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Dedicated to Full Member of the Russian Academy of Sciences O.N. Chupakhin on his 75th Anniversary

Steric Structure of Alkyl 2-Aryl(hetaryl)hydrazono-3-fluoroalkyl-3-oxopropionates

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Abstract—Steric structure of fluorinated 2-arylhydrazono-3-oxo esters was studied by ^{1}H, ^{19}F, and ^{13}C NMR spectroscopy and X-ray analysis. It was found that these compounds in the crystalline state and in solutions in acetone-d_6, DMSO-d_6, and $CDCl_3$ exist as *Z* isomers with the ester fragment involved in intramolecular hydrogen bond with the hydrazone NH proton. Exceptions are alkyl 2-arylhydrazono-4,4-difluoro-3-oxobutanoates which exist in acetone-d_6 as mixtures of *Z* and *E* isomers, the former prevailing. Unlike fluorinated analogs, ethyl 2-(4-methylphenyl)hydrazono-3-oxobutanoate in crystal has the structure of *E* isomer in which intramolecular hydrogen bond is formed between the NH proton and acetyl carbonyl group. The same compound in acetone-d_6, DMSO-d_6, and $CDCl_3$ gives rise to a mixture of *Z* and *E* isomers, the latter prevailing.

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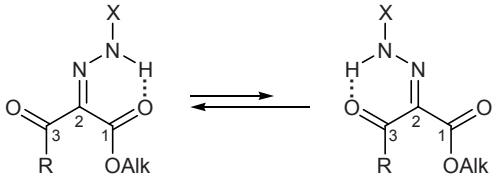
Fluorinated 2-aryl(hetaryl)hydrazono-3-oxo esters are extensively used in organic synthesis as building blocks for the preparation of various open-chain and heterocyclic systems [1–6]. Knowledge of the steric structure of such compounds is important for planning syntheses based thereon and predicting their reactivity.

We previously found that fluorinated 2-aryl(hetaryl)-hydrazono-3-oxo esters exist as hydrazone tautomers stabilized by intramolecular hydrogen bond [1]. It is well known that aryl(hetaryl)hydrazones could give rise to isomers differing by the position of the aryl-(hetaryl)amino group with respect to the double C=N bond. Geometric isomers of 2-aryl(hetaryl)hydrazono-3-oxo esters should be fairly stable due to formation of intramolecular hydrogen bond between the NH proton in the aryl(hetaryl)hydrazono fragment and carbonyl oxygen atom. The high strength of intramolecular hydrogen bond in these compounds follows from strong deshielding of the NH proton ($\delta_{NH} \approx 13$ ppm). Intramolecular hydrogen bond may involve the ester carbonyl group (*Z* isomer) or carbonyl oxygen atom in the polyfluoroacyl fragment (*E* isomer). This type of geometric isomerism was not studied previously for polyfluoroalkyl-containing 2-aryl(hetaryl)hydrazono-3-oxo esters. Therefore, in addition to esters **Ib**–**Ie**, **Ig**, **Ii**, and **Ik**–**In** synthesized by us previously [1, 5, 6], we prepared a number of alkyl 2-arylhydrazono-3-fluoroalkyl-3-oxopropionates **Ia**, **If**, **Ih**, and **Ij** by azo coupling of the corresponding fluorinated 3-oxopropi-



R = HCF_2, X = 4-MeC_6H_4, Alk = Me (**a**), Et (**b**); R = CF_3, Alk = Et, X = 4-$MeOC_6H_4$ (**c**), 1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl (**d**); R = HCF_2CF_2, Alk = Me, X = 4-MeC_6H_4 (**e**), 4-$MeOC_6H_4$ (**f**); Alk = Me, X = 4-MeO-C_6H_4, R = C_3F_7 (**g**), $HCF_2(CF_2)_3$ (**h**); R = C_4F_9: Alk = Me, X = 4-MeC_6H_4 (**i**), 4-$Me_2NC_6H_4$ (**j**), 1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl (**k**); Alk = Et, X = 4-$MeOC_6H_4$ (**l**), 4-MeC_6H_4 (**m**); Alk = Et, X = 4-MeC_6H_4, R = C_6F_{13} (**n**), Me (**o**).

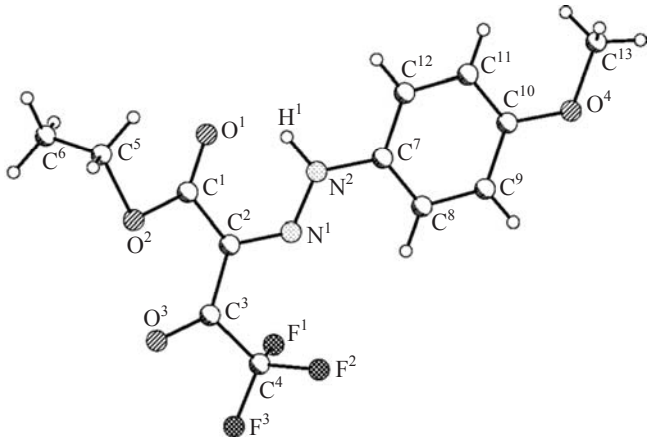


Fig. 1. Structure of the molecule of ethyl 4,4,4-trifluoro-2-[(4-methoxyphenyl)hydrazono]-3-oxobutanoate (**Ic**) according to the X-ray diffraction data.

onates with arenediazonium salts. For comparison, we also synthesized a nonfluorinated analog, ethyl 2-(4-methylphenyl)hydrazono-3-oxobutanoate (**Io**).

The goal of the present work was to study steric structure of fluoroalkyl-containing 2-aryl(hetaryl)hydrazono-3-oxo esters with a view to predict their reactivity. The structure of fluorinated esters **Ia**–**In** and nonfluorinated analog **Io** was studied by NMR spectroscopy and X-ray analysis.

According to the X-ray diffraction data for a single crystal of ethyl 4,4,4-trifluoro-2-(4-methoxyphenylhydrazono)-3-oxobutanoate (**Ic**) (Fig. 1), a strong intramolecular hydrogen bond is formed in its molecules between the NH proton in the hydrazone fragment and carbonyl oxygen atom in the ester moiety (*Z* isomer). The distance $O^1\cdots H^1$ is 1.83(2) Å, and the angles $N^2H^1O^1$ and $C^1O^1H^1$ are 134(2) and 101(2)°, respectively. Molecules **Ic** in crystal adopt *s-cis*,*s-trans* conformation in which the trifluoromethyl and ethoxy groups are oriented *trans* relative to the C(=O)–C(=NNHAr)–C(=O) fragment. For comparison, X-ray analysis was also performed for a single crystal of ethyl 2-(4-methylphenylhydrazono)-3-oxobutanoate (**Io**). Unlike trifluoromethyl analog **Ic**, compound **Io** was found to exist as *E* isomer in which intramolecular hydrogen bond involves carbonyl oxygen atom of the acetyl fragment (Fig. 2). The distance O^3–H^1 is 1.82(2) Å, and the angles $N^2H^1O^3$ and $C^3O^3H^1$ are 136(2) and 103(1)°, respectively.

