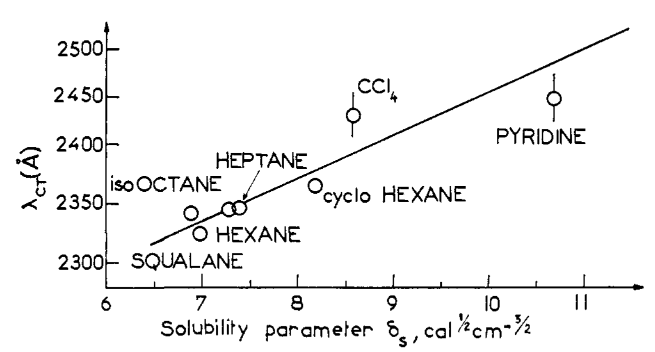


Figure 2. Displacement of the iodine-pyridine charge-transfer band with the solubility parameter of the solvents.

Furthermore, we have found that the maxima of the free and complexed iodine bands are strongly displaced in the same sense as a function of solvent (Table I). This result indicates that the iodine molecule in the complex is almost as sensitive to solvent effects as is the free molecule.

Finally, we wish to point out that the charge-transfer band of the complex is shifted significantly toward the red, corresponding to a decreasing transition energy $E_{CT} = h\nu_{CT}$, when the solubility parameter δ_s of the solvent increases (Figure 2). This result suggests that there is a larger decrease in the potential energy of the excited charge-transfer state than in that of the corresponding ground state. As δ_s is directly dependent on the vaporization energy and the molar volume of the solvent,[13] the decrease in transition energy can be correlated with both the dielectric and the cage effects of the solvent.

P. V. Huong, N. Platzer, M. L. Josien
Laboratoire de Spectrochimie Moléculaire
Faculté des Sciences de Paris, Paris, France, and
Laboratoire de Spectroscopie Infrarouge
Faculté des Sciences de Bordeaux, 33 Talence, France

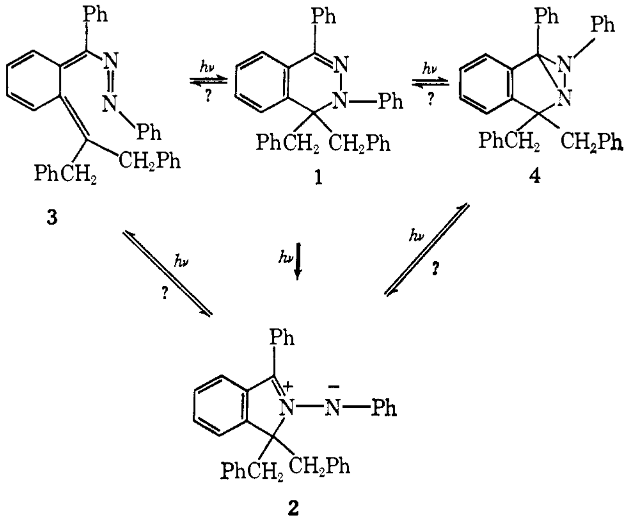
Received March 5, 1969

Photochemical Rearrangement of 1,1-Dibenzyl-1,2-dihydro-2,4-diphenylphthalazine. Photochemical Generation of Stable Azomethine Imines

Sir:

In an earlier communication[1] the light-induced rearrangement of a 2,3-benzoxazine was shown to produce an oxazirinodihydroisoindole. We now report what we believe is the first example of a photochemical generation of a stable azomethine imine from a 1,2-dihydrophthalazine, the nitrogen analog of the benzoxazine.[2]

Irradiation of 1,1-dibenzyl-1,2-dihydro-2,4-diphenylphthalazine [**1**;[3] $\lambda_{max}^{CH_3CN}$ 363 mμ (ϵ 8700), 246 (19,300)] in benzene solution with Pyrex-filtered light led to the formation of an orange-red compound. The reaction could be conveniently monitored by ultraviolet or nmr spectroscopy.



In the nmr spectrum[4] of the phthalazine **1**, the two benzyl groups (attached to C$_1$) appear as an AB quartet [**1**: nmr (CDCl$_3$) τ_A 6.77, τ_B 6.39 (q, 4 H, J_{AB} = 15.4 Hz, two CH_2Ph groups), τ 3.7–2.3 (m, 24 H, aromatic)] showing that the methylene hydrogens are magnetically nonequivalent.[5] On exposure to ultraviolet light, the original AB quartet was replaced by a second AB quartet, with slightly altered coupling constant, which grew in intensity with increased exposure time. By irradiation in benzene-diethylamine[6] (1:1, v/v) as before the azomethine imine **2** could be isolated[7] in 60–70% yield (dark red crystals with metallic luster): mp 162–163°; $\lambda_{max}^{CH_3CN}$ 460 mμ (ϵ 10,600), 346 (9900), 265 (14,000); nmr (CDCl$_3$) τ_A 6.43, τ_B 6.13 (q, 4 H, J_{AB} = 13.0 Hz, two CH_2Ph groups), τ 2.8–2.5 (m, 24 H, aromatic).

