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Unexpected cleavage and formation of C–C bonds by the nitration of 2,2'-biindanyl-1,1',3,3'-tetraone

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A novel compound, triindanylhexaone, is formed unexpectedly as a major product from the nitration of 2,2′-biindanyl-1,1′,3,3′-tetraone. The structure was clearly established by X-ray crystallography. The reaction mechanism is interpreted as involving an oxidation-induced radical addition.

Keywords: biindanyltetraone, nitration, radical addition, oxidation

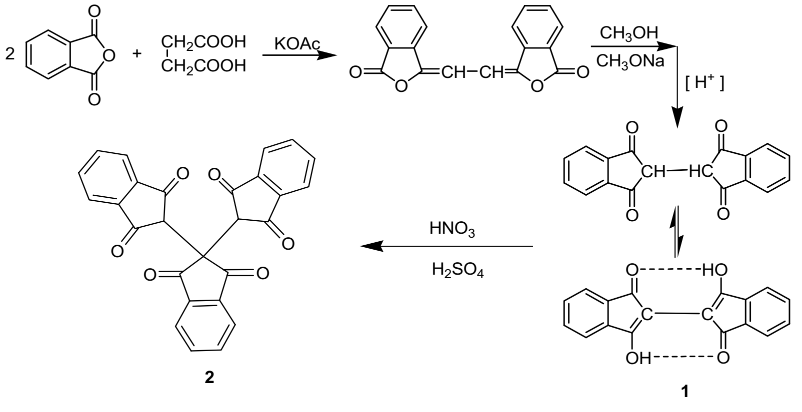
Photochromic compounds continue to attract considerable attention in view of their general applicability in optical information storage materials or switching devices.[1] Among many types of photochromic compounds, the biindenylidene derivatives, first investigated by Toda and coworkers in 1992, are unusual in that they simultaneously undergo photochromism in the crystalline state and generate radicals.[2] In our previous work,[3-5] we developed a novel approach to prepare a series of photochromic 3,3'-dialkyl biindenylidenedione derivatives, proposed the mechanisms of the reactions and the photomagnetism and presented the photochemical properties of the compounds in the crystalline state. In order to enlarge the conjugated system of this kind of compound and therefore enhance the photochromism and photomagnetism, we are interested in the nitration of 2,2'-biindanyl-1,1',3,3'-tetraone (**1**, Scheme 1). During the process, an unexpected product, the triindanylhexaone (**2**), was obtained and its structure was clearly established by X-ray crystallography.

2,2'-Biindanyl-1,1',3,3'-tetraone (**1**) was prepared as shown in Scheme 1.[6] Compound **1** was dissolved in concentrated sulfuric acid at 0°C, and concentrated nitric acid (69%) was added. After stirring at room temperature for 24 h and work-up, **2** was obtained in 24% yield as the major product and the byproducts were rather complex, showing a long line on TLC. When similar procedure was carried out without addition of concentrated nitric acid, compound **1** remained unchanged. Therefore, it was proved that the addition of concentrated nitric acid induced the formation of compound **2**. Since it was reported in our previous work that some derivatives of compound **1** could be induced to form biradicals by light[4,5] and the biradical **B** (Scheme 3) was stable for more than one year in darkness at room temperature, the following mechanism (Scheme 2) was proposed for the unexpected production of compound **2**.

On oxidation by HNO_3, compound **1B** lost two hydrogen radicals and the biradical **3B** (Scheme 2), similar in structure to the stable biradical **B** (Scheme 3), which was also proposed to be a relatively stable intermediate, was generated. Then, **3A**[7] and **4**, produced from **3B** and **1A** respectively, underwent a free radical addition. Due to a steric hindrance effect, only one equivalent of **4** was added to **3A** producing the free radical **5**, which was further quenched to give the product **2**.

The mechanism provides us with further understanding of the previously reported photochromic and photomagnetic properties[3-5] of **A** (Scheme 3) by comparing with its precursor **1B** which does not exhibit photochromism or photomagnetism. In compound **1B** (Scheme 2), oxygen atoms are strongly tied by hydrogen bonds and will not be oxidised to radicals until hydrogen bonds are broken under vigorous conditions. In compound **A** (Scheme 3), oxygen atoms are free to form radicals, since the presence of the R group prevents the formation of similar hydrogen bonds. Compound **1A** (Scheme 2) can be cleaved to form radical **4** which is stabilised by the two adjacent carbonyl groups. However, a similar procedure cannot happen to biradical **B** (Scheme 3), since the resulting carbene **C** is not stable enough. In conclusion, the presence of the R group facilitates the formation of biradical **B** and prevents **B** from decomposing, and therefore supported the photochromic and photomagnetic behaviour of **A**.

