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Abstract

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REGULARITIES IN THE MUTUAL INFLUENCE OF ATOMIC GROUPS ADJACENT TO A METHYLENE BRIDGE

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Clarifying the regularities and the nature of the mutual influence of atomic groups in complex molecules is of primary importance for chemistry; it leads to the establishment of relations between structure and properties and can considerably facilitate orientation in the search for compounds possessing the required properties. However, the highly varied specificity of the manifestations of mutual influence greatly complicates the classification, characterization, and interpretation of intramolecular interactions.

At present it is necessary, above all, to systematize the data of numerous scattered observations and, as far as possible, to characterize the most important types of combinations of atomic groups. Here we compare the parameters of molecules

$X—C \equiv N$, $X—CH_2—C \equiv N$, $X—CR_2—C \equiv N$, and X—cyclohexyl—$C \equiv N$

with the aim of establishing the elements of commonality and difference in the influence of substituents X through bridges, so different in their nature, between the groups X and CN (the letter R here and below denotes a methyl group).

Along with this, we shall compare molecules with a methylene bridge: $X—CH_2—C \equiv N$, $X—CH_2—CH = CH_2$, $X—CH_2—CO—CH_3$. We shall denote them by the common formula $X—CH_2—\Pi$.

From the vibrational spectra of these compounds one can obtain information about the stiffness of the multiple bond. The frequencies (ω_π) of the stretching vibrations $C = C$, $C \equiv N$, $C = O$ depend almost not at all on the force and kinematic parameters of the group X and depend comparatively little on the force constant K_{cc} of the single $C—C$ bond adjacent to the group Π. Thus, for acetonitrile derivatives,

$$\frac{\partial \omega_{CN}}{\partial K_{CC}} = 15 \cdot 10^{-6} \text{ cm}, \qquad \text{whereas} \qquad \frac{\partial \omega_{CN}}{\partial K_{CN}} = 37 \cdot 10^{-6} \text{ cm}.$$

Therefore, the experimentally observed differences in the frequencies ω_π can serve as a semiquantitative characteristic of the influence of substituents on the stiffness of the corresponding double or triple bond.

Table 1 gives the differences $\Delta\omega_{CN}$ between the CN frequency of compounds

Table 1*

Substituent X	$\Delta\omega_{CN}$, cm^{-1}	I_{CN}	$\Delta\mu$** for PhX	Substituent X	$\Delta\omega_{CN}$, cm^{-1}	I_{CN}	$\Delta\mu$** for PhX
$X—CH_2—C\equiv N$				R_2N	−24	48	1.5
NC	15***	38	−0.4	J	−10	150	0.2
EtOOC	10**	–	−0.2	$ClCH_2$	4**	–	−0.3
Cl	1	50	0.2	$NCCH_2$	0	39	0
$CH_2{=}CH$	1	52	0.1	R_2NCH_2	−5	60	0.3
H	0 [2255]	38	0	$X—CR_2—C\equiv N$			
C_6H_5	−1	60	0.3	H	0 [2244]**	–	–
R	−5	40	0.3	HO	−7	55	–
Et	−2	–	0.3	RHN	−21	62	–
RO	−9	40	0.9	R_2N	−24	62	–
H_2N	−16	45	0.9	morpholino-N	−25	55	–

* $\Delta\omega_{CN}$ and I_{CN} are given for solutions in ethyl acetate. In square brackets is ω_{CN}, taken as zero. Accuracy of determination of ω_{CN} $\pm1–2 cm^{-1}$. On measurements of I cm, see (1,2). For dinitriles, I_{CN} is calculated per one CN group.
** According to literature data.
*** Arithmetic mean between the values of $\Delta\omega_{CN}$ in the infrared and Raman spectra.

$X—CH_2—CN$ and the frequency of CN of unsubstituted acetonitrile (2225 cm^{-1}); I_{CN} is the coefficient of the integrated intensity of the line in combination scattering (Raman spectra).

Let us first turn to consideration of substituents that do not contain heavy atoms. From the values of ω_{CN} we obtain the series:

$$CN > COOEt > Cl,\ CH_2{=}CH,\ H,\ C_6H_5 > CH_3 > OR > NH_2 > NR_2. \quad (1)$$

The observed differences in frequencies are evidently not connected with differences in the polarity of the $C—X$ groups and, consequently, cannot be explained by the inductive effect. It may be noted, for example, that in compounds with

$X = H,\ F,\ Cl$ the dipole moments of the $C—X$ bonds differ greatly, while the values of ω_{CN} are almost identical.

