BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (8), 2445—2446 (1979)

Synthesis and Absorption Spectra of 1,4-Diazaanthraquinone Derivatives

Hiroyuki NAKAZUMI,* Testuro AGAWA, and Teijiro KITAO

Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture, Sakai 591

(Received February 20, 1979)

Synopsis. A new 5-amino-1,4-diazaanthraquinone and related compounds were prepared from 2,3-dichloro-1,4-naphthoquinone by two different methods. The transition energies and electron densities of 5-amino-1,4-diazaanthraquinone and 1-aminoanthraquinone were calculated by a variable β,γ-modification of the PPP method.

Anthraquinone dyes are of great value as synthetic coloring matter. We have attempted to prepare new azaanthraquinone derivatives for dyes. Although a few styryl derivatives of diazaanthraquinone dyes have been reported,[1)] the preparation and absorption spectra of other diazaanthraquinone derivatives for dyes are little known.

In this paper, we wish to report the syntheses and absorption spectra of new 5-amino-1,4-diazaanthraquinone **4** and related compounds which were prepared from 2,3-dichloro-1,4-naphthoquinone by two different methods (Scheme 1). Compound **4** was prepared as follows: Method A. Reduction of 5-nitro-1,4-diazaanthraquinone **3** prepared by the nitration of 1,4-diazaanthraquinone (DAQ) **2**,[2)] with sodium sulfide for 2 h gave **4** in 34% yield. Method B. Condensation of 2,3,5-triamino-1,4-naphthoquinone **6**[3)] prepared from 2,3-dichloro-1,4-naphthoquinone **1** *via* several steps (**1**→**5**→**6**), with 40% aqueous glyoxal at 90 °C for 3 h gave **4** in 92% yield. Method B is favorable as regards yield. No diazaanthraquinone derivative (**2**, X=CH_3) could be obtained by the Friedel-Crafts reaction of pyrazinedicarboxylic anhydride with toluene. Compounds **3** and **4** were confirmed by the appearance of peaks at 255 and 225, respectively, in the mass spectra. Since the purification of compound **4** was difficult, it was converted into acetylamino (**7**) and benzoylamino derivatives (**8**). These compounds gave satisfactory results of microanalysis. Bromination of **4** gave a mono bromo derivative **9**. The dye properties of these compounds are under investigation.

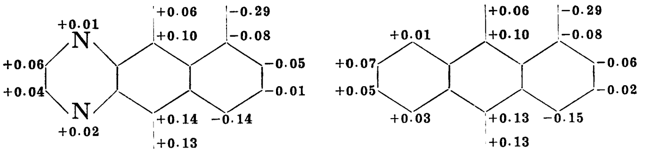
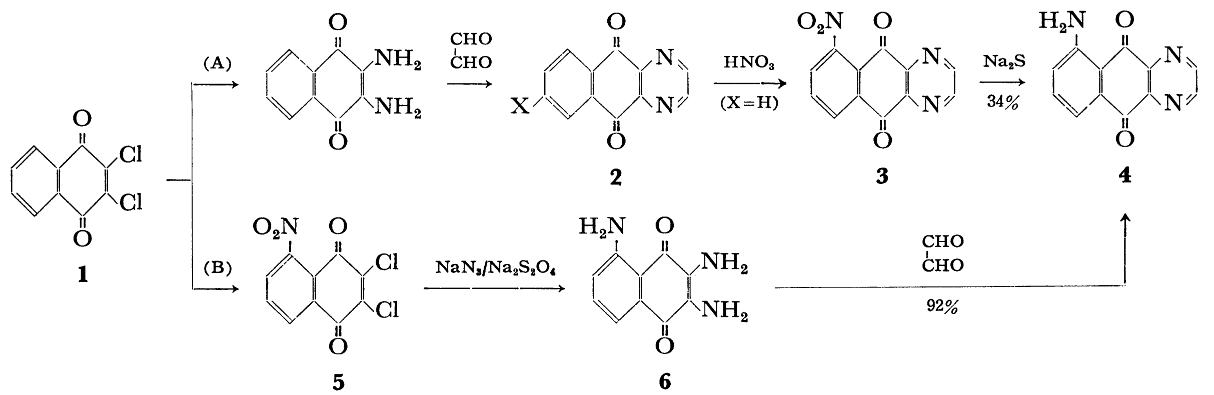


Fig. 1. Change in π-electron density accompanying electronic excitation to the first excited state for 5-amino-1,4-diazaanthraquinone **4** and 1-aminoanthraquinone **10**. A positive sign indicates an increase and a negative sign a decrease in π-electron density.

