Effect of the type of linkage between phenyl groups on the structure and photochemical properties of 2,2-diaryl-substituted pyridoannelated [2*H*]-chromenes

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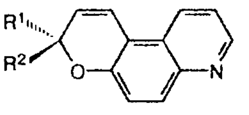
Three 2,2-diaryl-substituted pyridoannelated [2*H*]-chromenes have been studied by X-ray diffraction analysis. Bonding of the benzene rings through bridges of different nature and with different length affects substantially the orientation of the benzene rings, steric interactions at the C center, the conformation of the molecule, and the C—O bond length. A correlation between the photocolorability of chromenes under study and the orientation of the benzene rings with respect to the C—O bond, which provides different prerequisites to stabilization of the C(1)-centered cation formed upon cleavage of the C—O bond, was established. The effect of the orientation of the benzene rings on the dark reaction of ring closure was found.

Key words: chromenes, X-ray diffraction analysis, photochemistry in solutions, structure—property relationship.

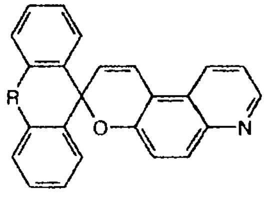
Previously,[1—3] we have discussed the structure and photochemical properties of R^1,R^2-chromenes, where $R^1 = R^2$ = Me; R^1 = Me and R^2 = Ph; or $R^1 = R^2$ = Ph, in detail.



It was demonstrated that an elongation of the C—O bond, which is cleaved upon photoexcitation, is dictated by steric interactions between the adjacent atoms in the C unit. The C—O bond lengths in Ph,Ph- and Ph,Me-chromenes are virtually equal (1.458(2) and 1.454(2) Å, respectively), and this bond in Me,Me-chromene is somewhat longer (1.468(3) Å). The R^1 and R^2 substituents have virtually no effect on the geometry of the pyran ring and on the energy of steric strains in this ring. The photocolorability of these compounds, which is characterized by the intensity of the absorption band (A_0) at λ_{max} of the open form that formed and which was measured under conditions of flash photolysis immediately after photoimpulse, appeared to be different. The photocolorability of these compounds increases in the series Me,Me-, Me,Ph-, and Ph,Ph-chromenes, which may be associated with an increase in the size of the π-system of the open form and hence with an increase in the extinction coefficient (ε_0) of their absorption.

We have synthesized Ph,Ph-chromenes,[4] whose naphthopyran fragments have different structures, and studied their structures and photochemical properties. It was demonstrated that the photocolorability of these compounds correlates with the energy of steric strain of the pyran ring.

With the aim of studying the effect of the mutual arrangement of the benzene rings on the structure and photochemical properties of chromenes, we studied chromenes **2**—**4** in which the benzene rings are bonded through different bridges.



1: R, the bridge is absent (3,3-diphenyl-3*H*-pyrano[3,2-*f*]quinoline);

2: R, the single bond between the benzene rings (spiro[3*H*-pyrano[3,2-*f*]quinoline-3,9′-9*H*-fluorene]);

3: R = CH=CH (spiro[11*H*-dibenzo[*a*,*e*]cycloheptene-11,3′-3*H*-pyrano[3,2-*f*]quinoline]);

4: R = CH_2—CH_2 (spiro[5,6-dihydro-11*H*-dibenzo[*a*,*e*]cycloheptene-11,3′-3*H*-pyrano[3,2-*f*]quinoline])

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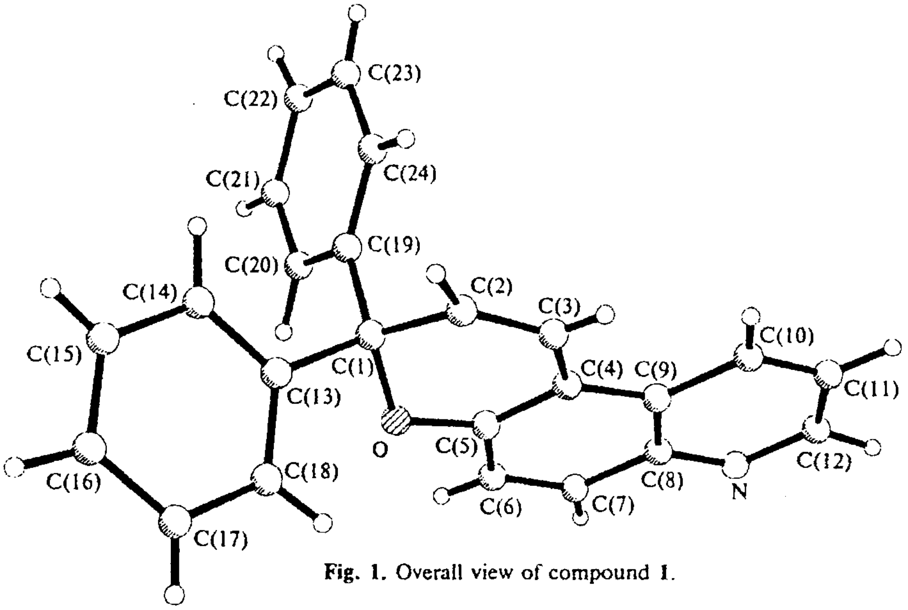


Fig. 1. Overall view of compound **1**.

