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# Features of the Reaction of 3(5)-Methyl-5(3)-trifluoromethylpyrazole with Chloroform. Synthesis and Structure of Fluorinated Analogs of Tris(pyrazol-1-yl)methane

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**Abstract**—Reaction of 3(5)-methyl-5(3)-trifluoromethylpyrazole (**I**) with chloroform leads to a complex mixture of compounds. The main components are {bis[(5-methyl-3-trifluoromethyl)pyrazol-1-yl](3-methyl-5-trifluoromethyl)pyrazol-1-yl}methane, bis{[(3-methyl-5-trifluoromethyl)pyrazol-1-yl](5-methyl-3-trifluoromethyl)-pyrazol-1-yl}methane, and tris[(3-methyl-5-trifluoro-methyl)pyrazol-1-yl]methane. The structure of isomeric substances was proved by XRD method.
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Tris(pyrazol-1-yl)methanes are isoelectronic analogs of tris(pyrazol-1-yl)hydroborates $[HB(Pz)_3]^-$. Besides the tris(pyrazol-1-yl)methane $HC(Pz)_3$ [1] a number of its methyl derivatives like tris(3,5-dimethylpyrazole-1-yl)methane, tris(4-methylpyrazol-1-yl)methane, tris-(3,4,5-trimethylpyrazol-1-yl)methane, and tris(3,5-dimethyl-4-bromopyrazol-1-yl)methane has been synthesized [1–6]. The studies are also known in which the $HC(Pz)_3$ analogs were obtained containing other substituents at the pyrazole rings, as well as the products of functionalization at the apical carbon atom [7, 8]. These compounds are promising in catalysis and in supramolecular, bioinorganic, and organometallic chemistry. Owing to the six nitrogen atoms in the three pyrazole rings, the tris(pyrazol-1-yl)methanes are interesting for the synthesis of transition metal coordination compounds, including magnetically active ones [8–11]. The review [8] considers the literature on the synthesis of metal complexes with tris(pyrazol-1-yl)methane until 2004. The studies on obtaining transition metal complexes with this class of compounds continue. Recently the complexes were synthesized of various iron(II) salts with $HC(Pz)_3$ displaying the spin transition and thermochromism [9, 10]. It was noted in [11] that the complexes with tris-(pyrazol-1-yl)methane can be considered as model substances of some metalloproteins.

No published data exist on fluorinated derivatives of $HC(Pz)_3$, in contrast to those of boron analogs $[HB(Pz)_3]^-$ [12]. Meanwhile, the introduction of fluoro-alkyl substituents significantly alters the physical properties and reactivity of many organic molecules [13–15].

With the aim of the synthesis of fluorinated analogs of tris(pyrazol-1-yl)methane we investigated a reaction of 3(5)-methyl-5(3)trifluoromethylpyrazole (**I**) with chloroform under the conditions used for the synthesis of $HC(Pz)_3$ [16]. This reaction, according to the data of $^1H$ and $^{19}F$ NMR spectroscopy, produces a complex mixture of substances. We studied the reaction mixture composition by gas chromatography–mass spectrometry. Despite the prolonged reaction duration, pyrazole (**I**) was always found in the reaction mixture (Fig. 1, peak $\tau_R$ = 11.72 min). The mixture chromatograms contain three groups of peaks of new compounds: **II**–**V**, **XI**–**XIX,** and **XX**–**XXXIX** (Fig. 1). Mass spectra of compounds belonging to each of the groups are similar, but the peaks of fragmentary ions

**Table 1.** Mass spectral data of compounds **II–V**

| *m*/*e* | $I_{rel}$, % | Ion |
|---|---|---|
| 460 | 0–1.3 | $[M]^+$ |
| 441 | 2.0–5.2 | $[M - F]^+$ |
| 391 | 0–0.3 | $[M - CF_3]^+$ |
| 311 | 100 | $[M - FPz]^+$ |
| 241 | 1.8–57.7 | $[M - FPz - CF_3]^+$ |
| 162 | 2.0–10.5 | $[M - 2FPz]^+$ |
| 149 | 2.4–8.1 | $[M - CH(FPz)_2]^+$ |
| 134 | 9.8–17.5 | $[M - CH(FPz)_2 - CH_3]^+$ |
| 84 | 0.5–0.9 | $[M - CH(FPz)_2 - CF_3]^+$ |
| 69 | 1.9–7.1 | $[CF_3]^+$ |

