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STRAINED HETEROCYCLIC SYSTEMS. 13.[1]
DIPOLE MOMENTS OF CYCLOALKA[b]QUINOLINES

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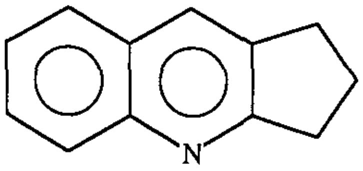
Abstract - The electric dipole moments of 2,3-dimethylnaphthalene (1), 2,3-dimethylquinoline (2), 2,3-dihydro-1H-cyclopenta[b]quinoline (3), and 1,2-dihydrocyclobuta[b]quinoline (4) have been determined experimentally. The measured values in benzene are 0.72, 2.04, 2.13, and 2.17 D, respectively. Ring strain effects thus do not significantly alter dipole moments.

Compounds such as pyridine and quinoline permit useful correlations between structures and physical properties, with substituent effects usually interpreted in terms of inductive and resonance contributions. Dipole moments and basicities are among the properties most often studied with these aza-aromatic systems, and the pair of nonbonded electrons of the nitrogen atom constitutes the primary center for both parameters. Reports by us[2-4] and others[5-7] have established that fusion of a strained ring adjacent to the hetero atom markedly decreases the basicity of such systems. This phenomenon is best accommodated by the orbital rehybridization hypothesis of Streitwieser, et al.[8] Since the dipole moment of pyridines and quinolines arises principally from the hybridization of the hetero atom,[9] we have undertaken the first assessment of ring strain effects on dipole moments.

For the present study we chose 2,3-dimethylnaphthalene (1), 2,3-dimethylquinoline (2), 2,3-dihydro-1H-cyclopenta[b]quinoline (3), and 1,2-dihydrocyclobuta[b]quinoline (4).[10]



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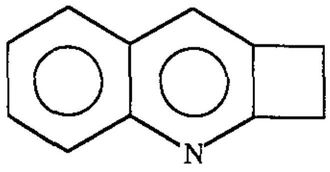

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Density, refractive index, and capacitance measurements were made at 25.00 ± 0.02 °C in benzene.[12] Duplicate experimental dipole moments were determined by the dielectric constant, density, and refractive index procedure of Smith,[13] using the method of least squares for calculation of the slopes and intercepts. Sample experimental data are given in Table 1 and the calculated parameters are given in Table 2.

Table 1

Mole fractions, densities, refractive indices, and dielectric constants at 25 °C in benzene

Mole fraction	Density (g/ml.)	Refractive index	Dielectric constant
2,3-Dimethylnaphthalene (1)			
0.011634	0.87584	1.5012	2.287
0.008520	0.87442	1.5005	2.285
0.004904	0.87415	1.4996	2.280
0.002352	0.87328	1.4992	2.277
0.000923	0.87286	1.4989	2.272
2,3-Dimethylquinoline (2)			
0.01979	0.8786	1.5021	2.40
0.01516	0.8810	1.5015	2.38
0.01021	0.8735	1.5004	2.34
0 00495	0.8768	1.4990	2.30
0.00349	0.8726	1.4990	2.30
2,3-Dihydro-1H-cyclopenta[b]quinoline (3)			
0.01720	0.8798	1.5035	2.39
0.01242	0.8809	1.5023	2.36
0.006645	0.8721	1.5006	2.32
0.007034	0.8774	1.5006	2.32
0.002824	0.8749	1.4995	2.29
1,2-Dihydrocyclobuta[b]quinoline (4)			
0.01859	0.8796	1.5034	2.40
0.01468	0.8803	1.5024	2.38
0.01079	0.8752	1.5014	2.35
0.007458	0.8781	1.5004	2.32
0.003479	0.8718	1.4994	2.29

Table 2

Linear regression data and dipole moments at 25 °C in benzene

E_1	a	n_1^2	c	p	μ
2,3-Dimethylnaphthalene (1)					
2.2722	1.3750	2.2460	0.6462	0.8727	0.719[a]
2.2694	1.6269	2.2458	0.6709	0.8730	0.825
2,3-Dimethylquinoline (2)					
2.2731	6.6122	2.2446	0.6150	0.8727	2.07[a]
2.2692	6.3105	2.2462	0.6498	0.8729	2.02
2,3-Dihydro-1<u>H</u>-cyclopenta[<u>b</u>]quinoline (3)					
2.2718	6.9559	2.2461	0.8469	0.8726	2.09[a]
2.2654	7.4896	2.2459	0.9059	0.8727	2.18
1,2-Dihydrocyclobuta[<u>b</u>]quinoline (4)					
2.2659	7.4652	2.2454	0.8014	0.8717	2.19[a]
2.2717	7.3763	2.2446	0.9187	0.8744	2.15

[a] Determined from data in Table 1

The experimental diploe moments of compounds **2**-**4** are compared to those of related carbocyclic and heterocyclic systems in Table 3. These data establish that fused strained rings exert no profound effects on the dipole moments of such frameworks as **3** and **4**. The influence of alkyl substituents, consistent over the range of compounds summarized here, conforms to previous interpretations.[22] Given the pattern of values for pyridine, 2-methylpyridine, and 2,3-dimethylpyridine as well as that for quinoline and 2-methylquinoline, the magnitude of the dipole moment for **2** is lower than anticipated. Its direction, however, is consistent with expectations. Using our value for **1**, the mean value for quinoline (Table 3), and the convention adopted for reporting the latter's direction,[34] we estimate by vector analysis a value of 2.28 D for **2** with Ø = +164°.

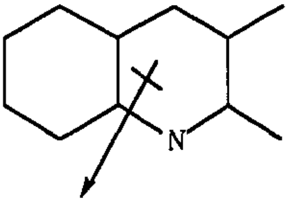

Table 3

Experimental dipole moments at 25 °C

Compound	Solvent[a]	μ D	Reference
toluene	B	0.33, 0.36	14, 15
o-xylene	C	0.54	16
indan	C	0.55	16
benzocyclobutene	C	0.40	16
2-methylnaphthalene	B	0.44	17
	C	0.45	16
2,3-dimethylnaphthalene (1)	[b]	0.69	18
	B	0.72	[c]
pyridine	B	2.22 ± .03	19-25
	C	2.21 ± .04	25-28
2-methylpyridine	B	1.96, 1.97	29, 21
	C	1.96	28
3-methylpyridine	B	2.40, 2.41	21, 30
	C	2.32	28
2,3-dimethylpyridine	B	2.20	21
quinoline	B	2.19 ± .02	17, 20, 31-33
2-methylquinoline	B	1.94, 1.95	17, 29
3-methylquinoline	B	2.29	17
2,3-dimethylquinoline (2)	B	2.04 ± .03	[c]
2,3-dihydro-1H-cyclopenta[b]quinoline (3)	B	2.13 ± .04	[c]
1,2-dihydro-cyclobuta[b]quinoline (4)	B	2.17 ± .02	[c]

[a] Solvents: B = benzene, C = cyclohexane
[b] Temperature and solvent unspecified
[c] Present work

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