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Polyfluorinated arylnitrosamines

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Dedicated to Prof. DWA. Sharp, on the occasion of his 70th birthday

Abstract

N-Methyl-, *N*-*n*-butyl-, *N*-*t*-butylperfluoroarylamines undergo nitrosation with nitrous acid to give the corresponding *N*-nitroso derivatives. Perfluoroaryl groups were selected from the benzene, indane, biphenyl, naphthalene and pyridine series. According to ^{1}H and ^{19}F NMR spectra, *N*-nitroso-*N*-methyl derivatives of polyfluoroarenes consist of *E* and *Z* isomers with the former prevailing. The more bulky *n*-butyl group promotes an increase in the formation of *Z* isomers. Only *Z* isomers have been obtained from *N*-*t*-butyl derivatives of perfluorinated 4-toluidine and 4-aminopyridine. The structure of the *Z* isomer of *N*-nitroso-*N*-methylperfluoro-4-toluidine is confirmed by X-ray data.

Keywords: Perfluoroaromatic chemistry; Nitrosation; *N*-nitroso-*N*-methyl-; *N*-nitroso-*N*-*n*-butyl-; *N*-nitroso-*N*-*t*-butylperfluoroarylamines; *E* and *Z* isomers; X-ray crystal structure of *N*-nitroso-*N*-methylperfluoro-4-toluidine

1. Introduction

Recently, interest in nitrosamines has increased in connection with the elucidation of their role as biologically active compounds [1]. Usually, *s*-nitrosamines are obtained by interaction of *s*-amines with nitrous acid. This method was used for the synthesis of *N*-nitrosodialkyl-, *N*-nitrosoalkylaryl- and *N*-nitrosodiarylamines [2,3].

Earlier, *N*-nitroso-*N*-acetylpentafluoroanilide was described. Its synthesis was achieved by interaction of pentafluoroacetanilide with NOCl in the medium of the mixture of acetic acid and acetic anhydride in the presence of CH_3COOK and P_2O_5 [4].

We have shown that *N*-alkylperfluoroarylamines react with nitric acid to give the corresponding *N*-nitroderivatives and small amounts of *N*-nitroso-*N*-alkylperfluoroarylamines [5]. This induced us to carry out nitrosation of *N*-alkylperfluoroarylamines by HNO_2 in order to synthesize various *N*-nitroso-*N*-alkylperfluoroarylamines and investigate their structures.

2. Results and discussion

As it turned out, nitrosation of *N*-alkylperfluoroarylamines was smoothly effected by HNO_2 prepared in situ from sodium nitrite in hydrochloric or acetic acid (Scheme 1):

In the reaction of *N*-methylpentafluoroaniline (**1**) with HNO_2, *N*-nitroso-*N*-methylpentafluoroaniline (**2**) was obtained (Scheme 2).

When the trifluoromethylhomologues of (**1**), such as *N*-methyl-perfluoro-4-toluidine (**3**) and *N*-methyl-perfluoro-2,4-xylidine (**4**) were taken, nitrosation resulted in *N*-nitroso-*N*-methyl-perfluoro-4-toluidine (**5**) and *N*-nitroso-*N*-methyl-perfluoro-2,4-xylidine (**6**) (Scheme 3). *N*-Methyl-5-aminoperfluoroindane (**7**) can be formally considered as an analogue of *N*-methyl-perfluoro-3,4-xylidine. In the reaction of **7** with HNO_2, *N*-nitroso-*N*-methyl-5-aminoperfluoroindane (**8**) was obtained (Scheme 4).

