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Abstract

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THE INFLUENCE OF SUBSTITUENTS ON THE PROPERTIES OF MOLECULES OF MONOSUBSTITUTED BENZENES

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Monosubstituted benzenes constitute one of the most important groups of organic compounds. The mutual influence of the substituents and the benzene ring in these compounds determines to a considerable extent the specific character of their chemical and physical properties. It is manifested in the heat of formation, interatomic distances, vibrational frequencies, ultraviolet absorption spectra, magnetic susceptibility, transition probabilities in infrared and combination spectra, dipole moments, and other properties.

In this work various monosubstituted benzenes PhX were investigated, containing as substituents X alkyl groups, halogen atoms, and other groups of various types.

We shall focus our main attention on whether there is any commonality in the various indicators of the influence of substituents on the benzene ring. One such indicator is the increased intensity of the characteristic lines of the benzene ring (1000 ± 10 cm^{-1} and 1600 ± 20 cm^{-1}) in combination-scattering spectra (Raman spectra). The line ~ 1600 cm^{-1} has a small intensity in benzene and alkylbenzenes and a much greater one in derivatives containing substituents capable of more or less strong interaction with the benzene ring. The intensity of the 1600 cm^{-1} line can serve for certain orienting judgments about the polarizability in that part which depends on the nuclear coordinates of the benzene ring.

In Table 1 are compared: 1) the results of measurements of the coefficients of integral intensity of the benzene-ring line ~ 1600 cm^{-1} in combination-scattering spectra (I_{1600}); 2) the values of exaltation of molecular refraction for $\lambda = 5893$ Å (EMR_D) and for $\lambda = 4361$ Å (EMR_γ)*; 3) the position of intense absorption bands (wavelength of the maximum λ in Å); in parentheses are given the values $\varepsilon/1000$, where ε is the molar (decimal) absorption coefficient at the band maximum**; 4) anomalies in the dipole moments ($\Delta\mu$, the difference of the μ vectors of the compounds PhX and AlkX ($\mathrm{Alk} = \mathrm{Me, Et}$) in debyes, according to data for μ in benzene); 5) Hammett constants σ_n, which determine the influence of substituents on the reactivity of groups located in the para position. The table uses averaged literature data for μ, MR, σ, λ; absorption-spectra data marked with an asterisk are from our measurements.

The intensity coefficients of the combination-scattering lines were measured by the photographic method in solutions in CCl_4; dimethylaniline and nitrostyrene were investigated in cyclohexane. Most of the coefficients were also redetermined by the photoelectric method by V. P. Bazov. In the event of discrepancies, mean values were taken. As the unit was adopted—

* EMR values were obtained by comparing the refraction of PhX and AlkX; the exaltation already present in AlkX, for example in Alk · CH:CH · NO_2, is not included here.

** We here neglect the presence of fine structure in the first band.

Table 1

Group X in PhX	I_{1600}	EMR_D	EMR_γ	Ultraviolet absorption spectra (in heptane), λ_1	Ultraviolet absorption spectra (in heptane), λ_2	Ultraviolet absorption spectra (in heptane), λ_3	$\Delta\mu$	σ_π
·C : C.NO_2	3500	4,0	—	—	3000 (17)	2290 (10)	—	—
·C : C.Ph	3000+	5,0	—	—	2950 (25)	2250 (15)	~ 0	0,3
·C : C.CHO	2000	3,3	5,1	—	*2790 (25)	2200 (13)	−0,2	—
·C : C.COOEt	1400	3,1	4,6	—	*2720 (21)	2160 (17)	—	—
·C : C.C : C	1100	3,0	—	—	2800 (25)	2230 (12)	~ 0	—
·Ph	360+	2,0	—	—	2470 (18)	2070 (27)	~ 0	0
·C : C	240+	1,4	2,0	2820 (0,8)	2450 (13)	2030 (22)	−0,1	0
·NO_2	210	0,9	1,4	2800 (1,5)	2520 (9,6)	—	−0,9	1,0
·CHO	200+	1,1	1,45	*2800 (1,5)	2420 (14)	—	−0,55	0,8
·NHCHO	190	—	—	*2750 (1)	2400 (13)	—	—	0

