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Molecular structure and photochromic properties of 1,3-dimethylindoline-3,3′-alkano-2-spiro-2′-(6′-nitro)benzopyrans☆

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Abstract

Photochromic properties of spiroindolinobenzopyrans in which a $-(CH_2)_3-$ or $-(CH_2)_5-$ moiety links the 3-position of indoline and the 3′-position of benzopyran have been studied. In this regard, a photochromic color change was observed only when the $-(CH_2)_5-$ bridging group was used. X-ray crystallographic data showed that the spiro-CO bond length in the pyran ring of the dye containing the $-(CH_2)_5-$ bridging group was slightly longer than that in the dye with th $-(CH_2)_3-$ bridging group. X-ray data also suggest that extended conjugation in the open form of the dye containing the $-(CH_2)_3-$ bridging group is inhibited because of the fixed conformation of the 6-membered ring. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Photochromism; Spiropyran; X-ray crystallography

1. Introduction

Spiropyrans are photochromic compounds that have been widely studied because of their potential utility in various high-tech applications [1–3]. Laser flash photolysis experiments have been conducted to characterise the complex photophysical and photochemical properties of the 1,3,3-trimethylindoline-2-spiro-2′-(6′-nitro)benzopyran (**1**). In this regard, it has been reported that dye **1** produces a cisoid ring-opened intermediate that undergoes isomerisation to a transoid form within 10 ns [4]. In related studies, results of MO (MNDO-PM3) calculations involving four possible transoid conformations (EE, EZ, ZE, and ZZ) of dye **1** indicated that the difference in stability among them is only 14.82 kJ mol^{-1} in vacuum [5] and 18.61 kJ mol^{-1} in DMSO [6].

In the present study, we prepared a pair of spirobenzopyrans containing a $-(CH_2)_n-$ bridging group linking the C-3 and C-3′ atoms, to restrict isomerisation to transoid conformations (Fig. 1). The photochromic properties of these dyes were studied at 173–293 K in ethanol.

2. Experimental

2.1. Materials

Spiropyrans **2a** and **2b** were prepared and purified by the method described in the literature [1]. Single crystals of these dyes were obtained by

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☆ A preliminary communication has been published [1].

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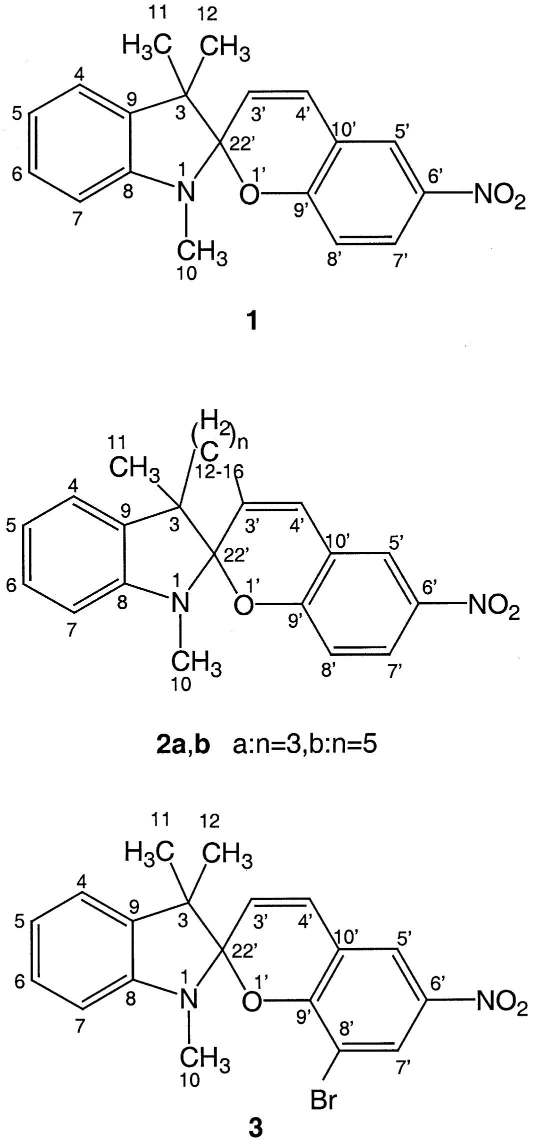
slow evaporation from EtOH solution at room temperature.