Table 1. Principal structural characteristics and photochemical data on compounds **1**—**4**

Compound	C(1)—O/Å	φ	θ	Dihedral angle/deg			γ	E_s	A_0	k_Δ/s^{-1}
		deg		C(R')C(1)C(R')	OC(1)C(R')	OC(1)C(R')$^\alpha$C(R')$^\beta$	/deg	/kcal mol^{-1}		
1	1.458(3)	23.0	12.3	112.9	108.4, 104.1	−38.5, 32.6	89	10.3	0.77	0.13
2	1.457(2)	20.4	6.7	102.0	112.2, 107.1	−65.6, 59.8	3	10.0	0.65	0.38 0.11 0.06
3	1.450(2)	30.7	11.8	109.1	111.1, 106.0	−5.3, 3.8	57.1	10.7	0.54	$4 \cdot 10^{-4}$
4	1.482(4)	7.9	4.6	119.5	103.9, 104.8	−44.6, 20.0	37.3	10.5	0.50	$\sim 10^{-4}$

Note: φ is the folding angle of the pyran ring along the O...C(2) line; θ is the folding angle of the pyran ring along the O...C(3) line; the dihedral angle: R' = Ph for **1** and R' = C_6H_4 for **2**—**4**; γ is the dihedral angle between the Ph substituents or the C_6H_4 fragments; E_s is the strain energy of the pyran ring (kcal mol^{-1}); A_0 is the photocolorability under conditions of flash photolysis;[5] k_Δ is the constant of dark decoloration (25 °C, toluene as the solvent).

Results and Discussion

In chromene **1**[4] (Fig. 1), the phenyl rings are perpendicular to each other. The dihedral angle between their planes is 89°. The pyran ring is nonplanar. The φ and θ folding angles are 23.0 and 12.3°, respectively (Table 1). The OC(1)C(19) and OC(1)C(13) bond angles in the OC(1)C(Ph) fragment are 108.4 and 104.1°, respectively. The C(1)—O bond length is 1.458(2) Å. The OC(1)C(19)C(20) and OC(1)C(13)C(18) torsion angles are −38.5° and 32.6°, respectively. The O...C(20) and O...C(18) distances are 2.80 and 2.68 Å, respectively.

In the molecule of the fluorenochromene **2** (Fig. 2), the C_6H_4 fragments are linked through the C(18)—C(19) bond (1.473(2) Å) resulting in the five-membered strained ring. The formation of this bond leads to the rigid mutual arrangement of the C_6H_4 fragments. The dihedral angle between the C_6H_4 fragments in molecule **2** is 3°. The fluorene fragment is planar. The C(18)—C(19) bond length is indicative of a pronounced π-conjugation between the C_6H_4 fragments. The formation of the five-membered ring leads to a substantial decrease in the $C(C_6H_4)C(1)C(C_6H_4)$ bond angle (102.0(1)°) and to a noticeable decrease in the remaining intraring angles (Table 1).

The formation of the planar fluorene ring results in a change in the orientation of the C_6H_4 fragments with respect to the oxygen atom. The OC(1)C(13)C(14) and OC(1)C(24)C(23) torsion angles (−65.6 and 59.8°, respectively) are larger than the analogous values in molecule **1**. This leads to the increase in the O...C(14) and O...C(23) distances to 3.225 and 3.069 Å, respectively. The OC(1)C(13) and OC(1)C(24) angles in the $OC(1)C(C_6H_4)$ fragments are −112.2° and 107.1°, respectively.

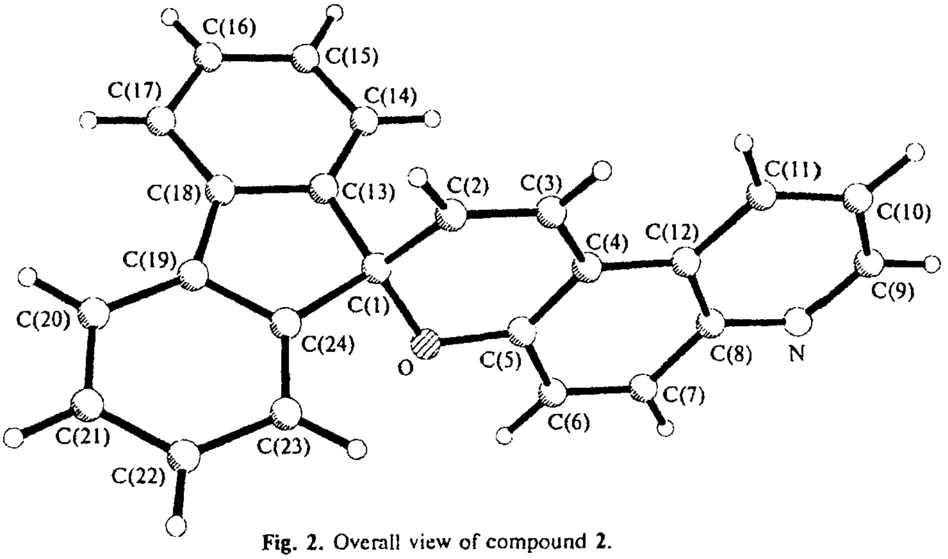
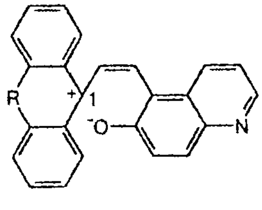


