

Geometric Isomerism in the Series of Fluoroalkyl-Containing 1,2,3-Trione 2-Arylhydrazones

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Abstract—According to the ¹H, ¹³C, and ¹⁹F NMR data, fluoroalkyl-containing 1,2,3-trione 2-arylhydrazones in CDCl₃ exist exclusively, while in (CD₃)₂CO preferentially, as isomers in which the acyl or aroyl group is involved in intramolecular hydrogen bond. The isomer structure was assigned on the basis of the chemical shifts of the carbonyl carbon atoms and fluorine atoms and carbon–fluorine spin–spin coupling constants *J*_{C–F}. X-Ray diffraction data showed that 1,2,3-trione 2-arylhydrazones in crystal have the same structure as in CDCl₃ solution. Quantum-chemical calculations were performed to rationalize predominant formation of 1,2,3-trione 2-arylhydrazone isomers with a free polyfluoroacyl group.

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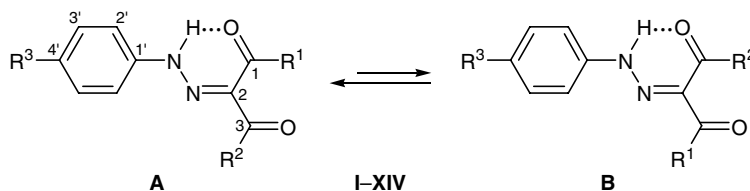
Fluoroalkyl-containing 1,2,3-trione 2-arylhydrazones are promising building blocks for the synthesis of various heterocyclic compounds [1, 2]. It is important to know specific features of their structure for planning syntheses on their base.

Pentane-2,3,4-trione 3-(4-methoxyphenylhydrazone) (**I**) and polyfluoroalkyl-containing 1,2,3-trione 2-arylhydrazones **III** and **V–VII** (Scheme 1) were synthesized previously by azo coupling of the corresponding 1,3-diones with arenediazonium salts [1, 3]. These compounds were found to exist as arylhydrazones in both crystalline state and in CDCl₃ and (CD₃)₂CO

solutions [1]. However, their geometric isomerism arising from different orientation of acyl substituents with respect to the C=N bond was not studied. Therefore, we synthesized compounds **II**, **IV**, and **VIII–XIV** (Scheme 1) according to the procedure described in [1] and examined NMR spectra of the series of polyfluorinated 1,2,3-trione 2-arylhydrazones with a view to reveal parameters ensuring identification of their geometric isomers.

Geometric isomers of 1,2,3-trione 2-arylhydrazones with respect to the C=N bond are fairly stable due to formation of intramolecular hydrogen bond between

Scheme 1.



I, R¹ = R² = Me, R³ = MeO; **II**, R¹ = R³ = Me, R² = CHF₂; **III**, R¹ = Me, R² = CF₃, R³ = MeO; **IV**, R¹ = Me, R² = CF₃, R³ = H; **V**, R¹ = Me, R² = CHF₂CF₂, R³ = MeO; **VI**, R¹ = R³ = Me, R² = CHF₂CF₂; **VII**, R¹ = Me, R² = CHF₂CF₂, R³ = H; **VIII**, R¹ = R³ = Me, R² = CHF₂(CF₂)₃; **IX**, R¹ = R³ = Me, R² = CF₃(CF₂)₃; **X**, R¹ = R² = CF₃, R³ = MeO; **XI**, R¹ = R² = CF₃, R³ = Me; **XII**, R¹ = Ph, R² = CF₃, R³ = Me; **XIII**, R¹ = Ph, R² = CHF₂CF₂, R³ = MeO; **XIV**, R¹ = Me(CH₂)₃, R² = CHF₂CF₂, R³ = Me.

the carbonyl oxygen atom and NH proton in the arylhydrazono group. The intramolecular hydrogen bond in these compounds is relatively strong, as follows from the deshielding [4] of the NH proton (δ_{NH} 13–15 ppm) (Table 1). The intramolecular hydrogen bond in unsymmetrical monofluoroalkyl 1,2,3-trione 2-arylhydrazones can involve either nonfluorinated acyl fragment (isomer **A**) or polyfluoroacyl group (isomer **B**), as shown in Scheme 1.

It is known [5] that solvents capable of forming hydrogen bonds induce a downfield shift of the carbonyl carbon atom in acetone. An analogous downfield shift of signals from the $\text{CH}_3\text{C}=\text{O}$ group (δ_{C^1} 197.50, $\delta_{\text{C}^{1'}}$ 31.37 ppm) involved in intramolecular hydrogen bond with the NH proton of the arylhydrazono group (cf. δ_{C^3} 196.60, $\delta_{\text{C}^{\alpha}}$ 26.65 ppm for free $\text{CH}_3\text{C}=\text{O}$ group) was observed by us previously in the ^{13}C NMR spectrum of pentane-2,3,4-trione 3-(4-methoxyphenylhydrazone) (**I**) (Table 2). Al-Rawi and Khayat [6] also reported on deshielding of carbon and hydrogen nuclei in acetyl and ethoxycarbonyl groups of arylhydrazones obtained by azo coupling of 2-ethoxycarbonylbenzenediazonium with active methylene compounds due to intramolecular hydrogen bonding.

The presence of only one set of signals in the NMR spectra of unsymmetrical monofluoroalkyl-containing 1,2,3-trione 2-arylhydrazones **III**, **IV**, **VI–IX**, and **XII–XIV** in CDCl_3 indicates that they exist as a single isomer (Tables 1, 2). Compounds **II**, **XII**, and **XIII** in $(\text{CD}_3)_2\text{CO}$ exist as equilibrium mixtures of two isomers (Tables 1, 2).

