

The higher density of the  $\alpha$  form is consistent with its greater stability. In this compound the polymorphism appears to be a consequence of the similarity of the energies of the two molecular conformations.

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## Studies in Crystal Engineering: Topochemical Photodimerization and Structure of *p*-Chlorobenzylidene-DL-piperitone

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#### Abstract

3-(*p*-Chlorophenylvinyl)-6-isopropyl-2-cyclohexen-1-one,  $C_{17}H_{19}ClO$ ,  $M_r = 274.7$ , triclinic,  $P\bar{1}$ ,  $a = 6.636$  (1),  $b = 10.537$  (2),  $c = 10.811$  (3) Å,  $\alpha = 95.31$  (2),  $\beta = 92.60$  (2),  $\gamma = 100.66$  (2)°,  $V = 738.2$  (2) Å<sup>3</sup>,  $Z = 2$ ,  $D_m = 1.23$ ,  $D_x = 1.236$  Mg m<sup>-3</sup>,  $Cu K\alpha$ ,  $\lambda = 1.5418$  Å,  $\mu = 2.09$  mm<sup>-1</sup>,  $F(000) = 292$ ,  $T = 298$  K,  $R = 0.050$  for 2220 observed reflections. The title compound undergoes a topochemical photodimerization giving an *anti* head-to-tail dimer instead of the *syn* head-to-head dimer expected on the basis of the ability of the chloro group to steer  $\beta$ -type packing. There are no significant Cl...Cl intermolecular interactions. Possible reasons for the observed  $\alpha$ -type packing of benzylidenepiperitones are advanced. The low dimer yield is also rationalized.

#### Introduction

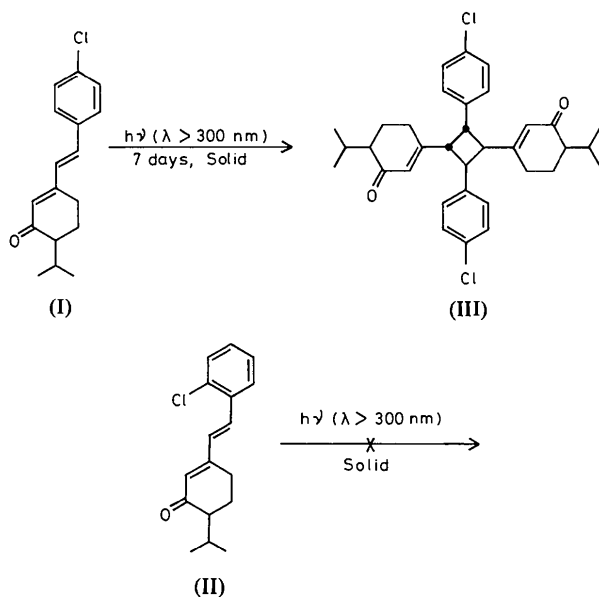
The product obtained from a photochemically induced reaction in the crystalline state is dictated by topochemical factors such as packing, local symmetry and the separation between reactive double bonds (Cohen & Schmidt, 1964; Cohen, Schmidt & Sonntag, 1964; Schmidt, 1964). The type of molecular packing which favours solid-state photochemical

reactions has been studied by a number of investigators. A predictive approach, focusing on organic solids, has led to the discovery of many steering groups such as chloro (Schmidt, 1971; Jones, Ramadas, Theocharis, Thomas & Thomas, 1981; Gnanaguru, Murthy, Venkatesan & Ramamurthy, 1984; Desiraju & Sharma, 1986), acetoxy (Ramassubbu, Gnanaguru, Venkatesan & Ramamurthy, 1982; Murthy, Ramamurthy & Venkatesan, 1988) and sulfur (Nalini & Desiraju, 1987). It has been observed that chloro substitution, in particular, favours  $\beta$ -type packing (Ramamurthy & Venkatesan, 1987; Desiraju, 1987) in organic crystals. In order to investigate this chloro-steering effect further and hence facilitate otherwise unattainable photoreactions, we have investigated the photostability of an  $\alpha$ -benzylidene-DL-piperitone, which contains two potentially reactive double bonds (Kanagapushpam, Ramamurthy & Venkatesan, 1987).

