

The Structure and Stereochemistry of the Solution Photodimer of 3-Phenyl-2-cyclopentenone by X-ray Diffraction

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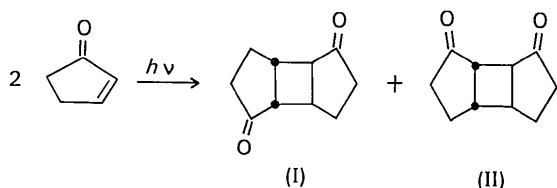
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Light-induced dimerization of 3-phenyl-2-cyclopentenone in a variety of solvents affords the head-to-head *cis-anti-cis* stereoisomer, $C_{22}H_{20}O_2$. The cyclobutane ring is bent with a dihedral angle of 152.4° . The cyclopentanone rings have an envelope-like conformation. Crystals are monoclinic, space group $C2/c$, with four molecules per unit cell of dimensions $a=17.018$ (3), $b=10.840$ (2), $c=9.097$ (2) Å, and $\beta=99.12$ (1°). 1406 independent reflections were collected on an automated diffractometer with Nb-filtered Mo $K\alpha$ radiation. The structure was solved by the symbolic addition procedure and refined by full-matrix least-squares calculation to $R=0.046$. Photodimerization in the solid state of 3-phenyl-2-cyclopentenone yields a different dimer whose structure is predicted to have the head-to-tail *cis-anti-cis* arrangement.

Introduction

Light-induced dimerization of 3-phenyl-2-cyclopentenone has been observed in solution and in solid state (Magnifico, O'Connell, Fratini & Shaw, 1972). Evidence such as n.m.r., infrared, and mass spectra suggests that dimerization occurs *via* a cycloaddition process to yield cyclobutane-centered structures. In the present investigation, we wish to clarify further the role of the monomer structure in governing the stereochemical course of the dimerization of simple cyclic enones by an X-ray structure determination of the solution photodimer of 3-phenyl-2-cyclopentenone.

Eaton (1962) has noted that cyclopentenone, upon irradiation in a variety of solvents, gives products (I) and (II) whose relative amounts show a moderate solvent dependency.



Margulis (1965) has verified by X-ray crystallographic methods Eaton's assignment of (I) as the head-to-tail *cis-anti-cis* dimer, where the relationship of the two five-membered rings with respect to the four-membered ring is *anti*. Irradiation of 3-phenyl-2-cyclopentenone, on the other hand, affords a single dimer. Spectral evidence indicates that the solution and solid-state dimers have different stereochemistry.

In addition, phosphorescence has been observed at 77K from polar glasses containing 3-phenyl-2-cyclopentenone (Magnifico *et al.*, 1972). Due to the scarcity

of simple enones which luminesce, derivatives of this compound could serve as model systems for comparison of their photochemical and spectroscopic properties.

Experimental

Crystals of 3-phenyl-2-cyclopentenone obtained from Dr E. J. O'Connell of Fairfield University were grown by evaporation from 2-propanol. They form colorless diamond plates with **b** and **c** coincident with the longer and shorter face diagonals, respectively. Two sets of intensities were recorded at room temperature (21°C). The first set, which was used to assign phases, was measured by the multiple-film Weissenberg technique with Cu $K\alpha$ radiation. The intensities were estimated visually by comparison with a calibrated film strip. Seven $h0l$ layers and the $hk0$ layer were measured, resulting in 1139 independent reflections.

The second set was collected on a diffractometer and used during refinement. A crystal with dimensions $0.40 \times 0.35 \times 0.20$ mm was mounted with **b** parallel to ϕ on a Picker automated diffractometer equipped with auxiliary disk memory. Diffractometer control programs were those of Lenhart & Henry (1970). Lattice parameters were obtained from least-squares refinement of 2θ angles for 11 Friedel pairs ($19.0^\circ < 2\theta < 42.8^\circ$). Nb-filtered Mo $K\alpha$ radiation (take-off angle 2.0°) was used to collect 4715 reflections by the θ - 2θ scan technique to a maximum 2θ of 50° . Aluminum foil attenuators were inserted into the diffracted beam whenever the count rate from the scintillation detector exceeded 8000 c.p.s.

Three standard reflections (314, $5\bar{1}0$, 641) were measured at two-hour intervals, with no observable decrease in intensity during the 408 h of data collection.

Absorption corrections were not applied since the maximum difference in corrected and uncorrected structure factors was approximately 1%, as calculated for a sample portion of the data by the method of Wehe, Busing & Levy (1962). Standard Lp corrections were applied, and equivalent reflections, whose $|F_o|$'s did not deviate by more than 4σ from the average, were averaged to produce 1406 independent observations. $\sigma(F)$'s were calculated by the method of Miller, Lenhart & Joesten (1972).