Comparison of the chemical shifts characterizing $\text{CH}_3\text{C}=\text{O}$ groups in **I** and **II–IX** showed that unsymmetrical hydrazones **III–IX** in CDCl_3 and $(\text{CD}_3)_2\text{CO}$ have structure **A** with the acetyl group involved in intramolecular hydrogen bond. An exception is difluoro-substituted pentane-2,3,4-trione 3-arylhydrazone **II**; in $(\text{CD}_3)_2\text{CO}$ it is a mixture containing 83% of isomer **A**. In the NMR spectra of **II**, more downfield signals from the methyl groups (δ 2.55–2.64, $\delta_{\text{C}^{1'}}$ 30.81–30.97 ppm) and carbon atom of the H-bonded carbonyl group ($\text{CH}_3\text{C}=\text{O}$, δ_{C^1} 197.50–197.73 ppm), corresponding to structure **A**, are considerably more intense than those belonging to structure **B** whose acetyl group gives signals in a stronger field (δ 2.44 ppm, $\delta_{\text{C}^{1'}}$ 26.07, δ_{C^1} 196.55 ppm).

Symmetric 1,2,3-trione 2-arylhydrazones **X** and **XI** derived from hexafluoroacetylacetone contain two nonequivalent $\text{CF}_3\text{C}=\text{O}$ groups. They are characterized by considerably different chemical shifts and coupling constants ($\Delta J_{\text{CF}} \approx 5\text{--}6$ Hz; Table 2).

Resonance signals from the $\text{CF}_3\text{C}=\text{O}$ group in the ^{19}F and ^{13}C NMR spectra were assigned for 4,4,4-trifluoro-1-phenylbutane-1,2,3-trione 2-(4-tolylhydrazone) (**XII**). The X-ray diffraction data for hydrazone **XII** (Fig. 1; single crystals of **XII** suitable for X-ray analysis were obtained from a solution in chloroform) unambiguously indicate formation of intramolecular hydrogen bond between the NH proton of the arylhydrazono group and carbonyl oxygen atom of the benzoyl fragment: the distance $\text{O}^1 \cdots \text{H}^1$ is 1.96(2) Å, and the angles $\text{N}^1\text{H}^1\text{O}^1$ and $\text{C}^1\text{O}^1\text{H}^1$ are 131(2) and 98(1)°, respectively. The IR spectra of a 0.1 M solution of **XII** in chloroform and of a crystalline sample dispersed in mineral oil were identical; this means that in both cases only one isomer (**A**) is present. We can conclude that the quartet signal in the ^{13}C NMR spectrum of compound **XII** in CDCl_3 belongs to the free $\text{CF}_3\text{C}=\text{O}$ group ($^1J_{\text{CF}} = 292.5$, $^2J_{\text{CF}} = 32.8$, $^4J_{\text{CF}} = 1$ Hz; Table 2). Similar coupling constants were found in [7] for the free $\text{CF}_3\text{C}=\text{O}$ groups in 2,6-bis(trifluoroacetyl)cyclohexan-1-one. The quartet with $^1J_{\text{CF}} = 291.8$ Hz (CDCl_3) was assigned to the CF_3 carbon atom of the free unconjugated $\text{CF}_3\text{C}=\text{O}$ group of the monoenol tautomer of 2,6-bis(trifluoroacetyl)cyclohexan-1-one, while that with $^1J_{\text{CF}} = 286.9$ Hz was attributed to the H-bonded $\text{CF}_3\text{C}=\text{O}$ group of the keto–enol fragment.

Analysis of the NMR spectra of trifluoroacetyl-containing 1,2,3-trione 2-arylhydrazones **III**, **IV**, and **X–XII** revealed the following general relations. The free $\text{CF}_3\text{C}=\text{O}$ group in 1,2,3-trione 2-arylhydrazones is characterized by the following spin–spin coupling constants and chemical shifts of fluorine atoms: $^1J_{\text{CF}} \approx 292$, $^2J_{\text{CF}} \approx 31\text{--}34$ Hz; CDCl_3 : $^4J_{\text{CF}} \approx 1$ Hz, $\delta_{\text{F}} \sim 91\text{--}92$ ppm, $^6J_{\text{FH}} \approx 1$ Hz; $(\text{CD}_3)_2\text{CO}$: $\delta_{\text{F}} \sim 93\text{--}94$ ppm. The H-bonded $\text{CF}_3\text{C}=\text{O}$ group in 1,2,3-trione 2-arylhydrazones has considerably different parameters: CDCl_3 : $^1J_{\text{CF}} \approx 287$, $^2J_{\text{CF}} \approx 40$, $^4J_{\text{CF}} \approx 1$ Hz, $\delta_{\text{F}} \sim 87\text{--}88$ ppm;

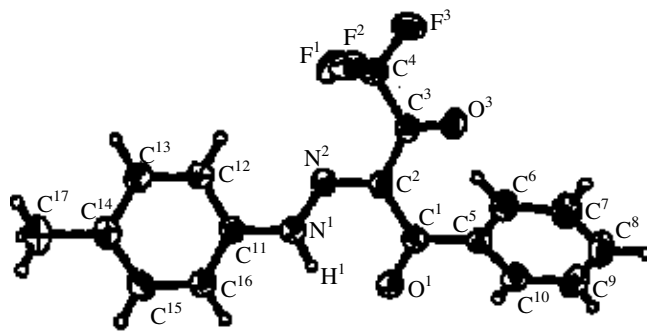


Fig. 1. Structure of the molecule of 4,4,4-trifluoro-1-phenylbutane-1,2,3-trione 2-(4-tolyl)hydrazone (**XII**) according to the X-ray diffraction data.