Fig. 2. Overall view of compound **2**.

The pyran ring in molecule **2** is insignificantly flattened compared to that in **1**. The φ and θ angles are 20.4° and 6.7°, respectively (Table 1). The strain energies of the pyran rings in molecules **1** and **2** are similar (−10.3 and 10.0 kcal mol^{-1}, respectively). In accordance with the structural characteristics of chromenes **1** and **2**, the C(1)—O bond length (1.457(2) Å) in molecule **2** is identical to the analogous value in molecule **1** (1.458(2) Å). However, unlike the labile structure of the Ph,Ph-C^+ cation in compound **1**, an increase in the $OC(1)C(C_6H_4)^{\alpha}C(C_6H_4)^{\beta}$ torsion angles and the rigid structure of the fluorene fragment in chromene **2** are less favorable for stabilization and flattening of the pyramidal structure of the C(1)-centered cation that formed upon cleavage of the C(1)—O bond.



Actually, in the pyramidal cation formed upon cleavage of the C(1)—O bond, the orientation of the nonbonding orbital is identical to that of the C(1)—O bond. The interaction between this orbital and the π-system of the Ph rings is favored by their parallel arrangement. This condition is fulfilled when the $OC(1)C(Ph)^{\alpha}C(Ph)^{\beta}$ torsion angles are close to 90°. In chromene **2**, these angles are −65.6 and 59.8°. Therefore, from the viewpoint of efficient orbital interactions in the cation that formed, the structure of **2** is less favorable than the structure of **1** in which the rotation of the Ph rings can provide any orientation. These peculiarities of the structure of **2** may be responsible for the decrease in the photocolorability of **2** (A_0 = 0.65) compared to that of **1** (A_0 = 0.77) even taking into account that the open form of compound **2** should be more planar than that of compound **1** and that the value ε_2 is larger than ε_1. The bathochromic shift of the open form of **2** (λ_{max} = 460 nm) compared to that of the open form of **1** (λ_{max} = 440 nm) confirms the fact that the π-system of **2** is more extended than that in the open form of compound **1**.

The presence of the vinyl bridge in chromene **3** results in formation of the seven-membered ring (Fig. 3). The $C(C_6H_4)C(1)C(C_6H_4)$ bond angle (109.1(1)°) is similar to the value typical of the C_{sp^3} atom. The $OC(1)C(C_6H_4)$ angles (111.1(1)° and 106.0(1)°) deviate insignificantly from the tetrahedral value. The $C(1)—C(C_6H_4)$ bond lengths (C(1)—C(13), 1.527(2) Å; and C(1)—C(21), 1.536(3) Å) are elongated compared to the analogous values in molecules **1** (1.504(4) and 1.528(4) Å, respectively) and **2** (1.516(2) and 1.522(2) Å, respectively). The dihedral angle γ between the C_6H_4 fragments is 57.1°. The benzene rings are rotated with respect to the plane of the vinyl bond about the C(18)—C(19) and C(20)—C(26) bonds by 28.9° and 29.9°, respectively. When this arrangement of the C_6H_4 fragments occurs, the oxygen atom lies simultaneously in the planes of the two C_6H_4 fragments. The OC(1)C(13)C(14) and OC(1)C(21)C(22) torsion angles are −5.3° and 3.8°, respectively. The O...H(14) and O...H(22) distances are 2.25 and 2.37 Å, respectively. This structure is favorable for the additional O...H(14) and O...H(22) intramolecular interactions although the OH(14)C(14) and OH(22)C(22) angles, which are determined by the geometry of the five-membered ring, are 103° and 102°, respectively. The H(14)OC(1) and H(22)OC(1) angles are 90° and 87°, respectively. The involvement of the O atom in additional interactions and the absence of additional steric interactions at the C(1) unit hinder elongation of the C(1)—O bond. In molecule **3**, this bond (1.450(2) Å) is the shortest one in the series of chromenes under study.

