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## Abstract

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# THE INFLUENCE OF SUBSTITUENTS SEPARATED FROM THE BENZENE RING BY AN ALIPHATIC CHAIN ON THE OPTICAL PROPERTIES OF SUBSTITUTED BENZENES

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The question of the intramolecular transmission of the influence of a functional group through a saturated aliphatic chain to an aromatic system in the excited state is important for understanding the chemical behavior of excited molecules of this type, which was previously studied in our laboratory ($^1$), as well as in the work of other authors ($^2$).

To clarify this question, in the present work we investigated the electronic absorption spectra and fluorescence quantum yields of molecules of the type $\mathrm{Ph}-(\mathrm{CH}_2)_n-X$, where Ph is phenyl, $X$ is a substituent, and $n = 1 \div 3$. Solutions of the investigated substances in cyclohexane at concentrations of $5 \cdot 10^{-2}$-$5 \cdot 10^{-3}$ mole/liter were used. Fluorescence was induced by light with $\lambda = 253.6$ m$\mu$. The fluorescence detector was an FEU-38 photomultiplier. The quantum yields of solutions carefully freed from air in vacuum were measured relative to a standard solution of toluene (quantum yield 0.23, ($^3$)). The measurement data are given in Table 1.

**1. Absorption spectra.** In the ultraviolet spectra of toluene and its substituted derivatives two characteristic absorption bands are observed, with maxima in the regions of 200 m$\mu$ ($p$-band) and 260 m$\mu$ ($\alpha$-band). The data of Table 1 show that, upon introduction of a substituent into the methyl group of toluene, the $p$-band is shifted into the long-wavelength region by 15–20 m$\mu$, while the $\alpha$-band is shifted into the short-wavelength region by $\sim 5$ m$\mu$. Lengthening of the methylene chain reduces the influence of the substituent, and the shifts of the $p$-band and $\alpha$-band approach their values for toluene. It is interesting that the position of the maximum of the $p$-band for phenylacetic acid (225 m$\mu$) and benzylamine (225 m$\mu$) is close to the position of the corresponding maxima for benzoic acid (230 m$\mu$, ($^4$)) and aniline (230 m$\mu$, ($^5$)). The oscillator strength also decreases upon introduction of a substituent into the methyl group of toluene.

To explain the observed change in the electronic spectra it is necessary to consider how introduction of a substituent affects the electronic structure of the benzene ring.

This consideration was carried out in ($^6$) for alternant hydrocarbons by solving the Hartree–Fock–Roothaan equations. Expressions obtained for the energies of the ground and excited states through the coefficients of MO expansion in AOs (in the LCAO MO approximation) are used in ($^7$) to explain the influence of substituents on the position and intensity of electronic spectra. In this work, the influence of a substituent is considered as a small perturbation, which makes it possible to represent the shift of the $\alpha$-band of a substituted benzene molecule in the form of the equation

$$\Delta E_{0\alpha} = nA + I_{0\alpha}\delta^2, \tag{1}$$

where $n$ is the number of substituents, $A$ is a constant taking into account the conjugation effect of the substituent and independent of the relative position of the substituents, $I_{0\alpha}$ is a coefficient depending only on the relative positions of the substituents and the energies and wave functions of the electronic states of benzene and independent of the type of substituent. $I_{0\alpha}$ is expressed through the coefficients of MO expansion in AOs. $\delta^2$ is a substituent parameter characterizing its inductive influence.

Table 1

| No. | Compound | $\lambda_p$(max), mμ | $\lambda_\alpha$(max), mμ | $(-\Delta E_{0\alpha})_{\text{obs}}$, eV | $f_{0\alpha} \cdot 10^{-3}$ | $\eta$ | $q_X/q_T$ |
|---|---|---|---|---|---|---|---|
| 1 | $PhCH_2OH$ | $< 215$ | 258 | 0.065 | 1.8±0.1 | 0.074 ± 5% | 1.25 ± 0.05 |
| 2 | $PhCH_2CH_2OH$ | $< 215$ | 259 | 0.075 | 2.3 | 0.094 | 1.25 |
| 3 | $PhCH_2CH_2CH_2OH$ | $< 215$ | 261 | 0.115 | 4.4 | 0.160 | 1.25 |
| 4 | $PhCH_2Cl$ | 227 | 260 | 0.090 | 2.6 | 0.009 | 15.6 |
| 5 | $PhCH_2COOH$ | 225 | 258 | 0.065 | 1.8 | 0.060 | 1.60 |
| 6 | $PhCH_2CH_2COOH$ | 220 | 259 | 0.075 | 2.5 | 0.125 | 0.95 |
| 7 | $PhCH_2CH_2CH_2COOH$ | 220 | 259 | 0.075 | 2.2 | 0.172 | 0.55 |
| 8 | $PhCH_2CH_2CH(COOH)_2$ | 220 | 259 | 0.075 | 2.6 | 0.126 | 1.00 |
| 9 | $PhCH_2CH_2COOC_2H_5$ | 220 | 259 | 0.075 | 2.9 | 0.090 | 1.60 |
| 10 | $PhCH_2NH_2$ | 225 | 259 | 0.075 | 2.4 | 0.041 | 3.00 |
| 11 | $PhCH_2CN$ | $< 215$ | 257 | 0.050 | 1.5 | 0.094 | 0.80 |
| 12 | $PhCH_3$ | $< 215$ | 262 | 0.145 | 5.3 | 0.23 | 1.00 |

* The oscillator-strength values were determined relative to toluene, for which the value $5.3 \cdot 10^{-3}$ was adopted (10).

