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P. P. Shorygin and Z. S. Egorova

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Abstract

Full Text

Physical Chemistry

P. P. Shorygin and Z. S. Egorova

THE INFLUENCE OF SUBSTITUENTS ON THE PROPERTIES OF MOLECULES OF PARA-DISUBSTITUTED BENZENE

(Presented by Academician B. A. Kazanskii, 11 IX 1957)

The frequencies of more or less local vibrations of atoms in groups attached to the benzene ring change noticeably when a second substituent is introduced into the ring in the para position. Thus, the frequency of the valence vibration of the nitro group under the influence of substituents may change by 10–50 cm^{-1} . These changes are apparently connected mainly with a change in the rigidity of the N–O bonds.

Absorption spectra and certain optical properties of aromatic compounds are more sensitive to the influence of substituents than are frequencies in vibrational spectra. Despite the difficulties in interpreting absorption spectra, in some cases it is possible to extract from them valuable information—not only about the excited state, but partly also about the ground state of molecules.

The use of various methods of investigation makes it possible to obtain a more many-sided picture of the mutual influence of atoms in complex molecules, and also makes it possible to check conclusions drawn on the basis of one method by other means. The latter is especially desirable because each of the methods has its own limitations and its own possible sources of errors and inaccuracies.

In the present work we studied the spectra and dipole moments of para derivatives of nitrobenzene $X-\langle \rangle-\text{NO}_2$ with various substituents X . The nitro group is among the most electronegative groups; signs of the influence of electropositive substituents are expressed especially distinctly in derivatives of nitrobenzene.

Table 1 gives the following quantities:

1. The magnitudes of the shifts ($\Delta\omega$) of the frequency of the valence symmetric vibration of the nitro group caused by the introduction of the substituent X , according to measurements of Raman spectra in benzene solutions (the frequency of the nitro group of unsubstituted nitrobenzene in benzene solution, and also in cyclohexane solution, is equal to 1347.5 cm^{-1}).
2. The coefficients of integral intensity of this line in Raman spectra, I_{NO_2} , measured in benzene solutions by the photographic method with excitation

of the spectrum by the mercury line 4358 Å (the unit adopted is 1/100 of the intensity of the 313 cm⁻¹ line of CCl₄, calculated per 1 mole; accuracy ±10%).

- The characteristics of intense absorption bands in the ultraviolet region: wavelength λ in Å, values of $\epsilon/1000$, where ϵ is the molar (decadic) absorption coefficient at the band maximum, and oscillator strength f from measurements of solutions in heptane, as well as the difference ($\Delta\lambda_1$) between the wavelengths of the intense absorption band of the compounds $X - \langle \rangle - \text{NO}_2$ and PhNO_2 , according to measurements of benzene solutions. The spectra were measured with a photoelectric spectrophotometer SF-4.

Table 1

Group	$\Delta\omega_{\{\text{NO}_2\}}$, cm ⁻¹		UV spectra (in heptane)	$\epsilon_1/1000$	f_1	λ_2	$\epsilon_2/1000$	$\Delta\lambda_1$ in benzene	$\Delta\mu$	$\sigma_{\{\text{para}\}}$
-H	0	700	2520	9.6	0.27	-	-	0	0	0
-	3	800	2470	11.5	0.34	-	-	-	-	0.6
SO ₂ R										
-F	0	900	2580	8.5	0.23	-	-	80	0.1	0.05
-	0	1100	2580	12	0.31	-	-	80	0.1	0.2
CH ₂ Cl										
-	-	-	2550	14.5	-	-	-	-	-	0.4
CCl ₃										
-	0	-	2540	13.5	0.36	-	-	50	-	0.5
COOEt										
-	-2	1000	2580	16.5	0.41	-	-	80	-0.1	0.4
CHO										
-	-1	1300	2670	11	0.29	-	-	130	0.15	0.2
Cl										
-	-3	1300	2700	12	0.30	-	-	170	0.15	0.2
Br										
-R	-2	1400	2650	10.2	0.28	-	-	130	0.1	-0.15
-	-2	1500	2650	10.5	0.29	-	-	130	0.1	-0.20
CR ₃										
-	-2	1600	2620	9	-	-	-	-	-	-
C·										
N·										
R ₂										
-I	0	2700	2880	12.5	0.32	2210	8	340	0.4	0.3

