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# DIPOLE MOMENTS AND STRUCTURES

# OF 1,5-DIPHENYL-3-ARYL-2-PYRAZOLINES AND THEIR

# FORMYL DERIVATIVES

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The dipole moments of 1,5-diphenyl-3-aryl- and 1-(p-formylphenyl)-3-aryl-5-phenyl-2-pyrazolines were measured in benzene solutions at 25°C and were estimated theoretically by a combination of quantum-chemical calculations by the self-consistent-field MO method within the Pariser−Parr−Pople approximation and the vector-additive scheme. It is shown that polarization of the $N_1-N_2$, $N_1-C_{ar}$, and C=N bonds makes a significant contribution to the resulting moment of 1,3,5-triphenyl-2-pyrazoline. The introduction of an electron-acceptor aldehyde group in the para position of the N-phenyl ring changes the polarization of these bonds substantially and leads to the appearance of considerable $\mu$ interaction. When electron-donor substituents are introduced into the 3-aryl grouping, one observed a similar but weaker effect that changes regularly as the electron-donor properties of the substituents increase.

The polarity of molecules containing a pyrazoline ring has already been the subject of a number of studies [1-5]. However, the data on the moment of the C=N bond in this system have been extremely contradictory up to now. No attempts have been made to take into account the asymmetry of the $N_1-N_2$ bond. In [2, 3] the application of a vector-additive scheme for the calculation of the dipole moments of 5-aryl- and 5-hetaryl derivatives of 1,3-diphenyl-2-pyrazoline, based on the assumption of the coplanarity of the entire molecule, contradicts the real geometry of these systems ($sp^3$ hybridization of the heteroring 5-C atom). A more accurate idea of the polarity of triaryl-2-pyrazolines and the factors that determine it would be extremely useful for the elucidation of the character of the electron interactions in such systems and its effect on the physicochemical properties, and, particularly, the spectral-luminescence properties of these compounds.
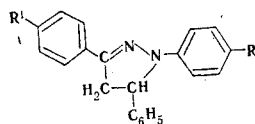
In the present research we attempted to refine and expand concepts regarding the electronic structures of triaryl-2-pyrazolines. For this we measured the dipole moments ($\mu_{exp}$) in benzene of two systematic series of compounds of this class (see Table 1) and also estimated them theoretically ($\mu_{calc}$) by a combination of a vector-additive scheme with the quantum-chemical calculations of some of the molecules by the self-consistent-field (SCF) MO method within the Pariser−Parr−Pople (PPP) $\pi$-electron approximation (see Fig. 1, diagrams a and b).

In previous calculations [2, 3] of the dipole moments of 2-pyrazolines it was assumed a priori that the $\mu$ value of the ring is determined primarily by the moment of the C=N bond, thereby ignoring the fact that the conjugation of the amine nitrogen atom with the azomethine group should weaken the polarization of the latter. At the same time, the polarization of the C=N group itself was completely ignored in [6, 7] during an interpretation of the spectral-luminescence properties of triaryl-2-pyrazolines.

| Compound | R | R' | $\alpha$ | $\beta$ | $MR_D$, cm³ | $P_\infty$, cm³ | $\mu_{exp}$ | $\mu_{calc}$ |
|---|---|---|---|---|---|---|---|---|
| I | H | H | — | — | — | — | 2,58* | 2,60 |
| II | | CH₃ | 9,3 | 0,83 | 98,2 | 217,8 | 2,42 | 2,52 |
| III | | OCH₃ | 12,8 | 0,61 | 99,8 | 281,4 | 2,98 | 2,81 |
| IV | H | N(CH₃)₂ | 17,5 | 0,90 | 106,7 | 345,3 | 3,41 | 2,71 |
| V | | Cl | — | — | — | — | 3,39* | 3,41 |
| VI | | NO₂ | 42,9 | 1,34 | 99,2 | 706,4 | 5,45 | 5,34 |
| VII | | H | 52,7 | 1,17 | 98,2 | 849,8 | 6,06 | 5,86 |
| VIII | | CH₃ | 55,9 | 1,10 | 102,8 | 903,7 | 6,25 | 6,03 |
| IX | | OCH₃ | 62,3 | 1,41 | 104,4 | 993,7 | 6,59 | 6,15 |
| X | CHO | N(CH₃)₂ | 86,7 | 1,15 | 111,36 | 1364,6 | 7,82 | 6,59 |
| XI | | Cl | 42,2 | 1,42 | 103,0 | 699,69 | 5,39 | 5,42 |
| XII | | NO₂ | 44,5 | 1,80 | 103,8 | 725,5 | 5,51 | 5,62 |
| XIII | | Phenyl | 46,1 | 1,50 | 122,4 | 768,6 | 5,62 | — |
| XIV | | Styryl† | 53,9 | 0,63 | 106,9 | 893,2 | 6,20 | — |

