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The Solid-state Photodimerisation of 2,5-Dibenzylidenecyclopentanone (DBCP): a Topochemical Reaction that yields an Amorphous Product

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When 2,5-dibenzylidenecyclopentanone (DBCP) is irradiated by u.v. light in the crystalline state the principal product formed by a [2 + 2] dimerisation is 2,9-dibenzylidene-6,12-diphenyldispiro[4.1.4.1]-dodecane-1,8-dione (DDBCP); a subsidiary dimeric species is formed in substantial amounts at low conversion but is consumed during the course of further reaction and is absent when the total conversion approaches 90%. Crystalline (+)-2,5-dibenzylidene-3-methylcyclopentanone [DB(+)3MeCP] under the same conditions is photostable. The contrasting photoreactivity of these two solids is interpreted in terms of the mutual disposition of potentially reactive olefinic bonds on neighbouring molecules. Even when such bonds are not parallel (and for DBCP they are inclined at an angle of 56°) reaction may ensue since the distances separating the carbon atoms are approximately 3.7 Å. It is argued that the photostability of DB(+)3MeCP, where the separation distances of the potentially reactive olefinic bonds on adjacent molecules are comparable to those in DBCP and where the bonds are again not parallel, is attributable to the non-coplanarity of the two π-bonds.

Many crystalline olefinic monomers dimerise readily under u.v. irradiation and almost invariably only one product is formed, in contrast to the reaction in solution where the same monomer yields a mixture of stereoisomers.[1-4] In certain instances, a well defined crystallographic relationship exists between the product and the monomer within which it is formed. This is expected [4,5] both for the situations in which dimerisation takes place randomly within the perfect structure, and, preferentially, at crystalline imperfections. On the other hand, in some instances the product is amorphous,[6,7] *e.g.* in the photodimerisation of *trans*-cinnamic acids. In each instance, however, the course of the reaction is governed by topochemical factors such as the packing characteristics, local symmetry, and separation distances between functional groups on neighbouring molecules.

We have recently discovered [8-11] a family of materials, based on 2-benzyl-5-benzylidenecyclopentanone (BBCP), for which photodimerisation proceeds to completion in a single crystal ⟶ single crystal fashion. These compounds constitute an ideal testing ground to explore the inter-relationships between photoreactivity and crystal packing, since they afford considerable scope for the ' engineering ' of crystals for

Table 1. Crystal and refinement data

Compound	DBCP	DB(+)3MeCP	DDBCP
Formula	$C_{19}H_{16}O$	$C_{20}H_{18}O$	$C_{38}H_{32}O_2$
Molecular weight	260.34	274.36	520.68
Crystallisation solvent	$CHCl_3$/MeOH	$CHCl_3$/MeOH	$CHCl_3$/MeOH
Crystal system	Orthorhombic	Monoclinic	Tetragonal
Space group	$C222_1$	$P2_1$	$P4_12_12$
a/Å	11.803(2)	10.325(3)	10.860(1)
b/Å	5.698(4)	7.723(4)	10.860(2)
c/Å	20.872(2)	10.483(2)	23.979(2)
β (°)		111.38(2)	
V/Å^3	1 403.6	776.8	2 828.2
D_c/Mg m^{-3}	1.232	1.173	1.223
Z	4	2	4
μ/cm^{-1}	5.01	5.13	5.37
Crystal size (mm)	0.15 × 0.15 × 0.20	0.20 × 0.15 × 0.20	0.30 × 0.20 × 0.20
θ (min, max)	3, 68	3, 70	3, 65
Total data unique	753	1 430	2 403
Total data observed	597	1 160	1 894
Significance test	$F_o > 2\sigma(F_o)$	$F_o > 3\sigma(F_o)$	$F_o > 3\sigma(F_o)$
No. of parameters	124	261	250
Weighting scheme	$[\sigma^2(F) + 0.0004F^2]^{-1}$	Unit weights	$[\sigma^2(F) + 0.0008F^2]^{-1}$
R	0.051	0.046	0.051
R_w	0.041	0.046	0.054
Absorption correction	No	No	Yes
Elemental analysis			
C (%) (theoretical)	87.42 (87.58)	86.55 (87.48)	85.38 (87.78)
H (%) (theoretical)	6.07 (6.15)	6.38 (6.56)	6.25 (6.15)
Melting point (°C)	198	157	242

