1,3,5-TRIARYL-Δ^2-PYRAZOLINES WITH A NITRO OR AMINO GROUP IN THE N-PHENYL RING

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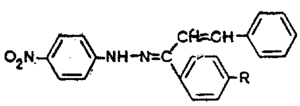
A number of p-nitrophenylhydrazones of chalcones and 1-(p-nitrophenyl)- and 1-(p-aminophenyl)-3-aryl-5-phenyl-2-pyrazolines were synthesized, and their UV and IR spectra were measured. It is shown that the direction of polarization in the π system of the ground and first excited states of the pyrazolines depends substantially on the character and position of the substituents introduced; the experimental data are compared with the results of calculation of the electronic states of the molecules by the Pariser–Parr–Pople (PPP) method. It was established that the nitro compounds have luminescence properties and that their absorption spectra in inert solvents have a vibrational structure.

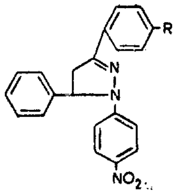
One of the important problems in the chemistry of pyrazolines is the problem of the participation of the 1- and 3-aryl rings in conjugation with the hydrazone fragment. Despite the large number of publications on this problem, research (mainly spectral studies) in this direction is continuing. In our opinion, this is to a considerable extent due to the ambiguity in the interpretation of the chromophore system of aryl-substituted Δ^2-pyrazolines. A review of some points of view with respect to this problem was presented in [1]. To supplement this, it should be emphasized that in their analysis of the UV spectra (particularly the long-wave absorption) researchers most often have in mind the $2p_z-\pi$ interaction of the hydrazone fragment [2-4]. Recently in [5] it was shown by the Hückel molecular orbital (HMO) method that the tertiary nitrogen atom is an electron donor both with respect to the 1-aryl group and the azomethine group; however, in this case also the entire attention of the researchers is concentrated on polarization of the hydrazone fragment.

In an attempt to make a definite contribution to the development of these concepts, we investigated triarylpyrazolines containing substituents with clearly expressed electronic character [for example, nitro or amino groups (II and III, respectively, Table 1)] in the N-phenyl ring. For comparison we studied p-nitrophenylhydrazones I, which are isomers of pyrazolines II.

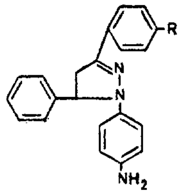
The long-wave absorption is the most sensitive to the electronic effect of substituents in I-III; the introduction of a substituent in both the 1- and 3-phenyl rings is reflected substantially in the spectra.



I a-f



II a-f



III a-d, f

I–III a R=H; b R=CH$_3$; c R=N(CH$_3$)$_2$; d R=Cl; e R=NO$_2$,
f R=—CH=CH—C$_6$H$_5$

In the present paper we will direct principal attention to precisely the long-wave absorption band. For an understanding of its nature it is extremely essential that the triarylpyrazoline molecules are cross-conjugated systems, since the $N_{(1)}$ atom is conjugated with the two π systems.

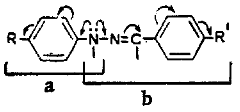


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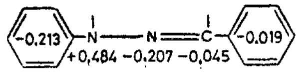
TABLE 1. Characteristics of the Synthesized Compounds

Compound	mp, °C	N found, %	Empirical formula	N calc., %	Yield, %
Ia	149—150	12,3	$C_{21}H_{17}N_3O_2$	12,2	42
Ib	148—149	11,7	$C_{22}H_{19}N_3O_2$	11,8	40
Ic	132	14,6	$C_{23}H_{22}N_4O_2$	14,5	45
Id	141—142	11,0	$C_{21}H_{16}ClN_3O_2$	11,1	60
Ie	250	14,5	$C_{21}H_{16}N_4O_4$	14,4	43
If*	164—165	11,6	$C_{23}H_{19}N_3O_2$	11,4	69
IIa	178	12,2	$C_{21}H_{17}N_3O_2$	12,2	100
IIb	167,5—168	11,8	$C_{22}H_{19}N_3O_2$	11,8	100
IIc	211—212	14,5	$C_{23}H_{22}N_4O_2$	14,5	100
IId	174	11,2	$C_{21}H_{16}ClN_3O_2$	11,1	100
IIe	192—193	14,5	$C_{21}H_{16}N_4O_4$	14,4	100
IIf*	202—203	11,4	$C_{23}H_{19}N_3O_2$	11,4	100
IIIa	173—174	13,1	$C_{21}H_{19}N_3$	12,9	40
IIIb	153—154	12,9	$C_{22}H_{21}N_3$	12,8	38
IIIc	177—178	15,8	$C_{23}H_{24}N_3$	15,7	32
IIId	164—165	12,1	$C_{21}H_{18}ClN_3$	12,1	35
IIIf*	172—173	12,4	$C_{23}H_{21}N_3$	12,4	42

*With a styryl rather than an aryl substituent.