The transformation of *N*-methyl-4-cyanotetrafluoroaniline (**9**) and *N*-methyl-4-aminotetrafluoropyridine (**10**) by HNO_2 into the corresponding *N*-nitroso derivatives (**11** and **12**) also demonstrates the synthetic range of *N*-nitrosation in the polyfluoroaromatic series, as does the synthesis of *N*-nitroso-*N*-methyl-4-aminononafluorobiphenyl (**13**) and 4,4′-bis(*N*-nitroso-*N*-methylamino)octafluorobiphenyl (**14**) from *N*-methyl-4-aminononafluorobiphenyl (**15**) and 4,4′-bis(*N*-dimethylamino)octafluorobiphenyl (**16**), and the

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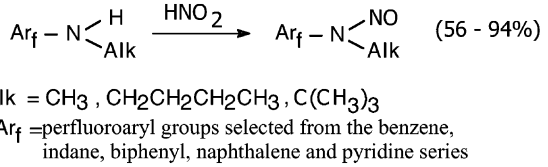
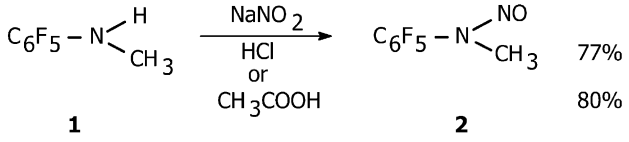


Scheme 1.



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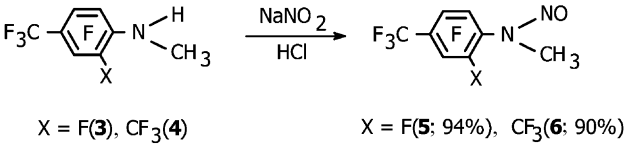

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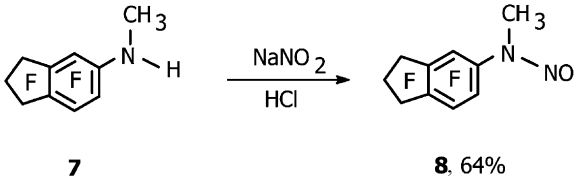

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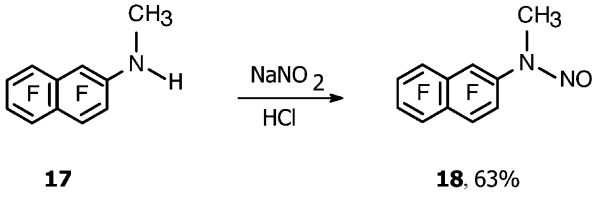
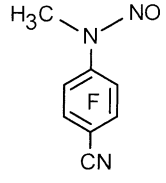


Scheme 5.

conversion of *N*-methyl-2-amino-heptafluoronaphthalene (**17**) to *N*-nitroso-*N*-methyl-2-aminoheptafluoronaphthalene (**18**) (Scheme 5).



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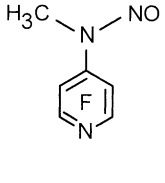

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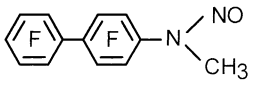

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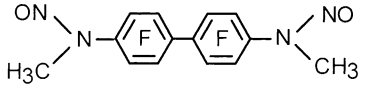

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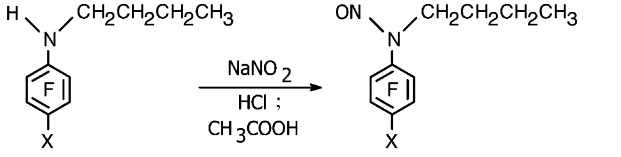
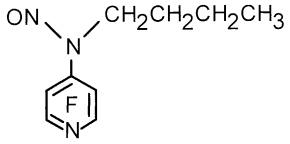


Scheme 6.

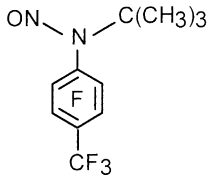
Nitrosation of *N*-*n*-butylpentafluoroaniline (**19**) and *N*-*n*-butylperfluoro-4-toluidine (**20**) gave *N*-nitroso-*N*-*n*-butylpentafluoroaniline (**21**) and *N*-nitroso-*N*-*n*-butylperfluoro-4-toluidine (**22**)(Scheme 6).

