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THE PROBLEM OF ACOPLANARITY OF AROMATIC AZOMETHINES

V. I. MINKIN, YU. A. ZHDANOV, E. A. MEDYANTZEVA and YU. A. OSTROUMOV

Chemistry Department, Rostov-on-Don State University, USSR

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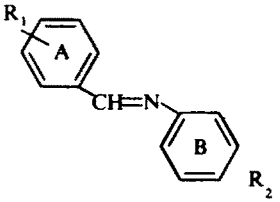
Abstract—The interaction of electronic and steric factors in aromatic azomethine molecules has been investigated. The theoretical calculations predict and the experimental data confirm that the azomethine molecule exists as a stable non-planar conformation in which the dihedrical angle between the amino nucleus and the rest of the molecule plane is 40–60° and that substituents in the aryl nucleus have little effect. Acoplanarity of the azomethine molecule suggests the possibility of finding atropoisomers and account for some specific features of their physical and chemical properties. The benzalaniline electronic spectra have been calculated by ASMO CI method. In addition the nature of electronic transitions and their connection with molecular conformation of benzalaniline have been investigated.

AROMATIC azomethines I exhibit a number of physical and chemical peculiarities, which cannot be explained by the planar structure traditionally accepted for them.



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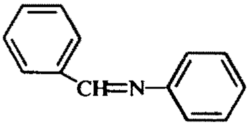

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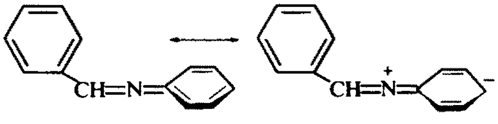

III

These peculiarities are: low intensity of the long-wave absorption band and absence of luminescence in contrast to the isoelectronic analogues—stilbenes and azobenzenes; low basity; nonisolation of *cis*-isomers and some other aspects, detailed in section IV. In order to define more precisely the azomethine structure (I) it was suggested[1-3] that instability of *cis*-isomers and anomalies in values of azomethine dipole moments (see below) were conditioned by the CH=N—Ar valency angle increase—the authors[1,2] assuming the angle to be 180° (structure II). Inadequency of this structure is now evident.

Izmailsky and Smirnov,[4] based on the studies of electronic spectra of compounds

[1] C. Weigand and E. Merkel, *Liebigs Ann,* **550**, 175 (1942).

[2] K. A. Jensen and N. H. Bang, *Liebigs Ann.* **548**, 106 (1941).

[3] E. Hertel and M. Schinzel, *Z. Phys. Chem.* **B 48**, 297 (1941).

[4] V. A. Ismailsky and E. A. Smirnov, *Zh. Obsch. Khim.* **26**, 342 (1956).

I (R_1, $R_2 = NO_2$, NMe_2), suggested that in azomethine molecules, besides π,π-conjugation, the conjugation of pair of nitrogen electrons n with π-electrons of the amino ring, i.e. n,π-conjugation may also be present. Optimal conditions for this kind of conjugation are created in conformations in which the angle between the plane of aldehyde and amino nucleus resulting from the turn around the N–Ar axis is 90°. In this connection it was supposed that the conformations for azomethines are realized either with $\theta = 90°$ or $\theta = 0°$, depending on R_1 and R_2. Later Ebara[5] applying his interpretation of spectra I to the ideas developed[1,2,4] suggested structure III with sp-hybridized nitrogen. Nevertheless such structure must have a very high dipole moment and structure III cannot explain the *cis-trans*-isomerism of azomethines.

In the third qualitive interpretation of spectral data it was pointed[6] out that the dihedrical angle θ has an intermediate value between 0° and 90°. Quite independently we have come to the same conclusion.[7] Measurements of dipole moments I and simple MO-calculation determine the angle θ as being approximately 60°[7].

In this paper more strict theoretical evidence for the acoplanarity of azomethine molecules is given and the interrelation of structure and properties in these compounds as well as the nature of spectral transitions in azomethine molecules is discussed.

Theoretical approach

HMO-calculations. The resultant effect of π,π- and n,π-conjugation upon azomethine molecular geometry may be calculated by comparing delocalization energies of the various conformations. The π-electronic configurations of benzalaniline and its *p*-substituted derivates with hypothetical substituents CH_2^- and CH_2^+ modelling strong electronodonor and electronoacceptor substituents were calculated for different angles θ.

In previous LCAO MO calculations of azomethines n-orbital was not included in the initial linear combination of AO[8,9]* (which corresponds to accepting planar configuration with $\theta = 0°$ *a priori*) or was taken into consideration indirectly.[7,10–12] In the present paper, the resultant effect of conjugations was calculated by including n-electrons in the basic AO and by variation heteroatomic parameters as function of angle θ (Table 1).

At $\theta = 0°$ all the parameters correspond to trigonally hybridized nitrogen,[7,13] and n-electrons are wholly localized. At $\theta = 90°$ $\beta_{\dot{N}-Ar} = 0$ and π,π-conjugation is

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[5] N. Ebara, *Bull. Chem. Soc. Japan* **33**, 534 (1960); **34**, 1151 (1961).

[6] P. Brocklehurst, *Tetrahedron*, **18**, 299 (1962).

[7] V. I. Minkin, E. A. Medyantzeva and A. M. Simonov, *Dokl. Acad. Nauk USSR* **149**, 1347 (1963).

[8] H. H. Jaffe, Si-Jung Yeh and R. W. Gardner, *J. Mol. Spectr.* **2**, 120 (1958).

[9] W. F. Smith, *Tetrahedron* **19**, 445 (1963).

[10] V. I. Minkin, E. A. Medyantzeva and Yu. A. Ostroumov, *Zh. Obsch. Khim.* **34**, 1512 (1964).

[11] V. I. Minkin, M. I. Gorelov, O. A. Ospipov and Yu. A. Ostroumov, *Optica and Spectroscopy*, **18**, 571 (1965).

[12] V. I. Minkin, Yu. A. Zhdanov, A. D. Garnovsky and I. J. Sadekov, *Dokl. Acad. Nauk USSR* **162**, 108 (1965).

[13] A. Streitwieser, *Molecular Orbital Theory for Organic Chemists*, Chap. 5, Wiley N.Y. (1961).

