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FORMATION OF BENZ[*cd*]INDAZOLE DERIVATIVES BY THE PHOTOLYSES OF DIAZIDONAPHTHALENES IN THE LOW-TEMPERATURE RIGID MATRICES

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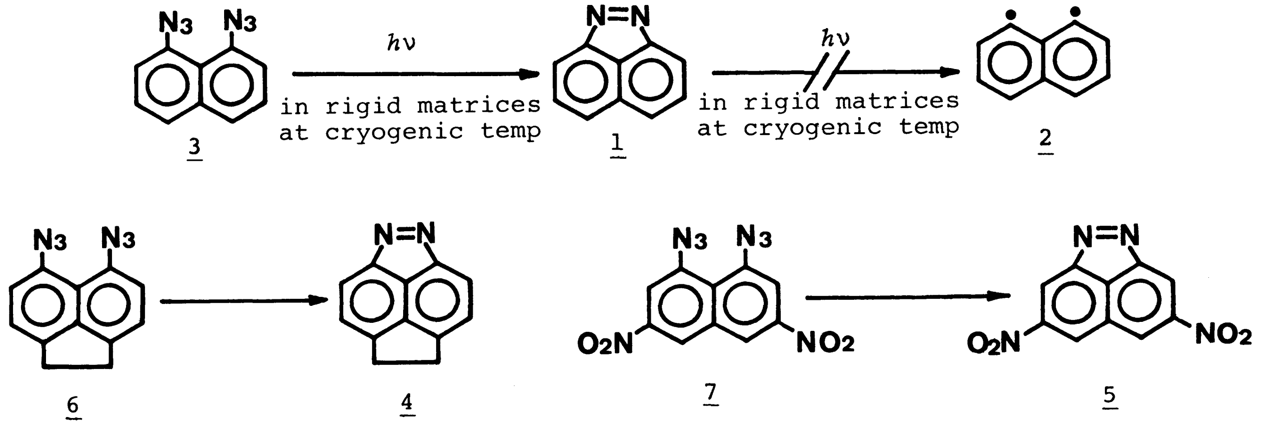
Two derivatives of benz[*cd*]indazole were formed in rigid matrices by low-temperature photolyses of *peri*-diazidonaphthalenes: 5,6-diazidoacenaphthene containing more strain energy than 1,8-diazidonaphthalene and 1,8-diazido-3,6-dinitronaphthalene having strong electron-attractive groups. These indazoles were stable to prolonged irradiation in low-temperature matrices.

Benz[*cd*]indazole (1) is of interest theoretically and experimentally as an aza-analogue of the nonalternant hydrocarbon, acenaphthylene, and as a possible precursor to 1,8-dehydronaphthalene (2). After much unsuccessful work directed towards the preparation of 1,1) we have succeeded in the first formation of 1.2,3) The product 1, which was given by the low-temperature photolysis of 1,8-diazidonaphthalene (3), could not be photolyzed to 2 on prolonged irradiation in the low-temperature rigid matrices. For further investigation of benz[*cd*]indazole chemistry, we intended to prepare two benz[*cd*]indazole derivatives, 4 containing more strain energy and 5 incorporating electron-attractive groups. In this paper, we wish to report the formation of benz[*cd*]indazoles 4 and 5 from 5,6-diazidoacenaphthene (6) and 1,8-diazido-3,6-dinitronaphthalene (7), respectively.

