

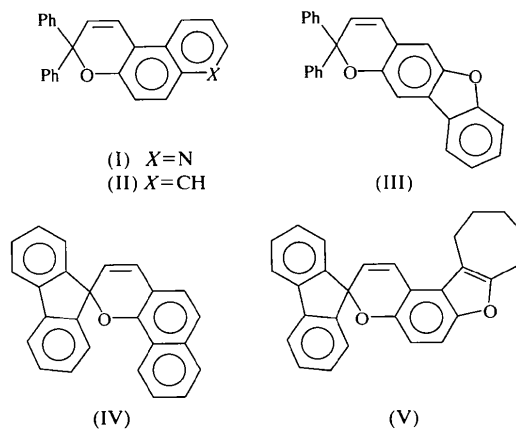
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Comment

The title compounds, (IV) and (V), were studied and compared with the previously analysed compounds (I), (II) and (III) (see scheme below) (Aldoshin *et al.*, 1995, 1996) in order to define the effect of replacing the C_{sp³} atom by a spiro atom on the structures and photochromic properties of chromenes.



The characteristic geometric parameters of compounds (I) to (V) are reported in Table 3. In compound (IV), the pyran ring is more planar than in compounds (I), (II) and (III), while in compound (V), the contrary is observed. In compound (V), the longer C15—C16 bond length of 1.470 (2) Å compared with the corresponding bonds in the other compounds [(I) 1.453 (2), (II) 1.454 (2), (III) 1.444 (4) and (IV) 1.448 (3) Å] confirms this assumption.

As a correlation between the strain energy (E_s) of the pyran ring and the photocolourability (A_0) (Miller *et al.*, 1975) has been found (Aldoshin *et al.*, 1996),

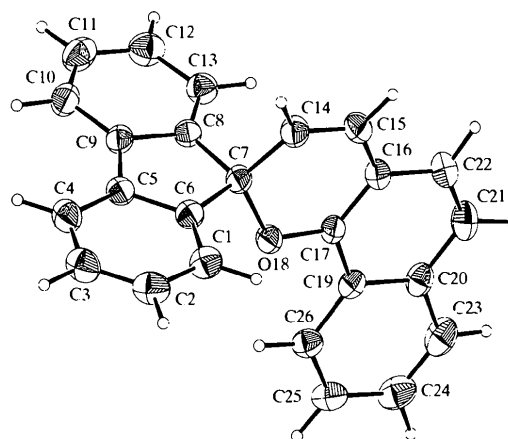


Fig. 1. ORTEP drawing (Johnson, 1976) of compound (IV) with displacement ellipsoids of 50% probability and H atoms drawn as small circles.

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Photochromic Properties of Spiro[fluorene-chromenes]

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Abstract

Two annelated spiro[fluorene–chromene] structures, spiro[2*H*-benzo[*h*]chromene-2,9'-fluorene], C₂₅H₁₆O, and 9,10,11,12-tetrahydrospiro[3*H*,8*H*-cyclohepta[4,5]furano-[3,2-*f*]chromene-2,9'-fluorene], C₂₈H₂₂O₂, have been analysed in order to define the effect of introducing a spiro-C atom into the pyran ring on the photochromic properties of the chromenes. The results are compared with those obtained for previously studied non-spiro 2,2-substituted chromenes.

similar *MMP2* (Allinger & Young, 1977) calculations were performed on chromenes (I) to (V) (Table 4). In the case of these compounds, a relationship is observed for the coloured forms with the shortest wavelengths in the visible region; the electronic spectra of compounds (III) and (IV) show three different bands, compared with only two bands for compound (V).

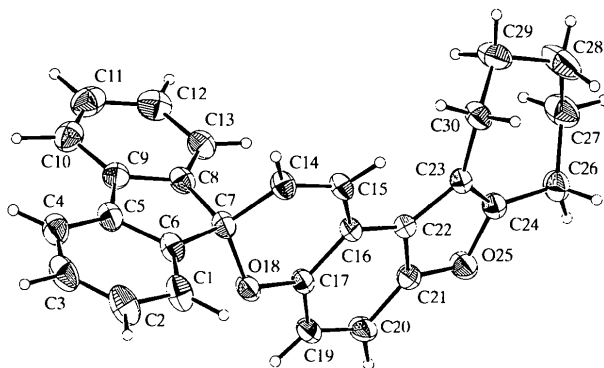


Fig. 2. ORTEP drawing (Johnson, 1976) of compound (V) with displacement ellipsoids of 50% probability and H atoms drawn as small circles.

