Structural Mimicry and the Photoreactivity of Organic Solids

William Jones,[a] Charis R. Theocharis,[a] John M. Thomas,[a] and Gautam R. Desiraju[b]

[a] *Department of Physical Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EP, U.K.*
[b] *School of Chemistry, University of Hyderabad, P.O. Central University, Hyderabad 500 134, India*

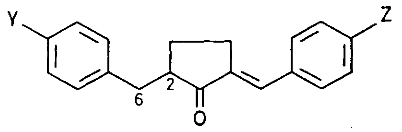
Molecules that are photostable in the solid state can be rendered photoactive if, by burial within crystals of closely analogous monomers, they can be made to mimic the molecular conformation of the latter; this fact is demonstrated for a pair of cyclopentanone derivatives, and the general significance of this result in solid-state synthesis is discussed.

The literature associated with the crystallography of organic molecules reveals firm evidence for the interchangeability of certain substituent groups in the sense that a given class of molecules (*e.g.*, aromatic hydrocarbons) possessing one particular substituent (*e.g.*, a halogen) tends to form solid solutions with other molecules in that class provided they have attached to them a substituent closely similar in size and shape to the first. Thus, chloro–methyl interchangeability (respective volumes 19.9 and 23.5 Å^3) is well known, and advantage has been taken of it in crystal engineering. Likewise, the comparable volumes of specific functional groups is a principal factor responsible for the difficulty in freeing, by zone-refining or other purification techniques, organic materials from impurities in solid solution, *e.g.*, pyrene from 4,5-phenanthrylene sulphide.[1]

In the light of these facts, it is not surprising that crystals of the cyclopentanones (**1**) and (**2**) are isomorphous, with very similar unit-cell dimensions [(**1**): $P2_1/c$, $Z = 4$, $a = 17.34$, $b = 10.68$, $c = 8.74$ Å, $\beta = 102.55°$; (**2**): $P2_1/c$, $Z = 4$, $a = 17.18$, $b = 10.59$, $c = 8.80$ Å, $\beta = 103.6°$] and each exhibits comparable solid state photoreactivity when irradiated with u.v. light, centrosymmetric cyclobutane dimers being produced smoothly in either case.[2] Moreover, we have found that, as expected, when a solution containing both (**1**) and (**2**) in 1:1 $CHCl_3$–MeOH is evaporated, mixed crystals are produced in which the components are randomly distributed on the lattice sites; no superstructures were detected. Such crystals yield, also as expected, unsymmetrical cyclobutane dimers upon u.v. irradiation in a transformation that, like that of the parent 2-benzyl-5-benzylidenecyclopentanone (**5**) is single-crystal → single-crystal from the monomeric to the dimeric state.

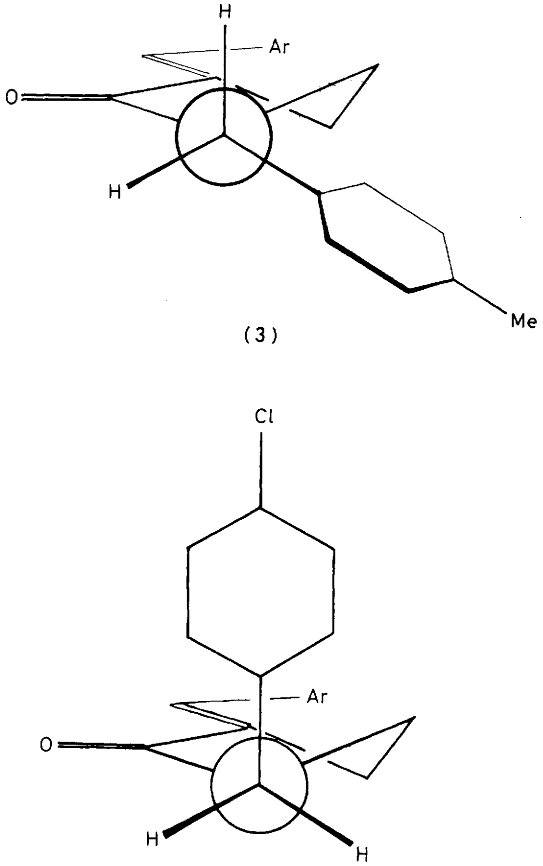
Cyclopentanone derivative (**3**) ($P2_1/c$, $Z = 4$, $a = 18.88$, $b = 11.21$, $c = 8.29$ Å, $\beta = 94.5°$) is also photoactive and it too, like (**1**) and (**2**), yields a centrosymmetric cyclobutane dimer. But derivative (**4**) ($P2_1/c$, $Z = 4$, $a = 17.53$, $b = 7.91$, $c = 11.89$ Å, $\beta = 91.2°$) even though it differs from (**3**) merely by the replacement of Me with Cl [*cf.* (**1**) and (**2**)] is photostable. We have shown[2] elsewhere that this arises from the subtle electronic (as well as spatial) influences of Cl substitution (Figures 1 and 2).

