BRIEF COMMUNICATIONS

DIPOLE MOMENTS OF MOLECULES OF 1, 3, 5-TRIARYL-Δ^2-PYRAZOLINES

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Khimiya Geterotsiklicheskikh Soedinenii, Vol. 3, No. 5, 948–949, 1967

UDC 547.772.2'543.253'426+541.67

The dipole moments of 1, 3, 5-triphenylpyrazole and a number of pyrazoline derivatives are determined. The presence of a C=C double bond in pyrazole does not lead to formation of a single π electron system in the heterocyclic ring. Comparison of found and calculated vector dipole moments confirms the appreciable effect of aromatic groups at position 1, and especially at position 3, and the slight effect at position 5.

Investigation of fluorescence [1], absorption, and luminescence spectra [2] and of polarographic reduction potentials [3] of Δ^2-pyrazoline derivatives, led to the conclusion that aromatic groups at positions 1 and 3 exert an appreciable effect on λ_m the maximum of the bands, and that at position 5 they have no effect. From this point of view it was of interest to consider the dipole moments (DM) of molecules of derivatives of 1, 3, 5-Δ^2-triphenylpyrazoline derivatives with substituents in the various benzene rings. For this purpose the densities and dielectric constants (beat method) of benzene solutions of 13 compounds tabulated were measured, and known formulas used to calculate the dipole moments of their molecules (μ_H, D). For comparison the DM (dipole moment) of the 1, 3, 5-triphenylpyrazole molecule was also measured.

μ_H for 1, 3, 5-triphenylpyrazole is almost the same as that of 1, 3, 5-triphenyl-Δ^2-pyrazoline (2.69 and 2.58 D). On the other hand the dipole moments of these molecules can be satisfactorily calculated vectorially, starting from the assumption of a planar molecule with the same angle between bonds (108°), and individual bond moments $\mu_{C\overset{\rightarrow}{=}N}$ = 2.47 D [4], $\mu_{\overrightarrow{het}-C_{ar}}$ = 0.4 D, and $\mu_{C\overset{\rightarrow}{-}N}$ = 0.45 D. The calculated moment is 2.53 D and it is directed along the conventional axis of the molecule passing through the N_1 nitrogen atom and the middle of the C_3—C_4 bond at an angle of 144°. DM for 1, 3, 5-triphenylpyrazoline, from other data [5] is 2.47 D. This is all intelligible only on a basis of assumption that the presence of a C=C bond in pyrazole does not result in formation of a single electron system in the heterocyclic ring, since the latter would lead to an appreciable difference between the resultant moments for pyrazole and pyrazoline molecules. Obviously μ_H for the molecules of the compounds considered are determined mainly by the C—N (C_6H_5)—N=C (C_6H_5)— group.

The simple vector method was also used to calculate DM for compounds with a para substituent in the phenyl group (μ_p), and values $\Delta\mu = \mu_p - \mu_H$ were obtained (table). In making the calculations the following DM values were taken respectively for molecules of monosubstituted benzenes C_6H_5X where X = Cl, Br, NO_2: 1.55, 1.52, 4.00 D. The components μ_x and μ_y of the resultant moment of 1, 3, 5-triphenyl-Δ^2-pyrazoline are respectively 1.52 and 2.09 D.

It can be seen that 5-aryl-substituted compounds have only low $\Delta\mu_H$ values (in the case of the nitro group only +0.19 D), while the nitro group introduced

