Acta Cryst. (1987). C**43**, 1128–1131

Structure of α-Benzylidene-(±)-piperitone,* an Exception to Topochemical Behaviour

By D. Kanagapushpam, V. Ramamurthy and K. Venkatesan

Department of Organic Chemistry, Indian Institute of Science, Bangalore–560 012, India

(*Received* 28 *July* 1986; *accepted* 6 *January* 1987)

Abstract. $C_{17}H_{20}O$, $M_r = 240{\cdot}2$, monoclinic, $P2_1/n$, $a = 6{\cdot}116$ (2), $b = 16{\cdot}127$ (3), $c = 14{\cdot}417$ (5) Å, $\beta = 96{\cdot}62$ (2)°, $V = 1412{\cdot}5$ (7) Å^3, $Z = 4$, $D_m = 1{\cdot}13$, $D_x = 1{\cdot}129$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 0{\cdot}454$ mm^{-1}, $F(000) = 520{\cdot}0$, $T = 298$ K, $R = 0{\cdot}062$ for the 1800 reflections used in the refinement. The two pairs of reactive double bonds which are related by a centre of inversion are properly oriented for [2+2] photocycloaddition. In spite of the favourable arrangement of the double bonds the molecule is photostable. A possible explanation for the inertness of the compound is provided in terms of a large atomic displacement of the styrene group upon excitation in the crystal lattice.

Introduction. A large number of crystalline olefinic monomers dimerize readily under UV radiation. The course of the reaction is generally governed by topochemical factors such as packing characteristics, local symmetry and separation distances between the potentially reactive double bonds (Cohen & Schmidt, 1964; Cohen, Schmidt & Sonntag, 1964; Schmidt, 1964). There are instances (Bhadbhade, Murthy, Venkatesan & Ramamurthy, 1984; Ramamurthy & Venkatesan, 1986) where on the basis of topochemical arguments one would expect photostability yet reaction does ensue. Also a few examples (Ariel, Askari, Scheffer, Trotter & Walsh, 1984) where, in spite of crystal-lattice alignment of the reactive double bonds, absence of [2+2] photocycloaddition in the solid state is known. In continuation of our studies on the subtler aspects (Gnanaguru, Ramasubbu, Venkatesan & Ramamurthy, 1985) of the topochemical principles we have been investigating the photobehaviour of dimerizable olefins in the solid state. The photobehaviour of benzylidene-(±)-piperitone reported here is exceptional viewed in the context of its structure in the solid state. It has been reported (Read & Smith, 1922) that this compound exists in dimorphic forms α and β which behave differently towards sunlight. The crystals of the α form cohere within a few minutes of exposure to sunlight, whereas the β form is quite stable. It was therefore considered worthwhile to investigate the crystal packing in the two forms which might account for the difference in their behaviour. It is noteworthy that there are three potentially reactive centres, namely two olefinic bonds and a carbonyl chromophore (Fig. 1). While the double bonds would be expected to participate in cycloaddition, the carbonyl chromophore is well situated for β or γ hydrogen abstraction. It is not easy to predict *a priori* which one of these chromophores would undergo transformation upon excitation. In this context a detailed crystallographic and photochemical study of the title compound appeared desirable.

Experimental. Benzylidene-(±)-piperitone was prepared by the reported procedure (Read & Smith, 1921), m.p. 331 K. Powdered crystals of the α form were exposed to UV radiation using a medium pressure mercury vapour lamp (450 W, $\lambda > 300$ nm). 3 h of irradiation gave a gummy material which did not reveal any changes according to spectral characteristics. The temperature of the sample did not go beyond 307 K during irradiation. The crystals were also irradiated at 278 K and under these conditions too they became gummy after 3 h. However, no melting occurred on irradiation at 199 K under nitrogen and there was no photoreaction at this temperature. It may be noted that the crystal did not undergo any physical changes during the data collection for structure analysis. Irradiation of a solution of this compound in deuterated benzene (300 m*M*) in an NMR tube resulted in *cis–trans* isomerization.