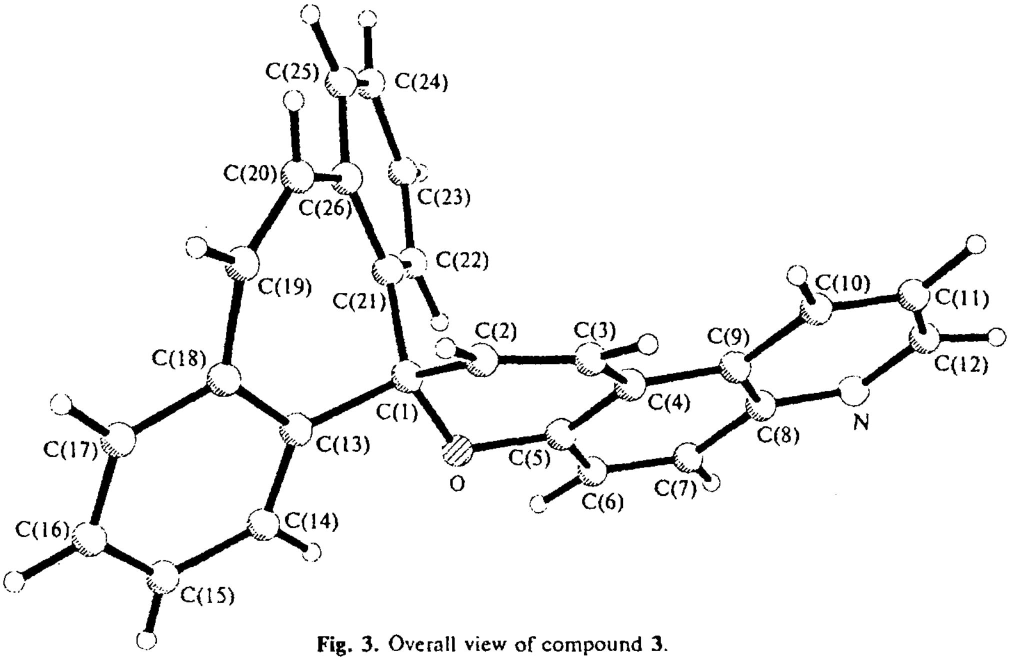


Fig. 3. Overall view of compound **3**.

The pyran ring in molecule **3** is the most distorted one. The φ and θ angles are 30.7° and 11.8°, respectively although the strain energy of the pyran ring (10.7 kcal mol^{-1}) is similar to those in molecules **1** and **2**.

The photocolorability of chromene **3** (A_0 = 0.54) is lower than those of **1** and **2** (0.77 and 0.65, respectively) in spite of the fact that the π-system of the open form is extended due to the presence of the vinyl bridge in the molecule. From the viewpoint of the structural characteristics of chromene **3**, this may be associated with substantially different orientations of the C_6H_4 fragments with respect to the C(1)—O bond rather than with the lesser elongation of the C(1)—O bond. This bond is virtually coplanar with the planes of the two C_6H_4 fragments, which results not only in additional O...H_{Ph} interactions in compound **3** but also in the absence of the structural possibility of stabilization of the C(1)-centered cation, which is formed upon cleavage of the C(1)—O bond, through interaction between the π-system of the C_6H_4 fragments and the nonbonding orbital of the C(1)-centered cation that coincides with the direction of the C(1)—O bond.

The replacement of the vinyl bridge in molecule **3** by the aliphatic bridge (—CH_2—CH_2—) in **4** (Fig. 4) leads to the arrangement of the C_6H_4 fragments such that they are approximately in a single plane (the dihedral angle between these fragments decreases to 37.3°) and results in a substantial increase in the $C(C_6H_4)C(1)C(C_6H_4)$ bond angle (119.5(4)°) with a simultaneous decrease in the $OC(1)C(C_6H_4)$ angles (OC(1)C(13), 103.9(3)°; and OC(1)C(18), 104.8(3)°). The increase in the $C(C_6H_4)C(1)C(C_6H_4)$ bond angle simultaneously with the coplanar arrangement of the C_6H_4 fragments leads to substantial flattening of the pyran ring (φ = 7.9° and θ = 4.6°) but has virtually no effect on the strain energy of this ring (E = 10.5 kcal mol^{-1}). The steric strain in the spiro center leads to the maximum elongation of the C(1)—O bond (1.482(4) Å) and of the C(1)—C(Ph) bonds (C(1)—C(13), 1.537(5) Å; and C(1)—C(18), 1.547(6) Å) compared to the corresponding values in chromenes **1**—**3**. Therefore, the structure of **4** is the most favorable one for the cleavage of the C(1)—O bond. However, the photocolorability of **4** (A_0 = 0.50) is virtually identical to that of **3**. Apparently, as in the case of **3**, this is due to the fact that the orientation of the C_6H_4 fragments with respect to the C(1)—O bond is unfavorable for stabilization and flattening of the C(1)-centered cation formed. Although the $OC(1)C(C_6H_4)^{\alpha}C(C_6H_4)^{\beta}$ torsion angles are larger (OC(1)C(18)C(19), −44.6°; and (OC(1)C(13)C(23), 20.0°) than those in **3**, the mutual orientation of the π-systems of the C_6H_4 fragments and the nonbonding orbital of the C(1)-centered cation remains unfavorable for their efficient interaction. Therefore, the increase in the photocolorability in the series **1** > **2** > **3** ≈ **4** correlates well with the orientation of the benzene fragments with respect to the C(1)—O bond, which determines the efficiency of stabilization and flattening of the C(1)-centered cation, rather than with the C(1)—O bond length in the initial molecule.