The starting materials 6 and 7 were prepared *via* the diamines from the corresponding dinitro compounds by conventional methods.4)



Figures 1(a) and 2(a) show the spectral changes of diazides 6 and 7, respectively, in ether-2-methylbutane (1:1) glassy matrices at 77 K upon irradiation (300-400 nm). Both 6 and 7 changed to the final photoproducts with the maximum intensity upon short irradiation with a 500 W high-pressure mercury lamp through

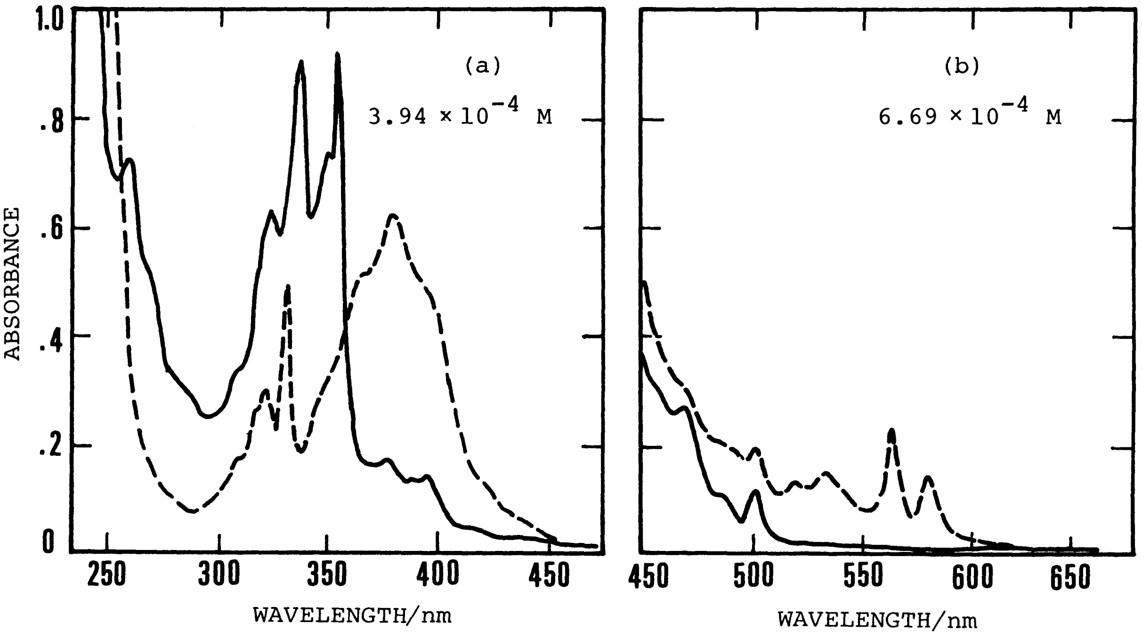


Fig. 1. Spectral changes in the photolysis of 6, (a) 6 before irradiation (——) and the final photoproduct (---); (b) 6 before irradiation (——) and the intermediate (---).

