Experimental and Quantum Mechanical Investigation on Dipole Moments of Some Oxazole Derivatives in Lowest Singlet Excited State *

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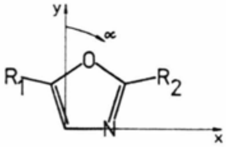
Electric dipole moments in the ground and lowest singlet excited state of four axazole derivatives were calculated theoretically using the PPPCI method, and determined experimentally on the basis of solvatochromic shifts in the electronic spectra.

Luminescent properties of substances belonging to a series of oxazoles (Fig. 1) have been the object of numerous theoretical and experimental investigations [1–4]. The reason for the particular interest in these compounds is their very high fluorescence quantum yield (close to 100%), which enables their extensive employment in scintillation and laser techniques. Knowledge of the electronic density distribution in the lowest singlet excited state permits to explain and, in many cases, predict the fluorescent properties of molecules.



Quantum mechanical calculations of the $S_0 \rightarrow S_1$ transition energies and the dipole moments were carried out using the PPPCI method, assuming standard geometry for the four oxazole derivatives. For α-NPO, the calculations predict the highest increase in the dipole moment on excitation to the S_1 state. Results of the calculations and experimental data are summarized in Table 1.

The dipole moment was determined experimentally basing on the solvatochromic shifts in the absorption and fluorescence spectra, similarly as in [5, 6]. The Onsager radius, a, was also determined experimentally by the Gorodyiskii and Bakhshiev method [7]. Surprisingly small Onsager radii (as related to the geometrical dimensions) were found for compounds I–III, which is due to the change in the electronic charge distribution occurring in the oxazole ring only. For the substances investigated, groups R_1 and R_2 play the role of additional solvent molecules. Therefore, in similar cases, one should not use the molecular geometry to estimate the onsager radius. For POPOP, with two oxazole rings, the Onsager radius obtained was markedly greater than that with BBO, although the geometrical dimensions of both molecules are comparable.

The 0-0 transition energies measured are in each case higher by about 1500 cm^{-1} than those calculated. The experimental results for the dipole moments in the excited state indicate, however, that the highest increase in $\Delta\mu$ occurs for α-NPO. Satisfactory agreement between the directions of the dipole moments in the excited state, calculated and determined experimentally, was also obtained.

Table 1.

No.	Substance	R_1	R_2	Theoretical results					Experimental data			
				$\Delta E(S_0 \rightarrow S_1)$ (kK)	μ_g* (D)	α_g	μ_e (D)	α_e	$\tilde{\nu}_{0-0}$** (kK)	a (Å)	μ_e (D)	α_e
I	PPO	phenyl	phenyl	27.92	1.24	351°	1.84	97°	29.459	3.8	1.6	51°
II	α-NPO	phenyl	1-naphtyl	25.25	1.14	353°	6.69	83°	26.672	4.0	3.6	25°
III	BBO	biphenyl	biphenyl	25.32	1.24	348°	0.64	69°	25.745	4.3	1.5	57°
IV	POPOP	phenyl	PPO	24.38	2.22	342°	1.97	342°	25.950	6.8	3.3	19°

* 1 Debye = 3.33×10^{-30} A · s · m. ** From Ref. [8].

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