Phosphorescence of 3-Phenylcyclopent-2-enone and Crystal Structure of its Solution Photodimer

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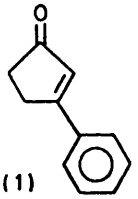
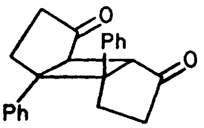
Summary Irradiation of 3-phenylcyclopent-2-enone in propan-2-ol affords a single photodimer, whose structure had been found to be the *cis-anti-cis* head-to-head cyclobutane dimer (**2**).

WE report here preliminary data on the photochemical and luminescence properties of 3-phenylcyclopent-2-enone (**1**) and the crystal structure of a photodimer of (**1**).

Irradiation of (**1**) in various solvents (C_6H_6, Pr^{i}OH, or MeCN) yields a single photodimer (**2**), m.p. 206—208°.

The gross dimeric structure of (**2**) was deduced from its elemental analysis, i.r., u.v., n.m.r., and mass spectra, and from its thermal and photochemical reversal to (**1**). The orientation of the cyclopentanone rings and the stereochemistry of (**2**) were unambiguously assigned by *X*-ray crystallography (Figure 1).


(1)



(2)

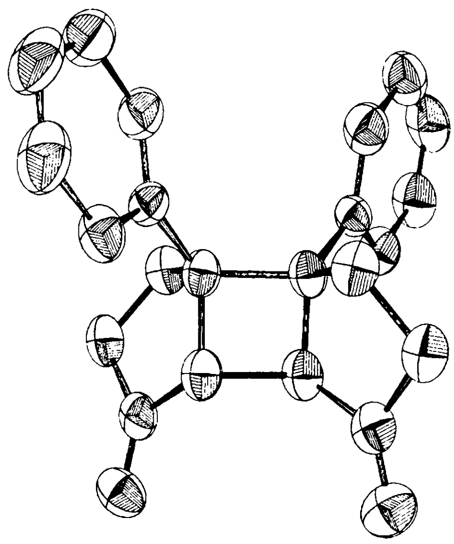


FIGURE 1. *The molecular structure of* (**2**)

Compound (**2**) crystallizes in the monoclinic system, space group C_2/c; $a = 17{\cdot}018(3)$, $b = 10{\cdot}840(2)$, $c = 9{\cdot}097(2)$ Å, $\beta = 99{\cdot}12(2)°$; $D_m = 1{\cdot}28$ g cm^{-3}; $D_c = 1{\cdot}27$ g cm^{-3} for $Z = 4$. The cyclopentanone rings are *anti* to each other and are not planar but distorted irregularly, the largest deviation of an atom from the least-squares plane being 0·2 Å The benzene ring is planar with an average aromatic distances of 1·390 Å. The cyclobutane ring is not planar, but bent with a dihedral angle of 152°. The average distance in the cyclobutane ring is 1·568 Å, and 1·536 Å in the cyclopentanone ring.

Irradiation of (**1**) in the solid state also yields a single dimer (**3**), m.p. 238—240°, whose i.r., n.m.r., and mass spectra are similar to those of (**2**) and are consistent with (**3**) being a cyclobutane derivative. The most notable difference between (**2**) and (**3**) is found in their respective ultraviolet absorption spectra. That of [$\lambda_{\max}$ (MeCN) 260 (ϵ 435) and 302·5 (ϵ 53) nm] is essentially identical to that reported by Yates[1] for the *cis-anti-cis* head to head photodimer of 3-phenylcyclohex-2-enone. In addition to the benzenoid absorption at 2600 Å, (**3**) shows a broad, partially resolved shoulder at 280 nm (ϵ 227) as well as a broad shoulder at 315 nm (ϵ 50). The crystal structure of (**3**) and of the monomer (**1**) are under investigation.

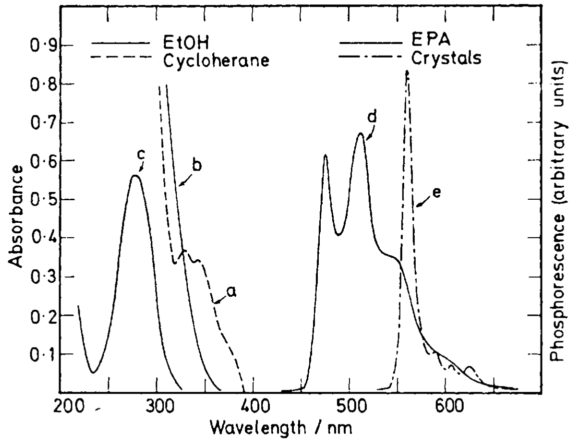


FIGURE 2. *Absorption and emission spectra of* (**1**). *Absorption* (298 K): (a) 4 × 10^{-3} M *in cyclohexane* (1 cm); (b) 1·2 × 10^{-3} M *in ethanol* (1 cm); (c) 2·3 × 10^{-5} M *in ethanol* (1 cm); *Phosphorescence* (77 K) (d) 10^{-3} M *in* EPA (Et$_2$O–isopentane–EtOH) (5:5:2 v/v); (e) *crystalline* (**1**).

Compound (**1**) is also interesting in that phosphorescence is observed, at 77 K, from polar glasses containing (**1**). Owing to the scarcity of simple enones which luminesce,[2–4] derivatives of (**1**) are a good model system for comparison of their photochemical and spectroscopic properties. The absorption and emission spectra of (**1**) are presented in Figure 2. The low-lying ($n \rightarrow \pi^*$) transition is well resolved in methylcyclohexane but in polar solvents is buried under an intense $\pi \rightarrow \pi^*$ transition. Phosphorescence is only observed from (**1**) in polar glasses at 77 K. The phosphorescence quantum yield in EPA at 77 K is *ca.* 1% and the measured decay time is 52 ms. These data suggest a π,π^* configuration for the emitting state. The lack of emission in hydrocarbon glasses is possibly due to the lowest triplet state of (**1**) having an n,π^* configuration in this medium. These observations are consistent with previous work which demonstrated the (n,π^*) and (π,π^*) triplet states of enones to be very close in energy.[2,5,6] The low energy phosphorescence of crystalline samples of (**1**) at 77° K is difficult to explain. This emission is also observed from hydrocarbon glasses where some crystallization of (**1**) has occurred on cooling at 77 K. The measured lifetime of this emission is 4 ms.

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[1] P. Yates, S. N. Ege, G. Buchi, and D. Knutson, *Canad. J. Chem.*, 1967, **45**, 2927.
[2] D. Kearns, G. Marsh, and K. Schaffner, *J. Chem. Phys.*, 1968, **49**, 3316.
[3] R. L. Cargill, A. C. Miller, D. M. Pond, P. deMayo, M. F. Tchir, K. R. Neuberger, and J. Saltiel, *Mol. Photochem.*, 1969, **1**, 301.
[4] R. L. Cargill, W. A. Bundy, D. M. Pond, A. B. Sears, J. Saltiel, and J. Winterle, *Mol. Photochem.*, 1971, **3**, 123.
[5] P. De May, J. P. Pete, and M. F. Tchir, *J. Amer. Chem. Soc.*, 1967, **89**, 5712.
[6] O. L. Chapman, T. H. Koch, F. Klein, P. J. Nelson, and E. L. Brown, *J. Amer. Chem. Soc.*, 1968, **90**, 1657.