Crystal data

$C_{22}H_{20}O_2$

F.W. 316; monoclinic ($C2/c$)
 $D_{meas} = 1.28 \text{ g cm}^{-3}$ (floatation
 in n-hexane- CCl_4 mixture)
 $D_{calc} = 1.27 \text{ g cm}^{-3}$
 $Z = 4$
 $F(000) = 672$
 $\mu = 0.86 \text{ cm}^{-1} (\text{Mo } K\alpha)$

$a = 17.018 (3) \text{ \AA}$
 $b = 10.840 (2)$
 $c = 9.097 (2)$
 $\beta = 99.12 (1)^\circ$
 $V = 1656.9 \text{ \AA}^3$

Structure determination and refinement

Phases were determined by the symbolic addition procedure for centrosymmetric crystals (Karle & Karle, 1966). There were 11 reflections with $|E| > 2.5$ and only

nine interactions with probabilities exceeding 0.97. The initial attempt at phase determination proved unsuccessful because the \sum_2 relation had incorrectly indicated the sign of the $824 (|E|=2.15)$ reflection. This reflection served as the initial entry into the subset of reflections with oee parity and thus was a key reflection during the early stages of the phase determination. A more judicious assignment of symbols which included two reflections of oee parity then led to the correct structure.

Atomic coordinates and thermal parameters were refined by full-matrix least squares calculation using the full data set. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1.0/\sigma^2(F)$. Atomic scattering factors for oxygen and carbon were taken from Cromer & Mann (1968) and hydrogen scattering factors were those of Stewart, Davidson & Simpson (1965). Refinement of scale, positional parameters and anisotropic temperature factors for O and C and isotropic temperature factors for H produced a final conventional R value of 0.046 and a weighted R of 0.028 for all reflections.* Maximum shift over error for the final cycle

* A structure factor list has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30409 (15 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

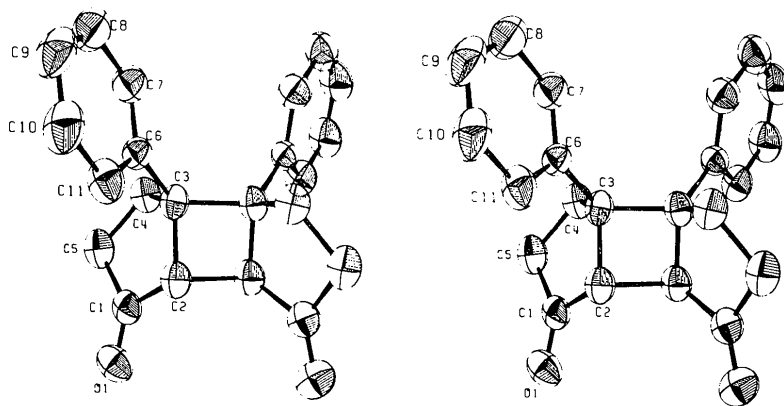


Fig. 1. Stereo view of the solution photodimer of 3-phenyl-2-cyclopentenone. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are scaled to enclose 50% probability.

Table 1. Final positional and thermal parameters for non-hydrogen ($\times 10^5$) and hydrogen ($\times 10^4$) atoms

Anisotropic thermal parameters are in the form $\exp[-(\beta_{11}h^2 + \dots + 2\beta_{12}hk \dots)]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O(1)	41000 (6)	-4125 (9)	5938 (12)	412 (5)	726 (12)	1442 (19)	-117 (6)	220 (8)	-246 (11)
C(1)	42307 (9)	6818 (14)	7837 (18)	241 (6)	745 (15)	1136 (23)	-23 (8)	152 (9)	-129 (15)
C(2)	45331 (8)	12914 (13)	22557 (17)	265 (6)	577 (13)	920 (21)	-22 (7)	134 (9)	-19 (41)
C(3)	45785 (8)	27060 (13)	19919 (15)	252 (6)	580 (13)	834 (21)	-5 (7)	86 (8)	6 (12)
C(4)	46350 (10)	27512 (15)	2978 (17)	308 (7)	726 (16)	883 (22)	-3 (8)	92 (9)	49 (14)
C(5)	41163 (11)	16817 (17)	-3980 (19)	376 (7)	871 (18)	934 (24)	-23 (9)	41 (11)	-89 (16)
C(6)	39359 (8)	35509 (13)	23902 (16)	247 (6)	676 (15)	898 (21)	29 (7)	11 (8)	-90 (13)
C(7)	39308 (10)	47929 (16)	19974 (19)	344 (7)	749 (17)	1278 (27)	51 (9)	71 (11)	-3 (17)
C(8)	33516 (12)	55898 (18)	23709 (22)	459 (9)	748 (18)	1518 (32)	167 (10)	-25 (13)	-53 (18)
C(9)	27678 (12)	51541 (19)	31285 (22)	356 (8)	1167 (23)	1611 (33)	227 (11)	51 (13)	-251 (21)
C(10)	27580 (11)	39320 (19)	35127 (22)	307 (7)	1161 (22)	1635 (31)	79 (10)	199 (12)	-146 (21)
C(11)	33415 (10)	31295 (16)	31579 (19)	284 (6)	816 (17)	1333 (26)	23 (8)	133 (10)	-68 (17)

