

Solid-State Photobehaviour and Crystal Packing of *o*-Chlorobenzylidene-DL-piperitone: Influence of Molecular Topology on Photobehaviour

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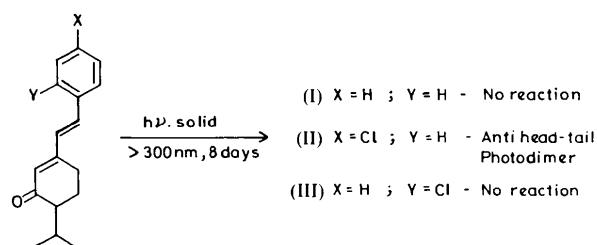
Abstract

$C_{17}H_{19}ClO$, $M_r = 274.7$, triclinic, $P\bar{1}$, $a = 11.154$ (3), $b = 12.685$ (2), $c = 12.713$ (2) Å, $\alpha = 100.68$ (1), $\beta = 113.58$ (1), $\gamma = 104.50$ (2)°, $V = 1511.1$ (6) Å³, $Z = 4$, $D_m = 1.22$, $D_x = 1.215$ Mg m⁻³, Cu $K\alpha$, $\lambda = 1.5418$ Å, $\mu = 2.16$ mm⁻¹, $F(000) = 584$, $T = 293$ K, $R = 0.057$ for 3481 observed reflections. The title compound is photostable in the crystalline state and lattice-energy calculations have been employed to rationalize the photobehaviour. The well-known β -steering ability of the chloro group is not operative in this system as there are no Cl...Cl interactions in the crystal lattice. All five benzylidene-DL-piperitone structures so far studied are α -packed and the molecular topology appears to be a deciding factor even in the presence of steering groups.

Introduction

Crystalline-state reactions, either thermal or photochemical are most often the result of the definite packing arrangement of the molecules unless defect initiated (Cohen & Schmidt, 1964; Cohen, Schmidt & Sonntag, 1964; Schmidt, 1964; Desiraju, 1987). 'Crystal engineering' may be defined as an attempt to preorganize molecules in a desired way. The various strategies adopted to attain the predictive design of organic solids include the use of steering groups such as chloro (Schmidt, 1971; Jones, Ramadas, Theocharis, Thomas & Thomas, 1981; Gnanaguru, Murthy, Venkatesan & Ramamurthy, 1984; Desiraju, 1987), acetoxy (Ramasubbu, Gnanaguru, Venkatesan & Ramamurthy, 1982; Murthy, Ramamurthy & Venkatesan, 1988), sulfur (Nalini & Desiraju, 1987), methylenedioxy (Desiraju, Kamala, Kumari & Sarma, 1984) *etc.* The steering ability of chlorine as a β -packing promoter involving a short axis of translation of 4 Å is well known (Gnanaguru *et al.*, 1982; Desiraju, 1987) and this encouraged us to examine the photobehaviour of photoinert benzylidene-DL-piperitone (Kanagapushpam, Ramamurthy & Venkatesan, 1987) after chloro substitution. The *p*-chloro derivative underwent

photocycloaddition whereas the *o*-chloro derivative remained photostable (see scheme below).



Structural investigations of (II) indicated that the juxtapositioning of the double bonds was favourable for photodimerization, giving an *anti* head-to-tail photoproduct (Venugopalan & Venkatesan, 1990). In order to gain insight into the behaviour of these systems, detailed lattice-energy calculations were performed. The inferences derived from these calculations are twofold. The influence of the nearest neighbours of the reacting partners in crystals of coumarins and other molecules with a rigid molecular skeleton may be described in terms of lattice-energy calculations (Murthy, Arjunan, Venkatesan & Ramamurthy, 1987). It is clear that constraints imposed by the neighbouring groups on conformational changes which may take place during photo-reaction appear to be one of the deciding factors in the photostability of the material. In addition, the role of the 'reaction cavity' (Cohen, 1975), that is the space available for the molecules to undergo necessary changes upon excitation, is also important. This paper is devoted to a detailed discussion of the crystallographic results obtained for (III) in relation to its solid-state photobehaviour. Based on the photobehaviour of benzylidene-DL-piperitone, and its *p*-chloro and *o*-chloro derivatives, the steering capacity of chlorine is also discussed.