Analytical[8] and mass spectral data for compound **2** require that it be isomeric with the starting material.[9] The ultraviolet and nmr data outlined above strongly suggest structure **2** for the photoisomer.

The azomethine imine structure **2** for the photoisomer is further substantiated by the facility with which it undergoes 1,3-dipolar additions with various dipolarophiles.[10] Treatment of **2** with dimethyl acetylenedicarboxylate in benzene solution at 60–70° yielded the

---

[1] B. Singh, *J. Am. Chem. Soc.*, **90**, 3893 (1968).

[2] For somewhat related cases of cyclohexadiene and hexatriene photochemistry see (a) W. G. Dauben and W. T. Wipke, *Pure Appl. Chem.*, **9**, 539 (1964); (b) J. Meinwald and P. H. Mazzochhi, *J. Am. Chem. Soc.*, **88**, 2850 (1966); (c) W. G. Dauben and J. H. Smith, *J. Org. Chem.*, **32**, 3244 (1967); (d) M. Pomerantz, *J. Am. Chem. Soc.*, **89**, 694 (1967); J. Meinwald and P. H. Mazzochhi, *ibid.*, **89**, 696 (1967); K. R. Huffman and E. F. Ullman, *ibid.*, **89**, 5629 (1967), and references therein.

[3] A. Mustafa, A. H. Harhash, and A. A. S. Saleh, *ibid.*, **82**, 2735 (1960).

[4] All nmr spectra reported here were taken on a Varian Associates 100-MHz spectrometer.

[5] This would be normally expected here because each methylene is attached to an asymmetric group. Since only one AB quartet is observed, the two CH$_2$'s are identical, indicating coplanarity of the NPh with the remainder of the molecule. This may also be indicative of a rapid inversion of the N–Ph bond.

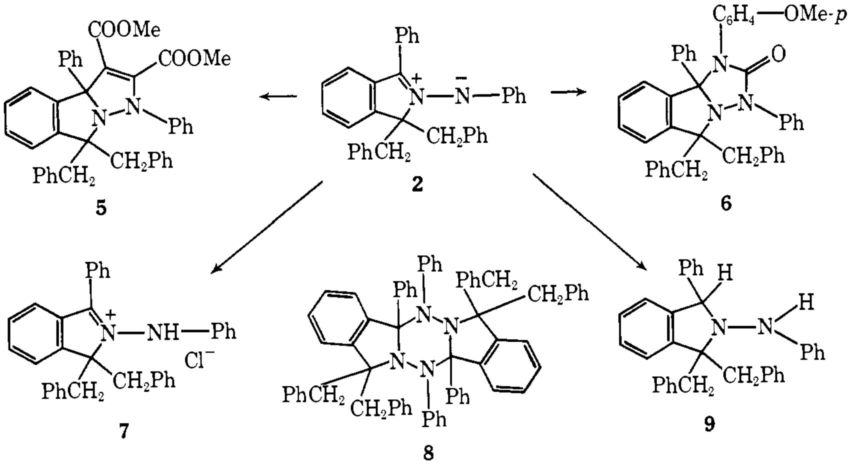
[6] As would be expected, the azomethine imine **2** is considerably stabilized toward further irradiation in the presence of relatively polar solvents such as ethanol, di- and triethylamines, pyridine ,and dimethylformamide. This may be due in part to the stabilization of the dipolar structure of the azomethine imine and in part due to the decreased energy of the excited state(s) of **2**. Maximum yields of **2** were obtained when irradiations were carried out in benzene–diethylamine (1:1, v/v).

[7] The red azomethine imine was extracted with a minimum volume of cold ethanol (in which **1** is virtually insoluble) followed by removal of the ethanol *in vacuo* and purification by recrystallization from ether.

[8] All new compounds reported here showed satisfactory elemental analyses and correct molecular ion peaks (M$^+$).

[9] The phthalazines **1** failed to show the molecular ion peak in the mass spectrum even at low voltages. The highest peak observed was at *m/e* 373, which corresponds to the loss of CH$_2$Ph group and not NPh group as was confirmed by high-resolution studies. Excellent elemental analyses and spectral data for **1** and its derivatives reported here confirm beyond doubt the assigned structure.

[10] For a summary of the azomethine imine reactions see R. Huisgen, *Proc. Chem. Soc.*, 357 (1961), and references cited therein.



colorless adduct **5** (88%): mp 220–222°; ir (Nujol) 5.72 μ (ester C=O), 5.91 (ester C=O); $\lambda_{max}^{CH_3CN}$ 332 mμ (ε 9400), 250 (8100). The nmr spectrum of **5** shows two AB quartets [**5**: nmr ($CDCl_3$) τ_A 7.31, τ_B 6.77 (q, 2 H, J_{AB} = 13.4 Hz, CH_2Ph), $\tau_{A'}$ 6.77, $\tau_{B'}$ 6.40 (q, 2 H, $J_{A'B'}$ = 12.6 Hz, CH_2Ph), τ 6.72 (s, 3 H, $COOCH_3$), 3.8–2.6 (m, 24 H, aromatic)], indicating that the two benzyl methylenes are no longer in an identical environment as would be expected from structure **5** for the adduct.

