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1958

SovietRxiv

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PHYSICAL CHEMISTRY

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THE INFLUENCE OF THE STRUCTURE OF ORGANIC MOLECULES ON THE PROBABILITY OF TRANSITION TO A METASTABLE STATE

(Presented by Academician A. N. Terenin, March 31, 1958)

In works ([1–3]) it was shown that at −196°, for substances whose fluorescence spectra in different media occupy different positions, the ratios of the quantum yields of phosphorescence and fluorescence, which we shall denote by δ, are determined mainly by the frequency of the maximum of the fluorescence spectrum $\nu_{\text{fl}}^{\max}$. In the present communication we consider the influence of certain structural features on the value of δ, and consequently on the probability of transition to a metastable state. On the basis of works ([4],[5]) it may be concluded that, in a series of phthalimide derivatives, on passing from one substance to another the capacity for phosphorescence decreases, in the general case, with a shift of the fluorescence spectrum toward lower frequencies.

The fact that δ is connected not only with the position of the fluorescence spectrum, but also with the structural features of the fluorescing molecules, can be demonstrated best by comparing δ for 3- and 4-acetylamino-*N*-methylphthalimides and 3- and 4-hydroxy-*N*-methylphthalimides (Fig. 1). Thus, at $\nu_{\text{fl}}^{\max} = 24000$ cm^{-1}, for 3-acetylamino-*N*-methylphthalimide, δ is 20 times greater than for its isomer at the same position of the fluorescence spectrum. At the same time, for 3-hydroxy-*N*-methylphthalimide, δ is approximately 10 times greater than for 4-hydroxy-*N*-methylphthalimide.

In works ([1–3]) it was shown that δ depends very little on the chemical nature of the medium and its state, but is determined mainly by the position of the fluorescence band. It is therefore clear that the relative capacity for phosphorescence of different substances must be compared not in one and the same solvent, but at one and the same $\nu_{\text{fl}}^{\max}$, even if, for the substances being compared, it is attained in different solvents.

Let us consider, in several examples, the influence of introducing a methyl group into the molecule on the value of δ. In Fig. 1 are presented the dependences of δ on $\nu_{\text{fl}}^{\max}$ for 3-acetylamino- and 3-methylacetylamino-*N*-methylphthalimides (curves *III* and *V*, respectively). The curve for the methylated derivative is shifted relative to the curve for 3-acetylamino-*N*-methylphthalimide toward lower frequencies. At the same $\nu_{\text{fl}}^{\text{max}}$, the values of δ for the first substance are considerably higher.

The influence of introducing a methyl group into the molecule on δ is seen most strikingly in the example of the 3,6-derivatives of *N*-methylphthalimide (Fig. 2). For 3-acetylamino-6-amino-*N*-methylphthalimide (*I*), δ at $\nu_{\text{fl}}^{\text{max}} = 20500$ cm^{-1} does not exceed 0.02, and at lower $\nu_{\text{fl}}^{\text{max}}$ phosphorescence is completely absent. On the same figure is plotted the curve of the dependence of δ on $\nu_{\text{fl}}^{\text{max}}$ for 3-acetylamino-6-dimethylamino-*N*-methylphthalimide (*II*). At $\nu_{\text{fl}}^{\text{max}}$ values lower than in the preceding case, this substance exhibits, although very slight, nevertheless distinct phosphorescence with $\delta = 0.02$ at $\nu_{\text{fl}}^{\text{max}} = 19000$ cm^{-1}. (In isopropyl formate and chloroform, $\nu_{\text{fl}}^{\text{max}}$ is located approximately at ···