Single crystals of the α form were obtained from ethanol by slow evaporation. Innumerable attempts to obtain the β form were met with failure. D_m by flotation in KI solution. Crystal approximately 0·4 × 0·2 × 0·15 mm. Preliminary Weissenberg photographs indicated crystal to be monoclinic. Nonius CAD-4 diffractometer; lattice parameters refined by least-squares fit to settings of 20 reflections. Intensity data collected using graphite-monochromated Cu $K\alpha$ radiation, scan speed 1° min^{-1}, $\theta \leq 75°$. During data collection three standard reflections (033, $\bar{1}\bar{1}2$, 006) showed only statistical variations within ± 2%. 2914 reflections collected, 2496 unique, $R_{\rm int} = 0{\cdot}089$, 1800 significant, $|F_o| \geq 3\sigma(|F_o|)$. No correction for absorption. h,k,l −7 to 7, 0 to 20, 0 to 17; structure solved by direct methods using *MULTAN*80 (Main, Fiske, Hull, Les-

---

* IUPAC name: 6-isopropyl-3-(2-phenylvinyl)-2-cyclohexen-1-one.

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* ($\times 10^3$) *for non*-H *atoms of benzylidene*-(±)-*piperitone*

E.s.d.'s are given in parentheses. The temperature factor is of the form: $U_{\rm eq} = \frac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j$.

	x	y	z	$U_{\rm eq}$(Å^2)
C(1)	8723 (4)	1068 (1)	2284 (1)	51 (1)
C(2)	10223 (4)	1266 (2)	1672 (2)	68 (1)
C(3)	9698 (5)	1206 (2)	719 (2)	81 (1)
C(4)	7627 (5)	945 (2)	362 (2)	75 (1)
C(5)	6120 (4)	740 (2)	953 (2)	66 (1)
C(6)	6636 (4)	799 (1)	1906 (1)	57 (1)
C(7)	9351 (4)	1160 (1)	3297 (2)	53 (1)
C(8)	8131 (4)	978 (1)	3975 (2)	54 (1)
C(9)	8811 (3)	1083 (1)	4972 (1)	50 (1)
C(10)	10943 (4)	1499 (2)	5305 (2)	65 (1)
C(11)	10997 (4)	1826 (2)	6301 (2)	66 (1)
C(12)	10367 (3)	1160 (1)	6968 (1)	51 (1)
C(13)	8140 (4)	806 (1)	6611 (2)	56 (1)
C(14)	7528 (4)	799 (1)	5599 (2)	59 (1)
C(15)	10542 (4)	1418 (1)	7997 (1)	53 (1)
C(16)	12929 (4)	1569 (2)	8392 (2)	65 (1)
C(17)	9139 (4)	2168 (2)	8168 (2)	67 (1)
O(18)	6912 (3)	501 (1)	7129 (1)	79 (1)

Table 2. *Selected bond distances* (Å) *and angles* (°) *involving non*-H *atoms in benzylidene*-(±)-*piperitone with their e.s.d.'s in parentheses*

C(1)–C(2)	1·382 (3)	C(9)–C(14)	1·344 (3)
C(1)–C(6)	1·398 (3)	C(10)–C(11)	1·527 (4)
C(1)–C(7)	1·474 (3)	C(11)–C(12)	1·521 (3)
C(2)–C(3)	1·378 (4)	C(12)–C(13)	1·511 (3)
C(3)–C(4)	1·377 (4)	C(12)–C(15)	1·533 (2)
C(4)–C(5)	1·366 (4)	C(13)–C(14)	1·464 (4)
C(5)–C(6)	1·377 (3)	C(13)–O(18)	1·222 (3)
C(7)–C(8)	1·329 (4)	C(15)–C(16)	1·524 (3)
C(8)–C(9)	1·459 (3)	C(15)–C(17)	1·520 (4)
C(9)–C(10)	1·496 (3)		