The absorption spectra of new 1,4-diazaanthraquinones in EtOH are as follows: 5-NH_2-DAQ **4**: λ_{max} 500 nm (ε 5.7×10^3), 5-$NHCOCH_3$-DAQ **7**: λ_{max} 414 nm (ε 4.5×10^3), 5-$NHCOC_6H_5$-DAQ **8**: λ_{max} 424 nm (ε 5.5×10^3), 5-NH_2-6(or 8)-Br-DAQ **9**: λ_{max} 490 nm (ε 6.2×10^3). The absorption maxima of diazaanthraquinone derivatives **4** and **7** were found at longer wavelength (10—20 nm) than those of their carbon analogues, *e.g.*, 1-aminoanthraquinone **10**: λ_{max} 478 nm, 1-acetylaminoanthraquinone **11**: λ_{max} 400 nm. In the benzene solution, the absorption maxima of **4** and **10** lie at 476 and 465 nm, respectively. The solvent-induced wavelength shift for **4** is larger than that for **10**. Calculation of the first excited energy by the variable β,γ-modification of the PPP method for **10** and **4** predicts a small bathochromic shift for the latter compound (**10**: 2.95 eV (f=0.246), **4**: 2.93 eV (f=0.226)). As shown in Fig. 1 the migration of π-electron accompanying the first electron exitation for **4** is from the donor amino group and substituted ring to two carbonyl groups and the pyrazine ring, as well as for carbon analogue **10**. From the result, it is expected that the characterization of the absorption properties of diazaanthraquinone derivatives is similar to that of anthraquinones.



Scheme 1.

Experimental

Infrared spectra were recorded on a Hitachi ESI-S2 spectrophotometer using KBr pellets, UV spectra on a Hitachi EPS-3T spectrophotometer, and mass spectra on a Hitachi RMU-6E mass spectrometer operating at 80 eV. Elemental analyses were recorded on a Yanaco CHN recorder MT-2.

5-Nitro-1,4-diazaanthraquinone **3**. 1,4-Diazaanthraquinone[1] (3.8 g, 0.018 mol) was dissolved in concd H_2SO_4 (10 g), and a mixture of concd H_2SO_4 (15 g) and fuming HNO_3 (d=1.52, 2.1 g) was added dropwise to this solution at 75—80 °C. The mixture was stirred at 75—80 °C for 5 h. After cooling, the mixture was poured into cold water. The resulting solid was separated and washed with water. Recrystallization from benzene gave **3** (1.0 g); yield 22%, mp 275—278 °C, Found: C, 57.64; H, 2.19; N, 15.67%; ν_{CO} 1690 cm^{-1}, NMR (DMSO-d_6) δ=9.10 (2H, s) and 7.50—8.50 (3H, m), MS (80 eV), *m/e* (rel intensity), 255 (M, 100), 225 (85), and 209 (54).

5-Amino-1,4-diazaanthraquinone **4**. Method A. Compound **3** (1.0 g, 0.0039 mol) was added to an aqueous solution (100 ml) of sodium sulfide (1.14 g) and sulfur (0.15 g). The mixture was stirred under reflux for 2 h, and the resulting solid was separated. Recrystallization from water and/or pyridine gave **4** (0.3 g). Method B. To a suspension of 2,3,5-triamino-1,4-naphthoquinone (7.7 g, 0.038 mol) in water (230 ml) was added 40% aqueous glyoxal (7.7 g) at 90 °C. *The mixture was stirred at 90 °C for 3 h. After cooling,* the resulting solid was separated. Recrystallization from water and/or pyridine gave **4** (7.9 g). Microanalysis of compound **4** gave unsatisfactory results as follows. Found: C, 62.98; H, 3.05; N, 18.34%. Calcd for $C_{12}H_7N_3O_2$: C, 64.00; H, 3.11; N, 18.67%, ν_{CO} 1680 and 1650 cm^{-1}, MS (80 eV), *m/e* (rel intensity) 225 (M, 100), 197 (39), 169 (33), and 143 (18).

