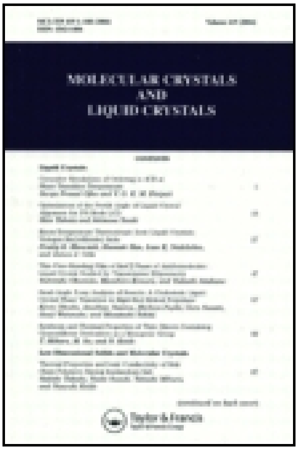

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Interpreting and Predicting the Photochemistry of Solid Cyclopentanone Derivatives

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Version of record first published: 17 Oct 2011.

To cite this article: S. K. Kearsley , N. Moulden , W. Jones & J. M. Thomas (1983): Interpreting and Predicting the Photochemistry of Solid Cyclopentanone Derivatives, Molecular Crystals and Liquid Crystals, 93:1, 41-51

To link to this article: http://dx.doi.org/10.1080/00268948308073514

Mol. Cryst. Liq. Cryst., 1983, Vol. 93, pp. 41–51
0026-8941/83/9304–0041/$18.50/0

Printed in the United States of America

INTERPRETING AND PREDICTING THE PHOTOCHEMISTRY OF SOLID CYCLOPENTANONE DERIVATIVES

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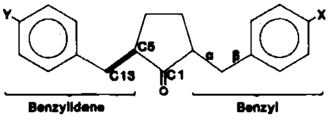
Abstract The principal packing motifs observed in a family of substituted benzyl - benzylidene - cyclopentanones are rationalised in terms of the interaction energies of isolated centrosymmetric pairs of molecules. Calculation of intermolecular interactions energies (using a non-bonding atom-atom potential approach) leads to a general understanding of the packing arrangements observed in these compounds.

Introduction

Single crystals of 2-benzyl - 5-benzylidene - cyclopentanone (BBCP) photodimerise in the solid state, when the reactive monomer units are related by a centre of inversion with the double bonds approximately 4.0 Å apart[1]. This observation prompted the structural investigation of several derivatives of BBCP, to analyse the effect of substituents on packing and various topochemical phenomena[2,3].

FIGURE 1.

Description of Benzyl-Benzyllidene-Cyclopentanone (BBCP)



C5-C13: reactive double bond

Torsional freedom about bonds α and β.

TABLE 1. Y →

X ↓

SUBSTITUTED	BENZYLIDENE	BROMO	CHLORO	METHYL
BENZYL	BBCP ● P_{bca} 31.30 S 10.78 8.69 120-2°	BpBrB ● P_{bca} 34.25 S 10.88 8.43 135-6°	BpClB P_{bca} 30.97 S 8.50 11.57	BpMeB P_{bca} 31.04 8.45 11.68
BROMO	pBrBB ● P_{2_1c} 17.46 S 10.55(103) 8.85 125-7°	pBrpBr P_{bca} 35.22 7.95 11.79 122-3°	pBrpCl 100-4°	pBrpMe 113-5°
CHLORO	pClBB ● P_{2_1c} 16.62 S 10.52(103) 8.98 119-20°	pClpBr P_{2_1c} 17.53 S 7.97(91) 11.85 115-7°	pClpCl 104-5°	pClpMe P_{bca} 33.19 8.42 11.79 135-7°
METHYL	pMeBB ● P_{2_1c} 17.34 S 10.67(102) 8.73 108-10°	pMepBr ● P_{2_1c} 18.38 S 11.21(94) 8.29 116-7°	pMepCl P_{bca} 32.72 8.62 11.58 126-7°	pMepMe P_{bca} 8.61 S 11.76 32.70 108-10° 119-21°

● Reactive to U.V. light S Crystal structure determined

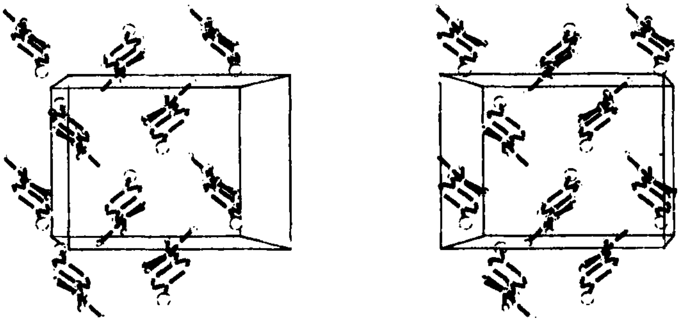
Figure 1 shows the relevant atom numbering scheme used, along with the position of the reactive double bond and positions of substitution within the molecular framework. Table 1 displays details of the sixteen permutations for the substituents H, Br, Cl and methyl at the para-positions X and Y. Also given are the acronyms, space groups, cell constants, melting points, reactivities and whether or not the structure has, at this stage, been determined.

