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Dipole Moments of Some Diazaarenes

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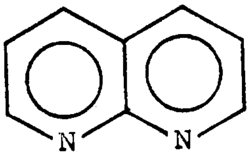
The electric dipole moments of 1,8-naphthyridine (1), 1,8-diazabiphenylene (2), and pyrido[3,2-*g*]quinoline (3) have been determined experimentally. The measured values in benzene are 4.10, 4.23, and 4.02 D, respectively. The larger value for 2 is attributed to its distorted molecular geometry.

Introduction

The dipole moments of quinoline and its derivatives are well-documented (**2**). This is not the case, however, with the naphthyridines for which only calculated values have been reported (*3*). The availability of 1,8-naphthyridine (**1**) (*4*) and the recently reported syntheses of 1,8-diazabiphenylene (**2**) (*5*) and pyrido[3,2-*g*]quinoline (**3**) (*6*) have prompted us to determine the dipole moments of this series of diazaarenes. Our principal interest was **2**, which extended current studies of strain effects on heterocyclic systems (*1*).



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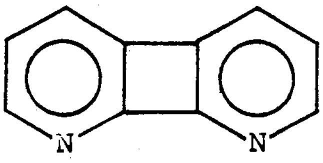

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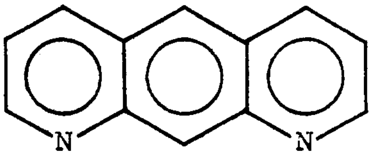

3

Results and Discussion

In Table I are presented data for pyridine, quinoline, and **1–3**. Previous reports from this laboratory have established that strained rings fused adjacent to the nitrogen atom decrease the basicity of heterocycles (*10–12*), but do not significantly affect the dipole moment (*1*). Although the data for **1–3** are broadly consistent with these relationships, the larger value for **2** prompts two observations. The dipole moments for this series do not correlate with the distance between the two nitrogen atoms. The latter parameter was calculated from the known molecular geometries derived from X-ray crystallographic analysis (*13–15*); in the case of **3** the distance was estimated from the calculated N(1)–C(8) separation for quinoline. Secondly, the value for **2** does reflect its abnormal geometry in which the distance between the aromatic rings, C(4a)–C(4b) or C(8a)–C(8b), is 1.518 Å and the N(1)–C(4) distance is 2.894 Å. Consequently, the delocalization of dipoles from one pyridine ring to the other (leading to charge separations which reduce the overall moment) is decreased, while the charge separation within one ring is increased. Such is not the case in the fully conjugated systems **1** and **3** with normal geometries, and their observed moments are smaller than that for **2**.

Table I. Data for Diazaarenes

compd	$\mu(C_6H_6)$, D	interatomic dist (calcd), Å N–N	 N(1)–C(4)	pK_a	ref
1	4.10 ± 0.08	2.307	2.802	3.39	*7*
2	4.23 ± 0.03	3.693	2.894	1.92	*8*
3	4.02 ± 0.04	4.792		(5.05)[b]	*9*
pyridine	2.22 ± 0.03[a]			5.23	*9*
quinoline	2.19 ± 0.02[a]		2.825	4.94	*9*

[a] From ref *1*. [b] Value for benzo[*g*]quinoline.

Table II. Mole Fractions, Densities, Refractive Indices, and Dielectric Constants at 25 °C in Benzene

compd	mole fracn	density, g/mL	refract index	dielec const
1	0.006 644	0.877 59	2.2500	2.441
	0.004 872	0.874 88	2.2488	2.399
	0.004 060	0.874 99	2.2482	2.378
	0.002 668	0.875 12	2.2478	2.342
	0.001 586	0.873 04	2.2470	2.316
2	0.004 751	0.876 36	2.2512	2.396
	0.003 736	0.875 55	2.2497	2.365
	0.002 646	0.876 36	2.2488	2.339
	0.001 780	0.875 85	2.2482	2.318
	0.001 145	0.875 55	2.2476	2.303
3	0.004 806	0.876 50	1.5008	2.378
	0.003 846	0.875 02	1.5005	2.368
	0.002 524	0.875 95	1.4997	2.331
	0.001 740	0.875 38	1.4994	2.303
	0.000 589	0.874 00	1.4988	2.282

