that specific *n–s** orbital interactions influence the length of the C—O bond which is broken upon photoexcitation. The efficiency of this interaction is influenced considerably by the conformation of the heterocycle, the nature of the substituents and their arrangement in the molecule. In this work we have carried out an X-ray study of the chromene (I), which contains a single pyran heterocycle, and in which an *n–s** interaction cannot affect the C—O bond length. Despite this, the compound is photochromic. The specific structural features of the chromene responsible for its photochromic properties are discussed.

(I)
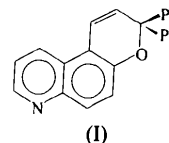
The pyran ring in (I) is nonplanar. The ring is bent along the C2—O and C3—O vectors by 23.2 (2) and 12.0 (2)°, respectively. The valence angles at the sp^3 hybridized C atom show substantial distortion away from the ideal value for tetrahedral geometry. The C1—O bond [1.458 (4) Å] is longer than a typical C—O bond in a six-membered heterocycle (1.41–1.43 Å; Birukov & Unkovskij, 1976), such as those in the photochromic spiropyrans studied earlier (Hoffman *et al.*, 1972; Shustov, Zolotoy & Kostyanovskii, 1982; Aldoshin, Kholmanskij & Atovmian, 1986; Aldoshin *et al.*, 1987).

The phenyl rings in the molecule are almost perpendicular to each other, the angle between the planes of the rings being 91.0 (2)°. The orientation of the rings with respect to the pyran ring is characterized by the angle between the plane formed by O, C1 and C2 and the plane of the phenyl ring C13–C18 [74.1 (2)°] and the angle between the plane formed by O, C1 and C2 and the plane of the phenyl ring C19–C24 [51.9 (2)°]. Analysis of the intramolecular contacts [O···H20 = 2.46 (3), O···C20 = 2.793 (3) Å, O···H20—C20 = 102 (2)°; C1—O···H20 = 79 (2)°; C5—O···H20 = 115 (1)°; O···H18 = 2.36 (2), O···C18 = 2.687 (3) Å, O···H18—C18 = 100 (2)°; C1—O···H18 = 83 (2)°; C5—O···H18 = 128 (1)°] allows us to assume the presence of weak C18—H18···O and C20—H20···O hydrogen bonds (Desideraju, 1989) which are apparently responsible for the orientation of the phenyl rings in the molecule. It should also be noted that the conditions for a secondary interaction between the C24—H24 bond and the p_z orbital of the C2=C3 bond are favorable [C24···C2 = 2.851 (3), H24···C2 = 2.48 (3) Å, C3—C2···H24 = 115 (2), C24—H24···C2 = 104 (2)°]. Geometrical modeling shows that a planar conformation of the pyran ring leads to a parallel orientation of the phenyl rings,

while bending the pyran ring towards one phenyl ring along the O—C2 and O—C3 vectors leads to a perpendicular orientation of the phenyl rings. A mutually orthogonal orientation of the phenyl substituents results in a short intramolecular contact of 2.915 Å between C14 and C19 and subsequent distortion of the tetrahedral configuration of C1. Short intramolecular contacts are absent when the orientation of the phenyl rings is parallel. The orthogonal orientation of the phenyl substituents in the crystal, despite the steric crowding that results, could be additional confirmation of the presence of CH—O interactions.

The bond lengths between the phenyl rings and the C1 atom differ considerably [C1—C19 = 1.504 (4), C1—C13 = 1.528 (4) Å]. The valence angle between the elongated C1—C13 and C1—O bonds [104.2 (2)°] is distorted the most from the value for ideal tetrahedral geometry (109.2°). As noted earlier, the distortion of the angles at C1 results from the steric crowding in this junction because of the orthogonal arrangement of the phenyl rings. The elongation of the C1—C13 and C1—O bonds can be explained by the repulsion of the valence electrons within these bonds as a consequence of the small O—C1—C13 angle.

This work has shown that the C—O bond in the chromene (I) which is broken upon photoexcitation is elongated and weakened in the ground state, as found in photochromic spiropyrans. In contrast to the spiropyrans, however, elongation of this bond is due to steric interactions between the substituents at the C1 atom. We are planning to study the role of steric interactions and their influence on photochromic properties of chromenes with various substituents at the C atom.

Fig. 1. An *ORTEP*II drawing (Johnson, 1976) of (I) with displacement ellipsoids at the 50% probability level.

