

1*H*-Benzo[*c*]pyrazolo[1,2-*a*]cinnolines: A Novel Photochromic System^{1†}

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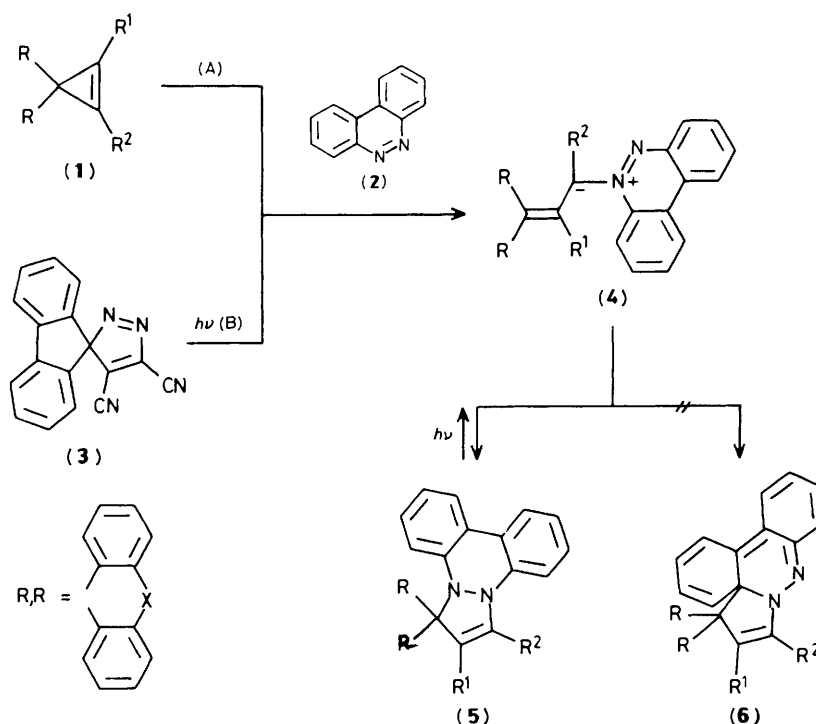
A novel photochromic system based on the pyrazolo[1,2-*a*]cinnoline structure (type 1,2-system) is described, together with syntheses, spectroscopic properties, and an X-ray analysis.

Photochromic compounds have attracted much attention in recent years,^{2a} largely because they can serve as silver-free materials for optical displays and data storage,^{2b} as actinometer substances and light filters^{2c}, as well as for solar energy conversion,^{2d} and recently for microelectronic computer chips.^{2e} We have previously reported on a photochromic

system based on a 1,5-electrocyclization both for the spiro-dihydroindolizines³ and the spiro-pyrazolo[1,5-*a*]pyridines (type 2,3-system).⁴ In this communication the syntheses, spectral properties, and an X-ray analysis of the new class of photochromic pyrazolo[1,2-*a*]cinnolines are presented.

Reaction of electrophilic spiro- and diaryl-cyclopropenes (**1**) with the 1,2-diazine benzo[*c*]cinnoline (**2**) in a 1:1 ratio in ether at room temperature (route A) afforded the title compounds (**5**). Unsymmetrically substituted spirocyclo-

† For Part 11 of the series Photochromic Systems, see ref. 4.



Scheme 1. Formation of compounds (5).

(5)	X	R ¹	R ²	% Yield	M.p./ °C	Route
a	— ^a	CO ₂ Me	CO ₂ Me	77	196	A
b	—	COMe	COMe	58	184	A
c	—	COPh	COPh	74	231	A
d	—	COMe	CO ₂ Me	46	198	A
e	—	CO ₂ Me	COMe	4	193	A
f	—	CN	CN	32	182	B
g ^b	H,H	CO ₂ Me	CO ₂ Me	36	174	A

^a Directly linked. ^b Ref. 5.

propenes (1) led to regioisomers (5d) and (5e) (12:1 ratio) which were separable by column chromatography on silica gel with methylene chloride as eluant [(5d) *R_f* 0.41; (5e) *R_f* 0.55]. Nucleophilic attack of the benzo[*c*]cinnoline (2) on C-2 or C-3 in (1) is responsible for the regioselectivity.

Photolysis (Pyrex filter, high pressure Hg lamp, HPK, 125 W) of the spiro-3*H*-pyrazole (3) in a 1% ethereal solution of (2) (route B) gave the photochromic (5f). The structures of (5) were assigned on the basis of *X*-ray crystallography, ¹⁵N, ¹³C, and ¹H n.m.r., i.r., u.v.-visible, and mass spectroscopy, and elemental analyses.

The ¹H n.m.r. data of (5a–f) indicate a symmetrical structure with regard to the fluorene skeleton. The aromatic protons of the benzocinnoline unit are in the shielding cone of the fluorene part of the molecule, and are shifted upfield to δ 5.48. A less symmetrical ¹H n.m.r. pattern is expected for (6). The ¹⁵N n.m.r. data[‡] should clearly distinguish between (5) and (6). Both absorptions observed appear in the tertiary amine range: δ –235.63 and –237.94 p.p.m., thus proving that structure (5) arises from the regioselective thermal cyclization.

The structure of the title compounds was unambiguously determined for (5g) by *X*-ray crystallography (Figure 1).[§]

These results demonstrate that the betaines (4) initially formed are converted in a regioselective 1,5-electrocyclic reaction into the pyrazolo[1,2-*a*]cinnolines (5); these molecules represent a novel pyrazole-based photochromic system (type 1,2-system).¹ Compounds (5) undergo a conrotatory 1,5-electrocyclic ring-opening reaction⁶ to give (4) photochemically. The long-wavelength maxima in the u.v.-visible spectra of (5a–g) lie between 399 and 470 nm with molar ε values of 5.5–11.1 × 10³; those of the coloured forms (4a–g), measured by low temperature u.v. spectroscopy in dichloromethane, show absorptions between 570 and 750 nm (see Table 1).