**Table 2.** Mass spectral data of compounds **XI–XIX**

| *m*/*e* | $I_{rel}$, % | Ion |
|---|---|---|
| 770 | – | $[M]^+$ |
| 751 | 1.0–3.5 | $[M - F]^+$ |
| 621 | 14.3–45.9 | $[M - FPz]^+$ |
| 551 | 0–0.4 | $[M - FPz - CF_3]^+$ |
| 471 | 5.7–26.3 | $[M - 2FPz]^+$ |
| 401 | 4.2–10.0 | $[M - 2FPz - CF_3]^+$ |
| 321 | 11.1–26.0 | $[M - 3FPz]^+$ |
| 311 | 100 | $[M - C(FPz)_3]^+$ |
| 241 | 2.7–15.0 | $[M - C(FPz)_3 - CF_3]^+$ |
| 162 | 1.5–2.8 | $[M - C(FPz)_3 - FPz]^+$ |

with the same *m*/*e* differ by relative intensity (Tables 1–3). The chloroform chlorine atoms were completely replaced by fragments of pyrazole **I**, since in the mass spectra of the reaction mixture there were no peaks of the ions characteristic of chlorine-containing compounds.

The first group of peaks concerns compounds **II–V**. Peaks with $\tau_R$ 17.59, 18.22 and 18.48 min belong to isomeric tris[(3-methyl-5-trifluoromethyl)pyrazol-1-yl]-methane (**II**), {bis[(3-methyl-5-trifluoromethyl)pyrazol-1-yl](5-methyl-3-trifluoromethyl)-pyrazol-1-yl}-methane (**III**) and {bis[(5-methyl-3-trifluoromethyl)-pyrazol-1-yl](3-methyl-5-trifluoromethyl)pyrazol-1-yl}methane (**IV**), respectively. The structure of compounds **II–IV** is confirmed by XRD analysis. Description of the structures is given below. The peak at $\tau_R$ 19.91 min presumably corresponds to the tris[(5-methyl-3-trifluoromethyl)pyrazol-1-yl]methane (**V**) (Scheme 1). The mass spectra of compounds **II–IV** contain the peak of molecular ion $M^+$ (*m*/*e* 460) of low intensity (less than 1.3%). The base peak is that of the fragment $[CH(FPz)_2]^+$ with *m*/*e* 311 formed by removing a pyrazole[1] fragment from $M^+$. The fragmentation of $M^+$ of compounds **II–IV** results in the structures of isomeric $CH(FPz)_3$ (Table 1).

In the mass spectra of compounds **XI–XIX** recorded in the range of $\tau_R$ 24.33–26.19 min, the base peak is that of the fragment $[CH(FPz)_2]^+$ with *m*/*e* 311. The maximum mass corresponds to the peak of the ion with *m*/*e* 751, which significantly exceeds the *m*/*e* value of $M^+$ for the isomers **II–V** (*m*/*e* 460) and indicates the formation of condensation products with higher molecular weight. In the reaction of non-fluorinated pyrazoles with $CHCl_3$ the formation of dichlorocarbenes was previously observed [8]. The reactions studied now can also incvolve such a process. The dichlorocarbene recombination followed by substitution of chlorine by the pyrazol substituents (and possibly the process with reverse sequence) may lead to the tetrapyrazolylethene isomers **VI–X**, which can add pyrazole molecule to form the isomeric pentapyrazolylethanes (*M* 770) (Scheme 1) . The mass spectra of compounds **XI–XIX** do no contain peaks of the ions with *m*/*e* 770, but there are peaks of ions with *m*/*e* 751 corresponding to the fragment $[M - F]^+$. The loss of a F atom by the molecular ion is typical of the fluoroalkyl compounds [17]. In addition, in the mass spectra of compounds **XI–XIX** there are peaks of ions corresponding to the sequential splitting off of four pyrazole fragments from the molecular ion with *m*/*e* 770. Further, a fragmentation occurs of the ion $[CH(FPz)]^+$ with *m*/*e* 162. It follows from the