2.2. Photochromism studies

Spiropyrans **2a** (4.0 mg) and **2b** (3.5 mg) were dissolved separately in EtOH (100 ml) and the solutions were transferred to 1-cm quartz cells. Each cell was maintained at constant temperature with a model DN1704 variable temperature liquid nitrogen cryostat equipped with a model ITC502 temperature controller (Oxford Instruments), and was irradiated with UV-light (250–400 nm) from a Xenon lamp (Ushio, UXL-500D) filtered by Toshiba UV-D33S. UV-visible spectra were obtained using a Shimadzu UV-3100PC spectrophotometer.



1

2a,b a:n=3,b:n=5

3

Fig. 1. Structures of dyes **1**, **2a** ($n=3$), **2b** ($n=5$) and **3**.

2.3. X-ray structure determination

The X-ray diffraction data were collected on **2a** and **2b** using a Rigaku AFC5R diffractometer and the ω-2θ scan technique at room temperature. The crystal structures were solved by the heavy-atom method and were expanded by successive Fourier syntheses. The non-hydrogen atoms were refined anisotropically using full-matrix least-squares techniques, while the hydrogen atoms were fixed at their standard geometries and were not refined. All calculations were performed using the teXsan crystallographic software package [7]. The crystallographic data obtained and the experimental details employed are summarised in Table 1. Selected atomic coordinates are given in Tables 2 and 3, and the numbering of the heavy atoms is shown in Fig. 1.

Table 1
X-ray crystal data collected on dyes **2a** and **2b**

Compound	**2a**	**2b**
Formula	$C_{21}H_{20}N_2O_3$	$C_{23}H_{24}N_2O_3$
Mol. wt.	348.40	376.45
Space group	$P2_1/n$	$P2_1/c$
a/Å	11.094 (1)	9.943 (4)
b/Å	12.265 (1)	11.511 (3)
c/Å	13.152 (2)	17.682 (2)
β/°	96.918 (9)	102.45 (2)
V/Å^3	1776.5 (6)	1976.0 (7)
Z	4	4
D_c/g cm^{-3}	1.303	1.265
μ(Mo K_α)/cm^{-1}	0.88	0.84
Crystal sizes/mm	0.4 0.3 0.3	0.15 0.1 0.3
No. unique reflections	2480	3848
No. observed reflections	1798 [$I>3\sigma(I)$]	907 [$I>3\sigma(I)$]
No. variables	235	349
F(000)	736.00	800.00
R	0.040	0.043
Rw	0.057	0.039

Table 2
Atomic coordinates and equivalent isotopic parameters for dye **2a**[a]

Atom	x	y	z	B_{eq}
O(1′)	1.0228 (1)	−0.0234 (1)	0.2623 (1)	4.70 (5)
O(6′A)	0.9925 (3)	−0.5109 (2)	0.3856 (2)	8.23 (8)
O(6′B)	1.1764 (2)	−0.5034 (2)	0.3506 (2)	7.71 (7)
N(1)	0.8547 (2)	0.0578 (2)	0.1640 (2)	4.13 (5)
N(6′)	1.0778 (3)	−0.4606 (2)	0.3591 (2)	5.84 (7)
C(22′)	0.9114 (2)	0.0402 (2)	0.2676 (2)	3.79 (6)
C(3)	0.9541 (2)	0.1560 (2)	0.3037 (2)	3.81 (6)
C(4)	1.0286 (2)	0.3044 (2)	0.1819 (2)	4.60 (7)
C(5)	1.0227 (3)	0.3395 (2)	0.0807 (3)	5.59 (8)
C(6)	0.9594 (3)	0.2794 (3)	0.0033 (2)	5.72 (8)
C(7)	0.9013 (3)	0.1826 (2)	0.0233 (2)	5.17 (7)
C(8)	0.9093 (2)	0.1489 (2)	0.1243 (2)	4.02 (6)
C(9)	0.9726 (2)	0.2086 (2)	0.2031 (2)	3.80 (6)
C(10)	0.8166 (3)	−0.0341 (3)	0.0985 (2)	5.79 (8)
C(11)	1.0663 (2)	0.1546 (2)	0.3818 (2)	5.38 (7)
C(12)	0.8509 (2)	0.2185 (2)	0.3469 (2)	4.63 (7)
C(13)	0.7856 (3)	0.1545 (2)	0.4211 (2)	5.27 (7)
C(14)	0.7295 (2)	0.0536 (2)	0.3683 (2)	4.96 (7)
C(3′)	0.8269 (2)	−0.0163 (2)	0.3323 (2)	3.84 (6)
C(4′)	0.8399 (2)	−0.1208 (2)	0.3574 (2)	3.93 (6)
C(5′)	0.9575 (2)	−0.2938 (2)	0.3547 (2)	4.34 (7)
C(6′)	1.0629 (3)	−0.3450 (2)	0.3352 (2)	4.67 (7)
C(7′)	1.1540 (2)	−0.2899 (3)	0.2932 (2)	5.13 (7)
C(8′)	1.1383 (2)	−0.1825 (2)	0.2678 (2)	4.80 (7)
C(9′)	1.0320 (2)	−0.1301 (2)	0.2861 (2)	4.01 (6)
C(10′)	0.9416 (2)	−0.1846 (2)	0.3313 (2)	3.84 (6)