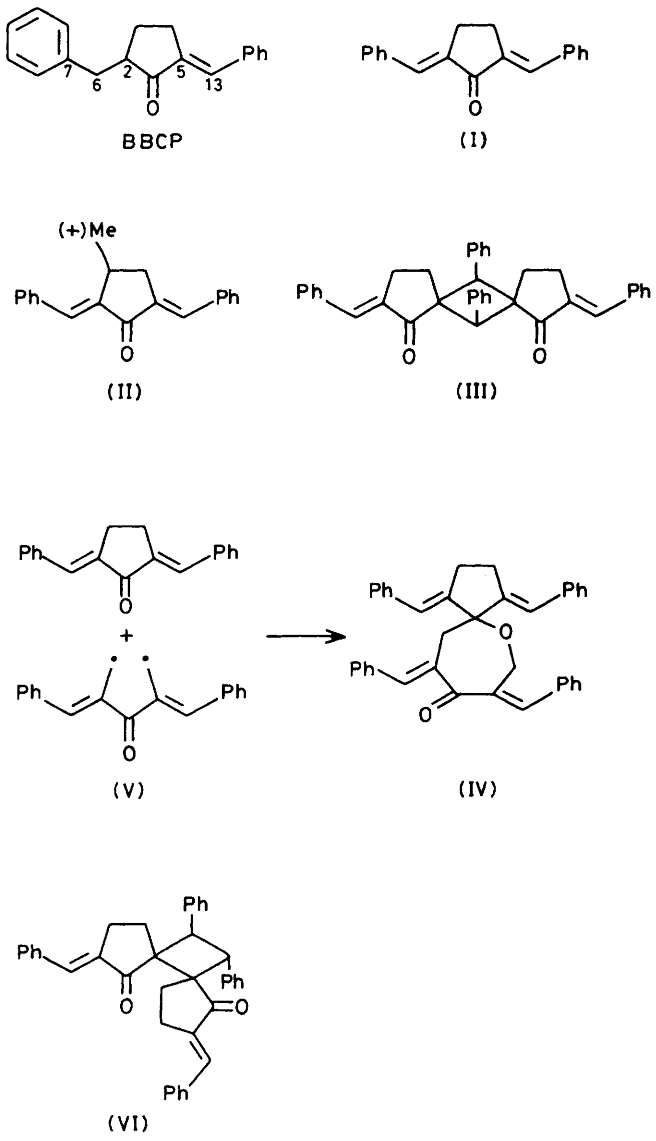

Figure 1. Molecular formulae of compounds. (IV) is derived from reaction of one molecule of (I) with the biradical (V) in the manner shown

which reactivity may, to a substantial degree, be designed and controlled.[12]

Table 2. Atom co-ordinates (× 10^4) for DBCP

	x	*y*	*z*
O(1)	4 132(2)	5 000	5 000
C(1)	3 107(3)	5 000	5 000
C(2)	2 379(2)	6 620(5)	5 366(1)
C(3)	1 169(3)	5 974(6)	5 255(2)
C(6)	2 838(2)	8 320(6)	5 727(1)
C(7)	2 315(3)	10 062(6)	6 147(1)
C(8)	3 011(3)	1 670(7)	6 456(2)
C(9)	2 570(4)	3 350(7)	6 867(2)
C(10)	1 439(4)	3 436(8)	6 980(2)
C(11)	731(4)	1 861(8)	6 684(2)
C(12)	1 171(3)	10 191(6)	6 271(1)

Table 3. Atom co-ordinates (× 10^4) for DDBCP

	x	*y*	*z*
O(2)	4 339(2)	4 440(2)	938(1)
C(1)	3 556(3)	3 628(3)	968(1)
C(2)	3 018(3)	3 118(3)	1 482(1)
C(3)	2 046(3)	2 197(3)	1 331(1)
C(4)	2 049(3)	2 092(3)	689(1)
C(5)	2 989(3)	3 019(3)	460(1)
C(6)	3 450(3)	3 500(3)	1 976(1)
C(7)	3 111(3)	3 159(2)	2 547(1)
C(8)	3 783(4)	3 665(4)	2 987(1)
C(9)	3 535(5)	3 413(4)	3 529(2)
C(10)	2 580(4)	2 627(4)	3 658(1)
C(11)	1 899(5)	2 120(4)	3 234(2)
C(12)	2 142(4)	2 383(3)	2 684(1)
C(13)	3 916(3)	2 544(2)	6(1)
C(14)	4 449(3)	1 270(2)	22(1)
C(15)	4 759(3)	667(3)	−464(1)
C(16)	5 376(4)	−449(4)	−451(1)
C(17)	5 665(4)	−994(3)	48(2)
C(18)	5 358(4)	−413(3)	539(1)
C(19)	4 759(3)	710(3)	523(1)
O(1)	5 642(4)	5 642(4)	0