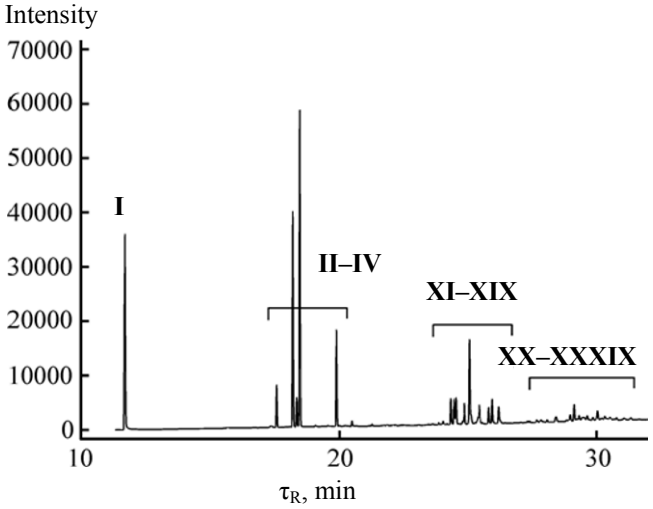
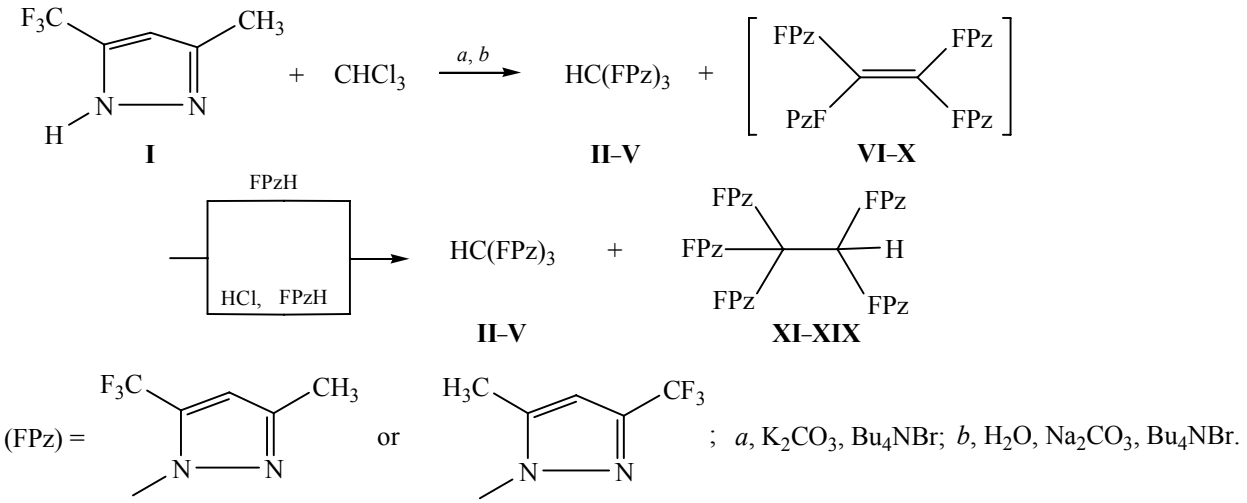



**Fig. 1.** Chromatogram of the reaction products of 3(5)-trifluoromethyl-5(3)-methylpyrazol **I** with chloroform.

[1] Here and hereinafter pyrazole fragments mean fragments of 3-methyl-5-trifluoromethylpyrazole and/or 5-methyl-3-trifluoromethylpyrazole.

**Scheme 1.**




foregoing, as we believe, that compounds **XI–XIX** are the pentapyrazolylethane isomers. (Scheme 1, Table 2). The isomers **XI–XIX** can also be formed through addition of HCl liberated in the reaction to the tetrapyrazolylethene isomers **VI–X** and the substitution of chlorine with pyrazolyl fragments (Scheme 1).

Another possible route to the formation of the pentapyrazolylethane isomers **XI–XIX** is the generation of carbanion $(FPz)_3C^-$ from compounds **II–V**, which interacts with $CHCl_3$ to form 1,1,1-tripyrazolyl-2,2-dichlorethene. The subsequent substitution of chlorine atoms by pyrazolyl groups produces the isomers **XI–XIX** (Scheme 2).

