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An unexpected dimerisation in ambient daylight

M. John Plater*, Matin Momeni and William T.A. Harrison

Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen AB24 3UE, UK

Base catalysed condensation of indan-1,3-dione with 2-naphthaldehyde gave a mixture of the expected products 2-naphthalen-2-ylmethylene-indan-1,3-dione and a four membered ring dimer resulting from a daylight catalysed photochemical dimerisation.

Keywords: dimerisation, Knoevenagel, ambient daylight

In the course of our exploratory studies on the condensation reactions of cyclic β-dicarbonyl compounds with aldehydes for Knoevenagel-Hetero-Diels-Alder reactions[1] we attempted the preparation of 2-naphthalen-2-ylmethylene-indan-1,3-dione **3**[2-3] from indan-1,3-dione **1** and 2-naphthaldehyde **2**. Indan-1,3-dione **1** readily undergoes Knoevenagel condensation reactions catalysed by acid or base.[4-9] Treatment with aqueous ethanolic alkali at room temperature for 3 days gave a single product by TLC analysis. However the NMR data were much more complicated than that expected for product **3**. Product **3** should have 20 peaks in the ^{13}C spectrum and two carbonyl groups. This compound, or mixture as we did not know at the time, had 33 peaks in the ^{13}C spectrum. There were 3 carbonyl groups and peaks at 51.2 and 59.8(q) ppm. This puzzle was solved by selecting a crystal and obtaining a single crystal structure analysis (Fig. 1). This analysis showed that the crystal consisted of a dimer **4** of two of the monomer units **3**.

The complete $C_{40}H_{24}O_4$ molecule is generated by crystallographic inversion symmetry and therefore the central four-membered C8/C10/C8^i/C10^i (i = 1–*x*, 1–*y*, 1–*z*) ring is perfectly flat. The C8–C10 and C8–C10^i bond distances are 1.588 (13) Å and 1.601 (14) Å, respectively, which are similar to those seen in some other sterically strained substituted cyclobutane rings.[10,11] The C8–C10–C8^i and C10–C8–C10^i bond angles are 92.4 (7)° and 87.6 (7)°, respectively. The dihedral angle between the indan-1,3-dione and naphthalene mean ring planes is 64.5 (2)°. The four-membered ring makes dihedral angles of 84.2 (5)° and 85.2 (4)° with the indan-1,3-dione and naphthalene mean planes, respectively, indicating that both the pendant ring systems are almost perpendicular to the central ring. Otherwise, the geometrical parameters of the molecule of **4** may be regarded as normal.

The dimer has symmetry and would possess 16 ^{13}C peaks. The monomer **3** would have 20 peaks giving a total of 36 peaks in the ^{13}C spectrum. Three peaks are therefore overlapping in the mixture. The dimer explains pertinent aspects of the observed data. Namely it has two aliphatic carbons, one of which is a quaternary carbon. The monomer has two carbonyl groups and the dimer has just one explaining the three observed carbonyl peaks.

We considered that the dimer **4** must form from monomer **3** by a photochemical cycloaddition reaction. The condensation reaction was therefore performed in a dark room and the product isolated under dark conditions. This gave a yellow product with a much simpler ^{13}C spectrum. Only 19 peaks were present and just two carbonyl groups. These peaks were apparent in the mixture and were manually subtracted to obtain the ^{13}C spectrum of the dimer. Monomer **3** has two IR carbonyl stretches at 1720 and 1686 cm^{-1} owing to symmetric and asymmetric stretches. Interestingly 1,3-indandione also has two carbonyl stretches at 1715 and 1734 cm^{-1}. A concentrated solution of the monomer was placed in a sample vial and irradiated overhead with a visible lamp for a few hours. The solvent DCM was replaced periodically. As the solution became nearly dry both white crystals and yellow crystals could be seen to precipitate from the solution. However when the sample was prepared for NMR analysis it was very difficult to dissolve presumably because of the greater purity.

This reaction is unusual. Photochemical dimerisations would typically require UV light to proceed.[12-14] A previous example is known of a dimerisation in ambient daylight during the formation of a coordination network.[15] The case reported here is only the second example of this type of reaction and it is the first which does not involve a coordination network.

