KERR CONSTANTS OF SOME NITROGEN-CONTAINING HETEROCYCLES

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The molecular Kerr constants $[_\infty(mK_2)]$ were measured for pyridine, 2- and 4-methylpyridines, quinoline, and acridine in dioxane. The molecular moments of pyridine and 4-methylpyridine are directed along the axis of maximum polarizability. The $\Delta B = B_{12} - B_1$ values for dilute solutions of azaaromatic compounds in dioxane are proportional to T^{-2}.

The double refraction effect (the Kerr effect) [1] in recent years has found application in the study of various types of molecular complexes [2-7]. In connection with measurements of the Kerr effect in dioxane for complexes of π acids with bases of various types [8], it was necessary to study this effect for the bases themselves in dioxane solutions. This was done in [5, 9-11] for aliphatic and aromatic amines; in the case of heterocyclic nitrogenous bases, the Kerr effect in benzene solution has been studied only for pyridine [12], piperidine [9], and piperazine and its derivatives [10].

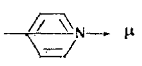
We have measured the concentration and temperature dependence of the Kerr constant (B_{12}) for solutions in dioxane of the following heterocyclic compounds: pyridine, 2- and 4-methylpyridines, quinoline, and acridine.* The apparatus for measuring the B constant is described in [13]. The necessary values of the dielectric permeability (ε_{12}), density (ρ_{12}), and refractive index (n_{12}) of the solutions as a function of concentration (c in weight percent) that were necessary for calculating the molecular Kerr constant $[_\infty(mK_2)]$ were measured, respectively, with a Dipol' DP-4 apparatus, by the method of hydrostatic weighing, and with an IRF-23 refractometer (at 546 nm). The $_\infty(mK_2)$ values of the compounds, calculated from the formula proposed in [14], are presented in Table 1, while the results of measurements of the B_{12} values of solutions of some of them at various temperatures (T) from 25 to 65° are presented in Table 2.

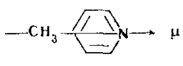
The $\Delta B = B_{12} - B_1$ value (B_1 is the Kerr constant of pure dioxane) for all of the studied compounds increases linearly with increasing c.

The $_\infty(mK_2)$ values of most of the compounds examined increases almost linearly with increasing μ^2 (μ is the dipole moment of the molecules in dioxane [15]). The structure of the molecules of these compounds is apparently such that the dipole term

$$\theta_2=\frac{1}{45k^2T^2}\mu^2(2b_3-b_2-b_1) \qquad (1)$$

plays the major role in the $_\infty(mK_2)$ value when the dipole moment lies on the axis of maximum polarizability or is close to it. The $_\infty(mK_2)_C$ values, calculated from the assumption of a planar structure for the indicated molecules and assuming that the axis of maximum polarizability passes through the oppositely situated H–C bond and ring nitrogen, viz.,





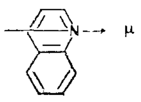


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TABLE 1. Molecular Kerr Constants of Heterocyclic Compounds

Compound	a*	b*	Concn. range c, wt.%	$(mK_2)_e \times 10^{12}$	$b_1 \cdot 10^{23}$	$b_2 \cdot 10^{23}$	$b_3 \cdot 10^{23}$	$\theta_1 \cdot 10^{35}$	$\theta_2 \cdot 10^{35}$	$(mK_2)_c \times 10^{12}$	$\frac{(mK_2)\text{calc.}}{(mK_2)\text{exp.}}$
Pyridine	0,069	0,104	0,153—1,840	125	1,072	1,043	0,645	4,08	23,05	114	0,92
2-Methylpyridine	0,070	0,040	0,157—2,990	61	1,249	1,252	0,800	2,2	23,3	107	1,75
4-Methylpyridine	0,070	0,152	2,180—6,160	231	1,229	1,198	0,800	2,4	51,4	226	0,98
Quinoline	0,075	0,062	0,168—0,768	1178	1,712	1,886	1,066	6,35	28,4	142,9	1,21
Acridine	0,074	0,03	0,094—1,156	78,7	2,296	2,677	1,469	13	37,5	210	2,7

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*a is an independent term, and b is the slope in the equation $B_{12} = a + bc$.

TABLE 2. Temperature Dependence of ΔB for Solutions of Heterocyclic Compounds in Dioxane

t, °C	Pyridine (c 1.55%)		2-Methylpyridine (c 2.99%)		4-Methylpyridine (c 2.18%)	
	$\Delta B_e \cdot 10^7$	$\Delta B_c \cdot 10^7$	$\Delta B_e \cdot 10^7$	$\Delta B_c \cdot 10^7$	$\Delta B_e \cdot 10^7$	$\Delta B_c \cdot 10^7$
25	0,084	0,084	0,124	0,124	0,304	0,304
35	0,083	0,078	0,123	0,116	0,282	0,285
45	0,082	0,075	0,119	0,109	0,253	0,277
55	0,076	0,069	0,117	0,102	0,241	0,251
65	0,070	0,065	0,094	0,096	0,210	0,236

are presented in Table 1.

The calculation was made from known dependences [2] for θ_1 and θ_2 values from the formula

$$({}_mK)=\frac{2\pi N_0}{9}(\theta_1+\theta_2). \tag{2}$$

The b_i values [the axes of the polarizability tensor adopted for the calculation of (mK_2) of these molecules] are presented in Table 1. As expected, the $(mK_2)_c$ values obtained (Table 1) are in good agreement with the experimental $(mK)_e$ values only in the case of pyridine and 4-methylpyridine, and are appreciably worse for quinoline and, particularly, 2-methylpyridine and acridine, for which the moment is sloped somewhat to the axis of maximum polarizability.

Since the dipole term (θ_2) makes the chief contribution to the molecular Kerr constant for the aza-aromatic compounds that we studied, it can be expected that the $\Delta B = B_{12} - B_1$ value for solutions of low concentrations will, for a sufficiently satisfactory approximation, be proportional to T^{-2}. In fact, the ΔB values observed at various temperatures in the case of solutions of pyridine and 2- and 4-methylpyridines agree satisfactorily with the values calculated from the expression

$$\Delta B_{T_2}=\Delta B_{T_1}\left(\frac{T_1}{T_2}\right)^2. \tag{3}$$

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