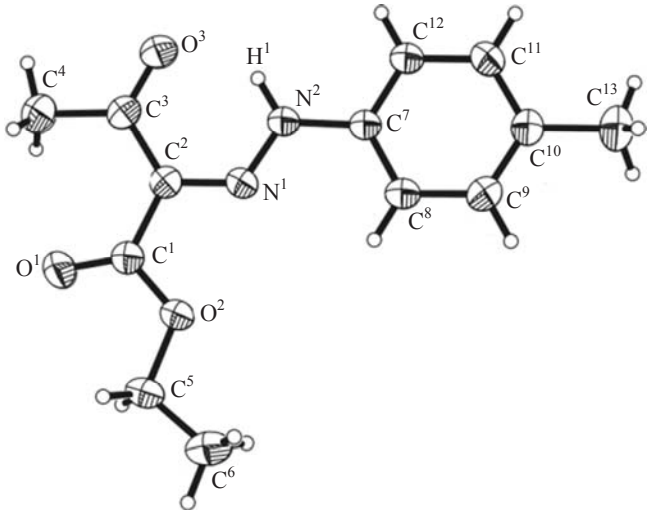


Fig. 2. Structure of the molecule of ethyl 2-[(4-methylphenyl)hydrazono]-3-oxobutanoate (**Io**) according to the X-ray diffraction data.

Comparison of the IR spectra of ethyl 2-(4-methylphenylhydrazono)-3-oxobutanoate (**Io**), recorded from a solution chloroform (*c* ~0.1 M) and from a crystalline sample using a diffuse reflectance accessory (DRA) revealed some differences in the absorption region corresponding to carbonyl stretching vibrations, as well as in the "fingerprint" region. In the IR spectrum of crystalline compound **Io**, carbonyl absorption bands are broadened in the region 1700–1695 cm^{-1}, whereas the corresponding bands in the spectrum recorded from chloroform solution are observed at 1700 and 1680 cm^{-1}. Therefore, we presume that the structures of ester **Io** in the crystalline state and in chloroform solution are not identical.

Mitchell and Nonhebel [7] previously showed by ^1H NMR spectroscopy that methyl and ethyl 2-phenylhydrazono- and 2-(4-chlorophenyl)hydrazono-3-oxobutanoates in $CDCl_3$ exist as mixtures of *Z* and *E* isomers, the latter prevailing (60–70%). Analysis of the ^1H and ^{13}C NMR spectra of ester **Io** in $CDCl_3$ and $(CD_3)_2CO$ also revealed the presence of *Z* and *E* isomers (two sets of signals were observed in each case). Signals were assigned to particular isomers taking into account that intramolecular hydrogen bonding induces downfield shift of the corresponding carbonyl carbon atom and neighboring carbon atoms relative to those belonging to the free carbonyl group. In the ^{13}C NMR spectrum of ester **Io**, signals from the H-bonded acetyl fragment of the *E* isomer are located in a weaker field [$\delta(C^3)$ 197.12, $\delta(C^4)$ 30.67 ppm] relative to the corresponding signals of the free $CH_3C{=}O$ group in the *Z* isomer [$\delta(C^3)$ 193.51, $\delta(C^4)$ 26.58 ppm]. On the other hand, the ester carbonyl carbon atom of the *E* isomer (free carbonyl group) resonates in a stronger field [$\delta(C^1)$ 164.14 ppm] as compared to the carbon atom in the H-bonded ester carbonyl group [$\delta(C^1)$ 165.49 ppm,

Z isomer]. Analogous downfield shifts of signals from methyl protons in the acetyl fragment of the *E* isomer of **Io** were observed in the ^{1}H NMR spectra, whereas methylene protons in the ethoxy group of the same isomer resonated in a stronger field. The fraction of the *E* isomer in weakly polar $CDCl_3$ was greater (90%) than in polar $(CD_3)_2CO$ (62%). In addition, the *E* isomer was characterized by downfield position of the NH proton (δ ~14 ppm) as compared to the *Z* isomer (δ ≈ 12 ppm), indicating that the intramolecular hydrogen bond in the *E* isomer is stronger.

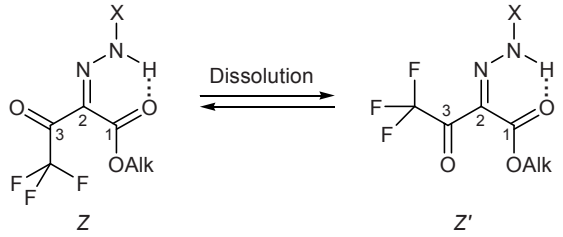
Unlike nonfluorinated 2-arylhydrazono-3-oxobutanoates, polyfluoroalkyl analogs **Ic**–**In** exist in solution [$CDCl_3$, $(CD_3)_2CO$, $(CD_3)_2SO$] as a single isomer: their ^{1}H, ^{19}F, and ^{13}C NMR spectra contain only one set of signals. Exceptions are 2-arylhydrazono-4,4-difluoro-3-oxobutanoates **Ia** and **Ib** which displayed in the ^{1}H and ^{19}F NMR spectra (acetone-d_6) two sets of signals corresponding to *Z* and *E* isomers. The signals were assigned to *Z* and *E* isomers on the basis of the same relations as those noted above for ester **Io**. In each case, the *Z* isomers with H-bonded ester carbonyl group were characterized by downfield signals from protons in the alkoxy groups, whereas the corresponding *E* isomers displayed upfield signals of these protons. A downfield shift was also observed for the NH signal of the *E* isomer (δ ~15 ppm) relative to that of the *Z* isomer (δ ~13 ppm).

While studying isomerism in the series of fluorinated 1,2,3-trione 2-arylhydrazones, we found that signals from fluorine atoms in the α-position with respect to the free carbonyl group appear in the ^{19}F NMR spectra in a weaker field relative to analogous signals from fluorine atoms in the α-position with respect to the H-bonded carbonyl group [8]. Following this relation, more intense fluorine signals in the region δ_F 35.89–35.90 ppm in the ^{19}F NMR spectra of compounds **Ia** and **Ib** should be assigned to their *Z* isomers, and those located in a stronger field, δ_F 35.73–35.78 ppm, to the *E* isomers.

The structure of trifluoromethyl-containing ester **Ic** was studied by IR spectroscopy. The IR spectra of **Ic** were recorded from a crystalline sample (dispersed in mineral oil) and a 0.1 M solution in chloroform. We observed no appreciable differences in the carbonyl absorption patterns (ν 1700 cm^{-1}) and concluded that ester **Ic** in solution, as well as in the crystalline state, has *Z* configuration. Similarity of the ^{1}H and ^{13}C NMR spectra of **Ic** in $CDCl_3$ and $(CD_3)_2CO$ indicates the presence of its *Z* isomer in these solvents.