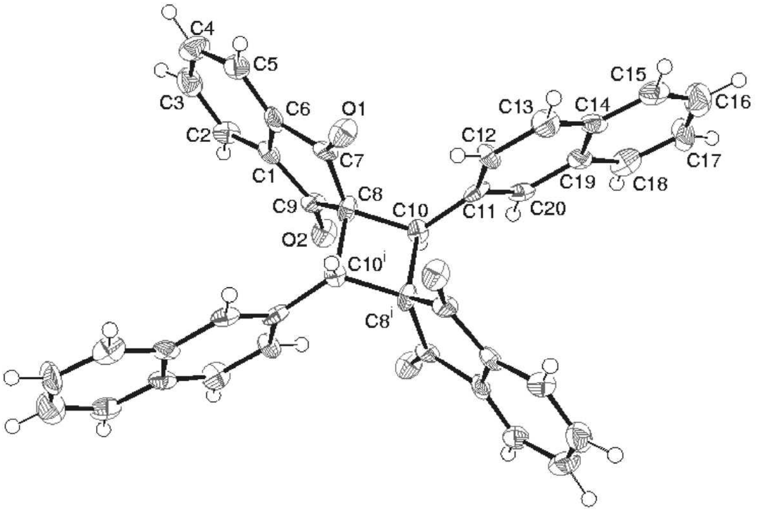

Fig. 1 The molecular structure of **4**, with 50% displacement ellipsoids for the non-hydrogen atoms. Symmetry code i: 1–*x*, 1–*y*, 1–*z*.

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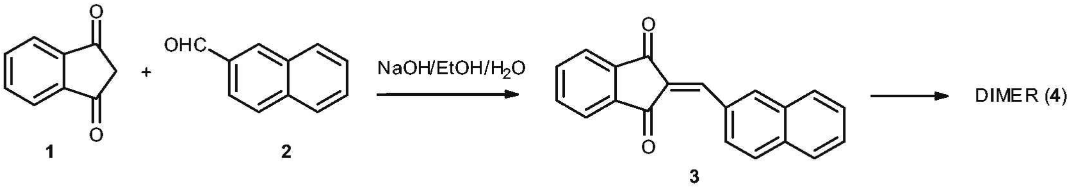
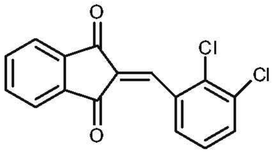
* Correspondent. Email: m.j.plater@abdn.ac.uk

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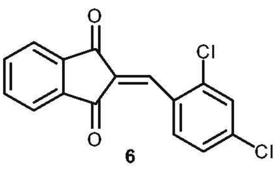
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It was not reported in the original work from two other research groups.[2-3] They appear to have only isolated the monomer possibly because the reactions were typically completed in a shorter time period of one hour in hot acetic acid with H_2SO_4 as catalyst. Their reported melting point of 232 °C is close to ours of 220–223 °C whereas that of the dimer is higher. They did have NMR but did not report NMR data on this compound. Product **3**, which contains a conjugated naphthalene ring, has a long wavelength broad shoulder absorbing at 402 nm in the UV spectrum which must account for the yellow colouration by the absorption of some blue light. The absorption of blue light from natural daylight must lead to the dimer **4** probably via efficient spin-crossover to a triplet state. The efficiency of this reaction is quite remarkable and rare. It is classified as a bimolecular light harvesting system.[16] Systems that can react with daylight or sunlight such as norbornadiene to give strained products have a potential value because catalytic reversal of the reaction on demand would be exothermic.[16]

We prepared two further derivatives **5** and **6** by similar condensation reactions to see if the naphthalene ring was critical to effect a dimerisation reaction. Both are yellow coloured so should absorb some blue light but they lack the longer wavelength shoulder present in stilbene **3**. No dimers were detected in their preparation or on standing in ambient daylight. It is not fully understood why the naphthalene derivative **3** so efficiently undergoes this reaction. Presumably exciplex formation may be involved which is thought to occur in the course of [2 + 2] photochemical dimerisations.[17-21] The larger π-surface area of the naphthalene ring may assist in the formation of exciplexes leading to a dimer.

