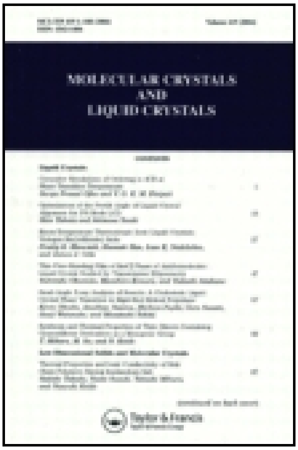

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Triplet Biradicals that are Stable in Crystals

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TRIPLET BIRADICALS THAT ARE STABLE IN CRYSTALS

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Abstract Three *trans-syn-* 3,3'-diaryl-2,2'-biindenylidene-1,1'-diones (**2a-c**) showed sharp photochromic phenomena in their crystalline forms. By exposure to sunlight, **2a-c** were converted to stable biradicals (**3a-c**). Although *N,N'*-dimethyl indigo (**6**) has an almost planar structure, **6** in its 1:1 inclusion crystal with the host 1,1,6,6-tetraphenyl-2,4-hexadiyne-1,6-diol (**7**) was found to have a twisted structure of dihedral angle 42.6° between the two rings.

Keywords: Triplet Biradical, Photochromic Phenomena, Inclusion Crystal, N,N'-Dimethyl Indigo

INTRODUCTION

Isolation of stable triplet biradicals is an interesting research subject. Triplet biradicals generated in crystals are expected to be stabilized because the crowded molecular assembly in the crystal may prevent intersystem crossing of the triplet to the singlet.

RESULTS AND DISCUSSION

Reduction of biindenyl (**1a-d**) with Zn-$ZnCl_2$ reagent[1] gave the corresponding *trans-syn-*3,3'-diaryl-2,2'-biindenylidene-1,1'-dione (**2a-d**) as yellow needles. For example, treatment of **1a** (3 g) with Zn-powder (6 g) and $ZnCl_2$ (1 g) in 10% aqueous THF (30 ml) under stirring for 30 min at room temperature gave **2a** in 45% yield. The yellow needles of **2a** were turned to reddish purple crystals on exposure to sunlight for a short time. In the dark, the reddish purple crystals were returned to the yellow crystals. Irradiation of **2a** in solution by a high pressure Hg-lamp, however, gave its *cis-anti* isomer (**5a**) quantitatively. The structures of **2a** and **5a** were elucidated by X-ray crystal structure analyses. In an ESR spectrum, the reddish purple crystals of **2a** showed strong signals which are assignable to a triplet biradical such as shown as **3a** (D=13.78G, E=1.377G, g_{xx}=2.0026, g_{yy}=2.0027, g_{zz}=2.0030). The data suggest that the distance between the two odd electrons in **3a** is approximately 12.6 Å. The biradical **3a** is stable with a half-life of about one hour, although **3a** is thermally labile and returned to **2a** immediately upon heating at 60 °C.

