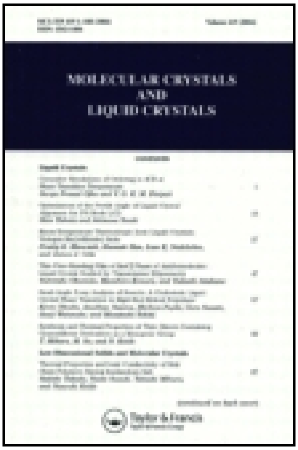

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ANALYSIS OF NON-BONDED INTERACTIONS IN 2-BENZYL-5-BENZYLIDENE CYCLOPENTANONES: THE ROLE OF SUBSTITUENTS IN DETERMINING MOLECULAR CONFORMATIONS AND CRYSTAL PACKING

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Abstract It is well known that the introduction of substituents into an organic molecule can affect its solid-state reactivity profoundly. A novel approach to the 'engineering' of photoreactive crystal structures is presented, with particular reference to 2-benzyl-5-benzylidene cyclopentanones.

INTRODUCTION

The crystal structures of eight derivatives of the title compound have been examined with particular reference to differences they exhibit in conformation and reactivity. The analysis outlined here is performed on a computer, and the graphical representations produced are of three kinds:

i) Radial distributions of the distances of non-bonded interactions of a given type from atoms of a centrally-placed molecule.
ii) Stereo-plots.
iii) Stereographic projections of these non-bonded interatomic vectors.

This approach has been applied to BBCP compounds with the molecular structure as given in figure 1, with substituents at the X and Y positions being interchanged between hydrogen, methyl, chloro and bromo groups.

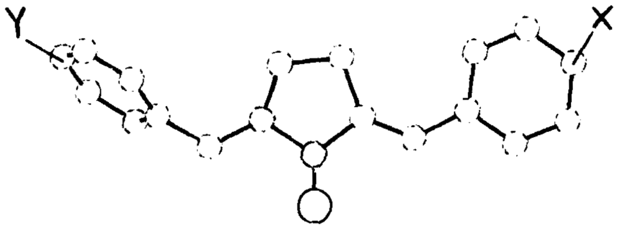

FIGURE 1. Skeletal outline of 2-benzyl-5-benzylidene cyclopentanone (BBCP)

The eight compounds considered are listed in table I, together with their corresponding substituents at the X and Y positions; the photoreactivity of the compounds is also indicated.

TABLE I. Description of the compounds analysed

Compound	X	Y	Reactivity*
BBCP	H	H	+
pMeBBCP	H	Me	+
pClBBCP	H	Cl	+
pBrBBCP	H	Br	+
BpClBCP	Cl	H	-
BpBrBCP	Br	H	+
pClBpBrBCP	Br	Cl	-
pMeBpBrBCP	Br	Me	+

* + Photoreactive

- Photostable

RESULTS

Figures 2 to 5 are radial distributions for C ··· C, C ··· H and H ··· H interactions respectively. The curves denoted by '++++' represent the radial distributions for the parent compound, BBCP. The other seven compounds give rise to distributions within the two curves separated by vertical bars.

The values on the x-axis represent the radius of the non-bonded interaction, r, and the ordinate values, f(r), indicate the number of interactions of length between r and (r + Δr), divided by $4\pi r^2 \Delta r$; Δr is taken to be 0.1Å in these plots. In addition, the ordinate values are divided by the number of atoms in the molecule contributing to the pairwise interactions.

So, for a molecule $C_xH_yO_z$, the distribution for C ··· C interactions is:

$$f(r) = \frac{N_1(r)}{4\pi r^2 \Delta r x}$$

Where $N_1(r)$ is the number of C ··· C interactions of length between r and (r + Δr). Similarly, if $N_2(r)$ is taken to represent the number of C ··· H interactions of length between r and (r + Δr), the distribution for C ··· H interactions is:

$$f(r) = \frac{N_2(r)}{4\pi r^2 \Delta r(x + y)}$$

Thus f(r) represents a spherically averaged coordination shell for each type of atom in the molecule. In order to model the thermal motion of atoms in a crystal, each atomic position has been broadened isotropically. This gives rise to the continuous distributions observed in the plots.