#### Experimental

*p*-Chlorobenzylidene-DL-piperitone (I) and the *o*-chloro derivative (II) were prepared following reported procedures (Read & Smith, 1921). Powdered samples of the compounds were exposed

to UV radiation using a Rayonet photochemical reactor ( $\lambda > 300$  nm). The results obtained from these experiments are shown below.



In the case of the *p*-chloro derivative (I),  $^1\text{H}$  NMR spectra established that an *anti* head-to-tail dimer (III) was obtained whereas the *o*-chloro derivative (II) is photostable. In order to relate the reactivity of these molecules to molecular packing, crystallographic investigations were carried out.

Single crystals of (I) were obtained from slow evaporation of a 75:25 ethanol–chloroform solution. (II) was crystallized from a 50:50 benzene–hexane solution. Preliminary oscillation and Weissenberg photographs indicated that both (I) and (II) belong to the triclinic system. The lattice constants were accurately determined by a least-squares fit of 21 standard reflections in the range  $14 < \theta < 30^\circ$  for the *para* derivative, and from 25 standard reflections in the range  $6 < \theta < 19^\circ$  for the *ortho* derivative ( $\lambda = 0.7107$  Å). In view of the photostability of (II), detailed crystallographic analysis of this compound was not carried out. Crystal data for (II):  $a = 11.127$  (3),  $b = 12.661$  (4),  $c = 12.686$  (3) Å,  $\alpha = 100.62$  (2),  $\beta = 113.56$  (2),  $\gamma = 104.50$  (2)°,  $V = 1502$  (27) Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.22$  Mg m<sup>-3</sup> (by flotation in KI solution),  $D_x = 1.215$  Mg m<sup>-3</sup>, space group  $P1$  or  $P\bar{1}$ . Three-dimensional intensity data for the *para* derivative were collected ( $2\theta = 130^\circ$ ) on an Enraf–Nonius CAD-4 diffractometer using a crystal of dimensions  $0.3 \times 0.2 \times 0.2$  mm. Graphite-monochromated  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5418$  Å) in  $\omega/2\theta$  mode with a scan speed of  $1^\circ \text{ min}^{-1}$  was employed. Three reflections were used as standard to monitor the stability and orientation of the crystal during the data collection. The intensity data of these

reflections ( $04\bar{2}$ ,  $\bar{2}14$ ,  $\bar{3}2\bar{4}$ ) varied by a maximum of 2%. A total of 2510 unique reflections were measured ( $h, k, l$  0 to 7,  $-11$  to 11,  $-12$  to 12) of which 2220 were significant ( $|F_o| > 3\sigma(|F_o|)$ ). Corrections were applied for Lorentz and polarization factors but not for absorption. The structure was solved by direct methods using *MULTAN84* (Main, Germain & Woolfson, 1984). Full-matrix least-squares refinement (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 converged at  $R = 0.050$ ,  $wR = 0.061$  and  $S = 1.57$ . The function minimized was  $\sum w(|F_o| - |F_c|)^2$  where  $w = 1.5534/(\sigma^2|F| + 0.001478|F|^2)$ .  $\Delta/\sigma_{\text{max}}$  for non-H atoms was 0.002; the residual electron density  $\rho_{\text{max}} = 0.2$ ,  $\rho_{\text{min}} = -0.4$  e Å<sup>-3</sup> in the final  $\Delta F$  map. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

## Discussion

The final positional and isotropic thermal parameters for the non-H atoms are given in Table 1.\* The bond lengths, angles and selected torsion angles are given in Table 2. A perspective view of the molecule (*ORTEP*; Johnson, 1976) is depicted in Fig. 1 and a packing diagram (*PLUTO78*; Motherwell & Clegg, 1978) is given in Fig. 2.

