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ELECTROPHILIC SUBSTITUTION REACTIONS IN TRISPYRAZOLEDIYLS. STRUCTURE OF TRIS(3-METHYL-4-ISOPROPYL-1,5-PYRAZOLEDIYL)

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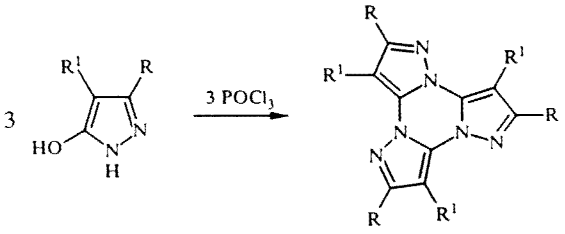
Halogenation, nitration, and sulfonation of previously obtained tris(1,5-pyrazolediyls) proceeds at position 4 of the pyrazole nucleus with the formation of symmetrical tris(4-substituted 1,5-pyrazolediyls) in quantitative yield. However, only a monoformyltrispyrazolediyl is obtained in the Vilsmeier reaction. An x-ray structural investigation has been carried out on the trispyrazolediyl nucleus of compound (Ic).

A new condensation of 5-pyrazolones occurring under the action of phosphorus oxychloride and leading to tris(1,5-pyrazolediyl) (I) was discovered by us previously [1].*



Ia-c

Ia R = Me, R¹ = H; b R = Ph, R¹ = H; c R = Me, R¹ = *i*-Pr

In general, the obtained heterocycles should differ little from pyrazoles with a free 4 position in ease of carrying out electrophilic substitution. However, the highly condensed nature of compounds (I) changed the expected result significantly.

To halogenate the trispyrazolediyls, we decided to use our previously developed method [3] for halogenating pyrazoles, which comprises reacting free halogen with pyrazole in concentrated hydrohalogen acid. However, the method proved to be of little use even for the most basic tris(3-methyl-1,5-pyrazolediyl) (Ia) since the introduction into the molecule of even one halogen atom (Br or Cl) sharply reduced its basicity and the halogen derivative precipitated from solution, subsequently the reaction occurs only in the heterogeneous phase. The reaction generally did not proceed with iodine and the phenylpyrazolediyl (Ib) was insoluble in hydrogen halide acids due to its low basicity [1]. By carrying out the reaction under more forcing conditions, particularly when using an excess of halogen (Cl_2 or Br_2) in chlorobenzene and heating, or iodine in the presence of I_2O_5 to oxidize the hydriodic acid formed, we succeeded in obtaining the trihalogen derivatives (II) in quantitative yield.

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*Regrettably, at the time of publication of [1] we mistakenly missed the short communication [2] in which the same condensation was described for 3-methylpyrazolone. We offer our apologies to the authors of the above-mentioned work and also thank J. Elguero for pointing out this oversight to us.

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TABLE 1. Yields and Constants of Trispyrazolediyls (II), (III), and (VI)

Tris(1,5-pyrazolediyl)	mp, °C	IR spectrum, cm^{-lvl}	UV spectrum, λ_{max}, nm (log ε)	Yield, %
IIa	333...336	1635	247 (4,35), 251 (4,29)	Quantitative
IIb	305...307	1630	247 (4,59), 254 (4,53)	Quantitative
IIc	315...317	1605	255 (4,64), 263 (4,66)	Quantitative
IId	334...337	1625	226 (4,29), 254 (4,53)	Quantitative
IIe	288...290	1615	224 (4,37), 276 (4,82)	Quantitative
IIf	330...332	1590	221 (4,53), 276 (4,66)	Quantitative
VI	334...336	1660	250 (4,20) †, 260 (4,15)	30
III	255...256	1645, 1525, 1390	222 (4,63) † 287 (4,48)	52

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*All substances melted with decomposition, mp were determined in sealed capillaries.

†Taken in ethyl alcohol.

