

Photochromism of the inclusion crystals of a new hydroperoxybiindenylidene

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Inclusion crystals of 3,1'-bis(4-fluorophenyl)-1'-hydroperoxy-3'-hydroxy-1',3'-dihydro-3H-[2,2']biindenyliden-1-one showed photochromic and photomagnetic properties in the solid state.

Organic photochromic compounds have received considerable attention in recent years due to their potential applications such as in information storage, electronic display systems, optical switching devices, ophthalmic glasses, and so on.¹ Several types of organic photochromic compounds such as naphthopyrans, spiropyrans, fulgides, *N*-salicylideneanilines and diarylthenes have been discovered and their properties investigated.² Recently, we have reported the photochromic and photomagnetic properties of *trans*-3,3'-diaryl-3H,3'H-[2,2']biindenylidene-1,1'-diones in the solid state.³ In the course of our studies of this new type of photochromic compound, we unexpectedly found that the title hydroperoxy compound (**3**) is also formed during the reduction of biindenylidene (**1**) to *trans*-biindenylidene-1,1'-diones (**2**) with Zn–ZnCl₂ in THF–H₂O, and the inclusion complex of **3** with some guest compounds showed photochromic and photomagnetic properties in the solid state (Scheme 1).

Treatment of 3,3'-bis(4-fluorophenyl)-[2,2']-biindenyl-1,1'-dione (**1**) with Zn–ZnCl₂ in 10% aqueous THF under stirring for 10 min at room temperature gave a mixture of 3,3'-bis(4-fluorophenyl)-3H,3'H-[2,2']-biindenylidene-1,1'-dione (**2**) and 3,1'-bis(4-fluorophenyl)-1'-hydroperoxy-3'-hydroxy-1',3'-dihydro-3H-[2,2']-biindenyliden-1-one (**3**) in 22 and 7% yields, respectively.[†] The hydroperoxy compound (**3**) could be formed via aerobic oxidation of a radical intermediate arising from the one-electron reduction of **1** with Zn under air.

The yellow prisms of **2** turned to red crystals, which immediately returned to yellow prisms in the dark as reported previously.³ Interestingly, however, the hydroperoxy compound (**3**) formed host–guest inclusion crystals with various guest compounds, which show stable photochromism from colorless to green in the solid state (Table 1). For example, single crystals of the 2 : 1 inclusion complex of **3** with toluene were changed from colorless to green irradiating with light. The green state of the crystal was stable in the dark for a couple of days at room temperature, with the color gradually changing to pale-red after two weeks in the dark. The UV spectra of the 2 :

1 inclusion complex of **3** with toluene before and after irradiation are shown in Fig. 1. The green crystals had EPR signals ($g = 2.004$) in the solid state similar to that previously reported³ (Fig. 2). The inclusion complexes of **3** with EtOH, acetone, cyclopentanone, AcOEt, γ -butyrolactone, ether, THF, dioxane, CH₂Cl₂ show similar photochromic and photomagnetic properties in the solid state, whereas the inclusion complexes with relatively small guests in volume, MeOH and MeCN, did not show any photochromic properties.

Table 1 Physical properties of the inclusion complex of **3**

Guest	Host : guest ^a	Mp/°C	Photochromism
MeOH	1 : 1	165–168	No
EtOH	1 : 1	163–166	Yes
Acetone	1 : 1	169–171	Yes
Cyclopentanone	2 : 1	154–156	Yes
AcOEt	2 : 1	159–164	Yes
γ -Butyrolactone	1 : 1	145–148	Yes
Ether	2 : 1	160–164	Yes
THF	2 : 1	164–167	Yes
Dioxane	2 : 1	157–160	Yes
CH ₂ Cl ₂	1 : 1	154–158	Yes
MeCN	1 : 1	155–158	No
Toluene	2 : 1	160–163	Yes

^a Host:guest ratios were determined by ¹H-NMR.