* The authors express their sincere appreciation to Dr. W. F. Smith for permission to get acquainted with his unpublished data.

broken, but n-electrons form a common MO with π-electrons of B ring, as in the aniline molecule. In this case α_N is taken as equal to the coulomb integral of arylamino nitrogen. It should be noted that the principal results of computations are stable in relation to the parameters.

Fig. 1 gives the graphic illustration of computation data of benzalaniline MO energy levels for various angles θ. Figure 2 represents the values of delocalization energies as functions of angle θ (curve B).

TABLE 1. COULOMB α AND RESONANCE β INTEGRALS OF AZOMETHINES

α	β
$\alpha_N = \alpha^\circ + (0{\cdot}5 + \sin\theta)\,\beta^\circ$	$\beta_{Ar-CH} = 0{\cdot}9\,\beta^\circ$; $\beta_{C=N} = 1{\cdot}1\,\beta^\circ$
$\alpha_{CN} = 0{\cdot}1\,\alpha_N$	$\beta_{\dot{N}-Ar} = \beta^\circ \cos\theta$; $\beta_{\ddot{N}-Ar} = 0{\cdot}5\,\beta^\circ \sin\theta$

$$DE = E^{\pi} - 6E_{C=C} - E_{C=N} - 2\alpha_N$$

where E^{π} is full π-electronic energy of a molecule, $E_{C=N}$ and α_N are energies of azomethine fragment electrons and coulomb nitrogen integrals correspondingly at given θ. Figure 3 (curve B) shows analogous dependencies for the substituted benzalanilines. Apparently inclusion of overlap[14] will not influence the conclusion given below.

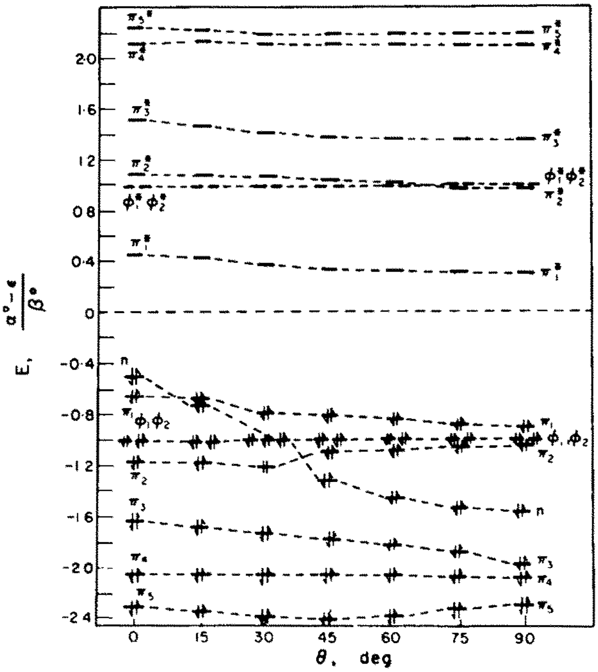

FIG. 1. Energies of HMO of benzalaniline at different θ.

Figs. 2 and 3 show that the minimum energy falls on conformations characterized by angle θ = 15–20°. Still the depth of the potential pit is very small and

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[14] G. Del Re, *Tetrahedron* **10**, 81 (1960).

delocalization energies of conformations with different θ are similar as the result of mutual compensation of π,π- and n,π-conjugations. In these conditions it is the steric effect that determines the conformation of the conjugated molecule. In compounds of type I this effect has been conditioned by space interactions (repulsion) between a hydrogen atom of the azomethine group and the *ortho*-hydrogen atoms of ring B—IV.

The repulsion energy E_{HH} depends on the distances between the centres of hydrogen atoms and, as they vary depending on θ, E_{HH} will also be a function of θ. As *m*-hydrogen atoms of ring B are far enough away from the azomethine hydrogen atom, these interactions need not be taken into consideration. Thus

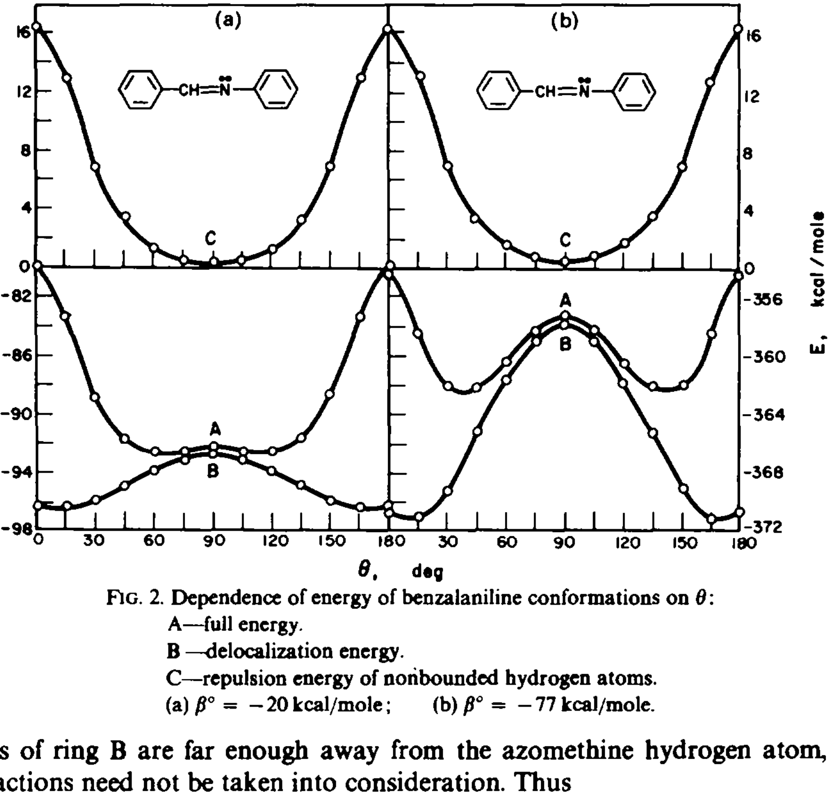
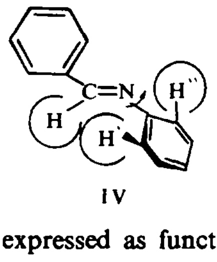


FIG. 2. Dependence of energy of benzalaniline conformations on θ:
A—full energy.
B—delocalization energy.
C—repulsion energy of nonbounded hydrogen atoms.
(a) $\beta^\circ = -20$ kcal/mole; (b) $\beta^\circ = -77$ kcal/mole.

$$E_{HH}(\theta) = E_{HH'}(\theta) + E_{HH''}(\theta)$$

The repulsion energies of non-bound hydrogen atoms may be estimated by solution of fourelectronic problem for the electrons of each of two corresponding C—H groups.[15, 16] The solutions are expressed as functions of overlap integrals, which



IV

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[15] R. S. Mulliken, *J. Am. Chem. Soc.* 72, 4493 (1950).