Table 1. ^1H and ^{19}F NMR spectra of 1,2,3-trione 2-arylhydrazones **I–XIV**

Comp. no.	Solvent	Fraction of isomer A, %	^1H NMR spectrum, δ , ppm (J , Hz)					^{19}F NMR spectrum, δ_{F} , ppm (J , Hz)
			R ¹	R ²	NH	R ³	Ar	
I	(CD ₃) ₂ CO		2.48 s	2.38 s	14.70	3.81 s	6.99 d (3'-H, J = 9.1), 7.48 d (2'-H, J = 9.1)	
II, A	(CD ₃) ₂ CO	83	2.55 s	6.95 t (2J = 54.0)	14.92	2.34 s	7.28 d (3'-H, J = 8.5), 7.50 d (2'-H, J = 8.5)	35.81 d (2J = 54.0)
II, B	(CD ₃) ₂ CO	17	6.85 t (2J = 54.0)	2.44 s	14.33	2.35 s	7.33 d (3'-H, J = 8.5), 7.56 d (2'-H, J = 8.5)	35.16 d (2J = 54.0)
III, A	CDCl ₃	100	2.62 s		15.40	3.85 s	6.98 d (3'-H, J = 9.1), 7.44 d (2'-H, J = 9.1)	91.65 d (J = 0.9)
	(CD ₃) ₂ CO	100	2.55 s		15.18	3.84 s	7.06 d (3'-H, J = 9.1), 7.58 d (2'-H, J = 9.1)	93.96 s
IV, A	CDCl ₃	100	2.64 s		15.19	–	7.50–7.30 m	91.56 d (J = 1.0)
V, A	(CD ₃) ₂ CO	100	2.56 s	6.71 t.t (2J = 52.8, 3J = 5.5)	13.30	3.87 s	7.09 d (3'-H, J = 9.2), 7.60 d (2'-H, J = 9.2)	26.65 d.t (HCF ₂ , 2J = 52.8, 3J = 7.8), 44.02 m (CF ₂)
VI, A	CDCl ₃	100	2.61 s	6.35 t.t (2J = 53.3, 3J = 5.6)	15.25	2.39 s	7.30 m	25.06 d.t (HCF ₂ , 2J = 53.3, 3J = 7.6), 44.26 m (CF ₂)
VII, A	CDCl ₃	100	2.62 s	6.35 t.t (2J = 53.2, 3J = 5.6)	15.20	–	7.44 m	24.96 d.t (HCF ₂ , 2J = 53.2, 3J = 7.3), 44.26 m (CF ₂)
VIII, A	CDCl ₃	100	2.61 s	6.17 t.t (2J = 2.0, 3J = 5.6)	15.34	2.38 s	7.25 d (3'-H, J = 8.5), 7.37 d (2'-H, J = 8.5)	24.71 m (HCF ₂ , 2J = 52.0), 32.58 m (C ^{γ} F ₂), 39.63 m (C ^{β} F ₂), 50.37 m (C ^{α} F ₂)
	(CD ₃) ₂ CO	100	2.56 s	6.79 t.t (2J = 51.0, 3J = 5.6)	15.14	2.37 s	7.34 d (3'-H, J = 8.5), 7.56 d (2'-H, J = 8.5)	25.65 d.t (HCF ₂ , 2J = 51.0), 34.72 m (C ^{γ} F ₂), 42.14 m (C ^{β} F ₂), 52.72 m (C ^{α} F ₂)
IX, A	CDCl ₃	100	2.61 s		15.33	2.38 s	7.25 d (3'-H, J = 8.5), 7.37 d (2'-H, J = 8.5)	36.74 m (C ^{γ} F ₂), 41.21 m (C ^{β} F ₂), 56.74 t (C ^{α} F ₂ , 3J = 12.2), 81.21 t.t (CF ₃ , 3J = 9.8, 4J = 2.4)
X	(CD ₃) ₂ CO				14.48	3.89 s	7.15 d (3'-H, J = 9.2), 7.77 d (2'-H, J = 9.2)	89.26 s, 93.10 s
XI	CDCl ₃				14.58	2.42 s	7.31 d (3'-H, J = 8.6), 7.44 d (2'-H, J = 8.6)	87.30 s (CF ₃), 90.8 d (CF ₃ , J = 1.0)
XII, A	CDCl ₃	100	7.37–7.57 m		14.11	2.37 s	7.23 d (3'-H, J = 8.4), 7.58 d (2'-H, J = 8.4)	91.46 d (J = 0.9)
	(CD ₃) ₂ CO	89	7.52–7.67 m		13.13	2.37 s	7.32 d (3'-H, J = 8.6), 7.72 d (2'-H, J = 8.6)	93.65 s
XII, B	(CD ₃) ₂ CO	11		7.38–7.74 m	13.92	2.33 s	7.25 d (3'-H, J = 8.4), 8.02 d (2'-H, J = 8.4)	91.01 s
XIII, A	CDCl ₃	100	7.40–7.56 m	6.37 t.t (2J = 53.1, 3J = 5.6)	14.30	3.86 s	7.00 d (3'-H, J = 9.0), 7.57 d (2'-H, J = 9.0)	24.54 d.t (HCF ₂ , 2J = 53.1, 3J = 7.9), 42.05 m (CF ₂)

Table 1. (Contd.)

Comp. no.	Solvent	Fraction of isomer A, %	¹ H NMR spectrum, δ , ppm (<i>J</i> , Hz)					¹⁹ F NMR spectrum, δ_F , ppm (<i>J</i> , Hz)
			R ¹	R ²	NH	R ³	Ar	
XIII, A	(CD ₃) ₂ CO	78	7.50–7.63 m	6.82 t.t. (² <i>J</i> = 53.0, ³ <i>J</i> = 5.8)	13.26	3.85 s	7.08 d (3'-H, <i>J</i> = 9.0), 7.69 d (2'-H, <i>J</i> = 9.0)	26.71 d.t (HCF ₂ , ² <i>J</i> = 53.0, ³ <i>J</i> = 7.5), 3.65 m (CF ₂)
	CD ₃ OD	74						26.73 d.t (HCF ₂ , ² <i>J</i> = 52.5, ³ <i>J</i> = 7.3), 43.74 m (CF ₂)
XIII, B	(CD ₃) ₂ CO	22	7.02 t.t. (² <i>J</i> = 53.0, ³ <i>J</i> = 6.0)	7.45–7.67 m	14.19	3.82 s	6.99 d (3'-H, <i>J</i> = 9.0), 8.02 d (2'-H, <i>J</i> = 9.0)	26.81 d.t (HCF ₂ , ² <i>J</i> = 53.0, ³ <i>J</i> = 7.5), 41.71 m (CF ₂)
	CD ₃ OD	26						26.73 d.t (HCF ₂ , ² <i>J</i> = 52.5, ³ <i>J</i> = 7.3), 41.69 m (CF ₂)
XIV, A	CDCl ₃	100	0.95 t (Me, <i>J</i> = 7.3), 1.40 m (3"-H, <i>J</i> = 7.3), 1.62 m (2"-H, <i>J</i> = 7.3), 3.00 t (1"-H, <i>J</i> = 7.3)	6.37 t.t. (² <i>J</i> = 53.3, ³ <i>J</i> = 5.6)	15.31	2.39 s	7.26 d (3'-H, <i>J</i> = 8.5), 7.33 d (2'-H, <i>J</i> = 8.5)	25.06 d.t (HCF ₂ , ² <i>J</i> = 53.4, ³ <i>J</i> = 7.7), 42.25 m (CF ₂)

