SPECTRAL PECULIARITIES OF ISOMERIC trans-STYRYLPYRAZOLES

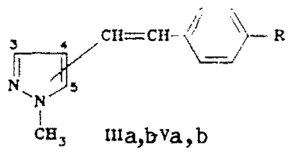
V. P. Perevalov, L. I. Baryshnenkova, G. V. Sheban,
A. K. Kh. Karim, S. S. Kramarenko, T. Yu. Koldaeva,
and B. I. Stepanov

UDC 547.773:535.34:530.-
145.001.24

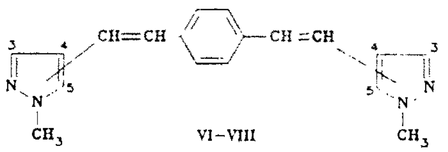
The regularities in the electronic absorption spectra of trans-styrylpyrazoles were interpreted on the basis of quantum-chemical calculations by the Pariser–Parr–Pople configuration-interaction (PPP CI) method and data from the photoelectron spectra taking into account the peculiarities of the formation of the boundary molecular orbitals of pyrazole. The difference in the electronic effects of the isomeric pyrazolyl radicals determines the degree of polarization of the ethylene fragment and the C–C bonds of the pyrazole ring in the styrylpyrazole molecules; this is reflected in their IR spectra.

The electronic absorption spectra (EAS) of isomeric phenylpyrazoles have been studied in detail [1-3]. 1,5-Disubstituted pyrazoles, in the molecules of which the coplanarity of the pyrazole and benzene rings is disrupted, occupy a special place among these compounds. This, for example, leads to a hypsochromic shift of the long-wave band in the EAS of 1-methyl-5-phenylpyrazole (I) [4] and to a shift to strong field of the signals of the proton in the 4 position of pyrazole and of the protons of the substituents in the PMR spectrum of I [5] as compared with the spectra of 1-methyl-3-phenylpyrazole (II). However, an interrelationship between the spectral and molecular-orbital characteristics of the isomers and regularities associated with differences in the electron structures of the 3-, 4-, and 5-pyrazolyl radicals were not established in a study of the EAS of phenylpyrazoles.

We have attempted to solve these problems in the case of pyrazole derivatives that contain a π-electron-acceptor styryl substituent, viz., trans-1-methyl-3-, trans-1-methyl-4-, and trans-1-methyl-5-(4-R-styryl)pyrazoles (IIIa-Va, R = NO_2; IIIb-Vb, R = NH_2) and trans,trans-1,4-bis(1-methyl-3-, -4-, and -5-pyrazolylvinyl)benzenes (VI-VIII) [6].



IIIa,bVa,b



VI–VIII

A comparison of the positions and intensities of the long-wave absorption band in the EAS of 3- and 5-substituted pyrazoles IVa,b, Va,b, VI, and VIII (Table 1) and an analysis of the PMR spectra of these compounds (Table 2) revealed the absence of the changes that are characteristic for the spectra of 3- and 5-phenylpyrazoles I and II. It may be concluded that the styryl and pyrazolyl fragments in IIIa,b, Va,b, VI, and VIII have an orientation that is close to coplanar, which should evidently be promoted by an s-cis configuration of the ethylene fragment relative to the C(pyrazolyl)–C(styryl) bond.

We carried out quantum-chemical calculations of the molecules of pyrazole, IIIa-Va, IIIb-Vb, and trans-3-, -4-, and -5-styrylpyrazoles IX-XI by the Pariser–Parr–Pople configuration-interaction (PPP CI) method with parametrization of the $N_{(1)}$ heteroring atom, which gives good results in the calculation of the position and intensity of the $CT_{NH_2}^{NO_2}$ band of 3- and 5-amino-1-methyl-4-nitropyrazoles [7]. The data obtained for IIIa-Va and IIIb-Vb are in good agreement with the positions of the long-wave absorption bands in the experimental EAS (Table 1). The calculation energies of the S_0–S_1 electron transition (ΔE) for the molecules of model compounds IX-XI increase in the order 5- < 4- < 3-isomer, which is retained, according to the EAS data, for bis(pyrazolylvinyl)benzenes VI-VIII (see Table 1 and the Experimental section).