[a] Values in parentheses are estimated standard deviations.

Table 3
Atomic coordinates and equivalent isotopic parameters for dye **2b**[a]

Atom	x	y	z	B_{eq}
O(1′)	0.7693 (5)	0.0823 (5)	0.3462 (3)	5.4 (2)
O(6′A)	0.6149 (7)	0.5538 (5)	0.4746 (4)	7.4 (2)
O(6′B)	0.8283 (7)	0.5460 (5)	0.5279 (3)	7.4 (2)
N (1)	0.6786 (6)	−0.0495 (5)	0.2494 (3)	4.3 (2)
N(6′)	0.7257 (9)	0.5047 (7)	0.4866 (4)	5.7 (3)
C(22′)	0.6532 (8)	−0.0011 (6)	0.3203 (4)	4.4 (2)
C (3)	0.6798 (8)	−0.1064 (7)	0.3781 (4)	4.9 (2)
C (4)	0.8698(10)	−0.2609 (8)	0.3767 (6)	6.5 (3)
C (5)	0.9531 (9)	−0.3120 (8)	0.3333 (7)	6.8 (3)
C (6)	0.9476 (9)	−0.2748 (9)	0.2583 (7)	6.7 (3)
C (7)	0.8611 (9)	−0.1866 (9)	0.2251 (6)	6.1 (3)
C (8)	0.7772 (8)	−0.1365 (7)	0.2695 (5)	4.2 (2)
C (9)	0.7838 (8)	−0.1722 (7)	0.3455 (5)	4.7 (2)
C(10)	0.681 (1)	0.0295(10)	0.1844 (6)	5.8 (3)
C(11)	0.738 (2)	−0.070 (1)	0.4614 (7)	8.2 (4)
C(12)	0.5531(10)	−0.1864 (8)	0.3708 (6)	5.9 (3)
C(13)	0.433 (1)	−0.141 (1)	0.4071 (8)	8.2 (4)
C(14)	0.298 (1)	−0.134 (1)	0.3501 (9)	8.7 (4)
C(15)	0.274 (1)	−0.026 (1)	0.3009 (7)	7.1 (3)
C(16)	0.3878 (9)	0.0042 (8)	0.2582 (6)	5.7 (3)
C(3′)	0.5154 (8)	0.0592 (7)	0.3083 (4)	4.4 (2)
C(4′)	0.5071 (8)	0.1625 (8)	0.3412 (4)	4.5 (2)
C(5′)	0.6136 (9)	0.3339 (8)	0.4176 (4)	4.6 (3)
C(6′)	0.7329(10)	0.3910 (8)	0.4514 (4)	4.8 (3)
C(7′)	0.861 (1)	0.3474 (8)	0.4504 (5)	5.9 (3)
C(8′)	0.8737(10)	0.2426 (9)	0.4160 (5)	5.9 (3)
C(9′)	0.7533 (9)	0.1838 (7)	0.3823 (4)	4.5 (2)
C(10′)	0.6249 (8)	0.2272 (7)	0.3829 (4)	4.0 (2)

[a] Values in parentheses are estimated standard deviations.

3. Results and discussion

3.1. Photochromism studies

Solutions of **2a** and **2b** were irradiated with xenon-light for 3 min at 173–293 K. While irradiation of **2a** did not change its absorption spectrum, the spectrum of **2b** underwent a significant change. The dependence of irradiation temperature on the absorption spectrum of **2b** is shown in Fig. 2. The solution of **2b** was stable to irradiation for more than 1 h at 193 K, whereas irradiation at 293 K led to decoloration. Warming the solution of **2b** to 193 K following irradiation at 173 K did not change its absorption spectrum, suggesting that the absorption coefficient of the colored form of dye **2b** was not affected by temperature.

