Photodimerization of 2-Phenylbenzoxazole and its Acid-catalysed Reversion as a New System for Light Energy Conversion

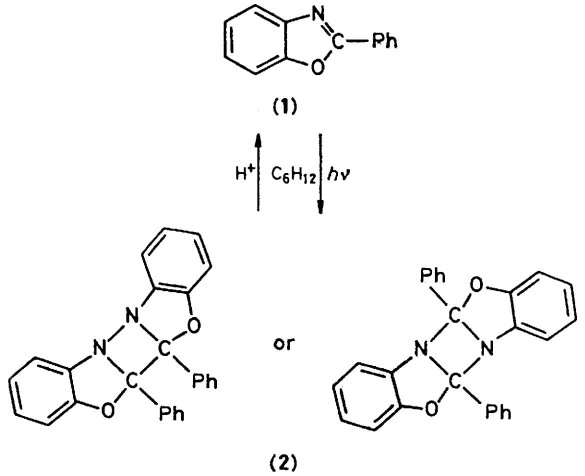
Jacques Roussilhe, Bernard Despax, André Lopez, and Nicole Paillous*

Laboratoire des Interactions Moléculaires et Réactivité Chimique et Photochimique, ERA au CNRS N° 264, Université Paul Sabatier, 118 Route de Narbonne, 31062 Toulouse Cedex, France

The photodimerization of 2-phenylbenzoxazole gives rise to a diazetidine whose acid-catalysed reversion to the starting material releases 116 kJ mol^{-1}.

The photostability of benzoxazoles, especially those which are 2-substituted by an aryl group, is of major interest because many industrial uses of these compounds as dye lasers,[1] solar screens,[2] or u.v. stabilizers in polymers[3] require light irradiation. However the few reported photochemical studies of benzoxazoles mainly concern non-substituted derivatives.[4,5] Here, we report on the photochemical behaviour of 2-phenylbenzoxazole which gives rise to a new [2 + 2] photodimerization in a concentrated medium.

Photolysis of a cyclohexane solution (0.1 M) of 2-phenylbenzoxazole (**1**) was carried out in degassed Pyrex tubes with a Rayonet R.P.R. apparatus ($\lambda = 300$ nm). A precipitate



(2)

formed (m.p. 178 °C) which could be easily isolated by filtration, and purified by benzene washing, with a 0.08 quantum yield. The structure of this photoproduct (2) [elemental analysis, $(C_{13}H_9NO)_2$, and desorption/chemical ionization mass spectrum, $MH^+ = 391$) was assigned on the basis of i.r. [disappearance of $\nu_{C=N}$ (KBr) 1620 cm^{-1} and $\nu_{N=C-O}$ (KBr) 1550 cm^{-1}] and u.v. spectral data. The 250 MHz ^1H n.m.r. spectrum [δ (C_6D_6) 7.83 (4H), 7.02 (4H), 6.91 (2H), 6.82 (2H), 6.65 (4H), and 6.47 (2H)] confirmed that the dimerization does not involve the aromatic ring but only the C=N double bonds. The two possible photodimer formulae (a 1,2 or a 1,3-diazetidine) were not distinguished since the amorphous structure of (2) did not allow an *X*-ray investigation to be made.

As far as we are aware, this photodimerization of 2-phenylbenzoxazole is the first example of a [2 + 2] intermolecular photocyclodimerization of C=N double bonds. Although [2 + 2] photocycloadditions of C=N and C=C are well known, the photocycloaddition of two C=N double bonds was only postulated by Searles to explain the structure of the compounds resulting from the photolysis of *N,N*-dimethyl-4-amino-(benzylidene)aniline.[6]

In the solid state, the photodimer (2) is stable at room temperature, but may revert thermally to 2-phenylbenzoxazole (1). In solution, the reversion occurs at room temperature. The first-order rate constant for the reversion at 25 °C was determined by following the reappearance of (1) using n.m.r. (in C_6D_6, $k_d = 1.70 \pm 0.05\ 10^{-5}\ s^{-1}$, $t_{1/2} = 11.1$ h) or u.v. spectral data (for cyclohexane solution, $k_d = 1.35 \pm 0.05\ 10^{-5}\ s^{-1}$, $t_{1/2} = 14.3$ h). The rate of reversion is highly enhanced by the addition of acid. Treatment of the benzene or cyclohexane solutions of (2) either with trifluoroacetic acid or with toluene-*p*-sulphonic acid gave (1) almost immediately. The influence of acids on diazetidines has been reported previously, protonation of the nitrogen atom facilitating the opening of the ring.[7,8]

The photochemical formation of a highly strained compound (2) which easily reverts to starting material (1) is a convenient system for light energy conversion. Its usefulness depends on the energy released during the acid-catalysed reversion. Using microcalorimetry† we measured the molar enthalpy of the decomposition of (2) in a benzene solution after the addition of trifluoroacetic acid: $\Delta\overline{H}_5$. The true value of the storage enthalpy $\Delta\overline{H}_S$ was calculated from $\Delta\overline{H}_5$ taking into account the interactions between the various reagents, interactions (gathered in Table 1) which were measured by independent microcalorimetric experiments (Table 1).