A peculiarity of cross-conjugated molecules is strong interaction of the chromophoric subsystems **a** and **b** with one another, which makes it possible to interpret the band under discussion as the absorption of the entire conjugated system. The contribution of chromophores **a** and **b** to the long-wave absorption depends on their polarization in the ground and excited states and therefore depends substantially on the electronic character of substituents R and R'.

An L_μ value, which characterizes the localization of the excitation on the chromophore fragments and can also be useful in the case of Δ^2-pyrazolines, was proposed in [6]. For its evaluation, the molecular diagram of diphenylpyrazoline in the ground (2) and first excited (3) states was calculated by the standard Pariser–Parr–Pople (PPP) method as in [7].



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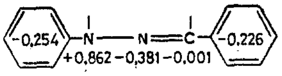
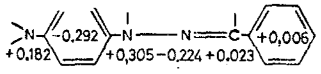


(3)

The results,* which have to do primarily with the electron density distribution in the ground and excited states, differ substantially from the data in [3, 4]. Both calculations are in agreement in the interpretation of the character of the long-wave absorption, since, as seen from diagrams 3 and 2, the $\pi-\pi^*$ transition under discussion is accompanied by delocalization of the electron density in two directions in accordance with scheme 1 above. According to our calculations, the degree of localization on chromophores **a** and **b** is ~30 and ~70%. The widely prevailing conclusion regarding the predominant shift of the electron density in the $N_{(1)} \rightarrow C_{(3)}$ direction in 1,3-diphenyl-Δ^2-pyrazoline itself (or in its 5-aryl-substituted derivatives) is confirmed by these data.

Unfortunately, the fact of the shift of the electron density from $N_{(1)}$ to the aryl group in the 1 position is frequently ignored, although it is not difficult to imagine that the introduction of electron-acceptor substituents in this aromatic ring should substantially intensify polarization of aniline fragment **a**. This is reflected in the UV spectra of II. Thus the introduction of a nitro group in the 1-phenyl substituent gives rise to a 60 nm bathochromic shift of λ_{max} of the long-wave absorption (λ_{max} 358 nm for 1,3,5-triaryl-Δ^2-pyrazoline) [8]). A λ_{max} value of such magnitude cannot be explained on the basis of concepts involving the predominant polarization in the direction of the azomethine group. The complex character of the interaction of chromophores **a** and **b** is well illustrated by the UV spectra of other compounds of this series (Table 2): substituents with any type of electronic character give rise to a bathochromic shift of the long-wave absorption band.



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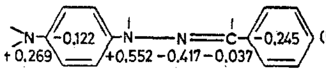

(5)

The amino group in the 4 position of the 1-phenyl substituent (III) sharply reduces the polarization of this chromophoric ring; this is well illustrated by molecular diagrams 4 and 5.

As seen from these diagrams, the character of the electron distribution, which is similar to the character of the distribution in 1,3-diphenyl-Δ^2-pyrazoline, is retained in the ground state, but in the first excited state

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*We thank A. A. Sukhorukov and M. Reinkhardt for their assistance in the calculations.

