C2—C3	1.381 (4)	C10—C11	1.385 (4)
C3—C4	1.389 (4)	C11—C12	1.474 (4)
C4—C5	1.386 (4)	C12—C13	1.495 (4)
C5—C13	1.402 (4)		
C14—O3—H3*B*	114 (2)	O1—C12—C13	127.3 (3)
C2—C1—C14	115.1 (3)	C1—C13—C12	132.4 (3)
C13—C1—C14	127.8 (3)	O2—C14—O3	119.6 (3)
O1—C12—C11	126.0 (3)	O3—C14—C1	119.0 (3)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3*B*···O1	0.93 (4)	1.66 (4)	2.596 (3)	174 (4)

All non-carboxy H atoms were placed in calculated positions and allowed to refine as riding. The carboxy H3*B* atom was found in an electron density difference map and the positional parameters were refined, but the displacement parameter was fixed.

Data collection: *XSCANS* (Siemens, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXTL*/*PC* (Sheldrick, 1990*b*), *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL*/*PC*. Software used to prepare material for publication: *SHELXTL*/*PC*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1139). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 1537–1539

Photochromic Pyrido-Annelated 2,2-Dimethylchromene

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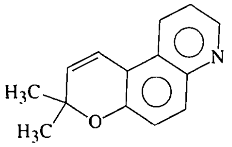
(*Received 7 July 1995; accepted 30 November 1995*)

Abstract

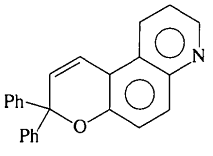
An X-ray analysis of the title photochromic pyrido-annelated 2,2-dimethylchromene, 3,3-dimethylpyrano-[3,2-*f*]quinoline, has been undertaken. It forms a crystallohydrate, $C_{14}H_{13}NO.H_2O$. The influence of the molecular structure on its photochemical properties has been investigated.

Comment

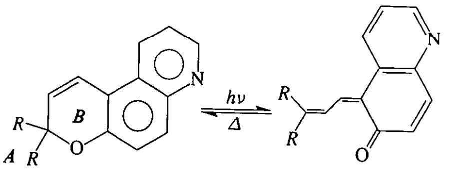
Aldoshin *et al.* (1995) have discussed the structure and photochemical properties of 2,2-diphenylchromene derivatives. Elongation of the C_{sp^3}—O bond, the rupture of which is responsible for the photochemical properties of chromenes, was shown to be due to steric repulsions at the sp^3 centre. Two different arrangements of the mutually orthogonal phenyl rings relative to the pyran O atom were revealed, the steric influence of each on the C—O bond length being the same. Changes in photochemical activity of different diphenylchromene derivatives are related to the specific structure of the pyran fragment of the molecule. The stability of open forms of diphenylchromenes depends on the π-system size and on the efficiency of π-conjugation in this system. In relation to this, it would be interesting to study the structure and photochemical properties of 2,2-dimethylchromene, the methyl groups of which have a steric influence on the sp^3 centre only. On the other hand, from such an investigation, the effect of the conjugated left moiety of chromenes, *A*, on the stability of their open forms can be determined. For this purpose we have synthesized the pyridino-annelated 2,2-dimethylchromene (I), an analogue of the previously studied diphenylchromene (II) (Aldoshin *et al.*, 1995), and studied its structure and photochemical properties.



(I)



(II)



A general view of (I) is shown in Fig. 1. The structure of the right, pyran part *B*, of chromene (I) is identical to the pyran part of (II). The C1 centre has a distorted tetrahedral structure. Similar to other diphenylchromene derivatives, one of the valence angles, O1—C1—C14 104.0 (2)°, is substantially decreased relative to the ideal tetrahedral angle (109.2°). Similarly decreased O—C—C(Ph) angles in diphenylchromenes lie in the range 104.2–105.8°.

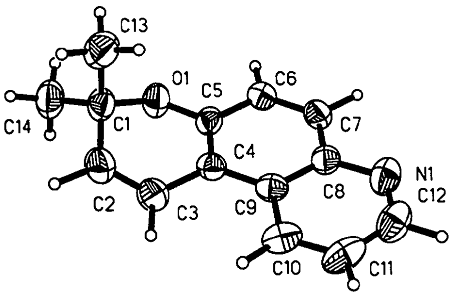


Fig. 1. *ORTEP*II drawing (Johnson, 1976) of the molecule of photochromic pyrido-annelated 2,2-dimethylchromene with 50% probability displacement ellipsoids.