The results of our previous study on the steric structure of a large series of various trifluoromethyl-containing 1,2,3-trione 2-arylhydrazones showed [6] that signals from fluorine nuclei in the trifluoroacetyl fragment involved in intramolecular hydrogen bonding with the NH proton in the arylhydrazone fragment appear in the ^{19}F NMR spectra at δ_F ~87 ppm in $CDCl_3$ or ~89 ppm in $(CD_3)_2CO$ and that the free CF_3CO group gives rise to signals at δ_F ~91 ppm in $CDCl_3$ or ~93 ppm in $(CD_3)_2CO$. Comparison of these values with those found for 2-arylhydrazono-4,4,4-trifluoromethyl-3-oxobutanoates **Ic** and **Id** indicated that intramolecular hydrogen bond therein is formed with participation of the ester carbonyl group (*Z* isomer with free CF_3CO group).

Furthermore, the CF_3 signal in the ^{19}F NMR spectrum of **Ic** in $CDCl_3$ was a doublet with a coupling constant $^6J_{FH}$ of 1 Hz (coupling with the hydrazone NH proton) which is typical of free $CF_3C{=}O$ group [7, 8]. In the ^{13}C NMR spectrum of the same compound in $CDCl_3$, the ester C^1 signal was split into quartet due to coupling with fluorine ($^4J_{CF}$ = 1.4 Hz). The existence of such coupling suggests *s-cis-s-cis* conformation of the conjugated C=O, C=N, and C=O double bonds; a different conformation is observed in crystal (Fig. 1). Presumably, dissolution of compound **Ic** in $CDCl_3$ is accompanied by rotation of the trifluoroacetyl group with respect to the single C^2–C^3 bond (*Z*′ conformer).



Other polyfluorinated esters **Ie**–**In** were assigned *Z* or *E* isomer structure by comparing their ^{19}F NMR spectra with those reported previously for polyfluoroalkyl-containing 1,2,3-trione 2-arylhydrazones [8]. Here, chemical shifts of fluorine atoms at the carbon atom directly attached to carbonyl group (involved or not involved in intramolecular hydrogen bond with the NH proton) were considered. The signal from the α-fluorine atoms in the H-bonded $H(CF_2)_2CO$ group is located at δ_F 41.0 ppm in the spectra recorded in $(CD_3)_2CO$ and $CDCl_3$, while the corresponding signal from the free $H(CF_2)_2CO$ group appears at δ_F 42.2 ppm in $CDCl_3$ and at δ_F 43.4 ppm in $(CD_3)_2CO$ [8]. The chemical shifts of the α-fluorine atoms in the ^{19}F NMR

Energies, charges on carbonyl carbon atoms, and Fukui indices of 2-arylhydrazono-3-oxo esters **Ia**, **Ic**, **If**, **Ii**, and **Io**

Comp. no., isomer	*E*, kJ/mol	Charges (Fukui indices for HOMO/LUMO)	
		C^3=O	C^1=O
Ia, *Z*	–638.52	0.2503 (0.0206/0.2621)	0.3422 (0.0349/0.2112)
E	–622.72	0.2313 (0.0580/0.4237)	0.3719 (0.0048/0.0651)
Ic, *Z*	–996.99	0.2972 (0.0041/0.3697)	0.3537 (0.0390/0.2929)
E	–984.37	0.2520 (0.0621/0.4431)	0.3740 (0.0089/0.0712)
If, *Z*	–1159.13	0.2869 (0.0199/0.2572)	0.3507 (0.0371/0.2116)
E	–1149.82	0.2383 (0.0575/0.4231)	0.3840 (0.0083/0.0688)
Ii, *Z*	–2139.14	0.2882 (0.0247/0.2824)	0.3545 (0.0358/0.1954)
E	–2110.76	0.2529 (0.0485/0.4088)	0.3726 (0.0106/0.0669)
Io, *Z*	–274.18	0.3123 (0.0155/0.0592)	0.3442 (0.0382/0.3003)
E	–273.45	0.2823 (0.0469/0.3528)	0.3742 (0.0037/0.0635)

spectra of esters **Ie** and **If** [δ_F 42.2 in $CDCl_3$ and 43.9 ppm in $(CD_3)_2CO$] fall into the range typical of tetrafluoropropionyl group not involved in intramolecular hydrogen bond (*Z* isomer).

According to [8], signals from the α-fluorine atoms in the free polyfluoroacyl group having more than three carbon atoms in 1,2,3-trione 2-arylhydrazones are located at δ_F ~49.4 ppm in chloroform-*d* and at δ_F 51.5 ppm in acetone-d_6. Esters **Ig**–**In** displayed in the ^{19}F NMR spectra signals from the $C^{\alpha}F_2$ group in the regions δ_F 49.6–50.5 ($CDCl_3$) and 52.1–52.8 ppm [$(CD_3)_2CO$], i.e., in the regions typical of *Z* isomers. Comparison of the ^{13}C NMR spectra of nonafluoropropyl derivative **Il** and trifluoromethyl analog **Ic** (see Experimental) whose structure was determined by X-ray analysis showed similarity in the chemical shifts of carbon nuclei in the ester fragment; these data provide an additional support to the *Z* configuration of ester **Il**.

Thus the results of our study showed that fluorinated 2-arylhydrazono-3-oxo esters **Ic**–**In** in the crystalline state and in solution [$(CD_3)_2CO$, $CDCl_3$] exist as *Z* isomers with the NH proton involved in intramolecular hydrogen bond with the ester carbonyl oxygen atom. Exception are difluoromethyl derivatives **Ia** and **Ib** for which both *Z* and *E* isomers were identified in $(CD_3)_2CO$ solution, the major isomer having *Z* configuration. Nonfluorinated ester **Io** in crystal exists as *E* isomer in which intramolecular hydrogen bond is formed between the NH proton and oxygen atom in the acetyl fragment. The same compound in $(CD_3)_2CO$ and $CDCl_3$ gives rise to a mixture of *Z* and *E* isomers, the latter prevailing.

We made an attempt to rationalize the observed differences in the steric structure of fluorinated and nonfluorinated 2-arylhydrazono-3-oxo esters on the basis of quantum-chemical calculations. The energy, charge, and orbital parameters were calculated for the most favorable conformers of esters **Ia**, **Ic**, **If**, **Ii**, and **Io** in terms of semiempirical AM1 approximation using MOPAC 7.10 software [9] (see table). The results showed that the *Z* isomers of fluorinated esters **Ia**, **Ic**, **If**, and **Ii** are energetically more favorable than their *E* isomers: the difference in the enthalpies of formation amounts to 9.31–28.38 kJ/mol. The corresponding difference for nonfluorinated analog **Io** is smaller by an order of magnitude (0.73 kJ/mol).

Presumably, the *Z* configuration of fluorinated 2-arylhydrazono-3-oxo esters **Ia**–**In** is favored by weaker proton-acceptor power of the carbonyl oxygen atom in the polyfluoroacyl group due to stronger negative inductive effect of polyfluoroalkyl group as compared to alkoxy. Moreover, it is known that the negative inductive effect of oxygen atom in alkoxy group is weaker than its positive mesomeric effect. All these factors favor intramolecular hydrogen bonding with participation of the ester carbonyl oxygen atom and hence *Z* configuration of esters **Ia**–**In**.