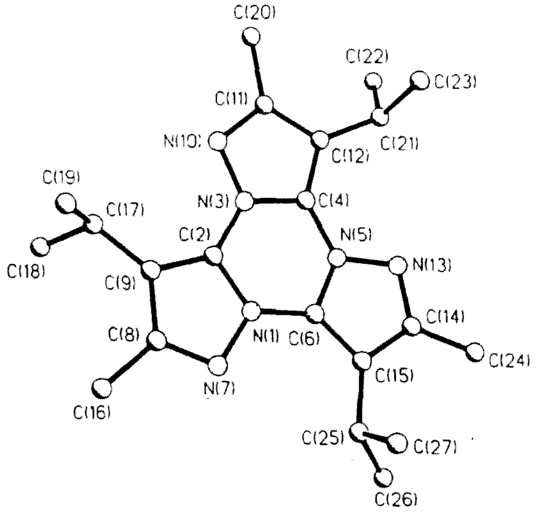
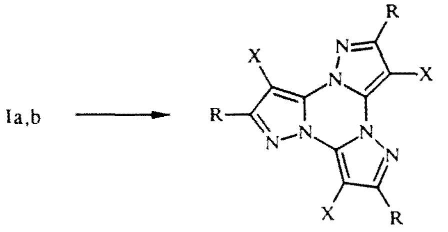


Fig. 1. Structure of the (Ic) molecule.



II-IV

II a R = Me, X = Cl; b R = Me, X = Br; c R = Me, X = I; d R = Ph, X = Cl; e R = Ph, X = Br;
f R = Ph, X = I; III R = Me, X = NO_2; IV R = Me, X = SO_3Na

The synthesized compounds were high-melting colorless powders, practically insoluble in the majority of solvents. All our attempts to isolate intermediate halogenated products (mono and di derivatives) proved to be unsuccessful. It was established chromatographically and with the aid of PMR spectra that with a large excess of trispyrazolediyl and slow addition of halogen to the mixture compounds were present, in addition to trispyrazolediyl and the trihalogenated derivative, with an R_f less than that of the trihalogen derivative but greater than that of the starting material. However, all our attempts to separate the mixture and identify mono- and dihalides proved unsuccessful.

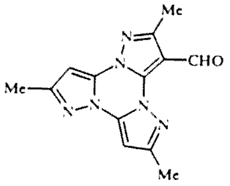
TABLE 2. Bond Lengths (Å) in Structure (Ic)

Bond	d, Å	Bond	d, Å
$N_{(1)}-C_{(2)}$	1,369(7)	$C_{(9)}-C_{(17)}$	1,482(9)
$N_{(1)}-C_{(6)}$	1,384(7)	$N_{(10)}-C_{(11)}$	1,341(7)
$N_{(1)}-N_{(7)}$	1,372(6)	$C_{(11)}-C_{(12)}$	1,416(8)
$C_{(2)}-N_{(3)}$	1,396(7)	$C_{(11)}-C_{(20)}$	1,49(1)
$C_{(2)}-C_{(9)}$	1,364(8)	$C_{(12)}-C_{(21)}$	1,497(8)
$N_{(3)}-C_{(4)}$	1,362(7)	$N_{(13)}-C_{(14)}$	1,325(7)
$N_{(3)}-N_{(10)}$	1,372(6)	$C_{(14)}-C_{(15)}$	1,401(7)
$C_{(4)}-N_{(5)}$	1,388(7)	$C_{(14)}-C_{(24)}$	1,496(9)
$C_{(4)}-C_{(12)}$	1,364(7)	$C_{(15)}-C_{(25)}$	1,517(8)
$N_{(5)}-C_{(6)}$	1,363(6)	$C_{(17)}-C_{(18)}$	1,48(1)
$N_{(5)}-N_{(13)}$	1,371(6)	$C_{(17)}-C_{(19)}$	1,49(1)
$C_{(6)}-C_{(15)}$	1,376(8)	$C_{(21)}-C_{(22)}$	1,52(1)
$N_{(7)}-C_{(8)}$	1,327(8)	$C_{(21)}-C_{(23)}$	1,51(1)
$C_{(8)}-C_{(9)}$	1,433(8)	$C_{(25)}-C_{(26)}$	1,52(1)
$C_{(8)}-C_{(16)}$	1,51(1)	$C_{(25)}-C_{(27)}$	1,51(1)

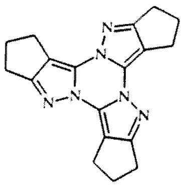
TABLE 3. Valence Angles (deg) in Structure (Ic)

