CHEMISTRY

V. I. MINKIN, E. A. MEDYANTSEVA, A. M. SIMONOV

1963

SovietRxiv

schematic molecular conformations I, II, III

Figure 1: schematic molecular conformations I, II, III

Abstract

Full Text

CHEMISTRY

V. I. MINKIN, E. A. MEDYANTSEVA, A. M. SIMONOV

ON THE ACOPLANARITY OF MOLECULES OF BENZALANILINE AND ITS DERIVATIVES

(Presented by Academician B. A. Arbuzov, 28.XI.1962)

For a correct interpretation of the chemical behavior and physical properties of anils of aromatic aldehydes, data are needed on their preferred molecular conformation.

As such, in almost all works devoted to the structure of anils, for example (1−3), the planar structure I is adopted (the angle between the planes of the two aromatic nuclei is $\theta = 0°$).

The lone pair of nitrogen electrons (the n-orbital) is thereby completely excluded from conjugation, since it is approximately sp^2-hybridized (4) and its axis lies in the plane of the molecule. Clearly, this should mean increased nucleophilicity of the azomethine nitrogen. Upon rotation of the amine nucleus about the C—N bond through an angle $\theta = 90°$, another limiting conformation II arises, in which the chain of π,π-conjugation is broken. However, the energetic destabilization of the ground state of the molecule that follows from this is to some extent compensated by involvement of the n-electrons in conjugation with the π-electrons of the amine series (5). The latter circumstance should lead to a decrease in the basicity of the nitrogen atom and to hindrance of quaternization reactions.

Finally, it should be pointed out that the possibility, usually not taken into account, exists for the realization of some intermediate conformation III ($0° < \theta < 90°$). In this conformation the stabilizing role of the effects of π,π- and n,π-conjugation taken separately is smaller than, respectively, in structures I and II, but their total contribution may prove to be more significant.

In the present work we set ourselves the aim of making a justified choice among conformations I—III and determining the angle θ_0 for the most stable configurations of the molecules of benzalaniline and its o-, m-, and n-derivatives. To solve this problem we carried out a semiempirical calculation of the energies of the indicated compounds by the LCAO-MO method in the Hückel approximation (neglect of overlap and resonance integrals between non-neighboring orbitals). The presence in the molecule of a heteroatom (nitrogen) was taken into account, as usual, by introducing dimensionless parameters h and k.

$$\begin{aligned} &\alpha_{\mathrm{N}} = \alpha + h\beta, \quad && \Delta\alpha_{\mathrm{N}} = \alpha_{\mathrm{N}} - \alpha = h\beta; \\ &\beta_{\mathrm{N}} = k\beta, && \Delta\beta_{\mathrm{CN}} = \beta_{\mathrm{CN}} - \beta = (k-1)\beta, \end{aligned} \tag{1}$$

where α and β are the standard (benzene) Coulomb and resonance integrals. The inductive effect exerted by the more electronegative

atom on the neighboring carbons was fixed in the form of additions $\Delta\alpha_C$ to their Coulomb integrals (^{6})

$$\Delta\alpha_C = 0.1\,\Delta\alpha_N. \tag{2}$$

Since in conformations I—III the σ-skeleton of the molecule and, consequently, the σ-electron energies remain constant, it may be assumed that the differences in the energies of these conformations reduce to differences in their π-electron energies (E_π). To calculate the latter we used the conclusions of first-order perturbation theory (^{7}), which, in particular, makes it possible to find the π-electron energies of benzal aniline and its o-, m-, and n-derivatives through the energies (E_π^0) of the corresponding alternant hydrocarbons IV—VII.

$$\begin{aligned} &\text{IV} \quad E_\pi^0 = 14\alpha + 18.878\beta; \qquad && \text{V} \quad E_\pi^0 = 15\alpha + 19.670\beta; \\ &\text{VI} \quad E_\pi^0 = 15\alpha + 19.595\beta; && \text{VII} \quad E_\pi^0 = 15\alpha + 19.665\beta. \end{aligned}$$

In this case the replacement in IV—VII of the carbon in position 8 by a nitrogen atom and the inductive action caused by the latter are regarded as perturbations of the initial structures, and for the π-electron energy the theory gives the expression

$$E_\pi = E_\pi^0 + \Delta E_\pi = E_\pi^0 + \sum_r \sum_j n_j c_{rj}^2 \Delta\alpha_r + 2 \sum_{r<s} \sum_j \sum_j n_j c_{rj} c_{sj} \Delta\beta_{rs}, \tag{3}$$

where c_{rj}, c_{sj} are the coefficients at the r-th and s-th atomic orbitals (φ) of the j-th occupied molecular orbital,

$$\Psi_j = \sum_r c_{rj}\varphi_r,$$

and n_j is the number of electrons in this orbit. If the concepts of electron densities q_r and mobile-bond order p_{rs} are used, (3) reduces to

Fig. 1. Dependence of $(E_\pi - E_{0\pi})/\beta$ on the angle θ.