The mass spectra of the compounds **XX–XXXIX** that contain a group of peaks with retention times 27.66–31.31 min, which includes the peak of the maximum mass ion of *m*/*e* 930 that suffers a fragmentation by successive elimination of the pyrazolyl fragments (Table 3). Given the possibility of the dichlorocarbene recombination with the formation of hexachlorocyclopropane, for the compounds of this group the formation of hexapyrazolylcyclopropane isomers ($M$ = 930) can be assumed. It should be noted that the hexa-(aryl, alkyl)-substituted cyclopropanes are known [18, 19].

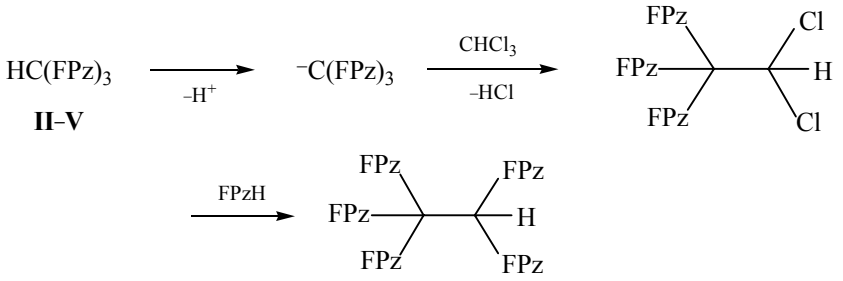
**Table 3.** Mass spectral data of compounds **XX–XXXIX**

| *m*/*e* | $I_{rel}$, % | Ion |
|---|---|---|
| 930 | 2.7–14.4 | $[M]^+$ |
| 781 | 0–1.2 | $[M - FPz]^+$ |
| 620 (621) | 1.2–2.9 | $[M - C(FPz)_2]^+$ |
| 471 | 13.6–24.4 | $[M - HC(FPz)_3]^+$ |
| 311 | 100 | $[M - HC_2(FPz)_4]^+$ |
| 241 | 3.0–7.2 | $[M - HC_2(FPz)_4 - CF_3]^+$ |
| 161 | 3.4–4.9 | $[M - HC_2(FPz)_4 - FPz]^+$ |

Thus, using the method of gas chromatography–mass spectrometry we revealed that the mixture components are all possible isomers of tris(pyrazolyl) methane trifluoromethyl derivatives (compounds **II–V**), and 9 out of 12 of possible isomers of the pentapyrazolylethane (compounds **XI–XIX** ). We suggest that the group of peaks with $\tau_R$ 27.66–31.31 min belongs to the hexapyrazolylcyclopropane isomers, whose number was not estimated exactly because of the low intensity and overlap of the peaks. The isomers belonging to each of the considered groups contain fragments of 3-methyl-5-trifluoromethylpyrazole and 5-methyl-3-trifluoromethylpyrazole in all possible combinations. The main component of the reaction mixture is {bis-[(5-methyl-3-trifluoromethyl)pyrazol-1-yl](3-methyl-5-trifluoromethyl)pyrazol-1-yl}methane (**IV**). Crystals of this compound were obtained at the prolonged keeping the oily substance isolated from the reaction mixture. From the residual oil by column chromatography followed by recrystallization of enriched fractions were isolated crystals of two isomers of compound (**IV**): tris[(3-methyl-5-trifluoromethyl)pyrazol-1-yl]methane (**II**) and {bis[(3-methyl-5-trifluoro-methyl)pyrazol-1-yl](5-methyl-3-trifluoromethyl)-pyrazol-1-yl}methane (**III**). The structure of compounds **II**, **III** and **IV** was proved by XRD analysis.