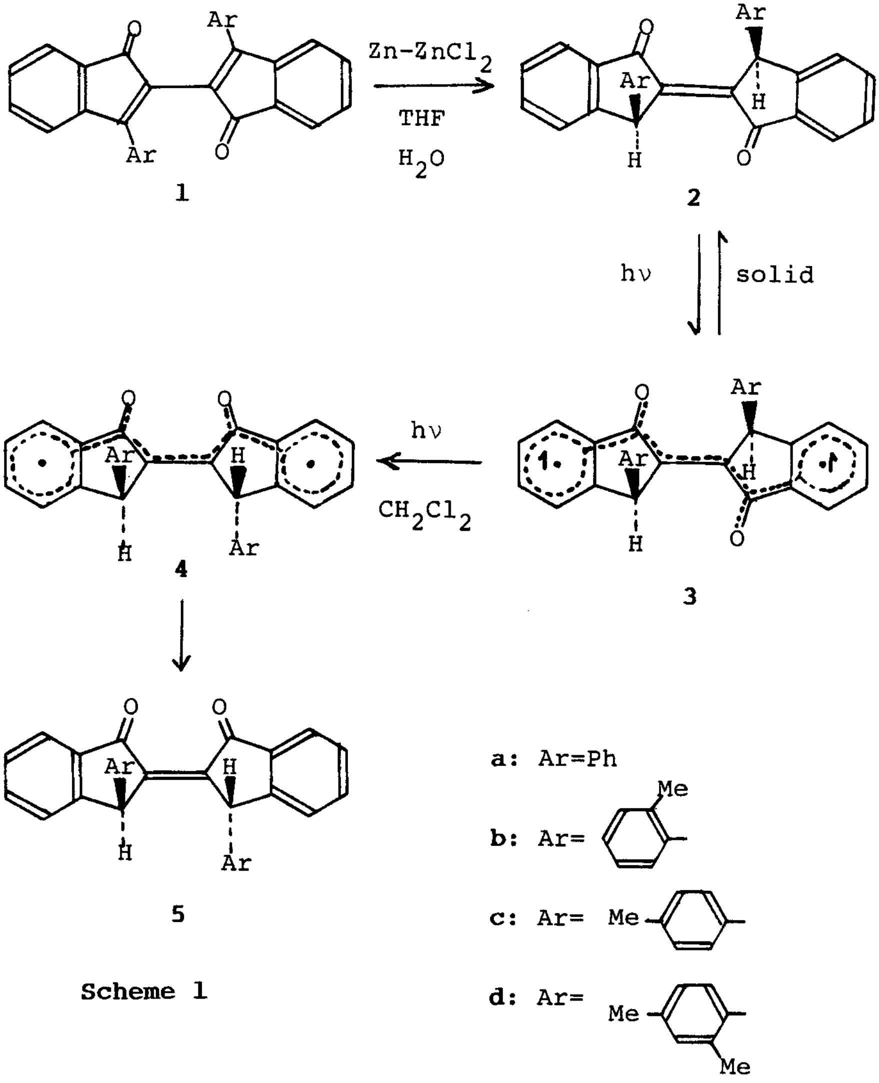
Similarly, **2b** and **2c** showed photochromism, and gave the stable triplet biradicals **3b** and **3c**, respectively. The stability of **3a-c** is probably due to a restricted rotation around the single bond binding the two indane rings in the crystal, because photoirradiation of **2a-c** in solution gave the corresponding *cis-anti* isomer (**5a-c**) (Scheme 1).

Nevertheless, **2d** did not show the photochromic phenomenon. X-ray crystal structure analysis showed clear structural difference between **2d** and **2a-c**. In the crystals of **2a-c**, biindenyl groups are arranged nearly parallel to each other. In **2d**, however, the biindenyl groups are arranged perpendicular to each other. An electronic interaction between the biindenyl groups might be a source of the stabilization of **3a-c**.

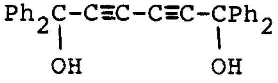
A nitrogen analogue of **2**, *N,N'*-dimethyl indigo (**6**) is expected to show photochromism similar to **2a-c**, but it is a photostable compound. Interestingly, however, **6** in the 1:1 inclusion crystal (**8**) with the host 1,1,6,6-tetraphenyl-2,4-hexadiyne-1,6-diol (**7**) was found to have a twisted structure, with a dihedral angle of 43° between the two rings, even though **6** itself has a coplanar structure. The twisted structure was also proven by measurement of a solid state UV spectrum of **8**, showing absorption bands of the twisted **6** (615 and 790 nm) at longer wavelengths than **6** itself (570 and 720 nm).

REFERENCES

1. F. Toda and K. Iida, Chem. Lett., **1978**, 695; F. Toda, K. Tanaka, and H. Tange, J. Chem. Soc. Perkin Trans. 1 **1989**, 1555; K. Tanaka, S. Kishigami, and F. Toda, J. Org. Chem., **55**, 2981 (1990).

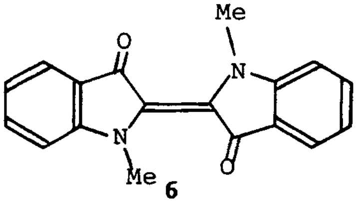


Scheme 1



$$\mathrm{Ph_2C(OH)\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}C(OH)Ph_2}$$

7



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