4-(o-Anilinimino)-2-thiazolidone (X). A mixture of 1.33 g (10 mmole) of isorhodanine I and 1.08 g (10 mmole) of o-phenylenediamine in 30 ml of methanol was stirred at room temperature for 30 min, after which the precipitated was removed by filtration, washed with methanol, and dried to give 1.4 g (68%) of a product with mp 145-146°C (dec., from propanol) and Rf 0.4 (elution with methanol). IR spectrum (cm$^{-1}$): 3395 m and 3300 s ($NH_2$), 3230 m (NH), 1690 s (CO, amide I), 1565 and 1530 m (amide II, Ar), and 1300 m and 1275 m (amide III). PMR spectrum, δ (ppm): 10.4 s (NH), 6.5-7.2 m ($4H_{ar}$), 5.2 broad s ($NH_2$), and 4.5 s ($CH_2$). Found, %: C 52.4; H 4.4; N 20.3; S 15.6. $C_9H_9N_3OS$. Calculated, %: C 52.1; H 4.3; N 20.2; S 15.4.

4-(o-Benzylideneanilinimino)-5-benzylidene-2-thiazolidone (XII). A mixture of 0.5 g (2.4 mmole) of 4-(o-anilinimino)-2-thiazolidone and 0.53 ml (5 mmole) of benzaldehyde in 5 ml of glacial acetic acid was heated until the starting components dissolved completely, after which the solution was allowed to stand at room temperature for 10 min. It was then diluted with water and filtered, and the solid was dried to give 0.8 g (87%) of a product with mp 197-198°C (from benzene) and $R_f$ 0.78 (elution with chloroform). IR spectrum (cm$^{-1}$): 3290 m (NH), 1735 s (CO, amide I), 1570 s and 1540 m (amide II, Ar), 1310 w and 1270 m (amide III). Found, %: C 72.1; H 4.2; N 11.1; S 8.1. $C_{23}H_{17}N_3OS$. Calculated, %: C 72.1; H 4.4; N 11.0; S 8.3.

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# EFFECT OF PERFLUOROPHENYL GROUPS ON THE NATURE OF THE ELECTRONIC ABSORPTION SPECTRA OF 1,3,5-TRIARYL-Δ$^2$-PYRAZOLINES

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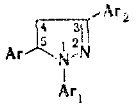
and V. T. Skripkina

UDC 547.778.2'221:535.34.001.5

The results of calculations by the self-consistent field (SCF) MO Pariser—Parr—Pople (PPP) method explain the nature of the electron transitions responsible for the electronic absorption spectra of 1,3,5-triphenylpyrazoline and its perfluorophenyl derivatives. The perfluorophenyl group behaves like a strong electron donor in the excited states. According to the results of the calculation, a perfluorophenyl group in the 1 position of the pyrazoline ring deviates markedly from the planar conformation.

Like their long-wave absorption, the luminescence of 1,3,5-triarylpyrazolines (I) is due to the electron transitions in the chromophore system (II), which includes 1- and 3-aryl groups [1-3]. The long-wave band is an intramolecular charge-transfer band in system II [3-5].



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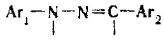

$Ar_1-\underset{|}{N}-N=\underset{|}{C}-Ar_2$

II

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Rostov State University, Rostov-on-Don 344006. All-Union Scientific-Research Institute of Single Crystals, Scintillation Materials, and Ultrapure Chemical Substances, Kharkov 310059. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 669-672, May, 1978. Original article submitted May 18, 1977.

TABLE 1. Results of the Calculation of the Spectral Characteristics of the Conjugated Fragments of Triarylpyrazolines

| Structure | Calc. |  | Exptl. |  |
|---|---|---|---|---|
|  | E, eV | λ, nm | E, eV | λ, nm |
| III | 3,71 | 334 | 3,44 | 360 |
|  | 4,40 | 282 | 4,00 | 310 |
| IV | 3,66 | 338 | 3,35 | 370 |
|  | 3,78 | 328 | 4,13 | 300 |
| V | 3,28 | 378 | — | — |
|  | 4,04 | 307 | 3,82 | 324 |
| VI | 3,54 | 350 |  |  |
|  | 4,18 | 296 | — | — |
| VII | 3,54 | 350 | 3,26 | 380 |
|  | 3,88 | 320 | 3,82 | 325 |
| VIII | 3,33 | 372 | — | — |
|  | 4,01 | 309 | 3,88 | 320 |

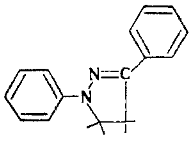
Data on the electronic absorption spectra of 1,3,5-triarylpyrazolines containing perfluorophenyl groups in the 1 and 3 positions are presented in the present communication. The experimental data are compared with the results of a quantum-chemical calculation, the goal of which was the assignment of the electron transitions and determination of the electronic effects of perfluorophenyl groups in the ground and electronically excited states.

