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Fluoroalkyl-containing 2-arylhydrazono-1,3-dicarbonyl compounds in the reactions with ethylenediamine and polyethylenepolyamines

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Abstract

Acyclic *N*,*N*′-(poly)ethylene-*bis*(2-arylazo-1,3-aminovinylketones) are the main products in the reactions of fluoroalkyl-containing 2-arylhydrazono-1,3-diketones with ethylenediamine, diethylenetriamine and triethylenetetramine. Nickel(II) and copper(II) chelates were obtained from *N*,*N*′-ethylene-*bis*(2-arylazo-1,3-aminovinylketones). 2-Arylhydrazono-3-fluoroacyl esters formed *N*,*N*′-ethylenediamides of 2-arylhydrazono-3-fluoroacylpropionic acids with ethylenediamine. Interaction of 2-arylhydrazono-3-fluoroacyl esters with diethylenetriamine and triethylenetetramine resulted in and decomposition products.

Keywords: 2-Arylhydrazono-1,3-diketone; 2-Arylhydrazono-3-oxo ester; Ethylenediamine; Diethylenetriamine; Triethylenetetramine

1. Introduction

The reaction of 1,3-dicarbonyl compounds with ethylenediamine can afford various products. 1,3-Diketones, including fluoroalkyl-containing, form either derivatives of 1,4-diazepine [1,2] or *N*,*N*′-ethylene-*bis*(1,3-aminovinylketones) [3] with this diamine, depending on the reaction conditions. In the presence of nickel(II) ion 1,3-diketones react with ethylenediamine to yield nickel chelates of *N*,*N*′-ethylene-*bis*(1,3-aminovinylketones) [4,5]. Polydentate *N*,*N*′-*bis*(1,3-aminovinylketones) are the products of the reactions of 1,3-diketones with polyethylenepolyamines [6]. Template nickel ion condensation of trifluoroacetylacetone or acetylacetone with triethylenetetramine leads to the formation of (1,4,7,10-tetraazacyclotrideca-10,12-dienato)-nickel(II) iodide [7]. Fluoroalkyl-containing 3-oxo esters interact with ethylenediamine to form the substituted 1,4-diazepin-5-ones [2,8], imidazolidines [8], acyclic aminoethylamides of 3-fluoroacylpropionic acids or dialkyl-*N*,*N*′-ethylene-*bis*(3-amino-2-bytenoates) [9] depending on the reaction conditions.

Previously we obtained fluoroalkyl-containing 2-arylhydrazono-1,3-dicarbonyl compounds and studied their reactions with α-*N*,*N*- and N,O-dinucleophiles resulting in heterocyclic compounds such as pyrazoles and isoxazoles [10]. To our knowledge there are no literature data on interaction of 2-arylhydrazonosubstituted 1,3-diketones and 3-oxo esters with ethylenediamine and polyethylenepolyamines.

In the present work the reaction of fluoroalkyl-containing 2-arylhydrazonosubstituted 1,3-diketones **1** and 3-oxo esters **2** with ethylenediamine, diethylenetriamine and triethylenetetramine has been studied.

2. Results and discussion

2.1. Reactions of 2-arylhydrazono-1,3-diketones with ethylenediamine, diethylenetriamine and triethylenetetramine

It has been found that fluoroalkyl-containing 2-arylhydrazono-1,3-diketones **1a–c** react differently with ethylenediamine depending on the structure of the fluorinated substituent. 2-Arylhydrazono-1,3-diketone **1a** with a difluoromethyl group cyclizes in methanol at room temperature into dihydro-1,4-diazepine **3**. Under similar conditions 1,3-diketones **1b**,**c** containing ''longer'' fluoroalkyl substituents afford acyclic *N*,*N*′-ethylene-*bis*(2-arylazo-1,3-aminovinylketones) **4b**,**c** (Scheme 1).

Unlike the fluorinated compounds **1b**,**c**, 2-arylhydrazonosubstituted acetylacetone **1d** under similar conditions

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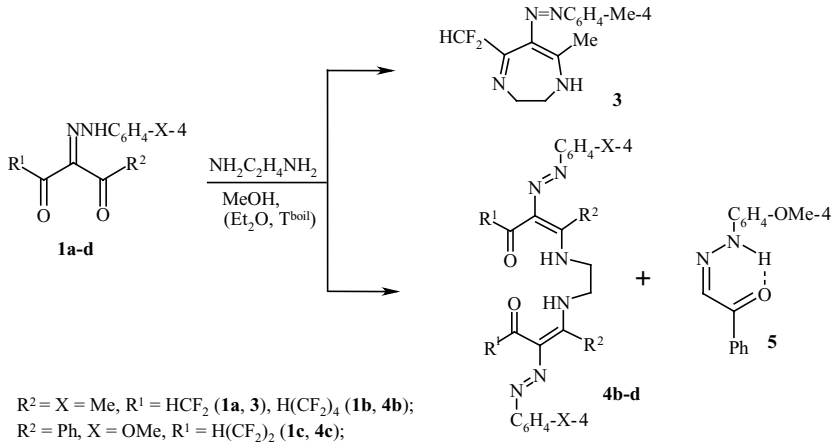


R^2 = X = Me, R^1 = HCF_2 (**1a**, **3**), $H(CF_2)_4$ (**1b**, **4b**);
R^2 = Ph, X = OMe, R^1 = $H(CF_2)_2$ (**1c**, **4c**);
R^2 = R^1 = Me, X = OMe (**1d**, **4d**).