According to the XRD study the crystals of the main reaction product, {bis[(5-methyl-3-trifluoromethyl)pyrazol-1-yl](3-methyl-5-trifluoromethyl)pyrazol-

**Scheme 2.**




**II**–**V** **XI**–**XIX**

1-yl}methane (**IV**), belong to the centrosymmetric space group of monoclinic system. The molecule as a whole has a helical configuration. The pyrazole ring at $N^1$ forms an angle of 73.9° with the $N^1N^3N^5$ plane, the ring at $N^3$ forms an angle of 56.6°, the ring at $N^5$ forms an angle of 58.6°. The lengths of the C–N bonds formed by methine fragment are close to each other, and their average value [1.442(3) Å] is somewhat less than the standard length of a single C–N bond [1.479(5) Å]. The lengths of the C–C bonds formed by $CF_3$ and $CH_3$ groups with pyrazole rings [1.468(3) Å and 1.476(5) Å, respectively] also are shorter than the standard single C–C bond. The group $CF_3$ at $C^7$ (Fig. 1) demonstrates the strong disordering of halogen atoms. It was simulated by introducing two positions of the fluorine atoms with the occupancy coefficients 0.6 and 0.4. The crystal packing is characterized by a number of short contacts, predominantly of the F···F type, with the deviation from the sum of the van der Waals radii not exceeding 0.05 Å.

Tris[(3-Methyl-5-trifluoromethyl)pyrazol-1-yl]-methane (**II**) and {bis[(3-methyl-5-trifluoromethyl)-pyrazol-1-yl](5-methyl-3-trifluoromethyl)pyrazol-1-yl}methane (**III**) (Figures 2 and 3) are quite similar structurally to the above considered {bis[(5-methyl-3-trifluoromethyl)pyrazol-1-yl](3-methyl-5-trifluoromethyl)pyrazol-1-yl}methane (**IV**). They also form crystals of the centrosymmetric space group of the monoclinic system (Table 4), have a helical configuration and are characterized by a disorder in the $CF_3$ groups. For compound **III** the angle of rotation of the pyrazole ring relative to the $N^1N^3N^5$ plane are 44.0°, 65.1°, and 69.8° (for the rings at $N^1$, $N^3$ and $N^5$, respectively), the distance from the $N^1N^3N^5$ plane to the central atom $C^{16}$ is 0.434(3) Å. For the tris[(3-methyl-5-trifluoromethyl)pyrazolyl]methane (**II**) the rotation angles of the pyrazolyl rings relative to the $N^1N^3N^5$ plane are 53.2°, 56.2°, and 56.9° (for the rings at $N^1$, $N^3$ and $N^5$, respectively), the distance from the $N^1N^3N^5$ plane to the central atom $C^{16}$ is 0.451 (3) Å. Thus, there is no clear relationship between the position of $CF_3$ groups and the angle of rotation of the pyrazole ring relative to the $N^1N^3N^5$ plane. A pronounced specific interactions in the molecular packing is also absent.

Thus, the main products of the reaction of 3(5)-methyl-5(3) trifluoromethylpyrazole (**I**) with chloroform are the fluorinated analogs of tris(pyrazol-1-yl)-methane, namely, {bis[(5-methyl-3-trifluoromethyl)-pyrazol-1-yl](3-methyl-5-trifluoromethyl)pyrazol-1-yl}methane (**IV**), {bis[(3-methyl-5-trifluoromethyl)-pyrazol-1-yl](5-methyl-3-trifluoromethyl)pyrazol-1-yl}methane (**V**) and tris[(3-methyl-5-trifluoromethyl)-pyrazol-1-yl]methane (**II**).

## EXPERIMENTAL

3(5)-Trifluoromethyl-5(3)methylpyrazole (**I**) was prepared by the method of [20]. The reaction progress was monitored by TLC (Silufol UV-254, eluent $CHCl_3$), the plates were developed by aqueous solutions of $Cu(OAc)_2$ and $KMnO_4$.

