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Abstract

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ON THE STRUCTURE OF 2-*p*-NITROPHENYLINDANDIONE-1,3

In studying amino derivatives of 2-arylindandiones-1,3, we included in the scope of our investigations also 2-*p*-nitrophenylindandione-1,3 (NPI) (I). It is of interest because, unlike the colorless 2-phenylindandione-1,3, it is a dark-red substance. 2-Chloro- and 2-bromo-NPI are colorless; bis-*p*-nitrophenylindandione-1,3 is also colorless, whereas 2-amino derivatives of NPI are yellow or orange substances, like the amino derivatives of 2-phenyl- and 2-anisylindandione-1,3 (1–4).

It is of interest to determine what causes the color of NPI. To explain this phenomenon solely by the empirical fact that introduction of a nitro group deepens the color of many compounds would be erroneous, since it is known that even 2,4-dinitrophenylindandione-1,3 is completely devoid of color (5). It has been noted in the literature (6,7) that phenylindandiones having an electrophilic substituent (Cl, Br, I) in the *p*-position of the phenyl radical exhibit the phenomenon of polychromism. Depending on the nature of the solvent from which these compounds are obtained, they possess different colors: from polar solvents they crystallize as red substances, from nonpolar ones as colorless substances. These compounds also show thermochromism. On determination of melting points, the red forms pass into colorless ones. There are indications (7) that the red form of NPI is stable and does not change under the influence of temperature and solvent. Some authors explain the change in color of arylindandiones in polar solvents by dis-

Fig. 1. U.-v. absorption spectra in abs. methanol:
a –NPI, *b* –Na salt of NPI;
c –Na salt of 2-phenylindandione

Fig. 2. U.-v. absorption spectra:
a –NPI in dichloroethane, *b* –methyl ether of NPI in dichloroethane; *c* –methyl ether of NPI in abs. methanol

Structural formulas (I)-(VI)

Figure 2: Structural formulas (I)-(VI)

placement of the keto-enol tautomeric equilibrium toward formation of the enol form (II) (^{7}). Apparently, elevated temperature

and low-polar solvents favor the opposite process—the formation of the diketo form (I). But one cannot fail to take into account the possibility of the existence of NPI also in the valence structures (III) and (IV). To resolve this question, we subjected NPI and some of its derivatives available to us to spectroscopic study in the ultraviolet and infrared regions. The methyl ether of its enolic form, obtained by the action of an ethereal solution of diazomethane on NPI, was also investigated (orange substance, m.p. 190–192°. Found, %: N 5.24. $C_{16}H_{11}O_4N$. Calculated, %: N 4.98).

The UV absorption spectra of NPI and of its Na salt in a solution of absolute methanol are characterized by identical absorption curves (Fig. 1). It is evident that the electronic structure of NPI in solution is the same as the electronic structure of its anion. Consequently, NPI is dissociated in a solution of absolute methanol. Comparison of the UV spectra of structurally similar Na salts of

2-phenylindandione-1,3 and NPI shows that the nature of the absorption of these enolate anions differs. This is quite understandable, since equalization of the electron density in the enolate anion of 2-phenylindandione-1,3 proceeds mainly toward the carbonyl group (V).

In the case of the enolate anion (VI), owing to the presence of a system of conjugated bonds, equalization of the electron density also proceeds toward the nitro group. Extension of the system of conjugated bonds entails intense absorption at 440 mμ ($\varepsilon = 22200$).

The UV spectrum of NPI in dichloroethane gives an absorption curve characteristic of the diketo form (Fig. 2), and is characterized by λ_{max} at 229 mμ and ε respectively 43000. The IR spectral data of a saturated solution of NPI in dichloroethane agree with the UV spectral data and are characterized by two frequencies of the carbonyl groups at 1717 and 1750 cm^{-1}. In 2-bromo-, 2-anilino-, and 2-piperidino derivatives of NPI, in which the diketo form is fixed, absorption of the carbonyl groups is observed respectively at 1718 and 1750 cm^{-1}, 1707 and 1747 cm^{-1}, 1705 and 1742 cm^{-1}.