Perusal of Table 1 shows that substitution of the benzyl ring (X) results in a change from orthorhombic to monoclinic crystal class but retention of the primary packing motif (a centre of symmetry) responsible for reactivity. pBrBB, pClBB and pMeBB are isomorphous regardless of the size of the substituent. Substitution on the benzylidene ring (Y) effects interchange of b and c axes and a change in the primary packing motif. BpBrB is an exception and has a structure seemingly isomorphous with BBCP, but comparison shows that the molecular positions within the unit cell differ slightly. Simultaneous substitution on both rings usually leads to light-stable compounds with the possiblity of conformational polymorphism, rotation being allowed about bonds α and β . For those molecules for which bromine has been substituted onto the benzylidene ring, chlorine or methyl substitution onto the benzyl ring (although having the same van der Waals radii), steer the molecule into different structural modes. In the case of pMeBB/pClBB and BpMeB/BpClB there is no distinction between chlorine and methyl and the structures are isomorphous.

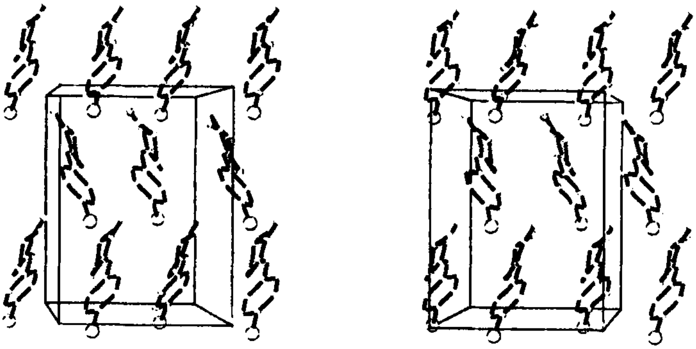
What has emerged from this study is (i) the long molecular axis for all derivatives lies approximately parallel to the [100] axis of the unit cell with the molecules packing in discrete layers in the (100) plane; (ii) reactivity results when the primary packing motif is glide-related centrosymmetric pairs of molecules in the (100) plane and non-reactivity exists when there are purely glide-related molecules in the (100) plane, see figure 2(a and b); and (iii) the greatest value of the factorised nonbonding energies between units corresponds to the plane-to-plane interaction of the incipient dimer pair. The rest of this paper will describe the energetics and properties of the isolated monomer pair.

FIGURE 2. For clarity only the benzylidene-cyclopentanone fragment is drawn.

(a) Shows the reactive inversion/glide motif (BpBrB)



(b) Shows the light stable glide/glide motif (BpClB)



Method

The analysis takes the form of investigating the interaction energy of all possible configurations of the isolated centrosymmetric pair of molecules. This is expressed in the form of contour maps, which are slices through the synthesised energy surface parallel to the plane defined by the benzylidene - cyclopentanone fragment. In the calculations the dispersive energy term alone is monitored as a superposition of pairwise atom-atom potentials (6-exp) over appoximately 12 Å radius. The coulombic contribution has not been included for several reasons; (i) although it is possible to add, explicitly, some contribution from the residual charges, we have relied upon the fact that the parameters used in the 6-exp potential partially incorporate some coulombic characteristics by the very nature of their derivation, (ii) that for this system the coulombic contribution is small compared to the dispersive energy, (iii) estimating the charge distribution reliably is a difficult task, (iv) there seems little benefit in refining the overall potential as the final orientations of the molecule within the crystal will be primarily dependent on the packing of surrounding units and (v) there was no significant difference to the outcome of the maps as a result of including tentative charge distributions.