N-Nitroso-*N*-n-butyl-4-aminotetrafluoropyridine (**23**) is synthesized from *N*-*n*-butyl-4-aminotetrafluoropyridine (**24**).



23

Interaction of *N*-*t*-butylperfluoro-4-toluidine (**25**) and *N*-*t*-butyl-4-aminotetrafluoropyridine (**26**) with HNO_2 resulted in the formation of the corresponding *N*-nitroso derivatives (**27**) and (**28**), which were stable as compared with the corresponding *N*-nitro derivatives [5]. Conditions for nitrosation of *N*-alkylperfluoroarylamines are given in Table 1.



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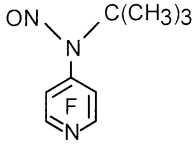


28

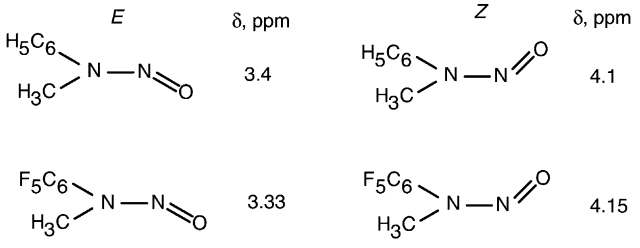
We have recently shown that nitration of bis(perfluoro-4-tolyl)amine affords the corresponding *N*-nitro derivative [5]. At the same time, an attempt at nitrosation of this amine by HNO_2 failed to show the corresponding *N*-nitroso derivative.

The presence of *E* and *Z* isomers of compound **2** was found by comparison of ^{1}H NMR spectra of these isomers with the corresponding non-fluorinated analogues described in [6]. Proton chemical shifts of *E* and *Z* isomers of compound **2** and its non-fluorinated analogue are shown in Scheme 7. According to this assignment, compound **2** consists of *E* and *Z* isomers (**2***E* and **2***Z*) in the ratio of ~2.3/1. ^{19}F NMR data of the previously described *N*-nitroso-*N*-acetylpentafluoroanilide [4] and **2***Z* isomer are in close agreement with each other. This could suggest the formation of the *Z* isomer of *N*-nitroso-*N*-acetylpentafluoroanilide. In the ^{19}F NMR spectrum of the **2***Z* isomer the chemical shift of the *ortho* fluorine atoms is downfield as compared to the

Table 1
Preparation of *N*-nitroso-*N*-alkylperfluoroarylamines **2**, **5**, **6**, **8**, **11–14**, **17**, **21–23**, **27** and **28**

Compound number	Amine (g)	$NaNO_2$ (g)	Molar ratio	HCl (CH_3COOH, ml)	Temperature (°C)	Time (h)	Isolated product		
							Compound number	Yield (g)	Yield (%)
1	2.0	2.0	1/1.45	(20)	18–24	20	**2**	1.85	80
1	25	17.5	1/2	200	0	1	**2**	25.5	77
3	0.5	0.2	1/1.45	(5)	18–22	20	**5**	0.32	58
3	2.0	1.1	1/2	20	−10 to 10	2	**5**	2.1	94
4	1.0	0.46	1/2	10	−7 to 0	1	**6**	1.0	90
7	1.0	0.45	1/2	10	−4 to 10	1	**8**	0.7	64
9	0.3	0.23	1/2	3	−5 to 5	1	–[a]	0.25	
9	0.2	0.4	1/2	2	22	3	**11**	0.17	74
10	0.3	0.23	1/2	3	0	1	**12**	0.23	65
15	0.25	0.1	1/2	3	−5 to 0	1	**13**	0.2	73
16	0.5	0.31	1/2	5	−2 to 0	1	**14**	0.43	75
17	0.5	0.24	1/2	5	−2 to 0	2	**18**	0.35	63
19	0.5	0.29	1/2	5	−4 to 0	1	**21**	0.33	59
20	0.57	0.18	1/1.5	(6)	20 to 22	20	**22**	0.35	56
24	0.5	0.31	1/2	5	−2 to 0	3	**23**	0.43	85
25	1.2	0.36	1/1.5	(12)	20 to 22	20	**27**	1.05	93
26	0.5	0.31	1/2	5	−2 to 0	1	**28**	0.43	75

[a] **11/9** ∼ 2.4/1 according to NMR spectra.

