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# FORMATION OF BENZ[cd]INDAZOLE BY LOW-TEMPERATURE PHOTOLYSIS OF 1,8-DIAZIDONAPHTHALENE IN A RIGID MATRIX1)

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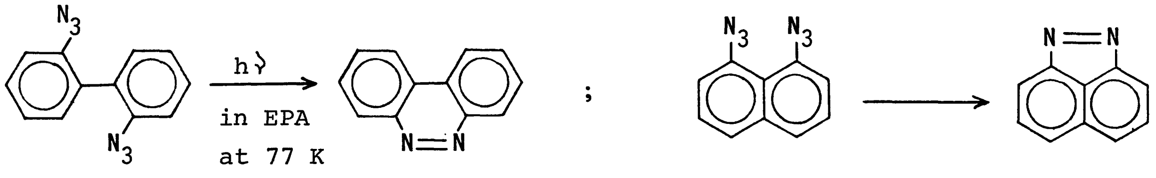
The absorption spectrum of benz[cd]indazole is observed by low-temperature matrix photolysis of 1,8-diazidonaphthalene and is identified tentatively on the basis of its chemical behavior and the prediction of the spectroscopic data by SCF MO-CI calculations.

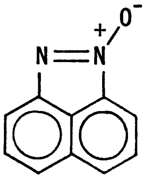
Benz[cd]indazole (I) is of interest in itself as an unprepared aza-analog of the nonalternant hydrocarbon, acenaphthylene, and as a possible precursor of the non-ortho-dehydroarene, 1,8-dehydronaphthalene by its thermolysis or photolysis.2) In spite of many attempts to prepare it, it has never been detected.3,4) In this paper we now report that the absorption spectrum of benz[cd]indazole is observed and is identified tentatively on the basis of its chemical behavior and the prediction of the spectroscopic data by SCF MO-CI calculations, although we could not yet isolate benz[cd]indazole.

Recently we have found that the low-temperature photolysis of 2,2'-diazidobiphenyl (IV) in rigid matrices leads to the intramolecular formation of the azo-linkage in an almost quantitative yield, whereas the unsensitized or sensitized photolysis at room temperature gives only little amounts of benzo[c]cinnoline (III).5) The same procedure for the peri-substituted naphthalene system is expected to be most promising route to benz[cd]indazole.6) Figure 1 shows the spectral changes of 1,8-diazidonaphthalene (II) in an EPA glassy matrix at 77 K by irradiation. Short irradiation ( ca. 10 min with a 500 W high-pressure mercury lamp through a Toshiba UV-D2 filter ) gave a final spectrum different from the starting azide (II). It is the new spectrum different from those of peri-NN-disubstituted naphthalene compounds reported previously such as benz[cd]indazole 1-oxide (V), benz[cd]indazole 1,2-dioxide (1,8-dinitrosonaphthalene),3) 1,3- or 1,5-dihydrobenz[cd]indazole, or related compounds.4) Melting of the irradiated



IV III II I

glassy sample showed no change in its absorption maxima except for their broadening ( Fig.1; dashed lines, the optical density is not corrected for volume changes). Upon subsequent refreezing at 77 K, the original spectrum obtained by irradiation at 77 K was completely reproduced. These observations indicate that the photoproduct is neither a nitrene nor a dinitrene. Furthermore, these spectral changes by irradiation are quite similar to those in other glassy solvents, e.g., 3-methylpentane, methylcyclohexane—2-methylbutane(3:1), or ethanol—glycerol(11:1) at 77 K, or even glycerol at 201 K. Therefore the photoproduct is independent of solvents. In addition, liquid phase chromatography of the irradiated sample showed the presence of a single product when it was treated in dilute solution. However, the isolation of the photoproduct by removal of the solvent turned it into the blue-purple product, which gave a wide streak on thin layer chromatography, among which a trace amounts of V was detected. Major product is a blue-purple solid having $\lambda_{max}$ ca. 550 nm. This product agrees with the compound which was found in the reductions of V or benz[cd]indazole 1,2-dioxide with a variety