Scheme 1.

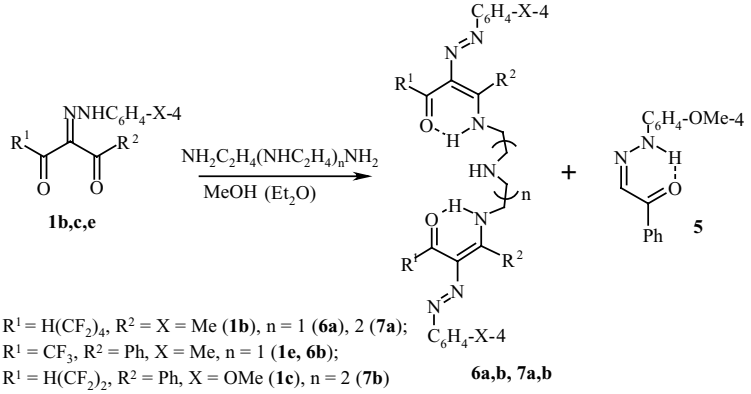
forms a mixture of products that is difficult to separate. However using diethyl ether as a solvent enabled *N*,*N*′-ethylene-*bis*(3-arylazo-4-aminopent-3-en-2-one) **4d** to be obtained (Scheme 1).

In the reactions of 2-arylhydrazono-1,3-diketones **1** with ethylenediamine we observed the single case of heterocyclic product formation (diazepine **3**), while non-substituted 1,3-diketones can form 1,4-diazepines with ethylenediamine [1,2]. Attempts to obtain 1,4-diazepines from 2-arylhydrazonosubstituted 1,3-diketones **1b-d** under conditions used to cyclize 1,3-diketones [1,2] failed.

2-Arylhydrazono-1,3-diketones **1b**,**c**,**e** react with diethylenetriamine and triethylenetetramine to give the penta- and hexadentate *N*,*N*′-*bis*(2-arylazo-1,3-aminovinylketones) **6a**,**b**, and **7a**,**b**, respectively (Scheme 2).

2-Arylhydrazono-1,3-diketones **1** condense with ethylenediamine (polyethylene-polyamines) in a ratio of 2:1 at one carbonyl group to give products **4**, **6** and **7**. In the case of the asymmetric fluoroalkyl-containing 2-arylhydrazono-1,3-diketones 1 the reaction may proceed either on the carbonyl connected with the non-fluorinated substituent or the carbonyl of the fluorinated moiety. The position of *N*,*N*′-(poly)-ethylenedi(poly)amine bridge in compounds **4**, **6** and **7** was established by ^{13}C NMR spectroscopy. In the ^{13}C NMR spectra of compounds **4c**, **6a** a triplet ($^2J_{C-F}$ = 23.3 Hz (**4c**), $^2J_{C-F}$ = 22.0 Hz (**6a**)) for the carbon atom attached to the polyfluoroalkyl substituent is located at ~180 ppm (Table 1), which is typical for a carbonyl carbon atom rather than a carbon at the C=C bond [11]. Thus, the attack of diamine proceeds on the carbonyl connected with non-fluorinated substituent. Such a direction for the addition is also typical for non-substituted fluorinated 1,3-diketones [3].

Experimental data obtained herein allow us to conclude that fluorinated 2-arylhydrazono-1,3-diketones **1** possess lower reactivity towards ethylenediamine (polyethylenepolyamines) compared with non-substituted analogues. Thus, the formation of acyclic *N*,*N*′-ethylene-*bis*(1,3-aminovinylketones) from fluoroalkyl-containing 1,3-diketones is an exothermal process carried out at lower temperatures [3], while 2-arylhydrazono-1,3-diketones **1** react with ethylenediamine (polyethylenepolyamines) at room temperature with incomplete conversion of starting compounds. However, by-products were formed already under these conditions, which was determined by thin-layer chromatography.

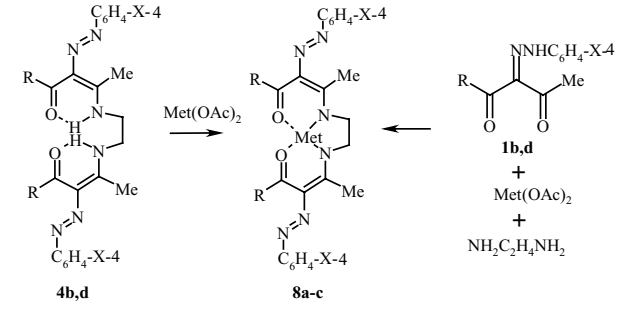


R^1 = $H(CF_2)_4$, R^2 = X = Me (**1b**), n = 1 (**6a**), 2 (**7a**);
R^1 = CF_3, R^2 = Ph, X = Me, n = 1 (**1e**, **6b**);
R^1 = $H(CF_2)_2$, R^2 = Ph, X = OMe (**1c**), n = 2 (**7b**)

Scheme 2.

Table 1
^{13}CNMR spectral data for compounds **4c**, **7a** (δC, ppm; $J(^{13}C–^{19}F)$, Hz) in $CDCl_3$

Compounds	C^1	$C^{2–5}$	C^6	C^7	C^8	C^9	C^{10}	C^{11}	C^{12}	C^{13}	C^{14}	$C^{15–16}$
4c	55.58	114.74–160.00					163.85	142.62	180.36 *T*(23.3)	107.76–115.03		46.29
7a, **I**	16.84	120.84–138.25	21.19	163.97	149.38	179.44 *T*(22.0)	105.46–113.20					43.77–52.74
7a, **II**	16.99	121.09–138.26	21.26	164.06	149.38	179.65 *T*(22.0)	105.46–113.20					41.34–56.04



R = $H(CF_2)_4$, X = Me (**1b, 4b**), Met = Cu (**8a**), Ni (**8b**);
R = Me, X = OMe (**1d, 4d**), Met = Ni (**8c**).