Experimental

o-Chlorobenzylidene-DL-piperitone (III) was synthesized following the reported procedure of Read & Smith (1921). A powdered sample of (III) was sealed

Table 1. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^4$) for non-H atoms of (III) with e.s.d.'s in parentheses

$$U_{\text{eq}} = \frac{1}{3} \sum_i U_{ij} a_i a_j a_i a_j$$

Molecule A	x	y	z	U_{eq}
Cl(1)	1192 (1)	7207 (1)	5560 (1)	930 (5)
O(1)	-1268 (3)	11578 (3)	1159 (3)	1248 (20)
C(1)	-1392 (3)	7236 (2)	4156 (3)	643 (14)
C(2)	-625 (3)	6705 (3)	4901 (3)	696 (15)
C(3)	-1270 (5)	5768 (3)	5139 (4)	879 (22)
C(4)	-2704 (5)	5346 (3)	4645 (4)	964 (24)
C(5)	-3498 (5)	5851 (3)	3917 (4)	913 (21)
C(6)	-2840 (4)	6782 (3)	3686 (3)	778 (17)
C(7)	-696 (4)	8205 (3)	3881 (3)	669 (15)
C(8)	-1289 (3)	8751 (3)	3155 (3)	683 (15)
C(9)	-539 (3)	9690 (3)	2884 (2)	619 (14)
C(10)	1024 (3)	10085 (3)	3428 (3)	680 (16)
C(11)	1588 (4)	10732 (3)	2735 (4)	761 (17)
C(12)	1021 (4)	11674 (3)	2489 (3)	752 (18)
C(13)	-565 (4)	11172 (3)	1853 (3)	838 (20)
C(14)	-1234 (4)	10209 (3)	2159 (3)	818 (19)
C(15)	1607 (4)	12385 (3)	1838 (3)	776 (18)
C(16)	1350 (5)	11672 (4)	629 (3)	901 (21)
C(17)	3165 (6)	13121 (5)	2639 (4)	1160 (27)
Molecule B				
Cl(1)	4302 (1)	7600 (1)	4691 (1)	1275 (6)
O(1)	-3992 (2)	3886 (2)	1559 (2)	822 (11)
C(1)	2951 (3)	8046 (3)	2597 (3)	887 (17)
C(2)	4204 (4)	8347 (3)	3664 (3)	1159 (26)
C(3)	5400 (5)	9202 (4)	3916 (5)	1177 (29)
C(4)	5379 (5)	9801 (4)	3135 (6)	1019 (27)
C(5)	4182 (5)	9543 (3)	2078 (5)	800 (18)
C(6)	2980 (4)	8680 (3)	1828 (4)	684 (15)
C(7)	1692 (3)	7105 (3)	2332 (3)	714 (16)
C(8)	512 (3)	6637 (3)	1289 (3)	680 (15)
C(9)	-711 (3)	5678 (2)	1008 (2)	599 (13)
C(10)	-753 (4)	5132 (3)	1946 (3)	788 (17)
C(11)	-2254 (4)	4444 (4)	1652 (3)	864 (20)
C(12)	-3064 (3)	3593 (3)	368 (3)	694 (15)
C(13)	-3045 (3)	4224 (3)	-521 (3)	648 (14)
C(14)	-1805 (3)	5243 (3)	-117 (3)	653 (14)
C(15)	-4535 (3)	2784 (3)	19 (4)	777 (18)
C(16)	-5522 (5)	3415 (5)	32 (6)	987 (28)
C(17)	-4475 (6)	1993 (5)	794 (6)	1182 (33)

in a Pyrex glass container, evacuated and exposed to UV radiation ($\lambda > 300$ nm) using a Rayonet photochemical reactor. The sample was shaken from time to time to ensure uniform exposure. After about one and a half days of irradiation, the material became slightly sticky. However, it did not reveal any photo-reaction according to spectral characteristics. Irradiating the sample at 275 K produced no gummy appearance even when exposed to UV light for 8 days, indicating the absence of photoreaction.