Table 4. Atom co-ordinates (× 10^4) for DB(+)3MeCP

	x	*y*	*z*
O(1)	−768(2)	1 199(6)	8 846(2)
C(1)	266(3)	840	9 842(3)
C(2)	312(3)	588(6)	11 268(3)
C(3)	1 800(3)	213(7)	12 182(3)
C(4)	2 584(3)	−114(8)	11 207(3)
C(5)	1 678(3)	599(7)	9 828(3)
C(6)	−841(3)	821(7)	11 536(3)
C(7)	−1 118(3)	740(6)	12 816(3)
C(8)	−224(4)	−46(8)	14 016(3)
C(9)	−554(4)	−66(8)	15 173(4)
C(10)	−1 737(5)	692(9)	15 180(4)
C(11)	−2 654(5)	1 450(8)	13 999(4)
C(12)	−2 344(4)	1 438(7)	12 824(4)
C(13)	1 974(3)	1 010(7)	8 735(3)
C(14)	3 268(3)	863(6)	8 481(3)
C(15)	4 411(3)	−131(8)	9 283(4)
C(16)	5 582(4)	−243(7)	8 962(4)
C(17)	5 674(4)	641(7)	7 865(4)
C(18)	4 568(4)	1 638(8)	7 055(4)
C(19)	3 377(4)	1 726(7)	7 362(4)
C(20)	2 433(5)	1 731(9)	13 127(5)

We embarked upon a study of 2,5-dibenzylidenecyclopentanone (DBCP) for four reasons. First, because the introduction of the extra double bond creates further potentially reactive centres in the monomer (just as with other compounds we have examined [5,13]). Secondly, to examine the photochemical consequences of rendering the monomer essentially planar, which arises in this case because of the presence of benzylidene groups. Thirdly, because of the chiral centre at C(2) in the benzyl–benzylidene framework all the molecules in the BBCP family necessarily crystallised in racemic space groups; with DBCP and its derivatives, however, we may expect a broadened range of space groups within which topochemical dimerisations can occur. Fourthly, it is, in principle, possible for subsequent chirality to be introduced by appropriate substitution within the pentanone ring. To this end, we have also studied (+)-2,5-dibenzylidene-3-methylcyclopentanone [DB(+)3MeCP], an archetype of such monomers. This derivative, in view of the disposition of double bonds on neighbouring molecules in the crystalline monomer, throws much light on the conditions that facilitate the solid-state photoreactivity of olefinic compounds.

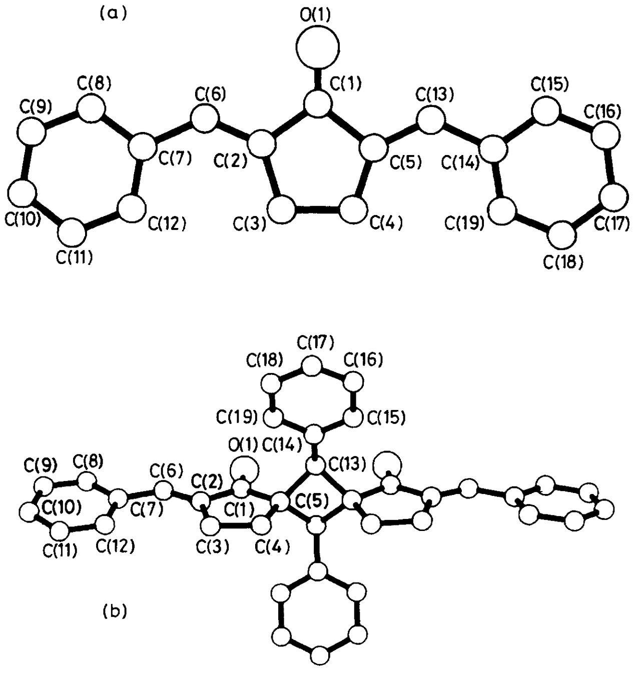

Figure 2. The numbering schemes used for DBCP, DB(+)3MeCP, and DDBCP

Experimental

DBCP (I) was prepared from the reaction of cyclopentanone with benzaldehyde in a 1 : 2 proportion in the presence of methanolic sodium hydroxide catalyst at room temperature. DB(+)3MeCP (II) was prepared from (+)-3-methylcyclopentanone using the same procedure. Crystallisation conditions, analytical results, and salient crystallographic data are given in Table 1. The dimer of DBCP [(III) in Figure 1], hereafter designated DDBCP, was prepared by irradiation through a Pyrex filter of a water–methanol (10% v/v) suspension of crystalline DBCP with a 500 W, low-pressure mercury lamp for 18 h. Nitrogen gas was bubbled through the suspension, which was cooled by a water jacket. Powder *X*-ray diffraction of the crude product showed it to be amorphous. Thin-layer chromatography from a chloroform solution on alumina indicated that one major (55%) and two minor products (15 and 20%) were obtained, whilst 10% of DBCP remained unreacted (*i.e.* a 90% conversion was achieved). Elemental analysis, n.m.r., and mass spectroscopy showed that the major product, DDBCP, had the molecular formula (III), and mass spectroscopy and chemical analysis confirmed that the minor products were not dimeric, and are probably photodegradation products; the latter were not examined further. Mass spectra showed that no product with mass larger than that of the dimer was obtained. The yields reported are based on the n.m.r. results of the crude product.

