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Abstract

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ON THE DEPENDENCE OF CONJUGATION CHARACTERISTICS ON THE ANGLE OF ROTATION OF METHOXYL AND DIMETHYLAMINO GROUPS RELATIVE TO THE PLANE OF THE BENZENE RING

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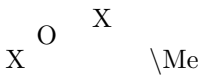
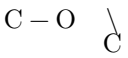
In the absence of steric hindrance, the signs of mutual influence between the group $-N(CH_3)_2$ or $-OCH_3$ and the benzene ring are readily observed. It is known that deviations from the data calculated by the additive scheme in the energies of the molecules anisole and dimethylaniline, determined from heats of combustion, reach 8-10 kcal/mol; anomalies in the dipole moments of these molecules are also very considerable. The introduction of $-OR$ and $-NR_2$ groups into the benzene ring leads to a considerable convergence and intensification of the absorption bands, to a strong increase in molecular polarizability, and to changes in other optical properties.

Judging from X-ray data, in the absence of ortho substituents the methoxyl group lies in the plane of the benzene ring.

In the presence of substituents (X) in molecules of the type



the position of the OMe group in the plane of the benzene ring becomes impossible; evidently, the plane



must make an angle θ with the plane of the benzene ring, the larger the dimensions of group X.

The OH group is more compact than OMe and therefore should be comparatively little subject to the influence of steric factors.

The NMe_2 group of dimethylaniline evidently has a pyramidal configuration; the line connecting the C atoms of the two methyl groups is apparently parallel to the plane of the benzene ring. In other compounds containing electron-acceptor groups (for example, in molecules of nitroamine and some others), the NR_2 group may also have a planar configuration. Ortho substituents should, naturally, disturb the coplanarity of the "benzene ring—dimethylamino group" system, but at the same time should have comparatively little effect on the more compact NH_2 group.

In studying the influence of ortho substituents (X), the greatest interest is presented by such groups X that have a large volume and at the same time exert little direct influence on the benzene ring and on the benzene spectrum. From this point of view, the study of tert-butyl derivatives is highly desirable; unfortunately, they are difficult to obtain. Among halogen substituents, the largest in size (bromine and iodine) substantially influence the benzene spectrum, causing convergence of absorption bands; this complicates the interpretation of the spectra of ortho-halo derivatives and judgments as to how much the influence of the OR and NR_2 groups changes.

The difficulties in interpreting spectra associated with the direct influ—

the effect of substituents X on the benzene ring becomes less significant if one passes to compounds of the type

$$O_2N\text{—benzene ring}\quad -C\begin{matrix}X\\X\end{matrix}-R \qquad \text{and} \qquad O_2N\text{—benzene ring}\quad -N\begin{matrix}X\\X\end{matrix}(R)_2.$$

It is known that *p*-nitrodimethylaniline has a very intense and sharply defined absorption band in the near ultraviolet region, which is associated with the presence of the system of conjugated bonds "nitro group—benzene ring—amino group" ; the same may be said of *p*-nitroanisole.

The signs of the influence of NR_2 and OR on the "nitro group—benzene ring" system are expressed much more distinctly than the signs of their influence on the benzene ring in the molecules $PhNR_2$ and PhOR.

The presence of the nitro group also makes it possible to obtain additional criteria for judging the influence of NR_2 and OR, at different angles of rotation (θ), on the system of conjugated bonds: the frequency of the valence vibration of the nitro group, observed in Raman spectra, can serve as an approximate measure of changes in the rigidity of the N—O bonds that are caused by substituents situated in the para position, i.e., by the groups NR_2 or OR. The intensity of the nitro-group line is especially sensitive to the influence of such substituents.

At the same time, substituents X in compounds

$$O_2N\text{—benzene ring}\quad \begin{matrix}X\\X\end{matrix}$$

have comparatively little effect on the absorption spectra and on the frequency of the nitro group, while the dipole moments of such compounds correspond to an additive scheme.

In Table 1, for each compound, the following are given:
1) the difference ($\Delta\omega$) between the frequency of the symmetric valence vibration of the nitro group of the given substance and the frequency of unsubstituted nitrobenzene (equal to 1347.3 cm^{-1}) according to measurements of the Raman spectra of benzene solutions; 2) the coefficient of the integral intensity of the corresponding nitro-group line, I_{NO_2}, according to measurements of benzene solutions; the intensity coefficient of the benzene line at 1176 cm^{-1} is taken as equal to 25 units (one unit is taken as 1/100 of the integral intensity of the 313 cm^{-1} line of CCl_4, calculated per 1 mole); accuracy $\pm 15\%$*; 3) the dipole moment according to measurements in benzene, μ in debyes (figures with the letter "l" in the subscript are from literature data); 4) the difference ($\Delta\mu$) between μ and the vector sum of the dipole moments of nitrobenzene (or, respectively, m,m-dichloronitrobenzene for the dichloro derivatives) and the aliphatic compound AlkZ (where $Z = OH, OR^{**}, NH_2$, or NR_2); roughly speaking, $\Delta\mu$ characterizes the displacement of electrons from Z toward the benzene ring and the nitro group; in calculating $\Delta\mu$, the deformation of the angles C—C—Cl, etc. was taken into account (by an approximate estimate); 5) the values of θ (the angle of rotation of the group NH_2, NR_2, OH, or OR about the bond C_{ar}—N or, respectively, C_{ar}—O), calculated from known data on interatomic distances in similar molecules and on the van der Waals radii of H and Cl atoms. In the calculation, allowance was made for the deformation of valence angles and for the approach of contacting H and Cl atoms to a distance smaller than the sum of their van der Waals radii under the influence of a force tending to rotate the NR_2 group (or, respectively, OR) into the plane of the benzene ring. According to an approximate estimate, this force should be about $5 \cdot 10^{-5}$ dyn. Such a force is sufficient to shorten the distance between contacting atoms by 0.1–0.2 Å. In the calculation, a planar model of the $-NR_2$ group was adopted.