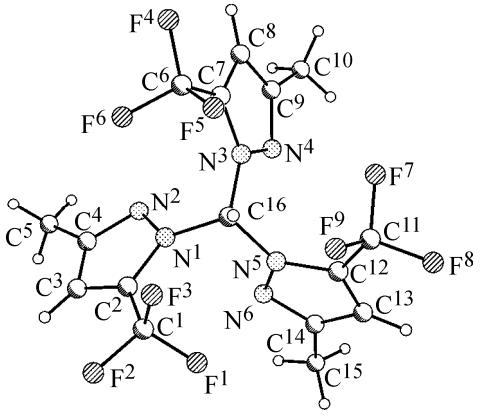



**Fig. 2.** The structure of tris[(3-methyl-5-trifluoromethyl) pyrazol-1-yl]methane **II** according to the XRD.

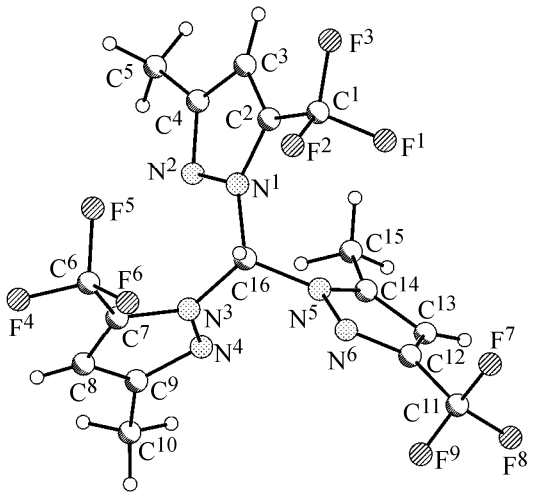



**Fig. 3.** The structure of {bis[(3-methyl-5-trifluoromethyl)-pyrazol-1-yl](5-methyl-3-trifluoromethyl)pyrazol-1-yl}-methane **III** according to the XRD.

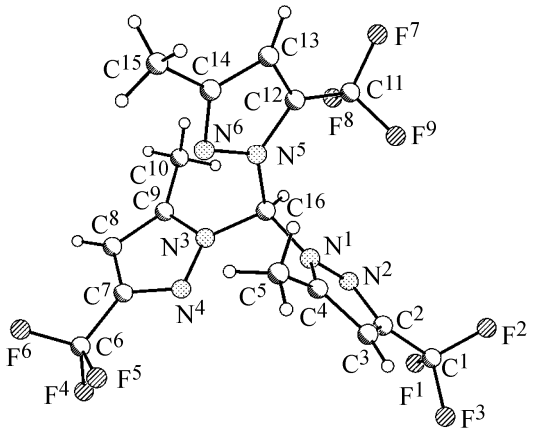



**Fig. 4.** The structure of {bis[(5-methyl-3-trifluoromethyl)-pyrazol-1-yl](3-methyl-5-trifluoro-methyl)pyrazol-1-yl}-methane **IV** according to the XRD.

The $^1$H and $^{19}$F NMR spectra were registered on a Bruker DRX-400 spectrometer (400 MHz for $^1$H, 376 MHz for $^{19}$F), internal references $Me_4Si$ ($^1$H) and $C_6F_6$ ($^{19}$F). The IR spectra were recorded on a Fourier-transform infrared spectrometer Spectrum One B (Perkin Elmer) using a diffuse reflectance attachment.

GC-MS analysis was performed on a GC-MS spectrometer Agilent GC 7890A MSD 5975C inert XL EI/CI (USA) with a quartz capillary column HP5-MS (polydimethylsiloxane, 5 wt % of phenyl groups), length 30 m, diameter 0.25 mm, film thickness 0.25 μm. The initial column temperature 40°C was maintained for 3 min, then it was heated at a rate 10°C per minute to the temperature 290°C, which was maintained for 30 min. Evaporator temperature 250°C. The temperature of the vaporizer 280°C, temperature of the sources 230°C, temperature of the quadrupole 250°C. Carrier gas helium, split ratio 1:50, flow through the column 1.0 ml min$^{-1}$. Scan of the full ion current in the range 20–1000 atomic mass units at the ionization energy of electrons 70 eV.

XRD of compounds **II**–**IV** was studied on an automatic four-circle diffractometer Xcalibur S with a CCD detector by standard procedure, $\lambda(MoK_\alpha)$ = 0.71073Å, graphite monochromator, ω-scanning, scan step 1°. For the analysis were used the fragments of colorless crystals of {bis[(5-methyl-3-trifluoromethyl)-pyrazolyl](3-methyl-5-trifluoro-methyl)pyrazolyl}-methane **IV** of the size 0.24×0.18×0.12 mm, {bis[(3-methyl-5-trifluoromethyl)pyrazolyl](5-methyl-3-trifluoromethyl)pyrazolyl}methane **III** 0.25×0.13×0.04 mm, and tris[(3-methyl-5-trifluoromethyl)-pyrazolyl]methane (**II**) 0.25×0.20×0.15 mm. The correction for extinction was not introduced. The structure was solved by the direct method with the SHELXS-97 software and refined with the SHELXL–97 [21] software by the full-matrix least square method with respect to $F^2$. Positional and thermal parameters of non-hydrogen atoms were refined in the isotropic and then anisotropic approximations. The hydrogen atoms were located in correspondence with the maxima of electron density and included in the refinement according to the *rider* model. The main crystallographic parameters and the refinement results are listed in Table 4.

