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Fig. 1

Figure 1: Fig. 1

Abstract

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MUTUAL INFLUENCE OF ATOMIC GROUPS IN MOLECULES CONTAINING HEAVY ATOMS AND SYSTEMS OF π-BONDS

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The peculiarities of the physical and chemical properties of compounds in whose molecules there is an alternation of double and single bonds, or in which certain atoms not forming double bonds adjoin double bonds, are in general quite well studied. However, this cannot be said of that range of compounds in which a double bond and a definite group of atoms are separated by two single bonds, for example by a bridge—$-CH_2-$. In other words, the mutual influence of directly adjacent groups A—B has been studied in detail, whereas systems A—M—B have been little studied. The terminology often used ("absence of transmission of conjugation through a bridge,""isolation"of two systems or chromophoric groups, etc.) is connected with the fact that in most cases no substantial deviations from additivity were observed in the properties of the corresponding complex molecules.

Fig. 1. Above—absorption spectra of allyl compounds of the type $H_2C=CH-CH_2-XZ_n$ (on the curves the atoms X in the groups XZ_n: CR_3, Cl, $B(OR)_2$, SiR_3, GeR_3, J, SnR_3, HgCl are indicated); below—spectra of tetramethyltin, trimethylvinyltin, and trimethylallyltin.

Comparison of compounds of the type Π—M—Π, in which two groups Π containing π-bonds, for example two phenyl or acetylene groups, are separated by various bridges M not containing multiple bonds ($-CH_2-$, $-S-$, $-NH-$, $-Hg-$, etc.), shows that signs of nonadditivity are often observed and depend on the nature of the bridge. In the ultraviolet absorption spectra they are weakly expressed for compounds with the bridge $-CH_2-$ (diphenylmethane, 1,1-dinitromethane) and rather pronounced for compounds with the bridge $-NH-$ (diphenylamine (^{1}), succinimide, vinylpyrrolidone (^{2})).

Turning to compounds of the type Π—M—XZ_n, in which groups XZ_n not containing multiple bonds are attached through bridges —M—to a system of π-bonds

Fig. 2

Figure 2: Fig. 2

Π, we sometimes encounter entirely different relationships.

Let us compare the ultraviolet absorption spectra* of a series of allyl compounds $H_2C = CH - CH_2 - XZ_n$ (see Fig. 1, top). We adopt the designations: R—methyl, Ph—phenyl, Et—ethyl group. It may be noted that the atoms X of the first period of the periodic system of elements adjoining the allyl group have little effect on the first absorption band characteristic of olefinic hydrocarbons. Similar conclusions may also be drawn in rela— ratio of the spectra of $Ph—CH_2—XZ_n$ (bands ~ 1800, 2000, and 2600 Å). Heavy atoms X, on the contrary, cause a considerable shift of the bands toward the long-wavelength side (and also a noticeable broadening of them); this shift cannot be the result of a simple superposition of the absorption characteristic of the group $—CH_2—XZ_n$ (see, for example, the data for SnR_4 in Fig. 1, below). Deviations from additivity are unquestionable, and they increase in the series of atoms X adjacent to the methylene bridge:

$$\mathrm{C,\ N,\ O,\ Cl < B < S < Si,\ Br < Se, Ge < J < Sn < Hg.}$$

Fig. 2. Absorption spectra of trimethylallylgermane and 1,1-dimethyl-1-germacyclopentene-3

As regards the influence of substituents on the frequency of the valence vibration $C = C$ in allylic compounds, approximately the same sequence is obtained. The lowering of the frequency reaches 10-20 cm^{-1}; it is apparently connected mainly with a decrease in the stiffness of the double bond.

Thus, the influence increases on going to elements of subsequent periods, i.e., to heavier atoms (see also (1)); a similar picture is observed for compounds $R—CO—CH_2—XZ_n$.

At the same time, judging from the available data, there is a tendency toward some weakening of the effect in a series of elements of one period when moving across D. I. Mendeleev' s table from left to right. Let us note that when the group XZ_n is directly adjacent to the double bond, for example in compounds $H_2C=CH—XZ_n$, other relationships are observed. In this connection it should be said that the degree of influence of $—CH_2—XZ_n$ on the UV absorption spectra $Π—CH_2—XZ_n$ clearly does not depend on the presence of a labile unshared electron pair at the atoms X (see the data for allylamine), in contrast to the

* For the measurements a photoelectric spectrometer was used, including a vacuum double monochromator with LiF prisms. The graphs give molar (decimal) absorption coefficients ε. Solvent—heptane.