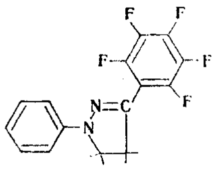
Fluorine atoms bonded to an aromatic ring display electron-acceptor inductive and electron-donor conjugation effects of comparable magnitude [6], and the overall electronic effect of fluorine is therefore close to zero. According to the data in [7], the perfluorophenyl group in the electronic ground state of the molecules is a stronger electron-acceptor substituent than the phenyl group.

To estimate the electronic effect of the perfluorophenyl group in various positions of the pyrazoline ring on the absorption spectra we calculated the energies of the electron transitions and electronic structures in the ground and excited states of triarylpyrazolines III-VIII.

The calculations were carried out by the SCF MO method within the π-electron approximation [the Pariser—Parr—Pople (PPP) approximation]. Twenty singly excited configurations were taken into account for the calculation of the spectral characteristics. The parameters and characteristics of the program for the calculation were presented in [8]. The III-VIII molecular fragments were assumed to be planar, and geometrical optimization was accomplished by the method of a variable resonance integral; the orbitals of the $sp^3$-hybridized atoms and the unconjugated system of the 5-aryl ring were disregarded. The results of the calculations and the experimental data on the absorption spectra are presented in Table 1.

The long-wave absorption bands of pyrazoline III are reproduced by the results of the calculation. The deviation of 0.3-0.4 eV can be eliminated by a more branched configuration interaction (allowance for 63 singly excited configurations). Since the aim of our calculation was not a precise matching of the experimental and calculated spectra but rather estab-


III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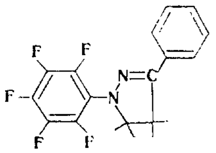
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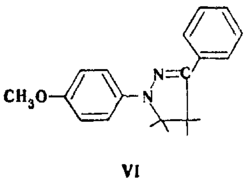
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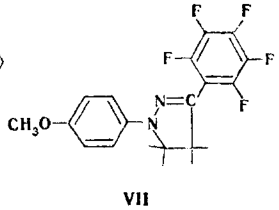
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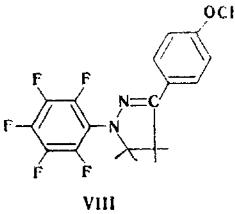
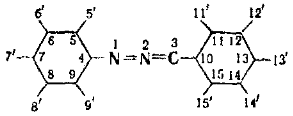

VIII

TABLE 2. π Charges on the Atoms in the Ground State ($S_0$) and First Excited Singlet ($S_1$ and $S_2$) States in the II Fragment of Triarylpyrazolines



| Atom No. | III |  |  | IV |  |  | V |  |  |
|---|---|---|---|---|---|---|---|---|---|
|  | $S_0$ | $S_1$ | $S_2$ | $S_0$ | $S_1$ | $S_2$ | $S_0$ | $S_1$ | $S_2$ |
| 1 | 0,276 | 0,613 | 0,477 | 0,266 | 0,463 | 0,320 | 0,272 | 0,527 | 0,303 |
| 2 | −0,234 | −0,396 | −0,208 | −0,284 | −0,413 | −0,450 | −0,233 | −0,467 | −0,431 |
| 3 | 0,083 | 0,005 | 0,108 | 0,101 | −0,085 | −0,094 | 0,055 | −0,059 | −0,133 |
| 4 | 0,002 | −0,019 | 0,039 | 0,007 | −0,031 | −0,008 | −0,087 | 0,002 | −0,085 |
| 5 | −0,006 | −0,011 | −0,117 | −0,073 | −0,046 | −0,071 | −0,099 | −0,090 | 0,047 |
| 6 | 0,005 | 0.004 | −0,135 | 0,004 | −0,001 | 0,004 | −0,055 | −0,019 | −0,004 |
| 7 | −0,035 | −0,002 | 0,086 | −0,043 | −0,039 | −0,043 | −0,076 | −0,014 | −0,064 |
| 8 | 0,007 | −0,004 | −0,123 | 0,004 | −0,005 | −0,000 | −0,065 | −0,074 | 0,049 |
| 9 | −0,055 | 0,075 | −0,120 | −0,064 | −0,027 | −0,054 | −0,070 | 0,044 | −0,030 |
| 10 | −0,009 | −0,068 | −0,009 | −0,121 | −0,072 | −0,124 | −0,004 | −0.081 | −0,040 |
| 11 | −0,004 | −0,039 | −0,009 | −0,014 | −0,122 | 0,096 | 0,001 | −0,053 | −0,046 |
| 12 | −0,000 | −0,008 | 0,000 | −0,083 | −0,002 | −0,032 | −0,001 | −0,010 | −0,002 |
| 13 | −0,007 | −0,063 | 0,013 | −0,035 | −0,084 | −0,100 | 0,001 | −0,075 | −0,037 |
| 14 | −0,001 | −0,007 | 0,001 | −0,082 | −0,087 | −0,064 | −0,001 | −0,008 | −0,002 |
| 15 | −0,014 | −0,020 | 0,020 | −0,001 | 0,070 | −0,076 | 0,006 | −0,055 | −0,045 |
| 5' |  |  |  |  |  |  | 0,045 | 0,052 | 0,084 |
| 6' |  |  |  |  |  |  | 0,078 | 0,086 | 0,113 |
| 7' |  |  |  |  |  |  | 0,076 | 0,096 | 0,091 |
| 8' |  |  |  |  |  |  | 0,078 | 0,077 | 0,123 |
| 9' |  |  |  |  |  |  | 0,080 | 0.120 | 0,108 |
| 11' |  |  |  | 0,088 | 0,076 | 0,143 |  |  |  |
| 12' |  |  |  | 0,075 | 0,100 | 0,104 |  |  |  |
| 13' |  |  |  | 0,084 | 0,087 | 0,087 |  |  |  |
| 14' |  |  |  | 0,076 | 0,081 | 0,131 |  |  |  |
| 15' |  |  |  | 0,035 | 0,137 | 0,103 |  |  |  |