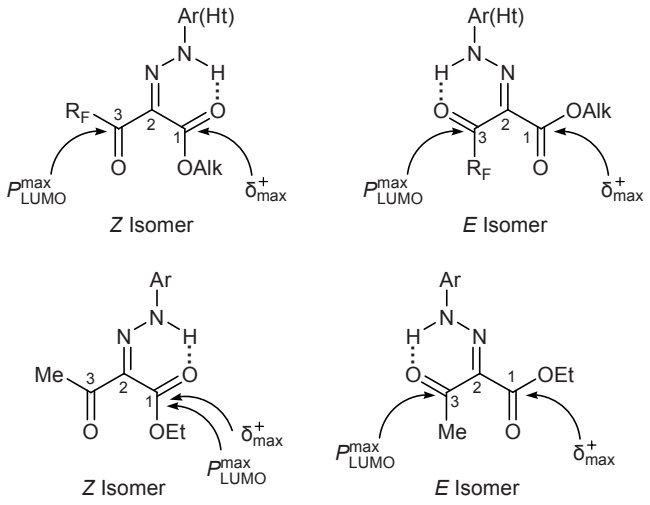
Positive inductive effect of methyl group {σ_I(Me) = –0.01 [10]} in nonfluorinated 2-arylhydrazono-3-oxobutanoates makes the acetyl oxygen atom preferable for hydrogen bonding with the NH proton in the arylhydrazone fragment, as compared to the alkoxy group exhibiting negative inductive effect {σ_I(OEt) = 0.28 [10]}. Therefore, such esters exist mostly as *E* isomers. On the other hand, the energies of formation of the *Z* and *E* isomers of nonfluorinated ester **Io** are fairly similar, so that the *E* isomer can readily be transformed into the *Z* isomer, and such transformation is observed in going from crystalline ester **Io** to solution in $CDCl_3$ and $(CD_3)_2CO$.

The presence of the second (*E*) isomer of 2-arylhydrazono-4,4-difluoro-3-oxobutanoates **Ia** and **Ib** in

$(CD_3)_2CO$ is likely to be related to the solvent properties. Electron-withdrawing carbonyl group in acetone molecule is capable of competing with the ethoxycarbonyl group in **Ia** and **Ib** for hydrogen bonding with the NH proton, which weakens the intramolecular hydrogen bond in the *Z* isomer and facilitates its transformation into the *E* isomer. The fact that *Z*/*E* isomerism is observed only for difluoromethyl-containing compounds **Ia** and **Ib** may be rationalized in terms of weaker negative inductive effect of difluoromethyl group $\{\sigma_I(HCF_2) = 0.28$ [10]$\}$ as compared to other fluoroalkyl substituents $\{\sigma_I(CF_3) = 0.40$, $\sigma_I(C_3F_7) \approx \sigma_I(C_4F_9) = 0.39$ [10]$\}$. In addition, the inductive effect of HCF_2 group is comparable to that of ethoxy group, which makes both carbonyl groups in **Ia** and **Ib** capable of binding the NH proton.

The results of quantum-chemical calculations showed that the C^3 atom in the polyfluoroacyl fragment of the *Z* and *E* isomers of fluorinated esters **Ia**, **Ic**, **If**, and **Ii** is characterized by the highest Fukui index in the LUMO, and that the largest positive charge is localized on the C^1 atom in the ester fragment. This means that kinetically controlled reactions of polyfluoroalkyl-containing 2-arylhydrazono-3-oxo esters with nucleophiles, other conditions being equal, should involve the C^1 center under charge control or C^3 center under orbital control. Analogous charge and electron density distribution over the C^1 and C^3 atoms was found for the *E* isomer of nonfluorinated ester **Io**. However, the ester carbonyl carbon atom in the *Z* isomer of **Io** has the highest Fukui index in the LUMO and the maximal positive charge.

Taking into account the above differences in the steric structure and energy, charge, and orbital parameters, fluorinated and nonfluorinated 2-arylhydrazono-3-oxo esters may be expected to exhibit different reactivities toward nucleophilic reagents. In fact, we previously found [2] that fluorinated esters react with ethane-1,2-diamine at the ester group to give the corresponding *N*,*N*′-ethylenebisamides; in contrast, 2-arylhydrazono-3-oxobutanoates reacted with the same diamine to form a "mixed" product as a result of nucleophilic attack at the ester group of one molecule and ketone group of the other.



EXPERIMENTAL

The ^1H NMR spectra were recorded on Tesla BS-567A (100 MHz) and Bruker DRX-400 (400 MHz) spectrometers using tetramethylsilane as internal reference; the ^{19}F and ^{13}C NMR spectra were measured on Tesla BS-587A (^{19}F, 75 MHz, C_6F_6) and Bruker DRX-400 instruments (^{19}F, 376 MHz, C_6F_6; ^{13}C, 100.6 MHz, TMS).

The IR spectra were recorded on a Specord 75IR or Perkin–Elmer Spectrum One instrument with Fourier transform from samples dispersed in mineral oil, using a diffuse reflectance accessory, or from solutions in chloroform ($c \approx 0.1$ M). The elemental compositions were determined on Carlo Erba CHN/S-O EA 1108 and Perkin–Elmer 2400 Series II analyzers. Column chromatography was performed on Merck 60 silica gel (0.063–0.200 mm) using chloroform as eluent. The melting points were measured in open capillaries using a Stuart SMP3 melting point apparatus.

Single crystals of ester **Ic** were obtained by crystallization from methylene chloride–hexane (4:1). The X-ray diffraction data were acquired on an Xcalibur 3 diffractometer equipped with a CCD detector [graphite monochromator, $\lambda(MoK_\alpha) = 0.71073$ Å, temperature 295(2) K, ψ/ω scanning]. Absorption by the crystal was taken into account analytically using a multifaceted crystal model with the aid of CrysAlis RED 1.171.28c4 software. The structure was solved by the direct method on the basis of Fourier difference syntheses using SHELXS-97 software [11]. The positions and temperature parameters of non-hydrogen atoms were refined by the least-squares procedure in full-matrix anisotropic approximation using SHELXL-97 software [11]. $C_{13}H_{13}F_3N_2O_4$. *M* 318.25; rhombic crystals, space group *Aba*2; $a = 15.440(3)$, $b = 26.143(3)$, $c = 6.939(5)$ Å; $V = 2801.2(8)$ Å^3; $Z = 8$, $d_{calc} = 1.509$ g/cm^{-3}; $\mu = 0.107$ mm^{-1}. Total of 1876 reflections were measured, 869 of which were independent ($R = 0.037$, 230 refined parameters).

Single crystals of ester **Io** were obtained by crystallization from methylene chloride. The X-ray diffraction data were acquired on an Enraf–Nonius CAD-4 diffractometer [graphite monochromator, $\lambda(MoK_\alpha)$ = 0.71073 Å, temperature 295(2) K, ω/2θ scanning]. The structure was solved by the direct method, followed by Fourier difference syntheses, using SHELXS-97 software [11] and was refined by the least-squares procedure in full-matrix anisotropic approximation for all non-hydrogen atoms using SHELXL-97 software [11]. The coordinates of hydrogen atoms were determined experimentally or calculated on the basis of geometry considerations and were refined in isotropic approximation. $C_{13}H_{16}N_2O_3$. *M* 248.28; rhombic crystals, space group *Pbcm*; *a* = 9.150(2), *b* = 22.100(4), *c* = 6.680(1) Å; *V* = 1350.8(4) Å^3; *Z* = 4; d_{calc} = 1.220 g/cm^3; μ = 0.088 mm^{-1}. Total of 2060 reflections were measured, 1109 of which were independent (*R* = 0.045, 138 refined parameters).