Experimental

Compounds (IV) and (V) were synthesized *via* the condensation of 1,1-diphenylpropyn-1-ol with heterocyclic phenols in toluene in the presence of a catalytic amount of *p*-toluenesulfonic acid (Pozzo, 1994). The mixture was heated under reflux for 2.5 h. The compounds were purified by crystallization from toluene and hexane–benzene (1:1), respectively. For (IV): m.p. 410 K; calculated C 90.34, H 4.85%; analysis found C 90.39, H 4.78%; ¹H NMR (solvent CDCl₃, δ in p.p.m. *versus* TMS): 5.56 (1H), 6.82 (1H), 7.21 (1H), 7.25 (2H), 7.36 (1H), 7.37 (1H), 7.41 (3H), 7.53 (2H), 7.67 (2H), 7.73 (1H), 7.95 (1H). For (V): calculated C 86.13, H 5.68%; analysis found C 86.38, H 5.62%; ¹H NMR (solvent CDCl₃, δ in p.p.m. *versus* TMS): 1.80 (3H), 2.88 (2H), 5.57 (1H), 6.57 (1H), 7.02 (1H), 7.15 (2H), 7.27 (1H), 7.31 (2H), 7.47 (2H), 7.57 (2H).

Compound (IV)

Crystal data

C₂₅H₁₆O
M_r = 332.38
 Monoclinic
*P*2₁/*n*
a = 14.768 (3) Å
b = 7.057 (1) Å
c = 17.999 (4) Å
 β = 112.81 (3)°
V = 1729.1 (6) Å³
Z = 4
D_x = 1.277 Mg m⁻³
D_m not measured

Cu *K*α radiation
 λ = 1.54178 Å
 Cell parameters from 25 reflections
 θ = 10–20°
 μ = 0.593 mm⁻¹
T = 293 (2) K
 Needle
 0.28 × 0.14 × 0.12 mm
 Colourless

Data collection

KM-4 diffractometer
 θ scans
 Absorption correction: none
 3618 measured reflections
 3520 independent reflections
 2189 reflections with
 $I > 2\sigma(I)$
R_{int} = 0.020

Refinement

Refinement on *F*²
R(*F*) = 0.038
wR(*F*²) = 0.105
S = 1.122
 3520 reflections
 299 parameters
 All H atoms refined
 $w = 1/[\sigma^2(F_o^2) + (0.0460P)^2 + 0.5461P]$
 where $P = (F_o^2 + 2F_c^2)/3$

θ_{\max} = 80.3°
 $h = -18 \rightarrow 17$
 $k = 0 \rightarrow 8$
 $l = 0 \rightarrow 21$
 3 standard reflections
 frequency: 60 min
 intensity decay: none

$(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.160 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.209 \text{ e } \text{Å}^{-3}$
 Extinction correction: none
 Scattering factors from
*International Tables for
 Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °) for (IV)

C6—C7	1.522 (3)	C14—C15	1.316 (3)
C7—O18	1.455 (2)	C15—C16	1.448 (3)
C7—C14	1.506 (3)	C16—C17	1.373 (3)
C7—C8	1.528 (3)	C17—O18	1.373 (2)
O18—C7—C14	111.7 (2)	C15—C14—C7	121.2 (2)
O18—C7—C6	106.5 (1)	C14—C15—C16	120.8 (2)
C14—C7—C6	114.1 (2)	C17—C16—C15	118.1 (2)
O18—C7—C8	111.2 (2)	C16—C17—O18	121.9 (2)
C14—C7—C8	111.4 (2)	C17—O18—C7	119.4 (1)
C6—C7—C8	101.3 (2)		
C8—C7—C14—C15	-100.7 (2)	C16—C17—O18—C7	17.9 (2)
C7—C14—C15—C16	-5.8 (3)	C8—C7—O18—C17	95.2 (2)
C14—C15—C16—C22	177.2 (2)	O18—C17—C19—C20	-175.2 (2)
C15—C16—C17—O18	2.8 (3)		

Compound (V)

Crystal data

C₂₈H₂₂O₂
M_r = 390.46
 Triclinic
P $\bar{1}$
a = 9.876 (3) Å
b = 11.156 (4) Å
c = 11.281 (4) Å
 α = 64.72 (2)°
 β = 65.51 (2)°
 γ = 80.78 (2)°
V = 1022.5 (6) Å³
Z = 2
D_x = 1.267 Mg m⁻³
D_m not measured