Table 1 (cont.)

	x	y	z	B
H(41)	5208 (9)	2614 (13)	154 (16)	4.1 (4)
H(42)	4478 (8)	3571 (13)	-118 (16)	4.1 (4)
H(2)	4255 (7)	988 (11)	3064 (14)	3.0 (3)
H(51)	3508 (10)	1915 (14)	-531 (17)	5.2 (4)
H(52)	4239 (9)	1370 (14)	-1372 (18)	5.1 (4)
H(7)	4352 (9)	5104 (14)	1443 (17)	4.9 (4)
H(8)	3370 (9)	6441 (15)	2070 (18)	5.4 (5)
H(9)	2338 (10)	5780 (16)	3398 (19)	6.8 (5)
H(10)	2310 (10)	3590 (15)	4073 (19)	6.2 (5)
H(11)	3344 (9)	2227 (14)	3467 (16)	4.5 (4)

was 0.08 and the average was 0.02. The residual electron density did not exceed $\pm 0.2 e \text{ \AA}^{-3}$. Final atomic parameters and e.s.d.'s are given in Table 1.

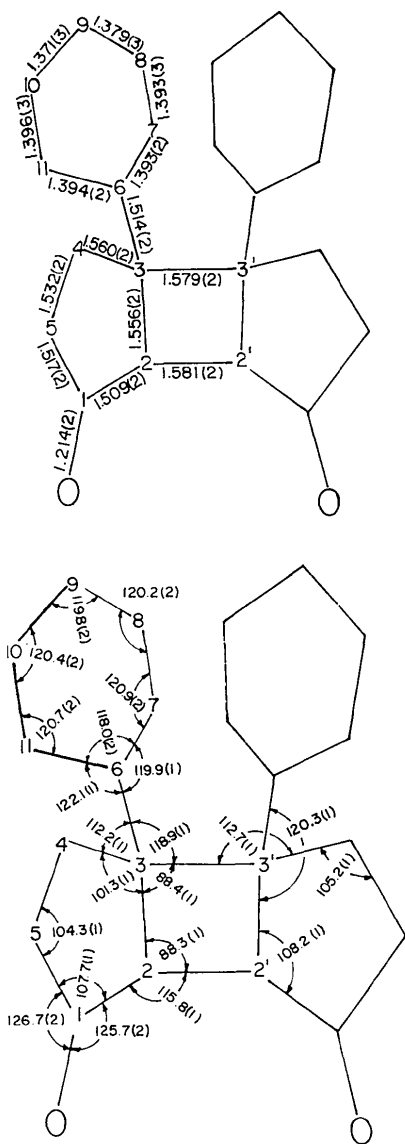
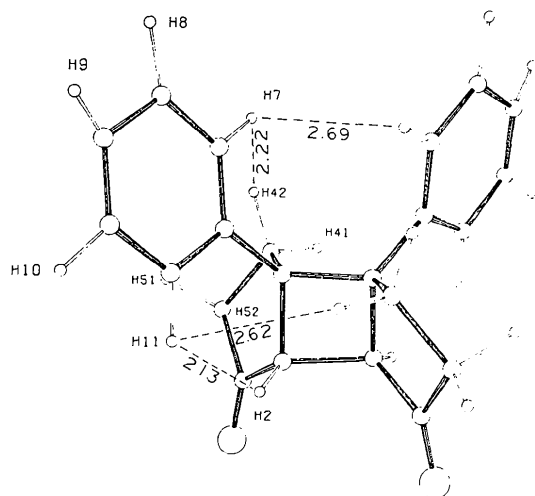


Fig. 2. Bond distances (Å) and angles (°) for the solution photodimer of 3-phenyl-2-cyclopentenone.



C(1)-C(2)-C(3)-C(4)	-22.8°
C(2)-C(3)-C(4)-C(5)	35.3
C(3)-C(4)-C(5)-C(1)	-35.0
C(4)-C(5)-C(1)-C(2)	20.3
C(5)-C(1)-C(2)-C(3)	2.1
C(2)-C(3)-C(6)-C(11)	7.3
C(4)-C(3)-C(6)-C(7)	-53.9

Fig. 3. Selected torsion angles and intramolecular H-H contacts for the solution photodimer of 3-phenyl-2-cyclopentenone. (See Fig. 1 for numbering of carbon atoms.)