Figure 3 shows the isolated pairs of molecules with variation in the z direction defining the separation of the molecular planes. Molecule A is fixed whilst molecule B is translated about the x-y grid maintaining the same symmetry operation and plane separation; thus defining a unique contour map. To associate the potential with a particular configuration of the molecules, it is necessary to designate a point in the molecule such that, for molecule A, this point is on the origin and for molecule B, wherever its position on the map gives the interaction energy. For the following set of maps the 'potential association point' (pap) is the C5 atom and the origin for each map corresponds to the orientation of the two molecules where the C5 atoms in each unit are superimposed in the z direction. C1 and C13 define the x axis and the line between these atoms must remain parallel to the x axis to maintain the symmetry operation. The crystallographic orientation of the isolated pair (+) are indicated on the contour maps. Associated with each map is a grid, to the same

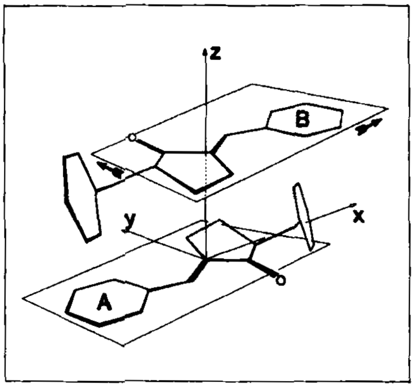


FIGURE 3. Depicts the frame of reference of the isolated monomer pair.

scale, with circles depicting areas where atom-atom contacts are less likely, i.e. less than the sum of their van der Waal radii. Thus they may be considered as a manifestation of the hard sphere potential, the advantage of which is that it can identify directly the effect of individual atom-atom contacts. Otherwise one bad contact may be masked by the overall summation of the positive energy contributions.

Minima on the contour map refer to the best energetic orientations of the isolated molecules (A and B) providing that the circle graph does not exclude the relevant areas.

Results and Discussion

For this system, without exception, where the centrosymmetric pair motif exists within the crystal, the minimum energy configuration corresponds to that found in the crystal structure. Figure 4 shows maps for BBCP, BpBrB, pClpBr and pMepBr. The maps for substituted benzyl derivatives are all very similar to that of BBCP.

(a) The method has the merit of predicting the amount of overlap between two isolated molecules which are related by inversion or translation. If it is possible to assess the likelihood that this arrangement will occur in the crystal structure, it ought, in turn to be possible to deduce whether reaction will occur, as well as predicting whether there are other properties related to this packing motif. For example substitution of hydrogen for bromine on BBCP (to mimic BpBrB)