Group X in PhX	I_{1600}	EMR_D	EMR_γ	Ultraviolet absorption spectra (in heptane), λ_1	Ultraviolet absorption spectra (in heptane), λ_2	Ultraviolet absorption spectra (in heptane), λ_3	$\Delta\mu$	σ_π
·COR	180+	0,85	1,15	2800 (1)	2380 (13)	–	–0,5	0,7
·NR_2	160	1,6	2,3	2970 (2)	2500 (14)	2000 (22)1760 (36)	1,5	–0,6
·CN	140+	1,0	1,2	2740 (0,6)	2250 (12)	–	–0,4	0,8
·COOR	120+	0,75	0,95	2770 (0,9)	2290 (12)	–	–0,2	0,6
·NHR	110	1,25	1,75	2880 (1,8)	2380 (14)	2000 (21)	–	–0,6
·SR	110	0,80	1,10	2790 (1,5)	2550 (10)	2050 (12)	0,5	0
·SH	100	0,50	0,70	2690 (0,7)	2360 (9)	–	0,5	–
·NH_2	85	0,95	1,30	2850 (1,7)	2330 (8)	2000 (20)	0,9	–0,5
·NEt · COR	80	–	–	–	*2380 (5,5)	–	–	–
·CCl_3	80	0,35	–	*2680 (0,6)	2240 (7)	–	–0,55	0,45
·OR	50+	0,35	0,50	2720 (1,8)	2200 (8)	–	0,9	–0,2
·OH	40	0,28	0,37	*2700 (1,8)	2130 (6)	–	0,7	–0,25
·I	42	0,15	0,20	2570 (0,7)	2310 (12)	–	0,2	0,3
·C.C.Ph	45	–	–	2600 (0,5)	$ $2050 (19)	1870 (100)	–	–
·R	39	0,27	0,31	2620 (0,3)	2050 (8,1)	1870 (55)	0,35	–0,15
·CR_3	32	0,20	0,24	2600 (0,3)	2060 (9)	1880 (80)	0,5	–0,2
·SO_2R	($ $30)	–	–	*2700 (1)	2160 (8)	–	–0,4	0,8

Group X in PhX	I_{1600}	EMR_D	EMR_γ	Ultraviolet absorption spectra (in heptane), λ_1	Ultraviolet absorption spectra (in heptane), λ_2	Ultraviolet absorption spectra (in heptane), λ_3	$\Delta\mu$	σ_π
·Br	33	0,10	0,15	*2650 (0,3)	2150 (9)	–	0,2	0,2
·Cl	33	0,15	0,17	*2650 (0,3)	2150 (8)	–	0,2	0,2
·F	$ $28	−0,05	−0,15	2670 (1,2)	2010 (7,3)	1810 (50)	0,2	0
·D	35	0	0	–	–	–	0	0
·H	35	0	0	2550 (0,2)	2020 (7,3)	1820 (50)	0	0

Note. The H atoms attached to carbon in the formulas have been omitted; R is a methyl group. One one-hundredth of the integrated intensity of the 313 cm^{-1} line of CCl_4 was taken in the calculation per mole. Accuracy $±10ˆ1$). For dibenzyl, stilbene, and diphenyl, the value given is $0,5 \cdot I_{1600}$*.

Benzene, toluene, fluorobenzene, and phenol have two lines in the region of 1600 cm^{-1}; the table gives the values of the summed intensity of both lines. Apparently, PhX has two forms of vibration of the benzene ring that are very close in frequency, one of them symmetric (with a significant influence of substituents the $ 1600*lineisratherstronglypolarized*(ˆ2$)).

* The intensity coefficients in Table 1 for some compounds studied previously differ from the old data and are more accurate (see data for dibenzyl and aniline). According to measurements in cyclohexane, the value $0,5I_{1600}$ for dibenzyl is about 70, i.e., greater than in CCl_4. For toluene, identical values of I_{1600} were obtained in both solvents.

As can be seen, alkyl groups have little effect on the chemical, electrical, and optical properties of PhX. Substituents containing double bonds C=C and benzene rings strongly affect the optical properties and only slightly the chemical properties and dipole moments. Strongly electropositive and strongly electronegative substituents significantly affect all these properties.

Among the indicators of the influence of substituents on various optical properties there is a certain commonality: the closer and more intense the absorption bands, the higher, in most cases, the intensity of the 1600 lines and the EMR.

At the same time, there is an undoubted connection between anomalies in dipole moments and the constants σ; electronegative substituents in most cases have positive σ_n, while electropositive ones have the opposite (roughly speaking, the larger $\Delta\mu$, the smaller σ_n^*). However, the optical properties mentioned are not in obvious correspondence with the electrical and chemical properties.