Scheme 3.

One such by-process is the acid decomposition of 2-arylhydrazono-1,3-diketones **1** resulting in product **5**, isolated from the reaction of 1,3-diketone **1c**.

It has been shown that *N*,*N*′-ethylene-*bis*(2-arylazo-1,3-aminovinylketone) **4** possesses a complexation ability like the non-substituted compounds of this class [3]. The treatment of compounds **4b**,**d** with nickel(II) or copper(II) acetate gives the corresponding metal chelates **8a–c** (Scheme 3).

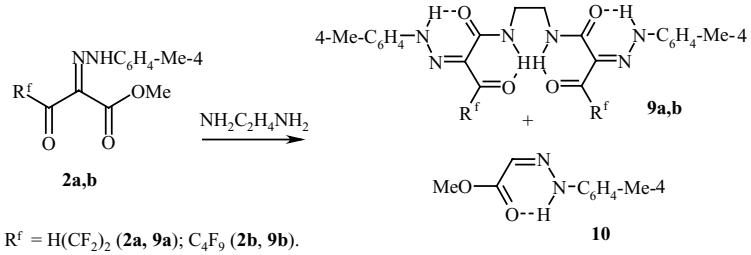
The template method is widely used for synthesis of similar nickel complexes [4,12,13]. However, it has been noted [12], that tri- and hexa-fluoroacetylacetones undergo Ni(II) template reactions with ethylenediamine to form nickel *bis*(1,3-diketonates) only. It has been also claimed [12] that in the case of 1,3-diketones having substituents (phenyl, methyl) in position 2, the complexation does not occur due to steric factors. We have found that nickel complexes **8b**,**c** can be obtained by a one-step template method from ethylenediamine and 2-arylhydrazono-1,3-diketones **1b**,**d** in the presence of nickel(II) acetate (Scheme 3).

Attempts to obtain *N*,*N*′-ethylene-*bis*(2-arylazo-1,3-aminovinylketone) **4a** with difluoromethyl substituents using a template method failed due to many by-products being formed.

2.2. Reactions of 2-arylhydrazono-3-fluoroacyl esters with ethylenediamine, diethylenetriamine and triethylenetetramine

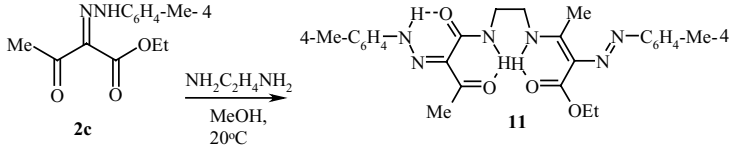
3-Oxo esters, including fluoroalkyl-substituted, can react with ethylenediamine at the keto group, ester fragment [9,14] or at both these centers [2,8,14]. We have found that 2-arylhydrazono-3-fluoroacyl esters **2a**,**b** condense with ethylenediamine at the ester group to give *N*,*N*′-ethylenediamides **9a**,**b** (Scheme 4).

Compared with 2-arylhydrazono-1,3-diketones **1**, fluoroalkyl-containing 2-arylhydrazono-3-oxo esters **2** in reactions with ethylenediamine have a greater tendency to undergo various side processes. The acid cleavage product **10** was isolated from the reaction of 2-arylhydrazono-3-oxo ester **2b** with ethylenediamine under mild conditions. Attempts to obtain cyclic products from these reactions were unsuccessful.

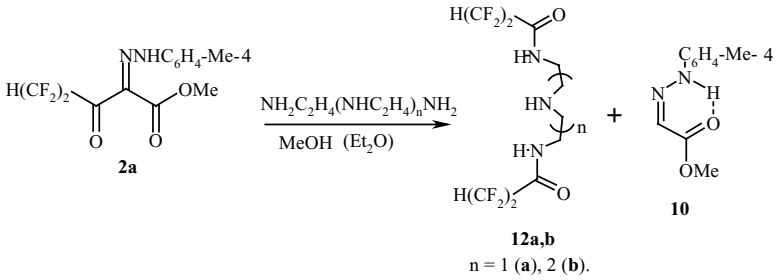


R^f = $H(CF_2)_2$ (**2a, 9a**); C_4F_9 (**2b**, **9b**).

Scheme 4.



Scheme 5.



Scheme 6.

In contrast to 2-arylhydrazono-3-fluoroacyl esters **2a**,**b**, under similar conditions 2-arylhydrazonosubstituted ethyl acetylacetate **2c** forms compound **11** as a result of addition of ethylenediamine on ester fragment of one 3-oxo ester and on ketogroup of other 3-oxo ester (Scheme 5).

Evidently 2-arylhydrazono-3-fluoroacyl esters **1a**,**b** react with ethylenediamine at the ester group to give symmetrical amides **9a**,**b** due to the presence of the electron-withdrawing fluoroalkyl substituents.

Acid decomposition is the basic process in the reactions of 2-arylhydrazono-3-fluoroacyl ester **2a** with diethylenetriamine and triethylenetetramine (Scheme 6) as shown by isolation of products **12a**,**b** and **10b**.