D. I. Mendeleev Moscow Institute of Chemical Technology, Moscow 125820. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1061-1064, August, 1990. Original article submitted June 28, 1988.

0009-3122/90/2608-0887$12.50

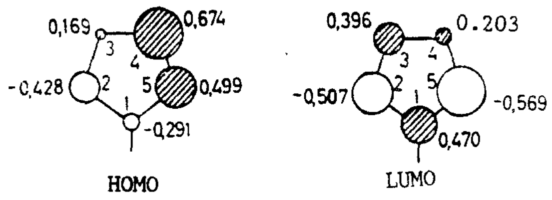


Fig. 1. Formation of the boundary molecular orbitals of pyrazole (according to the results of the calculations).

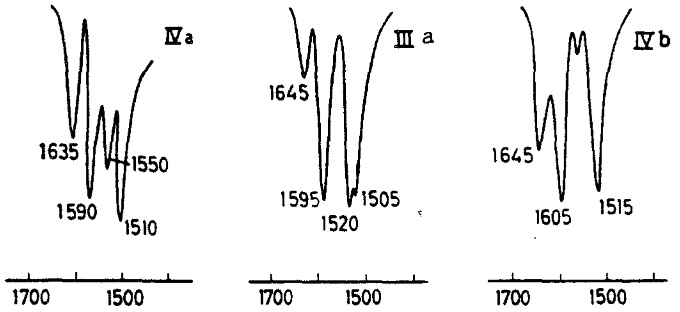


Fig. 2. IR spectra of IVa,b and IIIa (in KBr).

TABLE 1. Calculated and Experimental Characteristics of the Isomeric trans-Styrylpyrazoles and Their Derivatives*

Compound	E_{HOMO}, eV	IP_1 (PES)	E_{LUMO}, eV	$\|E_{HOMO} - E_{LUMO}\|$, eV	ΔE	λ_{max}, nm		ε
						calc.	exptl.	
III^a	−9,471	8,16	−3,409	6,062	3,553	349	351, *357***	20 500, 21 000
III^b	−8,301	6,60	−1,592	6,709	4,020	308	309, *310*	29 100, 28 100
IX	−9,053		−1,895	7,158	4,333	286	289	27 800
IV^a	−9,233	8,03	−3,370	5,863	3,404	364	361, *374*	23 900, 22 700
IV^b	−8,184	6,58	−1,438	6,746	4,010	308	306, *311*	30 000, 28 900
X	−8,839		−1,756	7,083	4,235	293	292	27 200
V^a	−9,513	8,51	−3,554	5,959	3,502	354	353, *359*	23 100, 21 200
V^b	−8,439	6,54	−1,859	6,580	3,870	321	336 (336)	27 000, 26 000
XI	−9,133		−2,158	6,975	4,134	300	—***	—

---

*IP) Ionization potential; PES) photoelectron spectrum.

**The EAS were recorded in ethanol; the data obtained in dioxane are given in italics, while the data obtained in benzene are given in parentheses.

***Compound XI was not obtained in individual form.

According to the calculations, the S_0–S_1 transitions in the molecules of styrylpyrazoles and substituted styrylpyrazoles are one-configuration transitions and the transition energy is determined by the difference $|E_{HOMO} - E_{LUMO}|$ (Table 1). The greatest change in the energy of the HOMO occurs when a styryl substituent is introduced into the 4 position of pyrazole (for pyrazole, $E_{HOMO}^{calc} = -10.27$ eV, $E_{LUMO}^{calc} = -0.49$ eV), while the greatest change in the energy of the LUMO occurs when a styryl substituent is introduced into the 5 position; this is due to the maximum contribution of the corresponding orbitals of the carbon atoms of the pyrazole ring that interact with the styryl residue to the boundary MO of pyrazole (Fig. 1).

This principle is confirmed experimentally in the case of a joint analysis of data from the PES and EAS of (4-nitrostyryl)pyrazoles IIIa-Va. According to the PES data used to evaluate the energies of occupied MO [8], 1-methyl-4-(4-nitrostyryl)pyrazole (IVa) has, in the series of isomers, the minimum value of the first ionization potential (IP_1), while 5-(4-nitrostyryl)pyrazole Va has the maximum IP_1 (Table 1). Since IIIa and Va have close ΔE values which, in turn, are determined by the $|E_{HOMO} - E_{LUMO}|$ differences, it may be concluded that 1-methyl-5-(4-nitrostyryl)pyrazole is characterized by the maximum E_{LUMO} value in the series of nitrostyrylpyrazoles (Table 1).