X-ray structural investigations

Single crystals of (III) were obtained by slow evaporation of a 50:50 benzene-hexane solution. Three-dimensional intensity data of (III) were collected on an Enraf-Nonius CAD-4 diffractometer using a crystal of dimensions $0.35 \times 0.25 \times 0.15$ mm. Lattice parameters were obtained by a least-squares procedure using 25 accurately centered reflections. A

search for higher symmetry using the program TRACER (Lawton, 1973) produced the triclinic cell as the one with the highest symmetry. The intensity data were collected using nickel-filtered Cu $K\alpha$ radiation to a limit of $\theta < 65^\circ$ in $\omega/2\theta$ mode. The intensities of three standard reflections (153, 211, 220), used for checking the stability and orientation of the crystal, showed only statistical fluctuations within $\pm 2\%$. A total of 4436 unique reflections were measured (h 0 to 12, k -14 to 14 and l -14 to 14) of which 3481 were considered significant [$|F_o| > 3\sigma(F_o)$], $R_{\text{int}} = 0.042$. Data were corrected for Lorentz and polarization factors, but not for absorption. The structure was solved using SHELXS86 (Sheldrick, 1986). Full-matrix least-squares refinement, using SHELX76 (Sheldrick, 1976), of scale factor, positional and anisotropic thermal parameters of non-H atoms as well as positional and isotropic thermal parameters of H atoms, located from a difference map, converged to a final R value of 0.057, $wR = 0.067$ and $S = 1.26$. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The function minimized in the least-squares refinement was $\sum w(F_o - F_c)^2$ where $w = 1.4093/[\sigma^2(F) + 0.00036|F|^2]$. $\Delta/\sigma_{\text{max}}$ for non-H atoms was 0.03; the residual electron density was $\Delta\rho_{\text{max}} = 0.24$, $\Delta\rho_{\text{min}} = -0.16 \text{ e \AA}^{-3}$ in the final ΔF map.

Results and discussion

The final positional coordinates of non-H atoms are given in Table 1.* A perspective view of the molecule (Johnson, 1976) with atomic numbering scheme is depicted in Fig. 1. The packing of the molecule (Motherwell & Clegg, 1978) is given in Fig. 2. The bond lengths and angles are given in Tables 2 and 3.

Even though (III) is photoinert in the crystalline state, the reactive double bonds are favourably juxtaposed, in the crystal lattice, for dimerization. This is clear from the packing of the molecules (Fig. 2). The distance separating the potentially reactive double bonds, as assessed by Schmidt and co-workers (Schmidt, 1976), must be within *ca* 4.2 Å. There are two potentially reactive double bonds such as C(7)=C(8) and C(9)=C(14) in (III) and the juxtaposition of the double bonds conducive for photo-dimerization is represented in Fig. 3 where the C(7)=C(8) bond is taken as an illustrative example. In this type of representation, θ_1 corresponds to

* Lists of structure factors, anisotropic thermal parameters, bond lengths and bond angles involving H atoms, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55040 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI0118]

rotation of one of the double bonds with respect to the other, θ_2 represents the angle of the parallelogram formed by the double bonds C(7), C(8), C(7ⁱ) and θ_3 is a measure of the angle between the least-squares planes passing through C(7), C(8), C(8ⁱ), C(7ⁱ) and C(1), C(7), C(8) and C(9). The parameter d represents the displacement of one of the double bonds with respect to the other. For ideal orientation of the molecules, θ_1 , θ_2 and θ_3 should be 0, 90, 90° respectively, with $d = 0$ Å.

The geometrical arrangement of the double bonds can be considered to be conducive for the topochemical dimerization reaction in (III). There are three such contacts observed within the two molecules of the asymmetric unit (hereafter *A* and *B*) and they are schematically represented in Fig. 4. These contacts are: (1) AC(7) at (1 + x , y , z) is at a distance of 4.204 Å from AC(8ⁱ) ($i = -x + 1, 2 - y, 1 - z$) with the geometrical parameters, $\theta_1 = 0$, $\theta_2 = 90.0$, $\theta_3 = 63.8^\circ$ and $d = 1.854$ Å. (2) BC(9) at (1 + x , y , z) comes close to BC(14ⁱ) ($i = -x + 1, 1 - y, -z$) at a distance of 3.77 Å with the displacement parameters $\theta_1 = 0$, $\theta_2 = 95.6$, $\theta_3 = 69.1^\circ$ and $d = 1.37$ Å. (3)

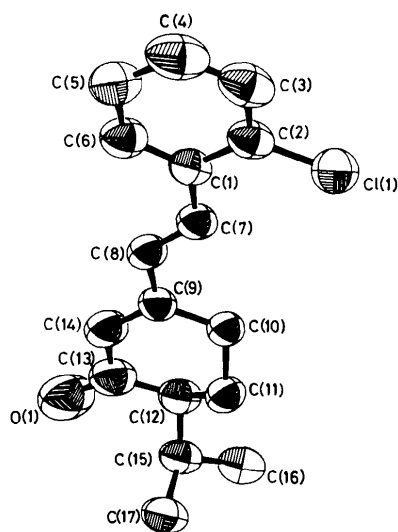


Fig. 1. A perspective view of molecule *A* with atomic numbering scheme (the two molecules in the asymmetric unit are similarly numbered and the thermal ellipsoids are at 50% probability level).

