

Communication

Guest-dependent photochromism of 3,3'-bis-(4-fluoro-phenyl)-3H,3'H-[2,2']biindenylidene-1,1'-dione in its inclusion crystals

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Received 6th November 2003, Accepted 19th December 2003

First published as an Advance Article on the web 8th January 2004

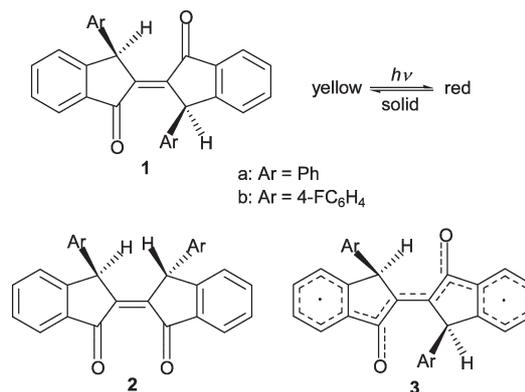
Inclusion crystals of 3,3'-bis-(4-fluoro-phenyl)-3H,3'H-[2,2']biindenylidene-1,1'-dione (**1b**) showed a reversible color change from yellow to red upon photoirradiation, although **1b** did not show photochromic property in the solid state.

Organic photochromic compounds have received much attention in recent years because of their potential applications such as information storage, electronic display systems, optical switching devices, ophthalmic glasses, etc.¹ Several types of organic photochromic compounds such as naphthopyrans, spiropyrans, fulgides, *N*-salicylideneanilines and diarylethenes have been discovered and their properties investigated.²

Recently, we have reported a new type of photochromic compound, *trans*-3,3'-diaryl-3H,3'H-[2,2']biindenylidene-1,1'-dione **1** which shows photochromism in the solid state.³ For example, the yellow crystals of **1a** turn reddish-purple when exposed to sunlight for a few minutes, and the reddish-purple crystals return slowly to yellow in the dark. However, irradiation of **1a** in a CH₂Cl₂ solution gives its *cis*-isomer **2a**, irreversibly. The reddish-purple crystals show EPR signals of triplet biradicals such as **3a** formed by twisting the central C=C bond of **1a** upon photoirradiation in the solid state.³

We have now found that the title compound **1b** forms inclusion crystals with various kinds of organic guest molecules, and these inclusion crystals show reversible color change from yellow to red upon photoirradiation in the solid state, although **1b** itself does not show any photocoloration. It was also found that the stability of the photochromism of inclusion crystals of **1b** depends on the type of guest molecule included.

trans-Biindenylidenedione **1b** was prepared according to the previously reported method.³ The biindenylidenedione **1b** was found to form inclusion complexes with various kinds of guest



compounds. (Table 1) For example, when **1b** was recrystallized from the CH₂Cl₂ solution, 1 : 1 inclusion complex crystals of **1b** with CH₂Cl₂ were obtained as yellow prisms. Similarly, the inclusion crystals with carbon tetrachloride (2 : 1), tetrachloroethylene (4 : 1), cyclopentanone (1 : 1), γ -butyrolactone (1 : 1), THF (1 : 1), 1,4-dioxane (1 : 1), DMSO (1 : 1), benzene (4 : 1), and toluene (4 : 1) were obtained as yellow crystals. (Table 1) Interestingly, these inclusion crystals show reversible color change from yellow to red upon photoirradiation in the solid state, whereas **1b** itself does not show any visible coloration (Fig. 1). For example, yellow crystals of the 1 : 1 inclusion complex of **1b** with CH₂Cl₂ turned into red crystals immediately upon photoirradiation. The red color faded in the dark on storage for 1 h at room temperature. The UV spectral changes of **1b** and its 1 : 1 CH₂Cl₂ inclusion complex are shown in Fig. 2 and Fig. 3, respectively.