Group	$\Delta\omega_{\{\text{NO}_2\}}$		UV	$\epsilon_1/1000$	f_1	λ_2	$\epsilon_2/1000$	$\Delta\lambda_1$	$\Delta\mu$	$\sigma_{\{\text{para}\}}$
X	cm^{-1}	$\text{I}_{\{\text{NO}_2\}}$	spec-					in		
in			tra					ben-		
X-			(in					zene		
C_6H_4			hep-							
-			tane)							
NO_2			λ_1							
-	-	-	2910	16	-	-	-	-	0.35	0
C C										
-	-5	3200	2850	10.5	0.26	2190	9	390	0.7	-0.35
OH										
-	-3	3200	2930	15	0.37	2200	14	420	0.6	-0.3
OPh										
-	-5	4000	2920	12	0.29	2200	9	460	0.45	-0.3
OR										
-	-7.5	5700	3050	12.7	0.32	2240	6	560	-	0.1
SH										
-	-1.5	5500	2940	18	0.45	2220	12	440	0.3	0
Ph										
-	-6	5500	3040	12	0.35	2240	10	540	-	-
R·										
CHO										
-	-8	16000	3260	15	0.30	2200	7	780	0.6	-0.05
SR										
-	-4.5	20000	3300	19	0.52	2370	13	720	0.5	-
C=C										
-										
Ph										
-	-	-	3000	15	-	2200	12	-	-	0
NHCOR										
-	-12	20000	3190	15	0.37	2260	8	820	1.0	-0.65
NH_2										
-	-	-	3250	24	0.64	2140	13	-	0.4	0.6
N Ph										
-	-16	38000	3250	15	0.45	2300	14	890	-	-
NH·										
NH·										
Ph										
-	-20	45000	3450	17	0.43	2200	8	870	2	-0.6
NHNH_2										
-	-12	-	3530	21	0.42	2350	8	-	0.8	-
NH·										
Ph										
-	-28	170000	3540	20	0.41	2260	8	1210	1.4	-0.7
NR_2										

Group	UV									
X	spec-									
in	tra									
X-	(in						$\Delta\lambda_1$			
C ₆ H ₄	hep-						in			
-	$\Delta\omega_{\text{NO}_2}$	{NO ₂ },	tane)					ben-		
NO ₂	cm ⁻¹	I_{NO ₂ }	λ_1	$\epsilon_1/1000$	f_1	λ_2	$\epsilon_2/1000$	zene	$\Delta\mu$	σ_{para}
ferroceny10	-	3900	4	0.06	2800	11	-	-	-	-
-	-	3120	16	0.37	2800	11	-	-	-	-
-	-									

Notes. 1. H atoms at carbon in the formulas are omitted; R is a methyl group; λ_1 of unsubstituted nitrobenzene in benzene solution is 2620 Å. The data for the 2200 Å band are considerably less reliable than those for the neighboring bands. Weak absorption bands were not taken into account. Figures with the letter “ ” were obtained by measurements of cyclohexane solutions. The NO₂ frequency in compounds with X = Cl, Br, NH · Ph, CHO, COOEt is split into 2 components; the table gives their total intensity and an intermediate value of the frequency.

2. Nitrodiphenyl, nitrohydrazobenzene, nitroazobenzene, nitroamines, and some other compounds were synthesized by T. I. Ambush and M. A. Geiderikh; *p*-nitrophenylferrocene was kindly provided by A. N. Nesmeyanov and R. V. Golovnya; the authors take this opportunity to express their gratitude to them.
3. The difference ($\Delta\mu$) between the observed value of the dipole moment of X-C₆H₄-NO₂ and the vector sum of the moments of X-C₆H₅ and C₆H₅-NO₂ (in debyes, according to literature data on dipole moments in benzene); $\Delta\mu$ characterizes the additional displacement of electrons (in the direction from X to NO₂) associated with the simultaneous presence of two substituents: X and NO₂.
4. Hammett constants σ_{para} , determined chiefly from the dissociation constants of X-C₆H₄-COOH.

Characterizing the dependence of the properties of compounds X-C₆H₄-NO₂ on the type of substituents X, we note that electropositive and electronegative substituents affect reactivity in opposite directions, but the optical properties (I_{NO_2} , λ_1 , f_1 , and polarizability) in the same direction.

In all cases, in X-C₆H₄-NO₂ molecules the influence of electropositive substituents is much stronger than that of electronegative substituents (in X-C₆H₄-NR₂ molecules, the reverse is true).

Fig. 1 qualitatively shows the tendency that is emerging in the relationship

Fig. 1

Figure 1: Fig. 1

between the quantities I_{NO_2} , λ_1 , ω_{NO_2} in the molecules $X - \langle \text{benzene ring} \rangle - \text{NO}_2$, the constants σ_{para} of the substituents X , and the anomalies in the dipole moments of PhX compounds ($\Delta\mu_{\text{phx}}$), according to the data of (1).

The points corresponding to the values of I and λ for the substituents $\text{C}_6\text{H}_5\cdot$ and $\text{CH}_2 : \text{CH}\cdot$ lie considerably above the curves shown; such substituents have little effect on the dipole moments and chemical properties, and strongly affect the optical properties.

Alkyl groups X affect the dipole moments of nitro compounds as weakly electropositive groups. The differences between the studied parameters of molecules (Table 1) with branched and unbranched alkyl groups do not exceed the possible experimental error. The differences in the constants σ are more substantial; however, it should not be forgotten that these quantities are of a very approximate character. Values of σ , often cited in the literature to three decimal places, may in this respect easily be misleading and create the impression of great possibilities for an exact and independent characterization of substituents.

In any case, the transition from $-\text{CH}_3$ to $-\text{CMe}_3$ is associated with very slight changes in the signs of the mutual influence of groups. The effect of methylation increases in the series $\text{CH}_3 < \text{OH} < \text{SH} < \text{NH}_2$.