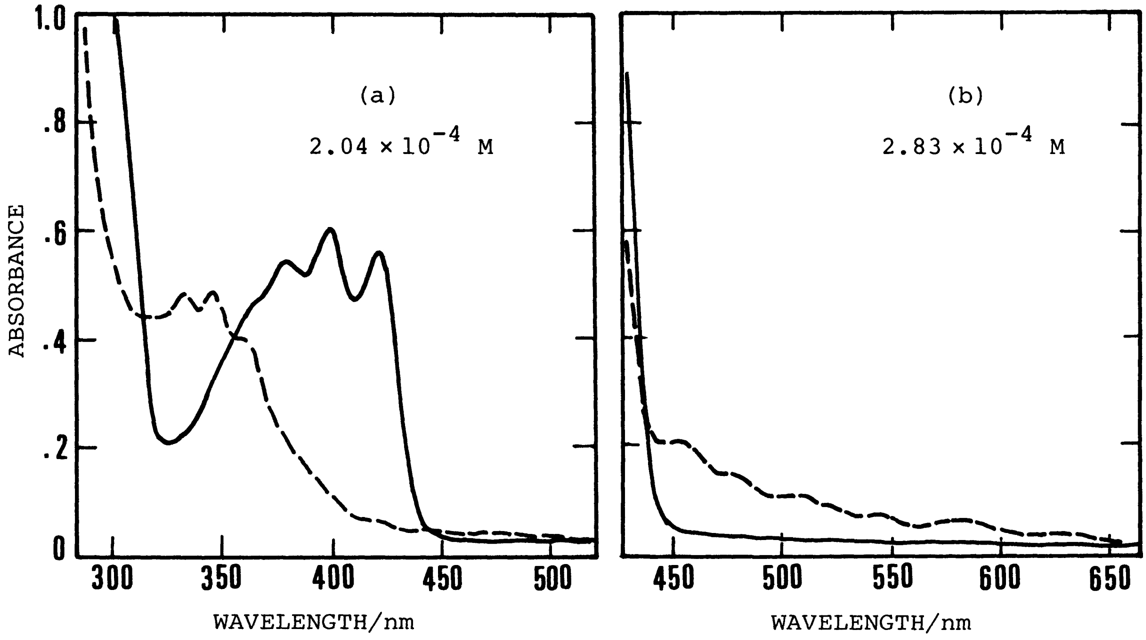


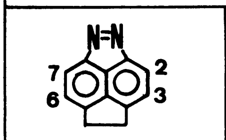
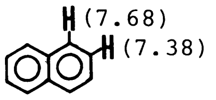
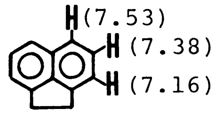
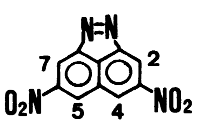
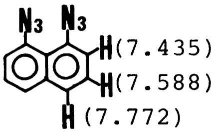
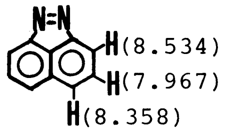
Fig. 2. Spectral changes in the photolysis of 7, (a) 7 before irradiation (——) and the final photoproduct (---); (b) 7 before irradiation (——) and the intermediate (---).

a 12.5%-transmittance neutral density filter : 60 s for 6 and *ca.* 300 s for 7. Melting of the matrices of photoproducts showed no change in the absorption maxima. However, the photoproducts were gradually decomposed at room temperature, and rapidly decomposed if the solutions were concentrated. The isolation of the photoproducts by removal of the solvents turned them into intractable compounds. This behavior was similar to that of 1. Therefore, the identification of the photoproducts which were given by the low-temperature photolysis was performed quickly *in situ* by NMR spectroscopy at room temperature. As the stability of the photoproducts from 6 and 7 was lower than that of 1 in the concentrated solutions at room temperature, only ^{1}H-NMR spectra could be measured with difficulty. Table 1 shows that the observed chemical shifts agree very closely with those calculated on the basis of the data for the mother compounds.$^{3)}$ These NMR signals show unusual shifts to lower field, compared with the corresponding azides and amines, suggesting that the indazoles include a distortion of the naphthalene ring as for single-atom *peri*-bridged naphthalenes.

For further confirmation of the photoproducts, the photolytic process of 6 was followed by IR spectroscopy in an argon matrix at 23 K using a cryostat system (Air Products, Displex Model CSA-202).$^{5)}$ With the decrease of the bands belonging to 6 upon irradiation, new bands appeared at 1595, 1463, 1435, 1400, 1200, 1030, and 913 cm^{-1}. Thus, the photoproduct was confirmed as the expected compound 6 on the basis of the data of 1.$^{6)}$

During the initial stages of the photolyses of 6 and 7, transient absorptions were observed in the 500-600 nm region as shown in Figs. 1(b) and 2(b). These transient species are assigned to the mononitrenes, since the ESR spectroscopy under the same conditions gave the characteristic absorptions of triplet nitrenes$^{7)}$ as shown in Fig. 3. Although the transients were indefinitely stable at 77 K in a rigid matrix, warming of the matrix resulted in rapid disappearance of both the UV-Vis and ESR spectra. Moreover, these spectra disappeared upon the further irradiation with longer wavelength light (>400 nm). Experiments on the light-intensity dependence suggested that the formation of the indazoles was a two-photon process at 77 K in a rigid matrix. Thus, the photolytic process of 6 to