Dipole Moments (μ, D) of 1,3,5-Triaryl-Δ^2-Pyrazolines

Compound	α	β	$P_{2\infty}$	P_{E+A}	P_{op}	μ_H	μ_p
1, 3, 5-Triphenylpyrazole	11.57	0.731	247.8	97.8	150.0	2.69	2.46
1, 3, 5-Triphenyl-Δ^2-pyrazoline	10.70	0.761	235.7	97.7	138.0	2.58	2.46
1, 5-Diphenyl-3-methyl-Δ^2-pyrazoline	13.88	0.464	270.3	76.0	194.3	3.04	—
1, 5-Diphenyl-3-p-chlorophenyl-Δ^2-pyrazoline	18.52	1.407	342.6	104.0	238.6	3.39	2.62
1, 5-Dipheny-3-p-bromophenyl-Δ^2-pyrazoline	14.55	1.570	294.5	107.0	187.5	3.01	2.51
1, 3-Diphenyl-5-o-chlorophenyl-Δ^2-pyrazoline	8.18	0.794	209.4	104.0	105.4	2.26	—
1, 3-Diphenyl-5-p-dimethylaminophenyl-Δ^2-pyrazoline	13.78	1.109	285.1	112.0	173.1	2.90	2.55
1, 3-Diphenyl-5-p-nitrophenyl-Δ^2-pyrazoline	25.20	1.198	450.6	103.2	347.4	4.10	3.91
1, 3-Diphenyl-5-m-nitrophenyl-Δ^2-pyrazoline	20.25	1.012	383.6	103.2	280.4	3.68	—
1-Phenyl-3-p-nitrophenyl-5-p-methoxyphenyl-Δ^2-pyrazoline	41.08	1.203	694.1	110.2	583.9	5.31	—
3, 5-Diphenyl-1-p-chlorophenyl-Δ^2-pyrazoline	23.57	1.498	414.0	104.0	310.0	3.87	3.91
3, 5-Diphenyl-1-p-nitrophenyl-Δ^2-pyrazoline	86.40	1.148	1351.6	103.2	1284.4	7.77	6.21
3, 5-Diphenyl-1-m-nitrophenyl-Δ^2-pyrazoline	33.75	0.713	590.9	103.2	487.7	4.86	—
3, 5-Diphenyl-1-o-methoxyphenyl-Δ^2-pyrazoline	11.61	1.324	242.1	104.3	137.8	2.57	—

into the 1-phenyl group, gives $\Delta\mu = +1.56D$, greater than the value for p-nitroaniline, and close to that for p-nitrodimethyl-aniline [5]. Appreciable too are the $\Delta\mu$ values for the cases where X = Cl and Br when they are introduced into the 3-phenyl group. Thus the abovementioned difference in the effects of aromatic groups at positions 1 and 3 on the one hand, and at position 5 on the other, is observed for properties of molecules not only in the excited state [4], but also in the ground state, as the dipole moments of the molecules show. A particularly considerable increase in moment with the p-nitro substituent in the 1-phenyl group may indicate that a pair of unextended electrons N_1 participates slightly in the conjugation in the actual heterocyclic ring, and this also determines the possibility of its being shifted appreciably for the nitro group.

We thank V. G. Tishchenko for allowing publication of material

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3 January 1967

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RESEARCH ON 2, 1, 3-THIA-AND SELENADIAZOLE

XLVIII.* Synthesis of α-Amino-β-(3, 4-Diaminophenyl) Propionic Acid

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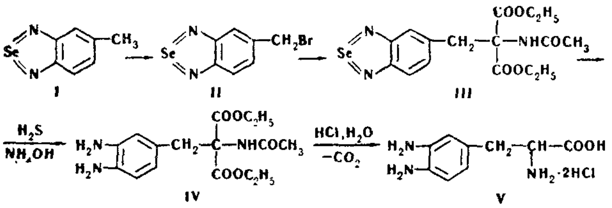
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 3, No. 5, 950–951, 1967

UDC 547.782.9'466:547.785.5

Reductive decomposition followed by hydrolysis of 5-(β, β-dicarethoxy-β-acetylamino)ethylbenz-2, 1, 3-selenadiazole gives β-(3, 4-diaminophenyl)alanine.

The present paper describes the hitherto undescribed synthesis of β-(3, 4-diaminophenyl)alanine (V) from 5-methylbenz-2, 1, 3-selenadiazole.



5-methylbenz-2, 1, 3-selenadiazole (I) is brominated with bromosuccinimide, to give 5-bromomethylbenz-1, 2, 3-selenadiazole (II), which is then reacted with sodioacetylaminomalonic ester, to give the malonate III. The latter is then reductively cleaved with hydrogen sulfide in aqueous alcoholic ammonia, to malonate IV. Acid hydrolysis and decarboxylation of the latter converts it to dihydrochloride V, paper chromatography of which gave one spot with a positive ninhydrin reaction. The reductive cleavage product, malonate IV, is also characterized as an o-diamine by reaction with phenanthraquinone.

An attempt was made to prepared V by reductive cleavage of 5-(β-carboxyoxy-β-amino) ethylbenz-2, 1, 3-selenadiazole (VI), in its turn obtained by acid hydrolysis and decarboxylation of malonate III, but the action of hydrogen sulfide on a solution of VI in ethanol

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*For Part XLVII see [1].