Synthesis and Absorption Spectra of Annelated 5-Amino-1,4-diazaanthraquinones and Related Compounds

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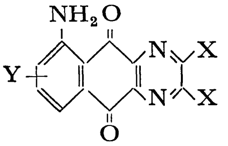
Synopsis. New annelated 5-amino-1,4-diazaanthraquinones and related derivatives were prepared from 2,3,5-triamino-1,4-naphthoquinone or 5-amino-2,3-dichloro-1,4-naphthoquinone. Their visible absorption spectra were examined by the PPP-SCF-MO calculation with a variable β approximation.

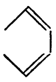
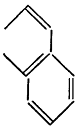
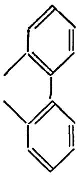
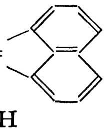
1-Amino- and 1,4-diaminoanthraquinones are of great value as coloring matter. We have attempted to prepare new diazaanthraquinones for dyes. The visible absorption maximum of 5-amino-1,4-diazaanthraquinone **2** prepared from 2,3,5-triamino-1,4-naphthoquinone **1** is found at a longer wavelength than that of its carbon analogue.[1)]

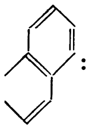
In this paper, we wish to report the preparation and visible absorption spectra of annelated derivatives of **2** and related compounds. Annelated 5-amino-1,4-diazaanthraquinones **5**—**7** were prepared by the reaction of 1,2-quinones (1,2-naphthoquinone, acenaphthenequinone and 9,10-phenanthrenequinone) with **1** in 50—86% yields. Benzo derivative **4** was prepared from 5-amino-2(or 3)-chloro-3(or 2)-anilino-1,4-naphthoquinone **3** and sodium azide. Bromination of **2** afforded 5-amino-6,8-dibromo-1,4-diazaanthraquinone **8**. No monobromo derivative[1)] was isolated under the same conditions. 5-Amino-8-anilino derivative **9** was prepared by the Ullmann amination of **8** with aniline, along with 6(or 8)-bromo-5-amino derivative **10**, debrominated product of **8** in trace amounts.

The observed and calculated absorption maxima of new annelated compounds and **9** are summarized in Table 1. All the annelated compounds showed a pronounced bathochromic shift of λ_{max} in polar solvents. In this PPP calculation, the parameters for the solvent effect were not included. Annelation to 6,7-positions of some 1,4-disubstituted anthraquinones produces a small hypsochromic shift.[2)] The hypsochromic shifts of 4—8 nm are accurately predicted by the PPP calculation.[3)] The observed absorption

Table 1. The absorption maxima of annelated 5-amino-1,4-diazaanthraquinones and related compounds



Compd No.	X, Y		λ_{max} (exptl)/nm ($\varepsilon\times10^{-4}$)			λ_{max}(calcd)/nm (f[a)])
			Benzene[b)]	DMF	EtOH	
2[1)]	X=H	Y=H	476	489	500(0.57)	423(0.226)
4	2X= 	Y=H	464	475(0.68)	484	422(0.304)
5[c)]	2X= 	Y=H	471	486(0.64)	493	419(0.309)
6	2X= 	Y=H	473	489(0.79)	498	420(0.306)
7	2X= 	Y=H	485	501(0.74)	511	422(0.300)
9	X=H	Y=6-Br-8-NHC_6H_5	598 634	598 634	598(1.2) 636(1.2)	—

a) Oscillator strength. b) The values of ε could not be measured due to the poor solubility. c) This structure was presumed by the comparison with the calculated λ_{max} of **5** and its isomer (2X= : 426 nm (f=0.343).

maxima of annelated derivatives **4**—**6** were found at wavelengths somewhat shorter than those of the parent compound **2**. The calculated values of all annelated compounds were very close to the value of **2**. The calculated changes in π-electron density accompanying electronic excitation to the first excited state for **4**—**6** were mainly from aniline moiety to two carbonyl groups. The changes were similar to those for **2**.[1)]

On the other hand, the $\lambda_{\max}$ of **7** was observed at a longer wavelength than that of **2**. The absorption band corresponds to changes in π-electron density away from aniline moiety to an acenaphthene ring. Thus, it is predicted that the character of charge transfer for the first excitation for **7** differs from that of the other 5-amino-1,4-diazaanthraquinones.