Angle	ω	Angle	ω
$C_{(2)}-N_{(1)}-C_{(6)}$	124,6(4)	$C_{(8)}-C_{(9)}-C_{(17)}$	130,7(6)
$C_{(2)}-N_{(1)}-N_{(7)}$	110,8(4)	$N_{(3)}-N_{(10)}-C_{(11)}$	103,8(4)
$C_{(6)}-N_{(1)}-N_{(7)}$	124,6(4)	$N_{(10)}-C_{(11)}-C_{(12)}$	113,1(5)
$N_{(1)}-C_{(2)}-N_{(3)}$	114,8(4)	$N_{(10)}-C_{(11)}-C_{(20)}$	117,9(6)
$N_{(1)}-C_{(2)}-C_{(9)}$	109,5(5)	$C_{(12)}-C_{(11)}-C_{(20)}$	129,0(6)
$N_{(3)}-C_{(2)}-C_{(9)}$	135,6(5)	$C_{(4)}-C_{(12)}-C_{(11)}$	103,0(5)
$C_{(2)}-N_{(3)}-C_{(4)}$	124,8(4)	$C_{(4)}-C_{(12)}-C_{(21)}$	127,7(5)
$C_{(2)}-N_{(3)}-N_{(10)}$	124,1(4)	$C_{(11)}-C_{(12)}-C_{(21)}$	129,2(5)
$C_{(4)}-N_{(3)}-N_{(10)}$	110,8(4)	$N_{(5)}-N_{(13)}-C_{(14)}$	103,6(4)
$N_{(3)}-C_{(4)}-N_{(5)}$	115,3(4)	$N_{(13)}-C_{(14)}-C_{(15)}$	114,2(5)
$N_{(3)}-C_{(4)}-C_{(12)}$	109,3(4)	$N_{(13)}-C_{(14)}-C_{(24)}$	117,9(5)
$N_{(5)}-C_{(4)}-C_{(12)}$	135,4(5)	$C_{(15)}-C_{(14)}-C_{(24)}$	127,9(6)
$C_{(4)}-N_{(5)}-C_{(6)}$	124,3(4)	$C_{(6)}-C_{(15)}-C_{(14)}$	102,8(5)
$C_{(4)}-N_{(5)}-N_{(13)}$	124,4(4)	$C_{(6)}-C_{(15)}-C_{(25)}$	125,8(5)
$C_{(6)}-N_{(5)}-N_{(13)}$	111,0(4)	$C_{(14)}-C_{(15)}-C_{(25)}$	131,1(5)
$N_{(1)}-C_{(6)}-N_{(5)}$	115,8(5)	$C_{(9)}-C_{(17)}-C_{(18)}$	115,3(7)
$N_{(1)}-C_{(6)}-C_{(15)}$	135,7(5)	$C_{(9)}-C_{(17)}-C_{(19)}$	111,9(7)
$N_{(5)}-C_{(6)}-C_{(15)}$	108,5(4)	$C_{(18)}-C_{(17)}-C_{(19)}$	110,3(8)
$N_{(1)}-N_{(7)}-C_{(8)}$	103,8(4)	$C_{(12)}-C_{(21)}-C_{(22)}$	113,8(6)
$N_{(7)}-C_{(8)}-C_{(9)}$	113,8(5)	$C_{(12)}-C_{(21)}-C_{(23)}$	112,3(6)
$N_{(7)}-C_{(8)}-C_{(16)}$	118,1(5)	$C_{(22)}-C_{(21)}-C_{(23)}$	111,5(7)
$C_{(9)}-C_{(8)}-C_{(16)}$	128,1(6)	$C_{(15)}-C_{(25)}-C_{(26)}$	112,5(6)
$C_{(2)}-C_{(9)}-C_{(8)}$	102,0(5)	$C_{(15)}-C_{(25)}-C_{(27)}$	110,1(5)
$C_{(2)}-C_{(9)}-C_{(17)}$	127,2(6)	$C_{(26)}-C_{(25)}-C_{(27)}$	111,2(6)

The nitration of the methylpyrazolediyl (Ia) takes place under comparatively forcing conditions (nitrating mixture, 95°C, 5 h) to the trinitro derivative (III). The nitration process is accompanied by oxidative processes revealed by the evolution of nitrogen oxides. Additional confirmation of the structure of (III) was obtained from PMR spectra with a singlet for the equivalent CH_3 groups at 2.59 ppm. The phenylpyrazolediyl (Ib) was not subjected to nitration due to possible competing nitration at the phenyl nucleus. Sulfonation of the pyrazolediyl occurred similarly (oleum, 150°C, 3 h) with the formation of the symmetrical molecule (IV). When carrying out the Vilsmeier reaction, only a monoformyl derivative (V) was obtained even under fairly forcing conditions (chlorobenzene, 120°, 3 h).