C(2)–C(1)–C(6)	117·8 (2)	C(9)–C(10)–C(11)	112·4 (2)
C(2)–C(1)–C(7)	119·5 (2)	C(10)–C(11)–C(12)	111·8 (2)
C(6)–C(1)–C(7)	122·6 (2)	C(11)–C(12)–C(13)	109·6 (2)
C(1)–C(2)–C(3)	121·7 (3)	C(11)–C(12)–C(15)	115·2 (2)
C(2)–C(3)–C(4)	119·5 (3)	C(13)–C(12)–C(15)	113·1 (2)
C(3)–C(4)–C(5)	119·9 (3)	C(12)–C(13)–C(14)	117·3 (2)
C(4)–C(5)–C(6)	120·8 (3)	C(12)–C(13)–O(18)	122·5 (2)
C(1)–C(6)–C(5)	120·3 (2)	C(14)–C(13)–O(18)	120·1 (2)
C(1)–C(7)–C(8)	127·0 (2)	C(9)–C(14)–C(13)	124·5 (2)
C(7)–C(8)–C(9)	125·3 (2)	C(12)–C(15)–C(16)	111·2 (2)
C(8)–C(9)–C(10)	120·5 (2)	C(12)–C(15)–C(17)	113·3 (2)
C(8)–C(9)–C(14)	120·0 (2)	C(16)–C(15)–C(17)	110·3 (2)
C(10)–C(9)–C(14)	119·5 (2)		

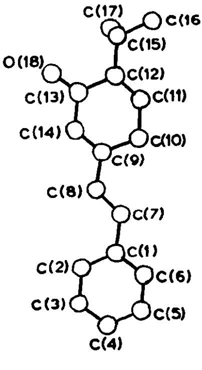

Fig. 1. A perspective view of the molecule.

Table 3. *Selected torsion angles* (°)

C(1)–C(7)–C(8)–C(9)	−179·6 (2)	C(11)–C(12)–C(13)–C(14)	30·0 (3)
C(7)–C(8)–C(9)–C(10)	6·3 (3)	C(12)–C(13)–C(14)–C(9)	0·2 (3)
C(7)–C(8)–C(9)–C(14)	−173·1 (2)	C(11)–C(12)–C(15)–C(16)	−66·8 (2)
C(14)–C(9)–C(10)–C(11)	−21·1 (3)	C(11)–C(12)–C(15)–C(17)	58·1 (2)
C(9)–C(10)–C(11)–C(12)	51·9 (3)	C(13)–C(14)–C(9)–C(10)	−5·1 (3)
C(10)–C(11)–C(12)–C(13)	−55·4 (3)		

singer, Germain, Declercq & Woolfson, 1980). The E map computed using the phases from the best set (ABSFOM = 1·1263, ψ_o = 1·186, R = 12·81, CFOM = 3·0000) led to the so-called chicken-wire pattern with two molecules displaced from each other along the a axis by ~0·4 Å and c axis by ~1·6 Å. The coordinates of these two molecules were averaged and subjected to refinement. Full-matrix refinement, scale factor, positional and anisotropic thermal parameters of non-H atoms as well as positional and isotropic thermal parameters of H atoms, $R = 0{\cdot}062$, $wR = 0{\cdot}070$, $S = 0{\cdot}27$; $\sum w(|F_o| - |F_c|)^2$ minimized, $w = 4{\cdot}1493/(\sigma^2|F| + 0{\cdot}000652|F|^2)$. *SHELX*76 (Sheldrick, 1976) used for full-matrix refinement. Δ/σ for non-H atoms ~ 0·003; residual electron density in final ΔF map ±0·3 e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Positional coordinates of non-H atoms are listed in Table 1.* Bond lengths and angles are given in Table 2. A perspective view of the molecule with the numbering of atoms is shown in Fig. 1.