The open forms of chromenes possess different stability characterized by the constant of dark decoloration k_Δ (Table 1). Unfortunately, data on the structures of the open forms are unavailable. However, it is evident that the open form of **2** should have the most planar structure. The open form of **1** should be less planar due to the steric repulsion between the adjacent hydrogen atoms of the Ph rings, which causes the rotation of the

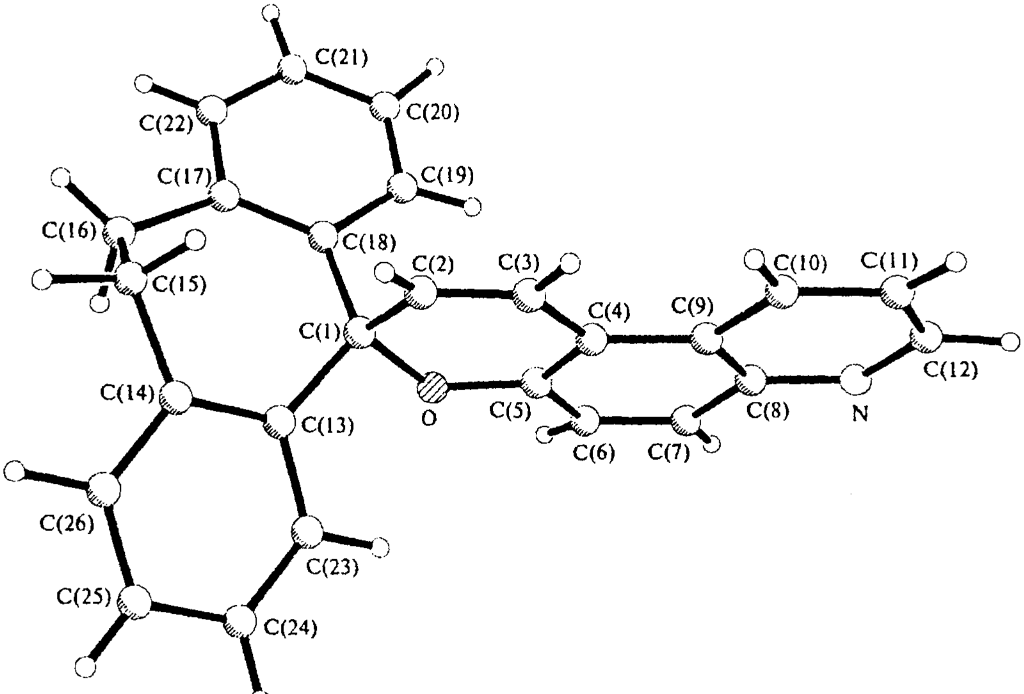
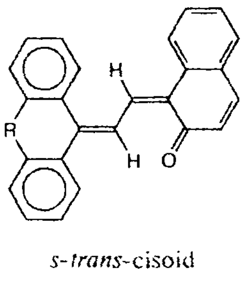


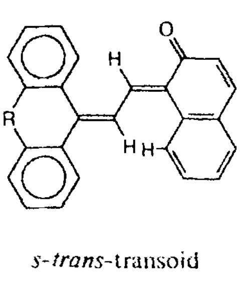
Fig. 4. Overall view of compound **4**.

Ph rings about the C(Ph)—C(1) bonds. According to this, the value λ_{max} of the open form of **1** (440 nm) is hypsochromically shifted relative to λ_{max} of the open form of **2** (460 nm). The orientations of the C_6H_4 fragments in the open forms of **3** and **4** are dictated by the rigid geometry of the seven-membered rings and are similar to their orientations in the closed forms of chromenes. Therefore, the open forms of **3** and **4** should be substantially less planar than the open forms of **1** and **2**. In the open form of **4**, the C_6H_4 fragments are coplanar with the molecule as a whole to a greater extent than in the case of the open form of **3**. However, in molecule **3** an additional π-bond of the vinyl group exists, which is rotated with respect to the planes of the C_6H_4 fragments by only 29.9° and 28.9°. Consequently, the value λ_{max} of the open form of **4** (424 nm) undergoes a larger hypsochromic shift than λ_{max} of the open form of **3** (440 nm).

Apparently, the *s-trans*-cisoid isomer is the most stable planar isomer of the open forms of chromenes under study.



s-trans-cisoid



s-trans-transoid

The formation of stable planar *s-trans*-transoid and *s-cis* isomers is impossible due to steric reasons. Modeling of the closure of the open forms of **1**—**4** in the ground electronic state demonstrated that this process is substantially hindered for the open forms of **3** and **4** compared to the open forms of **1** and **2**. This is associated with the fact that the orientations of the C_6H_4 fragments in chromenes **3** and **4** are such that when the nucleophilic O atom and the sp^2-hybridized C(1) atom approach each other to a C(1)...O distance of ~2.1 Å, short C(Ph)...O contacts (~2.3—2.8 Å) appear.