3. Conclusion

Introduction of the arylhydrazono-substituent in position 2 of fluoroalkyl-containing 1,3-dicarbonyl compounds affects their reactivity towards, ethylenediamine. In contrast to non-substituted analogues these compounds are converted to heterocycles with difficulty. 2-Arylhydrazono-1, 3-dicarbonyl compounds react with ethylenediamine and polyethylenediamine at the carbonyl associated with the non-fluorinated substituent to form acyclic products. The *N*,*N*′-ethylene-*bis*(2-arylazo-1,3-aminovinylketones) obtained are of interest due to their complexation ability.

4. Experimental

Melting points were measured in open capillaries and are uncorrected. Infrared spectra were recorded on a Specord 75 IR spectrophotometer at 4000–400 cm^{-1} in vaseline oil (compounds **4b**,**c**, **5**, **8b**,**c**, **9a**–**e**, **10**) and in 0.01 M $CHCl_3$ solution (**3**, **4b**,**d**, **8a**, **11**). ^1H and ^{13}C NMR spectra were measured on a Bruker DRX-400 spectrometer (^1H, 400 MHz, ^{13}C, 100.6 MHz) relative to $SiMe_4$. ^{19}F NMR spectra were obtained on a Tesla BS-587 A spectrometer (^{19}F, 75 MHz) using C_6F_6 as an internal standard. Mass spectra were measured on a Varian MAT-311A spectrometer. UV spectra were recorded on a Shimadzu UV-2401 PC spectrophotometer. Microanalyses were carried out on a Carlo Erba CHNS-O EA 1108 elemental analyzer. Copper and nickel were determined by the atomic absorption method on a Perkin Elmer PE 403 spectrophotometer. Column chromatography was performed on silica gel L 100/250.

4.1. Synthesis of compounds *3*, *4b-d*, *5*

Ethylenediamine (1 mmol) was added to a solution of 2-arylhydrazono-1,3-diketone **1a–d** (1 mmol) in methanol (8 ml) (diethyl ether for **4d**). The reaction mixture was kept for 24 h at room temperature (30 h at boiling temperature for **4d**). The precipitate formed was filtered off, recrystallized from a mixture of benzene: hexane (1:10) to give compounds **3**, **4b–d** as yellow powders, are **5** as a white powder.

4.1.1. 5-Difluoromethyl-6-(p-methylphenyl)azo-7-methyl-2,3-dihydro-^{1}H-1,4-diazepine (*3*)

Yield, 60%; mp, 172–173 °C. ^1H NMR ($CDCl_3$): δ 2.38 (3H, s, CH_3), 2.54 (3H, s, CH_3), 3.67 (2H, m, CH_2), 4.11 (2H, m, CH_2), 5.22 (^1H, br. s, NH), 6.68 (1H, t, HCF_2, $^2J_{H-F} = 56.0$ Hz), 7.36 (4H, m, C_6H_4) ppm. ^{19}F NMR ($CDCl_3$): δ 41.74 (4F, d, 2 HCF_2, $^2J_{H-F} = 56.0$ Hz) ppm. IR: 3430, 1590 (NH), 1625, 1555, 1535 (C=N, C=C, N=N) cm^{-1}. MS, *m*/*z* (I_{rel} (%)): 279 (10.06) $[M + 1]^+$, 278 (57.52) $[M]^+$, 131 (16.42), 130 (26.52), 120 (26.34) [HN=N–C_6H_4–CH_3]$^+$, 119 (31.09) [N=N–C_6H_4–CH_3]$^+$, 107 (19.91) [M–NH=N–C_6H_4–CH_3, CF_2H]$^+$, 104 (14.42), 91 (100) [C_6H_4–CH_3]$^+$, 65 (13.74). Analysis: Calc. for $C_{14}H_{16}F_2N_4$: C, 60.4; H, 5.8; F, 13.65; N, 20.1%. Found: C, 60.4; H, 5.9; F, 14.0; N, 20.0%.

4.1.2. N,N′-Ethylene-bis(6-(p-methylphenyl)azo-7-amino-1,1,2,2,3,3,4,4-octafluoro-6-octen-5-one) (*4b*)

Yield, 53%; mp, 134–135 °C. ^1H NMR ($CDCl_3$): δ 2.29 (6H, s, 2 CH_3), 2.59 (6H, s, 2 CH_3), 3.92 (4H, s, 2 CH_2), 6.20 (2H, tt, 2 $H(CF_2)_4$, $^2J_{H-F} = 52.0$, $^3J_{H-F} = 5.7$ Hz), 7.02 (8H, m, 2 C_6H_4), 15.78 (2H, br. s, 2 NH) ppm. ^{19}F NMR ($CDCl_3$): δ 24.58 (4F, dt, 2 HCF_2, $^2J_{F-H} = 52.0$, $^3J_{F-F} = 7.9$ Hz), 32.49 (4F, m, 2CF_2), 39.82 (4F, m, 2 CF_2), 51.66 (4F, m, 2 CF_2) ppm. IR: 3430, 1585 (NH), 1655 (C=O), 1600, 1585 (N=N, C=C) cm^{-1}. UV (chloroform), λ_{MAKC} (ϵ): 218 (10 500), 244 (15 860), 374 (40 140) nm. Analysis: Calc. for $C_{32}H_{28}F_{16}N_6O_2$: C, 46.16; H, 3.39; F, 36.51; N, 10.09%. Found: C, 46.07; H, 3.44; F, 36.62; N, 10.14%.