Similarly on gentle warming with *p*-methoxyphenyl isocyanate the photoisomer **2** yielded the adduct **6** (98%): mp 227–229°; ir (Nujol) 5.82 μ (C=O); $\lambda_{max}^{CH_3CN}$ 255 mμ (ε 18,300); nmr ($CDCl_3$) τ_A 7.07, τ_B 6.66 (q, 2 H, J_{AB} = 14.0 Hz, CH_2Ph), $\tau_{A'}$ 6.73, $\tau_{B'}$ 6.51 (q, 2 H, $J_{A'B'}$ = 12.6 Hz, CH_2Ph), τ 6.40 (s, 3 H, OCH_3), 3.7–2.5 (m, 28 H, aromatic).

On exposure to gaseous hydrogen chloride, solutions of the photoisomer **2** furnished the crystalline yellow hydrochloride **7** (quantitative): mp 218–220° (decomposes to yield **2**); $\lambda_{max}^{CH_3CN}$ 415 mμ (ε 3970), 284 (13,500); nmr ($CDCl_3$) 6.25 (s, sharp, 1 H, exchangeable with D, N*H*), τ_A 6.09, τ_B 5.37 (q, 4 H, J_{AB} = 13.4 Hz, two CH_2Ph groups), τ 3.5–2.0 (m, 24 H, aromatic).

That no skeletal rearrangement had occurred during treatment of **2** with hydrogen chloride was shown by the quantitative regeneration of **2** when **7** was treated with dilute aqueous alkali.

Attempts to methylate **2** with methyl iodide by refluxing in benzene solution for a prolonged period (2–3 days) were unsuccessful. Under these conditions the dimer **8** was isolated (45%) as yellow crystals: mp 235–237° (decomposes to **2**);[11] $\lambda_{max}^{CH_3CN}$ 400 mμ (ε 5760), 290 (22,600), 245 (35,000); nmr ($CDCl_3$) τ_A 6.03, τ_B 5.35 (q, 8 H, J_{AB} = 14.0 Hz, four CH_2Ph groups), τ 3.3–2.3 (m, 48 H, aromatic).

In conformity with structure **2**, the photoisomer undergoes facile reduction with metal hydrides. Titration of ethanolic solutions of **2** with ethanolic sodium borohydride (the orange-red color of **2** serves as an indicator) at ambient temperatures results in the quantitative conversion to the colorless dihydro derivative **9**: mp 126–127°; nmr ($CDCl_3$) τ_A 6.78, τ_B 6.65 (q, 2 H, J_{AB} = 13.2 Hz), 5.52 (s, 1 H, *CH*Ph), 4.74 (s, 1 H, exchangeable with D, *NH*), 3.7–2.6 (m, 24 H, aromatic).

Sensitization data suggest that the reaction **1** → **2** proceeds *via* the excited singlet state of **1**. Intervention of intermediates such as **3** or **4** in the photochemical reaction **1** → **2** cannot be excluded by the present data. Further studies are in progress and will form the subject of a future communication.

Acknowledgments. I wish to thank Dr. J. E. Lancaster for the nmr spectra and Drs. A. Zweig and A. K. Hoffmann for their valuable comments.

Balwant Singh
Central Research Division, American Cyanamid Company
Stamford, Connecticut 06904
Received March 28, 1969

Liquid-Crystal Polymorphism in Bis(4′-*n*-alkoxybenzal)-1,4-phenylenediamines

Sir:

We have found that bis(4′-*n*-alkoxybenzal)-1,4-phenylenediamine derivatives, in which the alkoxy chain lengths are C_5 to C_{18}, have a large number of first-order phase transitions. To our knowledge, no compound has been reported which has eight first-order phase transitions between condensed phases as observed in the case of C_7.

These dianils have been reported by Gray, *et al.*,[1] with only two liquid-crystal phases for those which have *n*-alkoxy chain lengths of C_5 to C_{12}, the higher temperature liquid-crystal phase being nematic and the lower one smectic. In the case of similar compounds with chain lengths C_{16} and C_{18}, only one smectic phase has been reported. Our observations of additional smectic phases with four of these compounds, prepared earlier for a comparison with the liquid-crystal phases of laterally substituted dianils,[2] encouraged us to prepare other homologs of the present series to investigate their liquid crystalline behavior.

Transition temperatures were determined by differential thermal analysis using a Du Pont DTA 900. The transitions with highest transition energy have been regarded as melting points (solid–liquid or solid–liquid-crystal transition). These transitions can be easily supercooled, whereas supercooling of liquid-crystal transitions is negligible. The assignments of the

---

(11) The dimer (tetrazine) dissociates into its monomer **2** on heating above its melting point (this was confirmed by spectral comparison of the melt with that of the pure compound **2**). The monomer–dimer equilibrium of this type has been observed previously (*cf.* ref 10).

(1) G. W. Gray, J. B. Hartley, A. Ibbotson, and B. Jones, *J. Chem. Soc.*, 4359 (1955).

(2) S. L. Arora, J. L. Fergason, and A. Saupe, Paper at the Liquid Crystal Conference, Kent, Ohio, 1968.