Table 1. ^{1}H-NMR chemical shifts (ppm from TMS) of benz[*cd*]indazoles 4 and 5

Positions of H		Observed	Calculated	by an additive rule using the following data
	$\delta(H_2,H_7)$	8.550	8.534	 
	$\delta(H_3,H_6)$	7.748	7.747	
	$\delta(H_2,H_7)$	9.830	9.373	 
	$\delta(H_4,H_5)$	10.572	9.623	

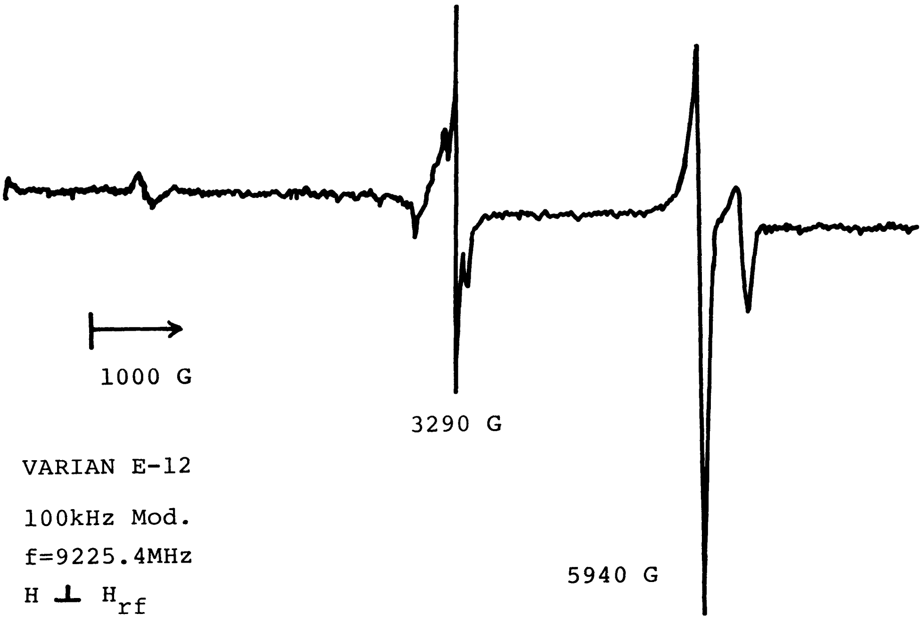
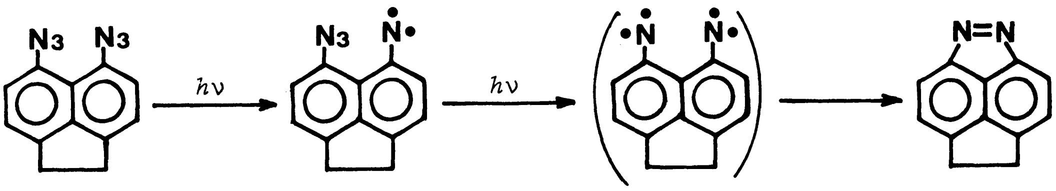


Fig. 3. ESR spectrum of photolyzed 4,5-diazidoacenaphthene (4) in 2-methyltetrahydrofuran at 77 K.

benz[*cd*]indazole 4 is shown as follows. The photolyses of the diazido compounds



are interesting in that the nitreno group formed by the first photon does not attack the neighboring azido group in a low-temperature rigid matrix.

Upon the prolonged irradiation of formed 4 and 5 with a low-pressure mercury lamp (184.9 and 253.7 nm), both 4 and 5 were not decomposed to the expected 1,8-dehydronaphthalenes by the elimination of nitrogen in low-temperature rigid matrices. Further investigation on the reactivity of benz[*cd*]indazoles is now in progress.

References

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