(CD₃)₂CO: δ_F ~89–90 ppm. We believe that the given fluorine chemical shifts and coupling constants J_{CF} may be used to distinguish isomers **A** and **B** of other 1,2,3-trione 2-arylhydrazones containing a CF₃ group.

The coupling constant $^6J_{FH} \approx 1$ Hz observed in the ¹⁹F NMR spectra of isomers having a free trifluoroacetyl group corresponds to interaction between the fluorine nuclei and NH proton. Addition of a drop of CD₃CO₂D or D₂O to a solution of hydrazone **IV** or **X** in CDCl₃ leads to appearance in the ¹⁹F NMR spectra of a singlet at δ_F 90.76–91.78 ppm due to fluorine atoms of the CF₃ group in addition to the doublet belonging to the free CF₃C=O group. This singlet results from partial replacement of the NH proton by deuterium.

Tri- and tetrafluoro-substituted 1,2,3-trione 2-arylhydrazones **XII** and **XIII** having a bulky benzoyl group showed in the NMR spectra two sets of signals from solutions in (CD₃)₂CO and one set of signals from solutions in CDCl₃. Comparison of the chemical shifts of the carbonyl carbon atoms in the benzoyl and tetrafluoroacetyl substituents of the isomers of **XIII** present in (CD₃)₂CO (Table 2) suggests that isomer **A** with the free polyfluoroacetyl fragment prevails. In addition, the signal from the α -CF₂ fluorine atoms of the major isomer (**A**) of hydrazone **XIII** in (CD₃)₂CO is displaced by ~2 ppm upfield relative to the corre-

sponding signal of the minor isomer **B** (Table 1). This is consistent with deshielding of fluorine nuclei in the CF₃ group of the major isomer of **XII**.

Hydrazones **XIII** and **XIV** are characterized by similar chemical shifts of fluorine and hydrogen nuclei of the tetrafluoroethyl group in the NMR spectra recorded from solutions in CDCl₃, which correspond to a single isomer. On the other hand, their IR spectra recorded from solutions in CHCl₃ and crystalline samples were identical. The structure of 1,1,2,2-tetrafluorononane-3,4,5-trione 4-(4-tolylhydrazone) (**XIV**) in crystal (from CHCl₃) was determined by X-ray

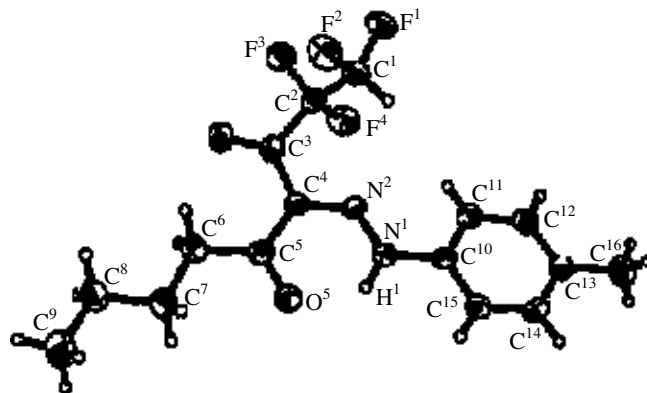


Fig. 2. Structure of the molecule of 1,1,2,2-tetrafluorononane-3,4,5-trione 4-(4-tolyl)hydrazone (**XIV**) according to the X-ray diffraction data.

Table 2. ^{13}C NMR spectra (δ_{C} , ppm, $J_{\text{C-F}}$, Hz) of 1,2,3-trione 2-arylhydrazones **I–IV** and **X–XIII** in $(\text{CD}_3)_2\text{CO}$

Comp. no.	C ¹	C ²	C ³	R ¹	R ²	C ^{1'}	C ^{2'}	C ^{3'}	C ^{4'}	R ³
I	197.50	136.27	196.60	31.37	26.65	133.47	118.48	115.73	158.93	55.87
II, A	197.50	137.84	183.93 t ($J = 23.0$)	30.84	109.04 t ($J = 245.0$)	131.07	131.07	117.87	139.81	20.98
II, B	196.55	137.81	183.95 t ($J = 23.0$)	26.07	108.71 t ($J = 244.8$)	130.93	117.96	117.79	139.94	20.98
III, A	197.52	135.53	177.18 q ($J = 31.2$)	30.81	118.74 q ($J = 292.5$)	128.39	119.72	116.23	160.27	56.02
IV, A^a	197.73 q ($^4J = 1.3$)	128.03	177.29 q ($J = 32.3$)	30.97	117.46 q ($J = 292.5$)	140.74	117.31	129.91	127.63	
X^a	176.43 q.q ($^2J = 39.7$, $^4J = 1.4$)	123.79	174.78 q ($J = 33.7$)	115.66 q ($J = 287.3$)	116.96 q ($J = 292$)	133.36	119.69	115.53	160.62	55.74
XI^a	176.67 q.q ($^2J = 39.7$, $^4J = 1.2$)	124.07	174.94 q ($J = 33.9$)	115.62 q ($J = 287.5$)	116.95 q ($J = 292$)	137.71	118.03	130.87	140.03	21.30
XII, A^a	192.36 q ($^4J = 1$)	137.59	176.79 q ($J = 32.8$)	137.93, 128.00, 128.29, 128.30	117.46 q ($J = 292.5$)	132.79	130.50	117.06	138.46	21.13
XIII, A	192.50	135.81	181.08 t ($J = 24.1$)	138.66, 129.26, 130.73, 131.36	112.35 t.t (C ^{α} , $^1J = 262.0$, $^2J = 27.0$), 111.23 t.t (C ^{β} , $^1J = 250.2$, $^2J = 30.5$)	133.84	119.35	115.93	159.61	55.98
XIII, B	191.72	135.60	182.10 t ($J = 26.4$)	137.89, 129.03, 129.53, 131.20	111.56 t.t (C ^{α} , $^1J = 260.6$, $^2J = 27.2$), 111.41 t.t (C ^{β} , $^1J = 251.0$, $^2J = 30.5$)	133.75	119.77	115.84	160.01	55.98