Bond lengths and angles are unexceptional. C(7) deviates significantly, by 0.047 (2) Å, from the phenyl ring, which is planar to within 0.006 (2) Å. From the torsion angles in Table 2, the cyclohexenone ring is observed to be in a sofa conformation (Romers, Altona, Buys & Havinga, 1969) as in  $\alpha$ -benzylidene-DL-piperitone (Kanagapushpam *et al.*, 1987).

There are two potentially reactive double bonds in the title molecule, both of which in principle could undergo photodimerization. Indeed, there are many instances of double photodimerization in molecules with multiple double bonds (Green & Schmidt, 1970; Hasegava, Saigo, Mori, Uno, Nohara & Nakanishi, 1985; Hasegava, Endo, Aoyama & Saigo, 1989; Venugopalan & Venkatesan, 1990a). However, in (I) the centrosymmetrically related pairs C(7)=C(8) and C(7<sup>i</sup>)=C(8<sup>i</sup>) [ $i$  1 -  $x$ ,  $-y - 1$ ,  $-z$ ] which lie at a distance of 3.897 (3) Å between C(7) and C(8<sup>i</sup>), participate in the reaction yielding the *anti* head-to-tail dimer. This confirms the stereochemistry assigned from  $^1\text{H}$  NMR spectra. Ideally, in a [2 + 2] photodimerization reaction, the  $\pi$  orbitals of the reactive

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53314 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates and equivalent isotropic temperature factors for non-H atoms of (I) with e.s.d.'s in parentheses

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	$U_{eq} (\text{\AA}^2)$
Cl	0.2384 (1)	0.0195 (1)	0.1946 (1)	0.0764 (3)
O	1.1123 (2)	-0.7241 (2)	-0.2622 (1)	0.0701 (6)
C(1)	0.4319 (3)	-0.2925 (2)	-0.0631 (2)	0.0500 (6)
C(2)	0.5530 (3)	-0.2350 (2)	0.0436 (2)	0.0549 (6)
C(3)	0.4948 (3)	-0.1404 (2)	0.1217 (2)	0.0588 (7)
C(4)	0.3124 (3)	-0.1009 (2)	0.0953 (2)	0.0558 (6)
C(5)	0.1861 (3)	-0.1565 (2)	-0.0084 (2)	0.0621 (7)
C(6)	0.2464 (3)	-0.2500 (2)	-0.0860 (2)	0.0577 (7)
C(7)	0.4914 (3)	-0.3891 (2)	-0.1505 (2)	0.0546 (6)
C(8)	0.6640 (3)	-0.4382 (2)	-0.1440 (2)	0.0545 (6)
C(9)	0.7206 (3)	-0.5340 (2)	-0.2321 (2)	0.0495 (6)
C(10)	0.5861 (3)	-0.5842 (2)	-0.3491 (2)	0.0564 (7)
C(11)	0.7012 (3)	-0.6461 (2)	-0.4502 (2)	0.0589 (7)
C(12)	0.8121 (3)	-0.7470 (2)	-0.4012 (2)	0.0520 (6)
C(13)	0.9557 (3)	-0.6849 (2)	-0.2887 (2)	0.0515 (6)
C(14)	0.8932 (3)	-0.5819 (2)	-0.2104 (2)	0.0535 (6)
C(15)	0.9192 (3)	-0.8213 (2)	-0.4978 (2)	0.0567 (6)
C(16)	1.0772 (4)	-0.7320 (3)	-0.5641 (2)	0.0747 (9)
C(17)	0.7659 (4)	-0.9093 (3)	-0.5913 (3)	0.0788 (9)

Table 2. Selected bond distances (Å), bond angles (°) and torsion angles (°) involving non-H atoms in (I) with e.s.d.'s in parentheses