The results of X-ray diffraction studies are deposited in the Cambridge Crystallographic Database under the numbers CCDC 852485–852487.

**Reaction of pyrazole I with chloroform.** *a*. To a mixture of 0.5 g of pyrazole **I**, 1.84 g of $K_2CO_3$, and 0.025 g of tetrabutylammonium bromide was added 25 ml of chloroform, and the mixture was heated under stirring to disappearance of the original pyrazole (TLC control). The inorganic precipitate was filtered off and washed on the filter with hot chloroform (3×5 ml). The filtrate was evaporated, the resulting oil was chromatographed on silica gel L 100/250 eluting sequentially with a hexane–methylene chloride (5:1) mixture and then with methylene chloride. Seven fractions were separated, each was analyzed by TLC and gas chromatography/mass-spectrometry. After removing the solvent from the first fraction crystals of

**Table 4.** The crystallographic parameters of the structures **II–IV**

| Parameter | **II** | **III** | **IV** |
|---|---|---|---|
| Empirical formula | $C_{16}H_{13}F_9N_6$ | $C_{16}H_{13}F_9N_6$ | $C_{16}H_{13}F_9N_6$ |
| Molecular weight | 460.32 | 460.32 | 460.32 |
| $T$, K | 295(2) | 295(2) | 145(2) |
| Crystal system | Monoclinic | Monoclinic | Monoclinic |
| Space group | $P2_1/c$ | $P2_1/c$ | $P2_1/c$ |
| $a$, Å | 16.9450(13) | 7.1745(5) | 8.8232(7) |
| $b$, Å | 13.0700(8) | 17.9203(14) | 16.7492(9) |
| $c$, Å | 9.1481(6) | 15.9228(15) | 12.8135(10) |
| α, deg | 90 | 90 | 90 |
| β, deg | 92.694(6) | 93.703(7) | 93.141(7) |
| γ, deg | 90 | 90 | 90 |
| $Z$, Å$^3$ | 2023.8(2), 4 | 2042.9(3), 4 | 1890.8(2), 4 |
| $d_{calc}$, g cm$^{-3}$ | 1.511 | 1.497 | 1.617 |
| μ, mm$^{-1}$ | 0.153 | 0.151 | 0.164 |
| $F$(000) | 928 | 928 | 928 |
| θ, deg | 2.72 < θ < 28.29 | 2.80 < θ < 26.38 | 2.61 < θ < 26.38 |
| Collected reflections | 12963 | 9970 | 7364 |
| Independent reflections | 4885 | 4023 | 3750 |
| $R_{int}$ | 0.0284 | 0.0430 | 0.0352 |
| Reflections with $I > 2\sigma(I)$ | 1762 | 1286 | 1962 |
| Completeness of the data collection (for θ, °) | 98.5 % (26.00) | 96.6 % (26.38) | 97.3 % (26.38) |
| $Q$-factor $S$ on $F^2$ | 1.007 | 1.004 | 1.003 |
| $R_1$ [$I > 2\sigma(I)$] | 0.0400 | 0.0506 | 0.0414 |
| $wR_2$ [$I > 2\sigma(I)$] | 0.0729 | 0.0997 | 0.0789 |
| $R_1$ (all reflections) | 0.1279 | 0.1880 | 0.0961 |
| $wR_2$ (all reflections) | 0.0777 | 0.1124 | 0.0852 |