Table 1. Molar enthalpy in benzene solution of all considered reactions.

Molar enthalpy	kJ mol^{-1}
$\Delta\overline{H}_1 = \Delta\overline{H}$[dissolution of solid (1)]	+ 15.5 ± 0.1
$\Delta\overline{H}_2 = \Delta\overline{H}$[dissolution of solid (2)]	+ 27.2 ± 0.3[a]
$\Delta\overline{H}_3 = \Delta\overline{H}$(dissolution of liquid CF_3CO_2H)	+ 7.5 ± 0.1
$\Delta\overline{H}_4 = \Delta\overline{H}$[interaction (1) $\longleftrightarrow$ CF_3CO_2H]	− 26.8 ± 0.1
$\Delta\overline{H}_5 = \Delta\overline{H}$[decomposition (2) → (1) on addition of CF_3CO_2H]	− 142.0 ± 0.5[a]

[a] Accuracy of $\Delta\overline{H}_2$ and $\Delta\overline{H}_5$ is lower because the decomposition of (2) begins even in the absence of acid catalysis.

$$\Delta\overline{H}_S = \Delta\overline{H}_5 - 2\Delta\overline{H}_4 - \Delta\overline{H}_2 = -116 \pm 1 \text{ kJ mol}^{-1}$$

This high value of the storage enthalpy compares favourably with those of other traditional systems of energy storage such as the norbornadiene/quadricyclene system ($\Delta\overline{H} = 77.3$ to 110 kJ mol^{-1} depending on substitution).

The efficiency *Q* of such systems also depends on the quantum yield of the photodimerization ($\phi = 0.08$ for 0.1 M) and on the longest useful wavelength (330 nm). The *Q*-factor for this reaction is 2.5%. Even if it is necessary to make some modifications in order to increase this *Q*-factor, the 2-phenylbenzoxazole/diazetidine system appears to be an interesting model for the reversible storage of light energy.

We thank Prof. Reisse for allowing us to perform all the microcalorimetric measurements in his laboratory (Laboratoire de Chimie Organique, Université de Bruxelles).

Received, 23rd December 1981; Com. 1463

References

1 C. Rulliere, J. C. Rayez, M. M. Denariez-Roberge, and J. Joussot-Dubien, in 'Lasers in Physical Chemistry and Biophysics,' ed. J. Joussot-Dubien, Elsevier, Amsterdam, 1975; C. Rulliere and J. C. Rayez, *Appl. Phys.*, 1976, **11**, 377; C. Rulliere, J. P. Morand, and O. de Witte, *Opt. Commun.*, 1977, **20**, 339; C. Rulliere and J. Joussot-Dubien, *ibid.*, 1978, **24**, 38; L. Ducasse, J. C. Rayez, and C. Rulliere, *Chem. Phys. Lett.*, 1978, **57**, 547; C. Rulliere, J. Bellocq, J. Joussot-Dubien, and A. T. Balaban, *J. Chim. Phys. Phys. Chim. Biol.*, 1978, **75**, 961.
2 Fr. P., 1,494,097; 1967.
3 G. Irick, Jr., C. A. Kelly, and J. C. Martin, U.S.P., 4,075,162; 1978; G. Irick, Jr., and C. A. Kelly, U.S.P., 4,096,115; 1978.
4 K. H. Grellman and E. Tauer, *Tetrahedron Lett.*, 1974, **4**, 375.
5 M. Maeda, Y. Iwase, and M. Kojima, *J. Heterocycl. Chem.*, 1976, **13**, 221.
6 S. Searles, Jr., and R. A. Clasen, *Tetrahedron Lett.*, 1965, **21**, 1627.
7 D. Mackay and C. W. Pilger, *Can. J. Chem.*, 1974, **52**, 1114.
8 D. Mackay and L. L. Wong, *J. Chem. Soc., Chem. Commun.*, 1974, 621.
9 K. B. Wiberg and H. A. Connon, *J. Am. Chem. Soc.*, 1976, **98**, 5411; D. S. Kabakoff, J.-C. G. Bunzli, J. R. M. Oth, W. B. Hammond, and J. A. Berson, *ibid.*, 1975, **97**, 1510; Proceedings reported in 'Solar Power and Fuels,' ed. J. R. Bolton, Academic Press, New York, 1977.
10 J. O. Hill, G. Ojelund, and I. Wadso, *J. Chem. Thermodyn.*, 1969, **1**, 111.
11 I. Wadso, *Sci. Tools*, 1966, **13**, 33.

---

† Microcalorimetric measurements were carried out in an LKB 8700-1 apparatus with 100 ml cells using the enthalpy related to the dissolution reaction of TRIS (ref. 10) for calibration. The corrections due to the energy transfer between the cell and the medium (ref. 11) were taken into account.