The study of the reaction of dark decoloration of the open forms of **1**—**4** demonstrated that under conditions of flash photolysis, the closure of the rings in the open forms of **3** and **4** is not observed, while under conditions of continuous irradiation, the constant of dark decoloration of the open forms of **3** and **4** is $\sim 10^{-4}$ s^{-1} (Table 1). The high stability of the open forms of **3** and **4** may be associated with the above-described peculiarities of their structures.

The ring in the open form of **1** is closed rather readily. Under conditions of flash photolysis, the constant of dark decoloration k_Δ = 0.13 s^{-1}. The relatively free rotation of the Ph rings about the C(1)—C(Ph) bonds does not prevent cyclization.

The reaction of decoloration of compound **2** is of interest. Under conditions of flash photolysis, three reactions (with constants of dark decoloration k_Δ = 0.38 (26%), 0.11 (35%), and 0.06 (39%)) are observed (Table 1). These peculiarities of decoloration of the open form of **2** can be explained only assuming that different associates of planar molecules of the open form of **2** are

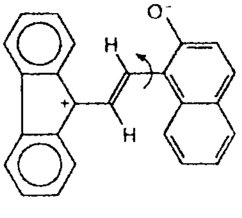
Table 2. Coordinates of nonhydrogen (×10^4) and hydrogen (×10^3) atoms in molecule **2**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
O	500(3)	695(4)	2048(2)	C(13)	−481(4)	3146(5)	2028(3)	H(6)	283(1)	−47(1)	216(3)
N	1848(4)	−2622(6)	4796(3)	C(14)	−4(5)	3616(7)	2773(3)	H(7)	197(1)	−32(1)	370(3)
C(1)	−653(4)	1537(5)	1783(3)	C(15)	233(6)	4980(7)	2914(4)	H(9)	253(2)	−371(2)	647(4)
C(2)	−1704(5)	869(6)	2050(3)	C(16)	−178(6)	5947(7)	2249(4)	H(10)	−39(1)	−202(1)	523(4)
C(3)	−1498(4)	50(5)	2730(3)	C(17)	570(5)	5470(6)	1491(4)	H(11)	−222(1)	−187(2)	388(3)
C(4)	−249(4)	−384(5)	3070(2)	C(18)	639(4)	3922(5)	1336(3)	H(14)	−44(1)	298(1)	335(4)
C(5)	768(4)	−135(5)	2726(2)	C(19)	1007(4)	3100(5)	642(3)	H(15)	178(2)	584(2)	393(4)
C(6)	2047(4)	−692(5)	3052(3)	C(20)	1429(5)	3461(7)	−269(3)	H(16)	−46(2)	737(1)	263(3)
C(7)	2338(4)	−1423(5)	3666(3)	C(21)	−1844(6)	2335(8)	−849(3)	H(17)	−91(2)	540(1)	137(3)
C(8)	1438(4)	−1732(5)	4112(3)	C(22)	−1639(5)	1023(8)	−528(3)	H(20)	−194(2)	625(2)	−34(3)
C(9)	1081(6)	−2672(8)	5239(4)	C(23)	−1412(5)	474(6)	320(3)	H(21)	−191(2)	402(1)	−186(3)
C(10)	−232(6)	−2356(8)	4981(4)	C(24)	−1033(4)	1685(6)	858(3)	H(22)	−154(1)	43(1)	−61(4)
C(11)	−624(5)	−1481(6)	4275(3)	H(2)	−160(1)	107(1)	177(3)	H(23)	−193(1)	−86(1)	63(3)
C(12)	198(4)	−1219(5)	3815(3)	H(3)	−220(1)	65(1)	291(3)				