25,500 cm^{-1}, and the corresponding $\hat{\delta}$ has a value of ~ 3; the exact position of the fluorescence spectrum is difficult to determine because of the large value of $\hat{\delta}$.) Curve *III* shows the dependence of $\hat{\delta}$ on $\nu_{\text{fl}}^{\text{max}}$ for a phthalimide derivative containing as many as 3 methyl groups—3-methylacetylamino-6-dimethylamino-*N*-methylphthalimide. This curve is shifted still further toward lower frequencies relative to curves *I* and *II*. The values of $\hat{\delta}$ for 3-methylacetylamino-6-dimethylamino-*N*-methylphthalimide reach 0.15. Figure 2 also schematically plots the dependences of $\hat{\delta}$ on $\nu_{\text{fl}}^{\text{max}}$ in various solvents for 3,6-diacetylamino- and 3-methylacetylamino-6-acetylamino-*N*-methylphthalimides. At equal $\nu_{\text{fl}}^{\text{max}}$, the value of $\hat{\delta}$ for the second compound is higher than for the first. Thus, at $\nu_{\text{fl}}^{\text{max}} = 22000$ cm^{-1}, for 3,6-diacetylamino-*N*-methylphthalimide $\hat{\delta} \simeq 0.15$, while for 3-methylacetylamino-6-acetylamino-*N*-methylphthalimide $\hat{\delta} = 0.4$. The same picture is also observed for 3- and 4-methoxy-*N*-methylphthalimides in comparison with the corresponding 3- and 4-hydroxy derivatives. In the case of 3-amino-6-nitro- and 3-dimethylamino-6-nitro-*N*-methylphthalimides (Fig. 3), the curve of the dependence of $\hat{\delta}$ on $\nu_{\text{fl}}^{\text{max}}$ for the second substance (*I*) is shifted to the long-wavelength side relative to the curve for the first compound *II*, i.e., in this case as well, at equal $\nu_{\text{fl}}^{\text{max}}$, the values of $\hat{\delta}$ are larger for the methylated compound.

Fig. 1. Dependence of $\hat{\delta}$ on $\nu_{\text{fl}}^{\text{max}}$ for derivatives of *N*-methylphthalimide: 3-hydroxy (*I*), 4-hydroxy (*II*), 3-acetylamino (*III*), 4-acetylamino (*IV*), 3-methylacetylamino (*V*). Numbering of solvents (for Figs. 1-5): 1 —crystalline state, 2 —water, 3 —benzene, 4 —carbon tetrachloride, 5 —menthol, 6 —α-chloronaphthalene, 7 —acetic acid, 8 —anisole, 9 —nitromethane, 10 —dioxane, 11 —triethylamine, 12 —formamide, 13 —propyl acetate, 14 —ethyl acetate, 15 —methyl orthoformate, 16 —acetone, 17 —tert-butyl alcohol, 18 —acetic anhydride, 19 —methyl alcohol, 20 —glycerol, 21 —chloroform, 22 —ethyl alcohol, 23 —diisopropyl ether, 24 —diisobutyl ether, 25 —diisoamyl ether, 26 —toluene, 27 —isooctane, 28 —pseudocumene, 29 —meta-xylene, 30 —pyridine, 31 —butyl alcohol, 32 —*n*-hexane, 33 —ortho-xylene, 34 —isobutyl alcohol, 35 —isopropyl alcohol, 36 —glue No. 235, 37 —diethyl ether, 38 —*n*-octane, 39 —propyl formate, 40 —chlorobenzene, 41 —isoamyl formate.

Fig. 2 and Fig. 3 graphs

Figure 1: Fig. 2 and Fig. 3 graphs

Fig. 4 graphs

Figure 2: Fig. 4 graphs

Thus, the introduction of methyls into the substituent group in various compounds invariably leads to an increase in $\hat{\delta}$, although almost always at the same time it shifts the fluorescence spectrum toward lower frequencies. However, on the other hand, the introduction of a methyl group in place of the imide hydrogen does not lead to a change in the dependence of $\hat{\delta}$ on $\nu_{\text{fl}}^{\max}$. Thus, $\hat{\delta}$ in ethyl alcohol and carbon tetrachloride for 3-hydroxyphthalimide falls on the same curve as for 3-hydroxy-*N*-methylphthalimide. The values of $\hat{\delta}$ for 3-acetylaminophthalimide fall on the curve $\hat{\delta}(\nu_{\text{fl}}^{\max})$ for 3-acetylamino-*N*-methylphthalimide.

Using 3-diphenylamino-*N*-methylphthalimide, phenylanthranilic acid, and phenyl-β-naphthylamine as examples, one can verify that the introduction of a phenyl into the molecule of a substance also increases $\hat{\delta}$. Comparing 3-diphenyl-

amino-N-methylphthalimide (Fig. 2, *IV*) and 3-amino-N-methylphthalimide (Fig. 3, *IV*) it can be seen that, although for 3-amino-N-methylphthalimide in ethyl alcohol, chloroform, toluene, and a number of other solvents $\nu_{\text{fl}}^{\max}$ has a larger value—

Fig. 2. Dependence of δ on $\nu_{\text{fl}}^{\max}$ for derivatives of N-methylphthalimide: 3-acetylamino-6-amino-(*I*); 3-acetylamino-6-dimethylamino-(*II*); 3-methylacetylamino-6-dimethylamino-(*III*); 3-diphenylamino-(*IV*); 3,6-diacetylamino-(*V*); 3-methylacetylamino-6-acetylamino-(*VI*).

