Engineering Organic Crystals so as to control the Photoreactivity of the Reactants and the Crystallinity of the Products

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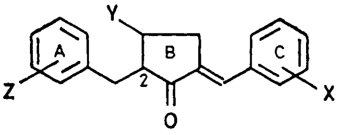
Summary A family of organic molecular crystals based on benzylidenecyclopentanone provides a basis for an assessment of topotactic and topochemical photoreactivity.

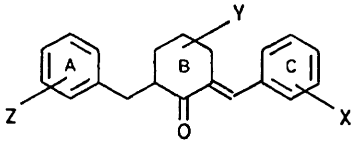
So extensive and subtle are the modifications that may be made to molecular structure, shape, and stereochemistry that it is, in principle, possible to design and engineer organic solids which display a desired photoreactivity and which generate crystalline products isomorphously and topotactically within the monomer matrix. Although design procedures cannot, at present, be evolved *de novo* we can, to a certain degree, and on the basis of accumulated experience, 'steer' molecules to crystallize into certain space groups which possess packing characteristics, symmetries, nearest-neighbour distances, and other so-called topochemical factors that are conducive to a required and specific photoreactivity. The strategy of crystal engineering (first discussed by Schmidt[1] and taken up by others[2–6]) has, *inter alia*, enabled solid-state synthesis of optically active dimers and polymers to be effected.[6,7] Almost all the systems studied to date, however, have disadvantages and very few have yielded crystalline products, a fact which limits the overall product yield and underlines the limitations of previously investigated systems. We report here a versatile system which, in addition to its wide scope, affords greater insight into solid-state reactivity, topotaxy, and crystal engineering.

The molecular frameworks (2-benzyl-5-benzylidenecyclopentanone, BBCP;[8] 2-benzyl-6-benzylidenecyclohexanone, BBCH; and 2,5-dibenzylidenecyclopentanone, DBCP) may be substituted in rings A, B, and C and 14 derivatives of the parent molecules have so far been studied crystallographically and their solid-state photoreactivity (100 W mercury lamp, Pyrex filter) analysed. We have, in addition, monitored the course of solid-state photo-induced reactions *in situ* on a four-circle diffractometer and charted the detailed crystallographic changes so as to probe the mechanisms of the reaction.[9,10]

Several noteworthy features relating to solid-state reactivity, specificity, and synthetic potential emerge. (i) Molecules (**1a**—**k**) and (**2**) (see Table) pack into one of the racemic space groups *Pbca*, $P2_1/c$, or $P\bar{1}$, not surprisingly in view of the formation of both stereoisomers (with respect to C-2) during synthesis. Of these (**1a**, **b**, **i**, and **j**) and (**2**) pack into photoreactive crystals, the changes in cell parameters merely reflecting different van der Waals radii of



(1)



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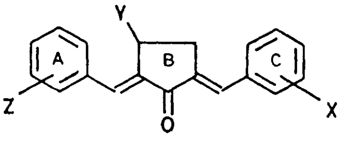

(3)

TABLE.

	X	Y	Z		a/Å(α °)	b/Å(β °)	c/Å(γ °)	Space group	Reactivity
(**1a**)	H	H	H	BBCP	31·30	10·78	8·69	*Pbca*	Yes
(**1b**)	*p*Br	H	H	B*p*BrBCP	34·25	10·88	8·43	*Pbca*	Yes
(**1c**)	*m*Br	H	H	B*m*BrBCP	12·91	27·13 (101·6)	9·21	$P2_1/c$	No
(**1d**)	*o*Br	H	H	B*o*BrBCP	28·93	8·82	12·28	*Pbca*	No
(**1e**)	*p*Cl	H	H	B*p*ClBCP	30·97	8·50	11·57	*Pbca*	No
(**1f**)	*o*Cl	H	H	B*o*ClBCP	14·38	11·60 (93·0)	9·24	$P2_1/c$	No
(**1g**)	*p*Me	H	H	B*p*MeBCP	31·04	8·45	11·68	*Pbca*	No
(**1h**)	*m*Me	H	H	B*m*MeBCP	10·09	10·27 (100·0)	15·20	$P2_1/c$	No
(**1i**)	H	H	*p*Cl	*p*ClBBCP	16·62	10·51 (76·33)	8·98	$P2_1/c$	Yes
(**1j**)	H	H	*p*Me	*p*MeBBCP	17·23	10·67 (77·0)	8·67	$P2_1/c$	Yes
(**1k**)	*p*Br	H	*p*Me	*p*MeB*p*BrBCP	33·62	11·82	8·66	*Pbca*	Yes
(**2**)	H	H	H	BBCH	13·30 (72·0)	11·14 (82·5)	5·93 (68·0)	$P\bar{1}$	Yes
(**3a**)	H	H	H	DBCP	11·75	5·69	20·89	$C222_1$	Yes
(**3b**)	H	±Me	H	DB-3-(±)-MeCP	17·11	9·02	19·61	*Pbca*	No
(**3c**)	H	+Me	H	DB-3-(+)-MeCP	10·43	7·71 (111·4)	10·30	$P2_1$	Yes

the substituent groups. In all cases delocalization is facilitated by the planarity of the carbonyl–benzylidene system. Nearest-neighbour molecules are related by centres of symmetry (they therefore yield centrosymmetric dimers), the double bonds being separated by 4·2, 3·8, 4·0, and 3·8 Å for (**1a**, **b**, and **i**) and (**2**), respectively. For the remaining molecules of group (**1**) photostability results from increased separation of the reactive double bonds. [For example, for (**1e**) nearest-neighbour molecules are related by a glide plane where the separation of the reactive groups is now *ca.* 6·2 and 4·7 Å.] (ii) Additional packing features are explained in terms of the molecules within group (**3**) formed by the removal of the chiral centre at C-2. Thus, for molecules (**3b**) and (**3c**) a new chiral centre is introduced by the addition of a methyl-group at the 3-position. Following this substitution the racemate packs into a photo-stable space group, whereas the pure enantiomer packs into a photoreactive phase. (iii) The conversion of BBCP (**1a**) into its dimer takes place topotactically (as well as topochemically), the maximum change in unit cell parameters in the course of this single-crystal→ single-crystal transformation being 0·7%.[9] (The cell parameters of the as-dimerized sample correspond closely to those obtained from dimer after recrystallisation.) (iv) By careful control of the rate at which dimerization occurs, it is possible to retain a homogeneous, single-crystal transformation (*i.e.* generate a crystalline product) even though the changes in unit cell parameters are relatively large. For example, in B*p*BrBCP (**1b**) where the cell parameter changes are 3·8, 5·6, and 6·5% for *a*, *b*, and *c*, respectively, a single-crystal to single-crystal photo-dimerization has been effected.

These facts permit novel avenues of solid-state chemistry to be explored: (iii) will enable the first full three-dimensional structure of partly photochemically converted reactant and its product to be established, thereby revealing the atomic rearrangements involved in a solid-state reaction; (ii) will enable the strength of the steering influence of alkyl substitution in cyclopentanones to be assessed; and (iv) offers a viable means of generating crystalline products in solid-state organic syntheses.

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