4.1.3. N,N′-Ethylene-bis(4-(p-methoxyphenyl)azo-5-amino-1,1,2,2-tetrafluoro-5-phenyl-4-penten-3-one) (**4c**)

Yield after reprecipitation from chloroform/ethanol, 55%; mp, 205–206 °C. ^{1}H NMR ($CDCl_3$): δ 3.42 (4H, m, 2 CH_2), 3.84 (6H, s, 2 OCH_3), 6.30 (2H, tt, 2 $H(CF_2)_2$, $^2J_{H-F} = 53.8$, $^3J_{H-F} = 5.6$ Hz), 6.87–7.46 (18H, m, 2 C_6H_4, 2 C_6H_5), 15.03 (2H, br. s, 2 NH) ppm. ^{19}F NMR ($CDCl_3$): δ 25.20 (4F, dt, HCF_2, $^2J_{F-H} = 53.8$, $^3J_{F-F} = 7.9$ Hz), 41.71 (4F, m, 2 CF_2) ppm. IR: 3310, 1590 (NH), 1655 (C=O), 1550, 1500 (N=N, C=C) cm^{-1}. Analysis: Calc. for $C_{38}H_{32}F_8N_6O_4$: C, 57.87; H, 4.09; F, 19.27; N, 10.66%. Found: C, 57.77; H, 3.94; F, 19.23; N, 10.73%.

4.1.4. N,N′-Ethylene-bis(3-(p-methoxyphenyl)azo-4-amino-3-penten-2-one) (**4d**)

Yield after recrystallization from acetone, 25%; mp, 184–185 °C. ^{1}H NMR ($CDCl_3$): δ 2.49 (6H, s, 2 CH_3), 2.55 (6H, s, 2 CH_3), 3.78 (6H, s, 2 OCH_3), 3.84 (4H, s, 2 CH_2), 6.91 (8H, s, 2 C_6H_4) ppm. IR: 3430, 1590 (NH), 1635 (C=O), 1570, 1490 (N=N, C=C) cm^{-1}. Analysis: Calc. for $C_{26}H_{32}N_6O_4$: C, 63.40; H, 6.55; N, 17.06%. Found: C, 63.05; H, 6.77; N, 16.75%.

4.1.5. 2-(p-Methoxyphenyl)hydrazono-1-phenyl-1-ethanone (**5**)

Yield after column chromatography (with $CHCl_3$ as an eluent), 35%; mp, 107–108 °C. ^{1}H NMR ($CDCl_3$): δ 3.82 (3H, s, OCH_3), 6.91–7.99 (9H, m, C_6H_4, C_6H_5), 7.68 (^{1}H, s, CH=), 14.67 (1H, ws, NH) ppm. IR: 3050, 1555 (NH), 1610 (C=O), 1590, 1520, 1500 (C=N, C=C) cm^{-1}. Analysis: Calc. for $C_{15}H_{14}N_2O_2$: C, 70.85; H, 5.55; N, 11.02%. Found: C, 70.46; H, 5.35; N, 10.72%.

4.2. Synthesis of compounds **6a**,**b**

Diethylenetriamine (1 mmol) was added to a solution of 2-arylhydrazono-1,3-diketone **1b**,**e** (1 mmol) in methanol (8 ml). The reaction mixture was kept for 24 h at room temperature (30 h at boiling temperature for **6b**). The formed precipitate was filtered off, recrystallized from CH_2Cl_2 to give compounds **6a**,**b** as yellow powders.

4.2.1. Amino-N,N′-diethylene-bis(6-(p-methylphenyl)azo-7-amino-1,1,2,2,3,3,4,4-octafluoro-6-octen-5-one) (**6a**)

Yield, 44%; mp, 163–164 °C. ^{1}H NMR ($CDCl_3$): δ 2.35 (6H, s, 2 CH_3), 2.48 (6H, s, 2 CH_3), 3.10 (4H, t, 2 CH_2, $^3J_{H-H} = 5.8$ Hz), 3.62 (4H, m, 2 CH_2), 6.22 (2H, tt, 2 $H(CF_2)_4$, $^2J_{H-F} = 52.2$, $^3J_{H-F} = 5.7$ Hz), 7.14–7.41 (8H, m, 2 C_6H_4), 15.06 (2H, br. s, 2 NH) ppm. ^{19}F NMR ($CDCl_3$): δ 24.48 (4F, dt, 2 HCF_2, $^2J_{F-H} = 52.2$, $^3J_{F-F} = 8.6$ Hz), 32.33 (4F, m, 2 CF_2), 39.69 (4F, m, 2 CF_2), 52.03 (4F, m, 2 CF_2) ppm. IR: 3440, 3385, 3280, 1550 (NH), 1645 (C=O), 1580, 1570 (C=C, N=N) cm^{-1}. Analysis: Calc. for $C_{34}H_{33}F_{16}N_7O_2$: C, 46.64; H, 3.80; F, 34.71; N, 11.20%. Found: C, 46.57; H, 3.93; F, 34.80; N, 10.92%.