V



VI

TABLE 4. Coordinates of Nonhydrogen Atoms (×10) in Structure (Ic)

Atom	x	y	z
$N_{(1)}$	-739(4)	7227(3)	1572(1)
$C_{(2)}$	-821(5)	6922(4)	1173(2)
$N_{(3)}$	-7(4)	6099(3)	1060(1)
$C_{(4)}$	827(5)	5614(4)	1314(2)
$N_{(5)}$	774(4)	5941(3)	1717(1)
$C_{(6)}$	58(5)	6769(4)	1855(2)
$N_{(7)}$	-1540(4)	8061(4)	1652(1)
$C_{(8)}$	-2118(5)	8223(5)	1300(2)
$C_{(9)}$	-1707(5)	7525(5)	981(2)
$N_{(10)}$	145(4)	5745(4)	668(1)
$C_{(11)}$	1077(5)	5029(4)	695(2)
$C_{(12)}$	1536(5)	4907(4)	1097(2)
$N_{(13)}$	1538(4)	5557(4)	2019(1)
$C_{(14)}$	1237(5)	6150(4)	2339(2)
$C_{(15)}$	330(5)	6934(4)	2259(2)
$C_{(16)}$	-3072(9)	9110(7)	1277(2)
$C_{(17)}$	-2116(7)	7439(7)	551(2)
$C_{(18)}$	-3472(9)	7269(10)	490(3)
$C_{(19)}$	-1674(13)	8365(9)	303(3)
$C_{(20)}$	1478(8)	4471(7)	317(2)
$C_{(21)}$	2599(6)	4232(5)	1248(2)
$C_{(22)}$	2530(10)	3068(7)	1112(3)
$C_{(23)}$	3862(9)	4721(8)	1152(4)
$C_{(24)}$	1877(7)	5914(7)	2734(2)
$C_{(25)}$	-169(6)	7840(5)	2521(2)
$C_{(26)}$	-596(9)	7461(8)	2939(3)
$C_{(27)}$	798(8)	8717(5)	2555(3)

Summarizing, it may be concluded that the reactivity of the trispyrazolediyls in electrophilic substitution reactions is less than that of alkylpyrazoles with a free 4 position on the nucleus and is close to the reactivity of 1-phenylpyrazole.