Experimental

Intensity data were collected on a Rigaku Mercury CCD diffractometer (Mo Kα radiation, $\lambda = 0.71073$ Å) at $T = 93$ K for a twinned crystal using the Twinsolve and Crystal clear programs. The structure was solved by direct methods with SHELXS-97 and refined using SHELXL-97. All the H atoms were geometrically placed and refined as riding. Crystal data: $C_{40}H_{24}O_4$, $M_r = 568.60$, triclinic, P1- (No. 2), $Z = 1$, $a = 7.366$ (6) Å, $b = 9.541$ (7) Å, $c = 10.776$ (9) Å, $\alpha = 96.99$ (5)°, $\beta = 104.59$ (5)°, $\gamma = 97.97$ (5)°, $V = 716.1$ (10) Å^3, $F(000) = 296$, $\rho = 1.319$ g cm^{-3}, $\mu = 0.084$ mm^{-1}, min., max. $\Delta\rho = -0.51, + 0.55$ e Å^{-3}, $R(F) = 0.173$, $wR(F^2) = 0.441$. As well as being twinned, the crystal quality was very poor, which probably correlates with the high residuals. CCDC deposition number: CSD-698301.

UV spectra were recorded on a Perkin-Elmer Lambda 15 UV-VIS spectrometer using DCM as the solvent. IR spectra were recorded on an ATI Mattson FTIR spectrometer. ^{1}H and ^{13}C NMR spectra were obtained at 250 MHz and 62.9 MHz respectively on a Bruker AC 250 spectrometer and at 400 MHz and 100.5 MHz respectively on a Varian 400 spectrometer. Chemical shifts (δ) are given in ppm relative to the residual solvent. Coupling constants (J) are given in Hz. Low resolution mass spectra were obtained using electrospray ionisation on a Finnigan Navigator Mass Spectrometer and accurate mass at the University of Wales, Swansea using CI and EI modes. Aldrich supplied starting chemicals.

Mixture of 2-naphthalen-2-ylmethylene-indan-1,3-dione **3** and *dimer* **4** *(light reaction) General procedure*: Indandione (0.2 g, 1.3 mmol) was added to 2-naphthaldehyde (0.1 g, 0.65 mmol) in a mixture of ethanol and water (20 ml, 4:1) NaOH (10 ml, 5M) was added and the mixture stirred for 72 h at room temperature The mixture was diluted with dil. HCl, extracted with DCM and dried over $MgSO_4$. The product was purified by flash chromatography on silica. Elution with dichloromethane:light petroleum (75:25) gave the title compound mixture (0.15 g, 75%) as a yellow solid. From this mixture a crystal was selected for X-ray single crystal structure determination. λ_{max}(DCM)/nm 370(log ε 3.65) and 400(3.79); ν_{max}(KBr)/cm^{-1} 1716 s, 1648 s, 1586 s, 819 m and 731 m; δ_H (400 MHz; $CDCl_3$) 5.60(2H, s), 7.30–7.36 (m), 7.43–7.63 (m), 7.69–7.72 (m), 7.78–7.84 (m), 7.86–7.92 (m), 7.98–8.06 (m), 8.58–8.60 (1H, dd, $J = 8.4$ and 1.8) and 8.92 (1H, s); δ_C (100.5 MHz; $CDCl_3$) 51.2, 59.8(q), 123.3, 123.5, 126.0, 126.2, 126.7, 127.4, 127.5, 127.7, 128.0, 128.4, 129.0, 129.1(q), 129.2, 129.2, 129.8, 130.9(q), 132.1(q), 132.6(q), 132.7(q), 132.9(q), 135.2, 135.4,135.5(q), 135.8, 136.8, 140.1(q), 142.1(q), 142.6(q), 147.1, 189.2(q), 190.4(q) and 199.0(q) (2 peaks are missing); m/z (ES) 285 ($M^+ + H^+$) and 569 ($M^+ + H^+$, 100%)