V

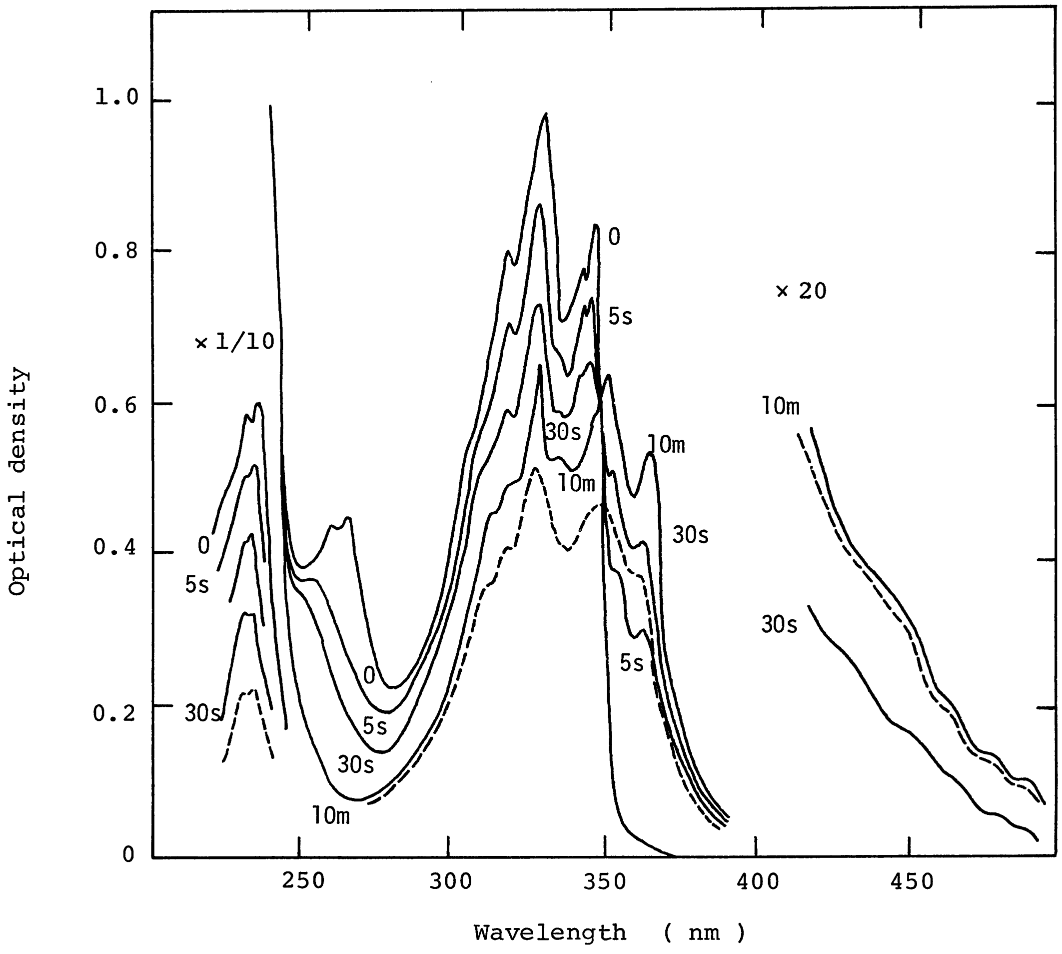


Fig.1 : Spectral changes of 1,8-diazidonaphthalene in EPA at 77 K with irradiation (——); the irradiated ( 10 min ) sample after warming to room temperature, whose spectrum was measured at 20°C (---).