An n.m.r. spectrum of DBCP crystals in $CDCl_3$, after a u.v. irradiation that was discontinued after 25% conversion, con-

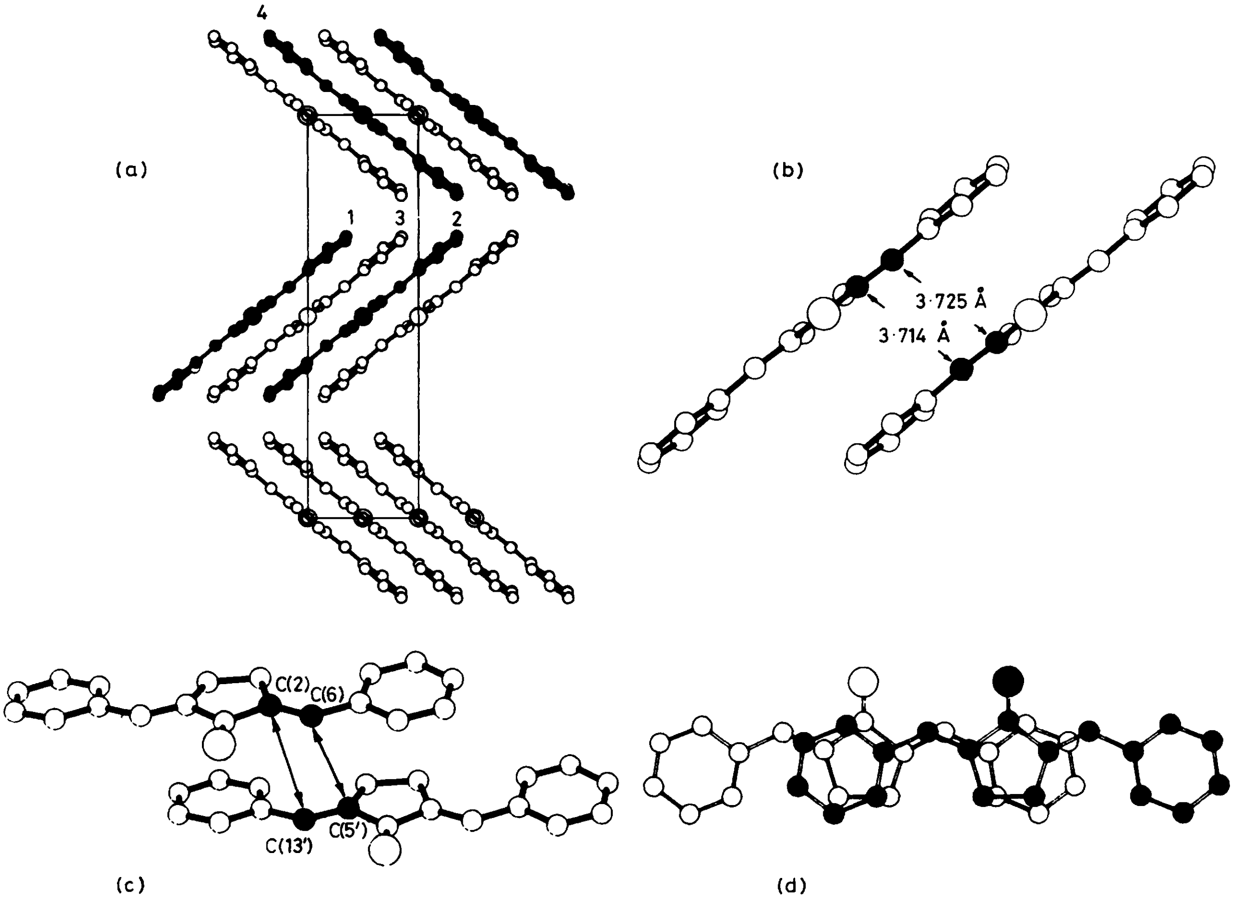

Figure 3. (a) DBCP structure viewed along the *a* axis. (b) The DBCP incipient dimer viewed along the *a* axis. (c) View of the DBCP incipient dimer of a low-symmetry direction. (d) The incipient dimer of DBCP viewed perpendicularly to the mean molecular plane. In (b) and (c) the reacting double bonds are shaded