There are, however, a few instances known where two compounds having completely different crystal structures nevertheless still form mixed crystals primarily as a result of forced changes imposed upon the molecular geometry of the minor component by the dominating second component. Thus, square planar diamagnetic bis(*N*-methylsalicylideneaminato)nickel(II) (Nisal-Me) assumes the crystal structure of the trigonal bipyramidal (Znsal-Me) becoming penta-co-ordinate and paramagnetic when crystallised from a solution rich in the latter compound.[3] Another interesting case of structural mimicry (unexpected isomorphism) in this family of compounds involves the forced assumption of a tetrahedral structure by a planar Ni^{II} complex in a host crystal structure of the corresponding Zn^{II} complex.[4] Several other examples are known[5] in which organic molecules readily form solid solutions; tetrathiafulvalene and tetraselenafulvalene,[6] and reaction products in the reactant matrices of their monomers[7] are specific instances.



	Z	Y
(**1**)	H	Me
(**2**)	H	Cl
(**3**)	Br	Me
(**4**)	Br	Cl
(**5**)	H	H

Recognising, therefore, the phenomenon of structural mimicry, where a molecule which adopts a given conformation in its own (pure) matrix may be induced to take up the con-



(3)

(4)

Figure 1. Molecular conformations as found in the crystal structures of pure (**3**) and (**4**), shown as Newman projections down the C(2)–C(6) bond. The photoactive methyl derivative (**3**) has an essentially linear conformation, whereas the photostable chloro derivative (**4**) has a 'bent' conformation.