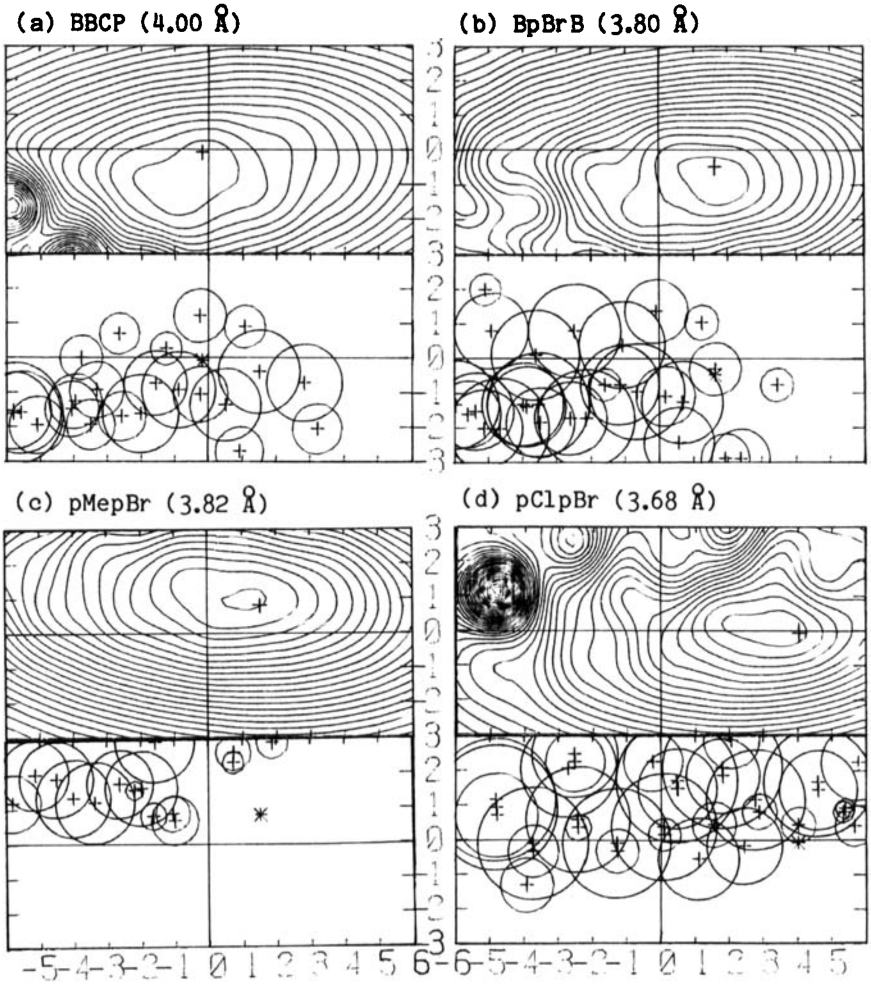


FIGURE 4. See text for detailed explanation of contour maps. The grid increments are in Ångstroms, contour intervals are 2kJ/mol apart and the number in brackets is the plane separation.

did reproduce the map of BpBrB and, as a consequence, the correct spatial relationship of the double bonds. Furthermore any conformational polymorphs similar to pClpBr are likely to be unreactive even though they may pack in the potentially reactive motif; the maps show that the double bonds are too far apart for reaction to ensue.

(b) The method has diagnostic value and can be used in conjunction with other forms of molecular packing analyses.

Compound	Fraction of LE	Motif	Reactivity
BpClB	77.6	glide/glide	No
BpBrB	82.2	inversion/glide	Yes
BBCP	83.5	inversion/glide	Yes
pBrBB	82.2	inversion/glide	Yes
pClBB	80.8	inversion/glide	Yes
pMeBB	84.4	inversion/glide	Yes
pMepBr	81.1	inversion/glide	Yes
pMepMe	78.3	glide/glide	No
pClpBr	68.4	inversion/glide	No

The above table gives the fraction (as a percentage) of the lattice energy contributed by each particular motif. It shows that the competing glide/glide packing motif contributes marginally less to the lattice energy in comparison to the inversion/glide motif, but as a consequence ensures a better interlayer contact in the [100] direction. Also the transition correlates directly with substituent size[4].

inversion/glide	glide/glide
I Br	Cl Me F

The resulting theoretical maps for chlorine and methyl are very similar to that of the bromine derivative implying that these should adopt isomorphous crystal structures (as observed in pXBBCP derivatives). One explanation for the fact that this is not observed may be that substituents smaller than bromine cannot be close-packed sufficiently in the [100] direction and, to do so, the molecules would have to be displaced from the optimal plane-to-plane orientation in the (100) plane. Thus the non-reactive glide/glide motif would become energetically more stable in comparison to a perturbed inversion/glide motif. It seems that a subtle change in volume of substituent in this position is enough to make the molecules adopt a different packing structure.

We conclude, therefore, that for the centrosymmetric primary packing motif, substitution within the (geometrically) remote benzyl group has little effect on structure and reactivity. Substitution within the benzylidene ring, however, directly affects the plane-to-plane contacts of the incipient dimer and depending on the type of substituent may radically change the overall crystal structure.

Acknowledgment

We acknowledge the financial support of the Science Research Council.

References

1 H. Nakanishi, W. Jones and J. M. Thomas, Chem. Phys. Letts., 71, 44,(1980)

2 W. Jones, H. Nakanishi, C. R. Theocharis and J. M. Thomas, J. Chem. Soc. Chem. Comm., 610, (1980)

3 W. Jones, S. Ramdas, C. R. Theocharis, J. M. Thomas and N. W. Thomas, J. Phys. Chem., 85, 2594, (1981)

4 M. J. Begley, M. A. Mazid and D. A. Whiting, Acta. Cryst., A34, 896, (1978)