The structure of compound (Ic) obtained by us previously [1] was studied by x-ray analysis (Fig. 1, Tables 2-4). The tetracyclic fragment was flat (the deviation of atoms from the mean square plane $N_{(1)}$-$C_{(15)}$ was less than 0.04 Å). Bond lengths in it were equal to a significant extent, which indicates its aromatic character. The endocyclic valence angles of the triazine ring at the nitrogen atoms were increased to 124.8-115.8(5)° and at the carbon atoms to 114.8-115.8(5)°. The isopropyl groups have a conformation with a close to syn-periplanar disposition of the hydrogen atom at the tertiary carbon atom with the $C_{(2)}-C_{(9)}$, $C_{(4)}-C_{(12)}$, and $C_{(6)}-C_{(15)}$ bonds. Torsion angles were as follows: $C_{(2)}-C_{(9)}-C_{(17)}-C_{(18)}$ 124.2(8)°, $C_{(2)}-C_{(9)}-C_{(17)}-C_{(19)}$ −108.7(9)°, $C_{(4)}-C_{(12)}-C_{(21)}-C_{(22)}$ 133.5(7)°, $C_{(4)}-C_{(12)}-C_{(21)}-C_{(23)}$ −98.7(8)°, $C_{(6)}-C_{(15)}-C_{(25)}-C_{(26)}$ 135.9(6)°, and $C_{(6)}-C_{(15)}-C_{(25)}-C_{(27)}$ −99.4(7)°. Notice the difference in the angle of deflection of the isopropyl substituent at the $C_{(9)}$ atom from the same groups at the $C_{(12)}$ and $C_{(15)}$ atoms, which leads to loss of a third order axis of symmetry for the molecule. Molecular mechanics calculations of the equilibrium geometry of an isolated (Ic) molecule gave the same deflection angles for all the isopropyl groups. Consequently, the difference in orientation of the isopropyl groups may only be caused by intermolecular interactions in the crystal. Analysis of the contributions of the isopropyl group atoms to the overall energy of the intermolecular interactions calculated by the method of atom−atom potentials showed that these substituents are not equivalent in the crystal. The smallest contribution to the overall energy of the intermolecular interactions was made by the isopropyl group at $C_{(9)}$ and the largest by that at $C_{(15)}$. Correspondingly these substituents must also have different mobilities in the crystal. Calculation by the atom−atom potential method showed (Fig. 1) that the isopropyl group at $C_{(9)}$ possesses a practically free rotation (the intermolecular interaction energy changed by less than 0.5 kcal/mole on turning it by ±60°). The orientation of the isopropyl group at the $C_{(15)}$ atom on the other hand was fixed fairly rigidly (E ~6 kcal/mole). The rotation of the isopropyl group at $C_{(12)}$ proved to be intermediate.

The packing of the molecules in the crystal was a normal Van der Waals distances [4] and had no special features.

In the Experimental section we give the synthesis of one further new trispyrazolediyl, viz. tris(3,4-trimethylene-1,5-pyrazolediyl) (VI), in addition to those described previously [1].

TABLE 5. Data of Elemental Analysis

Compound	Tris(1,5-pyrazolediyl)	Empirical formula	Found, % / Calculated, %		
			C	H	N
IIa	4-Chloro-3-methyl	$C_{12}H_9Cl_3N_6$	41,46 41,86	3,36 2,62	
IIb	4-Bromo-3-methyl	$C_{12}H_9Br_3N_6$	30,45 30,18	2,02 1,89	17,30 17,60
IIc	4-Iodo-3-methyl	$C_{12}H_9I_3N_6$	24,13 23,30	1,62 1,46	
IId	4-Chloro-3-phenyl	$C_{27}H_{15}Cl_3N_6$	60,77 61,12	3,10 2,86	
IIe	4-Bromo-3-phenyl	$C_{27}H_{15}Br_3N_6$	49,81 48,87	2,79 2,28	
IIf	4-Idodo-3-phenyl	$C_{27}H_{15}I_3N_6$	40,02 40,30	2,16 1,82	
VI	3,4-Trimethylene	$C_{18}H_{18}N_6$	67,94 67,92	5,53 5,66	26,32 26,32
III	3-Methyl-4-nitro	$C_{12}H_9N_9O_6$	38,89 38,35	2,74 2,42	32,81 33,69
V	Monoformyl-3-methyl	$C_{13}H_{12}N_6O$	58,21 58,13	4,48 4,80	31,10 31,10
IV	3-Methyl-4-sulfonyl sodium salt	$C_{12}H_9N_6Na_3O_9S_3$	25,81 26,37	2,4 1,61	

EXPERIMENTAL

The IR spectra were taken on a Perkin-Elmer 577 instrument in KCl disks, and UV spectra on a Specord M 40 spectrophotometer in isopropyl alcohol and in acetonitrile. The PMR spectra were taken on a Tesla 497 (100 MHz) instrument in CF_3COOH.

X-Ray Structural Investigation.* Crystals of (Ic) (from acetic acid) were rhombic. At 20°C a = 10.675(4), b = 12.486(4), c = 32.862(11) Å, V = 4380(5) $Å^3$, d_{calc} = 1.112 g/cm^3, space group Pbca, Z = 4. The unit cell parameters and the intensities of 1639 reflections with F > 7 (F) were measured on an automatic Siemens P3/PC four-circle diffractometer (MoK_α, graphite monochromator, $\theta/2\theta$ scanning, $2\theta_{max}$ = 60°).