4.2.2. Amino-N,N′-diethylene-bis(3-(p-methylphenyl)azo-4-amino-1,1,1-trifluoro-4-phenyl-3-butene-2-one) (**6b**)

Yield after reprecipitation from acetone/methanol, 42%; mp, 154-156 °C. ^{1}H NMR ($CDCl_3$): δ 2.37 (6H, s, 2 CH_3), 2.84 (4H, t, 2 CH_2, $^3J_{H-H} = 5.8$ Hz), 3.29 (4H, m, 2 CH_2), 7.17–7.19 (8H, m, 2 C_6H_4), 7.47–7.48 (10H, m, 2 C_6H_5), 14.91 (2H, br. s, 2 NH) ppm. ^{19}F NMR ($CDCl_3$): δ 92.01 (CF_3, s) ppm. IR: 3305, 3270, 2710, 1570, 1590 (NH), 1675 (C=O), 1650, 1550, 1530 (C=C, N=N) cm^{-1}. Analysis: Calc. for $C_{38}H_{35}F_6N_7O_2$: C, 62.04; H, 4.80; F, 15.49; N, 13.33%. Found: C, 62.03; H, 4.85; F, 15.67; N, 13.55%.

4.3. Synthesis of compounds **7a**,**b**

Triethylenetetramine (1 mmol) was added to a solution of 2-arylhydrazono-1,3-diketone **1b**,**c** (1 mmol) in diethyl ether (8 ml) (methanol for **7b**). The reaction mixture was refluxed for 24 h. The resulting precipitate was filtered off, recrystallized from ethanol to give compounds **7a**,**b** as yellow powders.

4.3.1. Ethylenediamino-N,N′-diethylene-bis(6-(p-methylphenyl)azo-7-amino-1,1,2,2,3,3,4,4-octa-fluoro-6-octen-5-one) (**7a**)

Yield, 40%; mp, 153–155 °C. ^{1}H NMR ($CDCl_3$, a mix of tautomers (I):(II) ~3:2) I: δ 2.33 (6H, s, 2 CH_3), 2.46 (6H, s, 2 CH_3), 2.85 (4H, s, 2 CH_2), 2.89 (4H, t, 2 CH_2, $^3J_{H-H} = 5.8$ Hz), 3.36 (4H, m, 2 CH_2), 6.24 (2H, tt, 2 $H(CF_2)_4$, $^2J_{H-F} = 52.2$, $^3J_{H-F} = 5.7$ Hz), 7.16–7.52 (8H, m, 2 C_6H_4); II: δ 2.38 (6H, s, 2 CH_3), 2.60 (6H, s, 2 CH_3), 2.63 (4H, br. s, 2 CH_2), 2.71 (4H, t, 2 CH_2, $^3J_{H-H} = 5.8$ Hz), 3.60 (4H, m, 2 CH_2), 6.25 (2H, tt, 2 $H(CF_2)_4$, $^2J_{H-F} = 52.2$, $^3J_{H-F} = 5.7$ Hz), 7.20–7.59 (8H, m, 2 C_6H_4) ppm. ^{19}F NMR ($CDCl_3$, (I):(II) ~ 3:2) I: δ 24.32 (4F, m, 2 HCF_2), 32.23 (4F, m, 2 CF_2), 39.58 (4F, m, 2 CF_2), 52.05 (4F, m, 2 CF_2); II: δ 24.57 (4F, m, 2 HCF_2), 32.39 (4F, m, 2 CF_2), 39.47 (4F, m, 2 CF_2), 50.24 (4F, m, 2 CF_2) ppm. IR: 3290, 2775, 1600 (NH), 1645, 1635 (C=O), 1570, 1545 (C=C, N=N) cm^{-1}. Analysis: Calc. for $C_{36}H_{38}F_{16}N_8O_2$: C, 47.06; H, 4.17; F, 33.09; N, 12.20%. Found: C, 47.69; H, 4.03; F, 33.30; N, 12.27%.

4.3.2. Ethylenediamino-N,N′-diethylene-bis(4-(p-methoxyphenyl)azo-5-amino-1,1,2,2-tetra-fluoro-5-phenyl-4-penten-3-one) (**7b**)

Yield after reprecipitation from chloroform/ethanol, 42%; mp, 232–234 °C. ^{1}H NMR ($CDCl_3$): δ 2.53 (4H, m, 2 CH_2, $^3J_{H-H} = 5.4$ Hz), 3.25 (4H, m, 2 CH_2), 3.77 (4H, s, 2 CH_2), 3.86 (6H, s, 2 OMe), 6.43 (2H, tt, 2 $H(CF_2)_2$, $^2J_{H-F} = 54.3$, $^3J_{H-F} = 5.7$ Hz), 6.86–7.63 (18H, m, 2 C_6H_4, 2 C_6H_5), 14.21 (2H, ws, 2 NH) ppm. IR: 2700, 2660, 1570, (NH), 1655 (C=O), 1590, 1525, 1490 (C=C, N=N) cm^{-1}. Analysis: Calc. for $C_{42}H_{42}F_8N_8O_2$: C, 57.66; H, 4.84; F, 17.37; N, 12.81%. Found: C, 57.52; H, 4.73; F, 17.59; N, 12.41%.

4.4. Synthesis of metal chelates **8a–c**

(a) A solution of copper(II) acetate monohydrate (nickel acetate tetrahydrate for **8b,c**) (1 mmol) in ethanol (5 ml) was added to a solution of *N,N′*-ethylene-*bis*(2-arylazo-1,3-aminovinylketone) **4b**,**d** (1 mmol) in ethanol (5 ml). The reaction mixture was refluxed for 10 min. The precipitation with water gave chelates **8a–c** as deep-brown powders.

(b) A mixture of nickel(II) acetate tetrahydrate (1 mmol), 2-arylhydrazono-1,3-diketone **1b**,**d** (2 mmol) and ethylenediamine (1 mmol) in ethanol (10 ml) was refluxed for 3 h. The solvent was removed under reduced pressure. Column chromatography (with $CHCl_3$ as an eluent) gave compounds **8b**,**c**.

