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Abstract

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On the Interaction of Atomic Groupings Remote from One Another through a System of Two Benzene Nuclei Linked by a Bridging Unit

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In the field of the quantitative study by chemical methods of the mutual influence of atoms or atomic groupings, manifested through such a simplest aromatic system as the benzene ring, an enormous amount of experimental material has now been accumulated. As regards investigations, from this point of view, of more complex aromatic systems that include several benzene nuclei, only isolated and scattered publications are still encountered here. Thus, on the basis of a study of the kinetics of the acylation reaction of a series of aminoderivatives of biphenyl, we showed that the interaction of substituents through a system consisting of two benzene rings directly linked to one another, although considerably weakened in comparison with what is observed in analogous benzene derivatives, is nevertheless still rather large (1–3).

It was of interest to determine whether, and if so in what way, the interaction of substituents sharply different in their nature—for example, the groups NO_2 and NH_2, located at opposite ends in the molecules of such compounds in which, in contrast to the previously studied biphenyl derivatives, the benzene rings are not joined directly but are isolated from one another by a unit separating them —would be manifested. We were unable to find in the literature indications that chemical methods of investigation had been used to solve such questions from a more or less quantitative point of view; however, for a number of such systems the optical properties have been studied. N. A. Valyashko and V. F. Lavrushin (4,5), from measurements of the absorption spectra of diphenylmethane and its derivatives, were able to establish that the benzene rings in these substances interact with one another through the bridging methylene group. R. S. Tsekhanskii (6) came to an analogous conclusion in studying the nature of the coloration arising in certain derivatives of diphenylmethane, and Jaffé (7), in comparing the absorption spectra of a series of compounds of elements of groups V and VI of the periodic system containing phenyl groups. A. Kh. Khalilov (8), by measuring the intensities of lines in Raman spectra, showed that in diphenylmethane and 1,2-diphenylethane there is a significant interaction of the benzene nuclei through the aliphatic groupings linking them, whereas the same method, applied to diphenyl oxide, does not make it possible to answer unambiguously the question of whether interaction of the benzene nuclei occurs in this case. In the opinion of V. A. Izmailskii and A. M. Simonov (9), replacement in a conjugated chain of the group $-\mathrm{CH}=\mathrm{CH}-$, -

···linking aromatic radicals, by atoms of N, O, or S leads to a change in the mechanism of transmission of electronic effects along this chain: the indicated atoms are insulators for the conjugation effect and can be conductors only of the induction effect. Koch ([10]) notes that in diaryl sulfides the so-called quasi-conjugation between aromatic nuclei is observed. A. A. Kharkharov ([11]) has recently expressed the view that the conjugation effect can be transmitted through the NH group. However, Brode ([12]), relying on the same spectroscopic data, concludes that the groups and atoms O, S, CH_2, and NH, which connect unsaturated organic radicals, are insulators for electronic interaction between the latter. Likewise, Mangini and Passerini ([13]) came to the conclusion that the sulfur bridge in aromatic sulfides cannot be regarded as a conductor of conjugation.

The present communication is devoted to the study of the indicated question by a chemical method. Here we set forth the results of an investigation of the kinetics of the acylation reaction of 4-aminodiphenyl oxide, 4-amino-4′-nitrodiphenyl oxide, and the corresponding sulfides with *p*-nitrobenzoyl chloride in benzene solution. The method used for measuring the acylation rate is an improved variant of the method proposed by us earlier ([14]) and consists in the fact that at a definite moment the reaction was interrupted by pouring diethylamine into the mixture of reacting substances, after which the unacylated amine was determined by potentiometric titration with sodium nitrite ([15]).

The bimolecular rate constants (k), the energy (E) and entropy (ΔS) of activation, and also the frequency factor (PZ) were calculated as indicated in previous communications ([2,3]). The numerical results for each of the reactions studied are collected in Table 1. Some data for reactions studied earlier are also given there.

Table 1

Amine	k 25°, l/mol · sec	k 50°, l/mol · sec	E, cal/mol	PZ, l/mol · sec	ΔS^{2+}, cal/deg · mol	f_{25°
4-Aminobiphenyl	0.533 ± 0.010	0.11 ± 0.02	5600	$7.1 \cdot 10^3$	−42.8	
4-Amino-4′-nitrobiphenyl	0.0505 ± 0.0011	0.118 ± 0.003	6500	$2.9 \cdot 10^3$	−44.7	10.6
4-Aminodiphenyl oxide	1.23 ± 0.03	2.60 ± 0.11	5550	$1.49 \cdot 10^4$	−41.5	