Fig. 3

Figure 3: Fig. 3

influence of the group $-XZ_n$ directly adjacent to the double bond, where this circumstance, on the contrary, is of greater importance (cf. the data for aniline).

With regard to the dependence of the influence of the group $-CH_2-XZ_n$ on its spatial arrangement relative to the system of π-bonds, the following can be said. In compounds $Ph-CH_2-XZ_n$ with a heavy atom X, the plane $C_{ar}-C\backslash X$ certainly does not lie in the plane of the benzene ring. The angle θ between these planes, determined by the repulsion of XZ_n from the hydrogen atoms of the benzene ring, for $X = Sn, \ Hg, \ J$ should be about $90 \pm 20°$. Under these conditions the influence of XZ_n on the absorption spectrum is very large. Judging from electron-diffraction data, something similar can be said about allyl iodide. At the same time, the absorption spectrum of the compound

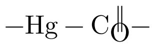
C=C
C C
\Ge/
C C

in which the Ge atom apparently lies in the plane $> C = C <$, is, on the contrary, quite close to the sum of the absorption spectra of an olefinic hydrocarbon and GeR_4 (see Fig. 2).

Fig. 3. Dependence of the energy of a molecule on the angle θ in the ground (a) and excited (b) electronic states

These data provide grounds for supposing that the influence of heavy atoms X is minimal when C–X is located in the plane of the π-bond system ($\theta = 0°$) and maximal at $\theta = 90°$, and that the dependence of the molecular energy E on θ in benzyl compounds has at $\theta =\sim 90°$ a more pronounced minimum in the excited state than in the ground state (Fig. 3 explains what has been said in a somewhat exaggerated form). Roughly speaking, the interaction of XZ_n and Π is manifested more strongly in the excited state.

In connection with the above, it is worth recalling the data from the chemical studies of A. N. Nesmeyanov and co-workers (^{3}), which showed that in systems



$$-Hg-\underset{\underset{O}{\|}}{C}-$$

the reactivity (lability) of the mercury atom depends strongly on the mutual spatial arrangement of the Hg–C and C=O bonds and is minimal in molecules with a planar system of bonds. Studies of tin and mercury compounds led them to the concept of σ, π-conjugation.

Fig. 4. Absorption spectra of trimethylbenzylstannane, trimethylphenoxystannane, anisole, tetramethylstannane, trimethylstannanol hydroxide

Figure 4: Fig. 4. Absorption spectra of trimethylbenzylstannane, trimethylphenoxystannane, anisole, tetramethylstannane, trimethylstannanol hydroxide

The question arises whether the methylene bridge plays only the role of an intermediate link that makes possible a suitable relative arrangement in space of the groups XZ_n and Π, in which modification of the system of electronic levels occurs, or whether the valence electrons of CH_2 participate in the formation of delocalized molecular orbitals.

In this connection, comparison of systems with different bridges is of interest. Investigation of UV spectra shows that in compounds $\Pi - M - XZ_n$ the influence of heavy atoms through the bridges $-CH_2-CH_2-$and $-CH_2-CH_2-CH_2$ is extremely small, whereas through the bridge $-CH_2-$, $-NH-$or $-O-$it is rather large. Let us compare the spectra of $Ph—CH_2—SnR_3$ and $Ph—O—SnR_3$, which should have similar geometrical configurations (the C–Sn and O–Sn bonds should lie in a plane almost perpendicular to the plane of the benzene ring). The bands in the UV spectra of both compounds are quite typical for monosubstituted benzenes with sufficiently "active" substituents. Thus, the spectrum of $Ph—CH_2—SnR_3$ is close to the spectrum of aniline (in the magnitude of the bathochromic shift of the benzene bands, the $—CH_2—SnR_3$ group even surpasses the amino group). However, the influence of the substituent with a heavy atom in the presence of an oxygen bridge is expressed considerably more weakly than in the presence of a methylene bridge (see Fig. 4). Thus, the influence of heavy atoms depends to a large extent on the nature of the bridge; obviously, the role of the bridge is not limited to its significance for the geometry of the molecule.