The C1—O1 bond in (I) [1.468 (3) Å] is elongated and is approximately equal to that in (II) [1.458 (4) Å]. Within the limits of experimental error, the O1—C5 bond lengths are also the same in (I) and (II) [1.373 (3) and 1.364 (4) Å, respectively].

Although chromenes (I) and (II) have similar structures, photochemical activity of (I) is much lower than that of (II). One can evaluate the photocolourability as the initial absorbance A_0 measured at λ_{max} of the photomerocyanine (see reaction scheme above) in standard conditions of flash photolysis (Pottier *et al.*, 1990). The photocolourability A_0 of (I) is 0.46, compared with 0.77 for (II). These data point out that substituents in the left fragment of chromenes, *A*, are essential participants in the process of cycle opening. Apparently, in diphenylchromenes, benzene-ring π systems stabilize and planarize a pyramidal carbocation at C1, that is formed upon elongation and rupture of the C1—O1 bond at the first stage of photoconversion. The absorption band of the open form of (I), λ_{max} = 381 nm, is essentially shifted into a short-wave area, compared with λ_{max} = 436 nm for (II), which is connected with a decrease of the size of the π-conjugated system of the open form of (I). This also determines an increase of the fading rate of (I) [$K\Delta$(I) = 1.16] compared with that of (II) [$K\Delta$(II) = 0.13], and hence a decrease of the lifetime of the open form of (I).

Experimental

The title compound was synthesized from the titanate salt of 6-hydroxyquinoline and 3-methyl-2-butenal as described by Pozzo (1994). Crystals were grown from heptane solution.

Crystal data

$C_{14}H_{13}NO.H_2O$
M_r = 229.28
Monoclinic
$C2/c$
a = 23.123 (4) Å
b = 11.484 (2) Å
c = 9.2200 (10) Å
β = 95.05 (3)°
V = 2438.8 (7) Å^3
Z = 8
D_x = 1.249 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 10.0–20.0°
μ = 0.084 mm^{-1}
T = 293 (2) K
Needle
0.35 × 0.1 × 0.05 mm
Colourless

Data collection

KM-4 diffractometer
θ scans
Absorption correction: none
1826 measured reflections
1700 independent reflections
922 observed reflections [$I > 2\sigma(I)$]

R_{int} = 0.0605
θ_{max} = 23.03°
$h = -25 \rightarrow 25$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 10$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F
R = 0.041
wR = 0.047
S = 1.188
1700 reflections
214 parameters
H-atom coordinates refined from calculated positions; U_{iso}(H) fixed at 0.05 Å^2
Unit weights applied

$(\Delta/\sigma)_{max} = -0.085$
$\Delta\rho_{max}$ = 0.174 e Å^{-3}
$\Delta\rho_{min}$ = −0.175 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	*y*	*z*	U_{eq}
O1	0.13782 (7)	0.3792 (2)	−0.5006 (2)	0.0510 (6)
N1	0.37017 (10)	0.4032 (2)	−0.3021 (3)	0.0553 (7)
C1	0.09437 (11)	0.3439 (2)	−0.4023 (3)	0.0501 (8)
C2	0.11662 (13)	0.2425 (3)	−0.3133 (3)	0.0566 (8)
C3	0.17315 (13)	0.2287 (3)	−0.2759 (3)	0.0529 (8)
C4	0.21455 (11)	0.3095 (2)	−0.3308 (3)	0.0395 (7)
C5	0.19473 (10)	0.3808 (2)	−0.4437 (3)	0.0386 (7)
C6	0.23234 (12)	0.4556 (2)	−0.5143 (3)	0.0446 (7)
C7	0.28952 (12)	0.4602 (2)	−0.4667 (3)	0.0448 (7)
C8	0.31239 (11)	0.3916 (2)	−0.3474 (3)	0.0415 (7)
C9	0.27493 (11)	0.3148 (2)	−0.2792 (3)	0.0408 (7)
C10	0.30027 (14)	0.2458 (3)	−0.1635 (3)	0.0549 (8)
C11	0.3584 (2)	0.2592 (3)	−0.1203 (4)	0.0652 (10)
C12	0.39126 (15)	0.3392 (3)	−0.1903 (3)	0.0607 (9)
C13	0.0828 (2)	0.4479 (3)	−0.3066 (5)	0.0695 (10)
C14	0.04104 (15)	0.3123 (4)	−0.5049 (5)	0.0681 (10)
O*W*	0.46867 (12)	0.5390 (3)	−0.3869 (3)	0.0764 (8)