Amine	k 25°, l/mol · sec	k 50°, l/mol · sec	E, cal/mol	PZ, l/mol · sec	ΔS^{2+}, cal/deg · mol	f_{25°
4-Amino-4′-nitrodiphenyl oxide	0.102 ± 0.003	0.273 ± 0.006	7500	$3.4 \cdot 10^4$	−39.9	12.1
4-Aminodiphenyl sulfide	0.120 ± 0.006	0.300 ± 0.012	7000	$1.70 \cdot 10^4$	−41.2	
4-Amino-4′-nitrodiphenyl sulfide	0.00504± 0.00018	0.0178 ± 0.0008	9700	$6.3 \cdot 10^4$	−38.5	23.8
Aniline	0.580 ± 0.018	–	–	–	–	

From Table 1 it is seen that, in contrast to the phenyl group, which possesses a very weak electron-acceptor property (^{1,2}), the group C_6H_5O—exhibits a rather noticeable electron-donor action, since the rate constant on passing from aniline to 4-aminodiphenyl oxide increases by more than a factor of two. The analogous group C_6H_5S, on the contrary, has a clearly pronounced electron-acceptor nature, because its introduction into the para position of the aniline molecule leads to a decrease in the acylation rate by almost a factor of five.

In comparing experimental data characterizing some molecular system from the standpoint of its conductivity of the mutual influence of substituents, it is convenient to use the ratio of constants⋯

of the rates for reactions of the unsubstituted and substituted compounds, showing how the reaction rate changes when the given substituent acts through such a system on the reacting group (for example, in our case the indicated characteristic is the ratio of the acylation rate constants of the amine without the NO_2 group and of the amine containing this group in the 4′-position). We shall call this ratio of constants the factor of transmission of the electronic interaction of substituents, denoting it by the letter f.

When comparing the molecular systems of diphenyl oxide and diphenyl sulfide with the biphenyl system, one might have expected that the presence in the first two systems of O and S atoms separating the benzene nuclei would cause here a considerably weaker interaction between the NO_2 and NH_2 groups than is observed in the case of the biphenyl system, where the aromatic rings are joined directly. However, the result obtained proved quite unexpected: comparison of the values of the factor f_{25° (see Table 1) shows that the interaction of the substituents under consideration, on passing from the biphenyl system to the systems of diphenyl oxide and the corresponding sulfide, not only did not decrease, but, on the contrary, even increased slightly in the case of the oxygen-containing compound and became appreciably stronger in the molecule of the diphenyl sulfide derivative. Thus the O and S atoms, by spatially moving apart the two benzene nuclei, in essence do not play the role of insulators between them in the transmission of electronic influences. With the still small amount of experimental material on the study of similar systems by chemical methods, the noted fact is not easy to explain at present; but, most probably, not only the features of the spatial structure of the compounds under consideration (which we shall not touch upon for the moment in the present communication) may be of essential importance here, but also the presence, at their O and S atoms, of unshared p-electrons participating in conjugation with the aromatic nuclei (p, π-conjugation according to the definition of A. N. Nesmeyanov and M. I. Kabachnik ([16])). But whatever the reason for the peculiar behavior of the amino derivatives studied by us, it nevertheless remains indisputable at the present time that the effect of separating one of the substituents under consideration from the other, both in the diphenyl oxide derivative and in its thio analogue, is overridden by some new factor promoting the transmission of the interaction of these substituents through a system of two benzene nuclei joined to one another by bridging O and S atoms.

It should be noted that optical methods of investigation, widely used for studying the mutual influence of atoms in systems similar to those considered here, often lead, as was already indicated above, to contradictory results and do not always make it possible to reveal the same aspects of the problem of interest to us as do chemical methods. Already by visual comparison of the intensely orange-red 4-amino-4′-nitrobiphenyl with the light-yellow 4-amino-4′-nitrodiphenyl oxide and the corresponding sulfide, it is easy to arrive at the conclusion of a much stronger interaction of the NO_2 and NH_2 groups in the biphenyl derivative, which in fact is also confirmed by spectroscopic investigations of such compounds ([13,17,18]). However, there are no grounds for attributing the noted contradiction in the results of studying the mutual influence of substituents in these systems by optical and chemical methods to any experimental shortcomings of either of these methods. The indicated contradiction, however, is only apparent. The point is that each of these methods by itself does not make it possible with sufficient completeness to characterize all the manifold aspects of that complex problem which we call the mutual influence of atoms and atomic groups not directly bonded to one another. The case considered by us is an example of this, and all that has been set forth above is clear evidence that such questions must be studied comprehensively, involving not only optical and, in general, physical methods, but also

chemical methods, giving preference to data on the kinetics and equilibrium of chemical reactions as the most rigorous and exact.

As to how the reactions investigated in this work may be characterized by invoking energetic indices, we limit ourselves only to the remark that the indicated reactions, like those studied earlier by us ([1]-[3]), proceed at very low values of the energies and entropies of activation.

Kharkov State University
named after A. M. Gorky

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