Let us now see whether there is similarity in the influence of substituents on the rigidity of the $C \equiv N$ bond through a methylene bridge and through a benzene ring. Comparison with the data for $X—C_6H_4—CN$ (1) shows that, despite the large differences in the character of the intermediate links for both types of molecules, the sequences of substituents that do not contain heavy atoms or atoms with especially low electronegativity are very similar. In these sequences there is a clear correspondence between a decrease in the frequency ω_{CN} and an increase in the "electron-donor ability" of group X, manifested in molecules PhX (which may be estimated from the vector difference $\Delta\mu$ of the dipole moments of PhX and AlkX; see the last column of Table 1).

Let us consider examples. The amino group, in the case of direct attachment to the benzene ring–in aniline–acts as an active electron-donor group; as substituent X in the molecules $X—CN$, $X—C_6H_4—CN$, and $X—CH_2—CN$ it lowers the rigidity of the $C \equiv N$ bond. The nitrile group in PhCN is an electron acceptor; as substituent X in $X—C_6H_4—CN$ and $X—CH_2—CN$ it increases the rigidity of $C \equiv N$.

If, in compounds with a methylene bridge, the amino group affects the nitrile group, then the question arises–does the nitrile group in turn affect the amino group? Let us again turn to comparison with aromatic compounds. It is known that in para derivatives of aniline,

$H_2N—C_6H_4—Y$,

nitrile and other electron-acceptor groups Y considerably decrease basicity (pK_a); along with this they increase the frequencies of the symmetric (ω^s_{NH}) and especially antisymmetric (ω^{as}_{NH}) vibrations of the amino group and increase the rigidity of the $N—H$ bonds. The increase in the frequency splitting $\omega^{as}_{NH} - \omega^s_{NH}$ in this case indirectly indicates some increase in the valence angle HNH. These circumstances cannot be explained by the inductive effect (see (2)). However, they can be satisfactorily described as the result of a "donor-acceptor" interaction of substituents, which is associated with a tendency toward transition of the N atom of the amino group into a tetravalent positive state. If a similar interaction is present in $H_2N—CH_2—CN$, then the properties of the amino group here should be modified in a similar way. Table 2 shows that this is so (data for ω_{NH} in CCl_4).

Additional information on the amino group of aminoacetonitriles is provided by UV spectra. Absorption in the region 1900-2300 Å here is probably caused by excitation of the electrons of the lone pair of the N atom of the amino group. The absorption spectrum of $R_2N—CH_2—CH_2—CN$ is close to the spectrum of R_3N; in contrast to these compounds, in $R_2N—CH_2—CN$ the absorption intensity is much smaller, apparently in connection with participation of the electrons of the lone pair in formation of a bond with CN. It should be noted that in the cation $(R_3NH)^+$ the absorption intensity in the region under consideration is quite small.

Thus, the interaction of the nitrile group and the amino group attached to the —CH_2— bridge is manifested both in the mechanical properties of the $C \equiv N$ and N—H bonds and in the absorption spectra and constants–

Table 2

Compound	ω_{CN}, cm^{-1}	ω^{as}_{NH}, cm^{-1}	ω^{s}_{NH}, cm^{-1}	pK_a	Compound	ω_{CN}, cm^{-1}	ω^{as}_{NH}, cm^{-1}	ω^{s}_{NH}, cm^{-1}	pK_a
C_6H_5CN	2230	–	–	–	C_2H_5CN	2250	–	–	–
$H_2NC_6H_5$	–	3481	3396	4.6	$H_2NC_3H_7$	–	3382	3328	10.6
$H_2NC_6H_4CN$	2229	3505	3412	1.7	H_2N-CH_2-CN	2239	3413	3348	5.3

of the basicity of such compounds. Probably it is effected both by the type of transannular interaction (which possibly includes the formation of a very weak covalent bond between the N atom of the amino group and the C atom of the nitrile group) and with participation of the methylene bridge, for example by changing its donor ability.

Judging from all the data, the interaction in compounds $X-CH_2-CH_2-CN$ is much weaker (see Table 1). Sayed's conclusion ([3]) about a significant influence of X on ω_{CN} in such compounds is based on a comparison of frequencies measured under noncomparable conditions, and cannot be accepted.

The electron-donor ability of the substituent X in $X-CH_2-CN$ in many cases determines its influence on the frequency of the electron-acceptor CN group, but is of no substantial importance for the almost "neutral" C=C group in allyl compounds $X-CH_2-CH=CH_2$ (in turn, the C=C group in allylamine does not affect ω_{NH}). Evidently, for interaction of two groups adjacent to a methylene bridge, the most favorable combination is that of an electron-donor group with an electron-acceptor group (of course, under conditions of a suitable mutual orientation of these groups).

It should be added that the electron-donor properties of X and the lowering of ω_π in the molecules XPh, X , $X-C_6H_4-$ are connected mainly with the presence of an unshared electron pair on atom Z of group X. However, in some compounds of the type $X-CH_2-$ –when the electronegativity of atom Z from group X adjacent to the bridge is small–they may be attributed to the valence electrons of the Z–C bond (and the CH_2 group may be regarded as an acceptor); an example may be $RHgCH_2COR$ (there are no such examples in Table 1).