^a In CDCl_3 .

analysis (Fig. 2). Molecule **XIV** is almost planar: the maximal deviations of atoms from the $\text{H}^1\text{N}^1\text{N}^2\text{C}^4\text{C}^5\text{O}^5$ and benzene ring $\text{C}^{10}-\text{C}^{15}$ planes are 0.04 (O^5) and 0.01 Å (C^{10}), respectively, and the dihedral angle between these planes is 6.6°. A strong intermolecular hydrogen bond is formed between the NH proton of the hydrazone fragment and carbonyl oxygen atom of the pentanoyl moiety. The distance $\text{O}^5 \cdots \text{H}^1$ is 1.85(2) Å, and the angles $\text{N}^1\text{H}^1\text{O}^5$ and $\text{C}^5\text{O}^5\text{H}^1$ are 134(1) and 104(1)°, respectively.

Using MOPS algorithm [8] we performed a search for most favorable conformers of 1,2,3-trione 2-arylhydrazones **I**, **III**, and **XII**, and the energies, charges on atoms, and orbital parameters of these conformers were calculated by the DFT B3LYP/6-31G(*d,p*) *ab initio* method (Table 3). Isomers **A** of **III** and **XII** were

found to be more favorable than isomers **B**; the difference in their total energies is 22.68 and 11.81 kJ/mol, respectively.

The results of calculations showed increase in the absolute value of the charge on the carbonyl oxygen atom involved in intramolecular hydrogen bonding ($\Delta\delta^- = 0.0148-0.0150$) in going from the acetyl group in pentane-2,3,4-trione 3-arylhydrazone **I** to the trifluoroacetyl group in less favorable isomers **B** of compounds **III** and **XII**. Electron-withdrawing effect of trifluoromethyl group reduces the negative charge on the neighboring carbonyl oxygen atom, and the probability for formation of isomers **B** with the H-bonded trifluoroacetyl group considerably decreases. In the more favorable isomer (**A**) of **III**, the trifluoromethyl group is fairly distant from the acetyl group involved

Table 3. Calculated total energies, charges on the carbonyl carbon and oxygen atoms, and Fukui indices of frontier molecular orbitals of 1,2,3-trione 2-arylhydrazones **I**, **III**, and **XII**

Comp. no.	E_{tot} , kJ/mol	Charges on carbonyl carbon and oxygen atoms (Fukui indices of HOMO/LUMO)			
		C ¹ =O	C ¹ =O	C ³ =O	C ³ =O
I	−1807816.84	0.4170 (0.0737/0.3101)	−0.4906 (0.1715/0.3230)	0.3900 (0.0452/0.1939)	−0.4591 (0.1924/0.2381)
III, A	−2592175.99	0.4323 (0.0701/0.2612)	−0.4897 (0.1716/0.2782)	0.2522 (0.0615/0.2558)	−0.4506 (0.2070/0.2845)
III, B	−2592153.31	0.3978 (0.0313/0.1068)	−0.4436 (0.1894/0.1685)	0.2853 (0.0904/0.3861)	−0.4758 (0.1870/0.3967)
XII, A	−3097171.06	0.4226 (0.0625/0.3225)	−0.5252 (0.1344/0.3348)	0.2523 (0.0674/0.1801)	−0.4437 (0.2037/0.2014)
XII, B	−3097159.25	0.3839 (0.0263/0.1405)	−0.4741 (0.1803/0.2099)	0.2879 (0.0927/0.3636)	−0.4756 (0.1844/0.3742)

in intramolecular hydrogen bond; therefore, it does not affect the charge on the acetyl carbonyl oxygen atom to an appreciable extent ($\Delta\delta^- = 0.0009$ relative to non-fluorinated analog **I**). The presence of a phenyl substituent (whose π -electron system acts as a donor) in isomer **A** of **XII** increases the negative charge on the neighboring carbonyl oxygen atom as compared to isomer **A** of **III** ($\Delta\delta^- = -0.0355$). Thus the existence of trifluoromethyl-containing 1,2,3-trione 2-arylhydrazones **III** and **XII** as isomer **A** may be rationalized in terms of the electronic factor. Presumably, the same factor is responsible for the isomer structure of the other polyfluorinated 1,2,3-trione 2-arylhydrazones.

Summarizing the NMR and X-ray diffraction data obtained in the present work, we can conclude that 1,2,3-trione 2-arylhydrazones **II–IX** and **XII–XIV** in the crystalline state and in solutions in CDCl_3 and $(\text{CD}_3)_2\text{CO}$ exist mainly as isomers like **A** in which the carbonyl group in the nonfluorinated fragment is involved in intramolecular hydrogen bond with the NH proton. Calculations of the energy and electronic parameters of different geometric isomers of hydrazones **III** and **XII** also showed that isomers **A** are more favorable.