The complete sets of crystallographic data for compounds **Ic** and **Io** were deposited to the Cambridge Crystallographic Data Centre (entry nos. CCDC 683849 and CCDC 623953, respectively; *www.ccdc.can.ac.uk/conts/retrieving.html*; 12 Union Road, Cambridge CB2 1EZ, UK; *e-mail: deposit@ccdc.cam.ac.uk*).

Fluorinated 2-arylhydrazono-3-oxo esters **Ic**, **Ig**, **Il**, **Im** [1], **Ib**, **Ie**, **Ii** [5], **Id**, and **Ik** [6] and fluorine-free compound **Io** [12] were synthesized according to known procedures and were purified by column chromatography. Newly synthesized esters **Ia**, **If**, **Ih**, and **Ij** were characterized by elemental analyses and IR spectra in addition to the NMR data.

Methyl 4,4-difluoro-2-(4-methylphenylhydrazono)-3-oxobutanoate (Ia). Yield 58%, orange powder, mp 102–103°C. Diffuse reflectance IR spectrum, ν, cm^{-1}: 3130 (NH); 1700, 1680 (C=O); 1590, 1530 (δNH, C=N, C=C); 1220–1125 (C–F). ^{1}H NMR spectrum, δ, ppm: in $CDCl_3$ (*Z* isomer, 100%): 2.37 s (3H, Me), 3.95 s (3H, OMe), 6.69 t (1H, HCF_2, $^2J_{HF}$ = 54.3 Hz), 7.22–7.29 m (4H, C_6H_4), 13.44 br.s (1H, NH); in $(CD_3)_2CO$: *Z* isomer (85%): 2.36 s (3H, Me), 3.89 s (3H, OMe), 6.99 t (1H, HCF_2, $^2J_{HF}$ = 54.1 Hz), 7.29–7.31 m and 7.50–7.54 m (4H, C_6H_4), 13.12 br.s (1H, NH); *E* isomer (15%): 2.31 s (3H, Me), 3.85 s (3H, OMe), 6.95 t (1H, HCF_2, $^2J_{HF}$ = 53.8 Hz), 7.33–7.35 m and 7.57–7.59 m (4H, C_6H_4), 14.58 br.s (1H, NH); in DMSO-d_6: 2.32 s (3H, Me), 3.85 s (3H, OMe), 7.06 t (1H, HCF_2, $^2J_{HF}$ = 53.6 Hz), 7.24–7.26 m and 7.48–7.51 m (4H, C_6H_4), 12.70 s (1H, NH). ^{19}F NMR spectrum, δ_F, ppm: in $CDCl_3$ (*Z* isomer, 100%): 34.55 d (HCF_2, $^2J_{FH}$ = 54.3 Hz); in $(CD_3)_2CO$: *Z* isomer (85%): 35.89 d (HCF_2, $^2J_{FH}$ = 54.1 Hz); *E* isomer (15%): 35.73 d (HCF_2, $^2J_{FH}$ = 53.8 Hz); in DMSO-d_6: *Z* isomer (100%): 35.23 d (HCF_2, $^2J_{FH}$ = 53.6 Hz). Found, %: C 53.48; H 4.42; F 14.00; N 10.12. $C_{12}H_{12}F_2N_2O_3$. Calculated, %: C 53.34; H 4.48; F 14.06; N 10.37.

Ethyl 4,4-difluoro-2-(4-methylphenylhydrazono)-3-oxobutanoate (Ib). Yield 54%, yellow crystals, mp 96–97°C. ^{1}H NMR spectrum, δ, ppm: in $CDCl_3$ (*Z* isomer, 100%): 1.42 t (3H, OCH_2**Me**, $^3J_{HH}$ = 7.1 Hz), 2.38 s (3H, Me), 4.41 q (2H, OCH_2, $^3J_{HH}$ = 7.1 Hz), 6.70 t (1H, HCF_2, $^2J_{HF}$ = 54.3 Hz), 7.22–7.28 m (4H, C_6H_4), 13.45 s (1H, NH); in $(CD_3)_2CO$: *Z* isomer (90%): 1.36 t (3H, OCH_2**Me**, $^3J_{HH}$ = 7.1 Hz), 2.35 s (3H, Me), 4.37 q (2H, OCH_2, $^3J_{HH}$ = 7.1 Hz), 6.98 t (1H, HCF_2, $^2J_{HF}$ = 54.1 Hz), 7.28–7.30 m and 7.49–7.52 m (4H, C_6H_4), 13.13 br.s (1H, NH); *E* isomer (10%): 1.35 t (3H, OCH_2**Me**, $^3J_{HH}$ = 7.1 Hz), 2.36 s (3H, Me), 4.33 q (2H, OCH_2, $^3J_{HH}$ = 7.1 Hz), 6.94 t (1H, HCF_2, $^2J_{HF}$ = 53.8 Hz), 7.31–7.33 m and 7.56–7.58 m (4H, C_6H_4), 14.54 br.s (1H, NH). ^{19}F NMR spectrum, δ_F, ppm: in $CDCl_3$: *Z* isomer (100%): 34.44 d (HCF_2, $^2J_{FH}$ = 54.3 Hz); in $(CD_3)_2CO$: *Z* isomer (90%): 35.90 d (HCF_2, $^2J_{FH}$ = 54.1 Hz); *E* isomer (10%): 35.78 d (HCF_2, $^2J_{FH}$ = 53.8 Hz).

Ethyl 4,4,4-trifluoro-2-(4-methoxyphenylhydrazono)-3-oxobutanoate (Ic). Yield 60%, yellow crystals, mp 130–131°C. ^{1}H NMR spectrum, δ, ppm: in $CDCl_3$ (*Z* isomer, 100%): 1.42 t (3H, OCH_2**Me**, $^3J_{HH}$ = 7.1 Hz), 3.84 s (3H, OMe), 4.40 q (2H, OCH_2, $^3J_{HH}$ = 7.1 Hz), 6.95–6.99 m and 7.36–7.40 m (4H, C_6H_4), 13.61 br.s (1H, NH); in $(CD_3)_2CO$ (*Z* isomer, 100%): 1.35 t (3H, CH_2**Me**, $^3J_{HH}$ = 6.8 Hz), 3.86 s (3H, OMe), 4.38 q (2H, OCH_2, $^3J_{HH}$ = 6.8 Hz), 7.06–7.10 m and 7.57–7.60 m (4H, C_6H_4), 13.42 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: in $CDCl_3$ (*Z* isomer, 100%): 55.57 (OMe), 14.02 and 61.64 (OEt), 117.27 q (C^4, $^1J_{CF}$ = 292.8 Hz), 115.06, (C^o), 118.00 (C^m), 120.34 (C^i), 134.49 (C^2), 158.61 (C^p), 174.41 q (C^3, $^2J_{CF}$ = 32.3 Hz), 164.09 q (C^1, *J* = 1.4 Hz); in $(CD_3)_2CO$ (*Z* isomer, 100%): 55.94 (OMe), 14.32 and 62.16 (OEt), 118.40 q (C^4, $^1J_{CF}$ = 292.9 Hz), 115.83, (C^o), 119.04 (C^m), 121.36 (C^i), 135.77 (C^2), 159.59 (C^p), 174.29 q (C^3, $^2J_{CF}$ = 31.5 Hz), 164.09 (C^1). ^{19}F NMR spectrum, δ_F, ppm: in $CDCl_3$ (*Z* isomer, 100%): 91.43 d (CF_3, $^6J_{FH}$ = 0.8 Hz); in $(CD_3)_2CO$ (*Z* isomer, 100%): 93.78 s (CF_3).

