

PHOTOCHEMICAL REACTIONS OF INTRAMOLECULARLY  
HYDROGEN-BONDED AZOBENZENE-CARBOXYLIC ACIDS

G.P. Joshua and V.N. Rajasekharan Pillai\*

Department of Chemistry, University of Kerala, Trivandrum, India - 695001.

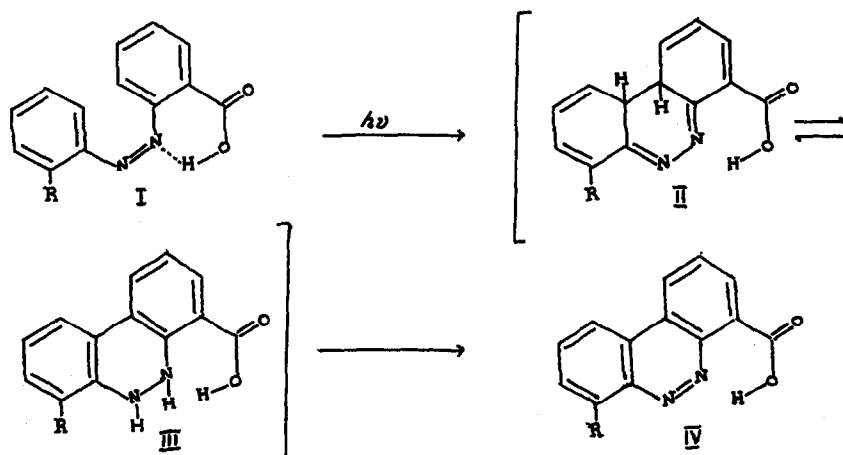
(Received in UK 24 July 1973; accepted for publication 31 July 1973)

Stilbenes<sup>1</sup>, diphenylamines<sup>2</sup> and schiff bases<sup>3</sup> undergo photochemical cyclodehydrogenation in organic solvents. But azobenzene did not cyclize under these conditions<sup>4</sup>. The failure of azobenzene to photocyclize in organic solvents was attributed to the fact that the lowest excited state is of the  $n \rightarrow \pi^*$  type. But if the nitrogen atom is protonated<sup>5</sup> or is complexed with a Lewis acid<sup>6</sup>, a  $\pi \rightarrow \pi^*$  state becomes the lowest photoexcited state and cyclodehydrogenation occurs. The observation that hydrogen-bonding increases the energy of the  $n \rightarrow \pi^*$  level above that of the  $\pi \rightarrow \pi^*$  level<sup>7</sup>, prompted an examination of the photochemical reactions of azobenzene-carboxylic acids in organic solvents. Here we report instances in which intramolecular hydrogen-bonding between a carboxyl group in the ortho position and the azonitrogen in azo compounds raises the energy of the  $n \rightarrow \pi^*$  transition above that of the  $\pi \rightarrow \pi^*$  transition and thereby assists photochemical cyclodehydrogenation.

Irradiation of a solution of azobenzene-2,2'-dicarboxylic acid (I: R = COOH, 200 mg.) in 1,2-dichloroethane (850 ml.) in an Engelhard Hanovia one litre photochemical reactor with a Philips HPK 125 W mercury-quartz lamp for 200 hrs. followed by working-up and chromatography on a column of silica gel yielded benzo[c]cinnoline-4,7-dicarboxylic acid (IV: R = COOH, 25 mg.) and benzo[c]cinnoline-4-carboxylic acid (IV: R = H, 10 mg.). Similar irradiation of azobenzene-2-carboxylic acid (I: R = H, 200 mg.) for 200 hrs. followed by working-up and chromatography on silica gel column gave azobenzene<sup>8</sup> (15 mg.) and benzo[c]cinnoline-4-carboxylic acid (IV: R = H, 20 mg.).

---

\*U.G.C. Research Fellow



Dimethyl azobenzene-2,2'-dicarboxylate (100 mg.) was irradiated for 300 hours under the same conditions as in the above cases. During irradiation a slight intensification of the colour of the solution was observed<sup>9</sup>; but chromatography of the reaction mixture on an alumina column resulted in only one band due to the starting compound. Similarly, diethyl azobenzene-2,2'-dicarboxylate, methyl azobenzene-2-carboxylate and ethyl azobenzene-2-carboxylate did not undergo any change on prolonged irradiation. But all these esters underwent photochemical cyclodehydrogenation in 98% sulphuric acid yielding the corresponding benzo[c]cinnoline-carboxylates along with some hydrolysed products. In the cases of the dimethyl- and diethyl esters of azobenzene-2,2'-dicarboxylic acid, besides the cyclodehydrogenation products, small quantities of indazolo[2,1-a]indazole-6,12-dione<sup>10</sup> were also formed.