Figures 2 and 3 show that BBCP itself has the most favourable C ··· C and C ··· H interactions for stabilisation. However the other seven substituted compounds do not show any major change in structural detail.

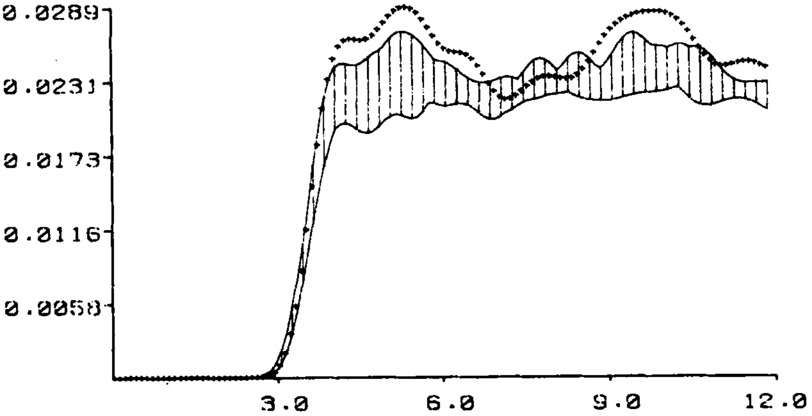

FIGURE 2. C ··· C interactions in BBCP (++++) and the other seven derivatives.

Figure 4 shows that there are comparatively fewer H ··· H interactions at low r, (note the ordinate values), and that the H ··· H interactions build up slowly to a fairly steady concentration at radii greater than 6Å.

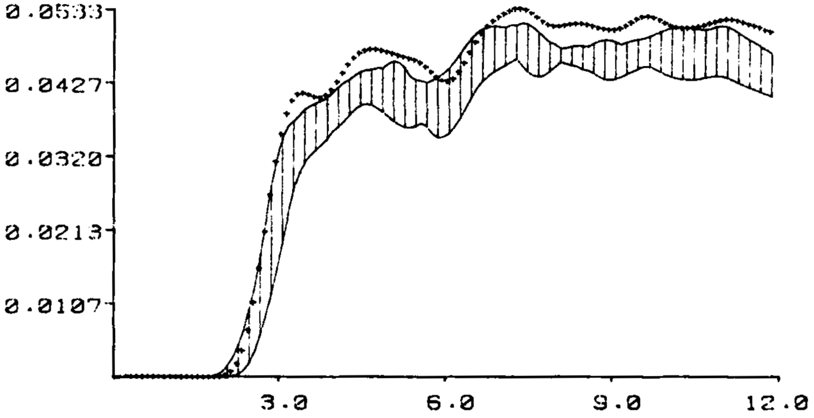

FIGURE 3. C ··· H interactions in BBCP (++++) and the other seven derivatives.

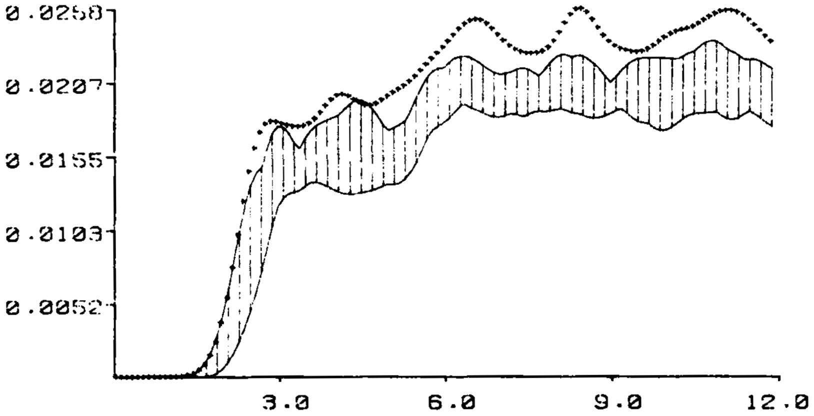

FIGURE 4. H ··· H interactions in BBCP (++++) and the other seven derivatives.