Ethyl 2-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-ylhydrazono)-4,4,4-trifluoro-3-

oxobutanoate (Id). Yield 57%, yellow powder, mp 158–159°C. ^{1}H NMR spectrum, δ, ppm: in $CDCl_3$ (*Z* isomer, 100%): 1.39 t (3H, CH_2**Me**, $^3J_{HH}$ = 7.1 Hz), 2.52 s (3H, Me), 3.15 s (3H, NMe), 4.39 q (2H, OCH_2, $^3J_{HH}$ = 7.1 Hz), 7.35–7.51 m (5H, C_6H_5), 13.37 s (1H, NH); in DMSO-d_6 (*Z* isomer, 100%): 1.30 t (3H, CH_2**Me**, $^3J_{HH}$ = 7.1 Hz), 2.48 s (3H, Me), 3.20 s (3H, NMe), 4.31 q (2H, OCH_2, $^3J_{HH}$ = 7.1 Hz), 7.38–7.58 m (5H, C_6H_5), 13.18 s (1H, NH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm (*Z* isomer, 100%): 10.49 (CH_2**Me**), 13.86 (Me), 35.13 (NMe), 61.22 (OCH_2), 111.42 ($C^{4'}$), 117.03 q (C^4, $^1J_{CF}$ = 292.7 Hz), 121.23 (C^2), 124.94 (C^o), 127.60 (C^p), 129.34 (C^m), 133.74 (C^i), 144.04 ($C^{3'}$), 158.00 ($C^{5'}$), 162.87 (C^1), 172.39 q (C^3, $^2J_{CF}$ = 31.3). ^{19}F NMR spectrum ($CDCl_3$): δ_F 90.81 ppm, s (CF_3, *Z* isomer, 100%).

Methyl 4,4,5,5-tetrafluoro-2-(4-methylphenylhydrazono)-3-oxopentanoate (Ie). Yield 71%, orange powder, mp 79–80°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*Z* isomer, 100%): 2.38 s (3H, Me), 3.93 s (3H, OMe), 6.34 t.t (1H, HCF_2, $^2J_{HF}$ = 53.2, $^3J_{HF}$ = 5.6 Hz), 7.23–7.30 m (4H, C_6H_4), 13.48 br.s (1H, NH). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm (*Z* isomer, 100%): 24.59 d.t (2F, HCF_2, $^2J_{FH}$ = 53.2, $^3J_{FF}$ = 7.9 Hz), 42.20 m (2F, 4-F).

Methyl 4,4,5,5-tetrafluoro-2-(4-methoxyphenylhydrazono)-3-oxopentanoate (If). Yield 73%, yellow powder, mp 100–101°C. Diffuse reflectance IR spectrum, ν, cm^{-1}: 3135 (NH); 1700, 1655 (C=O); 1610, 1590, 1520 (δNH, N=N, C=C); 1220–1125 (C–F). ^{1}H NMR spectrum, δ, ppm: in $CDCl_3$ (*Z* isomer, 100%): 3.85 s and 3.93 s (3H each, OMe), 6.34 t.t (1H, HCF_2, $^2J_{HF}$ = 53.2, $^3J_{HF}$ = 5.6 Hz), 6.97–6.99 m and 7.34–7.36 m (4H, C_6H_4), 13.60 s (1H, NH); in $(CD_3)_2CO$ (*Z* isomer, 100%): 3.86 s and 3.89 s (3H each, OMe), 6.72 t.t (1H, HCF_2, $^2J_{HF}$ = 52.7, $^3J_{HF}$ = 5.8 Hz), 7.06–7.10 m and 7.54–8.01 m (4H, C_6H_4), 13.35 br.s (1H, NH); in DMSO-d_6 (*Z* isomer, 100%): 3.78 s and 3.86 s (3H each, OMe), 6.84 t.t (1H, HCF_2, $^2J_{HF}$ = 52.0, $^3J_{HF}$ = 5.6 Hz), 7.05–7.09 m and 7.50–7.52 m (4H, C_6H_4), 12.94 br.s (1H, NH). ^{19}F NMR spectrum, δ_F, ppm: in $CDCl_3$ (*Z* isomer, 100%): 24.45 d.t (2F, HCF_2, $^2J_{FH}$ = 53.2, $^3J_{FF}$ = 7.7 Hz), 42.23 m (2F, 4-F); in $(CD_3)_2CO$ (*Z* isomer, 100%): 24.47 d.t (2F, HCF_2, $^2J_{FH}$ = 52.7, $^3J_{FF}$ = 7.7 Hz), 43.94 m (2F, 4-F); in DMSO-d_6 (*Z* isomer, 100%): 25.84 d.t (2F, HCF_2, $^2J_{FH}$ = 52.0, $^3J_{FF}$ = 8.0 Hz), 43.56 m (2F, 4-F). Found, %: C 46.60; H 3.72; F 22.80; N 8.30. $C_{13}H_{12}F_4N_2O_4$. Calculated, %: C 46.44; H 3.60; F 22.60; N 8.33.

Methyl 4,4,5,5,6,6,6-heptafluoro-2-(4-methoxyphenylhydrazono)-3-oxohexanoate (Ig). Yield 77%, yellow crystals, mp 95–96°C. ^{1}H NMR spectrum, δ, ppm: in $CDCl_3$ (*Z* isomer, 100%): 3.84 s and 3.93 s (3H each, OMe), 6.95–6.99 m and 7.34–7.40 m (4H, C_6H_4), 13.66 s (1H, NH); in $(CD_3)_2CO$ (*Z* isomer, 100%): 3.86 s and 3.90 s (3H each, OMe), 7.07–7.09 m and 7.56–7.60 m (4H, C_6H_4), 13.43 s (1H, NH). ^{19}F NMR spectrum, δ_F, ppm: in $CDCl_3$ (*Z* isomer, 100%): 37.50 m (2F, 5-F), 49.66 m (2F, 4-F), 81.40 m (3F, CF_3); in $(CD_3)_2CO$ (*Z* isomer, 100%): 39.64 m (2F, 5-F), 52.09 m (2F, 4-F), 81.44 m (3F, CF_3).