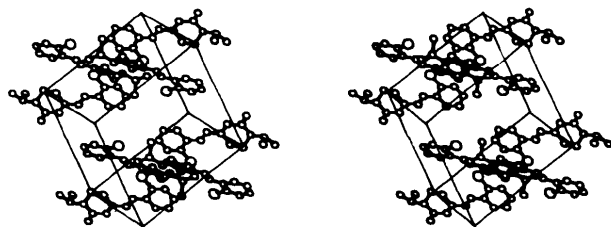


Fig. 2. Stereoview of the packing of the molecules in the unit cell.

Table 2. Selected bond distances (Å) involving non-H atoms in (III) with *e.s.d.*'s in parentheses

	Molecule <i>A</i>	Molecule <i>B</i>
C(1)—C(2)	1.736 (4)	1.735 (4)
O(1)—C(13)	1.214 (5)	1.221 (4)
C(1)—C(2)	1.400 (5)	1.401 (5)
C(1)—C(6)	1.390 (6)	1.381 (6)
C(1)—C(7)	1.461 (5)	1.464 (5)
C(2)—C(3)	1.379 (6)	1.365 (7)
C(3)—C(4)	1.371 (8)	1.354 (8)
C(4)—C(5)	1.378 (7)	1.370 (9)
C(5)—C(6)	1.373 (6)	1.375 (7)
C(7)—C(8)	1.321 (5)	1.328 (5)
C(8)—C(9)	1.457 (5)	1.445 (5)
C(9)—C(10)	1.496 (5)	1.496 (4)
C(9)—C(14)	1.339 (5)	1.346 (4)
C(10)—C(11)	1.516 (6)	1.533 (7)
C(11)—C(12)	1.511 (6)	1.525 (5)
C(12)—C(13)	1.513 (6)	1.505 (5)
C(12)—C(15)	1.529 (6)	1.532 (6)
C(13)—C(14)	1.467 (6)	1.462 (5)
C(15)—C(16)	1.505 (5)	1.517 (8)
C(15)—C(17)	1.532 (8)	1.526 (8)

Table 3. Selected bond angles (°) involving non-H atoms in (III) with *e.s.d.*'s in parentheses

	Molecule <i>A</i>	Molecule <i>B</i>
C(2)—C(1)—C(6)	116.4 (3)	116.4 (4)
C(2)—C(1)—C(7)	121.3 (3)	120.8 (3)
C(6)—C(1)—C(7)	122.3 (3)	122.8 (3)
Cl(1)—C(2)—C(1)	120.7 (3)	120.6 (3)
Cl(1)—C(2)—C(3)	117.4 (3)	117.5 (4)
C(1)—C(2)—C(3)	121.9 (4)	121.8 (4)
C(2)—C(3)—C(4)	119.5 (4)	119.7 (5)
C(3)—C(4)—C(5)	120.5 (5)	120.9 (6)
C(4)—C(5)—C(6)	119.4 (4)	119.2 (5)
C(1)—C(6)—C(5)	122.3 (4)	122.0 (4)
C(1)—C(7)—C(8)	127.7 (4)	126.2 (3)
C(7)—C(8)—C(9)	125.2 (3)	126.4 (3)
C(8)—C(9)—C(10)	119.7 (3)	120.5 (3)
C(8)—C(9)—C(14)	120.6 (3)	120.0 (3)
C(10)—C(9)—C(14)	119.7 (3)	119.4 (3)
C(9)—C(10)—C(11)	112.8 (3)	112.4 (3)
C(10)—C(11)—C(12)	113.1 (4)	111.3 (3)
C(11)—C(12)—C(13)	109.3 (3)	109.6 (3)
C(11)—C(12)—C(15)	115.0 (3)	115.6 (3)
C(13)—C(12)—C(15)	112.7 (3)	113.2 (3)
O(1)—C(13)—C(12)	121.9 (4)	122.2 (3)
O(1)—C(13)—C(14)	120.7 (4)	120.2 (3)
C(12)—C(13)—C(14)	117.4 (3)	117.5 (3)
C(9)—C(14)—C(13)	124.4 (4)	124.4 (3)
C(12)—C(15)—C(16)	113.2 (3)	113.0 (4)
C(12)—C(15)—C(17)	111.8 (4)	111.4 (4)
C(16)—C(15)—C(17)	111.0 (4)	111.8 (4)