In molecules $Z \cdot \text{NH} - \langle \text{benzene ring} \rangle - \text{NO}_2$, the effect of Z on the spectra is similar to the effect of the same substituents in molecules $Z - \langle \text{benzene ring} \rangle - \text{NO}_2$, but is expressed more weakly. The influence of similar substituents Z through the bridges $\cdot\text{CH}_2\cdot$ and $\cdot\text{CH}_2 \cdot \text{CH}_2\cdot$ is very small.

Fig. 1

The sequences of electronegative substituents arranged according to the degree of their influence on the dipole moments, the frequency and intensity of the nitro-group line, the absorption spectra, the exaltation of refraction (and also according to the values of the constants σ_{para}) are very similar. In individual cases discrepancies are observed; in part, they are explained by differences in experimental conditions (differences in solvents, etc.). Unfortunately, it is difficult to achieve complete uniformity in the measurement conditions. However, differences in experimental conditions are not the main cause of such discrepancies. It may be noted that the OH group affects dipole moments more strongly than OR, whereas for optical properties the reverse is true. Substantial differences between the effects of substituents on chemical and physical properties may be noted in a number of compounds (for example, at $X = \text{SH}, \text{SR}, \text{C} : \text{C}, \text{C} : \text{C} \cdot \text{Ph}$).

A more complete correspondence is observed in the signs of the effect of substituents on various optical properties of the molecules $X - \langle \text{benzene ring} \rangle - \text{NO}_2$.

Fig. 2

Figure 2: Fig. 2

In monosubstituted benzenes, PhX, on the contrary, significant discrepancies were observed ⁽¹⁾. This is connected with the fact that in $X \cdot C_6H_4 \cdot NO_2$ compounds (unlike PhX) there is a nearby intense absorption band whose influence on the optical properties dominates.

Judging from the data on the dependence of I_{NO_2} on the frequency of the incident light and on the dispersion of the refractive index, it may be concluded that the nearby intense absorption band of para derivatives of nitrobenzene, lying in the region 2500-3500 Å, mainly determines the intensity of the nitro-group line and the dispersion. According to calculation, in *p*-nitroaniline it determines by 90% the observed dispersion in the region 4500-5500 Å and the exaltation of refraction associated with the introduction of the amino group ($\sim 8 \text{ cm}^3$).

The differences in the intensity of the Raman line of NO_2 in various compounds $X - \langle \rangle - NO_2$ are greater than follows from the relation $I \sim (\nu_1^2 - \nu^2)^{-2}$ and, as is seen from Fig. 2, smaller than follows from the expression

$$I \sim \nu_1^2 f_1^2 (\nu_1^2 - \nu^2)^{-4}. \quad (1)$$

These relations are obtained by differentiating the expression for the polarizability

$$\alpha = \text{const} \cdot \sum_e \frac{f_e}{\nu_e^2 - \nu^2}$$

with respect to the nuclear coordinate:

$$\frac{\partial \alpha}{\partial Q} = \text{const} \sum_e \frac{1}{\nu_e^2 - \nu^2} \frac{\partial f_e}{\partial Q} - \frac{2\nu_e f_e}{(\nu_e^2 - \nu^2)^2} \frac{\partial \nu_e}{\partial Q}$$

(ν is the frequency of the incident light, e is the index of the electronic level).

Formula (1) describes more or less satisfactorily the dependence of I_{NO_2} on ν (at constant ν_1 , i.e., for one and the same compound), but, as is seen from Fig. 2, gives large deviations when ν_1 changes under conditions of constant ν (i.e., in a series of nitro compounds with different ν_1 , when the spectrum is excited by one and the same frequency ν). If differences in the anisotropy of the scattering tensors are taken into account, the deviations are still more considerable.

Fig. 2

These deviations do not have the character of a completely random scatter of points; one can note a gradually increasing deviation from the straight line. Within the framework of a semiclassical treatment of combinational scattering, this deviation may be attributed to a decrease, in the series of nitro compounds, of the quantity $\partial\nu_e/\partial Q$ (in compounds with especially close absorption bands, damping may also have an effect).

By an approximate estimate, the derivative of the polarizability of the molecule with respect to the nuclear coordinate $q_{\text{N-O}}$ for the symmetric vibration of the nitro group of *p*-nitroaniline is about 100 \AA^2 . If it is assumed that

$$\frac{\partial\alpha_X}{\partial q} = -14 \cdot 10^9 f_1 \nu_1 (\nu_1^2 - \nu^2)^{-2} \frac{\partial\nu_1}{\partial q} \text{ \AA}^2,$$

and that the absorption band is polarized in the direction *X* (substituting $3 \cdot 0.37$ for f_1), then the derivative $(\partial\nu_1/\partial q)_0$ should have an order of magnitude of $-20000 \text{ cm}^{-1}/\text{\AA}$; such a value is quite possible with changes in the equilibrium distances between the N and O atoms upon electronic excitation by an amount of the order of $0.03\text{-}0.1 \text{ \AA}$.

Physicochemical Institute
named after L. Ya. Karpov,

N. D. Zelinsky Institute of Organic Chemistry
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