These same authors, using the relation between absorption intensity and the transition moment, obtained an equation for the change in oscillator strength of the $\alpha$ band:

$$f_{0\alpha} = K \cdot (\Delta E''_{\alpha})\,(E_{0\alpha})_{\text{obs}}, \tag{2}$$

where $K$ is a constant, $\Delta E''_\alpha$ is the displacement of the level corresponding to the $\alpha$ band under the influence of a substituent of inductive character, with $\Delta E''_\alpha = I_\alpha \delta^2$, where $I_\alpha$ is the coefficient calculated for the $\alpha$ level analogously to the coefficient $I_{0\alpha}$. $(E_{0\alpha})_{\text{obs}}$ is the energy of the observed $\alpha$ transition. The constant $K$ is calculated from known data for benzene: $K = f_{0\beta}/2(E_\alpha - E_\beta)(E_\beta - E_0)$, where $f_{0\beta}$ is the oscillator strength of the $\beta$ band of benzene (0.69), $(E_\beta - E_0)$ is the transition energy corresponding to the $\beta$ band (6.74 eV), and $(E_\alpha - E_0)$ is the difference in energies of the levels corresponding to the $\alpha$ and $\beta$ bands (−2.05 eV). $K = -0.025$ eV$^{-2}$.

Since $(E_{0\alpha})_{\text{obs}}$ changes only slightly, it may be taken as constant. Then from (1) and (2) one may obtain:

$$f_{0\alpha} = a(\Delta E_{0\alpha})_{\text{obs}} - b, \tag{3}$$

where $a = K(I_\alpha/I_{0\alpha})(E_{0\alpha})_{\text{obs}}$ eV$^{-1}$, $b = K(I_\alpha/I_{0\alpha})(E_{0\alpha})_{\text{obs}}\, nA$.

Thus, the change in the intensity of the $\alpha$ band for monosubstituted benzenes is a linear function of the displacement of the position of the maximum of this band in the case where the influence of the conjugation effect remains constant. Figure 1 shows the dependence of the oscillator strength on the displacement of the maximum of the $\alpha$ band relative to benzene for the compounds we studied, which can be expressed by the equation (the oscillator strength of benzene is taken as zero, $\lambda_\alpha(\text{max}) = 255$ mμ)

$$f_{0\alpha} = 0.04(-\Delta E_{0\alpha})_{\text{obs}} - 0.0008. \tag{4}$$

The satisfactory adherence to a linear correlation makes it possible to conclude that the change in the intensity of the $\alpha$ band for this class of compounds is associated mainly with the inductive influence of the substituent.

The constant $A$, obtained from equation (3), is equal to −0.02 eV. This value is close to the magnitude −0.04 eV, given in (8) for the methyl group and obtained from analysis of the absorption spectra of various methyl-substituted benzenes. Thus, one may consider that the conjugation effect of the methyl group with the benzene ring does not change substantially when one substituent is introduced into this group.

The ratio $I_\alpha/I_{0\alpha}$, obtained from equation (4), is equal to 0.35, if for toluene one takes $(E_{0\alpha})_{\text{obs}} = 4.74$ eV. This same ratio, calculated from the values of $I_\alpha$ and $I_{0\alpha}$ calculated theoretically in (7), is equal to 2.6. The smaller

the value $\overline{I}_\alpha/I_{0\alpha}$ obtained from experiment, in comparison with the calculated value, apparently indicates the necessity of taking into account the influence of the substituent not only on that carbon atom in the ring with which it is directly

Fig. 1

Figure 1: Fig. 1

bonded, but also on the atoms adjacent to it. Indeed, the ratio $I_\alpha/I_{0\alpha}$ for 1,2,3-substituted benzene is equal to zero, i.e., the influence of the substituent on the neighboring atoms must greatly reduce the value of this ratio.

**Fig. 1.** Dependence of the oscillator strength of the $\alpha$-band on the shift of the maximum (the numbering of the points corresponds to the table)

The shift of the $\alpha$-band into the short-wavelength region and the associated decrease in its intensity upon introduction of a substituent into the methyl group of toluene can evidently be explained by a decrease in the total inductive effect. The inductive effect of the methyl group depends on the total electronegativity of the atoms bonded to the methyl carbon atom; therefore the electronegativity of the $CH_3$ group will be greater than that of the $CH_2X$ group if the electronegativities of the hydrogen atoms and of the substituent have opposite signs with respect to the carbon [(9)]. The increase in the total electronegativity can also explain the decrease in the influence of a substituent, for example the OH group, upon lengthening of the methylene chain.