The absorption maximum of 5-amino-8-anilino derivative **9** was found at the same wavelength as that of its carbon analogue (1-amino-2-bromo-4-anilinoanthraquinone: $\lambda_{\max}$ (benzene) 634 nm (ε, 1.35×10^4)).[4)] It is suggested that the substitution of a pyrazine ring for 1,4-disubstituted anthraquinone series produces no bathochromic shift.

Experimental

Most melting points of 1,4-diazaanthraquinones were not measured owing to the fact that no melting takes place below 300 °C. The absorption spectra were recorded on a Hitachi EPS-3T spectrophotometer, IR spectra on a Hitachi EPI-S_2 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.

Method of SCF-MO Calculation. The calculations were carried out by the PPP-SCF-CI method with a variable β approximation, using the parameters reported,[1)] except for the core resonance integrals (β). The following β_{rs}'s were used for all the annelated compounds.

$$\beta_{CC}/\text{eV} = -1.81 - 0.51\,P_{CC}$$
$$\beta_{CN}/\text{eV} = -1.98 - 0.53\,P_{CN}$$
$$\beta_{CO}/\text{eV} = -2.17 - 0.56\,P_{CO}$$

5-Amino-2,3-benzo-1,4-diazaanthraquinone (4). A solution of aniline (3.5 g) in EtOH (8.3 ml) was added dropwise to a solution of 5-amino-2,3-dichloro-1,4-naphthoquinone (3.7 g)[5)] in EtOH (160 ml) at 75 °C. After the mixture had been refluxed for 3 h, the solid was separated. The filtrate was evaporated, and the combined solids were dissolved in pyridine and filtered. Water was added to the filtrate and the resulting solid was separated. The crude product was purified by dissolution in a minimum quantity of pyridine and reprecipitating with water to give **3**; yield 48%, mp 213—216 °C (dec), Found: C, 64.61; H, 3.76; N, 10.11%. Calcd for $C_{16}H_{11}N_2O_2Cl$: C, 64.32; H, 3.69; N, 9.38%. *m/e* (rel intensity), 300 (M+2, 30), 298 (M, 86), 264 (23), and 263 (100). A solution of NaN_3 (0.7 g) in water (2.2 ml) was added dropwise to a solution of **3** (2.2 g) in DMF (17 ml) at room temperature. The mixture was stirred at 120 °C for 4 h. After cooling, the resulting solid was separated, water being added to the first filtrate to precipitate crude product. The combined crude products were dissolved in EtOH and filtered. The filtrate was evaporated, and the residue was washed with hot xylene. Recrystallization from *o*-dichlorobenzene gave **4**; yield 18%, *m/e* (rel intensity), 275 (M, 100), 247 (35), 219 (35), and 192 (7), IR: 3400 and 3290 cm^{-1} (NH_2), 1670 and 1648 cm^{-1} (CO): Found, C, 69.17; H, 3.59; N, 14.39%. Calcd for $C_{16}H_9N_3O_2$: C, 69.82; H, 3.27; N, 15.27%.