According to the data of Table 1, the groups OH, OR, NH_2, and NR_2 in the molecules of *p*-nitrophenol, *p*-nitroanisole, *p*-nitroaniline, and *p*-nitrodimethylaniline affect the frequency of the nitro group in the direction of lowering it, and the intensity

* Excitation by Hg 4358 Å. For details of the measurements of ω, I, μ, see (1).
** In the text and in Table 1 the letter R denotes a methyl group.

Table 1

Compound	$\Delta\omega_{NO_2}$	I_{NO_2}	U.-v. absorption spectra in heptane λ_{max}*	μ	$\Delta\mu$	θ
nitrobenzene	0	700	2800 (1.5) 2520 (9.6)	4.00	0	–
chloro-nitrobenzene	1.5	600	2900 (1.2) 2520 (7.4)	3.40	−0.1	–
dichloro-nitrobenzene	0	500	3070 (1.2) 2570 (6.2)	2.55	0.1	–
p-nitroaniline, H_2N–Ar–NO_2	−12	20000	3190 (15) 2260 (8)	6.20	1.8	0°
dichloro-*p*-nitroaniline, H_2N–Ar–NO_2	−13	18000	3220 (14.4) 2400 (8)	4.87	1.8	0°
p-nitro-*N*, *N*-dialkylaniline, R_2N–Ar–NO_2	−28	200000	3540 (20) 2260 (8)	6.87	2.8	0°
chloro-*p*-nitro-*N*, *N*-dialkylaniline, R_2N–Ar–NO_2	−16	100000	3450 (12) 2200	5.50	1.8	55°

Compound	$\Delta\omega_{NO_2}$	I_{NO_2}	U.-v. absorption spectra in heptane λ_{max}*	μ	$\Delta\mu$	θ
dichloro-*p*-nitro-*N*, *N*-dialkylaniline, R_2N—Ar—NO_2	−12	90000	3650 (7.5) 2590 (5)	4.05	1.4	65°
p-nitrophenol, HO—Ar—NO_2	−5	3000	2850 (10.5)	5.04	1.4	0°
dichloro-*p*-nitrophenol, HO—Ar—NO_2	−5	2000	2850 (6.5)	3.30	1.2	0°
p-nitroanisole, RO—Ar—NO_2	−5	4000	2920 (12)	4.90	1.4	0°
dichloro-*p*-nitroanisole, RO—Ar—NO_2	−2.5	1300	2720 (8.4)	3.42	1.2	60°

* In parentheses are the data $\varepsilon_{max} \cdot 10^{-3}$.

the Raman line of the nitro group—in the direction of increase; on the absorption spectrum—in the direction of strengthening and approach of the absorption band. The anomalies in the dipole moments are especially large in nitroamines.

Comparison of the data for 4-nitrophenol and 2,6-dichloro-4-nitrophenol shows that in the spectra of the latter no obvious signs are observed of a weakening of

Fig. 1

Figure 1: Fig. 1

the influence of the OH group on the "benzene ring–nitro group" system; the intensity of the absorption band (and also I_{NO_2}) in this compound is somewhat lowered, but to approximately the same extent as in m,m-dichloronitrobenzene in comparison with nitrobenzene. It may be assumed that the orientation of the OH group (angle θ) as a result of chlorination does not change appreciably.

The methoxyl group is less compact than OH and should be more subject to the influence of steric factors. Indeed, when chlorine atoms are introduced into the molecule of p-nitroanisole, a clear weakening of the influence of OR on the spectra is observed. However, the value of $\Delta\mu$ decreases only insignificantly (approximately as in the analogous phenol). Whether this is explained by the inaccuracy of the obtained value of μ or by other circumstances is as yet unclear.

Thus, the indications of the influence of OR on the spectra depend on the angle θ and weaken as it increases; no dependence of $\Delta\mu$ on θ is found here.

Fig. 1

Comparison of the parameters of the molecules of 4-nitroaniline and 2,6-dichloro-4-nitroaniline shows that the chlorine atoms have very little effect on the spectra and on the indications of the influence of NH_2 on the "benzene ring–nitro group" system, observed in the spectra and dipole moments (for absorption spectra see Fig. 1).

An entirely different picture is observed when chlorine atoms are introduced into the molecule of p-nitrodimethylaniline: already upon introduction of one chlorine atom, the indications of the influence of NR_2 on the system of conjugated π bonds are clearly weakened; two chlorine atoms give an still greater effect: the NO_2 frequency becomes closer to the frequency of unsubstituted nitrobenzene than to the frequency of the initial p-nitrodimethylaniline; the intensity of the nitro-group line (I_{NO_2}) is weakened by a factor of two, the absorption band is weakened still more strongly (see Fig. 2), and the anomalies in the dipole moments ($\Delta\mu$) are reduced by half.

Obviously, the influence of the group NR_2 on the spectra and dipole moments of aromatic compounds depends strongly on the angle of rotation θ of this group relative to the plane of the benzene ring; as θ increases from 0 to 60°, the indications of the influence of NR_2 weaken, roughly speaking, by a factor of two (it should be noted that rotation of the nitro group by an angle of about 60° [2] leads to a sharper weakening of the indications of conjugation of the nitro group with the benzene ring).

Unfortunately, at present there are no data for molecules in which the angle θ is close to 90°. However, the data already available allow one to suppose that the inductive effect is not a factor determining the anomalies in the spectra and

Fig. 2

Figure 2: Fig. 2

dipole moments of molecules in which the NR_2 group is attached to the system of π bonds.

Fig. 2

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