The explanation of the shift of the $p$-band presents greater difficulties than the explanation of the shift of the $\alpha$-band. This is connected with the necessity of taking into account higher-lying excited states, whose contribution could be neglected in considering the shift of the $\alpha$-band. When a substituent is introduced into benzene, the $p$-band shifts into the long-wavelength region, whereas, according to (7), with a purely inductive influence of the substituent, a shift into the short-wavelength region should occur (coefficient $I_{0p} > 0$). Allowance for hyperconjugation should have led to a shift into the short-wavelength region. Indeed, introduction of a heteroatom in place of the $\beta$-carbon atom of styrene leads to such a shift (11). Apparently, the inductive effect and the hyperconjugation effect are masked by another effect. Apparently, the shift of the band into the long-wavelength region, and in some cases the appearance of a new band with a maximum in the region of 225 m$\mu$ (phenylacetic acid, benzylamine), is associated with a transition to the so-called charge-transfer state, by which in work (8) the absorption of aniline in the region of 230 m$\mu$ is explained. From this point of view one can explain the changes in the spectrum of compounds containing the COOH substituent upon lengthening of the methylene chain. From the data of Table 1 it is seen that in this case no substantial changes are observed in the position and intensity of the $\alpha$-band, i.e., no substantial changes occur in the magnitude of the inductive influence ($\delta^2 \approx$ const). This is probably connected with the fact that the relative distance between the ring and the COOH group changes little upon lengthening of the chain up to $n = 3$, while their relative arrangement, i.e., the angles of rotation and inclination of the $2p\pi$-orbitals, apparently changes substantially. This will lead to a decrease in overlap and an increase in the energy of the charge-transfer state. In the absorption spectrum this will manifest itself in a shift of the corresponding band into the short-wavelength region, which is indeed observed for the band with $\lambda_{\max} = 225$ m$\mu$.

**2. Fluorescence.** Upon introduction of a substituent into the methyl group of toluene, the fluorescence quantum yields for most of the selected substituents, as is seen from the data of Table 1, decrease considerably.

Using the expression of the quantum yield in terms of the rate constants

photobleaching and radiationless deactivation, and also the relation between the bleaching constant and the oscillator strength, can be written as

$$\frac{q_X}{q_T} = \frac{f_X}{f_T}\frac{\eta_T}{\eta_X}\frac{1-\eta_X}{1-\eta_T}, \tag{5}$$

where $q_X$ and $q_T$ are the rate constants of radiationless deactivation for substituted and unsubstituted toluene, respectively; $f_X$ and $f_T$ are the oscillator strengths; $\eta_X$ and $\eta_T$ are the quantum yields. Expression (5) is valid if the absorption spectra lie in the same region.

Table 1 gives, for the compounds studied, the values of $q_X/q_T$, which characterize the rate of intramolecular radiationless processes. It is seen from Table 1 that introduction of a substituent into the methyl group of toluene in all cases (with the exception of the CN group) increases the rate of radiationless deactivation ($q_X/q_T > 1$), and in the following sequence: $\mathrm{Cl} > \mathrm{NH_2} > \mathrm{COOH} > \mathrm{OH} > \mathrm{H} > \mathrm{CN}$.

If the substituents are arranged in a series according to their effect on the shift of the absorption maximum in the 220 mμ region, the sequence proves to be the same. Since absorption in the 220 mμ region is apparently due to a transition to a state with charge transfer, it is possible that the approach of this level to the $\alpha$-level contributes to an increase in the rate of radiationless deactivation. As is seen from the data of Table 1, a change in the inductive effect of the substituent evidently does not affect the rate of radiationless deactivation. Thus, for the OH group, when the methylene chain is lengthened (i.e., when the parameter $\delta^2$ is increased), the value of $q_X/q_T$ remains practically constant, and the position of the maximum in the 220 mμ region also changes hardly at all. At the same time, for the COOH group, lengthening of the methylene chain leads to a decrease in the value of $q_X/q_T$ by several times, while the shift of the maximum in the 220 mμ region also decreases. The inductive effect of the COOH group upon lengthening of the methylene chain changes only slightly. This apparently confirms the supposition that the approach of the $\alpha$-level to the level corresponding to absorption in the 220 mμ region contributes to an increase in the rate of radiationless deactivation.

Thus, a study of the electronic absorption spectra of compounds of the type $\mathrm{Ph}-(\mathrm{CH_2})_n-\mathrm{X}$, where $\mathrm{X} = \mathrm{Cl}, \mathrm{OH}, \mathrm{NH_2}, \mathrm{CN}, \mathrm{COOH}, \mathrm{COOC_2H_5}$, shows that substituents act through the methylene chain on the excited state of the benzene ring. The influence of these substituents is mainly inductive in character and leads to a decrease in the inductive effect of the methyl group. The inductive effect of substituents does not affect the probability of radiationless transitions.

On the basis of the data obtained, the supposition is advanced that the charge-transfer state plays an essential role in changing the probability of radiationless transitions.

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