

Photodimerization of Coumarins in the Solid State

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Photochemical dimerization of 7-methoxycoumarin occurs in the solid state to give high yields of a *syn*-head-to-tail dimer although the potentially reactive double bonds are not favourably oriented in the crystal of the monomer.

There is much to be learnt about organic solid state reactions before they can be routinely exploited for molecular transformations.¹ Towards this end we have undertaken systematic crystallographic and photochemical investigations of coumarins in the solid state. Coumarin itself is known to be photostable in the solid state.² It was our intent to see if any of the substituted coumarins would undergo [2 + 2] photodimerization in the solid state owing to favourable orientation of the reactive double bonds brought about by crystal packing.¹

Of the several coumarins examined by us (Table 1) only 7- and 8-methoxycoumarins, as well as 4-chlorocoumarin, underwent photodimerization in the solid state upon u.v. irradiation, yielding 90, 50, and 40% of the dimer, respectively. From an X-ray crystallographic study, we found that the dimer[†] of 7-methoxycoumarin is *syn*-head-to-tail (Figure 1). Much to our surprise, a crystallographic study of the 7-methoxycoumarin monomer[‡] showed that the orientation of

the potentially reactive double bonds of the monomer molecules is not topochemically favourable^{1,4} for dimerization;[‡] the two double bonds are actually rotated by 115° (or 65°) with respect to each other (see Figures 2 and 3). Such an orientation of the double bonds makes it necessary to invoke a mechanism by which the double bonds are brought to a proper orientation before they can participate in dimerization.

The observed high yield of the dimer cannot be accounted for on the basis of orientational point defects.⁵ Glissile edge dislocations providing a means for the translation of one molecule with respect to the other cannot be invoked as the dimer would then be *anti*-head-to-tail rather than the observed *syn*-head-to-tail. A simple rotation of molecules as shown in Figure 3 is difficult to visualize, particularly in view of the high yield of the dimer. A favourable disposition of the monomer molecules can however be brought about by a translation-*cum*-rotation involving a screw dislocation or a screw axis. A (022) <100> type of screw dislocation, with a

Table 1

Compound	Dimerization in the crystalline state
(1) 7-methoxycoumarin ^{a,b}	Yes
(2) 8-methoxycoumarin ^b	Yes
(3) Coumarin ^c	No
(4) 5,7-dimethoxycoumarin ^d	No
(5) 4-methoxycoumarin ^b	No
(6) 7-hydroxycoumarin ^c	No
(7) 4-methyl-7-hydroxycoumarin ^c	No
(8) 4,7-dimethylcoumarin ^b	No
(9) 4-methyl-7-methoxycoumarin ^b	No
(10) 4-chlorocoumarin ^c	Yes

^a The photodimerization of this compound in the solid state had been reported earlier (ref. 3), but systematic studies were not carried out. ^b Crystallised from benzene. ^c Crystallised from ethanol. ^d Crystallised from chloroform.

[†] *Crystal data*: photodimer of 7-methoxycoumarin, orthorhombic, space group *Pbcn*, $a = 14.767(3)$, $b = 12.868(5)$, $c = 18.798(2)$ Å, $Z = 8$. The intensity data were collected on a CAD-4 diffractometer using graphite-monochromated Mo- K_{α} radiation ($\lambda = 0.7107$ Å). The structure was solved by direct methods using Multan-78.⁶ Full-matrix least squares refinement of positional and anisotropic thermal parameters for all non-hydrogen atoms, and isotropic refinement of hydrogen atoms resulted in the final R value of 5.8% for 1715 reflections with $|F_o| \geq 2\sigma(|F_o|)$.

Crystal data: 7-methoxycoumarin, triclinic, space group $P\bar{1}$, $a = 6.83(3)$, $b = 10.672(4)$, $c = 12.660(7)$ Å, $\alpha = 108.19(3)$, $\beta = 95.23(4)$, $\gamma = 95.22(3)^\circ$, $Z = 4$. The direct method programme Multan-80⁷ was used for the structure solution. Karle's recycling operations⁸ in the initial stages were necessary for arriving at the whole structure. The positional and anisotropic refinement of non-hydrogen atoms and isotropic refinement of hydrogen atoms yielded the R value of 6.8% for 1395 reflections with $|F_o| \geq 2\sigma(|F_o|)$. The molecules are packed on either side of the (022) plane as shown in Figure 2, the distance between the planes being ca. 3.6 Å.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

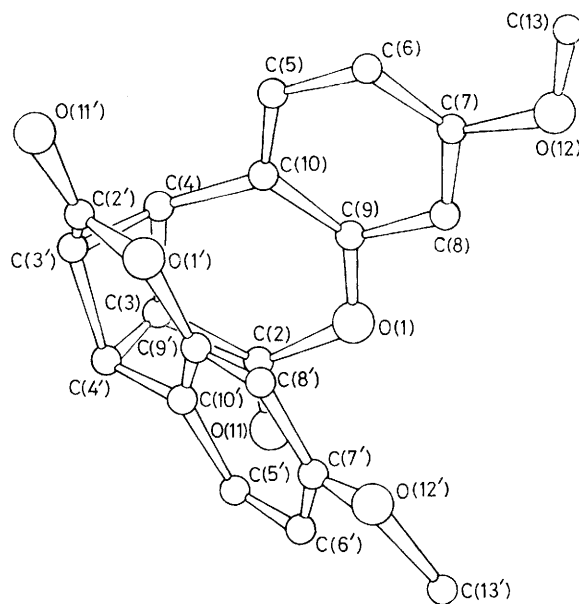


Figure 1. Photodimer of 7-methoxycoumarin; C(3)-C(4)-C(3')-C(4') is the cyclobutane ring.