Taken together, these plots indicate how, as expected, all the compounds in the series pack with optimised C ··· C and C ··· H interactions for their overall stabilisation and minimization of lattice energy. The introduction of substituents does not prevent the molecule from obtaining this basic packing requirement.

Figure 5 shows C ··· Y interactions for the compounds BBCP, PClBBCP, pMeBBCP and pBrBBCP, where Y = H, Cl, Me and Br respectively. The distribution for BBCP is indicated by '++++'. The other three compounds show a remarkable similarity in distribution, each falling within the range indicated by the vertical bars. These three compounds also show a distribution that is similar in detail to that of BBCP, apart from a shift to a higher radius for the shortest interactions. This shift is directly attributable to the increased Van der Waals radii of Cl, Me and Br compared to H. We may conclude, therefore, that para-substituents in the benzyl moiety do not have sufficient influence in perturbing the structure.

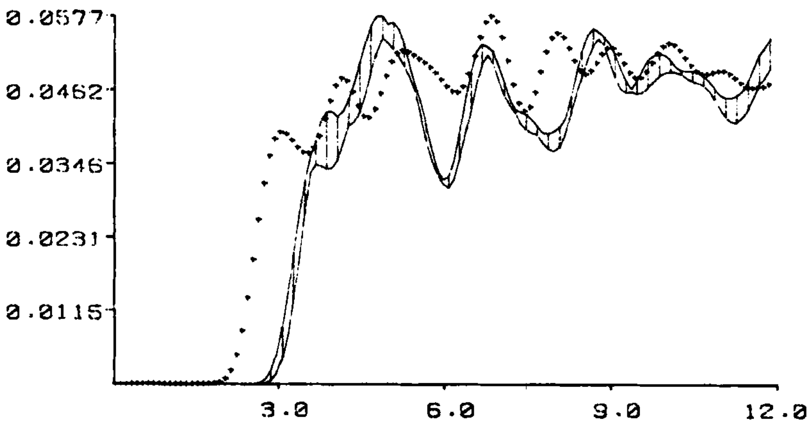

FIGURE 5. C ··· Y interactions in BBCP (++++) and in pClBBCP, pMeBBCP and pBrBBCP.

On the other hand, the C ··· X curves in figure 6 clearly bring out the unusual behaviour of the chloro substituent in the benzylidene moiety of BpClBCP, compared to the BBCP and BpBrBCP structures. In this figure, the continuous line represents BBCP, the dashed line represents BpClBCP, and the crossed line corresponds to BpBrBCP. It is the C ··· Cl interactions (and also H ··· Cl, not shown here) that seem to steer the BpClBCP molecule into a geometry unfavourable for topochemical reactivity.

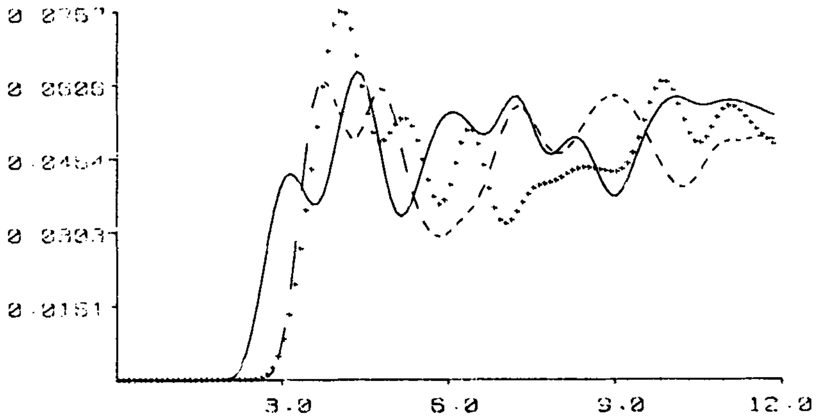

FIGURE 6. C ··· X interactions in BBCP (———), BpClBCP (----) and BpBrBCP (++++).

