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Structural formulas I and II: tautomeric forms of anils of o-hydroxyaldehydes

Figure 1: Structural formulas I and II: tautomeric forms of anils of o-hydroxyaldehydes

Abstract

Full Text

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DIPOLE MOMENTS AND ABSORPTION SPECTRA OF ANILS OF *o*-HYDROXYALDEHYDES

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Recently interest has increased in anils and alkylimines of *o*-hydroxyaldehydes (^{1,2}), on the basis of which a number of intracomplex compounds with valuable properties have been obtained. In the study of the indicated anils, structural problems arise that are connected with the possibility of prototropy of the type:

$$\text{(I)} \rightleftharpoons \text{(II)}$$

Regardless of whether structure I or II is realized, these compounds contain a strong intramolecular hydrogen bond (^{3}); moreover, on the basis of data on the dipole moment (^{4}) and electronic absorption spectra (^{5}), preference was given to the quinoid form II. It was noted (^{1,2}) that solutions of alkylimines of salicylaldehyde and 2-hydroxynaphthaldehyde also contain appreciable amounts of the quinoid form, as can be judged from the appearance of a long-wavelength absorption band (410 mμ), the intensity of which increases in polar solvents. Finally, the spectral changes of salicylideneanilines in the glassy state under ultraviolet irradiation were also proposed to be explained (^{6}) by the benzenoid-quinoid transformation I → II.

However, a careful study of the cited works ($^{4-6}$) shows that the tautomerism of anils of *o*-hydroxyaldehydes is rather a convenient hypothesis for explaining certain anomalies in their physical properties than a rigorously proven fact. In connection with this, we have carried out a further study of anils of *o*-hydroxyaldehydes.

The dipole moments of a series of anils were determined, and the values obtained were compared with calculated quantities. The measurements were carried out in benzene at 25° in accordance with the method (^{7}). The nature of the dependence of molecular polarization on concentration and cryoscopic data indicate the absence of association due to intermolecular hydrogen bonds at concentrations up to 0.03 mole fractions.

In calculations, for the moment of the C=N bond the value 1.4 D ([8]) was taken, and for Ar → N, 0.6 D ([9]); the remaining moments are given in reviews ([10,11]). Taking into account the tendency of the atoms forming the hydrogen bond toward collinearity, the valence angle of oxygen was taken to be tetrahedral, the angles at the double bond equal to 120°, and the other angles were calculated from the values of covalent radii ([12]).

The data from measurements and calculations are presented in Table 1.

In the absence of polar substituents in the anil molecules, the experimental values of the dipole moments agree satisfactorily with the values calculated both for structure I and for structure II, which does not allow a choice to be made between them and may lead to an erroneous

Table 1

No.	R_1	R_2	μ, D	For I μcalc, D	For II μcalc, D	mOH···N, D
1	H	H	2.39	2.7	2.8	0.4
2	H	4-Br	2.28	2.5	3.9	0.4
3	H	4-CH_3	2.63 (13)	2.9	2.6	0.4
4	H	2,4-di CH_3	2.37	2.5	2.4	0.2
5	H	2,4,6-tri CH_3	2.81	2.7	2.8	0
6	H	3-NO_2	3.81	4.3*	5.3	0
7	H	4-NO_2	4.18	4.5**	6.1	–
8	5,6-C_6H_4	H	2.18	2.7	2.8	0.6
9	5,6-C_6H_4	4-CH_3	2.43	2.9	2.6	0.6
10	5-NO_2	H	4.03	4.4**	1.2	1.5
11	5-NO_2	2,4-di CH_3	4.47	4.7**	1.6	1.5
12	5-NO_2	2,4,6-tri CH_3	3.95	4.4**	1.2	1.5
13	5-NO_2	4-Br	2.97	3.1**	1.7	0.4
14	Benzylideneaniline	Benzylideneaniline	1.61	1.6	–	–
15	*o*-Methoxybenzylideneaniline	*o*-Methoxybenzylideneaniline	2.87	2.5	–	–

* Calculated for a conformation in which the aniline aromatic nucleus lies in a plane perpendicular to the plane of the aldehyde nucleus. For coplanar conformations the calculation gives $\mu = 1.3$ D and 6 D.

structural formulas III and IV

Figure 2: structural formulas III and IV

** In the calculations the influence of the mesomeric effect of the nitro group was taken into account.

interpretation of the structure (^{4}). If, however, substituents with a sufficiently large group moment are present in one or both aromatic nuclei, comparison of the experimental and calculated values of μ convincingly testifies in favor of structure I. At the same time, one more proof of the presence of a strong intramolecular hydrogen bond can be obtained.