From the position and intensity of the absorption bands one can determine the contributions R_i of individual electronic levels to the value of the molecular refraction MR according to the formula $R_i = 18 \cdot 10^9 \cdot f_i(\nu_i^2 - \nu^2)^{-1}$, where ν_i is the frequency of the i-th absorption band, ν is the frequency of the incident light in cm^{-1}, and f_i is the oscillator strength.

Table 2

Compound	1st λ_1	1st R_1	1st ΔR_1	2nd λ_2	2nd R_2	2nd ΔR_2	3rd (and 4th) λ_3	3rd (and 4th) R_3	3rd (and 4th) ΔR_3	ΣR	$\frac{MR_\gamma - MR_D}{\Sigma\Delta R}$ calc.	$\frac{MR_\gamma - MR_D}{\Sigma\Delta R}$ found
Benzene	255	0.06	0.01	204	1.3	0.16	184	7.3	0.70	8.7	0.87	0.96
Fluorobenzene	267	0.4	0.11	200	1.2	0.15	181	7.0	0.67	8.6	0.93	0.87
Toluene	262	0.1	0.02	205	1.6	0.20	189	7.9	0.78	9.6	1.00	1.10
tert-Butylbenzene	260	0.1	0.02	206	1.6	0.22	188	11.9	1.26	13.6	1.50	1.36
Styrene	282	0.3	0.11	245	3.6	0.73	203	4.0	0.50	7.9	1.33	1.80
Dimethylaniline	297	0.9	0.37	250	3.8	0.82	200	3.9	0.46	–	–	–
Dimethylaniline	297	0.9	0.37	250	3.8	0.82	176	4.7	0.43	13.3	2.08	2.06
Cinnamaldehyde	–	–	–	279	10.1	3.20	220	3.0	0.48	13.1	3.68	3.55

In Table 2 are given the values of R_i in cubic centimeters, calculated for the sodium D line, and the increments (ΔR_i) of these values on going from the D line to the hydrogen line H_γ (4361 Å).

As can be seen, ΣR_i for some compounds greatly exceeds ΣR_i of benzene; in this case the difference is much greater than the EMR found experimentally. If the calculation formula and the experimental data for ε are correct, this means that consideration of the first three absorption bands is entirely insufficient for explaining exaltation and that further bands may influence EMR in the direction of decrease (i.e., be weaker and farther away than in benzene). Undoubtedly, the exaltation cannot be ascribed to a single absorption band.

For the dispersion and intensity of the lines of combination scattering, the proximity of absorption bands should have greater significance than for refraction (because of the peculiarities of the resonance denominators). The same bands in the region > 1700 Å can already, in the main, explain the experimentally observed values of $MR_\gamma - MR_D$; indeed, the latter do not differ greatly from the calculated values $\Sigma\Delta R$ (see Table 2).

* The correspondence, however, is very approximate. Here one should bear in mind not only the specificity of chemical processes (the significance of which can partly be judged from the fact that the constants σ for different reactions vary over wide limits), but also differences in solvents.

Judging from the known data on the dependence of I_{1600} for styrene and benzonitrile on the frequency of the incident light ν, the electronic levels having the greatest significance for I_{1600} must lie in the region 1700-2500 Å.

The observed similarity in the changes of EMR and I_{1600} may be interpreted as an indication of commonality in at least some of the parameters on which these quantities depend; such parameters may be ν_i and f_i of the intense absorption bands.

The attribution of the exaltation of refraction of PhX to the atoms of the substituents X (Ingold(3)) or to the bonds C_{ar}—X (4) is not justified. Its attribution to the benzene ring is more justified, although nevertheless it is rather conventional. The intensity of the 1600 cm^{-1} line is probably associated to a greater extent with the benzene ring. It should be borne in mind that the intense absorption bands in the region 1800-3000 Å belong to a considerable degree to the benzene ring or to the "benzene ring—substituent" system.

Table 1 shows that no general parallelism is observed between the various manifestations of the mutual influence of atomic groups in PhX molecules. In this connection it should be noted that the concepts of a "stronger" or "weaker" interaction of atomic groups can be applied only in a narrow and conventional sense, with reference to definite manifestations of it in series of similar compounds in which it has approximately the same character.

Between the manifestations of the mutual influence of groups in the various optical properties of PhX, a greater correspondence is observed. For more detailed comparisons, more complete information on all levels of electronic excitation is necessary.

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Note: Figure translations are in progress. See original paper for figures.