[16] H. E. Simmons and J. K. Williams, *J. Am. Chem. Soc.* 86, 3222 (1964).

depend on the distances between centres of hydrogen atoms.

$$E_{\mathrm{HH}} = \frac{A_{\mathrm{HH}}I_{\mathrm{H}}}{2}\sum_{i<j}\frac{S_{ij}^2}{1 - S_{ij}^2}$$

$\frac{1}{2}(A_{\mathrm{HH}}I_{\mathrm{H}})$ is here a constant equal to 149·05 kcal/mole,[16] S_{ij} are overlap integrals for I S-orbitals of i- and j-hydrogen atoms.

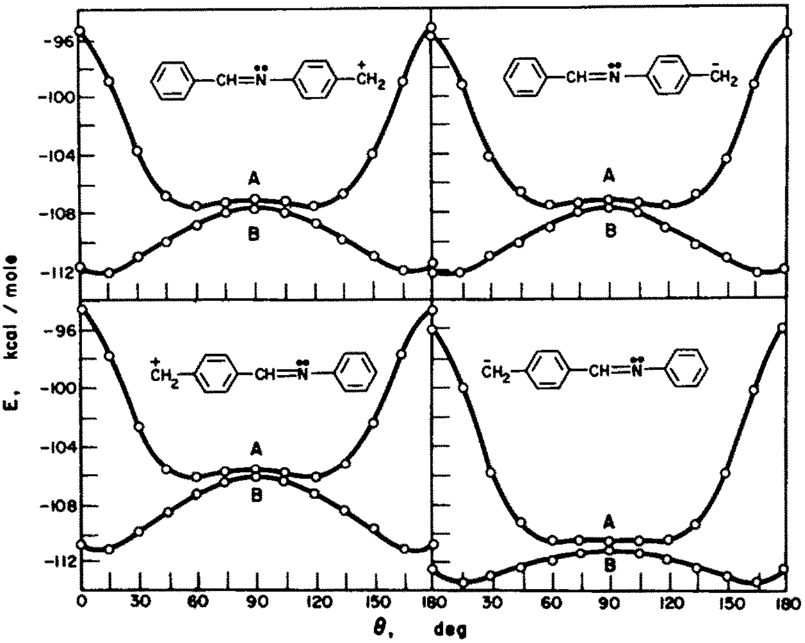

FIG. 3. Energies of conformations of substituted benzalanilines.

Based on the numerical calculations of values E_{HH} for different distances[16] the dependence $E_{\mathrm{HH}} = f(\theta)$ for compounds type I can be determined provided the geometrical structure I with $\theta = 0°$ closely corresponds with that of salicylalaniline (I, $R_1 = o$-OH, R_2 = H).[17] This kind of dependence is shown graphically in Fig. 2 (curve C) and it can be seen that the conformation with $\theta = 90°$ is the least hampered sterically.

Figure 2 shows the resultant potential curves of benzalaniline (addition of curves B and C) calculated at thermochemical $\beta° = -20$ kcal/mole (Fig. 2a) and estimated spectral values $\beta° = -77$ kcal/mole (Fig. 2b). These are considered extreme values, as angle θ for a stable molecular conformation is between 60–40° (120–140°).

The data represented in Fig. 3 show that introduction of electronodonor and electronoacceptor substituents in p-positions of nucleus A and B does not essentially influence the θ values.

Experimental evidences of acoplanarity of aromatic azomethines molecules

In order to confirm the results obtained by calculation it is necessary to prove

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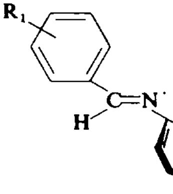
[17] J. Bregman, L. Leiserowitz and K. Osaki, *J. Chem. Soc.* 2086 (1964).

that molecules of type I compounds have a non-planar structure and that the predicted value $\theta = 40$–$60°$ is substantiated by experimental data. A new type of atropoisomerism realized in azomethines,[18, 19] is decisive proof of acoplanarity. Non-planar conformations of type I compounds are dissymmetrical (Y, YI), while activation energy of racemization of optical antipodes is, according to approximate evaluation, 8–15 kcal/mole (if $\theta = 0°$ in transition state, as is the case with *m*-substituted compounds).



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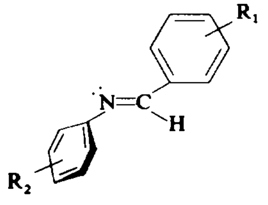

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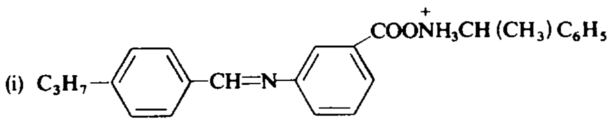

VII

The higher value is sufficient to determine experimentally the presence of optical isomers under common conditions.[20] By interaction of cuminal-*m*-aminobenzoic acid with (+) and (−)-α-phenylethylamines, salts (YII), with the sign of the rotation angle inverse to the original optically active amine, were prepared. By consecutive crystallization the initial rotation angle could be changed, but salts in solutions mutarotate quickly to the same limiting angle. Some results of the experiments are shown in Fig. 4.

These phenomena are not connected with any changes in the optical system of the amine, as α-phenylethylamine with initial rotation angle can be regenerated from any sample of the salts. Thus composition of the mixture of the diastereomers changes with each crystallization.