The potentially reactive pair, $BC(7)=BC(8)$ and $BC(14^i)=BC(9^i)$ ($i = -x, 1 - y, -z$), are also placed within the reactive distance. Here, $BC(7)\cdots BC(14^i) = 3.77$ and $BC(8)\cdots BC(9^i) = 3.86$ Å and the potentially reactive partners are not strictly parallel. This is revealed by θ_1 which is 6.6° . The other geometrical parameters are $\theta_2 = 65.7$, $\theta_3 = 87.2^\circ$ and $d = 0.17$ Å.

There are many instances where despite the favourable molecular packing molecules are photostable, as in the case of (III) discussed in this paper (Nakanishi, Parkinson, Jones, Thomas & Hasegawa, 1979; Ariel, Askari, Sheffer, Trotter & Walsh, 1984; Hanson, 1975; Sen & Venkatesan, 1991; Seinreich &

Batzer, 1973; Mez & Rihs, 1973). It has also been shown, based on lattice-energy calculations, that the photostability is in many cases due to the severe restrictions imposed upon the motions of the molecules by the environment upon excitation (Murthy *et al.*, 1987).

In this context it was considered worthwhile to carry out lattice-energy calculations for (II) and (III) in order to understand their photobehaviour. These calculations were performed using the program *WMIN* (Busing, 1981). The energy was calculated by the pairwise van der Waals attractive and repulsive potential given below.

$$E = \sum_i^{\text{one cell}} \sum_{i \neq j}^{\text{all cells}} (-A_{ij}/r_{ij}^6) + \sum_i^{\text{one cell}} \sum_{i \neq j}^{\text{all cells}} (D_{ij}/r_{ij}^{12}). \quad (1)$$

The nonbonded interaction parameters used for the lattice-energy calculations (A_i and D_i) were taken from Mirsky (1978). Contributions arising from the Coulombic interaction energy were not included.

The lattice energy was calculated for the initial orientations of the molecules (θ_1 , θ_2 , θ_3 and d as mentioned above). When these values deviated significantly, they were brought back to their ideal values by the necessary rotations and translations and the energy was recalculated. A right-handed coordinate system was chosen in which the origin lies at the midpoint of the reactive double bonds. Deviations of the final values of the geometrical parameters were within 1° of the ideal values, except for θ_1 of the third contact of (III). In all the calculations the molecules were treated as rigid bodies and the neighbouring molecules were also given appropriate rotations and translations so as to preserve the space-group symmetry. The energies computed for

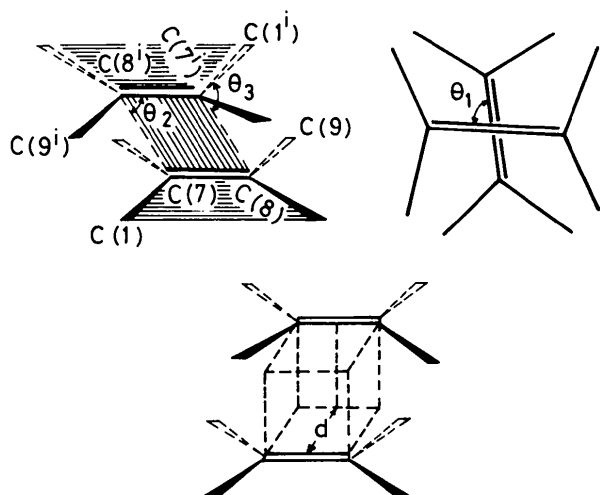


Fig. 3. Geometrical parameters used in the relative representation of the reactive double bonds.

the X-ray-determined positions of (II) and (III) were -7.1 and -12.9 kJ mol $^{-1}$ respectively. The increase in lattice energy after achieving ideal geometry was 12.9 kJ mol $^{-1}$ for (II) and 15.4, 15.7 and 8.3 kJ mol $^{-1}$ for (III), for the three contact geometries. This is not a very large increase in energy compared to the values calculated for all the cases that are found to be photostable. For example, in the case of a tetrahydronaphthalene derivative, the increase in energy was 359.6 kJ mol $^{-1}$ (Murthy *et al.*, 1987). The energy calculation is consistent with the photoreactivity of (II) but shows that (III) could also react.