The structure of **2** was clearly established by a single-crystal X-ray diffraction as shown in Fig. 1. The planes of C1–C2–C7–C8–C9 and C1A–C2A–C7A–C8A–C9A are almost vertical to each other (99.8°), and they show equal dihedral angles to the plane C10–C11–C12–C12A–C11A (63.8°). The crystal packing is shown as regular alternant planes and layers (Fig. 2).



Scheme 1 Unexpected formation of the target compound **2**.

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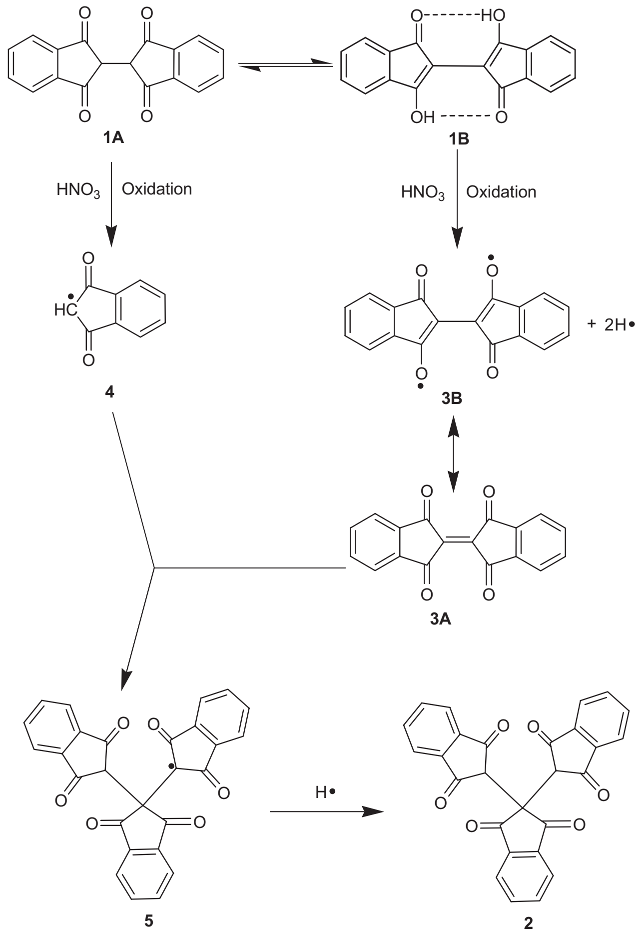
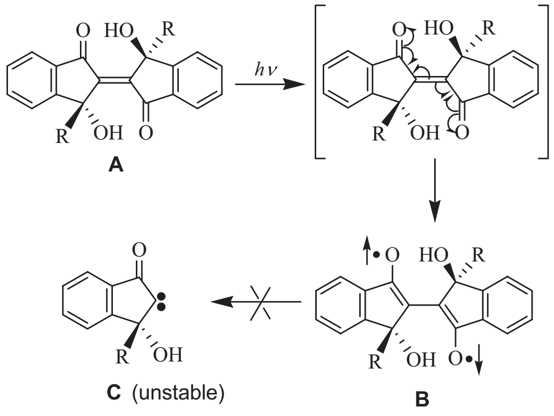


Scheme 2 Reaction mechanism.



Scheme 3

Experimental

Melting points were determined with a Yanagimoto MP-35 melting point apparatus and were uncorrected. The NMR spectra were recorded with a Bruker AV300 spectrometer, using tetramethylsilane as the internal standard. Coupling constants are given in Hertz. The Mass spectra were recorded on a Thermo Finnigan LCQAdvantage spectrometer in ESI mode, I Spray Voltage 4.8 kV. A Yamaco CHN corder MT-3 apparatus was used for elemental analysis. X-ray crystallographic analysis was performed on a Bruker SMART 1000 diffractometer.

