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Abstract

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ON THE NON-COPLANARITY OF PHENYL NUCLEI IN DIPHENYL DERIVATIVES

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It has been established that in the biphenyl molecule in the crystalline state the phenyl nuclei are situated in one plane, despite the partial overlap of the spheres of the hydrogen atoms (located in the ortho positions) (^{1}). Evidently, the coplanarity of crystalline biphenyl is due to the special conditions of packing of the molecules in the crystal, the energy of slight compression of the hydrogen-atom spheres being compensated by the advantage of a planar arrangement (^{2}). At the same time it is known that in biphenyl in the liquid and vapor phases the phenyl groups are arranged non-coplanarly (^{3,4}). The non-coplanarity of the biphenyl nuclei in the absence of substituents in the *o*-positions has also been shown for a number of n, n'-substituted biphenyls in solution ($^{5-8}$). Data on the structure of such derivatives in the crystalline state, however, have hitherto been lacking.

One possible way of studying this question is the spectroscopic investigation of crystals of biphenyl compounds in the infrared region. In the present work this method was applied to the study of the structure of biphenyl ketones of the following structure:

$$\mathrm{CH_3O}-\between-\mathrm{CO}-\between-\between \tag{I}$$

$$\between-\mathrm{CO}-\between-\between-\mathrm{OCH_3} \tag{II}$$

$$\mathrm{H_2N}-\between-\mathrm{CO}-\between-\between \tag{III}$$

$$\between-\mathrm{CO}-\between-\between-\mathrm{NH_2} \tag{IV}$$

In biphenyl-*p*-anisyl ketone (I) and biphenyl-*p*-aminophenyl ketone (III), the electron-donor effect of the methoxyl and amino groups is transmitted to the ketone group through the phenyl rings, whereas in *p*-methoxydiphenyl phenyl ketone (II) and *p*-aminodiphenyl phenyl ketone (IV) this effect is transmitted through the biphenyl system.

It could be expected that, in the case of non-coplanarity of the phenyl nuclei in biphenyl, the mutual influence of the methoxy and amino groups with the carbonyl group in compounds II and IV, owing to disruption of conjugation, would be smaller than in compounds I and III. To verify this, it was necessary to characterize those changes that occur in the carbonyl under the influence of these groups when the effect is transmitted through phenyl and biphenyl systems. For this purpose we used determination of the frequency of the stretching vibration of the carbonyl group in the infrared spectrum.

As is known, the frequency of the stretching vibration of the carbonyl group shifts toward longer wavelengths as the π-electron interaction of the carbonyl group with other electron-donor groups of the molecule increases ($^{9-13}$). Accordingly, in the case of non-coplanarity of the nuclei, the frequency

vibration of the carbonyl group in compound I should be lower than in compound II, and in compound III lower than in compound IV.

Simultaneously with the spectroscopic study of the ketones in the crystalline state, they were also studied in dioxane solution.

For the study of solutions, polarographic determinations were also used. It is known that, upon reduction of ketones at a dropping mercury electrode, the half-wave potential ($\varphi_{1/2}$) shifts toward more negative values as π-electron conjugation increases, i.e., as the influence of the electron-donor group on the C=O group increases and the electron density at the latter increases (^{14}). It follows from this that, in compounds II and IV, in the case of noncoplanarity of the nuclei of the diphenyl residue, where conjugation will be smaller, $\varphi_{1/2}$ will be more positive than in compounds I and III. In the case of coplanarity, however, the values should be identical or should change in the opposite direction.

In the study, in addition to the indicated diphenyl ketones (I–IV), the corresponding benzophenones were also used for comparison (see Tables 1 and 2). The spectra were recorded on an IKS-II infrared spectrometer in the region 5-14 μ with a NaCl prism, and for the amines also in the region 2-5 μ with a LiF prism.

The substances were recorded in the crystalline state (as a suspension in a fluorinated hydrocarbon) and in dioxane solution. The accuracy of determining the frequency of vibration of the carbonyl group was ±2-3 cm^{-1}.

The polarographic studies were carried out on a Heyrovský micropolarograph in ammonia buffer (pH 8.2). The accuracy of determination was ±0.005 V.

All compounds were synthesized according to literature data and recrystallized to constant melting points.