As the energy calculations could not provide a satisfactory rationale for the photostability of (III), one tends to think about the limitations of such an approach and to look for other possible explanations for photostability. It should be mentioned that in the unsubstituted benzylidene-DL-piperitone, the attainment of ideal geometry by the reactive partners only increased the energy by 0.2 kJ mol $^{-1}$ although the crystal is photostable (Kanagapushpam *et al.*, 1987).

In the calculations described above, the molecular geometry and the dispersion constants used correspond to the ground state. However it is to be expected that these are different in the excited state. Although the approach adopted here has been successful in rationalizing the photobehaviour of rigid molecular systems such as coumarins (Ramamurthy & Venkatesan, 1987), it cannot always be expected to be satisfactory for systems with conformational flexibility unless the crystal packing allows such large-scale changes without producing severe inter-

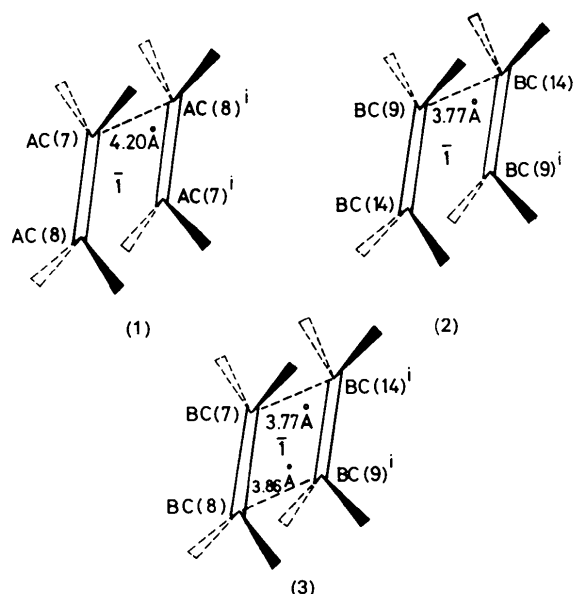


Fig. 4. Schematic representation of the three reactive pairs of double bonds in (III).

molecular short contacts. Obviously in the case of the photoreactive compound (II), the reaction-cavity volume is sufficient to allow photodimerization to take place. The situation with regard to the photo-inert compound (III) seems complex. Unlike the case of (II), there are two independent molecules (*A* and *B*) in the asymmetric unit. These two molecules are placed in such a way that the styrenic double bonds make an angle of 49.7° with respect to each other (see Fig. 5). Further, they are placed such that the angle between the least-squares plane passing through C(1), C(7), C(8) and C(9) of both molecules is 31.8° . Along the reaction pathway, which involves changes in hybridization of the reactive atoms C(7), C(8), C(9) and C(14) from sp^2 to sp^3 , the atoms must undergo considerable positional changes in the crystal lattice. Such large-scale displacement of atoms within the existing lattice may not be compatible with intermolecular energy considerations. Further, with two independent molecules in the asymmetric unit, there are no symmetry restrictions imposed on their concerted movements. Thus, it is inconceivable that the crystal would have a sufficiently large reaction-cavity volume to permit all the movements necessary for the molecules to attain the required geometry of the incipient dimer and still possess lattice stability. In order to further investigate this situation, it was considered worthwhile to perform lattice-energy calculations, even if they were only approximate.

In these energy calculations the necessary movements of the phenyl and cyclohexenone rings to produce the anticipated dimer from the initial positions of the monomers were conceived from a molecular model of the dimer. These conformational changes were performed in order to attain a final geometry close to that of the dimer. This was carried out in two steps. Firstly, rotations of 15° were performed about the C(7)=C(8) axis in such a way that the distance between C(1) and C(9') increased – this would be the direct consequence of a change in

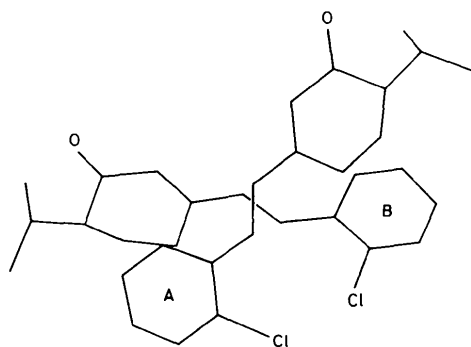


Fig. 5. The relative orientation of the two molecules (*A* and *B*) in the asymmetric unit.