It is also remarkable that the stability of the photochromism depends on the type of guest molecule. For example, the red color developed upon photoirradiation of the 1 : 1 inclusion

Table 1 Photochromism of the inclusion complex of **1a** and **1b** in the solid state

Guest	Inclusion complex of 1b			Inclusion complex of 1a		
	h : g ratio ^a	Photochromism	Half-life/h ^b	h : g ratio ^a	Photochromism	Half-life/h ^b
none	—	no	—	—	yes	1
CH ₂ Cl ₂	1 : 1	yes	0.5	1 : 1	yes	6
CCl ₄	2 : 1	yes	6	— ^c	—	—
Tetrachloroethylene	4 : 1	yes	3	— ^c	—	—
Cyclopentanone	1 : 1	yes	24	1 : 1	yes	12
γ -Butyrolactone	1 : 1	yes	12	1 : 1	yes	12
THF	1 : 1	yes	24	— ^c	—	—
1,4-Dioxane	1 : 1	yes	12	— ^c	—	—
DMSO	1 : 1	yes	36	— ^c	—	—
Benzene	4 : 1	yes	5	— ^c	—	—
Toluene	4 : 1	yes	12	— ^c	—	—

^a The host-guest ratio was determined by TG. ^b The half-life was determined by solid-state UV spectra and the average error in $t_{1/2}$ is about 10 min. ^c No inclusion complexation occurred.

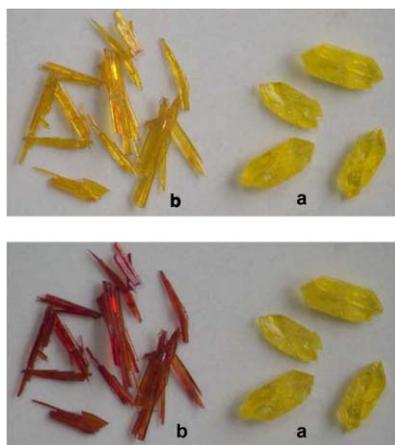


Fig. 1 Photographs of (a) **1b** (crystal size: 3.5 mm \times 1.5 mm \times 0.2 mm) and (b) 1:1 CH₂Cl₂ complex of **1b** (crystal size: 5.0 mm \times 0.5 mm \times 0.3 mm) before (top) and after photoirradiation (bottom).

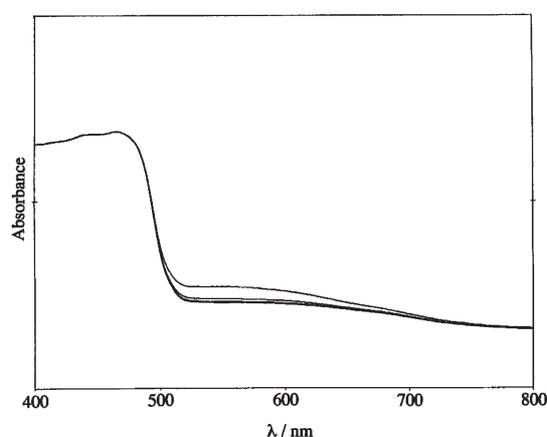


Fig. 2 UV spectral changes of **1b** in the solid state. Measurement was successively made every 30 min from the top (after irradiation) to the bottom.

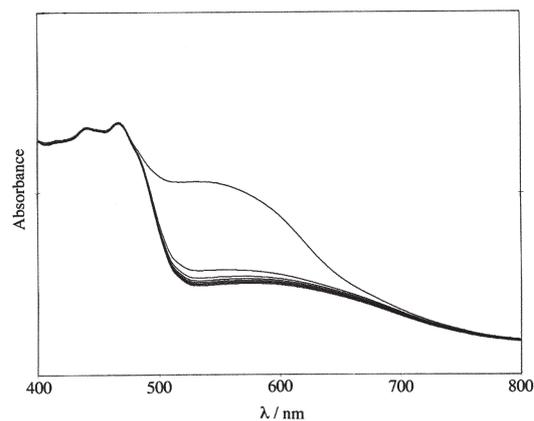


Fig. 3 UV spectral changes of 1:1 inclusion complex of **1b** with CH₂Cl₂ in the solid state. Measurement was successively made every 30 min from the top (after irradiation) to the bottom.

crystals of **1b** with cyclopentanone was more stable, and its half-life was 24 h in the dark (Fig. 4).