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*Data from [2].

†The aryl group in the 3 position of the pyrazoline ring was replaced by a styryl group.

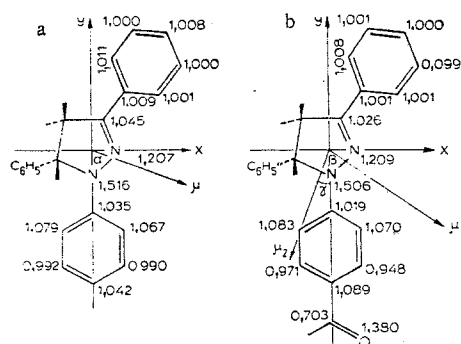

Fig. 1. $\pi$-Electron distribution in:
a) 1,3,5-triphenylpyrazoline (1), $\mu$ =
2.6 D, $\alpha$ = 70°; b) 1-(p-formylphenyl)-
3,5-diphenyl-2-pyrazoline (VII), $\mu_1$ =
6.74 D, $\beta$ = 55°; $\mu_2$ = 4.82 D, $\gamma$ = 20°C.

Our calculation of the $\pi$-electron distribution in the conjugated planar [8] fragment of the 1,3,5-triphenyl-2-pyrazoline (TPP) molecule (see Fig. 1, diagram a) clearly shows that the factors indicated above play an extremely important role. Moreover, as expected, the $\pi$-electron polarization of the $N_1 - C_{ar}$ and $N_1 - N_2$ bonds, which was previously disregarded by everyone, is extremely significant. The $\pi$ component of the dipole moment of TPP was found to be 1.63 D with the vector directed at an angle of 68° to the $N_1 - C_{ar}$ axis (the Y axis). Allowance for the $\sigma$ component was made by vector addition of the bond moments taken from [9]. The total value was 2.3 D, which is $\sim 0.3$ D lower than $\mu_{exp}$ of TPP. Considering that the p orbital of the $N_2$ atom lies in the plane of the heteroring, one may assume the development of its asymmetry and, as a consequence, the appearance of electrical moment $\mu_p$. We therefore assumed a vector difference $\vec{\mu}_{exp} - (\vec{\mu}_\pi + \vec{\mu}_\sigma) = \vec{\mu}_p = 0.3\,D$.

Diagram a in Fig. 1 also shows that, despite the considerable delocalization of the p electrons of the amine nitrogen atoms in the $N_1 - C_3$ direction, the polarization of the C = N bond remains significant ($\mu_{C=N} = 0.97$ D). The moment of the C = N bond is much lower than the value assumed in [2, 3] for the calculation of the $\mu$ values of TPP derivatives ($\mu_{C=N} = 2.4$-2.47 D) and somewhat lower than the $\mu_{C=N}$ value (1.5 D) used in [10] for the calculation of the moments of a hydrazone structure. The moment of the $N_1 - N_2$ bond ($\mu_\pi$), which we obtained from the data in the molecular diagram, is 2.22 D, as compared with 1.8 D for the $N_1 - C_{ar}$ bond ($\mu_\pi$). Thus these two bonds are maximally polarized in the TPP molecule. The total moment of TPP was found to be directed at an angle $\alpha$ of $\simeq 70°$ to the Y axis (see Fig. 1, diagram a).