Experimental

Crystal data

C24H17NO
$M_r = 336.39$
Monoclinic
$P2_1/n$
$a = 11.830 (20)$ Å
$b = 8.361 (20)$ Å
$c = 18.315 (40)$ Å
$\beta = 71.55 (3)°$
$V = 1718.4 (63)$ Å^3
$Z = 4$
$D_x = 1.30$ Mg m^{-3}
$D_m = 1.32 (2)$ Mg m^{-3}
D_m measured by flotation

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25
    reflections
$\theta = 1$–$17.5°$
$\mu = 0.079$ mm^{-1}
$T = 293 (2)$ K
$0.20 \times 0.15 \times 0.10$ mm
Colourless
Crystal source: heptane
    solution

Data collection

Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction:
    none
2612 measured reflections
2352 independent reflections
1590 observed reflections
    $[I > 2.0\sigma(I)]$

$R_{int} = 0.0285$
$\theta_{max} = 23.28°$
$h = 0 \rightarrow 13$
$k = -8 \rightarrow 0$
$l = -19 \rightarrow 20$
3 standard reflections
    frequency: 60 min
    intensity variation: 3%

Refinement

Refinement on F
$R = 0.0547$
$wR = 0.0547$
$S = 0.766$
2348 reflections
303 parameters
H-atom parameters not
    refined
Unit weights applied

$(\Delta/\sigma)_{max} = -0.473$
$\Delta\rho_{max} = 0.217$ e Å^{-3}
$\Delta\rho_{min} = -0.337$ e Å^{-3}
Extinction correction: none
Atomic scattering factors
    from *International Tables
    for X-ray Crystallography*
    (1992, Vol. C, Tables
    4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)
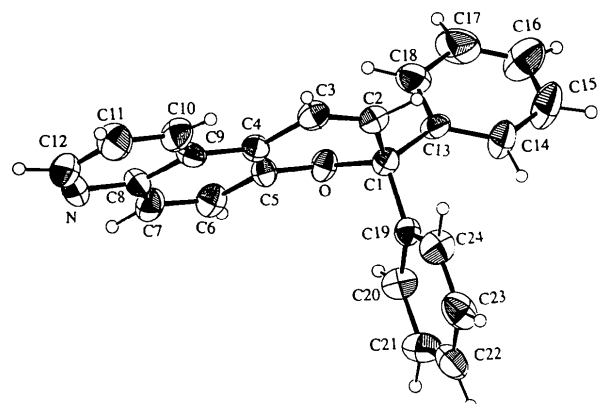
$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O	0.90597 (15)	0.1563 (2)	0.96089 (9)	0.034 (4)
N	0.9322 (2)	0.1460 (2)	0.65543 (13)	0.045 (5)
C1	0.7946 (2)	0.1821 (3)	1.02290 (13)	0.031 (6)
C2	0.7201 (2)	0.3059 (3)	0.9985 (2)	0.035 (7)
C3	0.7314 (2)	0.3263 (3)	0.9255 (2)	0.037 (7)
C4	0.8186 (2)	0.2365 (3)	0.86535 (14)	0.032 (6)
C5	0.9035 (2)	0.1542 (3)	0.88694 (13)	0.030 (6)
C6	0.9969 (2)	0.0726 (3)	0.8336 (2)	0.040 (6)
C7	1.0054 (2)	0.0733 (3)	0.7582 (2)	0.042 (7)
C8	0.9200 (2)	0.1526 (3)	0.73194 (15)	0.036 (7)
C9	0.8251 (2)	0.2339 (2)	0.78650 (15)	0.033 (5)
C10	0.7407 (3)	0.3078 (3)	0.7576 (2)	0.046 (8)
C11	0.7538 (3)	0.3013 (4)	0.6816 (2)	0.055 (9)
C12	0.8513 (3)	0.2177 (3)	0.6325 (2)	0.051 (8)
C13	0.8337 (2)	0.2454 (3)	1.08941 (14)	0.033 (6)
C14	0.7671 (3)	0.2166 (4)	1.1649 (2)	0.049 (9)
C15	0.8022 (3)	0.2782 (5)	1.2247 (2)	0.065 (10)
C16	0.9026 (4)	0.3670 (4)	1.2097 (2)	0.074 (10)
C17	0.9697 (4)	0.3970 (4)	1.1350 (2)	0.071 (10)
C18	0.9347 (3)	0.3379 (3)	1.0747 (2)	0.050 (8)
C19	0.7295 (2)	0.0252 (3)	1.04159 (13)	0.032 (6)
C20	0.7927 (3)	-0.1150 (3)	1.0402 (2)	0.043 (8)
C21	0.7339 (3)	-0.2566 (3)	1.0603 (2)	0.053 (8)
C22	0.6117 (3)	-0.2642 (4)	1.0820 (2)	0.051 (9)
C23	0.5485 (3)	-0.1286 (4)	1.0834 (2)	0.054 (9)
C24	0.6059 (3)	0.0147 (3)	1.0628 (2)	0.046 (8)