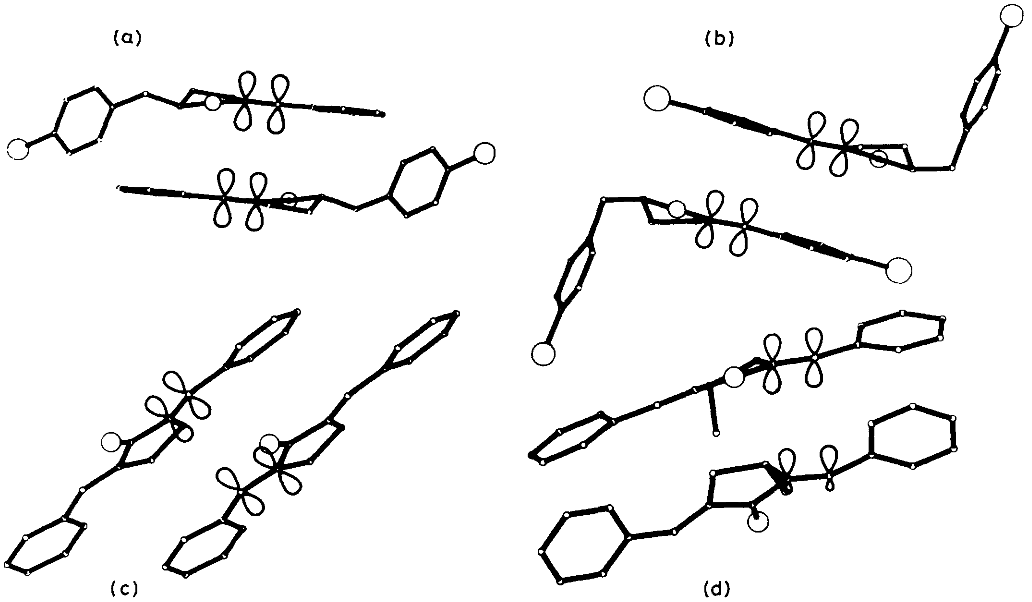

Figure 4. Illustration of different kinds of disposition of reacting double bonds in adjacent molecules in crystals of BBCP, DBCP, and some of their derivatives. These dispositions and the relevant separation distances are the principal determination of photoreactivity. (a) Double bonds in adjacent molecules are parallel and separated by *ca.* 4 Å in crystals of 2-*p*-chlorobenzyl-5-benzylidenecyclopentanone. This crystalline solid is photoreactive. (b) Double bonds are parallel but quite far apart (*ca.* 4.7 Å) in crystals of 2-*p*-chlorobenzyl-5-*p*-bromobenzylidene-cyclopentanone. This solid is photostable. (c) Double bonds are not parallel, but the planes of the benzylidene groups are, and the separation distance is only *ca.* 3.7 Å in DBCP. This solid is photoreactive. (d) Neither the double bonds nor the planes of the benzylidene groups are parallel in DB(+)3MeCP; the molecular planes are almost perpendicular to one another, despite the short separation distance (*ca.* 3.9 Å) this crystalline solid is photostable

tained peaks that were assigned to structure (IV) and that were absent from the spectrum after 90% conversion reported above. This dimer, which was obtained with a yield of 8% compared with 15% of structure (III) (DDBCP), was also reported by Kaupp and Zimmermann,[14] who postulated that it is the product of a reaction between a DBCP molecule and the biradical (V) (see Figure 1). It is clear that this second dimer degraded upon further irradiation to give the two minor products (at least in part) observed at 90% conversion. Kaupp and Zimmermann [14] reported a third dimer (VI), which was not detected in this work.

Irradiation of a solution of DBCP in chloroform under the above-mentioned conditions yielded a dimer (along with a few degradation products) shown by n.m.r. to be compound (VI). Its crystal structure will be reported elsewhere.

The proton n.m.r. spectra for (III), (IV), and (VI) are identical with those reported by Kaupp and Zimmermann.[14]

Data Collection.—Preliminary unit-cell and space-group data for all the crystals cited in Table 1 were obtained from oscillation, Weissenberg, and precession photographs. Accurate cell parameters and intensity data were obtained on an Enraf-Nonius CAD-4 diffractometer in the manner described elsewhere [15] using Ni-monochromatised Cu-K_α radiation, in an $\omega/2\theta$ scan mode.

The structures were solved by direct methods and refined using full-matrix least-squares techniques. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were located from difference maps and assigned isotropic thermal parameters. All calculations were performed on an ICL2980 (Queen Mary College) and on IBM 370/165 (Cambridge) computer using MULTAN-80, SHELX-76, PLUTO-78, and private programs. Scattering factors were obtained from reference 16.

Results

Final atomic co-ordinates are presented in Tables 2 for DBCP, 3 for DDBCP, and 4 for DB(+)3MeCP, and the numbering schemes employed are shown in Figure 2. Thermal parameters, bond lengths, and bond angles as well as lists of observed and calculated structure factors are given in Supplementary Publication No. SUP 23719 (29 pp.).*

Discussion

We begin by noting the more relevant structural features of the monomeric crystals that we have examined. These convey valuable information about the topochemically allowed reactions.