compound **IV** were obtained**,** 0.06 g (12%), mp 83–84°C. IR spectrum, ν, cm$^{-1}$: 1128 s, 1181 s, 1230 s, 1267 s (C–F), 1489 s, 1565 m, 1575 m (C=C–C=N). $^1$H NMR spectrum ($CDCl_3$), δ, ppm, $J$, Hz: 2.09 s (6H, $CH_3$), 2.27 s (3H, $CH_3$), 6.38 s (2H, =CH–), 6.62 s (1H, =CH–), 8.40 s (1H, CH). $^{19}$F NMR spectrum ($CDCl_3$), $\delta_F$, ppm: 98.91 s (6F, $CF_3$), 101.78 s (3F, $CF_3$). Chromatogram of the sample contains a peak with $\tau_R$ 18.48 min. Mass spectrum $m/e$ ($I_{rel.}$, %): 460 $[M]^+$ (0.2), 441 $[M - F]^+$ (7.0), 311 $[M - FPz]^+$ (100), 241 $[M - FPz–CF_3]^+$ (46.2), 162 $[M - 2FPz]^+$ (6.1), 149 $[M - CH(FPz)_2]^+$ (5.5), 134 $[M - CH(FPz)_2 - CH_3]^+$ (14.5) , 84 $[M - CH(FPz)_2–CF_3]^+$ (0.7), 69 $[CF_3]^+$ (4.0).

Single crystals of compound **III** were obtained by removing the solvent from the second fraction and were purified by crystallization from hexane–methylene chloride (5:1) mixture. We obtained 0.047 g (9.2%) of compound **III**. Chromatogram of a sample along with the main peak with $\tau_R$ 18.22 min contains minor peaks of the isomers **II**, **IV**, and **V**. $^1$H NMR spectrum ($CDCl_3$), δ, ppm, $J$, Hz: 2.12 s (3H, $CH_3$), 2.27 s (6H, $CH_3$), 6.38 s (1H, =CH–), 6.60 s (2H, =CH–), 8.41 s (1H, CH). $^{19}$F NMR spectrum ($CDCl_3$), $\delta_F$, ppm: 99.32 s (3F, $CF_3$), 101.50 s (6F, $CF_3$). Mass spectrum, $m/e$ ($I_{rel.}$, %): 441 $[M - F]^+$ (4.5), 311 $[M - FPz]^+$ (100), 241 $[M - FPz–CF_3]^+$ (20.6), 162 $[M - 2FPz]^+$ (2.8), 149 $[M - CH(FPz)_2]^+$ (3.5), 134 $[M -$

$CH(FPz)_2 - CH_3]^+$ (10.0), 84 [$M$ – $CH(FPz)_2 - CF_3]^+$ (0.5), 69 $[CF_3]^+$ (2.3).

Single crystals of compound **II** were obtained by removing the solvent from the fourth fraction and were purified by crystallization from hexane–methylene chloride (5:1) mixture. We obtained 0.05 g (9.8%) of compound **II**. Chromatogram of a sample along with the main peak with $\tau_R$ 17.59 min contains minor peaks of the isomers **III**, **IV**, and **V**. mp 64–65°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm, $J$, Hz: 2.28 s (9H, $CH_3$), 6.62 s (3H, =CH–), 8.43 s (1H, CH). $^{19}$F NMR spectrum ($CDCl_3$), $\delta_F$, ppm): 101.50 s ($CF_3$). Mass spectrum, $m/e$ ($I_{rel.}$, %): 460 $[M]^+$ (0.3), 441 $[M - F]^+$ (2.1), 311 $[M - FPz]^+$ (100), 241 $[M - FPz - CF_3]^+$ (2.1), 162 $[M - 2FPz]^+$ (1.9), 149 $[M - CH(FPz)_2]^+$ (2.3), 134 $[M - CH(FPz)_2 - CH_3]^+$ (9.8), 84 $[M - CH(FPz)_2 - CF_3]^+$ (0.6), 69 $[CF_3]^+$ (1.9).

*b*. To a mixture of 1.1 g of pyrazole (**I**), 0.055 g of tetrabutylammonium bromide, and 7 ml of distilled water was added at vigorous stirring 3.09 g (0.03 mol) of $Na_2CO_3$ and 20 ml of chloroform. The reaction mixture was heated under stirring until disappearance of the original pyrazole (TLC monitoring). Isolation, purification, and identification of reaction products was carried out as in the previous experiment.

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