Table 3. Coordinates of nonhydrogen (×10^4) and hydrogen (×10^3) atoms in molecule **3**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
O	8376(7)	1425(2)	3684(4)	C(14)	7998(1)	−0018(2)	2807(8)	H(6)	786(1)	042(3)	451(1)
N	8548(1)	4660(3)	5537(7)	C(15)	7716(1)	−0671(3)	2357(9)	H(7)	789(1)	197(3)	533(1)
C(1)	8938(1)	1781(2)	3295(6)	C(16)	8061(1)	−0298(3)	1899(8)	H(10)	942(1)	676(3)	436(1)
C(2)	9016(1)	3661(2)	3245(7)	C(17)	8708(1)	0652(3)	1893(1)	H(11)	954(1)	805(2)	521(1)
C(3)	8961(1)	4614(2)	3655(7)	C(18)	9033(1)	1252(2)	2346(1)	H(12)	888(2)	669(2)	592(1)
C(4)	8750(1)	3879(2)	4143(7)	C(19)	9772(1)	2071(2)	2304(1)	H(14)	774(1)	−024(2)	314(1)
C(5)	8426(1)	2320(2)	4130(6)	C(20)	10332(1)	2090(2)	2647(1)	H(15)	727(1)	−130(3)	237(1)
C(6)	8099(1)	1579(3)	4562(8)	C(21)	9697(1)	0977(2)	3445(1)	H(16)	783(1)	−068(3)	157(1)
C(7)	8128(1)	2404(3)	5020(8)	C(22)	9763(1)	−0014(2)	3879(1)	H(17)	897(1)	086(2)	156(1)
C(8)	8498(1)	3953(3)	5063(7)	C(23)	10461(1)	−0635(3)	4031(1)	H(19)	988(1)	250(2)	196(1)
C(9)	8809(1)	4705(2)	4622(7)	C(24)	11106(1)	−0265(3)	3754(1)	H(20)	1080(1)	258(2)	254(1)
C(10)	9176(2)	6251(3)	4684(9)	C(25)	11048(1)	0683(3)	3318(1)	H(22)	931(1)	−019(2)	409(1)
C(11)	9225(2)	6938(4)	5157(1)	C(26)	10345(1)	1275(2)	3145(1)	H(23)	1049(1)	−129(3)	432(1)
C(12)	8903(2)	6099(4)	5570(1)	H(2)	911(1)	414(2)	289(1)	H(24)	1161(1)	−066(3)	388(1)
C(13)	8647(1)	0966(2)	2807(7)	H(3)	902(1)	585(3)	363(1)	H(25)	1151(1)	092(2)	310(1)

formed as in the case with the open forms of spiropyrans.[6] Alternatively, this may be associated with an increase in the contribution of the zwitterionic form due to formation of the strained five-membered ring resulting in a substantial decrease in the bond angle at the C(1) atom. When the open form has the zwitterionic structure, the formation of the nonplanar *s-trans*-transoid isomer is possible.



s-trans-transoid

Therefore, the linkage between the benzene rings in molecules of R,R-chromenes (R = C_6H_4) through bridges of different nature and with different bond lengths affects substantially the orientation of the C_6H_4 fragments, steric interactions in the spiro unit, the conformation of the molecule, and the C(1)—O bond length. In the chromenes under study, their photocolorability is substantially affected by the orientation of the C_6H_4 fragments with respect to the C(1)—O bond, which provides different prerequisites to stabilization of the C(1)-centered cation that formed upon cleavage of the C(1)—O bond, rather than by the C(1)—O bond length in the initial state. When the C_6H_4 fragments are linked through a bridge formed by two carbon atoms to form the seven-membered ring, the C_6H_4 fragments are pushed apart and deviate from a single plane so that the dark reaction of ring closure is hindered and the lifetime of the open forms is increased.

Experimental

Crystals of **1**,[4] **2**,[5] **3**,[5] and **4**[5] were prepared by recrystallization from heptane. Photochemical studies were carried out by flash photolysis.[7] The intensity of absorption of the open form A_0 (λ_{max}) immediately after photoirradiation (photo-

Table 4. Coordinates of nonhydrogen ($\times 10^4$) and hydrogen ($\times 10^3$) atoms in molecule **4**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
O	3128(2)	−1913(3)	−0487(3)	C(15)	4854(4)	−4318(5)	2409(5)	H(10)	143(3)	048(4)	188(5)
N	431(3)	1564(4)	−1423(5)	C(16)	4340(4)	−5173(5)	1367(6)	H(11)	026(5)	198(6)	136(7)
C(1)	3496(3)	−2617(4)	0661(4)	C(17)	3302(4)	−4831(4)	0594(4)	H(12)	−033(3)	262(4)	−074(4)
C(2)	3249(3)	−2056(4)	1726(4)	C(18)	2936(3)	−3754(5)	0301(4)	H(15)	547(3)	−477(4)	304(5)
C(3)	2668(3)	−1177(4)	1598(4)	C(19)	1923(4)	−3606(6)	−0364(5)	H(151)	439(3)	−392(4)	281(4)
C(4)	2212(3)	−0642(4)	0376(4)	C(20)	1311(5)	−4519(6)	−0752(6)	H(16)	434(4)	−600(5)	162(5)
C(5)	2473(3)	−1050(4)	−0618(4)	C(21)	1666(6)	−5588(7)	−0474(6)	H(161)	480(5)	−506(6)	073(7)
C(6)	2080(3)	−0604(5)	−1836(4)	C(22)	2649(5)	−5750(6)	0188(6)	H(19)	159(4)	−284(4)	−055(4)
C(7)	1419(3)	0261(4)	−2073(5)	C(23)	5051(3)	−1740(4)	0511(5)	H(20)	057(7)	−443(8)	−124(8)
C(8)	1113(3)	0721(4)	−1106(4)	C(24)	6062(4)	−1610(5)	0864(6)	H(21)	125(4)	−632(4)	−069(4)
C(9)	1513(3)	0264(4)	0124(4)	C(25)	6662(4)	−2336(5)	1758(6)	H(22)	295(4)	−648(5)	042(6)
C(10)	1173(4)	0755(4)	1056(5)	C(26)	6250(4)	−3166(5)	2252(6)	H(23)	461(3)	−114(3)	000(4)
C(11)	0489(4)	1603(5)	0736(6)	H(2)	356(3)	−230(4)	248(4)	H(24)	635(4)	−092(4)	051(5)
C(12)	0130(4)	1957(5)	−0524(6)	H(3)	254(3)	−094(4)	238(5)	H(25)	736(5)	−229(6)	195(6)
C(13)	4620(3)	−2595(4)	0992(4)	H(6)	226(4)	−092(5)	−242(6)	H(26)	670(4)	−376(4)	282(5)
C(14)	5236(3)	−3332(4)	1899(4)	H(7)	112(4)	057(4)	−286(5)				