Similarly, the half-lives of the red color of the inclusion crystals were 3 h (tetrachloroethylene), 5 h (benzene), 6 h (CCl₄), 12 h (γ -butyrolactone, 1,4-dioxane and toluene), 24 h (THF), 36 h (DMSO), respectively. The stable photochromism of **1b** in inclusion crystals may be due to the molecular arrangement suitable for twisting the central C=C bond of **1b** upon photoirradiation in the crystal.

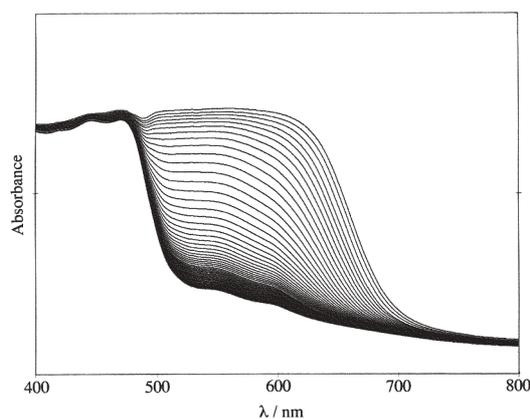


Fig. 4 UV spectral changes of 1:1 inclusion complex of **1b** with cyclopentanone in the solid state. Measurement was successively taken every 30 min from the top (after irradiation) to the bottom.

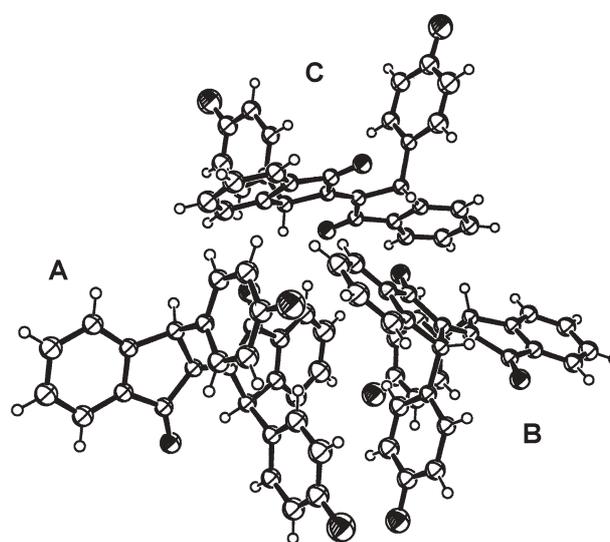


Fig. 5 The three independent molecules in the asymmetric unit of compound **1b**.

The high inclusion ability of **1b** may be attributed to the substituent effect of the 4-fluoro-phenyl groups, since biindenylidene-1,1'-dione **1a** includes only limited guest molecules (Table 1). For example, **1a** formed inclusion complexes with CH₂Cl₂ (1:1), cyclopentanone (1:1), and γ -butyrolactone (1:1) as yellow prisms. The photochromism of the inclusion crystals of **1a** is more stable than that of **1a** itself. The half-lives of the red color of the inclusion crystals of **1a** were 6 h (CH₂Cl₂), 12 h (cyclopentanone) and 12 h (γ -butyrolactone), respectively.

In order to clarify the reason for the drastic changes in photochromicity of **1b** by complexation with guest molecules, the X-ray crystal structures of the inclusion complex were studied.⁴ Figs. 5–7 show the asymmetric units in the crystals of **1b** and its inclusion complexes with CH₂Cl₂ and cyclopentanone, respectively.⁵ Thermal ellipsoids are drawn at the 50% probability level. In the crystal of the pure host, the asymmetric unit comprises three independent molecules while in the solvates the asymmetric unit is a 1:1 host–guest unit.

The molecular structure of the host in the three compounds was carefully analysed in order to identify structural features which might correlate with the observed stabilities of photochromism. Fig. 8 shows all of the host molecules viewed from a common direction, namely normal to the central C=C double bond and with the respective biindenylidene dione units seen on edge.

