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RESEARCHES ON PYRAZOLES

LIII. UV and Fluorescent Spectra of Some 1-Phenylpyrazoles. The Ortho-Effect of Substituents at Position 5*

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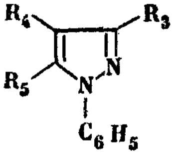
The existence of an ortho effect in 1-phenyl-5-substituted pyrazoles is proved by analyzing the UV and fluorescent spectra of a number of 1-phenylpyrazoles. The effect leads to destruction of the coplanarity of the phenyl and pyrazole rings.

The UV spectra of 1-phenylpyrazoles substituted at position 5 differ markedly from those substituted at position 3 or 4, by their absorption maximum being more on the short wave side (Table 1). As a chromophore, pyrazole itself absorbs in the region 210 mμ, lg ε 3.9 [1]. Substitution at position 1 by a phenyl substituent leads to conjugation of the π electron systems, and this naturally shows itself by a marked bathochromic shift of the maximum and a considerable increase in intensity of absorption (λ_{max} 251 mμ, lg ε 4.41 [2].). When there is any substitution at position 3 or 4 in the 1-phenylpyrazole ring, the spectrum changes in just the same way that the spectrum of benzene [3, 4] or pyridine [5] changes on substitution. The values for the bathochromic shifts (Table 2) are close to those for benzene compounds.

Table 1

UV Spectra of 1-Phenylpyrazoles (in Methanol)



Exp. No.	R_3	R_4	R_5	λ_{max}, mμ	lg ε
1	H	H	H	251	4.41
2	C_6H_5	H	H	278	4.40
3	H	H	C_6H_5	246	4.25
4	CH_3	H	H	256	4.15
5	H	H	CH_3	246	4.01
6	Cl	H	H	256	4.28
7	H	Cl	H	260	4.21
8	H	H	Cl	237	4.10
9	OH	H	H	271	4.32
10	H	OH	H	276	4.20
11	H	H	OH	241	4.20
12	NH_2	H	H	284	4.32
13	H	NH_2	H	282	4.16
14	H	H	NH_2	240	4.17
15	CH_3	H	NH_2	245	4.22
16	$NHCOCH_3$	H	H	274	4.44
17	H	$NHCOCH_3$	H	275	4.22
18	H	H	$NHCOCH_3$	238	4.09
19	CH_3	H	$NHCOCH_3$	246	4.26
20	COOH	H	H	263	4.54
21	H	COOH	H	262	4.17
22	H	H	COOH	250*	3.9

*A well-defined maximum was not found in the region investigated. See [10] regarding the possibility of using data of that kind for calculations.

In the case of 5-substituted 1-phenylpyrazoles, introduction of electron-donating and of electron-accepting substituents at position 5 led to shift of the absorption maximum to the shortwave side, with a hypsochromic effect (for 1-phenyl-5-carboxylic acid lg ε 3.90, while for 1-phenylpyrazole itself lg ε 4.41). This can be attributed to the displace-

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*For Part LII see [19].

ment of the benezene ring from coplanarity (ortho effect) by the substituent. This kind of effect is known in the case of 2-substituted 1-phenylpyrroles [6].

Table 2

Value of the Bathochromic Shift in mμ for Different Substituents at Positions 3 and 4 in the Pyrazole Ring of 1-Phenylpyrazole

Substituent	Position	
	3	4
CH_3	+5	—
Cl	+5	+9
COOH	+12	+11
OH	+20	+25
$NHCOCH_3$	+23	+24
C_6H_5	+27	—
NH_2	+33	+31

Usually the departure of aromatic systems from coplanarity is assessed by the intensity of the hypsochromic effect (Braude equation) [5, 9]:

$$\frac{\varepsilon}{\varepsilon^{\circ}} = \cos^2 \Theta$$

Angles Θ have been calculated from the data of Table 1 for various 5-substituted 1-phenylpyrazoles (Table 3). The starting point when calculating was the planarity of the 1-phenylpyrazole molecule in methanol solution. Despite the general acceptability of this assumption, it is necessary to bear in mind the results of a paper [7] where it is maintained that, for example, in solution, the phenyl rings in diphenyl are displaced through an angle of 23° (see also [8]).