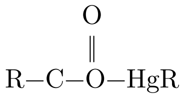
Fig. 4. Absorption spectra of trimethylbenzylstannane, trimethylphenoxystannane, anisole, tetramethylstannane, trimethylstannanol hydroxide

In this connection it is interesting that in the absorption spectrum of $HOSnR_3$ the absorption band lies in a shorter-wavelength region than in SnR_4. This gives grounds for relating the influence of the heavy atom X to the properties of the M–X bond and to the position of the electronic levels of the group $M—XZ_n$ in molecules $R—M—XZ_n$. At the same time, attention should be paid to the fact that in $Ph—M—SnR_3$ the bathochromic shift extends to all three observed absorption bands (regions) and is not limited to the third (short-wavelength) band, which lies especially close to the absorption band of SnR_4. The greatest shift is undergone by the 2000 Å band and, consequently, by that electronic level which is genetically connected with the benzene level B_{1u}. The low sensitivity of the position of this band to the influence of polar solvents is not consistent with assigning it to the electronic transitions associated with charge transfer.

The influence of XZ_n on the UV spectra of benzyl and allyl compounds of the type Π—CH_2—XZ_n depends little on the electronegativity of X and on the polarity of the group —CH_2—XZ_n. Therefore it is hardly possible here to attach great

significance to the inductive effect. However, one cannot ignore the fact that in vibrational spectra (the frequency of the double bond) and, apparently, in dipole moments, when an electronegative group Π is combined with an electropositive group XZ_n, the signs of influence through the methylene bridge are more distinct. This applies to an even greater extent to similar molecules with an oxygen bridge. Here substantial differences are already expressed between the manifestations of the influence in the UV and in the vibrational spectra. Thus, in some systems the features of the wave functions of the excited state are more significant and interesting, while in others those of the ground state are.

In this connection let us dwell on a specific example. In the vibrational spectra of the undissociated form



$$R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}HgR$$

the C=O frequency is strongly lowered (1630 cm^{-1} for a solution in CCl_4) and has a value intermediate between those characteristic of the molecules R–CO–OR (1740 cm^{-1}) and the anions R–COO′ (1560 cm^{-1}). It is therefore not excluded that some displacement of electron density from Hg to the oxygen atoms takes place here. At the same time, in the UV absorption spectrum of RCOOHgR no large deviations from additivity were observed; in practice the spectrum of this compound is very similar to the spectrum of HOHgR (esters in the region 1700–3000 Å do not have any intense absorption bands, so that the group –O – Hg– largely determines the absorption spectrum of RCOOHgR).

We have sometimes used the term "transmission of influence through bridges," which, however, is not entirely successful; in fact, the influence of the group $-CH_2 - XZ_n$ in some cases is much greater than the influence of $-XZ_n$ directly adjacent to a double bond (one may refer, for example, to the UV spectra of mercury compounds).

The specific character of the influence of the groups $\cdot CH_2 \cdot XZ_n$ with a heavy atom X can apparently be connected with the fact that the electronic levels characteristic of the systems Π and $M - XZ_n$ are in these cases sufficiently close, while the symmetry of the corresponding wave functions makes possible, in the molecules $\Pi - M - XZ_n$, appreciable perturbations that may lead to a displacement of levels (especially excitation levels). The peculiarities of the state of chemical bonds in the ground electronic state of the molecule are apparently associated not only with the interaction of the occupied orbitals Π and $M - X$, but also with the contribution of vacant levels to the actual wave function of the ground state. Here, however, one should not overestimate the role of vacant *d*-orbitals; as is known, the energy of these orbitals in the series Si, Ge, Sn in any case does not decrease; at the same time, experience shows that the SiF_3 group affects the spectrum even less than SiR_3. As for the possible role of free-valence indices at heavy atoms, the available data are still insufficient for definite conclusions. Regarding the significance of the polarizability of the heavy atom, we note that no parallelism is observed between the increment of the polarizability of atom X and the influence of the group $CH_2 - XZ_n$ on the UV spectra; in this respect the comparison of the groups $-CH_2 - I$ and $-CH_2 - HgR$ is quite revealing.

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