TABLE 2. Electronic (Absorption and Luminescence). and IR Spectra

Compound	UV spectra				IR spectra, ν, cm^{-1}			
	λ_{max}^{abs}, nm ($\varepsilon \cdot 10^{-3}$)		λ_{max}^{em}, nm		NH	C=N	NO_2, *as*	NO_2, *s*
	in isooctane	in ethanol	in isooctane	in ethanol				
Ia	—	417 (38,8), 332* 270 (15,4), 248 (14,3)	—	—	3320	1608	1513	1325
Ib	—	425 (38,3), 340* 275 (15,4), 250*	—	—	3310	1603	1508	1330
Ic	—	284 (12,5), 247 (10,3), 406, 308, 270	—	—	3330	1610	1512	1320
Id	—	420 (42,9), 280 (23,3), 245 (14,6)	—	—	3305	1603	1508	1330
Ie	—	424, 322, 268	—	—	3300	1595	1575	1320
If	—	433 (47,6), 304 (18,3), 240 (16,1)	—	—	3313	1596	1503	1320
IIa	405, 385, 333, 304, 245, 237	418, 339, 309, 265*, 230	470	490	—	1603	1490	1320
IIb	408, 388, 333, 307, 257, 245	422, 337, 310, 265, 237	475	500	—	1605	1570	1310
IIc	460, 294	452, 348, 322, 272*	486, 458	530	—	1600	1515	1320
IId	411, 391, 372* 337, 309, 248, 235	421, 343*, 311, 269*, 245*, 235	442	490	—	1600	1500	1315
IIe	434, 414, 385* 317	438, 332	482, 455	500	—	1595	1510	1310
IIf	425, 401, 381* 330, 300	432, 342, 301, 275, 247	458, 435	500	—	1600	1510	1310
IIIa	376, 305*, 252	373, 337, 252	477	497, 462	3466, 3381	1616		1520 †
IIIb	374, 305*, 255	372, 335*, 253	471	510, 462	3468, 3382	1615		1520 †
IIIc	384, 370, 294, 260	370, 334, 302*, 258	482*, 460	490, 465*	3467, 3378	1620		1525 †
IIId	386, 335*, 256	383, 335*	496	492, 465	3465, 3380	1615		1520 †
IIIf	405, 273	403, 275	486	515, 415	3468, 3384	1618		1520 †

*Shoulder.

†This is the band of deformation vibrations of the NH_2 group.

the entire phenylenediamine fragment acts as an electron donor with respect to the remaining π system. This is undoubtedly due to the fact that the degree of the electronic effect of the amino group is of the same order of magnitude as in the case of the $N_{(1)}$ atom of the molecule. The conclusion that charge is transferred from the aromatic ring in the 1 position to the ring in the 3 position is valid in this case. Hence it becomes comprehensible why electron-donor substituents (IIIb, c) give rise to a hypsochromic shift: they counteract the given polarization of the molecule, as is particularly graphically displayed in the case of dimethylamine derivative IIIc (Table 2). Electron-acceptor substituents and lengthening of the chain (IIId, f) favor the given polarization; hence one observes a red shift in the band.

On the basis of the above it can be concluded that the 1,3-diphenylhydrazone grouping is a cross-conjugated system, both portions of which, because of strong interaction, are responsible to a considerable extent for the long-wave absorption. In this sense one can call this grouping the principal chromophore system of aromatic hydrazones and pyrazolines. However, it should also follow from this that such useful concepts as "charge transfer from the 1-aryl substituent to the 3-aryl substituent" [1] or in the opposite direction are valid only in exceptional cases in which the effect of the substituents introduced is comparable to the electronic effect of the $N_{(1)}$ atom.

Although in the present research the principal emphasis in the calculation was placed on Δ^2-pyrazolines, the above conclusion applies to an equal extent to the isomeric arylhydrazones. A certain correction should be introduced by taking into account the presence in the hydrazones of another center of cross-conjugation of the carbon atom of the azomethine group. In addition, the geometries and rigidities of hydrazone and pyrazoline molecules are somewhat different; in the case of pyrazolines the hydrogen atom of the amino group is substituted by an aralkyl grouping, and this should also reinforce its electron-donor properties. As seen from the data in Table 2, these effects are on the whole insignificant and give rise to only small fluctuations in the λ_{max}

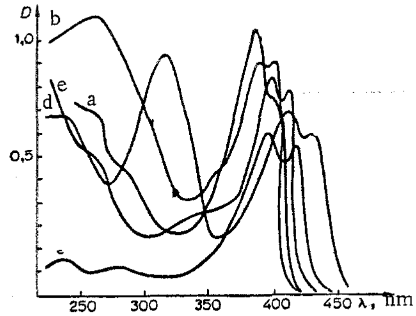

Fig. 1. Absorption spectra of 1-(4-nitrophenyl)-3-aryl-5-phenyl-Δ^2-pyrazolines (II) in isooctane.

values of the long-wave bands of compounds of the two series. At the same time, the short-wave regions of the UV spectra of hydrazones and pyrazolines differ to such an extent that in a number of cases they can serve as a basis for the identification of the class of compounds.

On passing from isooctane to alcohol, a slight hypsochromic shift of λ_{max} of the long-wave band is observed. This fact contradicts the well-known criteria for the identification of $\pi-\pi^*$ bands [9], but one should bear in mind the participation of the $2p_z$ electrons of the $N_{(1)}$ atom in conjugation; alcohol, which forms intermolecular hydrogen bond, weakens their interaction with the π system and thereby increases the energy of the corresponding electron transition. This is confirmed by data according to which protonation of this atom completely changes the character of the absorption.