Data collection

KM-4 diffractometer
 θ scans
 Absorption correction: none
 5307 measured reflections
 5307 independent reflections
 3601 reflections with
 $I > 2\sigma(I)$

Mo *K*α radiation
 λ = 0.71073 Å
 Cell parameters from 25 reflections
 θ = 10–20°
 μ = 0.078 mm⁻¹
T = 293 (2) K
 Needle
 0.42 × 0.16 × 0.11 mm
 Colourless

θ_{\max} = 30°
 $h = -12 \rightarrow 12$
 $k = -14 \rightarrow 14$
 $l = 0 \rightarrow 13$
 3 standard reflections
 frequency: 60 min
 intensity decay: none

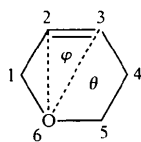
Refinement

Refinement on F^2
 $R(F) = 0.044$
 $wR(F^2) = 0.090$
 $S = 1.227$
 5307 reflections
 337 parameters
 H-atom positions refined
 with $U_{iso}(H) = 1.2U_{eq}(C)$

$w = 1/[\sigma^2(F_o^2) + (0.0230P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 0.158 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{min} = -0.211 \text{ e } \text{Å}^{-3}$
 Extinction correction: none
 Scattering factors from
*International Tables for
 Crystallography* (Vol. C)

Table 2. Selected geometric parameters (Å , $^\circ$) for (V)

C6—C7	1.513 (2)	C14—C15	1.321 (2)
C7—O18	1.455 (2)	C15—C16	1.470 (2)
C7—C14	1.519 (2)	C16—C17	1.406 (2)
C7—C8	1.524 (2)	C17—O18	1.383 (2)
O18—C7—C6	106.3 (1)	C15—C14—C7	120.4 (1)
O18—C7—C14	109.4 (1)	C14—C15—C16	120.0 (1)
C6—C7—C14	115.5 (1)	C17—C16—C15	116.7 (1)
O18—C7—C8	112.8 (1)	O18—C17—C16	120.6 (1)
C6—C7—C8	101.7 (1)	C17—O18—C7	116.6 (1)
C14—C7—C8	111.1 (1)		
C8—C7—C14—C15	-91.7 (2)	C16—C17—O18—C7	29.6 (2)
C7—C14—C15—C16	-3.3 (2)	C8—C7—O18—C17	78.3 (1)
C14—C15—C16—C22	166.7 (1)	O18—C17—C19—C20	-178.6 (2)
C15—C16—C17—O18	3.1 (2)		

Table 3. Folding angles ($^\circ$) of the pyran ring in compounds (I) to (V)

φ is the dihedral angle (6,2,3)/(2,1,6) and θ is the dihedral angle (6,2,3)/(3,4,6).

	(I)	(II)	(III)	(IV)	(V)
φ	23.1 (2)	22.9 (2)	27.0 (3)	20.7 (2)	28.5 (1)
θ	12.0 (2)	10.0 (2)	15.3 (3)	7.4 (2)	14.6 (1)

Table 4. Photochromic parameters and strain energies of the pyran ring in compounds (I) to (V)

	λ_1 (nm)	A_1	λ_2 (nm)	A_2	λ_3 (nm)	A_3	E_s (kcal mol ⁻¹)†
(I)	436	0.77					9.9
(II)	432	0.84					10.2
(III)	427	1.43	452	1.39	549	0.48	13.1
(IV)	409	0.70	436	0.93	495	1.32	9.8
(V)	447	1.26	534	0.39			12.1

† 1 kcal mol⁻¹ = 4.184 kJ mol⁻¹.

For both compounds, program(s) used to solve structures: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1220). Services for accessing these data are described at the back of the journal.

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A Water Adduct of Tris(pentafluorophenyl)borane: (C₆F₅)₃B(OH₂)–Dioxane–CH₂Cl₂ (1/1/1)

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Abstract

The dichloromethane solvate of the 1:1 aquatris(pentafluorophenyl)borane–dioxane adduct, [B(C₆F₅)₃(H₂O)]·C₄H₈O₂·CH₂Cl₂, is a water complex of tris(pentafluorophenyl)borane, which was crystallized from dioxane–methylene chloride solution. The water molecule was carried in either through improperly dried solvent or during the process of crystallization. The structure contains one dioxane and one CH₂Cl₂ molecule per formula unit. Two dioxane molecules form hydrogen bridges to the water molecule and also bridge between two different adduct moieties, so that an infinite chain of borane–water adducts and dioxane molecules is created.