colorability) was taken as the characteristic of the photochromic properties along with the thermal stability (the constant of dark decoloration k_Δ/s^{-1}) and the position of the maximum of the long-wavelength absorption ($\lambda_{\max}$).

The strain energies of the pyran rings were calculated by molecular mechanics (MM2).[8]

Colorless crystals of **2** belong to the monoclinic system. The principal crystallographic data are as follows: $C_{24}H_{15}NO$, M = 333.36, *a* = 10.800(2), *b* = 9.390(2), *c* = 17.363(3) Å, β = 107.90(3)°, *Z* = 4, d_{calc} = 1.322(2) g cm^{-3}, *V* = 1675.6(6) Å^3, space group $P2_1/n$. The experimental data set was collected from the crystal of **2** of dimensions 0.20×0.10×0.20 mm^3 on an automated four-circle KM-4 diffractometer (MoKα radiation). The number of reflections with $I > 2\sigma(I)$ was 2203. The final value of the *R* factor was 0.038.

Colorless crystals of **3** belong to the monoclinic system. The principal crystallographic data are as follows: $C_{26}H_{19}NO$, M = 361.42, *a* = 14.446(3), *b* = 11.796(2), *c* = 11.281(2) Å, β = 109.68(3)°, *Z* = 4, d_{calc} = 1.326(2) g cm^{-3}, *V* = 1810.1(6) Å^3, space group $P2_1/c$. The experimental data set from the crystal of **3** of dimensions 0.15×0.15×0.20 mm^3 was collected as described above. The number of reflections with $I > 2\sigma(I)$ was 1650. The final value of the *R* factor was 0.080.

Yellow crystals of **4** belong to the orthorhombic system. The principal crystallographic data are as follows: $C_{26}H_{17}NO$, M = 359.41, *a* = 17.618(4), *b* = 8.019(2), *c* = 26.240(5) Å, *Z* = 8, d_{calc} = 1.288(2) g cm^{-3}, *V* = 3707.2(14) Å^3, space group *Pbca*. The experimental data set from the crystal of **3** of dimensions 0.20×0.15×0.10 mm^3 was collected as described above. The number of reflections with $I > 2\sigma(I)$ was 2304. The final value of the *R* factor was 0.040.

The structures were solved by direct methods using the SHELX-86 program package[9] and refined anisotropically by the full-matrix least-squares method (SHELX-93).[10] The positions of the hydrogen atoms were located from the difference Fourier synthesis, and only their positional parameters were refined. The atomic coordinates are given in Tables 2—4, respectively.

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References

1. S. Aldoshin, I. Chuev, O. Filipenko, V. Lokshin, J.-L. Pozzo, G. Pepe, and A. Samat, *Acta Crystallogr.*, 1996, **C52**, 1537.
2. S. Aldoshin, I. Chuev, A. Utenyshev, V. Lokshin, A. Samat, G. Pepe, and R. Guglielmetti, *Acta Crystallogr.*, 1997, in press.
3. S. Aldoshin, I. Chuev, A. Utenyshev, V. Lokshin, J.-L. Pozzo, G. Pepe, and R. Guglielmetti, *Acta Crystallogr.*, 1995, **C51**, 141.
4. S. Aldoshin, I. Chuev, A. Utenyshev, O. Filipenko, V. Lokshin, J.-L. Pozzo, and R. Guglielmetti, *Acta Crystallogr.*, 1996, **C52**, 1834.
5. G. Harie, *PhD Thesis*, Universite d'Aix-Marseille II, 1996.
6. S. M. Aldoshin, *Mol. Cryst. Liq. Cryst.*, 1987, **149**, 251.
7. J. A. Miler, P. Levoir, J. C. Fontaine, F. Garnier, and J. F. Dubois, *Anal. Chem.*, 1975, **47**, 29.
8. N. L. Allinger and Young Yuh, *Molecular Mechanics. MM2 and MMP2 programs*, QCPE-395, 1977.
9. G. M. Sheldrick, *Program for Crystal Structure Determination*, University of Cambridge, England, 1986.
10. G. M. Sheldrick, *Program for the Refinement of Crystal Structures*, University of Gottingen, Germany, 1993.

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