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structural formulas (1) and (2)

Figure 1: structural formulas (1) and (2)

coordinate axes and conformations A–D

Figure 2: coordinate axes and conformations A–D

Abstract

Full Text

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FEATURES OF THE INTRAMOLECULAR HYDROGEN BOND IN MOLECULES OF ANILS OF *o*-HYDROXYALDEHYDES AND *o*-HYDROXYANILS

(Presented by Academician Ya. I. Syrkin, 27 VIII 1964)

In the present work we studied the features of intramolecular hydrogen bonds (I.H.B.) in six- and five-membered rings, using as examples anils of types (1) and (2), for which the presence of a strong I.H.B. has been well established ([4–8]) and a nonplanar structure has been demonstrated ([9]).

Delocalization of π-electrons through the I.H.B., if it occurs, will evidently lead to the appearance of an additional electric dipole moment, the vector $\Delta\vec{\mu}$ of which can be determined by comparing the experimental value $\vec{\mu}_{\mathrm{op}}$ with the value $\vec{\mu}_{\mathrm{r}}$, calculated without taking into account the perturbation introduced by the I.H.B.:

$$\Delta\vec{\mu} = \vec{\mu}_{\mathrm{op}} - \vec{\mu}_{\mathrm{r}}.$$

The method we used for calculating $\vec{\mu}_{\mathrm{r}}$, which makes it possible to exclude the influence of intramolecular conjugation effects not caused by the I.H.B. ([10]), may be illustrated by the examples of salicylalaniline (1) $R_1 = R_2 = H$ and benzal-*o*-aminophenol (2), $R_3 = C_6H_5p$.

A: $m_x = -1.34$ (here and below all values of μ and their projections are given in debyes), $m_y = 0.78$; **B:** $m_x = 0.84$, $m_y = 0.95$; **C:** $m_x = 1.34$, $m_y = 0.55$, $m_z = -0.55$; **D:** $m_x = -0.84$, $m_y = -0.47$, $m_z = 0.82$; **E:** $m_x = -0.84$, $m_y = 0.47$, $m_z = -0.82$.

In the specified coordinate system $\vec{\mu}_{\mathrm{r}}$ of salicylalaniline can be represented as the sum of the moment vectors of benzalanyline and phenol in configuration A, while μ_{r} of benzal-*o*-aminophenol can be represented as the sum of the moment vectors of benzalanyline and phenol in configuration B. The moment vector of phenol (as also of anisole and *p*-bromophenol) is known (^{10}); it is only necessary to transform it correspondingly into the coordinate system, while the moment vector of benzalanyline is calculated from μ_{op} of benzalanyline, benzal-*p*-toluidine, and the moment of the CH_3 group (0.4 D). In an analogous way $\vec{\mu}$ values are determined for other anils whose molecules are bases of compounds with I.H.B. (Table 1).

Let us first consider compounds with a six-membered I.H.B. ring (1). Table 2 gives the values, calculated by the above method, of $\vec{\mu}_{\mathrm{r}}$ (not taking into account the redistribution of electrons upon closure of the I.H.B.) and $\vec{\mu}_{\mathrm{op}}$, in which this effect is taken into account. The vector $\vec{\mu}_{\mathrm{op}}$ was determined, as also for the anils given in Table 1, from the moments of compounds (1) with $R_2 = H$ and $R_2 = n\text{-}CH_3$.* The last column gives the vector $\Delta\vec{\mu}$.

The data of Table 2 show that the formation of an I.H.B. leads to a decrease of the dipole moment in comparison with the additive value μ_{r} by 0.5–0.9 D. In this case the vector of the additional moment $\Delta\vec{\mu}$ has negative x- and y-components, i.e., its positive pole is located

Table 1

Skeleton of a molecule with an IHB	Anil moments from which the skeleton projections were calculated	$\vec{\mu}\ m_x$	$\vec{\mu}\ m_y$	Skeleton of a molecule with an IHB	Anil moments from which the skeleton projections were calculated	$\vec{\mu}\ m_x$	$\vec{\mu}\ m_y$
I	Benzalaniline, 1.60(6)	0	1.60	VI	*p*-Bromobenzalaniline, 1.79	−0.80	1.60

* μ of salicylal-*p*-toluidine is 2.65 D; 5-bromosalicylal-*p*-toluidine, 2.58 D; 2-hydroxynaphthal-*p*-toluidine, 2.43 D (^{5,6}).