The effects of irradiation time on the absorption spectrum of **2b** in EtOH at 193 K are shown in Fig. 3. An isosbestic point near 375 nm was observed until the 10-min point. Another isosbestic point near 330 nm was observed after irradiating **2b** for 10 min or more. This means that isomerisation to the colored form is complete in 10 min and that irradiation beyond that point causes dye degradation, even at 173 K. We also found that changes in absorbance at various temperature levels were caused by differences in the concentration of colored species and that the viscosity of the irradiated solutions affected the rates at which these species formed.

3.2. Crystal structures

The molecular structures of **2a** and **2b** are shown in Figs. 4 and 5, respectively. Selected bond distances, bond angles and torsion angles are given in Table 4, along with the previously reported values

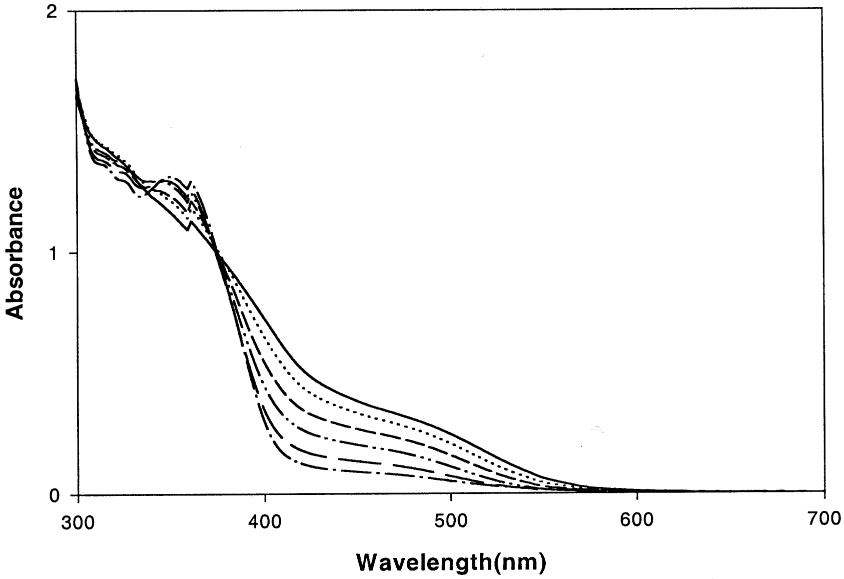


Fig. 2. The dependence of irradiation temperature on the absorption spectrum of **2b** in EtOH following irradiation for 3 min. Plots are arranged in decreasing order of absorbance values at 450 nm, for 273, 253, 233, 213, 193 and 173 K.

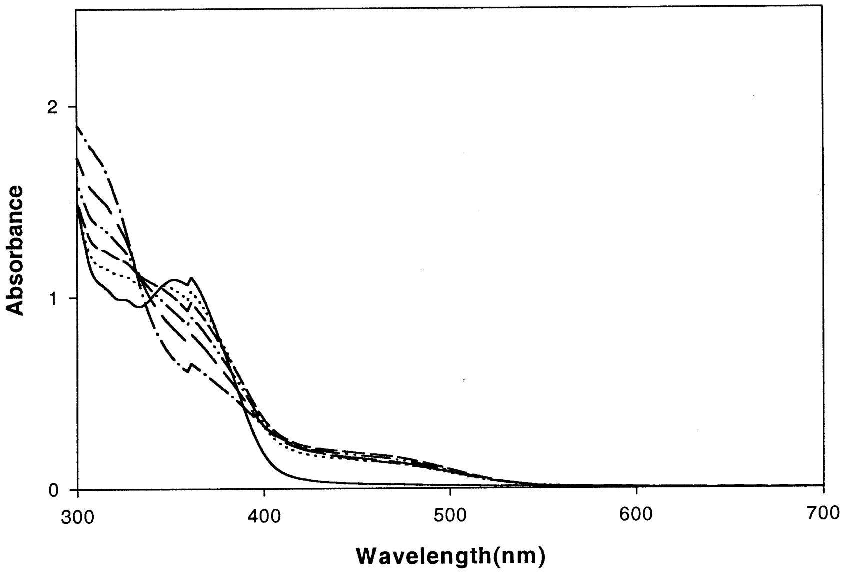


Fig. 3. The change in the absorption spectrum of **2b** in EtOH following irradiation at 193 K. Plots are arranged in decreasing order of absorbance values at 350 nm, for 0, 3, 10, 30, 60 and 120 min.