Thus the $\mu$ vector, at least in the TPP molecule, is actually close in direction to the axis of the $C=N$ bond; however, this is not responsible for the predominant contribution of the moment of this bond but rather is the result of the addition of several dipoles, primarily, $N_1-C_{ar}$, $N_1-N_2$, and $C=N$.

It should be noted that the calculation of the $\mu$ values of 3-aryl derivatives of TPP by the vector-additive scheme with the application of the $\mu$ values of TPP and the 2-aryl grouping (II-VI, Table 1) confirms the correctness of the calculated $\mu$ components and the orientation of the resulting vector. The introduction of substituents with a weakly expressed electronic effect ($CH_3$, $OCH_3$, Cl) has little effect on the electron distribution in the pyrazoline ring, a consequence of which is the good agreement between $\mu_{exp}$ and $\mu_{calc}$. The dimethylamino group (IV) enters into strong conjugation with the $C=N$ bond, intensifying the polarization of the latter; this is reflected in the significant interaction moment ($\mu_{int}=0.85$ D). On the other hand, the counter-polarization effect of the nitro group (VI) with respect to the $C=N$ bond determines the relative autonomy of the nitrophenyl grouping and the absence of a substantial difference in the $\mu_{calc}$ and $\mu_{exp}$ values.

The data obtained on the electronic interactions in the TPP derivatives are in good agreement with their chemical properties. Thus formylation is directed strictly to the para position of the N-phenyl group [11], and even the introduction of a nitro group in the 3-phenyl ring (VI) does not lead to substantial deactivation of the molecule in this reaction (XII was obtained by direct formylation of VI). The impossibility of the introduction of a formyl group in the benzene ring in the 3 position of the pyrazoline ring, which was noted in [12], is due to the deactivating effect of the azomethine grouping.

It might have been expected that the introduction of an electron-acceptor aldehyde group, which is capable of entering into direct polar conjugation with the amine nitrogen atom of the heteroring [11, 13], in the N-phenyl radical of the investigated molecules would substantially affect the electrical asymmetry of the pyrazoline ring. As seen from Table 1, formyl-substituted TPP (VII) is an extremely polar compound ($\mu_{exp}=6.06$ D). The $\mu_{calc}$ value of VII, calculated by the additive scheme on the basis of the $\mu$ value of TPP (2.6 D) and the $\mu$ value of CHO (2.96 D [9]), is 4.45 D, i.e., considerably lower than $\mu_{exp}$. In this case $\mu_{int}$ for VII (2.02 D) was found to be even lower than $\mu_{int}$ of p-dimethylaminobenzaldehyde (1.53 D [9]), which, in our opinion, is due to the more complex character of the electronic system of 2-pyrazoline derivatives. In the investigated formyl derivatives, in addition to the direct polar conjugation of the amine nitrogen atom with the aldehyde group, which is responsible for the $\mu_{int}$ value of p-dimethylaminobenzaldehyde, weakening of the $\pi$-electron delocalization in the $N_1 \rightarrow C_3$ direction and an increase in the dipole of the $C=N$ bond are also important; this affects $\mu_{int}$ in nonexplicit form.

We were able to take this set of effects into account by quantum-chemical calculation of the $\pi$-electron distribution in the VII molecule (Fig. 1, diagram b). The $\pi$ component of the moment of this molecule was found to be 4.4 D (both planar orientations of the formyl group were assumed to be equally likely in the calculation*). The contribution of $\mu_\sigma$ (1.34 D) and $\mu_p$ (0.3 D) makes it possible to estimate the $\mu_{calc}$ value of VII to be 5.86 D, which is in good agreement with $\mu_{exp}$, i.e., the combination of vector-additive and quantum-chemical calculations in this case also makes it possible to reliably estimate the polarity of the compounds.