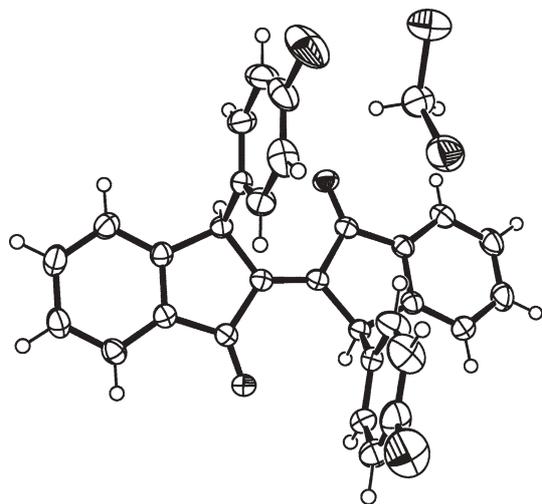


Fig. 6 Molecular structure of the 1:1 inclusion complex of **1b** with CH_2Cl_2 .

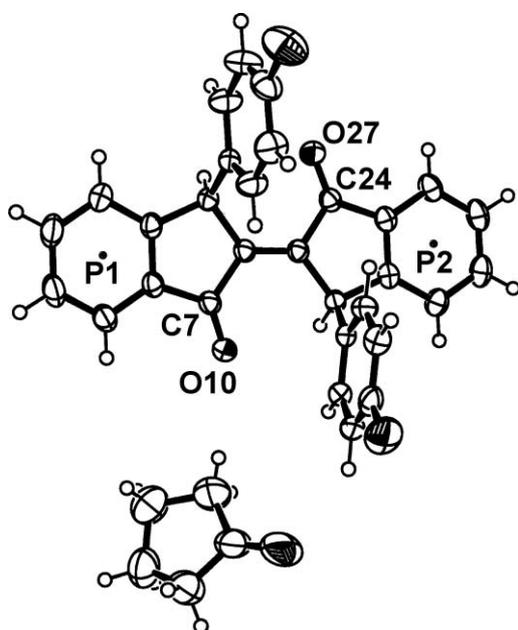


Fig. 7 Molecular structure of the 1:1 inclusion complex of **1b** with cyclopentanone. Labelled items are described in the text.

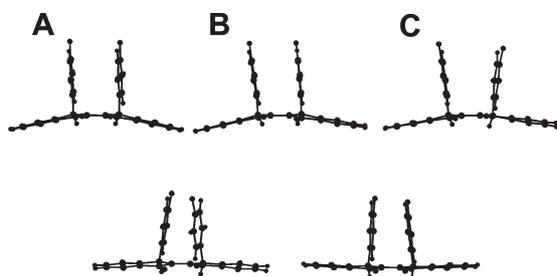


Fig. 8 The three independent host molecules in **1b** (A, B, C) and the host molecules in **1b**- CH_2Cl_2 (lower left) and **1b**-cyclopentanone (lower right).

A distinctly bowed conformation is adopted by the biindenylidene diene unit in each of the three independent host molecules in **1b**. In contrast, this effect is hardly evident in the host molecules of **1b**- CH_2Cl_2 and **1b**-cyclopentanone. To quantify the molecular distortions, separate parameters were selected to isolate the twist around the central double bond and

Table 2 Molecular parameters defining host conformations^a

Parameter	1b (A)	1b (B)	1b (C)	1b - CH_2Cl_2	1b - $\text{C}_5\text{H}_8\text{O}$
$\tau/^\circ$	5.7	-0.2	-0.8	-15.2	-18.6
$\text{P1}\cdots\text{P2}/\text{\AA}$	8.159	8.161	8.204	8.270	8.278

^a average e.s.d.'s are 0.3° and 0.005 \AA

the bowing effect, namely the pseudo-torsion angle $\text{C7-O10}\cdots\text{C24-O27}$ (τ) and the centroid-centroid distance $\text{P1}\cdots\text{P2}$, respectively (Fig. 7). The former parameter is zero when there is no twist and the latter has its maximum value of $8.278(5) \text{ \AA}$ in the case of the least bowed host molecule in **1b**-cyclopentanone. These parameters are listed in Table 2.