2-Naphthalen-2-ylmethylene-indan-1,3-dione **3** *(dark reaction)*
The reaction was performed in the dark to give the title compound (0.16 g, 80%) m.p. 220–223 °C (lit. 232 °C[2], 228–229 °C[3]) which was stored in the dark; λ_{max}(DCM)/nm 355 (log ε 4.2) and 402(broad sh) (4.0); ν_{max}(KBr)/cm^{-1} 1720 s, 1686 s, 1602 m, 1587 m, 1460 s and 1378 s; δ_H (400 MHz; $CDCl_3$) 7.45–7.62(2H, m), 7.80–8.10(8H, m), 8.6 (1H, d, $J = 8.4$) and 8.86(1H, s); δ_C (100.5 MHz; $CDCl_3$) 123.3, 126.8, 127.7, 128.4, 129.0, 129.1, 129.3, 129.8, 130.9, 133.0, 135.2, 135.4, 135.5, 136.8, 140.1, 142.6, 147.1, 189.2 and 190.4 (2 resonances are overlapping. Peak 136.8 is twice as intense); m/z 283.0755 ($M + H^+$), $C_{20}H_{13}O_2$ requires 283.0754

Data for the dimer by subtraction: δ_C (100.5 MHz; $CDCl_3$) 51.2, 59.8(q), 123.5, 126.0, 126.2, 127.4, 128.0, 129.2, 132.1(q), 132.6(q), 132.7(q), 135.8, 142.1(q), and 199.0(q)(2 peaks are missing)

Mixture irradiation: A mixture of the monomer **3** and dimer **4** dissolved in dichloromethane was irradiated in a sample vial under a visible lamp for 5 h. The solvent evaporates and was periodically replaced to maintain a concentrated solution. Product precipitates during the reaction. The formation of white crystals from the yellow solid was easily observed, m.p. > 240 °C.

2-(2,3-Dichlorobenzylidene)indan-1,3-dione **5**: The title compound was obtained as a yellow solid (0.20 g, 68%) m.p. 177–179 °C (from dichloromethane:light petroleum) λ_{max}(DCM)/nm 350 (log ε 2.4); ν_{max}(KBr)/cm^{-1} 1728 s, 1696 s, 1624 m, 1588 m, 1448 m, 1414 m, 1225 s, 732 s and 582w; δ_H (400 MHz; $CDCl_3$) 7.30 (1H, m), 7.58 (1H, d, $J = 6.4$), 7.81 (2H, m), 8.0 (2H, d, $J = 8.4$), 8.23 (1H, s), 8.30 (1H, d, $J = 6.4$); δ_C (100.5 MHz; $CDCl_3$) 123.6, 123.6, 126.9, 131.3, 131.5, 132.8, 133.4, 133.6, 134.7, 135.7, 135.7, 140.3, 141.4, 142.4, 188.2 and 189.1; m/z (ES) 302 (M^+, 100%) m/z (ES) 301.9907 (M^+, 100%) $C_{16}H_8O_2Cl_2$ requires 301.9907

2-(2,4-Dichlorobenzylidene)indan-1,3-dione **6**:[7] The title compound was obtained as a yellow solid (0.22 g, 73%) m.p. 184–187 °C (from dichloromethane:light petroleum) λ_{max}(DCM)/nm 350 (log ε 2.4); ν_{max}(KBr)/cm^{-1} 1730 s, 1693 s, 1619w, 1580w, 1463 s, 1290 s, 1243 m, 1151 m, 1106 m, 1017 m, 1048 m, 1075 m, 777w, 733vs and 681w; δ_H (400 MHz; $CDCl_3$) 7.22 (1H, s), 7.33 (1H, d, $J = 6.4$), 7.81 (2H, m), 8.00 (2H, d, $J = 8.4$), 8.23 (1H, s) and 8.30 (1H, d, $J = 6.4$); δ_C (100.5 MHz; $CDCl_3$) 123.5, 123.6, 127.1, 129.1, 129.8, 130.7, 134.5, 135.6, 135.7, 138.2, 139.0, 140.2, 140.5, 142.4, 188.5 and 189.3; m/z (ES) 302.9976 ($M^+ + H^+$) $C_{16}H_9O_2Cl_2$ requires 302.9974

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