Similar analyses can be carried out on the disubstituted compounds, pClBpBrBCP and pMeBpBrBCP. The radial curves in figure 7 show C ··· Br interactions for pClBpBrBCP (++++) and pMeBpBrBCP (———).

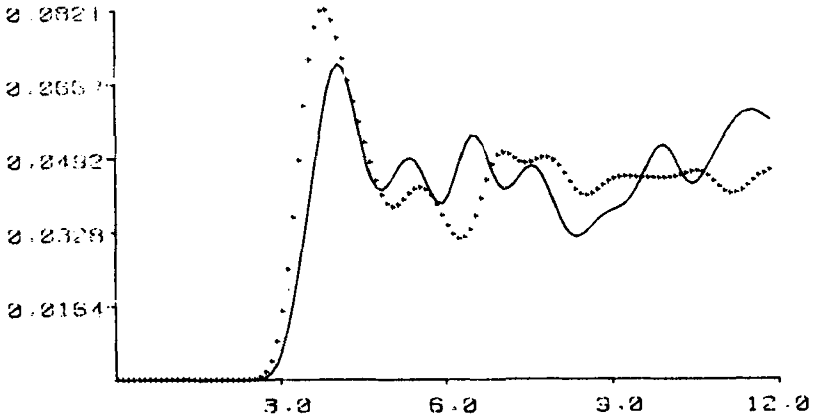

FIGURE 7. C ··· Br interactions in pClBpBrBCP (++++) and in pMeBpBrBCP (———).

The first of these compounds shows a very sharp peak at low r, with an ordinate value of 0.0821, the largest value observed for the whole range of compounds. It is interesting to probe what particular structural conformation gives rise to the very strong coordination of the bromine atom by carbons in pClBpBrBCP. For this reason, stereo vector-plots are invoked to bring out the strongly directional nature of the interactions causing a tight coordination-shell at low r.

Figure 8 is a stereo vector-plot of C ··· Br interactions in pClBpBrBCP. The thin lines represent the directions of non-bonded interactions from carbon atoms in the molecule drawn to bromine atoms in adjacent symmetry-related molecules. Note how the benzyl ring has undergone a major conformational change in order to be closely coordinated to an adjacent bromine atom.

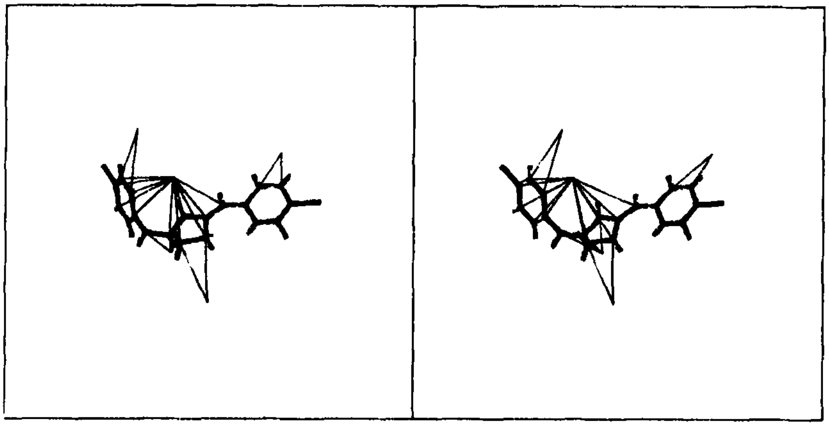

FIGURE 8. Stereo vector-plot of C ··· Br interactions in pClBpBrBCP.

Figure 9, by comparison, shows that no major conformational change of the benzyl moiety has occurred in the pMeBpBrBCP compound. The bromine atom is not as closely coordinated in this compound.