Experimental Section

Samples of **1–3**, provided by the principal investigators of the original syntheses (*4–6*), were vacuum sublimed immediately prior to use. Density, refractive index, and capacitance measurements were made at 25.00 ± 0.02 °C in benzene (spectroquality grade dried over sodium). Capacitances were determined on a General Radio 1-MHz bridge, Type 1610-AH, with a two-electrode cell of nominal 20 pF air capacitance; the cell was calibrated with liquids of known dielectric constant. Density measurements were made in calibrated 10-mL volumetric flasks. Refractive indices were measured at the sodium D line on a Bausch and Lomb, Abbe 3L refractometer. Duplicate experimental dipole moments were determined by the procedure of Smith (*16*), using the method of least squares for calculation of the slopes and intercepts. Sample experimental

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Table III. Linear Regression Data and Dipole Moments at 25 °C in Benzene

compd	E_1	a	n_1^2	c	ρ	μ
1	2.2767	24.8345	2.2461	0.5695	0.8721	4.17[a]
	2.2927	23.2203	2.2469	0.5464	0.8727	4.02
2	2.2726	25.5534	2.2464	0.9553	0.8756	4.20[a]
	2.2692	26.1664	2.2464	0.8857	0.8737	4.26
3	2.2666	24.3511	2.2456	1.4573	0.8742	4.06[a]
	2.2627	23.6998	2.2450	1.6300	0.8737	3.98

[a] Determined from data in Table II.

data are given in Table II and the calculated parameters are given in Table III.

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Registry No. 1, 254-60-4; 2, 259-84-7; 3, 260-67-3; benzene, 71-43-2.

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Diffusivities of CO_2 and N_2O in Aqueous Alcohol Solutions

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The molecular diffusivities of CO_2 and N_2O were measured in aqueous solutions of glycerol and 1,5-pentanediol at 25 °C and 1 atm by the laminar-jet technique. Experimental results show that an equation of the form $(D/D_w)_{CO_2} = (D/D_w)_{N_2O}$ can also be applied to the gas–aqueous alcohol solutions studied in this work.

Introduction

Removal of gases from effluents is often encountered in industrial operations and is usually carried out by gas–liquid contacting. The design of gas–liquid contactors requires a knowledge of solubility and diffusivity data of the gas into liquid solution. There are correlations for the estimation of diffusivities of gases into nonreacting liquids, such as the Wilke–Chang (*1*) and the Akgerman–Gainer (*2*) equations, besides several empirical correlations (*3–5*). However, in the case of reacting gases the estimation or experimental measurement of solubilities is not possible because of the difficulty in modeling the simultaneous processes of mass-transfer and chemical reaction.

It has been suggested that the solubility and diffusivity of CO_2 in reacting solutions can be estimated by using the "N_2O analogy" (*6*). In view of the similarities of the CO_2 and N_2O molecules, it has been proven (*7–9*) for aqueous solutions of amines that solubilities and diffusivities of CO_2 and N_2O are related as follows:

$$\log (\alpha/\alpha_W)_{CO_2} = \log (\alpha/\alpha_W)_{N_2O} \qquad (1)$$

$$(D/D_W)_{CO_2} = (D/D_W)_{N_2O} \qquad (2)$$

The N_2O analogy for solubilities has been shown to be valid for alcohol solutions of analogous structures with some previously tested amines such as MEA and DEA (*10*). In the present work diffusivities of N_2O and CO_2 in glycerol and 1,5-pentanediol solutions were measured at 25 °C and it has been shown that a modified form of eq 2 also holds for alcohol solutions.

Experimental Section

Aqueous solutions of alcohols were prepared from distilled water and reagent grade alcohols, glycerol, and 1,5-pentanediol. All solutions used in absorption experiments were previously degassed by stirring under vacuum. The gases N_2O and CO_2 were supplied from commercial cylinders with purities of 99.5% and 99.998%, respectively.

Diffusivities were measured by the laminar-jet technique. The experimental setup was similar to the apparatus described by Scriven and Pigford (*11*). The laminar-jet chamber consists of a 36 cm long, 4 cm i.d. glass vessel with a hole in the bottom that allows draining of any liquid overflow. It is placed inside a constant temperature air bath, provided with a 500-W heating element, a small fan, and an electronic temperature controller. The solution is preheated to the desired temperature and fed to the capillary nozzle through a glass tube (30 cm long, 0.8 cm i.d.) with a bell-shaped entrance to the capillary of 0.14 cm i.d., similar to that used by Raimondi and Toor (*12*). The liquid from the nozzle flows to a capillary receiver (2 cm long, 0.18 cm i.d.) connected to a glass tube (30 cm long, 0.8 cm i.d.). The downstream end was connected to a constant-level overflow. The jet length was measured with a vernier caliper with an accuracy of ±0.005 cm. The gas was preheated to the experimental temperature and saturated with the solution. The liquid flow rate was obtained by measuring the volume of effluent liquid from the system as a function of time.

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