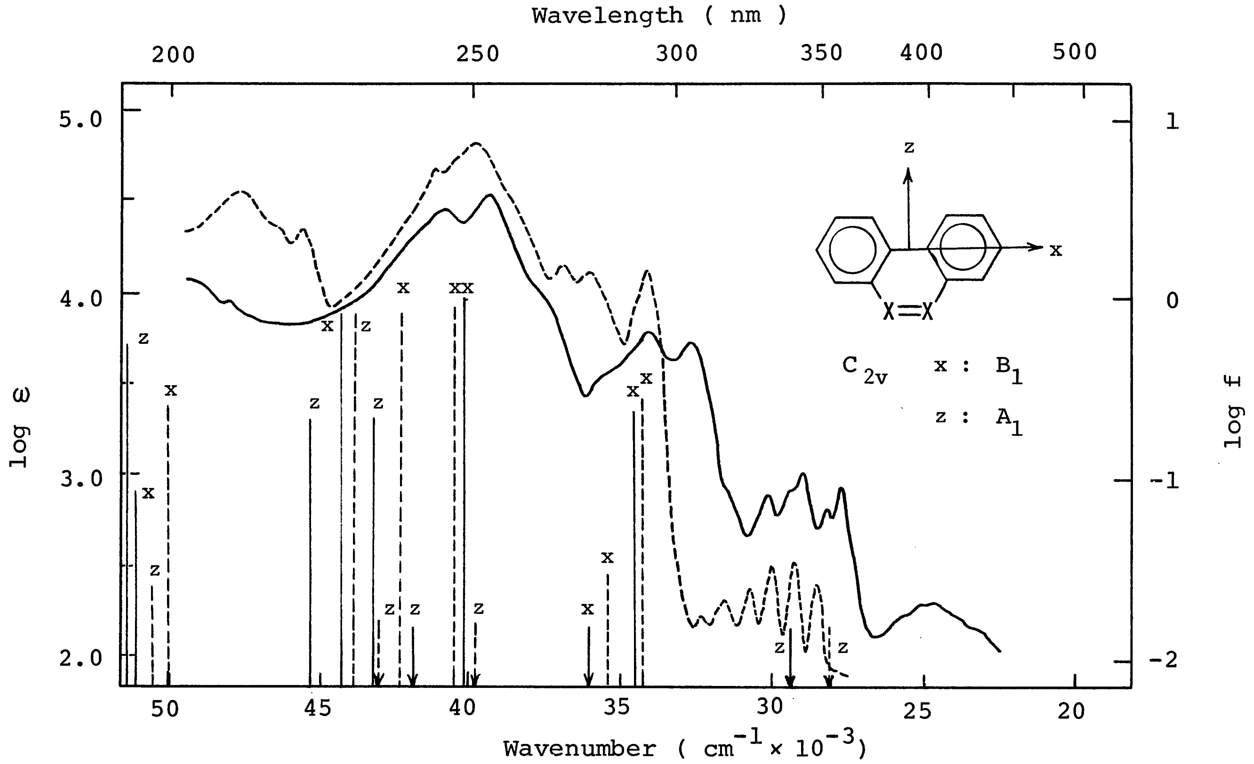


Fig.2 : Absorption spectra of phenanthrene (---) and benzo[c]cinnoline (——) in hexane, and their calculated transition energies and oscillator strengths; weak transitions are shown by arrows.

