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CRYSTAL STRUCTURE AND SOLID STATE PHOTOREACTIVITY OF 2,5-DIBENZYLIDENECYCLOPENT-3-ENE-1-ONE AND ITS TETRACHLORO DERIVATIVE

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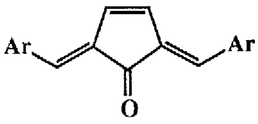
Abstract: The synthesis and crystal structure of a molecule designed to undergo triple solid state photodimerisation are described. The alternate single photodimerisation actually observed is discussed.

While the literature on topochemical [2+2] photodimerisations is extensive,[1,2] not much is known about double [2+2] cycloadditions of crystalline diolefinic compounds. The dimerisation of *bis*(3,4-dichlorostyryl)ketone[3], **3b**, and of 1,4-dicinnamoylbenzene[4,5] are perhaps among the few reported examples. This communication reports our initial approaches towards the construction of a crystal structure, represented conceptually in Figure 1, where three double bonds in a single molecule are aligned for topochemical photodimerisation. If formed, such dimers would have novel structures with unusual symmetries. Additionally, it is possible that the stacked structures of such monomers have interesting electronic properties.[6]

Crystal engineering of 2,5-dibenzylidenecyclopent-3-ene-1-one, **1a**,which was identified as a target structure,



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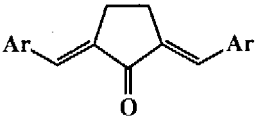

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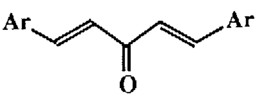

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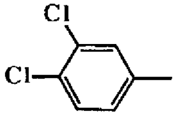
$Ar_1 = C_6H_5$

Ar_2 =



a: $Ar = Ar_1$

b: $Ar = Ar_2$

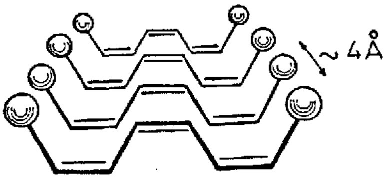


Figure 1. Conceptual representation of stacking leading to alignment of three reactive bonds.

can in principle proceed from either **2a** or **3a**. Cyclopentanone **2a** is planar in the crystal and potentially photoreactive molecules are related by a *ca.* 5.7 Å translation such that non-parallel double bonds are at a distance of 3.93 Å[7].The four out-of-plane methylene hydrogens in **2a** are replaced by the two in-plane olefinic hydrogens of **1a**. It was felt that such a change would perhaps optimize molecular stacking interactions, thereby approximating Figure 1 closely[8]. Alternatively, we argued that the crystal structures of **1a** and **1b** should be closely related to those of ketones **3a** and **3b**. While **3a** adopts a non-4Å structure[9] and is photoreactive when taken in KBr pellets[9], the early work of Schmidt and Green has shown that in crystalline **3b**, molecules stack with a 4 Å repeat such that [2+2] cycloaddition to yield a mirror-symmetrical tricyclic dimer is possible[3].

Accordingly, triene **1a** was prepared from **2a** in 65% overall yield by bromination with NBS/CCl_4 to give a mixture of diastereomeric dibromides (m.p.'s 131°C, 135°C) followed by debromination with Zn/MeOH. Recrystallisation from Et_2O or MeOH gave a pale yellow solid (m.p. 147°C; IR (KBr) 3050, 1720, 1610, 1240, 1080, 980, 920, 820 cm^{-1}; NMR(CDC^{13}) 7.3-7.7 (m); ^{13}C NMR($CDCl_3$) ppm 194.1(>C=O), 135.7, 134.4, 133.2, 130.1, 129.3, 129.1, 128.9).[10]

In the crystal[11], molecules of **1a** are bisected by two-fold symmetry axes at $x=0$, $z = \pm 0.25$ passing through the carbonyl groups. Figure 2 shows that potentially photoreactive molecules are stacked across centres

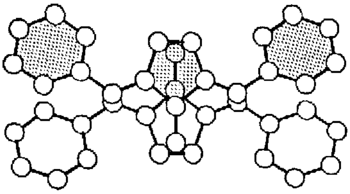
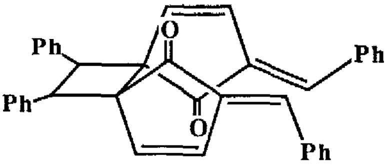
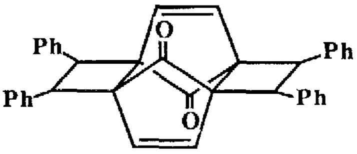


Figure 2. Overlap of adjacent molecules along the stacking direction in the crystal structure of **1a**.

of inversion rather than translated as shown in Figure 1. Nearest double bonds are non-parallel but at a distance of 3.92 Å from one another and photodimerisation can, in principle, involve two such pairs of double bonds to give compound **5** in a manner similar to the 1,4- dicinnamoylbenzene reaction. In practice, however, irradiation of crystalline **1a** at room temperature using sunlight or an Hg lamp (5% Ph_2CO/benzene filter) resulted in conversion to mostly a single product **4** which was separated by preparative tlc (silica gel, 5% EtOAc/hexane).