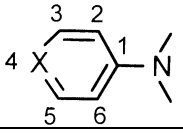


Scheme 7.

2*E* isomer(approximately by 5 ppm). A similar downfield shift of the *ortho* fluorine atoms relative to *N*-nitroso-*N*-methyl group takes also place in other *Z* isomers: **5***Z*, **11***Z*, **12***Z*, **13***Z* (Table 2). A downfield shift of the *ortho* fluorine atoms was also used to assign the structures of the others *Z* isomers. The ratio of *E* and *Z* isomers of *N*-nitroso-*N*-alkylamino derivatives of perfluoroarenes are given in Section 3 and Table 2.

In the case of *N*-nitroso-*N*-methylaniline, the *E* isomer with the phenyl group *trans* to the nitroso group is 104 times

Table 2
^{19}F and ^{1}H NMR data for *N*-nitroso-*N*-alkylperfluoroarylamines **2**, **5**, **11–14**, **21–23**, **27** and **28**:



Compound number	Ratio (*E*/*Z*)	*E*/*Z* chemical shifts (ppm)			
		2,6-F (multiplet)	3,5-F (multiplet)	4-F	CH_3
2	2.3/1	15.5/20.4	1.05/1.00	9.7 (t, J = 20.5 Hz)/10.8 (t, J = 20.5 Hz)	3.33/4.15
5	2.8/1	17.1/23.1	23.1/23.1	105.9/105.7 (multiplet)	3.37/4.17
11	3/1	18.3/24.5	31.0/30.7	–	3.37/4.18
12	5.5/1	13.9/21.1	74.3/74.3	–	3.41/4.21
13[a]	3/1	16.0/21.5	23.0–25.3	–	3.43/4.21
14	3[b]/1	16.1/21.7	25.5/25.2, 25.5/26.0	–	3.53/4.32, 3.53/4.31
21[c]	0.56/1	16.5/21.0	1.1/1.3	10.0 (tt, J = 20.7 and 1.5 Hz)/11.3 (tt, J = 20.5 and 2.5 Hz)	0.82/0.91
22[c]	0.74/1	17.6/22.5	22.9/22.9	105.6/105.6(multiplet)	0.89/0.98
23[c]	1.1/1	14.7/21.1	74.4/74.4	–	0.84/0.93
27	*Z*	23.9	22.2	105.4 (t, J = 21.7 Hz)	1.64
28	*Z*	21.5	74.1	–	1.64

[a] Chemical shift of signals *p*-C_6F_5: ∼23.0–25.3 (m, $2F_o$), 12.6 (tt, 1F, J = 20.5 and 3.2 Hz, F_p), 1.8 (m, $2F_m$).

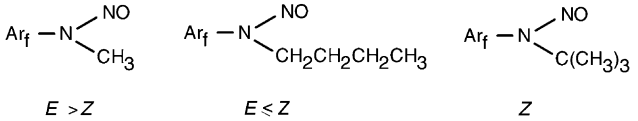
[b] The ratio of *E* and *Z* isomeric contributions. Formally, it can mean that the ratio of $E,E'/[E,Z'(E',Z)+Z,Z'] = 1/1$.

[c] Other proton chemical shifts for the $CH_{2\alpha}$–$CH_{2\beta}$–$CH_{2\gamma}$–CH_3 group (α, β, γ, respectively)—**21***E*: 3.82, 1.41, 1,23; *Z*: 4.49, 1.66, 1.41; **22***E*: 3.82, 1.45, 1.25; *Z*: 4.55, 1.72, 1.45; **23***E*: 3.92, 1.44, 1.23; *Z*: 4.58, 1.70, 1.44. For *E* isomers: H_α (t, J ∼ 7.2–7.3 Hz), H_β (m), H_γ (m), H, CH_3 (t, J ∼ 6.7–6.8 Hz); for *Z* isomers: H_α (t, J ∼ 7.2–7.3 Hz), H_β (tt, J ∼ 7.2 Hz), H_γ (m), H, CH_3 (t, J ∼ 7.2–7.3 Hz).