In the present case calculations using the Braude equation assume that the phenyl substituent rotates solely around the bond between the two rings, and that like the valence angle of the substituent at position 5, the valence angle for this inter-ring bond does not depart from standard. Finally, the starting point for the calculation is that the change in spectrum is due only to the ortho effect. Subject to the conditions mentioned above, it is justifiable to determine in this way the steric effect of a substituent. It has been shown that the present Θ values are comparable with those obtained by other authors, including those obtained by other computing methods for o-substituted dimethylanilines [5, 7, 10], and that the general sequence of groups in order of increasing steric effect is

$$C_6H_5 < OH \cong NH_2 < Cl <$$
$$NHCOCH_3 < CH_3 < COOH .$$

Table 3

Value of the Angle Θ Defined by the Deviation from Coplanarity of the Phenyl Ring of 5-Substituted 1-Phenylpyrazoles (According to Braude's Equation)

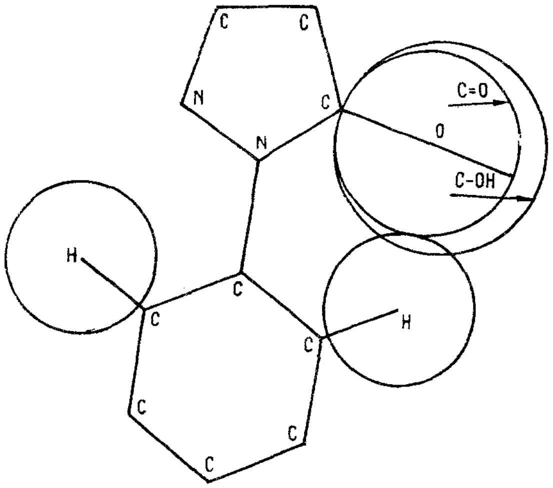
Expt. No.	R_5	R_3	lg ε—lg ε°	lg CosΘ	Θ
1	H	H	0	0	0
2	$NHCOCH_3$	CH_3	−0.15	−0.075	33°
3	C_6H_5	H	−0.16	−0.08	33°
4	H_2	CH_3	−0.19	−0,095	36°
5	OH	H	−0,21	−0,105	38°
6	H_2	H	−0.23	−0,115	40°
7	Cl	H	−0,31	−0,155	45°
8	$NHCOCH_3$	H	−0,32	−0,16	46°
9	CH_3	H	−0.40	−0,20	51°
10	CH_3	CH_3	−0.40	−0,20	51°
11	COOH	H	−0,51	−0,255	56°

Fluorescent spectra also confirm the presence of an ortho-effect in 5-substituted 1-phenylpyrazoles, as fluorescence is often determined by coplanarity of conjugated aromatic rings [11]. Actually 1-phenyl-4-amino- and 1-phenyl-3-aminopyrazole are strongly fluorescent, and have maxima at 380 and 360 mμ respectively, while 1-phenyl-5-amino- and 1-phenyl-3-methyl-5-aminopyrazole, which are isomeric with them, are not fluorescent. The same obtains for the corresponding 1-phenyl-x-hydroxypyrazoles (3- and 4-substituted ones fluoresced, the 5-substituted ones did not).

If a geometric model is built for the 1-phenyl-5-substituted pyrazole, the ortho effect becomes clear, even for the hydroxyl group (minimum volume).

Experimental

The UV spectra were measured in methanol, with a SF-4 instrument. Fluorescent spectra were measured with a SE-4 registering spectrophotometer equipped with a diffraction grating, and adapter for measuring fluorescence, made by the firm of Optica (Italy).* The filter transmitted the 313 mμ Hg line.



Geometric model of 1-phenyl-5-hydroxypyrazole, distances in Å.

In the pyrazole ring:

$(N_1\text{-}N_2) = 1.86$[12]; $(N_2\text{-}C_2) = 1.34$[12]; $(C_3\text{-}C_4) = 1.33$[12]; $(C_4\text{-}C_5) = 1.41$[12]; $(C_5\text{-}N_1) = 1.31$[12]; angle $N_2N_1C_1'$ 118° 15'[13]; $(N_1\text{-}C_1') = (C_1\text{-}C'_1)$ in diphenyl = 1.48[16].

In the phenyl ring:

$(C_1\text{-}C_2) = 1.397$[14,15]; $(C-H) = 1.084$[14,15]. Bond C–O; $C{=}O(CH_2O) = 1.21$[16]; $C{=}O(HCONH_2) = 1.25$[17]; C–O $(CH_3OH) = 1.43$[18].

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