Cl—C(4)	1.741 (2)	C(8)—C(9)	1.436 (3)
O—C(13)	1.219 (2)	C(9)—C(10)	1.509 (3)
C(1)—C(2)	1.397 (3)	C(9)—C(14)	1.353 (3)
C(1)—C(6)	1.404 (3)	C(10)—C(11)	1.526 (3)
C(1)—C(7)	1.446 (3)	C(11)—C(12)	1.520 (3)
C(2)—C(3)	1.368 (3)	C(12)—C(13)	1.527 (3)
C(3)—C(4)	1.377 (3)	C(12)—C(15)	1.527 (3)
C(4)—C(5)	1.384 (3)	C(13)—C(14)	1.448 (3)
C(5)—C(6)	1.363 (3)	C(15)—C(16)	1.525 (3)
C(7)—C(8)	1.343 (3)	C(15)—C(17)	1.517 (3)
C(2)—C(1)—C(6)	117.0 (2)	C(10)—C(9)—C(14)	119.2 (2)
C(2)—C(1)—C(7)	123.2 (2)	C(9)—C(10)—C(11)	112.5 (2)
C(6)—C(1)—C(7)	119.7 (2)	C(10)—C(11)—C(12)	111.7 (2)
C(1)—C(2)—C(3)	121.5 (2)	C(11)—C(12)—C(13)	109.4 (2)
C(2)—C(3)—C(4)	119.5 (2)	C(11)—C(12)—C(15)	115.6 (2)
Cl(1)—C(4)—C(3)	119.6 (2)	C(13)—C(12)—C(15)	112.6 (2)
Cl(1)—C(4)—C(5)	119.5 (2)	O(1)—C(13)—C(12)	121.6 (2)
C(3)—C(4)—C(5)	120.9 (2)	O(1)—C(13)—C(14)	120.9 (2)
C(4)—C(5)—C(6)	118.9 (2)	C(12)—C(13)—C(14)	117.4 (1)
C(1)—C(6)—C(5)	122.0 (2)	C(9)—C(14)—C(13)	124.7 (2)
C(1)—C(7)—C(8)	127.3 (2)	C(12)—C(15)—C(16)	112.7 (2)
C(7)—C(8)—C(9)	126.4 (2)	C(12)—C(15)—C(17)	111.7 (2)
C(8)—C(9)—C(10)	120.3 (2)	C(16)—C(15)—C(17)	110.6 (2)
C(8)—C(9)—C(14)	120.6 (2)		
C(14)—C(9)—C(10)—C(11)	-21.1 (3)	C(11)—C(12)—C(13)—C(14)	31.9 (2)
C(9)—C(10)—C(11)—C(12)	51.4 (2)	C(12)—C(13)—C(14)—C(9)	-2.3 (4)
C(10)—C(11)—C(12)—C(13)	-55.9 (2)	C(13)—C(14)—C(9)—C(10)	-3.6 (3)

double bonds should overlap, which would require the angles  $\theta_1$ ,  $\theta_2$  and  $\theta_3$  (Fig. 3) to adopt values of 0, 90 and 90° respectively with  $d$  (displacement of the reactive double bonds with respect to each other) being 0 Å. In the present structure these values are  $\theta_1 = 0$ ,  $\theta_2 = 87.1$  and  $\theta_3 = 66.8^\circ$  with  $d = 1.53$  Å. It should be mentioned that in many photoreactive crystalline compounds  $\theta_1$ ,  $\theta_2$ ,  $\theta_3$  and  $d$  deviate significantly from the ideal values (Ramamurthy &

Venkatesan, 1987). This suggests that appreciable translational and rotational motions from the X-ray determined positions are required before the cycloaddition reaction begins. A theoretical study of structural response to excitation in mixed molecular crystals (Craig, Lindsay & Mallett, 1984) has shown that it is necessary to view solid-state photochemical

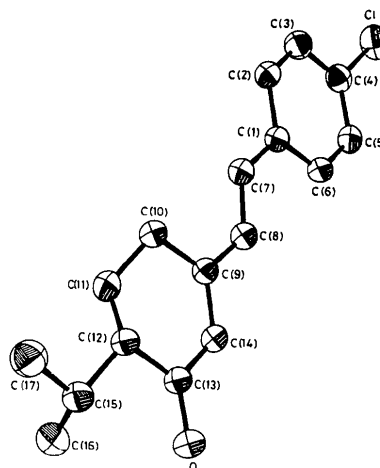


Fig. 1. A perspective view of the molecule with atomic numbering scheme.