The bond lengths and angles are unexceptional. The phenyl ring is planar to within 0·004 (3) Å with C(7) 0·031 (2) Å from this plane. The cyclohexenone ring is in a sofa conformation (Romers, Altona, Buys & Havinga, 1969) and the torsion angles of interest are given in Table 3.

From the packing diagram (Fig. 2) it is observed that the nearest neighbouring molecules are related by an inversion centre. Further, it is observed that there are two potentially reactive pairs of double bonds in the nearest neighbours of α-benzylidene-(±)-piperitone: the centrosymmetrically related pairs C(9)=C(14) and C(14$^{\rm i}$)=C(9$^{\rm i}$) at a distance of 3·915 (3) Å and the other C(7)=C(8) and C(14$^{\rm i}$)=C(9$^{\rm i}$) at distances of 3·932 (3) Å [C(7)···C(14$^{\rm i}$)] and 4·025 (3) Å [C(8)···C(9$^{\rm i}$)] [(i): 2−x, −y, 1−z]. Although the mean distances separating the potentially reactive centres is well within the limits of about 4·2 Å assessed to be necessary for [2+2] dimerization reaction (Schmidt, 1964), there is no evidence whatsoever for the presence of a dimer in the irradiated sample.

---

* 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 43707 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Absence of reactions in spite of favourable arrangement has been coming to light in the last few years and consideration of this allows us to know more about the subtler aspects of photoreactivity in crystals. One of the polymorphs of 2,5-distyrylpyrazine (Nakanishi, Parkinson, Jones, Thomas & Hasegawa, 1979), where the potentially reactive double bonds are separated by 4·19 Å, is photostable and its photostability has been ascribed to the layered structure which suppresses the molecular deformation necessary for the cycloaddition reaction. Another example by Ariel *et al.* (1984) is photostable, in spite of the fact that the reactive double bonds are parallel with a centre-to-centre distance of 3·79 Å. The probable reason for the lack of solid-state reactivity in this case is the steric compression experienced by the reacting molecules at the initial stages of photocycloaddition.

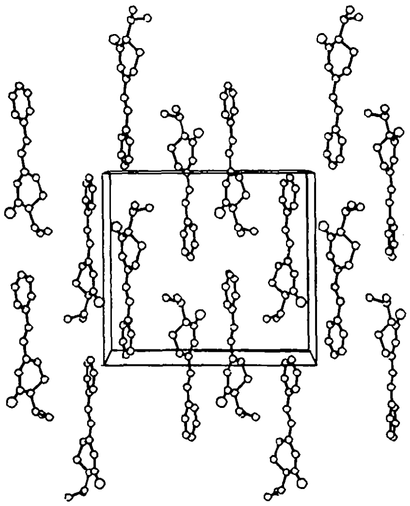

Fig. 2. Packing of the molecules in the unit cell.

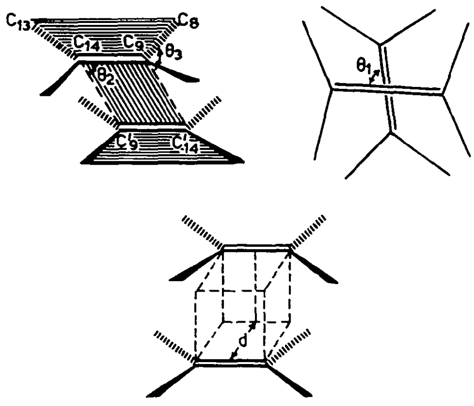

Fig. 3. Geometrical parameters used in the relative representation of reactive double bonds.