Figure 2: Fig. 1. Dependence of $(E_\pi - E_{0\pi})/\beta$ on the angle θ.

$$E_\pi = E_\pi^0 + \sum_r q_r \Delta\alpha_r + 2 \sum_{r<s} \sum p_{rs} \Delta\beta_{rs}. \tag{4}$$

The quantities E_π^0 and p_{rs} were calculated by us and are presented in the form of molecular diagrams*; since IV—VII are alternant hydrocarbons, all q_2 are equal to 1 (^{7}).

Fig. 1

The next stage is the choice of parameters. In conformation I the nitrogen atom donates one electron to the π-ensemble of the molecule; for it the values $h_N = 0.5$ and $k = 1$ are adopted (^{8}). In conformation II the π-electrons of the amino nucleus are delocalized with two n-electrons, as in aniline, and the nitrogen atom acquires a partial positive charge, increasing its effective field, which is reflected in the value $h_{\dot{N}} = 1.5^8$. $\beta_{8,9}$ upon rotation of the plane of the nuclei through an angle θ undergoes changes for two reasons. On the one hand, at $\theta = 90^\circ$ the overlap between the p_z-orbitals of nitrogen and of the 9th carbon atom; consequently, k becomes zero. On the other hand, upon rotation by 90°, the axes of the n-orbital and the p_z-orbital of carbon 9 pass into a common plane, which leads to an exchange interaction between them: $\beta_{n,9} = k'\beta$. Taking into account that the axes of these orbitals are not parallel because of the sp^2-hybridization of the n-orbital, we adopted the value 0.5 for k' $^{(9)}$. Noting now that the resonance integrals of p-orbitals rotated through an angle θ are proportional to $\cos\theta$ $^{(10)}$, owing to the proportionality of the overlap and resonance integrals, we can write $\Delta\beta_{8,9}$ for any conformation as

$$\Delta\beta_{8,9} = \Delta\beta_{\mathrm{CN}} + \Delta\beta_{n,9} = [(\cos\theta - 1) + 0.5\sin\theta]\,\beta. \tag{5}$$

We also assume that the change in the Coulomb integral of nitrogen upon rotation through an angle θ will obey an analogous dependence

$$\Delta\alpha_{\mathrm{N}} = (0.5 + \sin\theta)\,\beta. \tag{6}$$

Then, for benzalanyline and its substituted derivatives, expression (4) becomes

$$\frac{\Delta E_\pi}{\beta} = 1.2(0.5 + \sin\theta) + 2\rho_{8,9} \cdot [(\cos\theta - 1) + 0.5\sin\theta]. \tag{7}$$

Table 1

---

* For IV (stilbene), the literature (^{11}) gives p_{rs} values that coincide with ours.

structural formula: substituted benzalanyline

Figure 3: structural formula: substituted benzalanyline

Dipole moments

R	X	μ_{calc} (D) for conformation I, $\theta = 0^{\circ}$	μ_{calc} (D) for conformation II, $\theta = 90^{\circ}$	μ_{calc} (D) for conformation III, $\theta = 60^{\circ}$	μ_{exp}, D
H	H	1.60	1.60	1.60	1.61
H	NO_2	5.35	4.25	4.80	4.69
2,4,6-tri CH_3	NO_2	5.35	4.25	4.80	4.64
n-CH_3	NO_2	5.50	4.45	5.00	4.90
n-NO_2	NO_2	2.85	4.35	3.70	3.61
m-NO_2	NO_2	1.60	6.10	4.45	4.72
n-$(CH_3)_2N$	NO_2	7.25 **	6.40	6.80	6.68
H	Br	3.00	2.10	2.55	2.36
2,4,6-tri CH_3	Br	3.00	2.10	2.55	2.34
n-NO_2	Br	3.35	3.90	3.65	3.74

* For VIII, two planar conformations are possible. Thin-layer chromatography of anils on aluminum oxide indicates their identity. Since μ_{III} must have a value intermediate between μ_I and μ_{II}, the choice of the initial conformation I presents no difficulty.