Packing Considerations.—(a) *DBCP*: From Figure 3(a)—(d) it is seen that atoms O(1) and C(1) are at special positions located on the two-fold axis parallel to [100], all other atoms being at general positions. Since the molecular and the crystallographic two-fold axes coincide, the asymmetric unit is half the molecule. Nearest neighbour molecules are related by translation along [010] [molecules 1 and 2 in Figure 3(a)], such that C(2)$\cdots$C(13′) is 3.714(5) and C(6)$\cdots$C(5′) is 3.725(5) Å. (The primes indicate symmetry-related molecules). Since the essentially planar carbonyl–benzylidene moieties C(1)–C(5)–C(13)–C(14)$\cdots$C(19) and C(1)–C(2)–C(6)–C(7)$\cdots$C(12) subtend a dihedral angle of only 9.7°, the molecule as a whole is almost planar. As a consequence, the double bonds C(2)=C(6) and C(5′)=C(13′) lie in planes that are parallel to each other, but the bonds themselves are not parallel, as is

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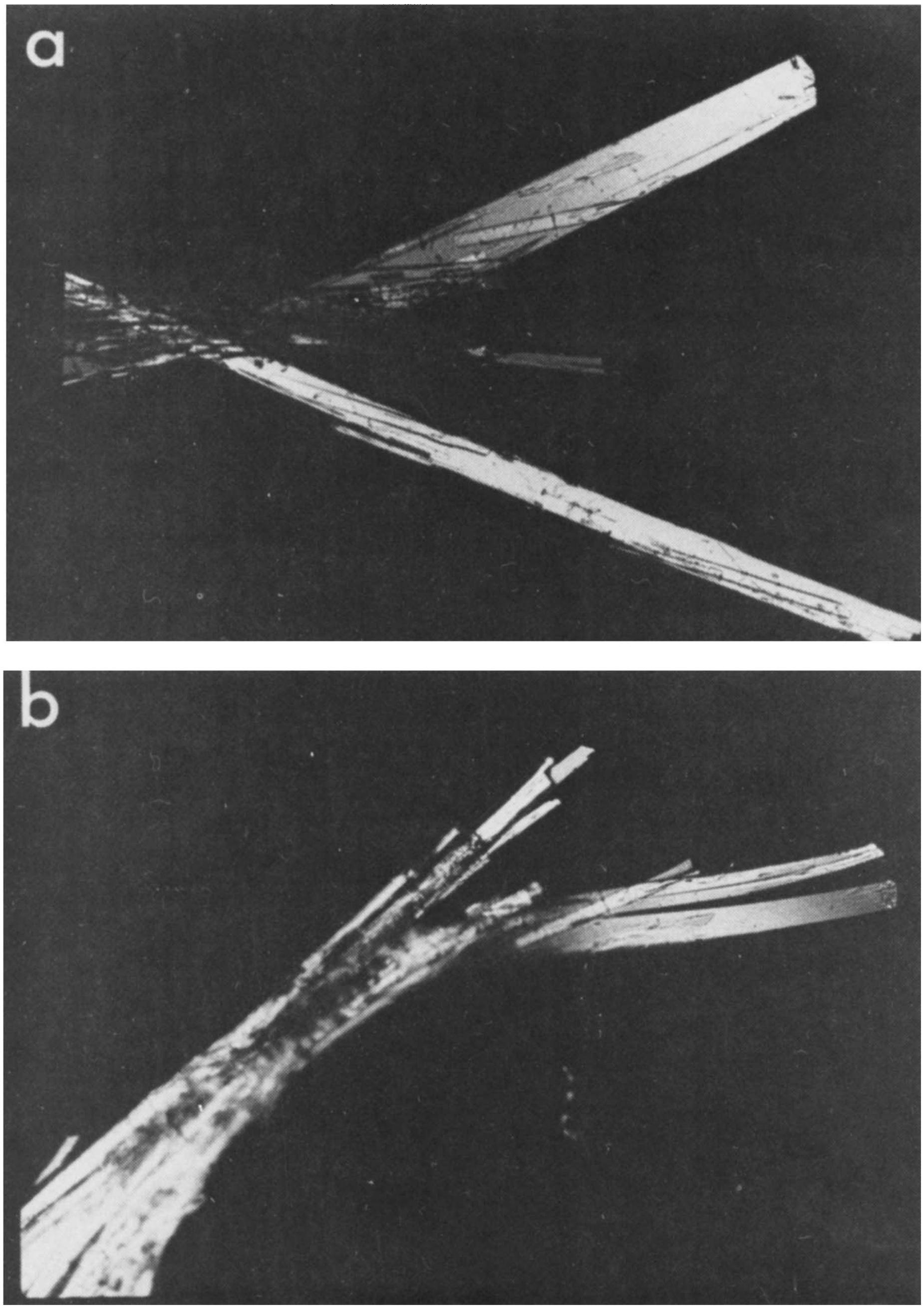
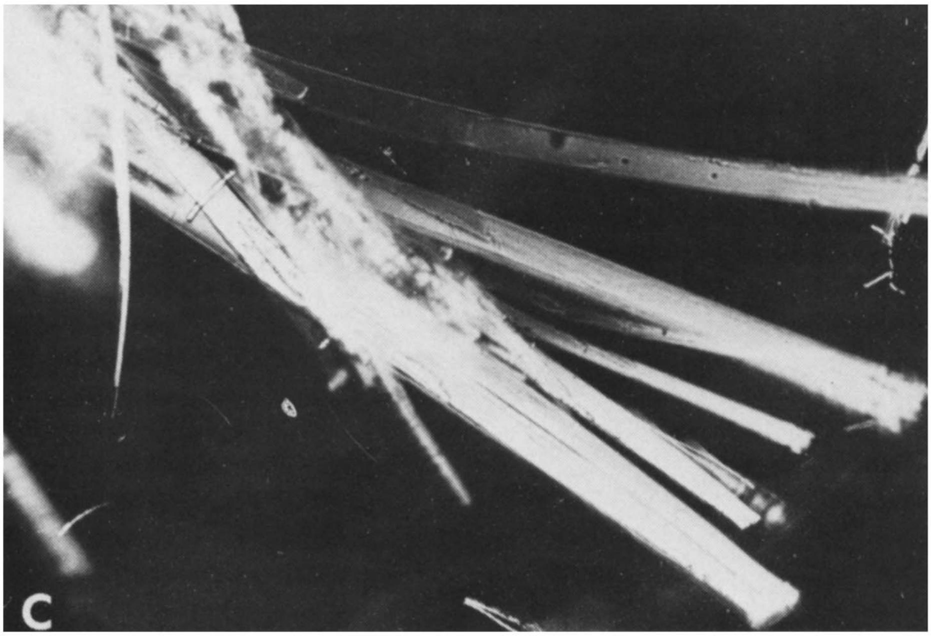
* For details of the Supplementary Publications Scheme see Instructions for Authors, *J. Chem. Soc., Perkin Trans. 2*, 1984, Issue 1.