It was considered worthwhile to carry out lattice-energy calculations on the present compound in order to understand its photostability. It would be expected that, before the reactions start, overlap of π orbitals of the reactive double bonds should be good. For the ideal situation the geometrical parameters θ_1, θ_2 and θ_3 (Fig. 3) should be 0, 90 and 90° respectively with d (displacement of the reactive bonds with respect to each other) being 0 Å. θ_1 corresponds to the rotation of one double bond with respect to the other, θ_2 corresponds to the angle of the parallelogram formed by the double-bonded C(9), C(14), C(9^i) and C(14^i) atoms, whereas θ_3 measures the angle between the least-squares plane through the reactive bonds C(9), C(14), C(9^i) and C(14^i) and that passing through C(8), C(9), C(14) and C(13). The values for these parameters in the present case are $\theta_1 = 0$, $\theta_2 = 105{\cdot}2$, $\theta_3 = 86{\cdot}4°$ and $d = 0{\cdot}161$ Å for the pair C(9)=C(14) and C(9^i)=C(14^i), whereas $\theta_1 = 6{\cdot}1$, $\theta_2 = 104{\cdot}3$, $\theta_3 = 70{\cdot}7°$ and $d = 1{\cdot}301$ Å for the pair C(7) = C(8) and C(9^i)=C(14^i). From these values it is reasonable to expect the dimerization to occur between the centrosymmetrically related sites.

The energy calculations were carried out using the program *WMIN* (Busing, 1981). The energy was calculated by a pairwise potential as follows:

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

In (1), the first and second terms represent van der Waals attractive and repulsive contributions respectively. The contribution of Coulombic energy was not included. The constants used are taken from Mirsky (1978); A_i for O = 33·0, C = 42·0, H = 11·0 kJ$^{1/2}$ mol$^{-1/2}$ Å^3, $D_{ij} \times 10^3$ for O···O = 639·91, O···C = 1271·53, O···H = 146·16, C···C = 2653·55, C···H = 298·73, H···H = 28·93 kJ mol^{-1} Å^{12}. The molecules were treated as rigid bodies. The energy calculated using the crystal position was −106·32 kJ mol^{-1}, and the increase in energy to achieve the ideal geometry ($\theta_2 = 0$, $\theta_2 = 90$, $\theta_3 = 90°$ and $d = 0$ Å) in the crystal lattice was small, 3·34 kJ mol^{-1}. This very small increase in energy suggests that there is enough freedom for the molecules to move in the lattice which should allow them to reach the ideal geometry and therefore should be expected to yield a centrosymmetric dimer.

It must be pointed out that in our calculations the molecular geometry and the dispersion constants used correspond to the ground state and these were expected to be different in the excited state. In spite of the approximations, this approach was successful in rationalizing the rigid systems like coumarin derivatives (Murthy, Arjunan, Venkatesan & Ramamurthy, 1986). We have assumed in these calculations that the overall topography of the excited molecule is the same as in the ground state. This clearly is not true and this assumption is more serious in the present molecule than in rigid molecules such as coumarins. In its reaction pathway involving change in the hybridization of the reactive atoms C(9) and C(14) from sp^2 to sp^3 with a lengthy styrene side group at C(9), it would be expected that the side group undergoes considerable positional changes in the existing crystal lattice which might not be favourable from the intermolecular energy calculations. It seems most likely that the available cavity volume (Cohen, 1975) is insufficient as the molecular topology undergoes very large changes in the course of the reaction path from the reactant to the product.

We record our grateful thanks to Professor A. J. Birch, FRS, Australian Academy of Sciences, for suggesting this problem and Professor V. Ramakrishnan for useful discussions.

References

ARIEL, S., ASKARI, S., SCHEFFER, J. R., TROTTER, J. & WALSH, L. (1984). *J. Am. Chem. Soc.* **106**, 5726–5728.

BHADBHADE, M. M., MURTHY, G. S., VENKATESAN, K. & RAMAMURTHY, V. (1984). *Chem. Phys. Lett.* **109**, 259–263.

BUSING, W. R. (1981). *WMIN*. A computer program to model molecules and crystals in terms of potential-energy functions. Report ORNL-5747. Oak Ridge National Laboratory, Tennessee.