The value of the dihedric angle θ can be estimated by approximate formula $\cos^2 \theta = \varepsilon/\varepsilon_0$,[21] where ε and ε_0 are molar extinctions of compounds with non-planar and planar structures respectively. 2-arylbenzazoles[1, 22, 23] and stilbenes[24] were unsuit-

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[18] V. I. Minkin, Yu. A. Zhdanov, E. A. Medyantzeva and V. I. Naddaka, *Zh. Org. Khim.* **2**, 356 (1966).

[19] V. I. Minkin, Yu. A. Zhdanov and E. A. Medyantzeva, Abstr. of Symposium *Structure, Properties and Application of Azomethines*, p. 11. Kharkov (1965).

[20] D. M. Hall and M. M. Harris, *J. Chem. Soc.* 490 (1960).

[21] E. A. Braude and F. Sondheimer, *J. Chem. Soc.* 3754 (1955).

[22] B. M. Krasovitzky, B. M. Bolotin and R. N. Nurmuhametov, *Zh. Obsch. Khim.* **34**, 3736 (1964).

[23] V. I. Minkin, O. A. Osipov, V. A. Kogan, R. R. Shagidullin, R. L. Terentyeva and O. A. Raevsky, *Zh. Phys. Khim.* **38**, 1718 (1964).

[24] V. A. Ismailsky and Yu. A. Fedorov, Abstr. of Symposium *Structure, Properties and Application of Azomethines*, p. 5, Kharkov (1965).

able reference structures[19, 25, 26] and instead nitrones were chosen, as in their molecules n-electrons are occupied in the co-ordinate bond with oxygen, which excludes the effect of competing conjugation and results in almost complete planarity.

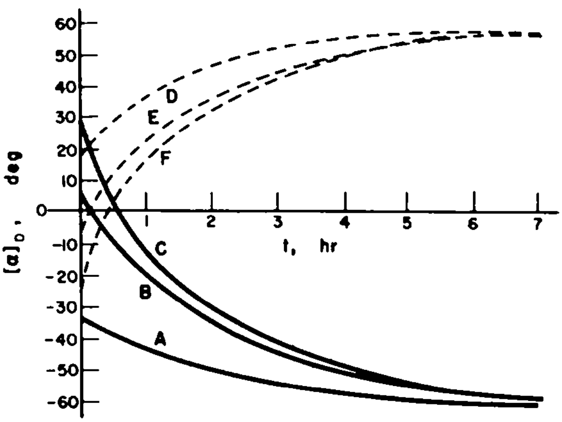
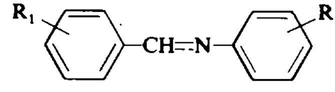
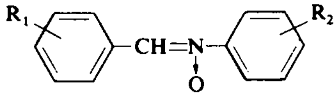


FIG. 4. Mutarotation VII in dioxane at 23°C.

The data concerning the intensity of long-wave absorption bands for compounds 1 and their nitrons and calculated values of angles θ are given in Table 2.

Thus a non-planar molecular conformation of azomethines predicted by HMO-calculations is confirmed by experimental data.

TABLE 2. THE CALCULATION OF THE ANGLES θ IN AZOMETHINES

R_1, R_2	 $\lambda_{max}(\varepsilon)$, mμ	 $\lambda_{max}(\varepsilon)$,[27] mμ	
$R_1 = R_2 = H$	310(6800), H[6]	322(19,900), Hp	55°
$R_1 = H, R_2 = p\text{-}Cl$	319(6500), C*	327(20,120), Hp	55°
$R_1 = H, R_2 = o\text{-}CH_3$	325(4200), Ch[9]	307(22,000), Hp	64°
$R_1 = H, R_2 = m\text{-}CH_3$	319(6150), Ch[9]	323(19,650), Hp	56°
$R_1 = H, R_2 = p\text{-}CH_3$	321(8070), Ch[9]	324(20,930), Hp	52°
$R_1 = p\text{-}OCH_3, R_2 = H$	315(10,800), Hp[27]	322(19,900), Hp	43°
$R_1 = p\text{-}NO_2, R_2 = H$	342(10,900), Hp[5]	365(20,830), C	44°

H—hexane, Hp—heptane, Ch—cyclohexane, C—carbon tetrachloride.

Acoplanarity and peculiarities of physical and chemical properties of azomethines

Some peculiarities of physical and chemical properties of azomethines are accounted for by its non-planar molecular configuration.

1. The lowered intensity of the long-wave absorption band caused by $\pi_1 \rightarrow \pi_1^*$

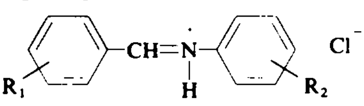
[25] V. I. Minkin, *Zh. Phys. Khim.* **41**, 556 (1967).

[26] H. H. Perkampus, *Theoretica Chimica Acta* **1**, 226 (1962).

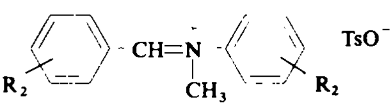
* Author's data.

electronic transition spreading along the whole π-system (section V) is evidently depended on acoplanarity of azomethines.

2. Non-planar structure of azomethine molecules is evidenced by the inability of crystal powders or solutions to luminescence,* while quarternary azomethine salts[28] having the planar structure VIII, IX luminescence intensely.



VIII

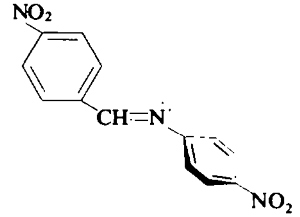


IX

Similarly non-planar quarternary salts of 2-arylbenzazoles have reduced luminescence as compared with planar initial bases.[29]

3. The distribution of MO levels in non-planar benzalaniline (Fig. 1) accounts for the absence of a n → π^* transition band in the spectra of type I compounds, while this band is clearly identified in saturated azomethines.[30, 31] n → π^* Transition may appear as a long-wave band (or tail) only in conformations where the dihedrical angle θ does not exceed 10–12°. The supposition[8] that the n → π^* transition band in benzalaniline spectra appears as a tail-form on the long-wave band has not been confirmed.[5, 6, 9, 23, 27, 32]

4. The dipole moment of *p,p'*-dinitrobenzalaniline (3·56 D[2]) exceeds that of benzalaniline (1·60 D[33]) and its other *p,p'*-substituted compounds.[34] This phenomenon is due to additional mesomeric interaction of n_N-electrons with π_{NO_2}-electrons possible only in non-planar conformations.