The structure was solved by the direct method using the SHELXTL PLUS [5] set of programs. Refinement for nonhydrogen atoms was carried out in an anisotropic approach by the full-matrix least squares method to R = 0.072 (R_W = 0.073, S = 1.94). Positions of hydrogen atoms were calculated geometrically and were further refined by the "ride-on" method with U_{iso} = 0.08 $Å^2$. Coordinates of the nonhydrogen atoms are given in Table 4.

The molecular mechanics calculations were carried out with the MMP2 program [6] modified for nitrogen-containing heterocycles [7]. Intermolecular interaction energies in the crystal were calculated by the atom—atom potential method with the NONVPOT program [8].

The data of elemental analysis for C, H, and N corresponded to calculated values (Table 5).

Tris(4-chloro-1,5-pyrazolediyl) (IIa, d). The appropriate trispyrazolediyl (0.001 mole) was dissolved in chlorobenzene (10 ml) for (Ib) and CCl_4 (10 ml) for (Ia) and water (2 ml) with heating in a flask with a reflux condenser, the mixture was cooled, and a slow stream of Cl_2 bubbled through, initially with no heating, and then with heating on a water bath in the dark. Overall approximately a twofold excess of chlorine (0.006 mole) was passed through the solution. The solvent was removed from the reaction mixture by steam distillation, the residue was made alkaline with ammonia, and the precipitate of (IIa,d) filtered off. Yield was quantitative. Purification was by recrystallization from a large volume of toluene. Constants are given in Table 1.

Tris(4-bromo-1,5-pyrazolediyl) (IIb, e). The trispyrazolediyl (0.001 mole) was dissolved in chlorobenzene (10 ml) and water (2 ml) by heating in a flask fitted with a reflux condenser and stirrer. After cooling, bromine (0.004 mole) was introduced under the liquid layer with vigorous mixing. After 1 h the mixture was heated to boiling on a water bath for 1 h,

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*The x-ray structural investigations were carried out in the A. N. Nesmeyanov Institute of Heteroorganic Compounds of the Russian Academy of Sciences (RAN) in the Laboratory of X-Ray Structural Investigations, Director Yu. T. Struchkov.

and treated as in the case of chlorination. Yield was quantitative. For purification the substance may be recrystallized from chlorobenzene. Constants are given in Table 1.

Tris(4-iodo-1,5-pyrazolediyl) (IIc, f). A mixture of trispyrazolediyl (0.001 mole), acetic acid (10 ml), water (1 ml), I_2 (0.002 mole), I_2O_5 (0.0002 mole) and carbon tetrachloride (2 ml) was placed in a flask fitted with a reflux condenser and stirrer. The reaction mixture was heated on a boiling water bath for 5 h, and then treated as for chlorination. Yield was quantitative. For purification the substance was recrystallized from chlorobenzene.

3,4-Trimethylenepyrazolone. Acetic acid (6 ml) and then 80% hydrazine hydrate solution containing hydrazine (0.105 mole) were added to freshly distilled 2-carbethoxycyclopentanone (15.6 g: 0.1 mole) dissolved in methanol (20 ml). The mixture was heated under reflux for 1 h, cooled, and filtered. After washing the precipitate with cold 60% methanol, the pyrazolone (11.2 g: 90%) having mp 268°C was obtained [9].

Tris(3,4-trimethylene-1,5-pyrazolediyl) (VI). A mixture of dry 3,4-trimethylene-5-pyrazolone (6.20 g: 0.5 mole) and $POCL_3$ (5.1 ml: 0.055 mole) was heated on an oil bath at 220°C for 5 h. After cooling to 60-70°C, water (25 ml) was added slowly. The violent reaction was allowed to subside, then 10% NaOH solution was added to pH 8-9. The contents of the flask were heated to boiling and then cooled. The solid was separated and heated to boiling with water (20 ml), cooled once again, and the crystalline tris-pyrazolediyl (4.27 g) filtered off. Recrystallization from acetic acid (25 ml) gave compound (VI) (1.57 g: 30%) of mp 334-336°C.