At the same time it must be noted that 0.0001 M solutions of NPI in dichloroethane are completely colorless. If a suspension of red NPI in chloroform or dichloroethane is left in a closed vessel at room temperature, then on prolonged standing a gradual transformation of the red form into a crystalline colorless form is observed, which is undoubtedly the diketo form. In the process of isolation from solution it is converted back into the red form. These data refute the view existing in the literature that NPI exists only in the red form, structural formula VII

Figure 3: structural formula VII

which is not interconvertible into the white form (7). Evidently, NPI differs in no way from other substituted in the *n*-position by electrophilic substitu-

derivatives of 2-phenylindandiones-1,3. The red form here is only more stable.

The UV spectrum of the methyl ether of the enol form of NPI in abs. methanol differs substantially from the spectrum of NPI itself. In dichloroethane solution, for the enol ether $\lambda_{\text{max}} = 245$ mμ ($\varepsilon = 29000$). For the enol ether in methanolic solution a small shift of the K band toward shorter wavelengths is observed ($\lambda_{\text{max}} = 242$ mμ; $\varepsilon = 24000$). The IR spectrum of the methyl ether of the enol form in a 0.01 M solution of dichloroethane confirms the correctness of its enol-ether structure, since absorptions of the CO group are observed at 1700 cm^{-1}, of the double bond in the 5-membered ring at 1622 cm^{-1}, and of ν_{NO_2} (asym.) at 1522 cm^{-1}. The elevated values of $\nu_{\text{C=O}}$ may be explained by the influence of strain in the 5-membered ring, which usually somewhat raises the vibrations of the CO group (9).

The IR absorption spectrum for red NPI, recrystallized from glacial acetic acid and suspended in paraffin oil, rules out its existence in the form of the diketo form (I), since no absorption of CO groups is observed. If the sample is recrystallized from water, then, alongside other vibrations, frequencies of CO groups appear at 1700 and 1735 cm^{-1} of medium intensity. We believe that partial conversion into the diketo form occurs under the influence of the solvent, since both samples were dried under identical conditions ($\sim 140^\circ$, 2 hours). The IR spectroscopic data also do not give us grounds to consider that the red form of solid NPI is an enol (II). We were unable to establish absorption of an enolic hydroxyl. The spectrum has little in common with the spectrum of its enol ether. The data obtained force us also to reject the structure of diketonitronic acid (IV), since the absorption characteristic of an α,β-unsaturated diketo grouping is not observed. The spectrum of red NPI shows great similarity to the spectrum of its Na salt. The overall picture of the spectrum in the double-bond region is thereby so complicated that it is unambiguously difficult to speak of the characteristic frequencies of individual groups. The very intense broad absorption maximum at 1514–1529 cm^{-1}, which is characteristic of the enolate anion of 2-phenylindandione, is not observed in the spectrum, although absorption is noted in the region of 1510 cm^{-1}. The substance absorbs intensely in the regions 1340–1350 cm^{-1} and 1560–1570 cm^{-1}.

The IR spectroscopic data thus show that NPI in the solid state probably exists as an ionized form with an equalized electronic structure. In such systems, as has been noted in the literature (8) in the study of the tautomerism of acetylacetone, it is difficult to speak of characteristic group frequencies.

VII $\left(\delta' > \frac{1}{2};\ 2\delta + 2\delta' = 2\right)$

We assume that in our case, in the crystal lattice of NPI, the proton is held in the electronic field of the carbonyl groups of two neighboring molecules (VII), and the equalization of electron density proceeds mainly toward the carbonyl groups. Similarly, in the case of diquinolyl-(2)-methane, it is assumed that the mobile proton is firmly held in the field of the free electron pairs of both nitrogen atoms of one molecule ([10]).

Thus, studies of NPI show that it is a highly mobile system which, in polar solvents and, probably, also in the solid state, exists as an anion with a leveled electronic structure and is capable of mutual interconversion. In weakly polar solvents it exists in the form of a colorless diketo form. The NPI anion possesses dual reactivity: thus, with diazomethane it gives the methyl ether of the enol form, while with bromine and chlorine it gives the 2-chloro and 2-bromo derivatives.

We believe that other hitherto known 2-arylindandiones-1,3 with electrophilic substituents in the *n*-position of the phenyl radical, in the red form, possess the properties and structural features of NPI.

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