X

5. One of the peculiarities of the azomethines I is the instability of the *cis-isomers*. It has been found[35–38] that preexponential factors usual for *cis-trans*-isomerization activation energies (13·5–17·5 kcal/mole) are considerably lower than that of stil-

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[27] T. Kubota, M. Yamakawa and Y. Mori, *Bull. Chem. Soc. Japan* **36**, 1552 (1963).

[28] V. I. Minkin, O. A. Osipov, M. I. Knyazhansky, A. D. Garnovsky and E. A. Medyantzeva, *Zh. Obsch. Khim.* **35**, 397 (1965).

[29] A. I. Kiprianov and V. A. Shrubovich, *Zh. Obsch. Khim.* **29**, 1290 (1959).

[30] M. B. Robin and W. T. Simpson, *J. Chem. Phys.* **36**, 580 (1962).

[31] R. Bonnet, N. J. David, J. Hamlin and P. Smith, *Chem. & Ind.* 1836 (1963).

[32] V. A. Ismailsky and Yu. A. Phedorov, *Dokl. Acad. Nauk. USSR* **158**, 900 (1964).

[33] V. I. Minkin, O. A. Osipov and V. A. Kogan, *Dokl. Acad. Nauk USSR* **145**, 236 (1962).

[34] O. A. Osipov and V. I. Minkin, *Dipole Moments Tables.* (2nd Ed.) Vysshya Shkola, Moscow (1965).

[35] E. Fischer and Y. Frei, *J. Chem. Phys.* **27**, 808 (1957).

[36] G. Wettermark and L. Dogliotti, *J. Chem. Phys.* **40**, 1486 (1964).

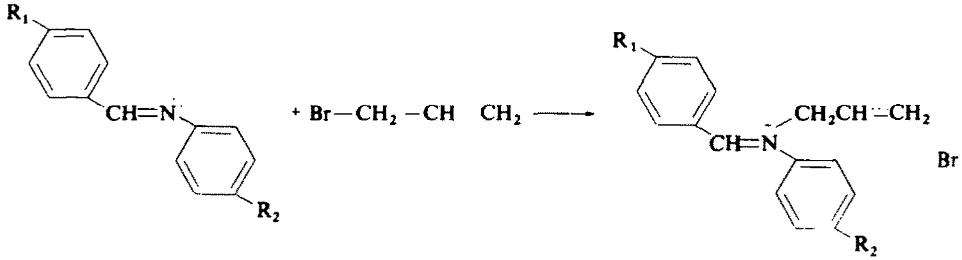
[37] G. Wettermark, J. Weinstein and J. Sousa, *J. Phys. Chem.* **69**, 1584 (1965).

[38] D. G. Anderson and G. Wettermark, *J. Am. Chem. Soc.* **87**, 1433 (1965).

* Derivatives of o-hydroxyaldehydes and azomethines containing p-NMe$_2$ groups are not included here.

benes[39] (34–37 kcal/mole) and alkylimines[40] (25–27 kcal/mole) due to the structural peculiarities of the transition state of the isomerization reaction. Accordingly[40,41] this state may be represented by structure III. Evidently, the initial acoplanarity of the aryl nucleus B will decrease the energetic barrier between the *cis*-form and structure III.

6. The azomethine nitrogen lone pair involved in conjugation in the non-planar conformation is responsible for certain specific reactions. The rate of azomethine quaternization with allylbromide in the reaction series XIa is correlated by Hammett σ-constants, while in the reaction series XIb this is accomplished by σ^--constants due to n, π-conjugation, possible only in non-planar conformation.[42]



XIa $R_1 = OCH_3, CH_3, F, Br, \overset{+}{N}Me_3, NO_2 \cdot R_2 = H$

XIb $R_1 = H \cdot R_2 = OH, OCH_3, CH_3, F, Br, \overset{+}{N}Me_3, COOCH_3, CN, NO_2$.

The basicity of azomethines[43–45] is lower than that of pyridines and 2-arylbenzazoles in which the lone pair is localized.

7. Other properties due to the non-planar structure of azomethines, include low conduction of electronic influences in nucleus A upon the reaction centre in nucleus B or *vice versa*[46–48] and the tendency of azomethine compounds to exist in a mesomorphic state.[49]

Electronic absorption spectra of azomethines

The various interpretations of the molecular structures of azomethines were based on data of their electronic spectra.[1,4–6,32] That is why the latter needed a more detailed examination.

The assignment of experimentally observed bands to certain electronic transitions and their correlation with various perturbations of the structure are the main problems in this connection. Spectra of benzalaniline[8,9] and salicylalaniline[11] were

[39] R. B. Cundall, in *Progress in Reaction Kinetics*, (Ed. G. Porter) vol. 2, p. 166. Pergamon Press, Oxford (1964).

[40] D. Y. Curtin and J. W. Hausser, *J. Am. Chem. Soc.* **83**, 3474 (1961).

[41] D. Y. Curtin and G. C. McCarty, *Tetrahedron Letters* 1269 (1962).

[42] V. I. Minkin and E. A. Medyantzeva, *Zh. Obsch. Khim.* **35**, 1956 (1965).

[43] A. Ricketts and C. S. Cho. *J. Org. Chem.* **26**, 2125 (1961).

[44] E. H. Cordes and W. P. Jencks, *J. Am. Chem. Soc.* **84**, 832 (1962).

[45] R. L. Reeves and W. F. Smith, *J. Am. Chem. Soc.* **85**, 724 (1963).

[46] V. I. Minkin, Yu. A. Zhdanov and E. A. Medyantzeva, *Dokl. Acad. Nauk USSR*, **159**, 1330 (1964).

[47] Yu. A. Zhdanov and V. I. Minkin, *Zh. Obsch. Khim.* **35**, 1270 (1965).

[48] Yu. A. Zhdanov and V. I. Minkin, *The Correlation Analysis in Organic Chemistry*. Chap I. Rostov-on-Don State University (1966).

[49] G. W. Gray, *Molecular Structure and the Properties of Liquid Crystals*. Chap. 10, Academic Press, N.Y. (1962).

studied earlier using the HMO method. A more detailed calculation of benzalaniline spectra by means of ASMO CI Pariser–Parr–Pople's (P–P–P) method[50-52] is now given.