Table 4. Torsion angles ($^\circ$) of the cyclohexenone ring in (III) with *e.s.d.*'s in parentheses

	Molecule <i>A</i>	Molecule <i>B</i>
C(14)–C(9)–C(10)–C(11)	–21.2 (5)	–22.3 (5)
C(9)–C(10)–C(11)–C(12)	49.8 (5)	51.9 (4)
C(10)–C(11)–C(12)–C(13)	–54.5 (5)	–55.9 (4)
C(11)–C(12)–C(13)–C(14)	32.5 (5)	32.0 (5)
C(12)–C(13)–C(14)–C(9)	–5.7 (6)	–2.9 (5)
C(13)–C(14)–C(9)–C(10)	–0.6 (6)	–2.5 (5)

hybridization at C(7) and C(8). The calculated lattice energy was $245.0 \text{ kJ mol}^{-1}$. Secondly, when the molecule, generated in the above manner, was further rotated by 15° about an axis perpendicular to the plane passing through C(1), C(7), C(8) and C(9), and the energy recalculated, it increased to $1651.9 \text{ kJ mol}^{-1}$. This indicates that the lattice does not permit these changes which are necessary for the reaction to take place and to yield a centrosymmetric dimer. The conformational changes simulated in these calculations are only approximate. In reality, there would be considerable single-bond rotations and other small-scale molecular movements occurring, along with the major hybridization changes. Nevertheless, the final configuration reached from the energy calculation is expected to be close to that of the dimer that would be expected from the packing arrangements.

In the case of (II) there are only two molecules in the unit cell which are inversion related. Hence symmetry-independent movements of the molecules in the crystal do not exist. It may be noted that the percentage yield of the photodimer is not very high (maximum 30% after 7 days of irradiation). Though the percentage yield depends upon factors such as the size of the crystallites, mosaicity and temperature, it is also possible that in this crystal restricted orientational flexibility may reduce the yield. However, it is not as stringent as in (III), probably due to the fact that there are no symmetry-independent neighbours to prevent photoreaction.

As mentioned earlier the ability of the chloro group to induce β -packing was the reason for the present study. However, there are no Cl...Cl short contacts less than sum of the van der Waals radii in either (II) or (III). Thus the chloro group is probably ineffective in inducing a β -packing mode in these crystal structures. It is observed that all the benzylidene-DL-piperitones studied, namely the unsubstituted compound (Kanagapushpam *et al.*, 1987), and the *o*-chloro, *p*-chloro (Venugopalan & Venkatesan, 1990), *p*-bromo (Venugopalan & Venkatesan, 1991) and *p*-fluoro derivatives (Kumar & Venkatesan, 1991) are α -packed. It is reasonable to conclude that the overall nonplanar nature of the molecule due to the presence of the cyclohexenone ring which is in a sofa conformation (Romers,

Altona, Buys & Havinga, 1969) (see the relevant torsion angles in Table 4) and an isopropyl group does not lead to efficient crystal packing in the β -mode. Another significant conclusion emerging from these studies is that the role of chlorine as a universal steering group is not applicable to all molecular frameworks, especially if it is significantly non-planar.

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Molecular Packing of Crystalline Azahydrocarbons

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Abstract

The crystal structures of 458 azahydrocarbons, that is, organic molecules containing C, H and N atoms without N—H \cdots N hydrogen bonding, have been retrieved from the Cambridge Structural Database. Statistical analyses of molecular and crystal parameters were performed, and the results compared with hydrocarbons and oxygen-containing compounds.

Average atomic contributions to molecular volumes, surfaces and packing energies were obtained. Packing coefficients are just slightly lower than for hydrocarbons, showing no clear sign of breakdown of close packing, while the crystal density increases with increasing nitrogen content as expected. Some evidence of weak C—H \cdots N hydrogen bonding appears, especially with nitrile N atoms, while no unusually short C \cdots N intermolecular distances are observed.