Fig. 3. Dependence of δ on $\nu_{\text{fl}}^{\max}$ for derivatives of N-methylphthalimide: 3-dimethylamino-6-nitro-(*I*), 3-amino-6-nitro-(*II*), 3-dimethylamino-(*III*), 3-amino-(*IV*).

—(21800 cm^{-1}) than for 3-diphenylamino-N-methylphthalimide in ethyl alcohol and isopropyl formate ($\nu_{\text{fl}}^{\max} = 18600$ cm^{-1}), nevertheless in 3-amino-N-methylphthalimide phosphorescence is completely absent, whereas in 3-diphenylamino-N-methylphthalimide, in the indicated media, phosphorescence with $\delta = 0.13$–0.16 is observed.

For phenyl-β-naphthylamine (Fig. 4, *III*) $\delta = 0.4$ occurs at $\nu_{\text{fl}}^{\max} = 24600$ cm^{-1}, whereas the same value of δ for β-naphthylamine is observed only at $\nu_{\text{fl}}^{\max} = 26000$ cm^{-1} (Fig. 4, *IV*). It is also evident from Fig. 4 that the curve $\delta(\nu_{\text{fl}}^{\max})$ for phenylanthranilic acid is shifted, relative to the analogous curve for anthranilic acid (*II*), to the left along the frequency axis.

Fig. 4. Dependence of δ on $\nu_{\text{fl}}^{\max}$ for phenylanthranilic acid (*I*), anthranilic acid (*II*), phenyl-β-naphthylamine (*III*) and β-naphthylamine (*IV*).

In contrast to methyl, which, when introduced in place of imino hydrogen, does not change δ, phenyl in this position sharply increases δ. 4-Acetylamino-N-phenylphthalimide in ethyl alcohol at $\nu_{\text{fl}}^{\text{max}} = 21000$ cm^{-1} has δ equal to 1.2, whereas for 4-acetylamino-N-methylphthalimide, at considerably larger $\nu_{\text{fl}}^{\text{max}}$, the value of δ does not exceed 0.15.

Comparing the results of determining δ for 3-amino- and 3-dimethylamino-N-methylphthalimides with those for 3-amino-6-nitro- and 3-dimethylamino-6-nitro-N-methylphthalimides (Fig. 3), one may be convinced that the nitro group also promotes the transition of molecules into the metastable state. Indeed, for 3-amino-N-methylphthalimide (IV) in ethyl alcohol $\nu_{\text{fl}}^{\text{max}} = 21800$ cm^{-1}

and phosphorescence is absent, whereas for 3-amino-6-nitro-N-methylphthalimide (II) in alcohols $\nu_{\text{fl}}^{\text{max}} = 20800$ cm^{-1}, and δ reaches values of the order of 2. Likewise, for 3-dimethylamino-N-methylphthalimide (III) in ethyl alcohol, at $\nu_{\text{fl}}^{\text{max}} = 19500$ cm^{-1}, phosphorescence is absent, whereas for the compound differing from it by the presence of a nitro group (I), at the same $\nu_{\text{fl}}^{\text{max}}$, $\delta \simeq 0.2$.

Thus, it has been shown that certain changes in the structure of luminescent molecules lead to an increase in the probability of transition to the metastable state. The considerable commonality in the action of structural factors should be especially noted.

Methylation in a substituent leads to an increase in δ, irrespective of whether an amino or a hydroxy group is methylated, and moreover in very different substances. Phenylation likewise leads to an increase in δ in a variety of organic compounds.

Worthy of attention is the fact that sometimes the position of the substituent plays a greater role than its character. For example, in 3-acetylamino- and 3-hydroxy-N-methylphthalimides, at the corresponding $\nu_{\text{fl}}^{\text{max}}$, larger δ values are observed than, respectively, in 4-acetylamino- and 4-hydroxy-N-methylphthalimides.

Received18 III 1958

CITED LITERATURE

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