** The moment of the $(CH_3)_2N$ group, equal to 3.25 D, was found from the moment measured by us for n-dimethylaminobenzalanyline (3.54 D).

The results of the calculation are presented graphically in Fig. 1, which shows that conformation I, contrary to the commonly accepted views, is the least stable of all possible conformations, while conformation III, with an angle between the planes of the nuclei of about 60°, proves to be the most energetically favorable. This conformation is more stable than I by 0.98β and than II by 0.21β.

It is evident from (7) that, after the parameters have been chosen, the value of the angle θ_0 depends only on $\rho_{8,9}$. In this connection, consideration of the molecular diagrams IV—VII leads to the following conclusions: a) introduction of a substituent into the aldehyde ring (N in position 8) has no effect on the value of θ_0, since $\rho_{8,9}$ is almost constant in all compounds; b) a substituent in the m-position of the aldehyde or amine ring likewise does not change the geometry of the molecule; c) a substituent in the o- or n-positions of the amine ring (N in position 7) has only a weak effect on the value of θ_0. The calculation shows that, in all the compounds considered, the value of θ_0 varies within the limits 59—62.5°.

For experimental verification of the calculated value we measured the dipole moments of a series of anils containing, in the *m*-position of the amine ring, a substituent with a sufficiently large group moment, and compared the values obtained with those calculated according to the vector scheme at different values of the angle θ. The measurement (12,13) and calculation (14) methods have been described previously. The choice of *m*-substituted anils is due to the fact that, for *o*-derivatives, an additional steric effect may be superimposed, while for *n*-derivatives rotation about the C—N bond should not change the dipole moment.

molecule. The results presented in Table 1, it seems to us, quite convincingly confirm the reliability of the molecular-orbital calculation.

Let us note that the quantity θ_0 obtained by the MO method depends not so much on the absolute values of the parameters as on the relative ones, which are almost constant in most of the sets used. Thus, taking for nitrogen the parameters ([15], [16]), we obtain $\theta_0 = 65$–$67°$. The picture, however, may change substantially when, in the *n*-position of the amine nucleus, there is such a strong acceptor as the nitro group, which noticeably increases the partial positive charge on the azomethine nitrogen. In the MO method this corresponds to an increase in the value of $h_{\ddot{N}}$, and this will lead to an approach of the value of θ_0 to 90°. Thus, we consider the conclusion drawn on the basis of consideration of the electronic spectra ([5])—that anils of this kind have configuration II—to be fundamentally correct.

Rostov-on-Don
State University

Received
22 XI 1962

CITED LITERATURE

[1] A. W. Baker, A. T. Shulgin, J. Am. Chem. Soc., **81**, 1523 (1859).
[2] H. H. Jaffe, Si Jung Yeh, R. W. Gardner, J. Mol. Spectroscopy, **2**, 120 (1958).
[3] J. Weinstein, E. McInnich, J. Am. Chem. Soc., **82**, 6064 (1960).
[4] H. A. Bent, Chem. Revs., **61**, 275 (1961).
[5] V. A. Izmail' skii, E. A. Smirnov, ZhOKh, **26**, 3042 (1956).
[6] G. W. Wheland, L. Pauling, J. Am. Chem. Soc., **57**, 2086 (1935).
[7] C. A. Coulson, H. C. Longuet-Higgins, Proc. Roy. Soc., A **191**, 39 (1947); A **192**, 16 (1947).
[8] A. Streitwiesen, Molecular Orbital Theory, N. Y., 1961.
[9] M. J. S. Dewar, Trans. Farad. Soc., **42**, 762 (1946).
[10] R. G. Rarr, B. L. Crawford, J. Chem. Phys., **16**, 526 (1948).
[11] C. A. Coulson, J. Jacobs, J. Chem. Soc., **1949**, 1983.
[12] O. A. Osipov, ZhOKh, **26**, 322 (1956).

[13] V. I. Minkin, O. A. Osipov et al., ZhFKh, **36**, 469 (1962).
[14] V. I. Minkin, O. A. Osipov, V. A. Kogan, DAN, **145**, 336 (1962).
[15] L. E. Orgel, T. L. Cottrell et al., Trans. Farad. Soc., **47**, 113 (1951).
[16] G. Del Re, Tetrahedron, **10**, 81 (1960).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.