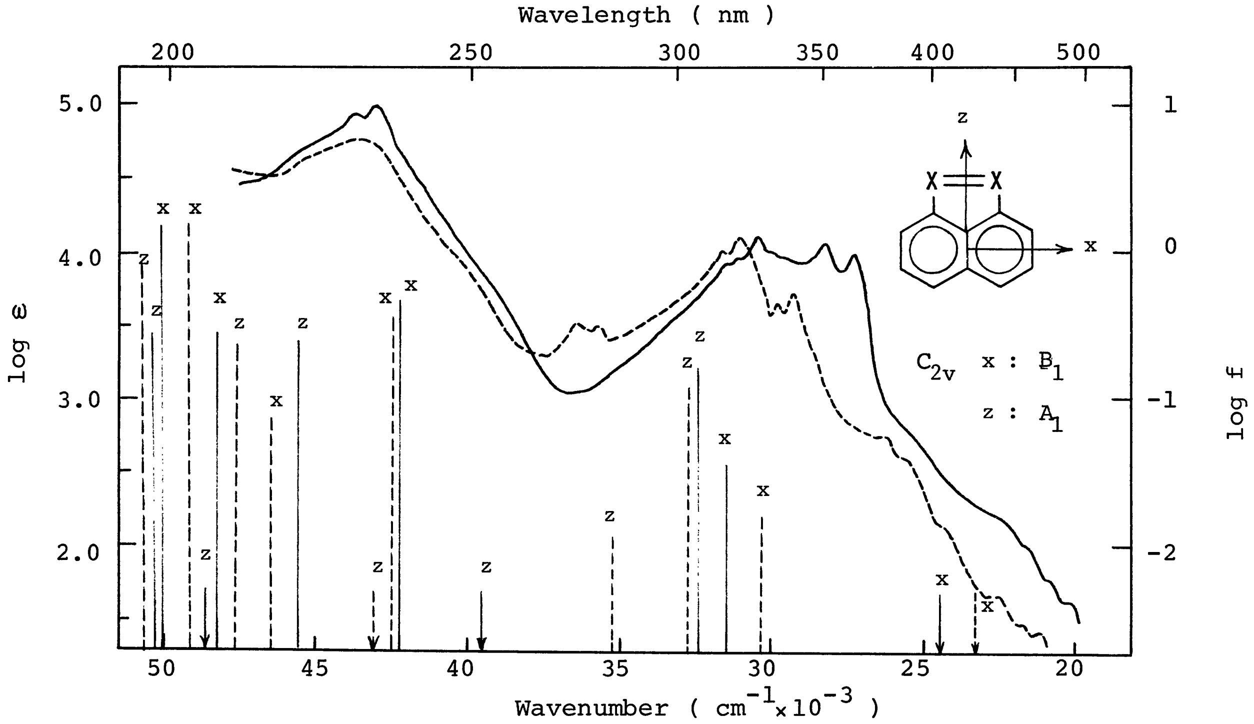


Fig.3 : Absorption spectra of acenaphthylene (---) and I (irradiated II) (——) in EPA at 77 K, and their calculated transition energies and oscillator strengths ; weak transitions are shown by arrows.

of reagents by Alder, Niazi, and Whiting,[3)] who presumed it to be the product from polymerization or self-condensation of benz[cd]indazole.

For the further confirmation of the photoproduct, the newly observed absorption spectrum is studied based on MO calculations. Marked resemblances of absorption spectra between some aromatic hydrocarbons and their aza-analogs have been shown qualitatively.[7,8)] We calculated the transition energies and intensities of benz[cd]indazole and acenaphthylene, together with those of benzo[c]cinnoline and phenanthrene, by ordinary procedure of PPP-CI method including all singly excited configurations. As Figures 2 and 3 show, the theoretical calculations reproduce the resemblances of two couples of the analogs, and these results support the newly observed spectrum to be that of benz[cd]indazole.

Although the newly observed spectrum is comparatively stable in dilute solution even at room temperature in the dark as described above,[9)] it is readily changed on irradiation at room temperature or on short heating. Attempts to trap 1,8-dehydronaphthalene expected to arise from its decomposition are in progress.

## References and Notes

1) Photolysis of Organic Azides. Part III. Preceding paper : A.Yabe and K.Honda, Bull. Chem. Soc. Japan, in press.
2) The two kinds of 1,8-dehydronaphthalene, which are represented by the symmetric and the antisymmetric combination of radical lobes, are predicted by R.Hoffmann, A.Imamura, and W.J.Hehre ( J. Amer. Chem. Soc., 90, 1499 (1970)). We may expect for them to be formed individually by pyrolysis or photolysis of benz[cd]indazole. The formation of 1,8-dehydronaphthalene by photolysis has not been reported previously.
3) R.W.Alder, G.A.Niazi, and M.C.Whiting, J. Chem. Soc.(C), 1970, 1693.
4) S.Bradbury, C.W.Rees, and R.C.Storr, J. Chem. Soc. Perkin I, 1972, 68.
5) (a) A.Yabe and K.Honda, Tetrahedron Lett., 1975, 1097.
   (b) A.Yabe and K.Honda, Bull. Chem. Soc. Japan, in press.
6) Conventional pyrolysis, and sensitized and unsensitized photolysis of 1,8-diazidonaphthalene gave only polymeric material and small amounts of 1,8-diaminonaphthalene ( cf. References 3) and 4)).
7) G.M.Badger, R.S.Pearce, and R.Pettit, J. Chem. Soc., 1951, 3199.
8) J.F.Corbett, P.F.Holt, and A.N.Hughes, J. Chem. Soc., 1961, 1363.
9) The spectrum is virtually invariant for a few days when the sealed cell irradiated at 77 K ( a ca. $5\times10^{-5}$M II solution ) is kept at room temperature in the dark. Under these conditions it is almost changed in about a month.

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