4.4.1. *N,N′-Ethylene-bis(6-(p-methylphenyl)azo-7-amino-1,1,2,2,3,3,4,4-octafluoro-6-octen-5-onato)copper(II) (**8a**)*

Yield after reprecipitation from chloroform/hexane, 96%; mp, 164–165 °C. IR: 1640 (C=O), 1570, 1535, 1490 (N=N, C=C) cm^{-1}. UV (chloroform), λ_{MAKC} (ϵ): 220 (12 200), 243 (19 120), 346 (33 920), 392 (31 180), 516 sh (1280) nm. Analysis: Calc. for $C_{32}H_{26}F_{16}N_6O_2Cu$: C, 42.99; H, 2.93; F, 34.00; N, 9.40; Cu, 7.11%. Found: C, 43.03; H, 2.88; F, 34.18; N, 9.43; Cu, 7.06%.

4.4.2. *N,N′-Ethylene-bis(6-(p-methylphenyl)azo-7-amino-1,1,2,2,3,3,4,4-octafluoro-6-octen-5-onato)nickel(II) (**8b**)*

Yield after column chromatography (with benzene as an eluent), 85% (a) and 65% (b); mp, 190–191 °C. ^1H NMR ($CDCl_3$): δ 2.24 (6H, s, 2 CH_3), 2.57 (6H, s, 2 CH_3), 3.47 (4H, br. s, 2 CH_2), 6.22 (2H, tt, 2 $H(CF_2)_4$, $^2J_{H-F} = 52.1$, $^3J_{H-F} = 5.6$ Hz), 6.98 (8H, m, 2 C_6H_4) ppm. ^{19}F NMR ($CDCl_3$): δ 24.45 (4F, dt, 2 HCF_2, $^2J_{F-I} = 52.1$, $^3J_{F-F} = 7.9$ Hz), 32.40 (4F, m, 2 CF_2), 39.60 (4F, m, 2 CF_2), 51.09 (4F, m, 2 CF_2) ppm. IR: 1640 (C=O), 1570, 1535, 1490 (N=N, C=C) cm^{-1}. UV (methanol), λ_{MAKC} (ϵ): 203 (36 500), 242 (30 620), 290 (28 460), 360 (42 200), 477 sh (7700) nm. Analysis: Calc. for $C_{32}H_{26}F_{16}N_6O_2Ni$: C, 43.22; H, 2.95; F, 34.18; N, 9.45; Ni, 6.60%. Found: C, 43.50; H, 2.89; F, 33.84; N, 9.42; Ni, 6.54%.

4.4.3. *N,N′-Ethylene-bis(3-(p-methylphenyl)azo-4-amino-3-penten-2-onato)nickel(II) (**8c**)*

Yield after reprecipitation from chloroform/hexane, 95% (a) and 57% (b); mp, 204–205°C. ^1H NMR ($CDCl_3$): δ 2.41 (6H, s, 2 CH_3), 2.53 (6H, s, 2 CH_3), 3.75 (6H, s, 2 OCH_3), 3.39 (4H, br. s, 2 CH_2), 6.87 (8H, m, 2 C_6H_4) ppm. IR: 1630 (C=O), 1590, 1525, 1490 (N=N, C=C) cm^{-1}. MS, *m/z* (I_{rel} (%)): 551 (14.64) $[M+1]^+$, 550 (44.64) $[M]^+$, 549 (33.33), 548 (100.00), 229 (14.98), 228 (90.73), 182 (12.14), 179 (10.91), 95 (21.68), 68 (12.14). UV (methanol), λ_{MAKC} (ϵ): 203 (39 500), 226 (32 400), 290 (27 600), 354 (39 600), 484 (11 000) nm. Analysis: Calc. for $C_{26}H_{30}N_6O_4Ni$: C, 56.86; H, 5.51; N, 15.30; Ni, 10.69%. Found: C, 56.55; H, 5.40; N, 15.40; Ni, 10.74%.

4.5. Synthesis of compounds **9a**,**b**, **10**, **11**

Ethylenediamine (1 mmol) was added to a solution of 2-arylhydrazono-3-oxo esters **2a–c** (1 mmol) in methanol (8 ml). The reaction mixture was kept for 48 h at room temperature. The resulting solid was filtered off, reprecipitated from acetone/methanol to give compounds **9a**,**b**, **11** as yellow powders**, 10** as a white powder.

4.5.1. *N,N′-Ethylene-bis(2-(p-methylphenyl)hydrazono-3-oxo-4,4,5,5-tetrafluoropentanamide) (**9a**)*

Yield, 48%; mp, 190–191 °C. ^1H NMR ($CDCl_3$): δ 2.38 (6H, s, 2 CH_3), 3.61 (4H, m, 2 CH_2), 6.35 (2H, tt, 2 $H(CF_2)_2$, $^2J_{H-F} = 53.4$, $^3J_{H-F} = 5.5$ Hz), 7.27 (8H, m, 2 C_6H_4), 9.02, 15.27 (4H, 2 br. s, 4 NH) ppm. ^{19}F NMR ($CDCl_3$): δ 25.59 (4F, dt, 2 HCF_2, $^2J_{F-H} = 53.4$, $^3J_{F-F} = 7.9$ Hz), 42.72 (4F, m, 2 CF_2) ppm. IR: 3320, 1580 (NH), 1660, 1650 (C=O), 1620, 1550, 1505 (C=N, C=C) cm^{-1}. Analysis: Calc. for $C_{26}H_{24}F_8N_6O_4$: C, 49.06; H, 3.80; F, 23.88; N, 13.20%. Found: C, 48.95; H, 4.05; F, 23.80; N, 13.19%.