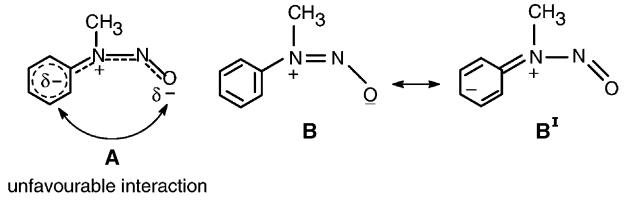
more abundant than the *Z* isomer [6]. An explanation of this result consists in conjugation of the π systems of the phenyl and nitroso groups lowering the total energy of the *E* isomer. The phenyl group of the latter is considered to be coplanar with the nitrosoamine group. In the *Z* isomer with the phenyl group *cis* to the nitroso group, steric hindrance prevents coplanarity, thus, making this isomer much less favorable energetically [6]. Steric hindrance in **2***Z* with the pentafluorophenyl group *cis* to the nitroso group can be more than in the *Z* isomer of *N*-nitroso-*N*-methylaniline taking into account the sizes of F and H [7]. Therefore, we would also expect the formation of small amounts of **2***Z* as compared with **2***E*. However, the difference between the ratio of *E*/*Z* for **2** (2.3/1) and *N*-nitroso-*N*-methylaniline (104/1) is large. This difference cannot be explained by steric hindrance of the pentafluorophenyl group *cis* to the nitroso group in **2***Z*. A steric interaction of the *N*-methyl substituent with the more bulky pentafluorophenyl group could prevent coplanarity of pentafluorophenyl ring with the nitrosoamine group to some extent and reduce conjugation of the π systems of the pentafluorophenyl and nitroso groups, thus, making the **2***E* isomer relatively less favorable energetically. This effect may also be expected in the **2***Z* isomer. In addition, steric hindrance in **2***Z* with the pentafluorophenyl group *cis* to the nitroso one could prevent coplanarity. The relatively small difference in the ratio of **2***E* and **2***Z* as compared with the difference in the ratio of *E* and *Z* isomers of *N*-nitroso-*N*-methylaniline favors the former effect. The ratio of *E* and *Z* isomers of *N*-nitroso-*N*-alkylperfluoroarylamines changes with increase in steric bulk of the *N*-alkyl substituent (Scheme 8). Thus, *N*-nitroso derivatives **21** and **22** containing *n*-butyl groups consist of *E* and *Z* isomer with the latter prevailing. In the case of **23**, the quantity of *E* and *Z* isomers is close to each other. *N*-Alkylamino derivatives containing the still more bulky *t*-butyl group give as *N*-nitroso derivative only the *Z* isomer (compounds **27** and **28**). Thus, the following change of the relationship of isomers takes place in the series of *N*-nitroso derivatives of *N*-methyl-, *N*-*n*-butyl-, *N*-*t*-butylaminopolyfluoroarenes (Scheme 8).

The form in which the more bulky alkyl group is *trans* to the NO group was found for *N*-alkyl-*N*-methylnitrosoamines [6].