COHEN, M. D. (1975). *Angew. Chem. Int. Ed. Engl.* **14**, 386–393.

COHEN, M. D. & SCHMIDT, G. M. J. (1964). *J. Chem. Soc.* pp. 1996–1999.

COHEN, M. D., SCHMIDT, G. M. J. & SONNTAG, F. J. (1964). *J. Chem. Soc.* pp. 2000–2013.

GNANAGURU, K., RAMASUBBU, N., VENKATESAN, K. & RAMAMURTHY, V. (1985). *J. Org. Chem.* **50**, 2337–2346.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

MIRSKY, K. (1978). In *Computing in Crystallography*, edited by H. SCHENK, R. OLITHOF-HAZEKAMP, H. VAN KONINGSVELD & G. C. BASSI, pp. 169–182. Delft Univ. Press.

MURTHY, G. S., ARJUNAN, P., VENKATESAN, K. & RAMAMURTHY, V. (1986). *Tetrahedron*. In the press.

NAKANISHI, H., PARKINSON, G. M., JONES, W., THOMAS, J. M. & HASEGAWA, M. (1979). *Isr. J. Chem.* **18**, 261–265.

RAMAMURTHY, V. & VENKATESAN, K. (1986). *Chem. Rev.* In the press.

READ, J. & SMITH, H. G. (1921). *J. Chem. Soc.* **119**, 779–789.

READ, J. & SMITH, H. G. (1922). *J. Chem. Soc.* **121**, 574–593.

ROMERS, C., ALTONA, C., BUYS, H. R. & HAVINGA, E. (1969). In *Topics in Sterochemistry*, Vol. 4, edited by E. L. ELIEL & N. L. ALLINGER, pp. 39–98. New York: John Wiley.

SCHMIDT, G. M. J. (1964). *J. Chem. Soc.* pp. 2014–2021.

SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Acta Cryst. (1987). C**43**, 1131–1134

Structure of 5-(*p*-Aminobenzenesulfonamido)-1-phenylpyrazole (Sulfaphenazole)*

BY H. C. PATEL AND T. P. SINGH

Department of Biophysics, All-India Institute of Medical Sciences, New Delhi – 110029, India

(*Received* 25 *August* 1986; *accepted* 12 *January* 1987)

Abstract. $C_{15}H_{14}N_4O_2S$, $M_r=314\cdot4$, monoclinic, $P2_1/n$, $a = 14\cdot760$ (3), $b = 11\cdot253$ (2), $c = 19\cdot213$ (4) Å, $\beta = 109\cdot90$ (3)°, $V = 3001$ (1) Å^3, $Z = 8$, $D_m = 1\cdot397$ (5), $D_x = 1\cdot3916$ (5) Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0\cdot216$ mm^{-1}, $F(000) = 1312$, $T = 293$ K, final $R = 0\cdot067$ for 3208 observed reflections. The two crystallographically independent molecules *A* and *B* in the structure have similar molecular dimensions but their conformations are substantially different. The six-membered benzene-ring planes in molecule *A* and in molecule *B* are inclined to the planar pyrazole rings at 53·5 (4) and 46·9 (4)°; 75·9 (3) and 69·1 (4)° respectively. The two benzene-ring planes in molecule *A* are mutually inclined at 12·8 (3)° while those in molecule *B* are oriented at 36·5 (4)°. Both molecules show *gauche* conformations about the S—N bonds with torsion angles of −73·7 (8) and 94·0 (8)° respectively. The molecules are packed in the form of hydrogen-bonded helices which are interconnected by hydrogen bonds and van der Waals forces through the amino N atoms and the sulfonyl O atoms.

---

* *Chemical Abstracts* name: 4-amino-*N*-(1-phenyl-1*H*-pyrazol-5-yl)benzenesulfonamide.

0108-2701/87/061131-04$01.50