EXPERIMENTAL

The melting points were determined in open capillaries and were not corrected. The IR spectra ($400\text{--}4000\text{ cm}^{-1}$) were recorded on a Perkin–Elmer Spectrum One spectrometer with Fourier transform from 0.1 M solutions in chloroform and samples dispersed in mineral oil. The ^1H and ^{13}C NMR spectra were measured on a Bruker DRX-400 spectrometer (400 and 100.6 MHz, respectively) relative to tetramethylsilane. The ^{19}F NMR spectra were obtained on the same instrument at 376 MHz using hexafluorobenzene as reference. The elemental compositions were determined on a Perkin–Elmer PE 2400 Series II analyzer.

Silica gel L (100–250 μm) was used for column chromatography.

X-Ray diffraction data for single crystals of compounds **XII** and **XIV** were acquired at room temperature on a Kuma Diffraction KM-4 diffractometer (MoK_α irradiation, graphite monochromator, $\omega/2\theta$ scanning). The structures were solved by the direct methods, followed by Fourier syntheses, using SHELXS-97 software [9] and were refined by the least-squares procedure in full-matrix anisotropic approximation for all non-hydrogen atoms using SHELXL-97 program [9]. The positions of hydrogen atoms were determined experimentally and were refined in isotropic approximation.

Crystallographic parameters of compound (**XII**).

$\text{C}_{17}\text{H}_{13}\text{F}_3\text{N}_2\text{O}_2$; M 334.29; monoclinic crystals, space group $P2_1/n$; $a = 13.997(3)$, $b = 4.554(1)$, $c = 24.767(5)$ Å; $\beta = 91.90(3)^\circ$; $V = 1577.8(5)$ Å³; $Z = 4$; $\lambda = 0.7107$ Å; $d_{\text{calc}} = 1.41\text{ g/cm}^3$; $\mu = 0.117\text{ mm}^{-1}$. Total of 2849 reflections were measured, 2780 of which were independent and 1854 were with $F_o > 4\sigma(F_o)$; 269 parameters were calculated; $2\theta_{\text{max}} = 50.14^\circ$; spherical segment $-16 \leq h \leq 18$, $-5 \leq k \leq 0$, $0 \leq l \leq 29$; $R = 0.040$ [$F_o > 4\sigma(F_o)$]. Principal bond lengths, Å: $\text{F}^1\text{--C}^4$ 1.313(2), $\text{F}^2\text{--C}^4$ 1.318(2), $\text{F}^3\text{--C}^4$ 1.325(2), $\text{O}^3\text{--C}^3$ 1.209(2), $\text{O}^1\text{--C}^1$ 1.224(2), $\text{O}^1\cdots\text{H}^1$ 1.96(2), $\text{N}^1\text{--N}^2$ 1.294(2), $\text{N}^1\text{--C}^{11}$ 1.405(2), $\text{N}^2\text{--C}^2$ 1.316(2), $\text{C}^3\text{--C}^4$ 1.545(2), $\text{C}^2\text{--C}^3$ 1.449(2), $\text{C}^1\text{--C}^2$ 1.478(2), $\text{C}^1\text{--C}^5$ 1.480(2), $\text{C}^5\text{--C}^{10}$ 1.376(3), $\text{C}^5\text{--C}^6$ 1.382(3), $\text{C}^6\text{--C}^7$ 1.379(3), $\text{C}^7\text{--C}^8$ 1.357(4), $\text{C}^8\text{--C}^9$ 1.363(4), $\text{C}^9\text{--C}^{10}$ 1.383(3), $\text{C}^{11}\text{--C}^{12}$ 1.372(3), $\text{C}^{11}\text{--C}^{16}$ 1.384(2), $\text{C}^{12}\text{--C}^{13}$ 1.376(3), $\text{C}^{13}\text{--C}^{14}$ 1.370(3), $\text{C}^{14}\text{--C}^{15}$ 1.385(3), $\text{C}^{14}\text{--C}^{17}$ 1.503(3), $\text{C}^{15}\text{--C}^{16}$ 1.375(3); bond angles, deg: $\text{N}^2\text{N}^1\text{C}^{11}$ 121.9(1), $\text{N}^1\text{N}^2\text{C}^2$ 121.2(1), $\text{O}^3\text{C}^3\text{C}^4$ 116.5(2), $\text{O}^3\text{C}^3\text{C}^2$ 124.2(2), $\text{C}^2\text{C}^3\text{C}^4$ 119.3(1), $\text{F}^1\text{C}^4\text{F}^2$ 107.8(2), $\text{F}^1\text{C}^4\text{F}^3$ 107.0(1), $\text{F}^2\text{C}^4\text{F}^3$ 106.9(2), $\text{F}^1\text{C}^4\text{C}^3$ 111.5(1), $\text{F}^2\text{C}^4\text{C}^3$ 113.6(1), $\text{F}^3\text{C}^4\text{C}^3$ 109.8(1), $\text{N}^2\text{C}^2\text{C}^3$ 115.4(1), $\text{C}^1\text{C}^2\text{N}^2$ 123.7(2), $\text{C}^1\text{C}^2\text{C}^3$ 120.9(1), $\text{O}^1\text{C}^1\text{C}^2$ 119.3(2), $\text{O}^1\text{C}^1\text{C}^5$

119.9(1), C²C¹C⁵ 120.6(1), C¹⁰C⁵C⁶ 119.7(2), C¹⁰C⁵C¹ 119.1(2), C⁶C⁵C¹ 121.1(2), C⁷C⁶C⁵ 120.0(2), C⁸C⁷C⁶ 120.1(2), C⁷C⁸C⁹ 120.3(2), C⁸C⁹C¹⁰ 120.6(3), C⁵C¹⁰C⁹ 119.3(2), C¹²C¹¹C¹⁶ 120.0(2), C¹²C¹¹N¹ 118.1(2), C¹⁶C¹¹N¹ 121.9(2), C¹¹C¹²C¹³ 120.0(2), C¹⁴C¹³C¹² 121.6(2), C¹³C¹⁴C¹⁵ 117.4(2), C¹³C¹⁴C¹⁷ 121.0(2), C¹⁵C¹⁴C¹⁷ 121.5(2), C¹⁶C¹⁵C¹⁴ 122.4(2), C¹⁵C¹⁶C¹¹ 118.6(2). The complete set of crystallographic data for compound **XII** is available from the Cambridge Crystallographic Data Center (entry no. CCDC 296475).