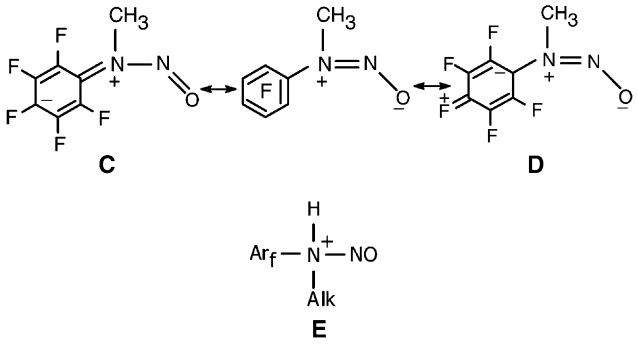
Other effects may also be taken into account when the difference in the ratio of *E*/*Z* for **2** and *N*-nitroso-*N*-methylaniline is examined. One may expect for the *Z* isomer of *N*-nitroso-*N*-methylaniline that unfavorable interaction (repulsion) of negative charges in the phenyl ring and on oxygen atom can arise as a result of conjugation (**A**). A contribution of resonance structure (**B**) is proposed on the basis of



Scheme 8.



Scheme 9.



Scheme 10.

data of work comparing NMR spectra of *N*-nitrosoamines and carbenium ions [8] (Scheme 9). More steric hindrance in **2***Z* than in the *Z* isomer of *N*-nitroso-*N*-methylaniline prevents coplanarity to a greater extent. Resonance contribution (**C**) could be reduced by this effect and by the resonance structure (**D**) (Scheme 10). In this case, a decrease of repulsion between the negative charges of the pentafluorophenyl ring and on the oxygen atom (**A**-like structure) can be expected. In consequence, an increase of **2***Z* compared with **2***E* isomer could occur. In **27***Z* the nitrosoamine group is practically orthogonal to the benzene ring according to X-ray data (Fig. 1). In this case, the contribution of a resonance structure **C** is practically impossible and unfavorable interaction of negative charges in structure like **A** can be small. Therefore, the formation of *Z* isomer could be expected.

The larger contribution of the **12***E* isomer as compared with **5***E* could be explained by the stronger unfavorable interaction (repulsion) of negative charges in the tetrafluoropyridine ring and on the oxygen atom; it can reflect a more strongly electron-withdrawing tetrafluoropyridyl group than perfluorotolyl [9].

It is possible that these factors can influence the formation of *E* and *Z* isomers in the course of the conversion of the intermediate **E** into polyfluorinated arylnitrosamines (Scheme 10). Other factors, for example inductive effect of fluorine atoms, intramolecular hydrogen bonds, the acid medium could also have an influence on the formation of *E* and *Z* isomers of polyfluorinated arylnitrosamines.

3. Experimental

^{19}F and ^{1}H NMR spectra were recorded on a Bruker AC-200 instrument at 188.3 and 200 MHz in $CHCl_3$ solution.

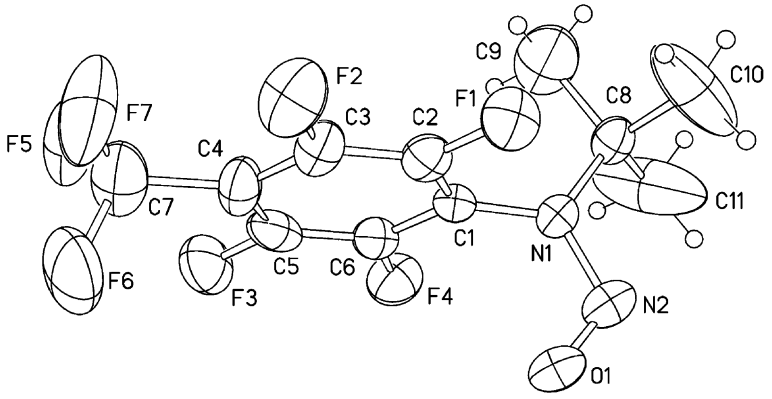


Fig. 1. ORTEP diagram of *N*-nitroso-*N*-*t*-butylperfluoro-4-toluidine (**27**).