Skeleton of a molecule with an IHB	Anil moments from which the skeleton projections were calculated	$\vec{\mu}\ m_x$	$\vec{\mu}\ m_y$	Skeleton of a molecule with an IHB	Anil moments from which the skeleton projections were calculated	$\vec{\mu}\ m_x$	$\vec{\mu}\ m_y$
II	Benzal-*p*-toluidine, 1.65α-Naphthalaniline, 1.66α-Naphthal-*p*-toluidine, 1.63	0.33	1.63	VII	*p*-Dimethylaminobenzalaniline, 3.54	3.16	1.60
III	Benzal-α-naphthylamine, 1.67*p*-Nitrobenzal-α-naphthylamine, 4.00	0.35	1.63	VIII	Ferrocenalaniline, 2.25Ferrocenal-*p*-toluidine, 1.98	1.63	1.55
IV	*p*-Nitrobenzalaniline, 4.10	−3.77	1.60	IX	2-Furalaniline, 2.012-Fural-*p*-toluidine, 1.87	0.88	1.81

Skeleton of a molecule with an IHB	Anil moments from which the skeleton projections were calculated	$\vec{\mu}$ m_x	$\vec{\mu}$ m_y	Skeleton of a molecule with an IHB	Anil moments from which the skeleton projections were calculated	$\vec{\mu}$ m_x	$\vec{\mu}$ m_y
V	*p*-Methylbenzalaniline, 1.93	1.07	1.60	X	5-Nitro-2-furalaniline, 4.02 5-Nitro-2-fural-*p*-toluidine, 4.34	−3.15	2.50

(Structural formulas I–X are shown in the source page.)

Table 2

Compound	$\vec{\mu}_p$ m_x	$\vec{\mu}_p$ m_y	μ_p	$\vec{\mu}_{\mathrm{OP}}$ m_x	$\vec{\mu}_{\mathrm{OP}}$ m_y	μ_{OP}	$\Delta\vec{\mu}$ m_x	$\Delta\vec{\mu}$ m_y	$\Delta\mu$
R_1=R_2=H	−1.34	2.38	2.73	−1.44	1.91	2.39	−0.10	−0.47	0.47
R_1=5-Br, R_2=H	−2.12	1.02	2.36	−2.16	0.16	2.16	−0.04	−0.86	0.86
R_1=4,5-C_6H_4, R_2=H	−1.01	2.41	2.62	−1.42	1.60	2.18	−0.41	−0.81	0.90
R_1=H, R_2=2,3-C_6H_4	−0.99	2.41	2.62			2.38			

on oxygen, and not on nitrogen. In order to make sure that the appearance of

$\Delta\mu$ is a consequence of the IHB, it is necessary to establish that the discrepancy between μ_{OP} and μ_p is not simply the result of enhanced conjugation of the p-electrons of the hydroxyl group with the π-electrons of the aromatic nucleus conjugated with the electron-acceptor arylazomethine group. If there is no such additional conjugation, then for methyl ethers (1) and (2) the values of μ_p and μ_{OP} should coincide. Indeed, as is seen from the data of Table 3, the agreement of these quantities is quite satisfactory.*

Thus, the differences between μ_{OP} and μ_p, determined by the indicated method, are caused by the formation of an IHB. At the same time it is very important that the appearance of $\Delta\mu$ in compounds of type (1) cannot be regarded (Coulson(11)) simply as the result of the contribution of ionic structures

$\overset{+}{\mathrm{O}}\mathrm{H} - \overset{+}{\mathrm{N}}=$,

included in the quantum-mechanical description(11–13) of the hydrogen bond. This is immediately indicated by the direction of the vector $\Delta\mu$ (Table 2), opposite to that which would occur upon the contribution of the noted ionic structure.

Calculations of $\Delta\vec{\mu}$ by the LCAO MO method show that the origin of this quantity is associated with delocalization of π-electrons through the IHB.**

* In calculating μ for methyl ethers (1) it was taken into account that the preferred(6) configuration is the B-configuration of the anisole fragment of the molecule, and in the case of methyl ethers (2) the configurations and are equally probable.