Tris(3-methyl-4-nitro-1,5-pyrazolediyl) (III). A cold mixture of 96% H_2SO_4 (2 ml) and HNO_3 (d 1.5) (2 ml) was added to methylpyrazolediyl (Ia) (480 mg: 0.002 mole). The mixture was heated on a boiling water bath for 5 h (significant evolution of nitrogen oxides was observed for the first 3 h and then stopped). Further HNO_3 (d 1.50) (2 ml) was then added to the reaction mixture which was then heated for 2 h more (nitrogen oxides were not evolved). The reaction mixture was cooled and then slowly added dropwise to water (15 ml) so that the temperature did not rise above 50°C. After cooling, concentrated ammonia solution (3 ml) was added dropwise. Next day the precipitated crystals were filtered off. After washing with water and drying, the crude tris(nitropyrazolediyl) (600 mg) was obtained. Pure tris(nitropyrazolediyl) (390 mg: 52%) was obtained after recrystallization from a mixture of benzene (12 ml) and hexane (8 ml). Constants are given in Table 1.

Monoformyltris(3-methyl-1,5-pyrazolediyl) (V). The pyrazolediyl (Ia) (2.4 g: 0.01 mole), phosphorus oxychloride (10.2 g: ~0.04 mole), and dry DMF (2.9 g: 0.04 mole) in dry chlorobenzene (40 ml) were boiled for 3 h, poured into water, and the chlorobenzene steam-distilled off. The precipitate was filtered off. After recrystallization from a benzene–hexane mixture, the monoformyl derivative (1.7 g: 63%) was obtained having mp 185-187°C. UV spectrum, λ_{max} (log ε): 231 (4.59), 251 (4.62), 279 (4.42) (in alcohol). IR spectrum: 1680 (C=O), 1620 cm^{-1}. PMR spectrum (CF_3COOH): 2.86, 2.78 and 2.68 (3 × 3H, three s, three CH_3), 7.09 and 6.97 (2 × 1H, two s, two 4-H), 10.32 ppm (1H, s, CHO).

Sodium Salt of Tris(3-methyl-4-sulfonyl-1,5-pyrazoldiyl) (IV). The methylpyrazolediyl (Ia) (2.4 g: 0.01 mole) was dissolved in 7% oleum (25 ml), the reaction mixture heated at 150°C for 3 h, cooled, and immediately poured into water (200 ml) with stirring. The solution was neutralized with $CaCO_3$ until cessation of CO_2 evolution and filtered. A solution of Na_2CO_3 was added to the filtrate with vigorous stirring to precisely pH 8. The mixture was filtered once again, the filtrate evaporated to 10 ml, and a mixture of acetone (5 ml) and methanol (5 ml) added to it. The precipitated sodium salt was filtered off, washed with methanol, and dried. The yield of salt was 1.85 g (33.9%). UV spectrum (water), λ_{max}, nm (log ε): 215 (4.06) (discontinuity), 248 (4.69), 282 (3.94) (discontinuity). IR spectrum (KCl disk): 1610, 1220 and 1035 cm^{-1} (SO_3^-). PMR spectrum (D_2O): 2.59 ppm (9H, s, CH_3).

REFERENCES

1. I. I. Grandberg and N. L. Nam, Khim. Geterotsikl. Soedin., No. 5, 616 (1994).
2. B. Bjorgvist, E. Helgstrom, and N. Stjepstrom, Acta Chem. Scand., **21**, 2295 (1967).
3. I. I. Grandberg and D. N. Bareeva, Authors Certificate 320493 SSSR; Byull. Izobret., No. 34 (1971).
4. Yu. V. Zefirov and P. M. Zorkii, Usp. Khim., **58**, 713 (1989).
5. G. M. Sheldrick, SHELXTL PLUS. PS Version. A system of computer programs for the determination of crystal structure from x-ray diffraction data. Rev. 4.2.1992.
6. J. T. Sprague, J. C. Tai, Y. Yuh, and N. L. Allinger, J. Comput. Chem., **8**, 581 (1987).
7. J. C. Tai and N. L. Allinger, J. Am. Chem. Soc., **110**, 2050 (1988).

8. V. I. Shil'nikov, NONVPOT, A Set of Programs for Crystallochemical Calculations, Center for X-Ray Structural Investigations [in Russian], Russian Academy of Sciences (RAN), 1994.
9. W. Dieckmann, Justus Liebigs Ann. Chem., **317**, 60 (1901).