Further evidence is given in figure 10 for the highly specific interactions between the bromine atom of pClBpBrBCP with carbons in the neighbouring benzyl moiety. It is a stereogram of the interatomic Br ··· C vectors, with the C-Br bond of the molecule pointing along the polar axis, marked by a cross. It is seen that the centre of the phenyl ring makes a very small angle with the C-Br bond, indicating that the C-Br bond is pointing almost directly into the benzyl ring.

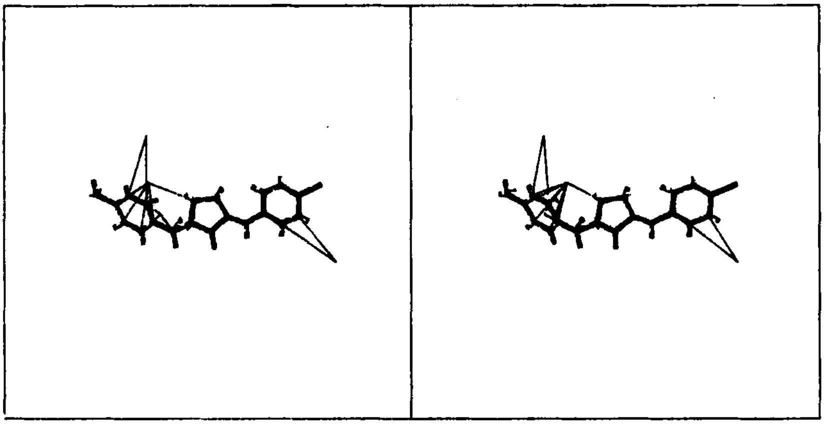

FIGURE 9. Stereo vector-plot of C ··· Br interactions in pMeBpBrBCP.

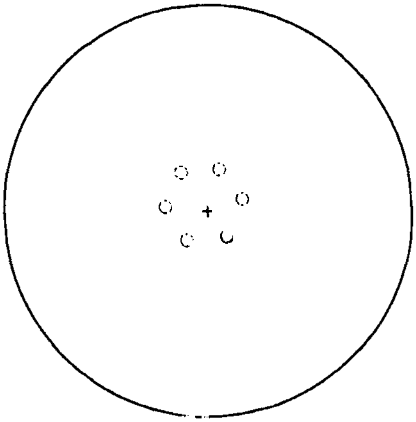

FIGURE 10. Stereographic projection of Br ··· C vectors in pClBpBrBCP. The polar axis is marked by a cross, and the circles represent the projection of Br ··· C vectors.

Figure 11 shows a similar projection for the pMeBpBrBCP compound. It is seen that the C-Br bond (parallel to the polar axis) no longer points directly into the neighbouring phenyl ring. By measuring the length XY, we infer that the centre of the phenyl ring makes an angle of approximately 40° with the C-Br bond.

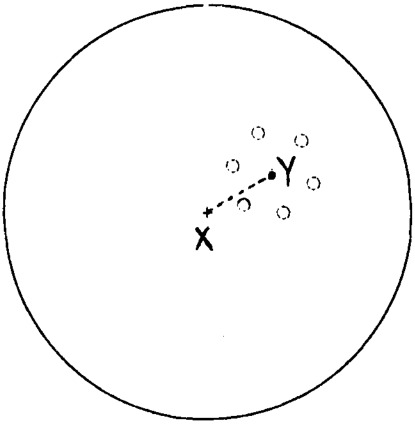

FIGURE 11. Stereographic projection of Br ··· C vectors in pMeBpBrBCP.

CONCLUSION

The three types of illustration shown here provide a simple, graphical basis for a semi-empirical analysis of non-bonded geometry and interactions. Since the analysis is based on observed crystal structures, it can be extended easily to a wider variety of families of compounds.

Such a semi-empirical approach can be incorporated into the general strategy of "crystal engineering".

For further details of the system see,
Jones et. al., J. Phys. Chem. (1981), 85, 2594.