Discussion

X-ray analysis reveals the structure of the solution photodimer of 3-phenyl-2-cyclopentenone as the head-to-head *cis-anti-cis* stereoisomer, as shown in Fig. 1. Since the molecule lies on a twofold axis, the cyclobutane ring is not required to be planar, and exhibits a dihedral angle of 152.4° . Bond distances and angles (uncorrected for thermal motion) are presented in Fig. 2. The C(2)-C(2') distance, $1.581(2) \text{ \AA}$, and the C(3)-C(3') distance, $1.579(2) \text{ \AA}$, are typical of strained cyclobutane derivatives, and compare with the corresponding value of $1.59(2) \text{ \AA}$ found for the dimer of cyclopentenone (Margulis, 1965). Dunitz & Schomaker (1952) have offered an explanation of the lengthened C-C bonds based on nonbonded C-C repulsions.

The cyclopentanone rings have an envelope-like conformation (see Fig. 3 for pertinent torsion angles). C(4) is 0.5 \AA out of the least-squares plane comprised of O(1), C(1), C(2), C(3), and C(5), whose maximum deviation is 0.02 \AA . By comparison, in the photodimer of cyclopentenone, C(3) and C(4) deviate 0.21 \AA and 0.45 \AA respectively from the plane formed by C(1) and its three substituents. Phenyl substitution has altered the angle C(2)-C(3)-C(4) from 107.9° in the unsubstituted cyclopentenone to 101.3° . The atoms of the benzene ring are coplanar to within 0.005 \AA , and the average aromatic distance is $1.388(1) \text{ \AA}$. The average C-H bond length is $1.013(5) \text{ \AA}$.

The significant intramolecular distances are between H(2)–H(11), 2.13 Å, and H(42)–H(7), 2.22 Å, as illustrated in Fig. 3. Solely from a consideration of the intramolecular H–H contacts, the observed orientation of the benzene ring would seem to be the most favorable, since rotation about the C(3)–C(6) bond in either direction in order to relieve these intramolecular H–H repulsions would increase others, notably H(7)–H(7') and H(11)–H(41'). The shortest intermolecular contacts are H(2)–O(1), 2.44 Å, and H(9)–H(11), 2.46 Å, where O(1) is generated by $x, \bar{y}, \frac{1}{2}+z$, and H(11) by $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$.

As previously mentioned the dimerization of 3-phenyl-2-cyclopentenone also occurs in the crystalline state. The solution photodimer undergoes thermal and photochemical monomerization while the solid-state dimer resists such decomposition. A preliminary study in this laboratory of the packing of the monomer, 3-phenyl-2-cyclopentenone, favors the head-to-tail *cis-anti-cis* structure of the solid-state photodimer. The monomer structure is characterized by double bonds which are approximately 3.7 Å apart, across a crystallographic center of symmetry. For dimerization to be effective in the solid state the reacting centers are usually less than 4 Å apart (Cohen & Schmidt, 1964; Schmidt, 1971). Crystals of the solid-state dimer have been prepared and further analysis is in progress.

Computations were performed on the CDC 6600 computer at WPAFB using the X-RAY system (Stew-

art, Kundell & Baldwin, 1970). Stereoscopic drawings were prepared by the ORTEP program of Johnson (1965).

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Structural Studies of Dibenz[*c,f*]azocines. I. *N*-Methyl-5,6-dihydro-7*H*,12*H*-dibenz[*c,f*]azocine*

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Crystals of the title compound, C₁₆H₁₇N, are orthorhombic, *Pna*2₁, with $a=15.400$, $b=16.041$, $c=5.055$ Å, and $Z=4$. The crystal structure has been determined by the tangent formula, and refined by the least-squares method to $R=0.042$ for the 849 observed reflexions. The eight-membered azocine ring is in the rigid boat-chair conformation, and the molecule has a non-crystallographic plane of symmetry through the N...C diagonal of the ring. The N–CH₃ bond is in an off-axial position, and its length of 1.435 (7) Å is about 0.04 Å shorter than expected for a N(*sp*³)–C(*sp*³) bond. The endocyclic angle at N is 117.5 (3)° and the exocyclic angles are 114.0 (3) and 114.7 (3)°; the mean at N being 115.4°. The length of the N...C diagonal is 3.34 Å.

Introduction

Several *N*-derivatives of 5,6-dihydro-7*H*,12*H*-dibenz[*c,f*]azocine (I), have been synthesized for pharmaco-

logical screening by Casadio, Pala, Crescenzi, Marazzi-Uberti, Coppi & Turba (1968), and by Pala, Mantegani & Zunga (1970). The conformational properties in solution of the *N*-methyl derivative have been determined by Renaud, Layton & Fraser (1973) from a study of its n.m.r. spectrum. The latter also plan to carry out further n.m.r. studies on different *N*-alkyl

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