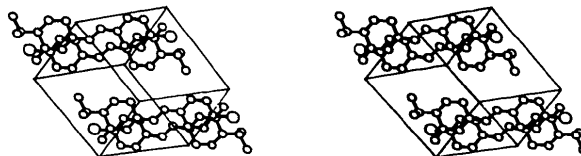


Fig. 2. Stereoview of the packing of the molecules in the unit cell.

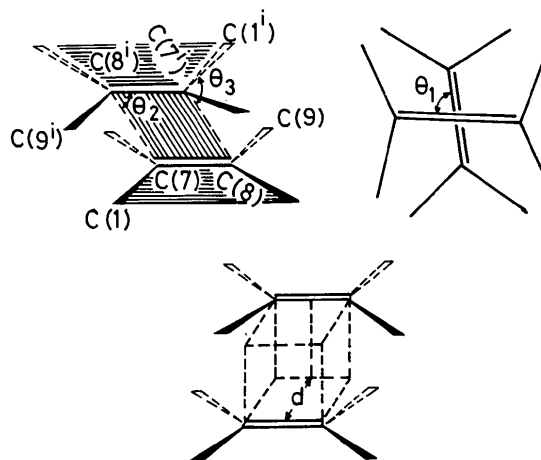


Fig. 3. Geometrical parameters used in the relative representation of the reactive double bonds.

reactions in the light of 'dynamic preformation'. It has also been shown from lattice-energy calculations that in many photoreactive crystals in which reactive double bonds are not ideally oriented, the increase in the lattice energy is considerably less than that in the photo-inert crystals (Murthy, Arjunan, Venkatesan & Ramamurthy, 1987). This indicates that there is sufficient cavity volume and hence freedom for the reacting partners to reorient themselves in the lattice.

As mentioned at the outset, the ability of the chloro group to induce the  $\beta$ -structure was the reason the present study was undertaken. Benzylidene-DL-piperitone is photostable but *p*-chloro substitution makes it photoactive. However, instead of the anticipated  $\beta$  packing,  $\alpha$ -type packing is observed. Interestingly, the *o*-chloro derivative (II) is not photoreactive at all. Thus, chloro substitution is ineffective in inducing the  $\beta$ -packing mode in these crystal structures.

It should also be mentioned that crystals of benzylidene-DL-piperitone, the *p*-chloro derivative discussed here, as well as the *p*-bromo derivative (Venugopalan & Venkatesan, 1990*b*), adopt the  $\alpha$ -packing mode. It seems reasonable to assume that the same kind of packing also occurs in the *o*-chloro derivative. The fact that  $\alpha$ -type packing prevails in all the benzylidenepiperitones investigated by us is noteworthy. The overall non-planar character of these molecules produced by a cyclohexenone ring adopting a sofa conformation (see the torsion angles in Table 2) along with an anisotropically shaped isopropyl group would prevent efficient close crystal packing by the  $\beta$  arrangement. This situation seems to lead to the observed  $\alpha$ -packing mode taking precedence over the halogen-halogen interaction. Indeed, this has been observed in benzylbenzylidene-cyclopentanones (Theocharis, 1989).

Another important observation is the slowness of the reaction for the title compound. The irradiation time *versus* percentage yield of dimer shows a significant induction time, the maximum yield being 30% after 7 days. From photochemical studies on crystalline coumarin derivatives it is known that the occurrence of an induction period is characteristic in cases where the reaction is defect-initiated (Gnanaguru, Ramasubbu, Venkatesan & Ramamurthy, 1985). However, as discussed earlier, the reaction of the title compound is topochemical (see the geometrical parameters mentioned above). Although stability of the crystal lattice would be an important factor in controlling the rate of the reaction as well as the percentage yield of the dimer, the observed induction period could arise as follows. The reactive partners in the crystal lattice are not ideally juxtaposed as seen from the calculated values of  $\theta_1$ ,  $\theta_2$ ,  $\theta_3$  and *d*. Upon excitation the molecules must undergo the necessary motions to achieve the overlap

of the  $\pi$  orbitals. Unlike the case of rigid molecules such as coumarins, in the title molecule there is an additional molecular aspect controlling the rate of reaction, namely the necessity for conformational changes during the course of the reaction. Considerable molecular movement must exist, involving changes in the conformations at the anisotropic isopropyl as well as the benzylidene groups, in order to release the intermolecular steric pressure. This additional factor may contribute to the presence of the induction period as well as the lower percentage yield of the dimer.