[‡] X-ray crystallographic studies of the monomers of 8-methoxy- and 4-chloro-coumarins just completed in this laboratory reveal that packing arrangements in these crystals also do not allow favourable orientation of the potentially reactive double bonds for dimerization to occur. The solid state dimerizations reported here appear to be some of the few instances where simple crystal engineering principles (ref. 1) do not seem to hold.

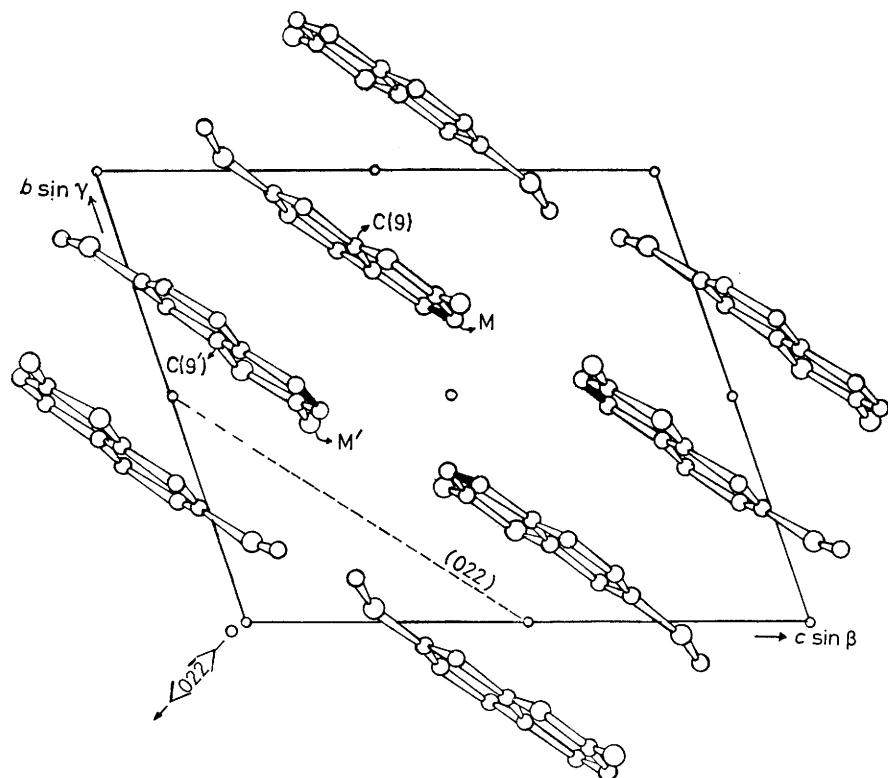


Figure 2. Packing arrangement of monomer molecules of 7-methoxycoumarin (down *a*). The (022) plane and $\langle 0\bar{2}2 \rangle$ directions are indicated. The disposition of two monomer molecules, M and M', looking along C(9)–C(9') direction is shown in Figure 3. Shaded bonds are the potentially reactive double bonds.

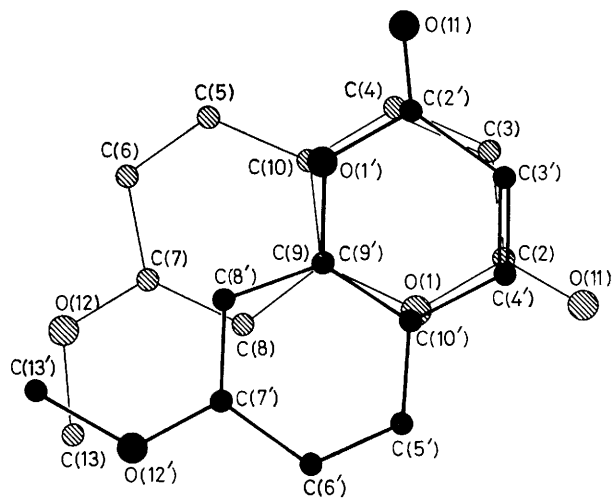


Figure 3. Disposition of the potentially reactive double bonds [C(3)–C(4) and C(3')–C(4')] in the asymmetric unit of 7-methoxycoumarin. It can be seen that the molecule with the C(3')–C(4') bond has to be rotated by 115° (65°) to bring the two potentially reactive double bonds into the proper orientation.

core considerably removed from the reacting molecules, can, in principle, be propagated by the resulting geometry of the dimer. The photostability of compounds (3)–(9) (Table 1) in the solid state is not due to any inherent electronic or steric properties of these molecules as they are all known to dimerize

in solution. It must be attributed to an unfavourable arrangement of these molecules in the crystal lattices both in the macro- and micro-regions.

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