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

O—C5	1.364 (4)	C9—C10	1.412 (4)
O—C1	1.458 (4)	C10—C11	1.353 (5)
N—C12	1.307 (4)	C11—C12	1.404 (5)
N—C8	1.364 (5)	C13—C18	1.377 (4)
C1—C19	1.504 (4)	C13—C14	1.379 (5)
C1—C2	1.515 (4)	C14—C15	1.388 (5)
C1—C13	1.528 (4)	C15—C16	1.353 (6)
C2—C3	1.312 (5)	C16—C17	1.370 (6)
C3—C4	1.457 (4)	C17—C18	1.386 (5)
C4—C5	1.374 (4)	C19—C20	1.386 (4)
C4—C9	1.422 (5)	C19—C24	1.393 (5)
C5—C6	1.399 (4)	C20—C21	1.363 (5)
C6—C7	1.352 (5)	C21—C22	1.374 (5)
C7—C8	1.413 (4)	C22—C23	1.354 (5)
C8—C9	1.418 (4)	C23—C24	1.370 (5)
C5—O—C1	118.5 (2)	C10—C9—C4	123.8 (3)
C12—N—C8	117.5 (3)	C8—C9—C4	120.0 (3)
O—C1—C19	108.6 (2)	C11—C10—C9	120.2 (3)
O—C1—C2	109.7 (2)	C10—C11—C12	118.9 (3)
C19—C1—C2	111.1 (3)	N—C12—C11	124.0 (3)
O—C1—C13	104.2 (2)	C18—C13—C14	118.6 (3)
C19—C1—C13	112.5 (2)	C18—C13—C1	120.2 (2)
C2—C1—C13	110.5 (2)	C14—C13—C1	121.2 (3)
C3—C2—C1	120.6 (2)	C13—C14—C15	120.6 (4)
C2—C3—C4	121.5 (3)	C16—C15—C14	120.4 (4)
C5—C4—C9	118.3 (2)	C15—C16—C17	119.8 (3)
C5—C4—C3	116.6 (3)	C16—C17—C18	120.4 (4)
C9—C4—C3	125.0 (3)	C13—C18—C17	120.2 (3)
O—C5—C4	121.8 (2)	C20—C19—C24	117.7 (3)
O—C5—C6	116.0 (2)	C20—C19—C1	120.0 (3)
C4—C5—C6	122.1 (3)	C24—C19—C1	122.4 (2)
C7—C6—C5	119.8 (3)	C21—C20—C19	120.2 (3)
C6—C7—C8	121.3 (3)	C20—C21—C22	121.2 (3)
N—C8—C7	118.4 (3)	C23—C22—C21	119.4 (3)
N—C8—C9	123.1 (3)	C22—C23—C24	120.3 (3)
C7—C8—C9	118.4 (3)	C23—C24—C19	121.1 (3)
C10—C9—C8	116.2 (3)		

Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1994). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *Word* 5.0 on a Macintosh LCII.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: PA1125). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Diethyl Methano-C60-fullerene-61,61-dicarboxylate Chloroform Solvate at 193 K, $C_{60}C(CO_2C_2H_5)_2.CHCl_3$

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Abstract

The structure of fullerene can be interpreted as a condensation of 20 cyclohexatriene rings [with single- and double-bond lengths of 1.450 (4) Å and 1.390 (4) Å, respectively] to form a highly symmetrical sphere. The addition of the bis(ethoxycarbonyl)methano group to a double bond prevents the known disorder of the unsubstituted fullerene molecule in the solid phase.

Comment

The title compound (I) crystallizes with two molecules in the asymmetric unit together with two chloroform solvent molecules. The fullerene molecule can be interpreted as an arrangement of 12 five-membered rings on the surface of a sphere connected by double bonds. In this way, 20 six-membered rings are generated, all of which are formal cyclohexatriene rings.

(I)
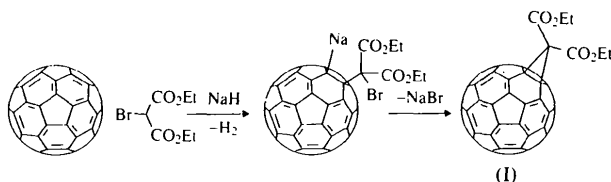
Even at low temperature (249 K), the crystal structure of unsubstituted C_{60}-fullerene is disordered (Bürgi *et al.*, 1992). Because in this case the malonic acid diethyl ester group is added to a double bond of the fullerene molecule, the orientation of the fullerene molecule is fixed in the cell. It is therefore possible to determine the dimensions of the fullerene molecule quite accurately because the coordinates of C atoms having the same local symmetry are determined many times. This situation is further enhanced by the fact that there are two molecules in the asymmetric unit.

The addition of the malonic acid diethyl ester group increases the C—C bond distance involved in the cyclopropane ring fusion from 1.393 (5) Å to an average of 1.606 (4) Å. This is contrary to the theory that the fullerene ring system is opened by the addition