Sequence of photographs following the break-up of DBCP crystals during conversion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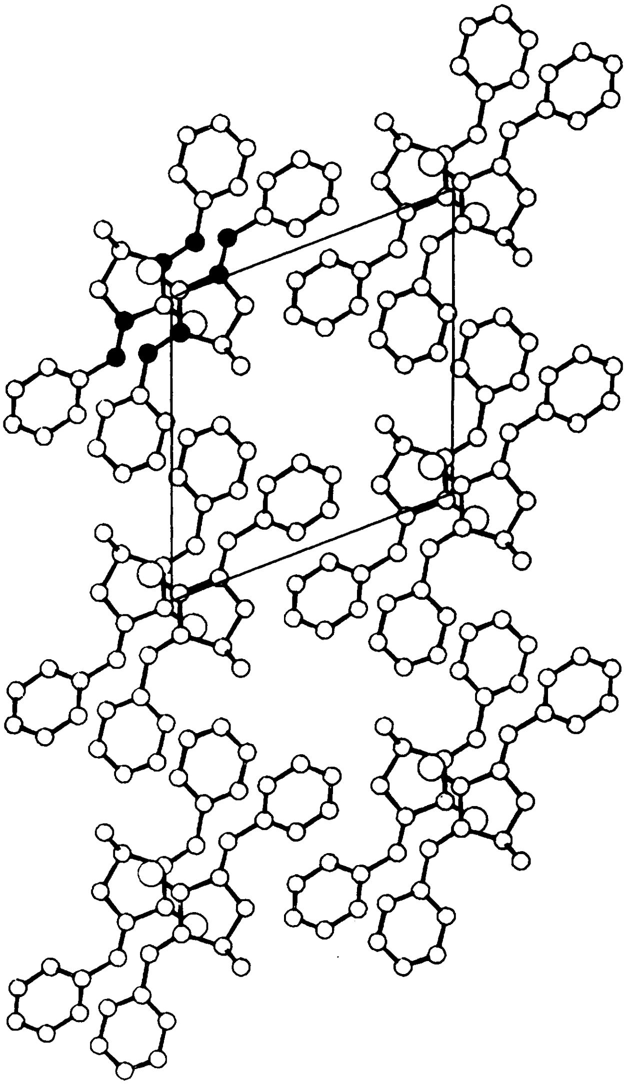