2,2'-Biindanyl-1,1',3,3'-tetraone.[6] Phthalic anhydride (25.0 g, 0.169 mol) and succinic acid (25.0 g, 0.212 mol) were heated to melting under stirring, and anhydrous potassium acetate (6.5 g) was added. The reaction mixture was stirred at 210°C for 2 h, and then cooled to 100°C. Hot water (100 ml) was added and the resulting mixture was stirred at 100°C for another hour. The resulting mixture was filtered and the solid was dried to get 14.7 g of a brick-red solid. The solid was suspended in methanol (50 ml), and sodium methoxide solution {prepared from sodium (3.5 g) and methanol (50 ml)} was added with stirring. The mixture was refluxed for 1 h, cooled, and filtered. The resulting black solid was boiled in water for 0.5 h and filtered. The filtrate was acidified to pH 3, and filtered to get purple solid. The purple solid was recrystallised from nitrobenzene and washed with ethanol to get 6.2 g of black needles, yield 23.5%. ^{1}H NMR (300 MHz, CDCl$_3$) δ 14.60 (s, 2H), 7.33–7.30 (m, 8H); MS (ESI) *m/z* 289 [M-H]$^-$; Anal. Calcd for $C_{18}H_{10}O_4$: C 74.5, H 3.5. Found: C 74.2, H 3.7.

The triindanylhexaone 2,2'-Biindanyl-1,1',3,3'-tetraone[6] (0.5 g) was dissolved in concentrated sulfuric acid (2 ml) at 0°C and concentrated nitric acid (69%) (0.3 ml) was added dropwise. The resulting solution was stirred at room temperature for 24 h, poured into ice water, and filtered. The residue was washed thoroughly with cold water, dried, and subjected to silica gel chromatography with elution by 10% methanol in chloroform. The appropriate fractions, as determined by TLC, were collected and the solvent was evaporated slowly to give 0.19 g **2** as colourless crystals: m.p. 249–250°C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.95–7.82 (m, 12H), 5.07 (s, 2H); MS (ESI) *m/z* 433 [M-H]$^-$; Anal. Calcd for $C_{27}H_{14}O_6$: C 74.65, H 3.25. Found: C 74.3, H 3.5. Crystal data for **2**. $C_{27}H_{14}O_6$, $M = 434.38$, orthorhombic, a = 12.586(3), b = 10.601(3), c = 15.721(4) Å, $\alpha = \gamma = 90°$, $\beta = 94.857(4)°$, U = 2090.0(9) Å^3, T = 294(2) K, space group *C2/c*, Z = 4, d = 1.380 Mg/m^3, μ(Mo-K$_\alpha$) = 0.098 mm^{-1}, 5838 reflections measured, 2173 unique (R_{int} = 0.0358), which were used in calculations. CCDC 299396.

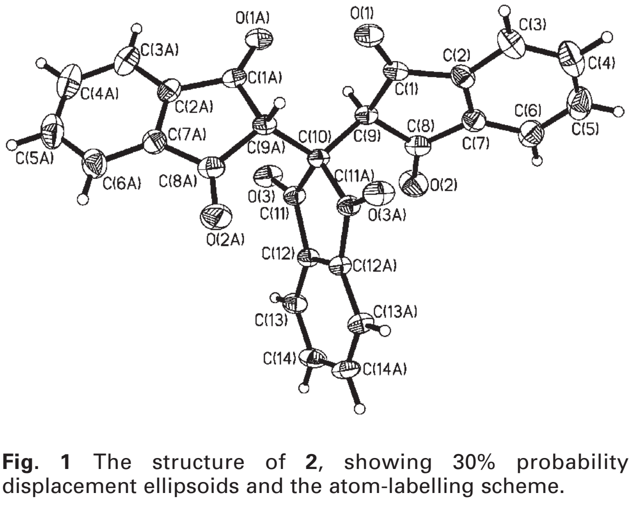


Fig. 1 The structure of **2**, showing 30% probability displacement ellipsoids and the atom-labelling scheme.

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CCDC 299396 contains the supplementary crystallographic data and collection parameters for **2**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request.cif.

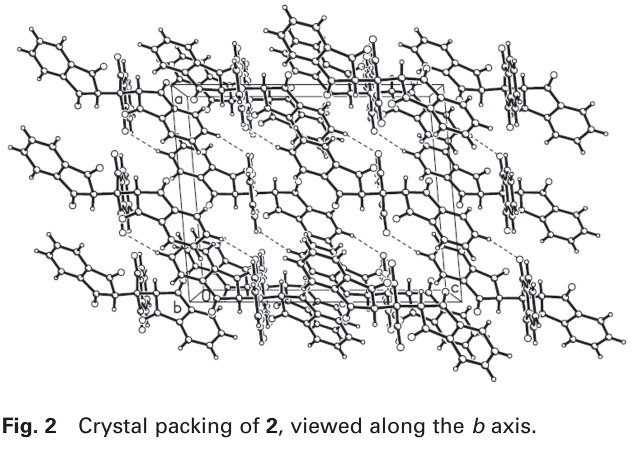

Fig. 2 Crystal packing of **2**, viewed along the *b* axis.

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