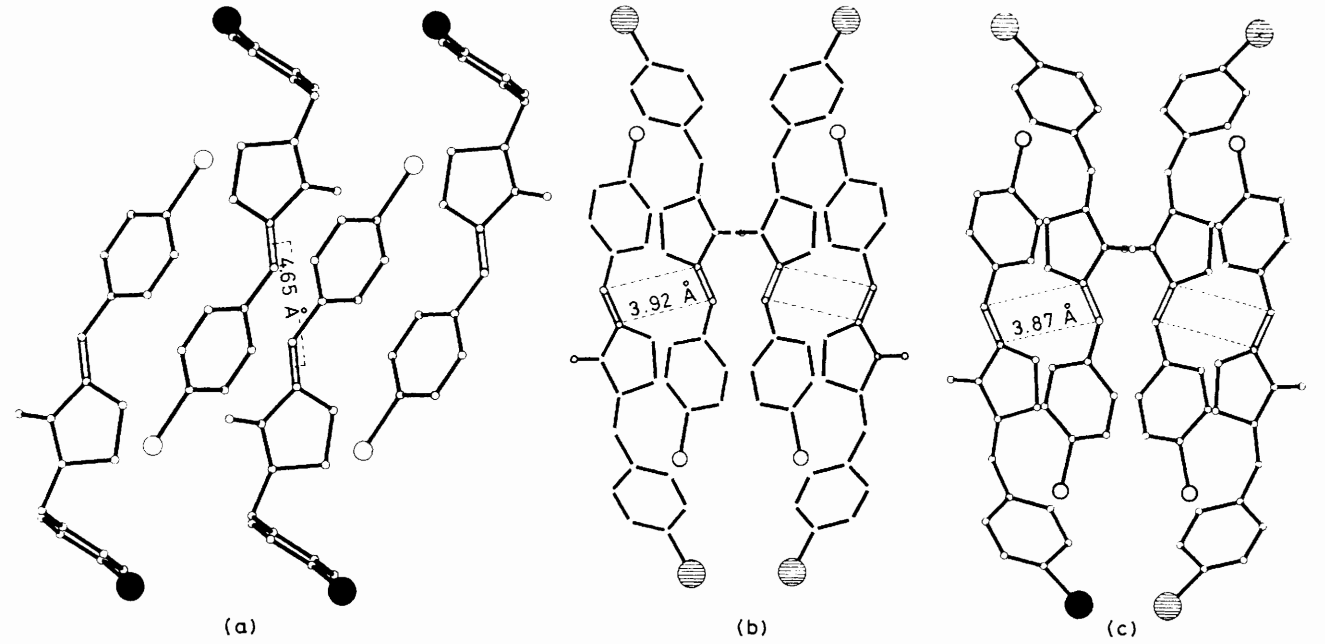


Figure 2. Packing of molecules in the crystal structures (viewed along *c*) of (a) pure (**4**), (b) pure (**3**), and (c) the mixed crystal. Note that the conformations of molecules in (a) and (b) are as shown in Figure 1. In pure (**4**), the nearest double bonds are 4.65 Å apart and the compound is photostable. In (b) [pure (**3**)], inversion related molecules are joined by dotted lines which define the incipient cyclobutane ring, separation distance 3.92 Å. In (c), molecule (**4**) is forced to adopt the 'linear' conformation of (**3**) and crystallises in a structure from which an asymmetric cyclobutane can be formed upon u.v. irradiation, separation distance of the double bonds now being 3.87 Å.

formation of a host matrix, we were prompted to explore whether molecules of (**4**), notwithstanding their solid state photostability in the pure crystalline state, could be rendered reactive when embedded, at low concentrations, in a matrix of (**3**). We were encouraged to explore this possibility since the energy differences, corresponding to the distinct conformations adopted by (**3**) and (**4**) in the pure solids are minor. We report here that such photoreactivity does indeed occur.

When compounds (**3**) and (**4**) were dissolved in 1 : 1 $CHCl_3$–MeOH, typically in 9 : 1 ratio, and the solution was slowly evaporated, crystals were obtained in about one day. Single crystals from this batch have cell parameters which are slightly but significantly different from those of pure (**3**). *X*-Ray intensity data were collected for such crystals and structure solution, phasing on the Br position, showed that the atoms in the benzylbenzylidenecyclopentanone framework were very similar to the corresponding positions in the crystal structure of (**3**). Further difference maps revealed both methyl and chloro groups and showed that mixed crystals contain both (**3**) and (**4**) molecules in a statistically averaged fashion. This disordered model could be refined satisfactorily to an *R* value of 0.058 (R_w 0.0518), the partial occupancy factors of (**3**) and (**4**) being 0.7 and 0.3 at convergence.† By analogy with the closely related (**3**), the mixed crystals were expected, and found, to undergo a topotactic and topochemical conversion into dimeric species.[8] As in the case of the (**1**)–(**2**) solid solution above, one of the products of the solid state reaction is an unsymmetrical cyclobutane (Figure 2). More details of the structures of these mixed crystals will be discussed elsewhere.

In summary, through the device of chloro–methyl exchange, the unreactive chloro compound (**4**) has been induced to adopt the molecular conformation, crystal structure, and solid state reactivity of the methyl compound (**3**). In particular, this work shows how the strategy of crystal engineering hitherto restricted to the use of various types of steering groups (*e.g.*, dichloro[9] or methylenedioxy[10] substitution of a pendant molecule) to 'drive' a molecule into a specific reactive packing mode of monocomponent crystals, can be significantly extended by harnessing the forces responsible for structural mimicry to the domain of mixed crystals. Such developments are likely to offer advantages in the solid state syntheses of certain organic species.

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† *Crystal data*: $a = 18.365(7)$, $b = 11.152(2)$, $c = 8.324(2)$ Å, $\beta = 94.51(3)°$, $U = 1699.5$ Å^3, $P2_1/c$, $Z = 4$, $F(000) = 744$, $\mu = 37.64$ cm^{-1} ($\lambda = 1.5418$ Å), 1185 reflexions with $F_o > 2\sigma(F_o)$. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.