Table 1

Compound	ν C=O, cm^{-1}: crystals in fluorinated hydrocarbon	ν C=O, cm^{-1}: solution in dioxane	$\varphi_{1/2}$, in relative N.C.E. (in ammonia buffer pH 8.4)
$C_6H_5-CO-C_6H_5$	1661	1664	−1.360
$C_6H_5-CO-C_6H_4-OCH_3$	1647	1653	−1.420
$CH_3O-C_6H_4-CO-C_6H_4-OCH_3$	1642	1647	−1.605
$C_6H_5-CO-C_6H_4-C_6H_5$	1653	1660	−1.275
$CH_3O-C_6H_4-CO-C_6H_4-C_6H_5$	1642	*	−1.340
$C_6H_5-CO-C_6H_4-C_6H_4-OCH_3$	1656	*	−1.275

* The products are insoluble in dioxane.

The results obtained are given in Tables 1 and 2. For illustration, the curves of part of the infrared spectrum for the methoxy compounds (Fig. 1) and the polarograms of the amino compounds (Fig. 2) are given.

As is seen from the data of Table 1, the influence of the electron-donor $-OCH_3$ group is manifested in a lowering of the characteristic frequency of vibration of the C=O group. The NH_2 group has the same influence (Table 2).

In compounds II and IV, where these groups interact through the diphenyl system, this influence is practically not observed, and the value of νC=O in these compounds is almost equal to the value of νC=O for unsubstituted diphenylphenyl ketone. A decrease in the magnitude of νC=O is observed for compounds both in solution and in the crystalline state.

All compounds with a methoxy and an amino group give a strong narrow band in the region 1595–1600 cm^{-1}, which may be assigned to vibrations of phenyl residues.

The observed considerable difference in νC=O for amines in the crystalline state and in solutions in dioxane is evidently due to intermolecular interaction of the NH_2- and C=O-groups through hydrogen bonds, which is diminished in dioxane solution.

For benzophenone amines the absorption bands for the C=O- and NH_2-groups coincide, since the absorption band of the stretching vibration of the C=O-group conjugated with the ring overlaps with the band of the deformation vibration of the NH_2 group in the aromatic ring. Only in the case of IV, owing to the merely insignificant interaction of these groups through the diphenyl residue (in dioxane solution), is a second band at 1622 cm^{-1} observed, which

Fig. 1. Infrared spectra of diphenyl-*p*-anisyl ketone (*I*) and *p*-methoxydiphenylphenyl ketone (*II*)

Table 2

Fig. 2. Polarograms of diphenyl-*p*-aminophenyl ketone (III) and *p*-aminodiphenylphenyl ketone (IV) (with addition of gelatin)

Figure 1: Fig. 2. Polarograms of diphenyl-*p*-aminophenyl ketone (III) and *p*-aminodiphenylphenyl ketone (IV) (with addition of gelatin)

Compound	ν C=O, cm^{-1}, crystals in polyfluorinated hydrocarbon	ν C=O, cm^{-1}, solution in dioxane	δ NH$_2$, cm^{-1} (solution in dioxane)	φ_2', in optical density units (in amyl ether)
$C_6H_5-CO-C_6H_5$	1661	1664	–	−1,360
$C_6H_5-CO-C_6H_4-NH_2$	1635	1646	1646	−1,450
$C_6H_5-CO-C_6H_4-C_6H_5$	1653	1660	–	−1,275
$NH_2-C_6H_4-CO-C_6H_4-C_6H_5$	1635	1650	1650	−1,380
$C_6H_5-CO-C_6H_4-C_6H_4-NH_2$	1652	1664	1622	−1,275

should be assigned to the deformation vibration of the NH_2 group (the vibration frequency of the NH_2 group in aniline is 1622 cm^{-1}).

Thus, from the IR-spectral data it may be concluded that the mutual influence of the groups in ketones II and IV, both in solution and in the crystalli-

state is accomplished through the diphenyl system to a considerably lesser extent than in the corresponding phenyl ketones.

The data of polarographic reduction are in full agreement with this conclusion. As is seen from Tables 1 and 2, the influence of the electron-donating groups OCH_3 and NH_2 through the phenyl ring is manifested in a certain shift of $\varphi_{1/2}$ toward negative values. At the same time, in ketones II and IV there is observed –

Fig. 2. Polarograms of diphenyl-*p*-aminophenyl ketone *(III)* and *p*-aminodiphenylphenyl ketone *(IV)* (with addition of gelatin)

–a shift toward positive values, which indicates a decrease in conjugation and a hindrance to the transmission of mutual influence through the diphenyl system.

All the data presented here on the hindrance to the transmission of the mutual influence of groups in ketones II and IV may be regarded as an indication of the nonplanarity of diphenyl in these compounds, both in solutions and in the crystalline state.

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