4.5.2. *N,N′-Ethylene-bis(2-(p-methylphenyl)hydrazono-3-oxo-4,4,5,5,6,6,7,7-nonafluoroheptan-amide) (**9b**)*

Yield after recrystallization from ethanol, 38%; mp, 76–78 °C. ^1H NMR ($CDCl_3$): δ 2.37 (6H, s, 2 CH_3), 3.62 (4H, m, 2 CH_2), 7.28 (8H, m, 2 C_6H_4), 9.03, 15.39 (4H, 2 br. s, 4 NH) ppm. ^{19}F NMR ($CDCl_3$): δ 36.59 (4F, m, CF_2), 41.14 (4F, m, 2 CF_2), 51.21 (4F, m, 2 CF_2), 80.93 (6F, m, 2 CF_3) ppm. IR: 3330, 1575 (NH), 1665, 1650 (C=O), 1515, 1500 (C=N, C=C) cm^{-1}. Analysis: Calc. for $C_{30}H_{22}F_{18}N_6O_4$: C, 41.30; H, 2.54; F, 39.19; N, 9.63%. Found: C, 41.02; H, 2.50; F, 39.00; N, 9.48%.

4.5.3. *Methyl-2-(p-methylphenyl)hydrazonoethanoate (**10**)*

Yield after recrystallization from mixture of benzene: hexane (1:1), 54%; mp, 177–178 °C. ^1H NMR (DMSO-d_6/CCl_4): δ 2.26 (3H, s, CH_3), 3.72 (3H, s, OCH_3), 7.01 (4H, m, C_6H_4), 7.10 (1H, m, CH=), 11.02 (^1H, br. s, NH) ppm. IR: 3240 (NH), 1690 (C=O), 1530, 1500 (C=N, C=C) cm^{-1}. Analysis: Calc. for $C_{10}H_{12}N_2O_2$: C, 62.49; H, 6.29; N, 14.57%. Found: C, 62.47; H, 6.23; N, 14.81%.

4.5.4. *N,N′-Ethylene-(2-(p-methylphenyl)hydrazono-3-oxobutanamide)(ethyl-2′-(p-methylphenyl)-azo-3′-amino-2′-butenoate) (**11**)*

Yield after recrystallization from acetone, 43%; mp, 139–140 °C. ^1H NMR ($CDCl_3$): δ 1.38 (3H, t, OCH_2CH_3, $^3J_{H-H} = 7.1$ Hz), 2.31 (3H, s, CH_3), 2.34 (3H, s, CH_3), 2.36 (3H, s, CH_3), 2.44 (3H, s, CH_3), 3.68 (2H, m, CH_2), 3.76 (2H, m, 2 CH_2), 4.30 (2H, q, OCH_2CH_3, $^3J_{H-H} = 7.1$ Hz), 7.09–7.34 (8H, m, 2 C_6H_4), 9.65, 14.60, 15.19 (3H, 3 br. s, 3 NH) ppm. IR: 3450, 3250 (NH), 1680, 1640 (C=O), 1575, 1500 (C=N, C=C) cm^{-1}. MS, *m/z* (I_{rel} (%)): 493 (20.24) $[M+1]^+$, 492 (67.23) $[M]^+$, 246 (13.93) $[CH_3–C(=O)–C(=N–NH–C_6H_4–CH_3)–C(=O)–NH–CH_2–CH_2]^+$ or $[C_2H_5O–C(=O)–C(=N–NH–C_6H_4–CH_3)–C(CH_3)=N]^+$,

155 (13.78) $[CH_3–C(=O)–C(=N–NH_2)–C(=O)–NH–CH=CH_2]^+$ or $[C_2H_5O–C(=O)–CH=C(CH_3)–NH–CH=CH_2]^+$, 132 (12.44) $[CH_2=N–N=C_6H_4=CH_2]^+$, 119 (41.51) $[N=N–C_6H_4–CH_3]^+$, 109 (13.05), 107 (75.23) $[H_2N–C_6H_4–CH_3]^+$, 106 (100) $[NH–C_6H_4–CH_3]^+$, 97 (12.02) $[HC(=N)–C(=O)–NH–CH=CH_2]^+$ or $[CH_2=N–CH=CH–NH–C(=O)]^+$, 91 (83.88) $[C_6H_4–CH_3]^+$, 79 (12.26). Analysis: Calc. for $C_{26}H_{32}N_6O_4$: C, 63.40; H, 6.55; N, 17.06%. Found: C, 63.71; H, 6.60; N, 17.17%.

*4.6. Reactions of 2-arylhydrazono-3-oxo ester **2a** with diethylenetriamine or triethylenetetramine*

A mixture of 2-arylhydrazono-3-oxo ester **2a** (1 mmol) and diethylenetriamine or triethylenetetramine (1 mmol) was stirred in 8 ml of methanol (diethyl ether) for 48 h. The solvent was removed. Column chromatography (with chloroform:methanol (1:10) as an eluent) gave products **10** (0.14 g, 66%) and **12a** (0.10 g, 63%; mp, 138–139 °C; [15]) or compounds **10** (0.12 g, 58%) and **12b** (0.09 g, 52%; mp, 116–117 °C; [15]) as white precipitates.

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