The data show that on proceeding from the pure host to the CH_2Cl_2 and cyclopentanone inclusion complexes, there is a definite increase in the extent of twist around the central $\text{C}=\text{C}$ double bond and an accompanying decrease in the extent of bowing. The former parameter shows the more significant changes (from an average of *ca.* 1.5° for molecules in **1b** to -18.6° in the cyclopentanone complex) and the degree of twist increases with the stability of photochromism (0.5 h for **1b**- CH_2Cl_2 , 24 h for **1b**-cyclopentanone, relative to the host in **1b** which is not photochromic). Thus, the X-ray structures reveal unequivocal differences in the host geometries in the solid state that can be correlated with the photochromic behaviour.

Crystal stabilisation in **1b** (Fig. 9) is based on π - π stacking (nine unique interactions with ring centroid \cdots centroid distances $< 4.00 \text{ \AA}$), ten $\text{C-H}\cdots\text{O}$ hydrogen bonds (both intra- and intermolecular), as well as one $\text{C-H}\cdots\text{F}$ hydrogen bond.

Enclathration of the guests CH_2Cl_2 and cyclopentanone by host **1b** results in a significant reduction in π - π stacking in crystals of the inclusion complexes. In the complex with CH_2Cl_2 (Fig. 10), pairs of guest molecules are trapped in cages formed by the fluorophenyl rings of four host molecules,

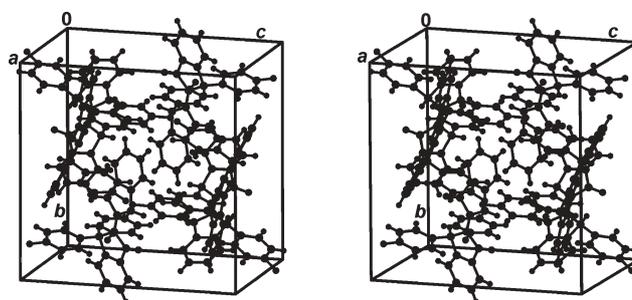


Fig. 9 Stereoview of the crystal packing in **1b**. Click here to access a 3D view of Fig. 9.

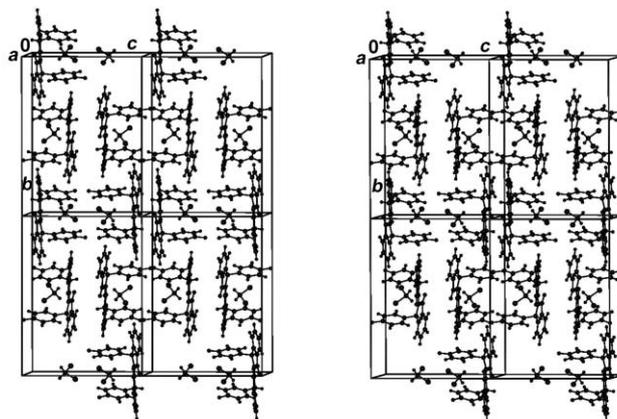


Fig. 10 Stereoview of the crystal packing in **1b**- CH_2Cl_2 . Four unit cells are drawn. Click here to access a 3D view of Fig. 10.

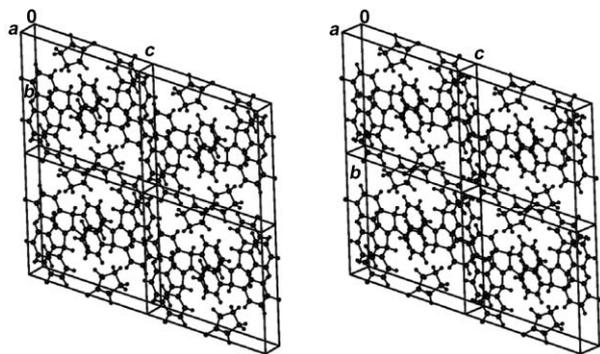


Fig. 11 Stereoview of the crystal packing in **1b**-cyclopentanone. Four unit cells are drawn. Click here to access a 3D view of Fig. 11.

host-guest interaction consisting of one (solvent)C–H \cdots O-10(host) hydrogen bond.