As seen from the data in Table 1, the $\mu_{calc}$ value is in good agreement with the $\mu_{exp}$ value for 3-aryl derivatives VII (VIII-XII) if the moments of VII and the corresponding aryl group are used in the vector-additive calculations. In this case the regularity typical for conjugated systems is observed: When an electron-acceptor formyl group is present, the introduction of electron-donor substituents leads to an increase of $\Delta\mu=\mu_{exp}-\mu_{calc}$. As in the case of IV, in this series of compounds one should speak of reinforcement of the polarization of the arylazomethine fragment rather than charge transfer from the 3-aryl group to the 1-aryl group. However, there is no doubt that the presence of an electron-acceptor aldehyde group in the 1-phenyl group promotes polarization of the phenylazomethine grouping by electron-donor substituents (for example, compare the $\Delta\mu$ values of IV and X). The introduction of an electron-acceptor nitro group in the 3-phenyl group of the formyl derivative of TPP, as in the case of VI, does not lead to a substantial change in the electron distribution in the starting molecule.

Lengthening of the conjugation chain by introduction of a styryl group in the 3 position of the pyrazoline ring (XIV), in conformity with principle, increases the $\mu$ value, whereas lengthening of this chain by introduction of a diphenylyl grouping gives rise to a decrease in the $\mu$ value. The latter is most likely a consequence of the effect of steric factors due to disruption of the planarity of the diphenylyl grouping itself.

Thus the electron distribution in the pyrazoline ring is subject to considerable perturbation under the influence of electron-acceptor substituents in the 1-phenyl ring or of strong electron-donor groups in the 3-

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*The dipole moments ($\mu_1$ and $\mu_2$) of both conformers due to the different orientations of the formyl group are presented in diagram b in Fig. 1.

phenyl ring or when both of these substituents are present in the molecule. At the same time, electron-acceptor substituents in the 3-phenyl ring do not interact substantially with the pyrazoline ring. It follows from this that the stronger effect of electron-acceptor substituents in the 3-phenyl ring, as compared with the 1-phenyl ring, on the spectral characteristics, which was noted, for example, in [7], is not associated with a corresponding change in the electron distribution in the ground state in the molecules.

## EXPERIMENTAL

The dipole moments were measured by the method described in [14] at $25 \pm 0.01°$ in dilute solutions in benzene.

The $\pi$-electron distribution in the conjugated fragment of the TPP molecule was calculated by the SCF MO method within the PPP $\pi$-electron approximation from the program in [15]. The following semiempirical parameters were used [16]: $\beta_{benz} = -2.4$ eV, $\beta_{C-C} = -2.1$ eV, $\beta_{C=O} = -3.3$ eV, $\beta_{C=\dot{N}} = -3.0$ eV $\beta_{C-\ddot{N}} = -2.5$ eV, $B_{\ddot{N}-\dot{N}} = -2.5$ eV; $\gamma_C = 11.13$ eV, $\gamma_O = 15.23$ eV, $\gamma_{\dot{N}} = 13$ eV, $\gamma_{\ddot{N}} = 13$ eV; $W_{\dot{C}} = -11.16$ eV, $W_{\dot{O}} = -17.7$ eV, $W_{\dot{N}} = -14$ eV, $W_{\ddot{N}} = -20$ eV. The bond lengths and valence angles from data from the x-ray diffraction analysis of 1,3-diphenyl-2-pyrazoline [8] were used in the calculations.

Compounds II and III were obtained by the method in [17] and purified by two recrystallizations from hexane—benzene with aluminum oxide. The melting points were, respectively, 151.5-152° and 139-140° [mp 154 and 141° (from acetic acid) [17]]. Compound VI was obtained by refluxing equimolar amounts of 4-nitro-chalcone and phenylhydrazine hydrochloride in ethanol for 12 h and had mp 177-178° (from ethanol) (mp 177° [18]).