An interesting peculiarity of 1-(4-nitrophenyl)-3-aryl-5-phenyl-Δ^2-pyrazolines (IIa-f) that has not been previously noted [5, 10] is the appearance of a vibrational structure in the spectra of solutions in a nonpolar solvent (Fig. 1). The smallest traces of moisture (up to the concentration permissible in solvents provided by industry) level out this type of structure. This property is absent in the case of I and III. The overall half-width of the long-wave absorption (~4000 cm^{-1}) and its position confirm the validity of the conclusion regarding the appearance of a vibrational structure. The difference in the frequencies of the maxima of the individual peaks (1280 cm^{-1}) probably corresponds to the frequencies of the stretching vibrations of the NO_2 group (Table 2), the absorption bands of which in the IR spectra have the maximum intensities.

A second peculiarity of II is the fact that they have fluorescent properties (Table 2); this also has not been observed previously [5, 10]. In addition, a basis for the reasons for the absence of fluorescence in the case of pyrazolines containing a 1-nitrophenyl group was presented in [10]. The presence in the nitro group of a nonradiative predissociation transition at 5000 A, which was previously noted in [11, 12], was considered to be the principal reason for quenching of the luminescence. Without rejecting this conclusion in principle, we would like to direct attention to the fact that the luminescence bands of IIa-f lie at 490-510 nm, i.e., in the same region as for the 3-(nitrophenyl) derivative discussed in [10], which has luminescence properties. The ratio of the energies of the $n-\pi^*$ and $\pi-\pi^*$ levels consequently corresponds to the requirements that determine the fluorescence; in other words, the energies of the $n-\pi^*$ levels in IIa-f are higher than the energies of the $\pi-\pi^*$ levels.

Pyrazolines IIIa-f (Table 2) also display luminescence properties. A peculiarity of the luminescence spectra of solutions of these compounds in ethanol is the appearance of a vibrational structure. The effect of the substituent in these spectra is subject to the same principles as in the case of the absorption spectra.

The relative quantum yields were measured for III (with 1,3,5-triphenylpyrazoline as the standard); they were found to be relatively low, ranging from 0.21 to 0.25.

The band of the stretching vibrations of the $C=N$ group is one of the most intense bands in the IR spectra of I and II, whereas its relative intensity is very low in the spectra of pyrazolines IIIa-f. This is probably due to the fact that the nitro group promotes polarization of the $C=N$ group, during which the moment of the transition and the intensity of the band increase, whereas an amino group introduced into the 1-aryl substituent has the opposite effect.

EXPERIMENTAL

The electronic spectra were measured with a Specord spectrophotometer, the luminescence spectra were measured with a Hitachi MPF-2A spectrofluorimeter, and the IR spectra were measured with a UR-20 spectrometer. The results of elementary analysis, the melting points, and the yields of the compounds obtained are presented in Tables 1 and 2.

4-R'-Chalcone p-Nitrophenylhydrazones (Ia-f). These compounds were obtained by the usual method [13].

1-(p-Nitrophenyl)-3-aryl-5-phenyl-2-pyrazolines (IIa-f). Nitrophenyl hydrazones Ia-f were cyclized to pyrazolines IIa-f by the method in [14].

1-(p-Aminophenyl)-3-aryl-5-phenyl-2-pyrazolines (IIIa-f). A 0.01-mole sample of 1-(p-nitrophenyl)-3-aryl-5-phenyl-2-pyrazoline (IIa-f) was dissolved by heating in 90 ml of ethylene glycol in a three-necked flask equipped with a stirrer, dropping funnel, and condenser, and ammonium hydroxide was added to the resulting solution to pH 8-9 (~10.5 ml). A solution of sodium hydrosulfite (14 g in 45 ml of water) was added slowly dropwise with stirring at 110-125 deg C until the mixture turned lemon-yellow. It was then heated for another 30 min, after which it was filtered, and the filtrate was diluted with dilute ammonium hydroxide until the mixture was weakly alkaline. Boiling water was then added until the mixture became turbid. The mixture was cooled, and the resulting precipitate was removed by filtration, dried, and chromatographed on Al_2O_3 (elution with benzene). The fraction with luminescence in UV light was collected, the solvent was removed with a rotary evaporater, and the residue was crystallized from benzene.

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