Further stabilisation is afforded by two intermolecular host–host C–H \cdots O hydrogen bonds and two π – π interactions with distances 3.847 and 3.875 Å.

In the cyclopentanone inclusion complex (Fig. 11), the guest molecules occupy isolated sites, each guest oxygen atom linking two adjacent host molecules *via* C–H \cdots O hydrogen bonds.

Further crystal stabilisation is provided by one intermolecular host–host C–H \cdots F hydrogen bond and four π – π interactions with ring centroid \cdots centroid distances in the range 3.827–3.998 Å.

CCDC reference numbers 221994–221996. See <http://www.rsc.org/suppdata/ce/b3/b314140c/> for crystallographic data in CIF format.

K.T. acknowledges financial support from The Suzuki Foundation. M.R.C. thanks the University of Cape Town and the National Research Foundation (Pretoria) for financial support.

Notes and references

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- Intensity data were collected on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo K α X-rays ($\lambda = 0.71069$ Å). Crystals were coated in Paratone N oil (Exxon Chemical Co., TX, USA) for data collection and cooled in a stream of nitrogen vapour. No phase changes were detected on lowering the temperature from ambient (293 K) to the final temperature of data collection (203(2) K).
- (a) Crystal data for **1b**: C₃₀H₁₈F₂O₂, $M = 448.44$, triclinic, space group $P\bar{1}$, $a = 12.8638(2)$, $b = 15.8214(2)$, $c = 16.1334(2)$ Å, $\alpha = 88.140(1)$, $\beta = 88.037(1)$, $\gamma = 84.747(1)^\circ$, $U = 3266.40(8)$ Å³, $Z = 6$, $D_c = 1.368$ g cm⁻³, $T = 203(2)$ K, $\mu(\text{Mo K}\alpha) = 0.096$ mm⁻¹. 15450 reflections were collected and the refinement was based on all data excluding 39 low-angle reflections truncated by the beamstop. The final $wR2 = 0.207$ (all data), $R1$ [11668 data with $F^2 > 2\sigma(F^2)$] = 0.0690, and goodness-of-fit on $F^2 = 1.121$ (CCDC number 221996); (b) Crystal data for **1b**-CH₂Cl₂: C₃₁H₂₀Cl₂F₂O₂, $M = 533.37$, monoclinic, space group $P2_1/n$, $a = 9.0486(1)$, $b = 19.3364(2)$, $c = 14.4056(2)$ Å, $\beta = 95.365(1)^\circ$, $U = 2509.47(5)$ Å³, $Z = 4$, $D_c = 1.412$ g cm⁻³, $T = 203(2)$ K, $\mu(\text{Mo K}\alpha) = 0.302$ mm⁻¹. Of the 49309 reflections collected, 5746 were unique ($R_{\text{int}} = 0.0472$). Refinement was based on all data excluding 11 low-angle reflections truncated by the beamstop. The final $wR2 = 0.1086$ (all data), $R1$ [4005 data with $F^2 > 2\sigma(F^2)$] = 0.0429, and goodness-of-fit on $F^2 = 1.022$ (CCDC number 221995); (c) Crystal data for **1b**-C₅H₈O: C₃₅H₂₆F₂O₃, $M = 532.56$, triclinic, space group $P\bar{1}$, $a = 8.7846(1)$, $b = 12.3272(2)$, $c = 13.4594(2)$ Å, $\alpha = 70.087(1)$, $\beta = 76.153(1)$, $\gamma = 83.096(1)^\circ$, $U = 1329.35(3)$ Å³, $Z = 2$, $D_c = 1.330$ g cm⁻³, $T = 203(2)$ K, $\mu(\text{Mo K}\alpha) = 0.093$ mm⁻¹. Of the 11116 reflections collected, 5835 were unique ($R_{\text{int}} = 0.0197$). Refinement was based on all data excluding 15 low-angle reflections truncated by the beamstop. The final $wR2 = 0.1395$ (all data), $R1$ [4362 data with $F^2 > 2\sigma(F^2)$] = 0.0481, and goodness-of-fit on $F^2 = 1.060$ (CCDC number 221994).