Method. The following assumptions were used: (1) zero differential overlap, (2) the neglect of non-neighboured resonance interactions, (3) the use of empirical values of mono and two-electronic repulsion integrals in accordance with recommendations[53,54]: $\gamma_{CC} = 7{\cdot}0$ eV, $\gamma_{NN} = 8{\cdot}5$ eV, $\gamma_{12} = 1{\cdot}7$ eV, (4) all bond lengths (except $l_{C=N} = 1{\cdot}31$ Å. $l_{C_6-C_7} = 1{\cdot}44$ Å and $l_{N-C} = 1{\cdot}44$ Å) were taken as equal to 1·39 Å, and values β_{12} were calculated by means of the exponential formulaes.[50,55]

To describe the ground and the lowest excited electronic states of a π-system ten configurations were taken into consideration

$$\chi_i = C_{i0}\Gamma_0 + \sum_{J.T} C_{iJT}\psi_J^{-1}\psi_T$$

with the lowest closed shell $\Gamma_0 = \| I\bar{I}\ 2\bar{2} \ldots J\bar{J} \ldots \mathrm{N}\bar{N} \|$ and nine singly excited singlet configurations

$$\psi_J^{-1}\psi_T = 2^{-\frac{1}{2}}\{\| I\bar{I}\,2\bar{2}\ldots J\bar{T}\ldots N\bar{N} \| + \| I\bar{I}\,2\bar{2}\ldots T\bar{J}\ldots N\bar{N} \|\}$$

(the normalization factor is implied in the symbol $\| \ldots \|$).

As basic functions ψ_J six HMO of benzalaniline were used as shown in Fig. 5. n-Orbital was not taken into consideration, but acoplanarity of a molecule was considered when the matrix $F_{\mu\nu}$ was constructed by means of the value $\beta^{60°}_{N-C} = \beta_{N-C}$ cos 60°. The marked MO define the nine possible singly excited configurations given in Table 3. The energy of each configuration corresponds to the expression

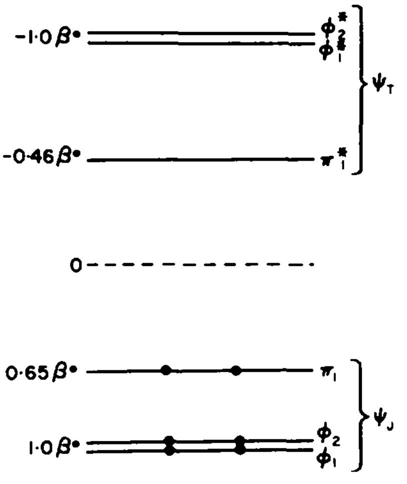


FIG. 5. HMO of benzalaniline involved in configuration interaction.

$$\langle\psi_J^{-1}\psi_T|\mathbf{H}|\psi_J^{-1}\psi_T\rangle - \langle\Gamma_0|\mathbf{H}|\Gamma_0\rangle = F_{TT} - F_{JJ} + 2\langle JT|TJ\rangle - \langle JT|JT\rangle$$

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[50] R. Pariser and R. G. Parr, *J. Chem. Phys.* **21**, 466, 767 (1953).

[51] J. A. Pople, *Trans. Far. Soc.* **49**, 1375, 1385 (1953).

[52] R. G. Parr, *The Quantum Theory of Molecular Electronic Structure*, Benjamin, N.Y. (1963).

[53] L. Salem and H. C. Longuet-Higgins, *Proc. Roy. Soc.* (*Lond.*), **A257**, 445 (1960).

[54] E. Weltin, J. P. Weber and E. Heilbronner, *Theoret. Chim. Acta*, **2**, 114 (1964).

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where **H** is the many electron Hamiltonian of the π-system and nondiagonal matrix elements of the interconfigurational matrix are determined as

$$\langle \psi_J^{-1} \psi_T | \mathbf{H} | \Gamma_0 \rangle = (\sqrt{2}) \mathrm{F}_{JT}$$

$$\langle \psi_J^{-1} \psi_T | \mathbf{H} | \psi_K^{-1} \psi_S \rangle = F_{TS} \delta_{JK} - F_{JK} \delta_{TS} + 2\langle KT. | SJ \rangle - \langle KT | JS \rangle$$

These matrix elements can be expressed through coefficients at AO in ψ_J according the known rules.[54, 56] The results of calculations are given in Table 3.

The electronic transitions moments $i \rightarrow k$ have been calculated as

$$\vec{M}_{ik} = \langle \chi_i | \vec{M} | \chi_k \rangle$$

where the operator of the moment is

$$\vec{M} = e \sum_j \vec{r}_j - \sum_\mu Z^c \vec{r}_\mu)$$

and $\vec{r}_j$, $\vec{r}_\mu$ are the position vectors of the electrons and the positive charges in the core, respectively. At $i = k$ one can get the value of π-component ($\vec{\mu}_\pi$) of the dipole moment of a molecule in the corresponding hybrid state χ_i. The values of π-electronic densities on the μ-th atom are determined by the integral (only on the space occupied by AO ϕ_μ).

$$Q_{i\mu} = \int_\mu \chi_i \sum_j e_j \chi_i \, \mathrm{d}\tau$$

The ground state. The distribution of π-electronic density in the ground state of a molecule is shown in Table 4. To estimate the dipole moment of a molecule $\vec{\mu} = \vec{\mu}_\pi + \vec{\mu}_\sigma$, the value of σ-component of the complete moment was calculated by a method,[57] where all σ-bonds are treated as localized MO. The values were found $\mu_\sigma = -0{\cdot}36\,\vec{i} + 0{\cdot}55\,\vec{j}$ and $\vec{\mu} = 0{\cdot}76\,\vec{i} + 1{\cdot}59\,\vec{j}$. The scalar value of the complete moment (1·76D) well agrees with the experimental value (1·60D[33]).

The assignments of the bands in benzalaniline spectra are clear from Fig. 6 and Table 5.