Table 2. *Geometric parameters (Å, °)*

O1—C5	1.373 (3)	C4—C5	1.371 (4)
O1—C1	1.468 (3)	C4—C9	1.436 (4)
N1—C12	1.323 (4)	C5—C6	1.420 (4)
N1—C8	1.371 (3)	C6—C7	1.357 (4)
C1—C2	1.490 (4)	C7—C8	1.417 (4)
C1—C13	1.523 (4)	C8—C9	1.421 (4)
C1—C14	1.530 (4)	C9—C10	1.414 (4)
C2—C3	1.332 (4)	C10—C11	1.378 (4)
C3—C4	1.455 (4)	C11—C12	1.387 (5)
C5—O1—C1	116.9 (2)	C4—C5—C6	122.1 (2)
C12—N1—C8	117.8 (3)	O1—C5—C6	116.0 (2)
O1—C1—C2	109.5 (2)	C7—C6—C5	119.6 (3)
O1—C1—C13	107.8 (2)	C6—C7—C8	121.0 (2)
C2—C1—C13	111.3 (3)	N1—C8—C7	118.0 (2)
O1—C1—C14	104.0 (2)	N1—C8—C9	122.8 (2)
C2—C1—C14	112.0 (3)	C7—C8—C9	119.2 (2)
C13—C1—C14	111.8 (3)	C10—C9—C8	117.0 (3)
C3—C2—C1	121.2 (3)	C10—C9—C4	123.5 (2)
C2—C3—C4	119.7 (3)	C8—C9—C4	119.5 (2)
C5—C4—C9	118.4 (2)	C11—C10—C9	119.0 (3)
C5—C4—C3	117.3 (2)	C10—C11—C12	120.0 (3)
C9—C4—C3	124.2 (2)	N1—C12—C11	123.4 (3)
C4—C5—O1	121.8 (2)		

Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *ORTEP*II (Johnson, 1976). Material was prepared for publication using an IBM PC AT 486 .

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PA1202). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C52, 1539–1543

Comparison of the Geometries of 3,7,10-Tribenzyl-3,7,10-triaza[3.3.3]propellane, (1), 7,10-Dibenzyl-3-*p*-tolyl-3,7,10-triaza[3.3.3]propellane, (2), and 7,10-Dibenzyl-3-oxa-7,10-diaza[3.3.3]propellane, (3)

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(*Received 18 September 1995; accepted 27 November 1995*)

Abstract

Room-temperature crystal structures are reported for three analogous [3.3.3]propellanes. Compound (1), $C_{29}H_{33}N_3$, is trigonal, (2), $C_{29}H_{33}N_3$, triclinic and (3), $C_{22}H_{26}N_2O$, orthorhombic. All three molecules have eclipsed conformations about the central conjoining bond and the five-membered rings all have envelope conformations (C_s-*m* symmetry).

Comment

A [*p*,*q*,*r*]propellane is a tricyclic compound whose (*p* + 2),(*q* + 2),(*r* + 2)-membered alicyclic or heterocyclic rings share a common (conjoining) C—C bond; for an overview refer to Ginsburg (1975) and subsequent updates. Using the crystal structures of eighteen dithia[*n*.3.3]propellanes (*n* = 1, 2, 3) and dithia[4.3.3]-propellenes (in various forms) as a basis (Herbstein *et al.*, 1986), we proposed two generalizations for the conformations of propellane-type molecules: (*a*) propellane molecules are either eclipsed or staggered about the conjoining bond, intermediate situations not being found, *i.e.* τ(C2—C1—C4—C3) $\simeq$ 0 or 60° (atom numbering as in scheme below, in which the conjoining bonds are emphasized); (*b*) it follows from (*a*) that the three rings of a propellane molecule all have the same conformation and symmetry, *e.g.* considering only five-membered rings (*n* = 3), all three have envelope