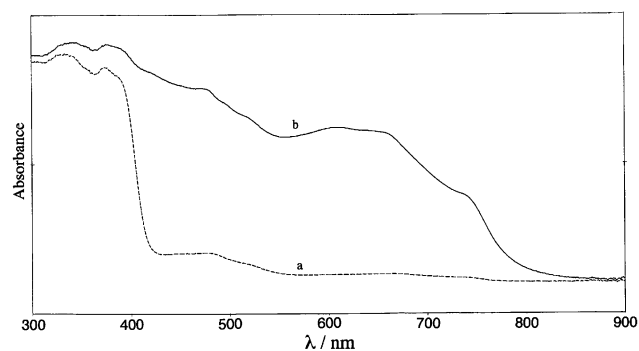
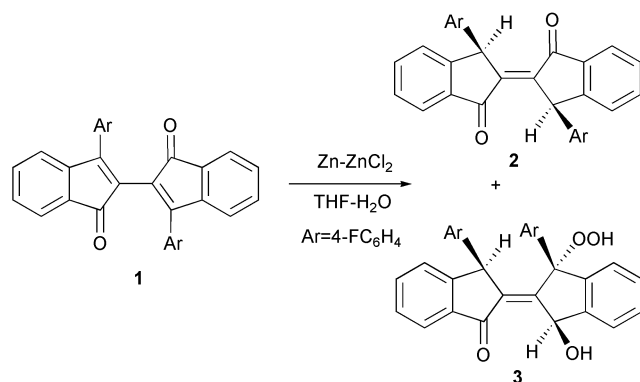


Fig. 1 UV spectra of the 2 : 1 inclusion complex of **3** with toluene a) before and b) after photoirradiation in the solid state.



Scheme 1

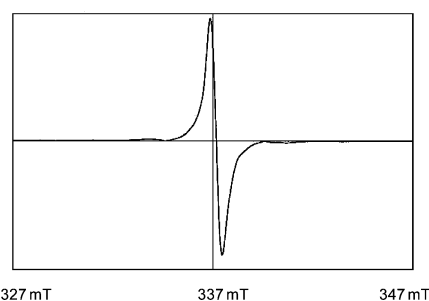


Fig. 2 ESR spectrum of the 2 : 1 toluene complex of **3** after photoirradiation in the solid state.

The $^1\text{H-NMR}$ and IR spectra of the green crystals of the inclusion complexes of **3**, after photoirradiation, were almost identical with those of the colorless crystals before photoirradiation. In the inclusion crystals of **3** with relatively large guest molecules, the central C=C double bond may twist to form biradicals upon photoirradiation in the solid state.

In order to investigate the relationship between the photo-reactivity and the structure, X-ray crystal structure analyses have been carried out for compounds, **3**-MeOH, **3**-MeCN, and **3**-CH₂Cl₂.[‡] The molecular structures of **3** and molecular packing in crystals of **3**-MeOH, **3**-MeCN, and **3**-CH₂Cl₂ are similar to each other. The two indene rings of **3** make an angle of 20.2(1)–27.0(1)°, and the peroxy O–O bond distance is 1.447(2)–1.454(3) Å. There is an intramolecular hydrogen bond between the hydroxy and keto groups of **3** (the O5 and O6 atoms in Fig. 3). There is also intermolecular hydrogen bonding between the peroxy and hydroxy groups, which form zigzag chains along the *b* axis (Fig. 4). The host molecules **3** forms a ladder structure, and the guest molecules accommodated show orientational disorder and/or large atomic displacement parameters. There is a tendency that the larger the size of the guest molecule (larger the volume of asymmetric unit), the longer the crystal *b* axis, *i.e.* 11.939(3), 11.972(1), and 12.138(3) Å, for **3**-MeOH, **3**-MeCN, and **3**-CH₂Cl₂, respectively. The photo-

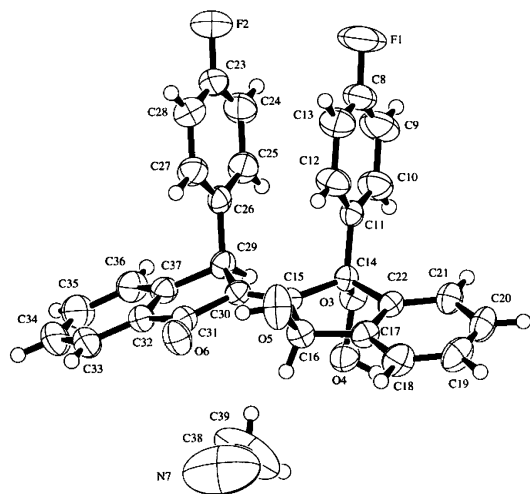


Fig. 3 Molecular structure of **3**-MeCN.