When nitrile compounds $X-CH_2-CN$ are compared with ketones $X-CH_2-COR$, it is noteworthy that the mutual influence of the amino group (X) and COR is expressed very weakly in spectroscopic and chemical constants; thus, the C=O frequency in

$$\text{(piperidyl)}-\text{N}-\text{CH}_2-\text{CO}-\text{R}$$

(1717 cm^{-1} for a solution in CCl_4) is only 3 cm^{-1} lower than that of acetone. Apparently, these differences between ketones and nitriles are connected with the relationships between the real and the "optimal" conformations of the molecules.

Let us now turn to very interesting and distinctive compounds containing, in group X, heavy atoms Z adjacent to the π bond in group Π directly (X−), or through a benzene ring (X−C_6H_4−), or through a methylene bridge (X−CH_2−).

In such molecules X− the frequency ω_π, as a rule, is considerably lower than in compounds Alk . However, in the force constants of the π bond there are in most cases no substantial differences; the lowering of the frequency is due mainly to the low rigidity of the single Z−C bond to the heavy atom and to its large mass. In UV spectra of compounds X− the deviations from additivity are also comparatively small.

In compounds X−C_6H_4− , heavy atoms for the most part have almost no effect on the frequency and on the rigidity of the π bond in group Π, but cause

only a small bathochromic shift of the UV absorption bands and an increase in the intensity of the Raman lines. In the presence of lone electron pairs at the atoms Z, the influence on the rigidity of the π-bond and on the optical properties of $X - \Pi$ and $X - \quad - \Pi$ is in most cases more strongly expressed.

The influence of heavy atoms is manifested quite differently in the spectra of molecules $X-CH_2-\Pi$. Here the frequencies ω_π are appreciably lowered, mainly owing to a decrease in the rigidity of the multiple bond; in UV spectra a considerable bathochromic shift of the bands is observed (4), and the intensity of the Raman lines (I_π) is much higher than the usual values (see, for example, the data for iodoacetonitrile in Table 1*). These features, especially in the optical properties, are intensified on going to heavier atoms, but depend comparatively little on the type of π-bond. The presence of lone electron pairs is no longer of great importance, but with low electronegativity of the atom Z, donor-acceptor interaction of X and $CH_2\Pi$ with a lowering of ω_π is quite possible (nonspecific for heavy atoms).

The features of $X - CH_2 - \Pi$ molecules with a heavy atom in the group X can be correlated with the decrease in the rigidity and strength of the $C - X$ bond on going to heavier atoms and with the fact that the rigidity and dissociation energies of the $C - X$ bonds in the molecules $Ph - CH_2 - X$ and $CH_2 = CH - CH_2 - X$ are considerably lower than in saturated compounds Alk$X$ (the dissociation energies by an amount ~ 20 kcal/mole, corresponding to the energy gain due to conjugation in the radical $CH_2-\Pi$). Thus, when a system of π-bonds and a substituent X with a heavy atom are combined with a methylene bridge, the differences in the energies of the systems $X - CH_2 - \Pi$ and $X + CH_2\Pi$ are not very large. Within the framework of an approximate quantum-mechanical interpretation—the method of valence schemes—this corresponds to a certain contribution of the wave function of the radical $CH_2\Pi$ to the wave function of the real molecule $X - CH_2 - \Pi$.

In other words, it may be assumed that here there is a partial rehybridization of the valence orbitals of the carbon atom of the methylene bridge ($sp^3 \to sp^2 + p$), with a slight redistribution of electron density in the $CH_2\Pi$ group involving the p-orbital and an increase in the free-valence index of the heavy atom (in such a case the planar configuration of the chain should be least favorable for interaction in allylic and carbonyl compounds).

It is quite probable that in the excited state these features are expressed to a much greater degree; a simple calculation on the basis of the LCAO MO method agrees with this assumption. The large intensity of the Raman lines of the stretching vibrations of the $C - X$ bond and of the multiple bond makes it very probable that the corresponding interatomic distances increase considerably upon electronic excitation.

In connection with the above, it seems natural that in molecules $X{-}CH_2{-}CH_2{-}X$ with two heavy atoms, in a planar configuration of the chain, anomalies may be observed in the optical properties similar to those described above. Indeed, in 1,2-diiodoethane the intensity of the Raman lines of the stretching vibration of the $C - J$ bonds is several times higher than in compounds Alk$J$ and in 1,3-diiodopropane. This indicates the relative closeness of the effective levels of electronic excitation in diiodoethane.

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* The large value of I_{CN} here cannot be explained by the participation of the $C - J$ bond in a not entirely local "vibration of the nitrile group," since the amplitude of vibration of $C - J$ is then very small. Obviously, the matter here lies in modification of the level of electronic excitation.

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