for 1,3,3-trimethylindoline-2-spiro-2′-(8′-bromo-6′-nitro)benzopyran (**3**) [8]. The C(22′)–O(1′) bond lengths in **2a** and **2b** were found to be 1.470 (3) and 1.495 (8) Å, respectively. They are 0.04 and 0.07 Å longer than the normal C(sp^3)–O bond length of 1.43 Å. The C(22′)–O(1′) bond length in typical photochromic benzospiropyrans is 1.470 (2)–1.500 (8) Å [9]. Although the C(22′)–O(1′) bond length

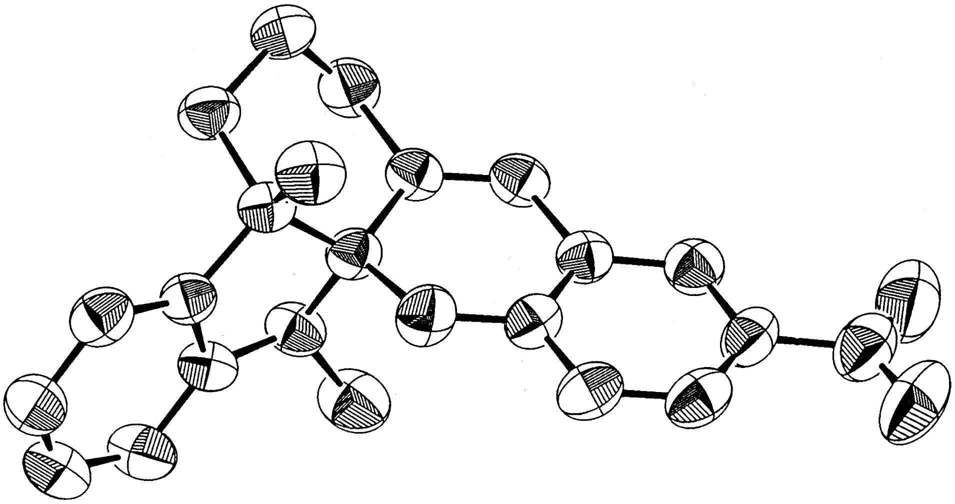


Fig. 4. The X-ray crystal structure of **2a**.

Table 4
Selected bond lengths (Å), bond angles (°), and torsion angles (°) for dyes **2a, 2b, 3**

	2a	**2b**	**3**[a]
Bond lengths			
O(1′)-C(22′)	1.470 (3)	1.495 (8)	1.496(4)
O(1′)-C(9′)	1.346 (3)	1.357 (8)	1.342(5)
N(1)-C(22′)	1.446 (3)	1.443 (8)	1.453(4)
C(22′)-C (3)	1.554 (4)	1.570 (9)	1.527(5)
C(22′)-C(3′)	1.509 (3)	1.508 (9)	1.483(5)
Bond angles			
N(1)-C(22′)-O(1′)	107.9 (2)	104.2 (6)	108.3(3)
C(3)-C(22′)-O(1′)	105.8 (2)	106.6 (6)	104.7(3)
C(3′)-C(22′)-O(1′)	111.5 (2)	111.5 (6)	110.0(3)
N(1)-C(22′)-C (3)	103.5 (2)	103.6 (6)	103.7(3)
N(1)-C(22′)-C(3′)	111.8 (2)	112.2 (7)	113.1(3)
C(3)-C(22′)-C(3′)	115.8 (2)	117.9 (7)	116.3(3)
Torsion angles[b]			
N(1)-C(22′)-O(1′)-C(9′)	−105.2 (2)	144.9 (6)	−97.5
N(1)-C(22′)-C(3)-C (9)	−27.6 (2)	29.2 (8)	−27.9
N(1)-C(22′)-C(3)-C(11)	−150.4 (2)	147.7 (9)	−152.0
N(1)-C(22′)-C(3)-C(12)	85.7 (2)	−83.7 (8)	85.8
N(1)-C(22′)-C(3′)-C(4′)	105.0 (3)	−135.6 (8)	101.9

[a] Ref. [8].