The K-band is caused by a charge transfer from nucleus B mainly to the azomethine bridge (Table 4). The considerable decreasion of electronic density on the *p*-carbon atom of ring B suggests that the introduction of electronodonor substituents into the *p*-position of nucleus B should bring about a batochromic shift of the K-band while the introduction of electronoaccepting substituents should cause a hypsochromic shift.[9, 56] This situation is graphically illustrated by Fig. 7. As the changes of electronic densities in *m,m'*-positions are insignificant, the K-bands positions in the spectra of various *m,m'*-substituted benzalaniline are almost the same.

E_2 band is the result of two electronic transitions: $\chi_0 \rightarrow \chi_2$ and $\chi_0 \rightarrow \chi_3$ being superimposed. The first is connected with the electronic transfer from nucleus A to the azomethine bridge, the second—from nucleus B. At low temperatures the E_2 band is resolved into two components of almost equal intensity. Jaffe[8, 58] has pointed out that the graphic splitting of the E_2 band is possible.

The E_1 band is due to four neighbouring transitions (Table 5). The splitting of this

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[56] J. N. Murrell, *Theory of Electronic Spectra of Organic Molecules*, Chap. 6, 9. Methuen, London (1963).

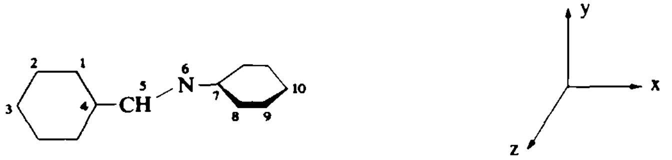
[57] G. Del Re, *J. Chem. Soc.* 4031 (1958).

[58] H. H. Jaffe and M. Orchin, *Theory and Applications of Ultraviolet Spectroscopy*. Chaps. 8, 12, Wiley, N.Y. (1962).

TABLE 3. THE GROUND AND THE LOWEST EXCITED ELECTRONIC STATES OF BENZALANILINE

χ_i	E, eV	Γ_0	$\psi_{\pi_1}^{-1}\psi_{\pi_1}^*$	$\psi_{\pi_1}^{-1}\psi_{\phi_2}^*$	$\psi_{\pi_1}^{-1}\psi_{\phi_1}^*$	$\psi_{\phi_2}^{-1}\psi_{\pi_1}^*$	$\psi_{\phi_2}^{-1}\psi_{\phi_2}^*$	$\psi_{\phi_2}^{-1}\psi_{\phi_1}^*$	$\psi_{\phi_1}^{-1}\psi_{\pi_1}^*$	$\psi_{\phi_1}^{-1}\psi_{\phi_2}^*$	$\psi_{\phi_1}^{-1}\psi_{\phi_1}^*$
χ_0	0	0·99999	0·0001	0	0	0	0	0	0	0	−0·0022
χ_1	4·53	0·0001	−0·9981	0	0	0	−0·0591	0	0	0	0·0170
χ_2	4·68	0	0	0	−0·4682	0	0	0	0·8836	0	0
χ_3	4·73	0	0	−0·3242	0	0·9460	0	0	0	0	0
χ_4	5·86	0	0	0	0	0	0	1·0000	0	0	0
χ_5	6·02	0	0	0	0	0	0	0	0	1·0000	0
χ_6	6·07	0	0	0·9460	0	0·3242	0	0	0	0	0
χ_7	6·10	0	0	0	0·8836	0	0	0	0·4682	0	0
χ_8	6·41	0·0021	−0·0001	0	0	0	0·2770	0	0	0	0·9608
χ_9	6·42	0·0006	0·0615	0	0	0	−0·9590	0	0	0	0·2765

TABLE 4. ELECTRONIC DENSITIES AND DIPOLE MOMENTS IN THE GROUND AND IN THE LOWEST EXCITED STATES OF BENZALANILINE



N of atom:	χ_0	χ_1	χ_2	χ_3
1	0·978	1·001	0·887	1·043
2	1·001	0·996	0·862	1·004
3	0·980	0·989	1·038	1·060
4	1·007	0·984	1·025	1·037
5	0·862	1·020	1·051	1·096
6	1·194	1·205	1·290	1·327
7	1·001	0·935	1·005	1·020
8	1·000	0·978	1·031	0·850
9	1·000	0·989	1·000	0·805
10	0·999	0·939	1·030	1·055
$\vec{\mu}_\pi$(D)	$1{\cdot}13\vec{i} + 1{\cdot}04\vec{j}$	$-2{\cdot}02\vec{i} + 0{\cdot}07\vec{j}$	$8{\cdot}78\vec{i} + 2{\cdot}11\vec{j}$	$-11{\cdot}77\vec{i} - 1{\cdot}55\vec{j}$
$\|\mu\|$(D)	1·76	2·46	8·83	12·17

band into two or three constituents occurs in many compounds of type I.[5, 27, 59, 60] The transition $\chi_0 \rightarrow \chi_8$ conditioned by local excitation (without the charge transfer) when transitions $\phi_1 \rightarrow \phi_1^*$ and $\phi_2 \rightarrow \phi_2^*$ are mixed, contributes largely to the E_2 band. Hence, the position of the observed integral band is almost independent of R_1 and R_2 in structure I.

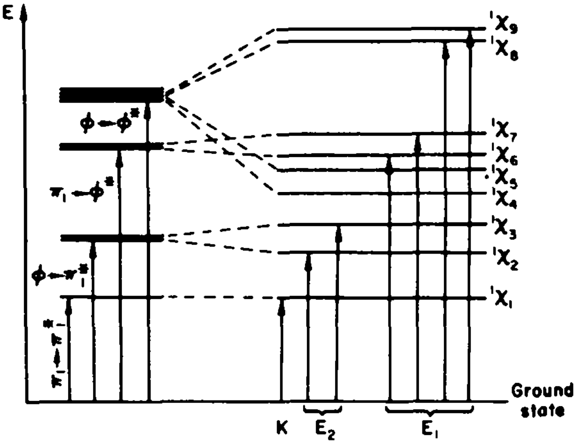


FIG. 6. The assignment of bands in the electronic spectra of benzalaniline.

As the assignment of azomethine absorption bands confirm the interpretations based on the HMO method,[8, 9, 11] some subsequent problems have been investigated by simple method. Table 6 illustrates the effect of the conformation of a benzalaniline

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[59] O. H. Wheeler and P. H. Gore, *J. Org. Chem.* **26**, 3298 (1961).