** Details of the calculations of such molecules and the justification for the choice of parameters for heteroatoms were given by us earlier(9,15). The calculations were carried out on an M-20 electronic digital computer using a program compiled by Yu. A. Ostroumov.

Table 3

Compound	μ_{op}	μ_{p}	Compound	μ_{op}	μ_{p}	Compound	μ_{op}	μ_{p}
(1) R_1, R_2 = H	2.87(6)	2.70	(2) R_3 = C_6H_5	1.91	2.00	(2) R_3 = C_6H_4Br-n	2.42	2.46
(1) R_1 = $4,5$ = C_6H_4, R_2 = H	2.79	2.82	(2) R_3 = $C_6H_4NO_2$-n	4.91	4.96	(2) R_3 = 5-nitrofuryl-2	4.64	4.78
(1) R_1 = H, R_2 = $2,3$ = C_6H_4	2.92	2.85						

molecular diagrams

Figure 3: molecular diagrams

In molecular diagram (3) the π-electron configuration, the delocalization energy, and the π-component of the dipole moment of salicylal-aniline are given, calculated under the assumption of orthogonality of the atomic orbitals; in this calculation the perturbation introduced by the intramolecular hydrogen bond was in no way taken into account. In describing this effect within the framework of the LCAO MO method, it is apparently best to abandon attempts to determine exactly the form of the hydrogen-provided orbital ([4,13,14]) and simply to assign a small exchange integral to the bond closed by the H bridge ([2,3]). Such a model corresponds well to the idea of delocalization through an intramolecular hydrogen bond. The choice of $\beta_{\mathrm{O-H...N}}$, of course, was made with regard to the qualitative nature of the problem posed; it is not especially important. In the present case we used the value $\beta_{\mathrm{O-H...N}} = 0.2\beta^{\circ}$. The electron configuration calculated with allowance for π-delocalization through the intramolecular hydrogen bond, and the values DE and $\vec{\mu}_{\pi}$ of salicylal-aniline, are given in molecular diagram (4).

(3) $DE = 21.46\,\beta^{\circ}$; $\vec{\mu}_{\Pi} = 4.33\mathbf{i}{+}2.23\mathbf{j}$ (4) $DE = 21.50\,\beta^{\circ}$; $\vec{\mu}_{\Pi} = 4.29\mathbf{i}{+}1.99\mathbf{j}$

Comparison of (3) with (4) makes it possible to calculate the increase in the dipole moment due to delocalization through the intramolecular hydrogen bond as the difference of their π-moments:

$$\Delta\vec{\mu} = \vec{\mu}_{\pi}^{\mathrm{H}} - \vec{\mu}_{\pi} = e\sum_{i}\left(q_i^{\mathrm{H}} - q_i\right)\vec{r}_i.$$

Here the index H refers to the charge distribution obtained with allowance for the intramolecular hydrogen bond (4), q_i is the charge, and $\vec{r}_i$ is the radius vector of the i-th atom. The calculation gives

$$\Delta\vec{\mu} = -0.04\mathbf{i} - 0.24\mathbf{j} \qquad (\Delta\mu = 0.25\,D).$$

In this case $\Delta\mu$ is subtracted from μ_{p}, as is required by the experimental results. The latter are also consistent with the predicted direction of $\Delta\mu$, whose vector, according to the calculation, forms an angle of 99.5° with the x axis, whereas the experiment gives 102°. The absolute value of $\Delta\mu$ obtained in the calculation, somewhat underestimated in comparison with the experimental value, indicates that π-delocalization through the intramolecular hydrogen bond is apparently still more significant than was allowed for by the conditions of the calculation. Thus it is clear that the appearance of an increment $\Delta\mu$ in molecules of type

(1) is associated with delocalization of π-electrons through the intramolecular hydrogen bond.

A different picture is observed on going to compounds of type (2), with a five-membered ring of the intramolecular hydrogen bond. Because of the acoplanarity of this ring, due to the nonplanar structure of the backbone, π-delocalization through the intramolecular hydrogen bond is strongly weakened or does not appear at all. It is precisely this circumstance that accounts for the sharp differences in the character of the UV spectra (^{7,8}) and in the reactivity of compounds of this type and of (1). The results presented below of measurements and calculations of the dipole moments of compounds of type (2) confirm the conclusion that there is no interaction of π-electrons through—

···without H-bonding. As is seen from the data in Table 4, the experimental μ_{op} and calculated μ_p values agree well.