The synthesis of IV, VII-XI, XIII, and XIV was described in [11, 13, 19].

1-(p-Formylphenyl)-2-(p-nitrophenyl)-5-phenyl-2-pyrazoline (XII). This compound was obtained in 59% yield by formylation of VI with dimethylformamide in the presence of phosphorus oxychloride by the method described in [11]. The reaction product was purified by chromatography of a benzene solution on aluminum oxide, after which it was converted to the bisulfite derivative, which was washed with alcohol and decomposed by refluxing with 10% sodium carbonate solution. The resulting XII was obtained as bright-red crystals with mp 181-182° after two recrystallizations from isopropyl alcohol. IR spectrum: $\nu_{C=O}$ 1680, $\nu_{C=N}$ 1600 cm$^{-1}$, and other characteristic bands in conformity with [20]. Found: N 9.61%. $C_{22}H_{17}N_3O_3$. Calculated: N 10.13%.

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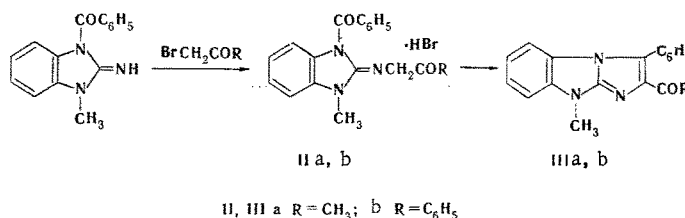
# RESEARCH ON IMIDAZO[1,2-a]BENZIMIDAZOLE DERIVATIVES

## XV.* 2-ACYL-SUBSTITUTED IMIDAZO[1,2-a]BENZIMIDAZOLES

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UDC 547.785.5.07

2-Acyl-substituted 3-methyl(phenyl)-9-methylimidazo[1,2-a]benzimidazoles were synthesized by three methods: by the reaction of α-halo ketones with 3-benzoyl-2-imino-1-methylbenzimidazoline, by reaction of acetic anhydride or acetyl bromide with 1-methyl-2-phenacylaminobenzimidazole, and by acylation of 3-substituted imidazo[1,2-a]benzimidazoles. Some of the properties of the resulting 2-acyl-substituted compounds were studied.

The synthesis of 2-acyl-substituted imidazo[1,2-a]benzimidazoles (III) by heating 3-benzoyl-2-imino-1-methylbenzimidazoline (I) with α-halo ketones in dimethylformamide (DMF) at 80-90° for 16-20 h was described in [2].



II, III a R = CH₃; b R = C₆H₅

As shown in the scheme above, the synthesis of 2-acyl derivatives of imidazo[1,2-a]benzimidazole (III) proceeds through a step involving the formation of N-(acylmethyl)imine salts (II). The latter can be obtained by the action of α-halo ketones on imine I in absolute DMF at room temperature. Incorporation of the phenacyl grouping in the imino group was confirmed by conversion of hydrobromide IIb to 1-methyl-2-phenacylamino-benzimidazole (X) by treatment with dilute sodium carbonate solution.

The IR spectra of IIIa and IIIb contain a distinct $\nu_{C=O}$ band at 1619 and 1690 cm$^{-1}$, respectively. The signals of protons of the COCH₃ and N—CH₃ groups in the PMR spectrum of 2-acetyl derivative IIIa show up in the form of singlets with identical intensities at 2.1 and 3.77 ppm. The signal of the protons of the N-methyl group of 2-benzoyl derivative IIIb is observed at 3.7 ppm. In addition to the chief reaction products III, their isomers (VI), which hinder purification of the final product, are formed in 5-10% yield. The formation of isomeric 3-acyl derivatives of imidazo[1,2-a]benzimidazole (VI) is due to partial isomerization of imine I [3] to 2-benzamido derivative IV during the reaction; the latter on reaction with α-halo ketones undergoes quaterniza-tion at the ring nitrogen atom to give salts V, which are subsequently converted to the previously described [4] VI.

* See [1] for communication XIV.