5-Acetylamino-1,4-diazaanthraquinone **7**. A solution of **4** (0.5 g) in acetic anhydride (25 ml) was stirred under reflux for 2 h. After cooling, the resulting solid was separated and washed with water. Recrystallization from xylene gave **7** in 67% yield: ν_{CO} 1700 and 1665 cm^{-1}, MS (80 eV), *m/e* (rel intensity), 267 (M, 17), 225 (100), 210 (19), and 197 (39). Found: C, 63.09; H, 3.30; N, 16.11%. Calcd for $C_{14}H_9N_3O_3$: C, 62.92; H, 3.37; N, 15.73%.

5-Benzoylamino-1,4-diazaanthraquinone **8**. Benzoyl chloride (2.6 g) was added dropwise to a solution of **4** (1.4 g) in nitrobenzene (45 ml) at 125 °C for 1.5 h. The mixture was then heated for 1.5 h at the same temperature. After cooling, the resulting solid was separated and washed with ligroin and methanol. Recrystallization from acetonitrile gave **8** (1.3 g) in 64% yield: ν_{CO} 1700 and 1665 cm^{-1}. Found: C, 69.21; H, 3.24; N, 12.93%. Calcd for $C_{19}H_{11}O_3N_3$: C, 69.30; H, 3.34; N, 12.77%.

5-Amino-6(or 8)-bromo-1,4-diazaanthraquinone **9**. Bromine (5.3 g) was added dropwise to a solution of **4** (3.0 g) in *o*-dichlorobenzene (100 ml) at 165—170 °C for 1 h. The mixture was stirred under reflux for 7 h. After cooling, the resulting solid was separated and washed with benzene, methanol, and water. Recrystallization from EtOH gave **9** in 45% yield: ν_{CO} 1700 and 1665 cm^{-1}. Found: C, 46.44; H, 2.08; N, 14.20%. Calcd for $C_{12}H_6N_3BrO_2$: C, 47.38; H, 1.97; N, 13.82%, MS (80 eV), *m/e* (rel intensity), 305 (100), 303 (99), 225 (90), 197 (44), and 169 (48).

Method of SCF-MO Calculation. The calculation was carried out by the Pariser-Parr-Pople method with variable β,γ-approximation. The resonance integrals, β_{rs}'s, were adjusted at each iteration of the SCF calculations by means of the following equations.[4]

$$\beta_{CC} = -1.84 - 0.51P_{CC}$$
$$\beta_{CN} = -2.02 - 0.53P_{CN}$$
$$\beta_{CO} = -2.20 - 0.56P_{CO}$$

where P_{rs} is a bond order between the r and s atoms. The two center repulsion integrals γ_{rs}'s were calculated by the Nishimoto-Mataga equation[5] using the following R_{rs}:

$$R_{CC} = 1.517 - 0.18P_{CC}$$
$$R_{CN} = 1.451 - 0.18P_{CN}$$
$$R_{CO} = 1.410 - 0.18P_{CO}$$

The ionization potentials, $I_{p(r)}$'s, and one-center repulsion integrals, γ_{rr}'s, for carbon, nitrogen, and oxygen atoms were chosen as:

$$\begin{array}{llll} I_p(C) & = 11.16\ eV & \gamma_{rr} & = 11.13\ eV \\ I_p(N) & = 14.12\ eV & & = 12.34\ eV \\ I_p(NH_2) & = 26.7\ eV & & = 17.44\ eV \\ I_p(O) & = 17.7\ eV & & = 15.23\ eV \end{array}$$

The authors would like to thank Mr. Y. Kogo, Nippon Kayaku Co., Ltd., for assistance in the molecular orbital calculations.

References

1) G. A. Efimova and L. S. Efros, *Zh. Org. Khim.*, **3**, 388 (1967); *Chem. Abstr.*, **67**, 3068 (1967).

2) G. A. Efimova and L. S. Efros, *Zh. Org. Khim.*, **2**, 531 (1966); *Chem. Abstr.*, **65**, 8910 (1966).

3) M. L. Mosby and M. L. Silva, *J. Chem. Soc.*, **1964**, 3990.

4) K. Nishimoto and L. S. Forster, *Theor. Chim. Acta*, **4**, 155 (1966).

5) K. Nishimoto and L. S. Forster, *Theor. Chim. Acta*, **3**, 407 (1965).