To summarize, the so called 'chloro effect' may not be operational for all kinds of molecular framework. When the molecule has a bulky chain at one end as, for example in (I), it is likely that the closest neighbours are centrosymmetrically related giving rise to (if photolabile) the *anti* head-to-tail dimer.

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## Oriental Disorder in Phenanthrene. Structure Determination at 248, 295, 339 and 344 K

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### Abstract

Phenanthrene, C<sub>14</sub>H<sub>10</sub>,  $M_r = 178.2$ , m.p. 374 K, shows a phase transition around 333–343 K. The structure is ordered at 295 K with  $a = 8.441$  (2),  $b = 6.140$  (1),  $c = 9.438$  (1) Å,  $\beta = 97.96$  (1)°,  $V = 484.4$  (1) Å<sup>3</sup>, monoclinic,  $P2_1$ ,  $Z = 2$ ,  $D_x = 1.221$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 0.064$  mm<sup>-1</sup>,  $F(000) = 188$ ,  $R = 0.043$  for 726 observed reflections. The high-temperature phase is orientationally disordered with the second possible position of the molecule related to the first by a center of symmetry. Two intensity data sets at 339 and 344 K were used in least-squares refinement. The occupancy of the second position was refined to 0.158 (5) and 0.446 (3) at 339 and 344 K, respectively. It is possible to quench the high-temperature phase by rapid cooling from 344 to below 260 K. The occupancy of the second position in the quenched phase was refined to 0.389 (3).

### Introduction

Phenanthrene is one of the simple aromatic hydrocarbons which has been intensively studied. The structural phase transition in phenanthrene has been studied by measurement of several physical properties (Kroupa *et al.*, 1988; and references therein). The structure of the room-temperature phase was determined by Basak (1950), Trotter (1963) and Kay, Okaya & Cox (1971). An X-ray powder diffraction study of the phase transition and the structure of the high-temperature phase were reported by Matsumoto & Fukuda (1967). They suggested the

same space group for both phases. The present diffraction study is the first attempt to solve and refine the structure of the high-temperature phase and the structure during the phase transition from X-ray diffraction single-crystal data.

### Experimental

Colorless transparent monocrystals were grown by the Bridgman method. A spherical sample ( $r = 0.6$  mm), prepared by cutting and polishing, was mounted in a Lindeman-glass capillary to decrease sublimation. A Hilger & Watts diffractometer (Mo  $K\alpha$ , Nb filter) controlled by an M7000 computer was used to collect crystal and intensity data at different temperatures. The learnt-profile method (Diamond, 1969; Clegg, 1981) was used to obtain intensities and their e.s.d.'s. The scan speed was varied from 1 to 8° min<sup>-1</sup>, determined from a rapid prescan. The intensities of three standard reflections (41 $\bar{1}$ , 132, 005) were measured every 30 reflections. Reflections with  $I < 1.96\sigma(I)$  were classified as unobserved, but were used in the refinement with  $|F_{\text{unobs}}| = \frac{2}{3}|F_{\text{min}}|$  and  $\sigma(|F_{\text{unobs}}|) = [1/(18)^{1/2}]|F_{\text{min}}|$  where  $|F_{\text{min}}|$  is the minimum observed value of  $|F|$ . The data were corrected for Lorentz and polarization effects. Crystal data and details of the data collection are given in Table 1.

The sample was heated (cooled) by a nitrogen stream. The temperatures quoted were deduced by measuring the temperature of the nitrogen stream with a thermocouple. Four temperatures 248, 295, 339 and 344 K, at which the quenched, room-