Methyl 4,4,5,5,6,6,7,7-octafluoro-2-(4-methoxyphenylhydrazono)-3-oxoheptanoate (Ih). Yield 81%, yellow crystals, mp 82–83°C. Diffuse reflectance IR spectrum, ν, cm^{-1}: 3110 (NH); 1680 (C=O); 1610, 1515 (δNH, N=N, C=C); 1230–1110 (C–F). ^{1}H NMR spectrum, δ, ppm: in $CDCl_3$ (*Z* isomer, 100%): 3.84 s and 3.94 s (3H each, OMe), 6.18 t.t (1H, HCF_2, $^2J_{HF}$ = 52.0, $^3J_{HF}$ = 5.6 Hz), 6.96–6.99 m and 7.36–7.40 m (4H, C_6H_4), 13.68 s (1H, NH); in $(CD_3)_2CO$ (*Z* isomer, 100%): 3.86 s and 3.90 s (3H each, OMe), 6.78 t.t (1H, HCF_2, $^2J_{HF}$ = 51.1, $^3J_{HF}$ = 5.6 Hz), 7.06–7.10 m and 7.57–7.61 m (4H, C_6H_4), 13.40 s (1H, NH); in DMSO-d_6 (*Z* isomer, 100%): 3.79 s and 3.86 s (3H, OMe), 7.05–7.07 m and 7.51–7.55 m (4H, C_6H_4), 7.08 (1H, HCF_2, $^2J_{HF}$ = 50.2, $^3J_{HF}$ = 5.6 Hz), 12.97 s (1H, NH). ^{19}F NMR spectrum, δ_F, ppm: in $CDCl_3$ (*Z* isomer, 100%): 24.41 d.m (2F, HCF_2, $^2J_{FH}$ = 53.0 Hz), 32.38 m (2F, 6-F), 39.20 m (2F, 5-F), 50.09 m (2F, 4-F); in $(CD_3)_2CO$ (*Z* isomer, 100%): 25.60 d.m (2F, HCF_2, $^2J_{FH}$ = 51.1 Hz), 34.69 m (2F, 6-F), 41.96 m (2F, 5-F), 52.53 m (2F, 4-F); in DMSO-d_6 (*Z* isomer, 100%): 24.34 d.m (2F, HCF_2, $^2J_{FH}$ = 50.2 Hz), 33.88 m (2F, 6-F), 40.99 m (2F, 5-F), 51.33 m (2F, 4-F). Found, %: C 41.50; H 2.65; F 34.80; N 6.38. $C_{15}H_{12}F_8N_2O_4$. Calculated, %: C 41.30; H 2.77; F 34.84; N 6.42.

Methyl 4,4,5,5,6,6,7,7,7-nonafluoro-2-(4-methylphenylhydrazono)-3-oxoheptanoate (Ii). Yield 72%, pale yellow powder, mp 94–95°C. ^{1}H NMR spectrum, δ, ppm: in $CDCl_3$ (*Z* isomer, 100%): 2.38 s (3H, Me), 3.94 s (3H, OMe), 7.23–7.32 m (4H, C_6H_4), 13.55 s (1H, NH); in $(CD_3)_2CO$ (*Z* isomer, 100%): 2.36 s (3H, Me), 3.91 s (3H, OMe), 7.32–7.35 m and 7.50–7.52 m (4H, C_6H_4), 13.30 s (1H, NH). ^{19}F NMR spectrum [$(CD_3)_2CO$], δ_F, ppm (*Z* isomer, 100%): 38.92 m (2F, 6-F), 43.39 m (2F, 5-F), 52.77 m (2F, 4-F), 82.80 m (3F, CF_3).

Methyl 4,4,5,5,6,6,7,7,7-nonafluoro-2-(4-dimethylaminophenylhydrazono)-3-oxoheptanoate (Ij).

Yield 59%, red powder, mp 110–111°C. IR spectrum (mineral oil), ν, cm^{-1}: 3080 (NH); 1680 sh, 1675 (C=O); 1600, 1585, 1525 (δNH, C=N, C=C); 1225–1100 (C–F). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*Z* isomer, 100%): 3.02 s (6H, Me), 3.92 s (3H, OMe), 6.73–6.75 m and 7.31–7.35 m (4H, C_6H_4), 13.83 s (1H, NH). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm (*Z* isomer, 100%): 36.64 m (2F, 6-F), 41.15 m (2F, 5-F), 50.48 m (2F, 4-F), 80.91 m (3F, CF_3). Calculated, %: C 41.13; H 3.02; F 36.59; N 8.99. $C_{16}H_{14}F_9N_3O_3$. Found, %: C 41.12; H 2.90; F 36.47; N 8.68.

Methyl 4,4,5,5,6,6,7,7,7-nonafluoro-2-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-ylhydrazono)-3-oxoheptanoate (Ik). Yield 68%, yellow powder, mp 129–130°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm (*Z* isomer, 100%): 2.49 s (3H, Me), 3.16 s (3H, NMe), 3.91 s (3H, OMe), 7.34–7.52 m (5H, C_6H_5), 13.40 s (1H, NH). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm (*Z* isomer, 100%): 36.88 m (2F, 6-F), 40.49 m (2F, 5-F), 49.56 m (2F, 4-F), 80.75 m (3F, CF_3).

Ethyl 4,4,5,5,6,6,7,7,7-nonafluoro-2-(4-methoxyphenylhydrazono)-3-oxoheptanoate (Il). Yield 80%, orange powder, mp 77–78°C. ^1H NMR spectrum [$(CD_3)_2CO$], δ, ppm (*Z* isomer, 100%): 1.35 t (3H, CH_2**Me**, $^3J_{HH}$ = 7.0 Hz), 3.84 s (3H, OMe), 4.38 q (2H, OCH_2, $^3J_{HH}$ = 7.0 Hz), 7.03–7.07 m and 7.15–7.55 m (4H, C_6H_4), 13.39 s (1H, NH). ^{13}C NMR spectrum [$(CD_3)_2CO$], δ_C, ppm (*Z* isomer, 100%): 55.92 (OMe), 14.30 and 62.16 (OEt), 112.58 q (C^4, $^1J_{CF}$ = 272.0, $^2J_{CF}$ = 32.0 Hz), 106.58–120.18 (C^5, C^6, C^7), 115.80, (C^o), 119.14 (C^m), 122.76 (C^i), 135.72 (C^2), 159.65 (C^p), 176.16 t (C^3, $^2J_{CF}$ = 22.7), 164.14. ^{19}F NMR spectrum [$(CD_3)_2CO$], δ_F, ppm (*Z* isomer, 100%): 38.86 m (2F, 6-F), 43.19 m (2F, 5-F), 52.69 m (2F, 4-F), 82.77 m (3F, CF_3).

Ethyl 4,4,5,5,6,6,7,7,7-nonafluoro-2-(4-methylphenylhydrazono)-3-oxoheptanoate (Im). Yield 59%, orange powder, mp 44–45°C. ^{1} NMR spectrum ($CDCl_3$), δ, ppm (*Z* isomer, 100%): 1.40 t (3H, CH_2**Me**, $^3J_{HH}$ = 7.1 Hz), 2.35 s (3H, Me), 4.38 q (2H, OCH_2, $^3J_{HH}$ = 7.1 Hz), 7.14–7.17 m and 7.24–7.35 m (4H, C_6H_4), 13.50 br.s (1H, NH). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm (*Z* isomer, 100%): 36.84 m (2F, 6-F), 41.26 m (2F, 5-F), 50.44 m (2F, 4-F), 81.10 m (3F, CF_3).