TABLE 2. Data from the PMR Spectra of IIIa,b, Va,b, VI, and VIII (d_6-DMSO)

Compound	Chemical shifts of the protons (δ, ppm) and SSCC (J, Hz)						
	$1\text{-}CH_3$	pyrazole ring protons			$J_{4\text{-}5(3)}$	CH=CH (d)	C_6H_4 (d)
		4-H, d	5H, d	3-H, d			
III a	3,87	6,58	7,67	—	2,5	7,24; 7,33	7,79; 8,17
III b	3,79	6,37	7,53	—	2,5	6,75; 6,87	6,55; 7,18
V a	3,97	6,74	—	7,42	2,0	7,29; 7,51	7,29; 7,51
V b	3,85	6,45	—	7,30	2,0	6,90*	6,58; 7,29
VI	3,84	6,54	7,67	—	2,5	7,12*	7,55*
VIII	3,92	6,61	—	7,37	2,0	7,16; 7,24	7,65*

---

*Singlet.

The addition of a 4-aminostyryl substituent (its mesomeric effect is close to zero) to any of the heteroring carbon atoms, in contrast to the introduction of a 4-nitrostyryl fragment – a typical electron acceptor [9] – leads, according to the PES data, to an approximately identical change in the energy of the HOMO. Consequently, the chief reason that the ΔE value is the minimum value for 5-(4-aminostyryl)pyrazole Vb as compared with the values of the isomers is the decrease in the energy of the LUMO caused by the effective interaction of the fragmental orbital of the 4-aminostyryl residue with the AO that makes the maximum contribution to the LUMO of pyrazole (Fig. 1).

The difference in the electronic effects of the isomeric pyrazolyl radicals that is due to the peculiarities in the distribution of the electron density in the heteroring is manifested, for example, in an increase in the order of the C(pyrazolyl)–C(styryl) bond in the 4-(4-nitrostyryl)pyrazole IVa molecule (0.344) as compared with the order of the same bond in 3-(4-nitrostyryl)pyrazole IIIa (0.320) and determines the degree of polarization of the ethylene fragment and the C–C bonds of the pyrazole ring in (4-R-styryl)pyrazole molecules. In the pyrazole IVa molecule the π charges (q_π) on the C atoms of the vinyl group are –0.044 and +0.039, as compared with –0.012 and +0.032 in the IIIa isomer and –0.010 and +0.004 in the Va isomer. The change in the π charges on the $C_{(4)}$ and $C_{(5)}$ atoms of the heteroring on passing from pyrazole IVa (q_π –0.104 and –0.032) to 4-(4-aminostyryl)pyrazole IVb (q_π –0.096 and –0.046) constitutes evidence for a decrease in the polarization of the corresponding bond of the pyrazole ring.

The indicated regularities are reflected in the IR spectra of substituted styrylpyrazoles. Sensitive (to a change in the π–π interaction) bands of stretching vibrations of the pyrazole ring at 1520-1560 cm^{-1} [10, 11] and of trans-ethylene bonds at 1625-1670 cm^{-1} [12], the intensities of which depend on the degree of polarization of the corresponding fragments of the molecules [13, 14], were identified in the spectrum of pyrazole IVa (Fig. 2). This is confirmed by the marked changes in the IR spectra of nitro compounds IIIa and Va as compared with the spectrum of pyrazole IVa and by the decrease in the intensity of the stretching vibrations of the heteroring at 1550 cm^{-1} in the spectrum of amine IVb (Fig. 2). In the spectra of (4-aminostyryl)pyrazoles IIIb-Vb the band at 1630-1650 cm^{-1} is due primarily to N–H deformation vibrations of the amino group [13] as evidenced by the absence of absorption in this region in the IR spectrum of trans-1-methyl-3-(4-N,N-dimethylaminostyryl)pyrazole (XII).