Crystallographic parameters of compound (XIV). C₁₆H₁₈F₄N₂O₂; *M* 346.32; monoclinic crystals, space group *P*2₁/*n*; *a* = 13.858, *b* = 8.544(2), *c* = 14.945(3) Å; β = 110.97(3)°; *V* = 1652.3(6) Å³; *Z* = 4; λ = 0.71073 Å; *d*_{calc} = 1.39 g/cm³; μ = 0.122 mm⁻¹. Total of 2403 reflections were measured, 2303 of which were independent and 1844 were with *F*_o > 4σ(*F*_o); 289 parameters were calculated; 2θ_{max} = 46.14°; spherical segment -15 ≤ *h* ≤ 14, 0 ≤ *k* ≤ 9, 0 ≤ *l* ≤ 16; *R* = 0.035 [*F*_o > 4σ(*F*_o)]. Principal bond lengths, Å: F³-C² 1.348(2), F⁴-C² 1.351(2), F¹-C¹ 1.343(2), F²-C¹ 1.343(2), N¹-N² 1.292(2), N¹-C¹⁰ 2.57, N²-C¹⁰ 1.411(2), N¹-C⁴ 1.328(2), O³-C³ 1.203(2), O⁵-C⁵ 1.226(2), O⁵...H¹ 1.85(2), C³-C² 1.564(3), C³-C⁴ 1.455(3), C¹-C² 1.507(3), C⁴-C⁵ 1.480(3), C⁵-C⁶ 1.496(3), C⁶-C⁷ 1.513(3), C⁷-C⁸ 1.508(3), C⁸-C⁹ 1.501(3), C¹⁰-C¹¹ 1.373(3), C¹⁰-C¹⁵ 1.377(2), C¹¹-C¹² 1.370(3), C¹²-C¹³ 1.386(3), C¹³-C¹⁴ 1.378(3), C¹³-C¹⁶ 1.496(3), C¹⁴-C¹⁵ 1.372(3); bond angles, deg: N²N¹C¹⁰ 120.4(1), N¹N²C⁴ 122.0(1), O³C³C² 115.9(2), O³C³C⁴ 124.9(2), C⁴C³C² 119.2(2), F³C²F⁴ 106.4(2), F³C²C¹ 107.7(2), F⁴C²C¹ 108.1(2), F³C²C³ 107.6(2), F⁴C²C³ 112.0(2), C¹C²C³ 114.7(2), N²C⁴C³ 112.6(2), N²C⁴C⁵ 123.2(2), C³C⁴C⁵ 124.2(2), O⁵C⁵C⁴ 118.4(2), O⁵C⁵C⁶ 119.8(2), C⁴C⁵C⁶ 121.8(2), F¹C¹F² 106.3(2), F¹C¹C² 110.3(2), F²C¹C² 108.1(2), C⁵C⁶C⁷ 114.3(2), C⁸C⁷C⁶ 112.6(2), C⁹C⁸C⁷ 114.1(2), C¹¹C¹⁰C¹⁵ 120.1(2), C¹¹C¹⁰N¹ 121.8(2), C¹⁵C¹⁰N¹ 118.2(2), C¹²C¹¹C¹⁰ 119.3(2), C¹¹C¹²C¹³ 122.1(2), C¹⁴C¹³C¹² 117.0(2), C¹⁴C¹³C¹⁶ 121.5(2), C¹²C¹³C¹⁶ 121.5(2), C¹⁵C¹⁴C¹³ 121.9(2), C¹⁴C¹⁵C¹⁰ 119.5(2). The complete set of crystallographic data for compound **XIV** is available from the Cambridge Crystallographic Data Center (entry no. CCDC 271114).

Pentane-2,3,4-trione 3-(4-methoxyphenyl)hydrazone (**I**) and polyfluorinated 1,2,3-trione 2-arylhydrazones **III** and **V–VII** were synthesized previously [1, 3]. The yields, melting points, IR spectra, and elemental analyses of newly synthesized compounds **II**, **IV**, and **VIII–XIV** are given below. The NMR data for compounds **I–XIV** are collected in Tables 1 and 2.

1,1-Difluoropentane-2,3,4-trione 3-(4-methylphenyl)hydrazone (II). Yield 50%, light yellow powder, mp 112–113°C (from propan-2-ol). IR spectrum, ν, cm⁻¹: 3060, 1580 (NH); 1690, 1660 (C=O); 1620, 1510, 1500 (C=N, C=C); 1150–1170 (C–F). Found, %: C 56.98; H 5.02; F 14.94; N 11.17. C₁₂H₁₂F₂N₂O₂. Calculated, %: C 56.69; H 4.76; F 14.94; N 11.02.

1,1,1-Trifluoropentane-2,3,4-trione 3-phenylhydrazone (IV). Yield 59%, light yellow powder, mp 110–111°C (isolated by column chromatography on silica gel using chloroform as eluent). IR spectrum, ν, cm⁻¹: 3060, 1595 (NH); 1700, 1680 sh (C=O); 1635, 1520, 1500 sh (C=N, C=C); 1160–1185 (C–F). Found, %: C 51.01; H 3.41; F 21.94; N 11.07. C₁₁H₉F₃N₂O₂. Calculated, %: C 51.17; H 3.51; F 22.07; N 10.85.

5,5,6,6,7,7,8,8-Octafluorooctane-2,3,4-trione 3-(4-methylphenyl)hydrazone (VIII). Yield 82%, light yellow powder, mp 78–79°C (from ethanol). IR spectrum, ν, cm⁻¹: 3060, 1580 (NH); 1680, 1650 sh (C=O); 1625, 1500 (C=N, C=C); 1100–1210 (C–F). Found, %: C 44.36; H 2.88; F 37.30; N 6.80. C₁₅H₁₂F₈N₂O₂. Calculated, %: C 44.57; H 2.99; F 37.60; N 6.93.