4



5

Dimer **4** was identified spectroscopically IR(KBr) 3050, 2925, 1720, 1620, 1020 cm^{-1}; NMR ($CDCl_3$) 4.72 (s,2H,cyclobutane), 6.94-7.48(m,26H); ^{13}C NMR ($CDCl_3$) 203.6, 138.0,137.9, 135.4,134.8, 131.5, 129.9, 129.3, 129.2, 128.8, 128.6, 127.4, 127.2, 62.0, 45.9 ppm;^{13}C NMR (off-resonance) 62.1, 46.9, 45.0 ppm. A similar product was not recovered in high yields in the case of 1,4-dicinnamoylbenzene since the second cycloaddition reaction was presumably easy. In the present case, the strained ring junctions in **5** probably hinder the **4**-->**5** conversion. Even dimer **4** is not very stable in solution, rapidly collapsing to **1a** under ambient conditions and in the mass spectrometer. Molecular mechanics calculations (MM2P) confirm the instability of dimers **4** and **5**. The total energies (difference in energy between minimised structure and ideal structure) for **1a**, **4** and **5** are respectively, 47, 117 and 218 kcal mol^{-1}. Irradiation of crystalline **1a** also results, not unexpectedly, in the formation of a small amount of polymer.[4,5]

The inversion-stacking of molecules in crystalline **1a** is distinct from the conceptualised arrangement in Figure 1 and also from the phenyl-cyclopentanone stacking in **2a**.[7] Attention therefore shifted to the *bis* (3,4-dichlorophenyl)triene **1b** which was expected to adopt a 4 Å structure in accordance with the well-known chloro-rule' for planar polychloro aromatics[14,15]. Triene **1b** (m.p. 197°C ; IR(KBr) 3050,1720, 1620, 1470, 1270, 1180, 1020, 940 cm-1; NMR ($CDCl_3$) 7.15-7.6 (m) was prepared from diene **2b** as described above. Despite several attempts, single crystals could not be obtained. While the solid state photoreaction was again rapid, no dimer was formed. The bulk of the product (>80%) was polymeric while a small amount of 3,4-dichlorobenzoic acid (15%) was recovered as an oxidation by-product. The molecular weight (retention chromatography. THF) of the purified polymer (Soxhlet, cyclohexane) showed the degree of polymerisation to be between 8 and 10. Statistical considerations show that dimer:oligomer ratios decrease dramatically with an increasing number of potentially photoreactive double bonds in the monomer.[5] Given that no dimer could be recovered from the solid state reaction of **1b**, it appears that its crystal structure is different from that of **1a**. An X-ray powder diffractogram (Cu K_{α}) of **1b** showed intense lines corresponding to d-values 3.175, 3.414 and 3.801 Å (van der Waals stacking of molecular layers). Further investigations on the dibenzylidenecyclopentenone family of compounds will therefore undoubtedly prove interesting.

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11. Thin platelets (MeOH) or prisms (Et_2O), almost invariably twinned. Structure solved and refined on one set of data of twinned crystal. **1a**: $C_{19}H_{14}O$, M= 258, monoclinic, C2/c, a = 29.855(9), b = 6.502(4), c =7.696(5) Å, β = 107.78(4)$^{\circ}$,V = 1422.6(1) Å^3, F(000)=544, Z=4, D_c = 1.20 g-cm^{-3}, λ (MoK_{α})=0.71069 Å, μ(MoK_{α}) =0.39 cm^{-1}; 1032 measured I, 677 had $I>1.5\sigma(I)$. Structure solution with SHELXS86[11] and refined anisotropically with SHELX76[11] (hydrogens isotropic), R=0.044 (wR=0.043). Careful examination of the structure factors at convergence did not reveal any discrepancies which would suggest that there was any serious overlap of reflections from the twin. Incidentally, it may be mentioned that the crystal structure analysis of **3a** was equally complex[9] and the problems never fully resolved. It is likely that twinning is not uncommon in this family of compounds.
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