[b] Torsion angles were calculated from the coordinates reported in Ref. [8].

in **2b** was practically the same as that in **3**, the corresponding value in **2a** was shorter than that in **3**, as shown in Table 4. In all three cases, the C(9′)–O(1′) bond length was longer than the 1.39 Å bond length reported elsewhere [9]. Although both **2a** and **2b** have the ability to undergo photochromic changes leading to a merocyanine structure of the type possible for dyes **1** and **3**, based on the observed bond length changes, only **2b** gave a color change in solution following irradiation.

Bond angles and torsion angles in **2a** and **2b** associated with the C(22′) atom were close to those found in **3**, except for torsion angles N(1)–C(22′)–O(1′)–C(9′) and N(1)–C(22′)–C(3′)–C(4′). These observations suggest that the C(22′) atomic orbitals in **2a** and **2b** are the typical sp^3 hybrid orbitals of photochromic spiropyrans such as **3**, even though **2a** did not exhibit photochromic behavior. Atoms C(22′), C(3), C(12), C(13), C(14) and C(3′) in **2a** form a cyclohexane ring. Two of them, C(22′) and C(3), are also members of the indole ring. On the other hand, 2b has a cyclooctane ring in which the ring strain is lower than that in the cyclohexane ring.

Among the merocyanine-like isomers of **2a** and **2b**, EE and EZ can be excluded, since it is not possible for the C(4′)–C(3′)–C(22′)–N(1) moiety to possess the *trans* configuration. When semi-empirical MNDO-PM3 quantum chemical calculations were carried out on the open-form isomers of **2a** and **2b**, optimization of the open-form structure of **2a** led to one minimum, which was not a merocyanine-like form. Instead, the structure was a cisoid type in which the indoline ring and nitro-

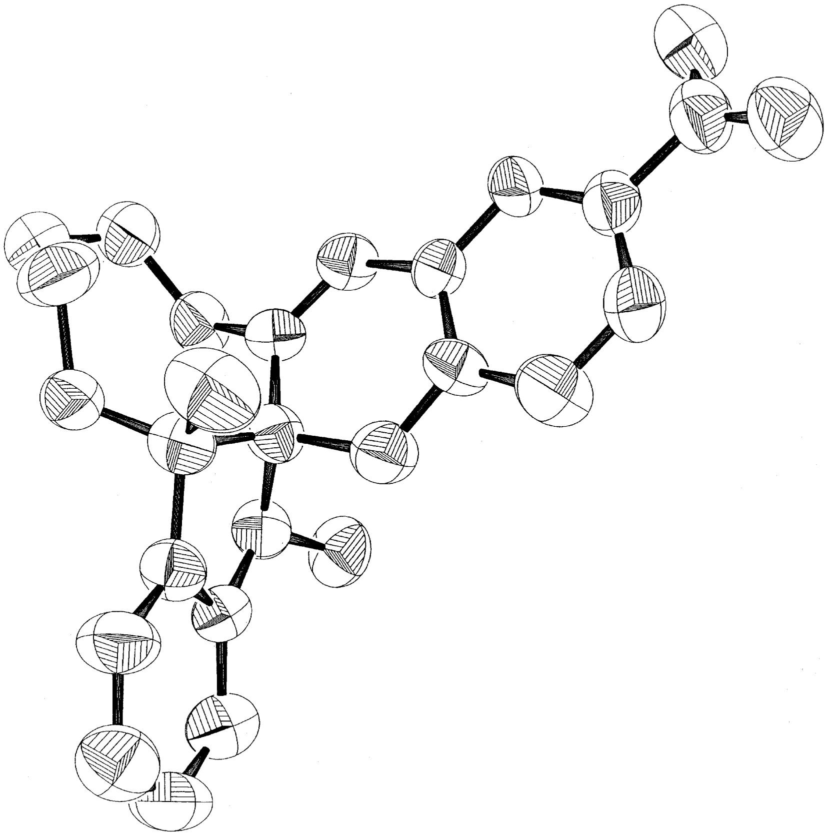


Fig. 5. The X-ray crystal structure of **2b**.

benzene ring were perpendicular, and the HOMO involved parts of indoline ring and C(3′). This isomer was colorless. On the other hand, the open-form structure of **2b** produced two minima. One was similar to **2a** and the other was also a cisoid type in which the two aromatic rings were almost parallel. In the latter case, the HOMO involved the indoline and nitrobenzene rings, and this isomer was colored.

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