Table 4

Compound (2), R_3	μ_{op}	μ_p	Compound (2), R_3	μ_{op}	μ_p	Compound (2), R_3	μ_{op}	μ_p
I	2.73	2.60	IV	5.08	5.02	VII	3.69	3.68
II	3.20	3.26	V	3.90	3.30—?	VIII	3.19	3.28
III	2.39	2.29	VI	2.85	2.80	IX	3.63	3.60

The values of μ_p in Table 4 and the projection of the phenol moment vector in configuration C were calculated for an angle $\theta = 45^\circ$ (and not 60°, as is usual). We note, however, that this is almost not reflected in the values of μ_p.

For comparison with (3) and (4), the electron-density distribution in the molecule of benzyl-*o*-aminophenol (2), $R_3 = \mathrm{C_6H_5}$ (without taking H-bonding into account and with $\beta_{\text{O–H...N}} = 0.1\,\beta^\circ$), was calculated by the LCAO MO method. The results of the calculations are presented, respectively, in the molecular diagrams (5) and (6).

$$DE = 21.38\,\beta^\circ; \quad \vec{\mu}_{\text{II}} = 24.63\,\mathbf{i} + 0.90\,\mathbf{j} - 2.53\,\mathbf{k}. \tag{5}$$

$$DE = 21.38\,\beta^\circ; \quad \vec{\mu}_{\text{II}} = -4.82\,\mathbf{i} + 0.97\,\mathbf{j} - 2.58\,\mathbf{k}. \tag{6}$$

The calculations show that, if in compounds of type (2) π-delocalization through H-bonding were to occur, this would lead not to a decrease, as in (1), but to an increase of the dipole moment in comparison with μ_p.

The established presence of π-delocalization through H-bonding in compounds (1), in contrast to (2), is in good agreement with the ideas on quasiaromaticity developed by D. N. Shigorin [4].

The synthesis and characteristics of the anils investigated by us are described in [16], and the method for measuring dipole moments in [17]. The measurements were carried out in benzene at $25 \pm 0.03°$. The errors in the values of μ_{op}, estimated according to [18], nowhere exceed ±1% of the measured value.

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CITED LITERATURE

1. A. Sent-Dyerdyi, *Bioenergetics*, 30, Moscow, 1960.
2. M. S. Evans, J. Gergely, *Biochim. et biophys. acta*, **3**, 188 (1949).
3. B. Pullman, A. Pullman, *Quantum Biochemistry*, N. Y., 1963.
4. D. N. Shigorin et al., *Izv. AN SSSR, ser. fiz.*, **14**, 395 (1953); *DAN*, **132**, 1372 (1960); *ZhFKh*, **37**, 2432 (1963).
5. V. I. Minkin, O. A. Osipov, V. A. Kogan, *DAN*, **145**, 336 (1962).
6. O. A. Osipov, V. I. Minkin, V. A. Kogan, *ZhFKh*, **37**, 1492 (1963).
7. G. M. Badger, A. G. Moritz, *J. Chem. Soc.*, 1958, 3437.
8. A. W. Baker, A. T. Shulgin, *J. Am. Chem. Soc.*, **81**, 1523 (1959).
9. V. I. Minkin, E. A. Medyantseva, A. M. Simonov, *DAN*, **149**, 1347 (1963).
10. B. Eda, K. Ito, *Bull. Chem. Soc. Japan*, **29**, 524 (1956); **30**, 164 (1957).
11. C. A. Coulson, *Hydrogen Bonding*, London, 1959, p. 339.
12. C. A. Coulson, *Research*, **10**, 149 (1957).
13. D. N. Sokolov, *UFN*, **57**, 242 (1955).
14. L. Paoloni, *J. Chem. Phys.*, **30**, 1045 (1959).
15. V. I. Minkin, E. A. Medyantseva, Yu. A. Ostroumov, *ZhOKh*, **34**, 1512 (1964).

16. Yu. A. Zhdanov, I. D. Sadekov et al., *Izv. Vyssh. ucheb. zaved.* (in press).

17. V. I. Minkin, O. A. Osipov, A. D. Garnovskii, *ZhFKh*, **36**, 469 (1962).

18. R. J. W. Le Fevre, *Dipole Moments*, London, 1948.

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