The u.v.-visible results prove that the λ_{max.} values of the

[§] Crystal data: C₃₁H₂₄N₂O₄, *M* = 488.5, monoclinic, space group *P*2₁/*a* (No. 14), *a* = 15.118(2), *b* = 11.061(2), *c* = 16.657(2) Å, β = 116.34(1)°, *U* = 2496 Å³, *D_c* = 1.30 g cm⁻³, *F*(000) = 1024, *Z* = 4, μ(Mo-*K*_α) = 0.81 cm⁻¹, λ = 0.71069 Å, crystal size: 0.14 × 0.43 × 0.53 mm, total reflections: 6112 (±*h+k+l*), independent reflections: 5626, observed reflections: 2922 [*I* < 2 σ(*I*)], 334 parameters, *R* = 0.058, *R_w* = 0.061, maximum electron density final difference Fourier ρ = 0.28 e Å⁻³. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

[‡] 40.56 MHz, inverse gated decoupling, 1 M in CDCl₃, internal standard: nitromethane (δ 0 p.p.m.); relaxation reagent: 0.05 M Cr(acac)₃ (Hacac = pentanedione).

Table 1. U.v.-visible data and kinetic parameters for the pyrazolo[1,2-*a*]cinnolines (**5**)^a and betaines (**4**)^b in CH₂Cl₂.

	X ^c	(5), $\lambda_{\max.}/$ nm (log ϵ)	(4), $\lambda_{\max.}/$ nm	$\Delta H^\ddagger/$ kcal mol ⁻¹	$\Delta S^\ddagger/$ cal K ⁻¹ mol ⁻¹	τ_1/s
a	—	405 (4.05)	660	15.2	0.73	0.02
b	—	435 (3.98)	750	15.3	-1.85	0.077
c	—	413 ^d (3.75)	475 ^e	16.2	-1.0	0.224
d	—	432 (3.98)	540, 685	13.3	-3.38	0.006
e	—	399 (3.96)	730	—	—	—
f	—	470 (3.94)	382, 605	15.0	-7.94	1.2
g	H,H	402 (4.00)	382, 570	—	—	—

^a Room temp. ^b U.v. spectroscopy at -78°C. ^c A dash signifies direct linkage. ^d Shoulder at 480 nm. ^e Shoulder at 700 nm.

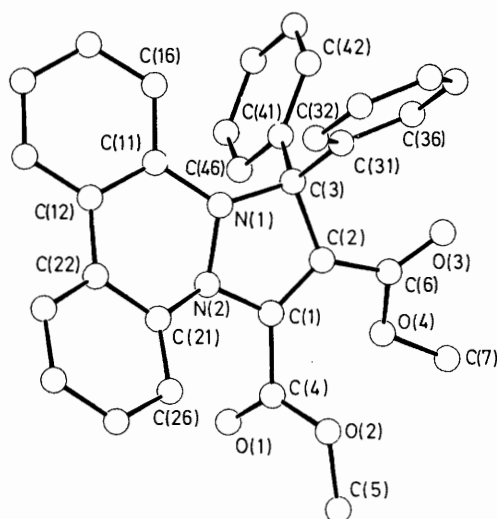


Figure 1. X-Ray analysis of the pyrazolo[1,2-*a*]cinnoline (**5g**). Selected bond distances: C(1)–C(2) 1.342(5), C(2)–C(3) 1.542(5), C(3)–N(1) 1.508(4), N(1)–N(2) 1.443(4), N(2)–C(1) 1.362(5), C(1)–C(4) 1.499(5), C(2)–C(6) 1.474(5), C(3)–C(31) 1.546(4), C(3)–C(41) 1.544(5), N(1)–C(11) 1.395(5), N(2)–C(21) 1.420(5) Å.

betaines (**4**) are dominated by the electron-attracting substituent R² at C-3 and are influenced weakly by R¹ at C-2. This is evident from a comparison of the maxima of (**4a,b**) (660 and 750 nm) with those of (**4d,e**) (685 and 730 nm). The weaker electron acceptor in the C-3 position shifts the $\lambda_{\max.}$ value to shorter wavelengths.

The kinetics of the cyclization reactions (**4**) → (**5**) were investigated in methylene chloride by flash photolysis in the temperature range 288–303 K. The observed decolouration was independent of the observation wavelength and showed monoexponential decay. Half lives (τ_1) are 293 K as listed in Table 1 together with activation parameters obtained from the temperature dependence of *k*.

The τ_1 values range from several milliseconds [(**4d**) 0.006 s] to seconds [(**4f**) 1.2 s]. The entropies of activation are around zero or slightly negative, indicating that no extreme steric hindrance or change in solvation accompanies the formation of the transition state during the cyclization. Although the changes in τ_1 or *k* are really sizeable, the accuracy of the activation parameters, which were obtained over a rather narrow temperature range, does not warrant a more detailed discussion as to whether these changes are due to a variation of ΔH^\ddagger or ΔS^\ddagger .

The reaction of (**1**) with cinnolines (**2**) thus provides an easy entry into the betaine series (**4**). This molecule has only a small barrier for the disrotatory cyclization to give (**5**). The energetically unfavourable regioisomer (**6**) is not formed. Pyrazolo-cinnolines (**5**) constitute a new class of photochromic molecule which give coloured betaines (**4**) having only small τ_1 values.

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