[60] J. Schulze, F. Gerson, J. N. Murrell and E. Heilbronner, *Helv. Chim. Acta*, **44** 428 (1961).

TABLE 5

Spectral band	P–P–P–						HMO						Experimental	
	Transition	E, eV	$\vec{Q}$ (Å)[c]			f_{theor}	Transition	E, eV	$\vec{Q}$ (Å)[c]			f_{theor}	E, eV	$f_{\text{exp.}}$[d]
			Q_x	Q_y	Q_z				Q_x	Q_y	Q_z			
K	$\chi_0 \rightarrow {}^1\chi_1$	4·53	1·94	0·55	0	1·60	$\pi_1 \rightarrow \pi_1^*$	[b]	1·15	0·28	0	0·50	4·07	0·27
E_2	$\chi_0 \rightarrow {}^1\chi_2$	4·68	0	0·27	0	0·03	$\phi_1 \rightarrow \pi_1^*$	4·52	0	0·61	0	0·15	4·59	0·22
	$\chi_0 \rightarrow {}^1\chi_3$	4·73	0	0·14	0·24	0·03	$\phi_2 \rightarrow \pi_1^*$	4·52	0	0·11	0·20	0·02	4·91	0·15
—	$\chi_0 \rightarrow {}^1\chi_4$	5·86	forbidden				$\phi_1 \rightarrow \phi_2^*$	6·8	forbidden					
	$\chi_0 \rightarrow {}^1\chi_5$	6·02	forbidden				$\phi_2 \rightarrow \phi_1^*$	6·8	forbidden					
E_1	$\chi_0 \rightarrow {}^1\chi_6$	6·07	0	0·41	0·72	0·38	$\pi_1 \rightarrow \phi_2^*$	6·29	0	0·41	0·72	0·38	5·4–6·1	
	$\chi_0 \rightarrow {}^1\chi_7$	6·10	0	0·79	0	0·33	$\pi_1 \rightarrow \phi_1^*$	6·29	0	0·36	0	0·07		
	$\chi_0 \rightarrow {}^1\chi_8$	6·41	1·20	0	0	0·81	$\phi_1 \rightarrow \phi_1^*$	6·8	0·98	0	0	0·57		
	$\chi_0 \rightarrow {}^1\chi_9$	6·42	0·78	0·03	0	0·34	$\phi_2 \rightarrow \phi_2^*$	6·8	0·98	0	0	0·57		

[a] Classification of spectral bands[33, 59]. [b] $\beta^\circ = -3{\cdot}4$ eV. [c] $e\vec{Q} = \vec{M}$. [d] Accordingly to[58].

on energy and intensity of spectral transitions. When the dihedric angle θ is increased the intensity of $\pi_1 \to \pi_1^*$ decreases in accordance with Braude's formula. $\phi_1 \to \pi_1^*$ transition intensity does not depend on θ. This transition connected mainly with charge transfer from nucleus B to the azomethine bridge and should appear at any conformations. The intensity of $\phi_2 \to \pi_1^*$ falls sharply when θ increases, and the preservation of the second component of the E_2 band is due to the mixing of $\phi_2 \to \pi_1^*$ transition with $\pi_1 \to \phi_2^*$ (Table 3). The energy and the intensity of $\phi_1 \to \phi_1^*$ and $\phi_2 \to \phi_2^*$ transitions are not depended on θ.

The above data show that the azomethine molecular structure must not be based only on empirical correlations of the position of absorption bands in spectra I with

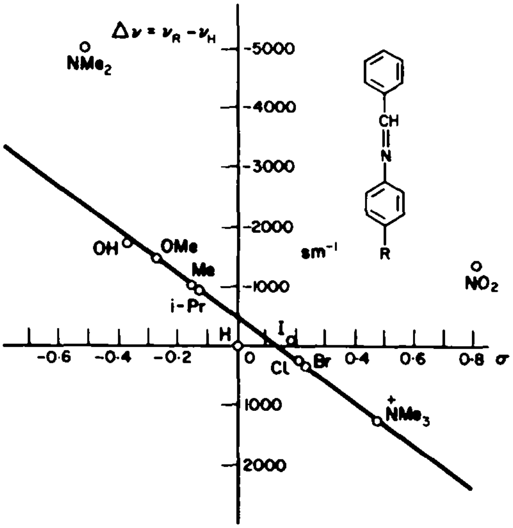

FIG. 7. Correlation of experimental energies of $\pi_1 \to \pi_1^*$ transitions in azomethine spectra.

TABLE 6. THE DEPENDENCE OF ENERGIES AND INTENSITIES OF BENZALANILINE ELECTRONIC TRANSITIONS ON THE MOLECULAR GEOMETRY

Transition	θ	E, $\beta°$	$\vec{Q}$(Å)			Q^2(Å^2)
			Q_x	Q_y	Q_z	
$\pi \to \pi^*$	0°	−1·1172	2·02	0·55	0	4·39
	30°	−1·1067	1·67	0·44	0	2·98
	60°	−1·1775	1·14	0·28	0	1·39
	90°	−1·2214	0	0	0	0
$\phi_1 \to \pi_1^*$	0–90°	see $\phi_2 \to \pi_1^*$	0	0·61	0	0·38
$\phi_2 \to \pi_1^*$	0°	−1·4620	0	0·62	0	0·38
	30°	−1·3783	0	0·36	0·21	0·17
	60°	−1·3283	0	0·11	0·20	0·05
	90°	−1.3108	0	0	0	0
$\phi_1 \to \phi_1^*$	0–90°	−2·0000	0·98	0	0	0·96
$\phi_2 \to \phi_2^*$	0–90°	−2·0000	0·98	0	0	0·96

various perturbations of the structure by introduction of substituents R_1 and R_2. Contrary to the point of view[5] it may be stated that the presence of absorption bands in azomethine spectra set up by autonomic transitions (localized in some molecular fragments) cannot prove the absence of conjugation between parts of a molecule at the ground state as the result of acoplanarity.

Summary

The effect of competing conjugation coupled with demands of stereofactors are responsible for the non-planar conformations of azomethine molecules and some peculiar properties of azomethines. Azomethines are, probably, the best known example of compounds in which the space structure is determined by interaction of two or more electronic effects (and not *vice versa* as in many cases).