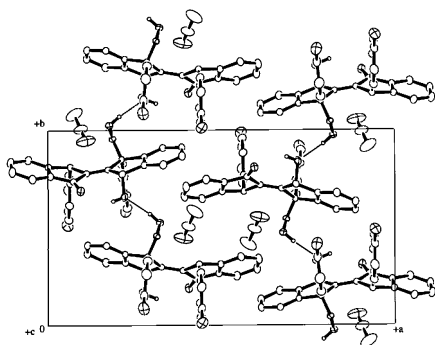


Fig. 4 Crystal structure of **3**-MeCN, with thin lines indicating intermolecular hydrogen bonding.

stability of **3**-MeOH and **3**-MeCN may be due to the shrinkage of the ladder structure in the crystals. Photochromism of these inclusion compounds may require enough flexible space to allow the conformational change of the biradical formed from **3** by irradiation.

In conclusion, we have discovered a novel hydroperoxybiindenylidene (**3**) which shows guest-dependent photochromism and photomagnetism in inclusion crystals. Further detailed studies of the mechanism of the photochromism of the inclusion crystals of **3** are in progress.

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Notes and references

[†] *Synthesis of 2 and 3*: A mixture of **1** (5.0 g, 11.2 mmol), Zn powder (20 g) and ZnCl₂ (1.5 g) in 10% aqueous THF (50 ml) was stirred for 10 min at room temperature. After removal of Zn powder by filtration, the filtrate was extracted with toluene. The toluene solution was washed with dil. HCl and then water, dried over MgSO₄, and evaporated *in vacuo* to give a crude product. Recrystallization of the crude product from AcOEt afforded a mixture of yellow crystals of **2** (1.1 g, 22% yield) and colorless crystals of **2**: 1 inclusion crystals of **3** with AcOEt, which, upon heating *in vacuo*, gave pure **3** as white powder (0.37 g, 7% yield). **2**: yellow prisms. Mp 205–207 °C. IR: 1691 (C=O), 1597 (C=C) cm⁻¹. UV: λ/nm (ϵ) 301 (24000). $^1\text{H-NMR}$: δ 5.80 (2H, s, CH), 6.91–7.79 (16H, m, Ar). Anal. calc. for C₃₀H₁₈F₂O₂: C, 80.35; H, 4.05. Found: C, 80.34; H, 4.11%. **3**: White powder. Mp 169–171 °C. IR: 3236 (OH), 1686 (C=O), 1600 (C=C) cm⁻¹. UV: λ/nm (ϵ) 282 (24800). $^1\text{H-NMR}$: δ 5.28 (1H, d, *J* = 3.5 Hz, OH), 5.51 (1H, s, CH), 6.29 (1H, d, *J* = 3.5 Hz, CH), 6.51–6.66 (4H, m, Ar), 7.62 (1H, s, OOH), 7.01–7.92 (12H, m, Ar). Anal. calc. For C₃₀H₂₀F₂O₄: C, 74.68; H, 4.18. Found: C, 74.71; H, 4.27%.

[‡] The X-ray intensities were measured on a Rigaku AFC-7R four-circle diffractometer up to $2\theta(\text{MoK}\alpha) = 50^\circ$. Crystal data of **3**-MeOH: C₃₁H₂₄F₂O₅, *Mr* = 514.52, monoclinic, space group *P2₁/n*, *a* = 18.717(5), *b* = 11.939(3), *c* = 11.695(3) Å, β = 98.51(2)°, *V* = 2584.6(12) Å³, *Z* = 4, *D_x* = 1.322 Mg m⁻³, *R*(*F*) = 0.056. Crystal data of **3**-MeCN: C₃₂H₂₃F₂NO₄, *Mr* = 523.53, monoclinic, space group *P2₁/n*, *a* = 21.239(1), *b* = 11.972(1), *c* = 10.217(1) Å, β = 92.746(8)°, *V* = 2594.9(4) Å³, *Z* = 4, *D_x* = 1.340 Mg m⁻³, *R*(*F*) = 0.045. Crystal data of **3**-CH₂Cl₂: C₃₁H₂₂Cl₂F₂O₄, *Mr* = 567.42, monoclinic, space group *P2₁/n*, *a* = 21.462(4), *b* = 12.138(3), *c* = 10.296(3) Å, β = 93.23(2)°, *V* = 2677.9(11) Å³, *Z* = 4, *D_x* = 1.407 Mg m⁻³, *R*(*F*) = 0.052. CCDC 209591–209593. See <http://www.rsc.org/suppdata/cc/b3/b305416k/> for crystallographic data in .cif or other electronic format.

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