lishment of the tendencies caused by the introduction of perfluorophenyl groups in various positions of the pyrazoline ring, the noted deviations are not of substantial significance.

It is apparent from the data in Table 2 that the first excited state of triphenylpyrazoline is associated with transfer of electron density from the nitrogen atom (0.35 e) to the $-N=C-C_6H_5$ grouping. The second excited state is of a different nature and is due to charge transfer (0.2 e) from the nitrogen atom to the adjacent aryl ring.

Replacement of the phenyl ring by a perfluorophenyl ring — conversion to IV — substantially changes the nature of the electron transitions (Table 2). The transition to the first excited state is accompanied by redistribution of the electron density in the $-N-N=C-$ chain, and the perfluorophenyl group participates relatively weakly in this redistribution. Electron density is transferred from the perfluorophenyl group to the azimethine bond in the second excited state. Thus, according to the results of the calculation, a perfluorophenyl group in the 3 position of the pyrazoline ring acts as a rather strong electron donor in the first and second excited states. Judging from the electron-distribution data, in the electronic ground state it behaves like a weak electron donor. However, one should bear in mind that because of the π-electron approximation used in the calculation, the role of the inductive effect of fluorine, which acts in the opposite direction, is not adequately taken into account in the electronic ground state.

The calculations predict that the introduction of fluorine atoms in the 1-aryl ring should lead to an appreciable bathochromic shift of the bands in the electronic spectra (V and VIII). The available experimental observations (Table 1) contradict these data. The disparity between the calculated and experimental energies of the long-wave transitions can be explained by the noncoplanarity of the 1-perfluorophenyl-substituted pyrazolines due to rotation about the N-Ar bond. The calculations show that a decrease in the resonance integral for this bond actually leads to a hypsochromic shift of the spectrum. The reasons for this rotation are evidently associated with an increase in the steric interactions of the fluorine atoms of the 1-aryl ring with the 5-phenyl ring and with repulsion of the unshared electron pairs of the fluorine atoms and the azomethine nitrogen atom.

The first excited state in V and VIII (Table 2) is associated with transfer of electron density from the perfluorophenyl group (0.35 e) and the nitrogen atom (0.3 e) to the azomethine bond (0.35 e) and the phenyl ring (0.3 e). The second excited state has a similar nature. The presence of a methoxy group in the 3-phenyl ring does not fundamentally affect the nature of the electron transitions. Consequently, according to the calculated values, the perfluorophenyl group in the 1 position of the heteroring acts as a weak electron acceptor in the electronic ground state and as a rather strong electron donor with respect to the phenyl group in the first and second excited states.

The authors thank B. Ya. Simkin for his useful discussion.

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# NMR SPECTRA OF PYRIMIDINES.

## EFFECT OF SUBSTITUENTS ON THE CHEMICAL SHIFTS OF THE "meta" PROTONS IN 2- AND 4-SUBSTITUTED PYRIMIDINES

O. P. Shkurko and V. P. Mamaev

UDC 543.422.25:547.853:541.67

The chemical shifts of the protons in the even positions of the pyrimidine ring in 2- and 4-substituted pyrimidines in dimethyl sulfoxide solutions were determined. The correlation equations that link the relative chemical shifts (with allowance for corrections for the magnetic anisotropy of the substituents and the ring) with the F and R substituent constants were calculated. The ratios obtained were analyzed by comparison with the corresponding correlation equations for monosubstituted benzenes. The reasons for the significant increase in the transmission of the conjugation effects of the substituents to the even positions of the pyrimidine ring as compared with the meta positions of the benzene ring and the appreciable weakening of the conductivity of their inductive effects when the heteroring nitrogen atom is situated between a resonating proton and the substituent are discussed.

We have previously [1] studied the effect of substituents on the chemical shifts of the 5-H and 2-H protons in 2- and 5-substituted pyrimidines and have ascertained the specific characteristics of the transmission of the electronic effects of substituents to the para position in the pyrimidine ring via both inductive and conjugation mechanisms. In the present communication we examine the effect of substituents on the chemical shifts of the protons of the pyrimidine ring that are located in meta positions relative to the substituent. The measured chemical shifts of the protons in the 4 position of the ring ($\delta_4$-H) for 2-substituted pyrimidines (series I) and in the 2 ($\delta_2$-H) and 6 ($\delta_6$-H) positions for 4-substituted

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