EXPERIMENTAL

The EAS spectra of solutions (c 10^{-4} mole/liter) of the compounds in ethanol, dioxane, and benzene were recorded with a Specord UV-vis spectrophotometer. The IR spectra of KBr pellets of the compounds were obtained with a UR-20 spectrometer. The PMR spectra of solutions of the compounds in d_6-DMSO were obtained with a Tesla BS-467 spectrometer (60 MHz) with hexamethyldisiloxane (HMDS) as the internal standard. The PES were recorded with a Perkin–Elmer PES-18 spectrometer and were calibrated relative to the $^2p_{1/2}$ and $^2p_{3/2}$ lines of Xe at 12.13 and 13.43 eV. The quantum-chemical calculations of the molecules were carried out by the PPP method [15] within the approximation of a variable β value [16] taking into account the configuration interaction (CI) and the additional introduction of optimization of the internuclear distances of the ground state with respect to the minimum atomization energy by means of a program that realizes the Dewar logarithm [17].

Substituted styrylpyrazoles IIIa-Va and IIIb-Vb and bis(pyrazolylvinyl)benzenes VI-VIII were synthesized by the method in [6], while IX, X, and XII were synthesized by the method in [18]. Electron absorption spectra, $\lambda_{max}(\varepsilon)$: in ethanol: VI 344 (63,400), VIII 356 (64,900), XII 340 (29,700); in dioxane: VI 346 (58,000), VII 352 (55,000), VIII 359 (54,000), XII 339 nm (29,400).

LITERATURE CITED

1. E. S. Krongauz, D. A. Bochvar, I. V. Stankevich, and V. V. Korshak, *Dokl. Akad. Nauk SSSR*, **179**, 94 (1968).
2. V. I. Minkin, A. F. Pozharskii, and Yu. A. Ostroumov, *Khim. Geterotsikl. Soedin.*, No. 4, 551 (1966).
3. P. Cohen-Fernandes and C. L. Habraken, *Rec. Trav. Chim.*, **86**, 1249 (1967).
4. I. L. Finar, *J. Chem. Soc. (B)*, No. 7, 725 (1968).
5. R. N. Butler, *Can. J. Chem.*, **51**, 2315 (1973).
6. V. P. Perevalov, A. K. Kh. Karim, M. A. Andreeva, E. G. Rumyantseva, and B. I. Stepanov, *Zh. Obshch. Khim.*, **52**, 2598 (1982).
7. V. P. Perevalov, V. V. Redchenko, G. V. Sheban, A. B. Kostitsyn, L. I. Baryshnenkova, and B. I. Stepanov, *Khim. Geterotsikl. Soedin.*, No. 12, 1629 (1986).
8. V. I. Vovna and F. I. Vilesov, *Advances in Photonics* [in Russian], No. 5, Leningrad State University, Leningrad (1975), p. 3.
9. H. Verschambre and A. Kergomard, *Bull. Soc. Chim. Fr.*, No. 1, 336 (1966).
10. Ya. A. Shuster V. A. Kozlova, and V. I. Seraya, *Khim. Geterotsikl. Soedin.*, No. 12, 1655 (1974).
11. B. V. Ioffe and N. L. Zelenina, *Khim. Geterotsikl. Soedin.*, No. 10, 1414 (1970).
12. M. A. Andreeva, A. K. Kh. Karim, E. A. Denisova, V. P. Perevalov, and B. I. Stepanov, *Zh. Obshch. Khim.*, **50**, 2370 (1980).
13. R. Silverstein, H. Bassler, and T. Morril, *Spectrometric Identification of Compounds* [Russian translation], Mir, Moscow (1977).
14. E. V. Titov, N. V. Poddubnaya, and L. N. Litvinenko, *Teor. Éksp. Khim.*, **2**, No. 3, 271 (1966).
15. P. Pariser and R. Parr, *J. Chem. Phys.*, **23**, 711 (1955).
16. V. P. Zvolinskii, Abstract, Master's Dissertation, Moscow (1970).
17. M. Dewar, *Molecular Orbital Theory in Organic Chemistry* [Russian translation], Mir, Moscow (1972), p. 220.
18. V. P. Perevalov, M. A. Andreeva, L. V. Shmelev, and B. I. Stepanov, *Khim. Geterotsikl. Soedin.*, No. 11, 1533 (1984).