Figure 5. The DB(+)3MeCP crystal structure, viewed along the *b* axis. The double bonds in one of the nearest neighbour pairs is indicated

seen from Figures 3(c) and (d), the angle between the two bonds being 56°. This is not the geometry generally considered conducive for a topochemical reaction,[1,17] although the mean distance separating the potentially reactive centres is well within the limits previously deduced to be necessary for such reactions. However, since the two bonds belong to molecules the planes of π-bonds of which are parallel, the p_z orbital on atom C(2) is oriented in the direction of the corresponding orbital on C(13′) (see Figure 4). These are the orbitals which initially form the π-component of the double bonds and subsequently form part of the cyclobutane ring. It appears, therefore, that on photo-excitation, interaction and overlap of these orbitals is still possible and this is probably why reaction ensues in the crystalline state. The ideal situation is achieved when the bonds are exactly parallel and not displaced with respect to one another, in which case the p_z orbitals of one bond are optimally disposed with respect to those of the second bond.[18]

The above packing considerations help us to understand the molecular structure of the dimer determined in this work [Figure 2(b)]. We note from Figure 3(a)—(d) that the dimer structure (III) (Figure 1) is the one formed [rather than, for example (VI)] on the basis of the topochemistry of the parent monomer structure. From Figure 3 it is seen that, in the monomer crystal, the carbonyl groups within the incipient dimer point in the same direction. The formation of DDBCP within the DBCP crystal is expected to result from reaction between C(2) and C(13′), on the one hand and C(6) and C(5′), on the other. The cyclobutane ring of the dimer is puckered, probably because of dipole–dipole repulsion between the two carbonyl groups. By contrast, the cyclobutane ring of the BBCP dimer,[11] which is centrosymmetric, is planar, there being no repulsion between carbonyl groups of the dimer. It is noteworthy that molecular structure (IV) can, in principle, be obtained from the DBCP crystal as described above, *via* reaction of molecules 1 and 3 (*i.e.* second nearest neighbours) in Figure 3(a) (see also Figure 1). Conversely, structure (VI) could also, in principle, be obtained *via* a reaction between molecules 1 and 4, a process not allowed topochemically in the defect-free crystal.

(b) *DB*(+)3*MeCP* [*structure* (II)]. This molecule, apart from the methyl group C(20), which lies 1.65 Å above the mean plane, is almost planar, with maximum deviation from the mean plane of 0.44 Å. Nearest-neighbour molecules are related by a two-fold screw axis (Figure 5) and the distance separating the carbon atoms of neighbouring double bonds C(5)=C(13) and C(2′)=C(6′) is 3.871(5) Å. Although this distance is apparently suitable for [2 + 2] topochemical cycloaddition, this crystal is photostable. We argue that this situation arises because benzylidene groups to which these two bonds belong are not parallel. This prevents the necessary overlap of potentially reactive orbitals.

The fact that the dimer obtained (DDBCP) from the irradiation of crystalline DBCP is the one predicted for a topochemical reaction in the perfect structure does not necessarily imply that reaction occurs within defect-free regions of the crystal. However, optical microscopic studies of DBCP single crystal undergoing photodimerisation (see Plate) show that cracks develop very rapidly in a direction parallel to [010], and this is in line [see Figure 3(a)] with expectations based on the strain induced by cyclobutane ring formation. There is no evidence of the nucleation of a new phase, and when structural defects were introduced in the monomer crystal (by deformation or heating) there was no significant consequential change in photoreactivity. Clearly, there is no preferential photodimerisation at structural faults, in contrast to the situation that is obtained in some other photoreactive organic molecular crystals[4,19] and also in the recently reported study on 9-methoxycoumarin.[17]

Contrast between BBCP and DBCP.—BBCP has been shown to undergo single crystal ⟶ single crystal dimerisation, unlike DBCP which yields an amorphous product. This difference in behaviour probably reflects the difference in the molecular structure of the two parent compounds. In BBCP, the benzyl group is not rigid, and can, therefore, change conformation [*via* rotation round the C(2)–C(6) and C(6)–C(7) bonds] to allow the dimeric molecule to relax within the reacting crystal during the course of dimerisation. The dimeric molecule can, therefore, occupy essentially the same volume as two monomeric ones, and it is not surprising that the process is accompanied by such a small change in cell parameters with the overall change being single crystal ⟶ single crystal. In DBCP, however, because of the intrinsic rigidity of the rather large molecular framework, no such change of molecular configuration is possible during reaction and the dimer molecule cannot fit compactly into the crystalline monomeric structure. Moreover the strain that develops as dimerisation progresses results in the loss of mechanical integrity of the crystal, and this loss in part is augmented by the other products generated in the reaction.

Acknowledgements

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