Azobenzene-3-carboxylic acid, azobenzene-3,3'-dicarboxylic acid, azobenzene-4-carboxylic acid and azobenzene-4,4'-dicarboxylic acid were also irradiated in 1,2-dichloroethane. They also did not undergo any change even when the irradiation was extended for much longer periods.

The above observations clearly show that the carboxyl group in the ortho position has some special role in the cyclization. That this effect is not steric in origin was indicated by the lack of photochemical reactivity of azo

compounds having a non-hydrogen-bonding group such as a carboalkoxy group in the ortho position. Thus, it must be the intramolecular hydrogen-bonding between the orthocarboxyl group and the azo nitrogen which facilitates cyclization. Infra red spectral measurements lent further support to this view: in the IR spectra of azobenzene-2-carboxylic acid and azobenzene-2,2'-dicarboxylic acid in 1,2-dichloroethane solutions, the only significant absorption in the  $3\mu$  region was broad bands with maxima near  $3060\text{ cm}^{-1}$  and  $3075\text{ cm}^{-1}$  respectively (bonded OH); and no marked change in the spectra occurred with dilution, confirming intramolecular hydrogen-bonding.

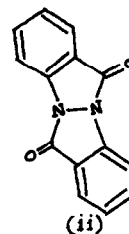
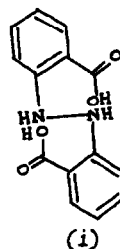
The absence of any reduction product<sup>10</sup> in these reactions indicates that the photochemical disproportionation mechanism<sup>5,6</sup>, which was found to operate in acidic solutions and in presence of Lewis acids, does not operate here. Therefore it may be reasonably assumed that the oxidation of 10a,10b-dihydrobenzo[c]cinnoline-4,7-dicarboxylic acid (II) formed as a result of cyclization and/or 5,6-dihydrobenzo[c]cinnoline-4,7-dicarboxylic acid (III) formed from II by subsequent prototropic shifts<sup>11</sup> is effected by the dissolved oxygen present. This was confirmed by the observation that traces of dissolved iodine slightly accelerates the reaction.

#### REFERENCES AND NOTES

1. P. Hugelshofer, J. Kalvoda and K. Schaffner, Helv.Chim.Acta., **43**, 1322 (1960).
2. K.H. Grellman, G.M. Sherman and H. Linschitz, J.Amer.Chem.Soc., **86**, 303 (1964).
3. F.B. Mallory and C.S. Wood, Tetrahedron Letters, 2643 (1965).
4. G.S. Hartley, Nature, **140**, 281 (1937)
5. G.E. Lewis, Tetrahedron Letters, 12 (1960).
6. C.P. Joshua and V.N. Rajasekharan Pillai, Tetrahedron Letters, 2493 (1972).
7. J. Rennert and J. Wisenfield, Photochem.Photobiol., **5**, 337 (1966).
8. Formed as a result of the photochemical decarboxylation of the starting material (C.P. Joshua and G.E. Lewis, Tetrahedron Letters, 4533 (1966)).

9. May be due to the reversible  $\text{trans} \rightleftharpoons \text{cis}$  isomerization of the azo compound.  
 (A.H. Cook, J.Chem.Soc., 876 (1938); A.H. Cook and D.C. Jones, J.Chem.Soc., 1309, (1939); G.S. Hartley, J.Chem.Soc., 633 (1938)).

10. Irradiation of azobenzene-2,2'-dicarboxylic acid in 98% sulphuric acid gives benzo[*c*]-cinnoline-4,7-dicarboxylic acid (IV: R = COOH) and indazolo[2,1*a*]indazole-6,12-dione (ii) in equal quantities. The latter product is formed by the elimination of two molecules of water from the hydrazobenzene-2,2'-dicarboxylic acid (i), formed as a result of photochemical disproportionation.  
 (C.P. Joshua and V.N. Rajasekharan Pillai, unpublished result).



11. G.M. Badger, R.J. Drewer and G.E. Lewis, Aust.J.Chem., 19, 643 (1966).