Preparation of Annelated 5-Amino-1,4-diazaanthraquinones (5—7). 1,2-Naphthoquinone (0.93 g, 5.9 mmol) was added to a suspension of 2,3,5-triamino-1,4-naphthoquinone (1.0 g, 4.9 mmol) in 10% acetic acid (50 ml) at 80 °C. The mixture was stirred at 90 °C for 2.5 h. After cooling, the solid was separated and recrystallized from xylene to give **5**. No other isomer was observed by means of TLC. The other annelated compounds **6** and **7** were similarly prepared and recrystallized from DMF. **5**: yield 86%, *m/e* 325 (M, 100), 297 (27), and 269 (27), IR (KBr): 3420 and 3300 cm^{-1} (NH_2), 1689 and 1645 cm^{-1} (CO), Found: C, 74.20; H, 3.72; N, 11.69%. Calcd for $C_{20}H_{11}N_3O_2$: C, 73.85; H, 3.38; N, 12.92%. **6**: yield 51%, *m/e* 375 (M, 100), 347 (17), 319 (15), and 318 (10), IR (KBr): 3440 and 3325 cm^{-1} (NH_2), 1678 and 1650 cm^{-1} (CO), Found: C, 76.65; H, 3.36; N, 11.08%. Calcd for $C_{24}H_{13}N_3O_2$: C, 76.80; H, 3.47; N, 11.20%. **7**: yield 56%, *m/e* 349 (M, 100), 321 (22), and 293 (17), IR (KBr): 3430 and 3300 cm^{-1} (NH_2), 1670 and 1645 cm^{-1} (CO), Found: C, 75.51; H, 3.20; N, 11.60%. Calcd for $C_{22}H_{11}N_3O_2$: C, 75.64; H, 3.15; N, 12.03%.

5-Amino-6,8-dibromo-1,4-diazaanthraquinone (8). To a suspension of **2** (0.91 g) in *o*-dichlorobenzene (46 ml) was added bromine (1.62 g) dropwise at 130 °C for 1 h. The mixture was heated at 140—145 °C for 5 h. After cooling, the solid was separated and washed with benzene, methanol, and water. The crude product was suspended in water (150 ml) and treated with aqueous sodium sulfite, and recrystallized from xylene to give **8**; yield 47%, *m/e* 385 (M+4, 52), 383 (M+2, 100), 381 (M, 52), 357 (8), 355 (16), 353 (9), 286 (23), and 284 (28), IR (KBr): 3400 and 3280 cm^{-1} (NH_2), 1680 and 1640 cm^{-1} (CO), $\lambda_{\max}$ (EtOH): 492 nm (ε, 6.6×10^3), Found: C, 37.58; H, 1.52; N, 10.93%. Calcd for $C_{12}H_5N_3O_2Br_2$: C, 37.62; H, 1.31; N, 10.97%.

5-Amino-6-bromo-8-anilino-1,4-diazaanthraquinone (9). A mixture of **8** (0.94 g), $CuCO_3$ (0.06 g), potassium acetate (1.3 g), and aniline (8.0 g) was stirred at 130—140 °C for 1 h. After being cooled to 80—90 °C, methanol (8 ml) was added to the mixture. The resulting solid was separated, washed with water and methanol, and recrystallized from benzene. The crude product was separated by column-chromatography on silica gel (developing solvent: benzene-acetone (1:2)) to give **9** and **10** in yields of 31% and ≈0.1%, respectively. Compound **9** was again recrystallized from benzene. The first filtrate was steam distilled, and the residue solution evaporated. The crude product was recrystallized from water to give **10** (yield 0.3%). **9**: *m/e* 396 (M+2, 100) 394 (M, 100) 379 (43), 377 (47), and 298 (38), Found: C, 54.87; H, 3.01; N, 12.94%. Calcd for $C_{18}H_{11}N_4O_2Br$: C, 54.70; H, 2.79; N, 14.18%, mp 254 °C (sublimed). **10**: $\lambda_{\max}$ (EtOH): 488 nm (ε, 6.8×10^3), *m/e* 305 (M+2, 100), 303 (M, 100), 277 (24), 275 (25), 249 (14), 248 (12), 247 (12), 197 (13), and 196 (20), Found: C, 47.85; H, 2.20; N, 13.12%. Calcd for $C_{12}H_6N_3O_2Br$: C, 47.38; H, 1.97; N, 13.82%.

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