5,5,6,6,7,7,8,8-Nonafluorooctane-2,3,4-trione 3-(4-methylphenyl)hydrazone (IX). Yield 84%, light yellow powder, mp 62–64°C (from ethanol). IR spectrum, ν, cm⁻¹: 3060, 1590 (NH); 1690, 1685 sh (C=O); 1630, 1510, 1500 (C=N, C=C); 1140–1240 (C–F). Found, %: C 42.37; H 2.58; F 40.25; N 6.80. C₁₅H₁₁F₉N₂O₂. Calculated, %: C 42.67; H 2.63; F 40.49; N 6.63.

1,1,1,5,5,5-Hexafluoropentane-2,3,4-trione 3-(4-methoxyphenyl)hydrazone (X). Yield 46%, light yellow powder, mp 97–99°C (isolated by column chromatography on silica gel using hexane–ethyl acetate, 17:1, as eluent). IR spectrum, ν, cm⁻¹: 3100, 1590 (NH); 1705, 1650 (C=O); 1620, 1580, 1505 (C=N, C=C); 1160–1190 (C–F). Found, %: C 42.02; H 2.34; F 33.11; N 8.29. C₁₂H₈F₆N₂O₃. Calculated, %: C 42.12; H 2.36; F 33.31; N 8.19.

1,1,1,5,5,5-Hexafluoropentane-2,3,4-trione 3-(4-methylphenyl)hydrazone (XI). Yield 43%, light yellow powder, mp 90–91°C (isolated by column chromatography on silica gel using hexane–acetone, 50:1, as eluent). IR spectrum, ν, cm⁻¹: 3110, 1595 (NH); 1710, 1655 (C=O); 1605, 1520 (C=N, C=C); 1160–1200 (C–F). Found, %: C 43.93; H 2.43; F 35.00; N 8.60. C₁₂H₈F₆N₂O₂. Calculated, %: C 44.19; H 2.47; F 34.94; N 8.59.

4,4,4-Trifluoro-1-phenylbutane-1,2,3-trione 2-(4-methylphenyl)hydrazone (XII). Yield 52%, light yellow powder, mp 133–134°C (from ethanol). IR spectrum, ν , cm^{-1} : 3040, 1570 (NH); 1690, 1680 sh (C=O); 1615, 1590, 1530, 1520, 1505 sh (C=N, C=C); 1150–1190 (C–F). Found, %: C 60.66; H 3.88; F 17.00; N 8.20. $\text{C}_{17}\text{H}_{13}\text{F}_3\text{N}_2\text{O}_2$. Calculated, %: C 61.08; H 3.92; F 17.05; N 8.38.

4,4,5,5-Tetrafluoro-1-phenylpentane-1,2,3-trione 2-(4-methoxyphenyl)hydrazone (XIII). Yield 60%, light yellow powder, mp 135–136°C (from ethanol). IR spectrum, ν , cm^{-1} : 3060, 1580 (NH); 1715 (C=O); 1615, 1600, 1520, 1500 (C=N, C=C); 1230–1250 (C–F). Found, %: C 56.59; H 3.79; F 19.91; N 7.24. $\text{C}_{18}\text{H}_{14}\text{F}_4\text{N}_2\text{O}_3$. Calculated, %: C 56.55; H 3.69; F 19.88; N 7.33.

1,1,2,2-Tetrafluorononane-3,4,5-trione 4-(4-methylphenyl)hydrazone (XIV). Yield 85%, light yellow square prisms, mp 66–67°C (ethanol). IR spectrum, ν , cm^{-1} : 3040, 1590 (NH); 1695, 1690 sh (C=O); 1630, 1515 (C=N, C=C); 1060–1150 (C–F). Found, %: C 55.64; H 5.29; F 21.91; N 8.26. $\text{C}_{16}\text{H}_{18}\text{F}_4\text{N}_2\text{O}_2$. Calculated, %: C 55.49; H 5.24; F 21.94; N 8.09.

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REFERENCES

1. Burgart, Ya.V., Fokin, A.S., Kuzueva, O.G., Chupakhin, O.N., and Saloutin, V.I., *J. Fluorine Chem.*, 1998, vol. 92, p. 101; Kuzueva, O.G., Burgart, Ya.V., and Saloutin, V.I., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 1997, p. 695.
2. Khudina, O.G., Burgart, Y.V., Saloutin, V.I., and Chupakhin, O.N., *J. Fluorine Chem.*, 2004, vol. 125, p. 401; Khudina, O.G., Shchegol'kov, E.V., Burgart, Ya.V., Saloutin, V.I., and Chupakhin, O.N., *J. Fluorine Chem.*, 2004, vol. 125, p. 1363.
3. Garg, H.G. and Joshi, S.S., *J. Indian Chem. Soc.*, 1960, vol. 37, p. 626.
4. Ebraheem, K.A.K., *Monatsh. Chem.*, 1991, vol. 112, p. 157; Burdett, J.L. and Rogers, M.T., *J. Am. Chem. Soc.*, 1964, vol. 86, p. 2105.
5. Ionin, B.I., Ershov, B.A., and Kol'tsov, A.I., *YaMR-spektroskopiya v organicheskoi khimii* (NMR Spectroscopy in Organic Chemistry), Leningrad: Khimiya, 1983, p. 46; Levy, G.C., Lichter, R.L., and Nelson, G.L., *Carbon-13 Nuclear Magnetic Resonance Spectroscopy*, New York: Wiley, 1980, 2nd ed., p. 143.
6. Al-Rawi, J.M.A. and Khayat, M.A.R., *Magn. Reson. Chem.*, 1989, vol. 27, p. 112.
7. Sevenard, D.V., *Cand. Sci. (Chem.) Dissertation*, Yekaterinburg, 2001, p. 68.
8. Sinyaev, A.A., Grishina, M.A., and Potemkin, V.A., *ARKIVOC*, 2004, part (xi), p. 43.
9. Sheldrick, G.M., *SHELXS-97 and SHELXL-97*, Göttingen: Univ. Göttingen, Germany, 1997.