Calculation of the dipole moment of salicylideneaniline under the assumption of free rotation about the C—O bond leads to a value of 1.6 D.

Some deviations of μ, calculated for I, from the experimental value might seemingly be attributed to the presence of small amounts of the quinoid form II; however, our measurements of the IR absorption spectra (in the solid phase and in CCl_4 solution) do not reveal a carbonyl group. Such a possibility is also ruled out by crystallographic studies of salicylideneanilines (^{6}). The calculated values μ of the dipole moments can be reconciled with the experimental ones if the moment arising upon formation of the hydrogen bond and resulting from its electrostatic nature is taken into account. The values of the moments mOH···N, calculated by the vector scheme, are given in Table 1. They agree well with the values obtained for intermolecular hydrogen bonds of a similar type (^{14}, ^{15}).

It is evident that the sharp increase in mOH···N for derivatives of 5-nitrosalicylaldehyde is due to a mesomeric displacement III that facilitates protonation

(III) (IV)

or, in other terms according to Coulson (^{16,17}), by an enhancement of the delocalization effect and an increasing contribution of structure IV in describing the molecules by the valence-bond method.

The results of dipole-moment measurements are supplemented and confirmed by data on the electronic absorption spectra (in methanol). In the spectra of the anils of *o*-hydroxyaldehydes (Table 2), four absorption bands can be distinguished.

Table 2

No.	R_1	R_2	Band* E_1	Band* E_2	Band* K	Band* R
1	Benzylideneaniline (^{18})		213 (5)	260	305	–

No.	R_1	R_2	Band* E_1	Band* E_2	Band* K	Band* R
2	*o*-Methoxybenzylideneaniline	–	220 (16600)	265 (11500)	325 (10400)	432 (44)
3	H	H	227 (17100)	268 (11600)	333 (10800)	432 (169)
4	H	4-CH_3	223 (20700)	269 (13300)	340 (15300)	431 (156)
5	H	2-OH	221 (26300)	270 (11700)	350 (14500)	445 (1600)
6	H	3-OH	227 (17000)	266 (10700)	340 (10900)	436 (260)
7	H	4-OH	218 (28500)	267 (13500)	329 (13600)	430 (170)
8	H	3-NH_2	223 (22100)	270 (21800)	340 (11000)	429 (57)
9	H	4-NO_2	–	–	358 (18600)	–
10	Disalicylidene-*o*-phenylenediamine		222** (22400)	256 (19000)	325 (11400)	400 (4500)
11	5,6-C_6H_4	H	232 (32400)	316 (9300)	456 (10800)	–
12	5,6-C_6H_4	4-CH_3	231 (40000)	317 (11800)	457 (14700)	–

* The wavelength is given in mµ. The value of ε is given in parentheses.
** Shoulder.

absorption, of which the bands E_1, E_2, K correspond, in all probability, to $N \to V$, and the R-band to $n \to \pi^*$ electronic transitions. The band E_2 has been proposed (^{18,19}) to be assigned to an electronic transition localized in the aromatic nucleus; it is associated with the band $\lambda = 203.5$ mµ of benzene. From the data in Table 2 it follows that this band is due to transitions in the aromatic nucleus of the aldehyde component.

The band E_2 is the result of an electronic transition involving the aldehyde aromatic nucleus and the π-electrons of the double bond, since the position of this band is almost independent of substituents in the amine nucleus. The band K apparently characterizes an electronic transition over the whole chain of conjugated bonds of the molecule. The most interesting consequences follow from consideration of the R-band. It had been assumed (^{2,5}) that this particular band owes its origin to the presence of the quinoid form, since it is absent in *m*-isomers or alkoxy compounds.

Our study of the absorption spectrum of *o*-methoxybenzylideneaniline, however, made it possible to establish for this compound the presence of a low-intensity *R*-band in the very same region as for derivatives of salicylideneaniline. In the latter case the intensity of the *R*-band is considerably increased owing to the intramolecular hydrogen bond, and it is more readily detected. An increase in the intensity of the *R*-band for the analogous case of benzaldehydes and salicylaldehydes had already been noted earlier (20) and may be regarded as a characteristic sign of an intramolecular hydrogen bond. Thus, the results of measurements of the dipole moments and absorption spectra of a series of anils of *o*-hydroxyaldehydes prove the presence of a strong intramolecular hydrogen bond leading to chelation. With the aid of the methods indicated, it is not possible to detect the tautomeric benzenoid-quinoid equilibrium postulated by a number of authors (4–6).

Let us note that the appearance of a long-wavelength band in the spectra of alkylimines of salicylaldehyde can also be successfully explained by means of the concept of an intramolecular hydrogen bond (^21), without invoking ideas of tautomerism.

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