Ethyl 4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoro-2-(4-methylphenylhydrazono)-3-oxononanoic acid (In). Yield 53%, yellow powder, mp 50–51°C. IR spectrum (mineral oil), ν, cm^{-1}: 3100 (NH); 1705, 1660 (C=O); 1595, 1530 (δNH, C=N, C=C); 1240–1120 (C–F). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.42 t (3H, CH_2**Me**, $^3J_{HH}$ = 7.0 Hz), 2.37 s (3H, Me), 4.40 q (2H, OCH_2, $^3J_{HH}$ = 7.0 Hz), 7.22–7.31 m (4H, C_6H_4), 13.55 br.s (1H, NH). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 35.73 m (2F, 8-F), 39.12 m (2F, 7-F), 40.57 m (2F, 6-F), 41.89 m (2F, 5-F), 50.34 m (2F, 4-F), 81.01 m (3F, CF_3). Found, %: C 39.40; H 2.31; F 44.70; N 5.12. $C_{18}H_{13}F_{13}N_2O_3$. Calculated, %: C 39.15; H 2.37; F 44.72; N 5.07.

Ethyl 2-(4-methylphenylhydrazono)-3-oxobutanoate (Io). Yield 65%, orange powder, mp 80–81°C; published data [12]: mp 75–76°C. Diffuse reflectance IR spectrum, ν, cm^{-1}: 3050 (NH); 1700, 1695 sh (C=O); 1625, 1590, 1505 (δNH, C=N, C=C). IR spectrum ($CHCl_3$), ν, cm^{-1}: 1700, 1680 (C=O). ^1H NMR spectrum, δ, ppm: in $CDCl_3$: *Z* isomer (10%): 1.44 t (3H, CH_2**Me**, $^3J_{HH}$ = 7.1 Hz), 2.35 s (3H, C_6H_4**Me**), 2.49 s (3H, Me), 4.37 q (2H, OCH_2, $^3J_{HH}$ = 7.1 Hz), 7.18–7.20 m and 7.31–7.33 m (4H, C_6H_4), 12.80 s (1H, NH); *E* isomer (90%): 1.40 t (3H, CH_2**Me**, $^3J_{HH}$ = 7.1 Hz), 2.35 s (3H, C_6H_4**Me**), 2.59 s (3H, Me), 4.33 q (2H, OCH_2, $^3J_{HH}$ = 7.1 Hz), 7.18–7.20 m and 7.31–7.33 m (4H, C_6H_4), 14.90 s (1H, NH); in $(CD_3)_2CO$: *Z* isomer (38%): 1.31 t (3H, CH_2**Me**, $^3J_{HH}$ = 7.1 Hz), 2.30 s (3H, C_6H_4**Me**), 2.38 s (3H, Me), 4.29 q (2H, OCH_2, $^3J_{HH}$ = 7.1 Hz), 7.20–7.24 m and 7.34–7.42 m (4H, C_6H_4), 12.24 s (1H, NH); *E* isomer (62%): 1.33 t (3H, CH_2**Me**, $^3J_{HH}$ = 7.1 Hz), 2.31 s (3H, C_6H_4**Me**), 2.50 s (3H, Me), 4.26 q (2H, OCH_2, $^3J_{HH}$ = 7.1 Hz), 7.20–7.24 m and 7.34–7.42 m (4H, C_6H_4), 14.67 s (1H, NH). ^{13}C NMR spectrum [$(CD_3)_2CO$], δ_C, ppm: *Z* isomer (38%): 20.91 (C_6H_4**Me**), 26.58 (C^4), 14.63 and 61.09 (OEt), 116.19–140.41 (C_{arom}), 136.13 (C^2), 165.49 (C^1), 193.51 (C^3); *E* isomer (62%): 20.83 (C_6H_4**Me**), 30.67 (C^4), 14.39 and 61.57 (OEt), 116.19–140.41 (C_{arom}), 136.13 (C^2), 164.13 (C^1), 197.12 (C^3). Found, %: C 62.97; H 6.47; N 11.02. $C_{13}H_{16}N_2O_3$. Calculated, %: C 62.89; H 6.50; N 11.28.

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REFERENCES

1. Kuzueva, O.G., Burgart, Ya.V., and Saloutin, V.I., *Izv. Ross. Akad. Nauk, Ser. Khim*., 1998, p. 695; Burgart, Ya.V., Fokin, A.S., Kuzueva, O.G., Chupakhin, O.N., and Saloutin, V.I., *J. Fluorine Chem*., 1998, vol. 92, p. 101.

2. Khudina, O.G., Burgart, Ya.V., Saloutin, V.I., and Chupakhin, O.N., *J. Fluorine Chem*., 2004, vol. 125, p. 401.
3. Khudina, O.G., Burgart, Ya.V., Murashova, N.V., and Saloutin, V.I., *Russ. J. Org. Chem*., 2003, vol. 39, p. 1421.
4. Shchegol'kov, E.V., Burgart, Ya.V., and Saloutin, V.I., *J. Fluorine Chem*., 2007, vol. 128, p. 779.
5. Khudina, O.G., Shchegol'kov, E.V., Burgart, Ya.V., and Saloutin, V.I., *Russ. J. Org. Chem*., 2004, vol. 40, p. 813; Khudina, O.G., Shchegol'kov, E.V., Burgart, Ya.V., Saloutin, V.I., and Chupakhin, O.N., *J. Fluorine Chem*., 2005, vol. 125, p. 1363.
6. Shchegol'kov, E.V., Sadchikova, E.V., Burgart, Ya.V., and Saloutin, V.I., *Izv. Ross. Akad. Nauk, Ser. Khim*., 2008, p. 599.
7. Mitchell, A. and Nonhebel, D.C., *Tetrahedron*, 1979, vol. 35, p. 2013.
8. Khudina, O.G., Shchegol'kov, E.V., Burgart, Ya.V., Kodess, M.I., Saloutin, V.I., Kazheva, O.N., Shilov, G.V., D'yachenko, O.A., Grishina, M.A., Potemkin, V.A., and Chupakhin, O.N., *Russ. J. Org. Chem*., 2007, vol. 43, p. 380.
9. Dewar, M.J.S., Zoebisch, E.G., Healy, E.F., and Stewart, J.J.P., *J. Am. Chem. Soc*., 1985, vol. 107, p. 3902.
10. Vereshchagin, A.N., *Induktivnyi effekt. Konstanty zamestitelei dlya korrelyatsionnogo analiza* (Inductive Effect. Substituent Constants for Correlation Analysis), Moscow: Nauka, 1988.
11. Scheldrick, G.M., *SHELXS-97 and SHELXL-97*, Göttingen, Germany: Univ. of Göttingen, 1997.
12. Garg, H.G. and Singh, P.P., *J. Med. Chem*., 1968, vol. 11, p. 1104.