The standards were hexafluorobenzene (162.9 ppm from CCl_3F) and hexamethyldisiloxane (0.04 ppm from TMS). IR spectra were measured on a UR-20 spectrophotometer for solutions in CCl_4. UV spectra were recorded on a Specord UV–VIS instrument for solutions in ethanol. Molecular weights of nitroso compounds were determined by mass spectrometrically on a Finnigan MAT-8200 instrument. The nominal energy of the ionizing electrons was 70 eV. X-ray structure analysis was performed on a Bruker P4 diffractometer (λ, Mo Kα, graphite monochromator) at -30 °C. The structure of *N*-nitroso-*N*-alkylperfluoroarylamines was established on the basis of ^{1}H and ^{19}F NMR, IR, UV spectral data, molecular weights and elemental analyses. An assignment of signals in the ^{1}H NMR spectra to *E* and *Z* isomers was carried out by comparison with data described in literature for non-fluorinated *N*-nitrosoamines [6]. The fluorine signals in the ^{19}F NMR spectra were assigned by comparison with ^{19}F NMR data of the corresponding starting compounds [5]. Comparisons of values of 2,6-F shifts in isomeric *N*-nitroso-*N*-*n*-butyl- and *N*-nitroso-*N*-*t*-butylperfluoroarylamines with 2,6-F of *N*-nitroso-*N*-methylperfluoroarylamines make it possible to assign *E* or *Z* isomers for compounds **21**–**23**, **27** and **28**. This assignment was confirmed by X-ray structure analysis of **27***Z* (Fig. 1).

3.1. N-Nitroso-N-alkylperfluoroarylamines

A water solution of $NaNO_2$ (~20%) was added to a stirred mixture of *N*-alkylperfluoroarylamine in acid (HCl or CH_3COOH). After reaction, cold water was poured into the reaction mixture. The mixture was extracted with chloroform. The chloroform layer was washed with water, dried over $MgSO_4$, the solvent distilled off and the residue was sublimed (details are given in Table 1). Compounds **6***E*, **6***Z*, **8***E*, **8***Z*, **17***E*, and **17***Z* showed the following NMR characteristics—(**6***E*) δ_F ppm: 105.7 (d, 3F, $J = 23.8$ Hz, 2-CF_3), 105.4 (t, 3F, $J = 22.8$ Hz, 4-CF_3), 49.9 (m, 1F, 3-F), 37.3 (m, 1F, 5-F), 20.1 (dd, 1F, $J = 21$ and 13 Hz, 6-F); δ_H ppm: 3.32. (**6***Z*) δ_F ppm: 103.2 (d, 3F, $J = 23.2$ Hz, 2-CF_3), 105.3 (t, 3F, $J = 23.0$ Hz, 4-CF_3), 49.4 (m, 1F, 3-F), 37.3 (m, 1F, 5-F), 22.1 (dd, 1F, $J = 21.8$ and 13.2 Hz, 6-F); δ_H ppm: 4.12. Ratio of *E*/*Z* ~ 2.5/1. (**8***E*) δ_F ppm: 55.2 and 54.7 (broadened peaks, 2F and 2F, 1-CF_2, 3-CF_2), 39.7 (m, 1F, 4-F), 34.1 (d, broadened peaks, 1F, $J \sim 20$ Hz, 6-F), 32.1 (m, 2F, 2-CF_2), 23.9 (tt, 1F, $J = 20$ and 7 Hz, 7-F); δ_H ppm: 3.39. (**8***Z*) δ_F ppm: 55.3 and 54.5 (broadened peaks, 2F and 2F, 1-CF_2, 3-CF_2), 45.0 (m, 1F, 4-F), 39.8 (m, 1F, 6-F), 32.1 (m, 2F, 2-CF_2), 23.3 (tt, 1F, $J = 20$ and 7 Hz, 7-F); δ_H ppm: 4.20. Ratio of *E*/*Z* ~ 2.5/1. (**18***E*) δ_F ppm: 36.1 (dd, 1F, $J = 66$ and ~16 Hz, 1-F), 19.5 (broadened peak, 1F, 3-F), 19.0 (dt, 1F, $J = 66$ and ~16 Hz, 8-F), 17.1 and 16.0 (dt, 1F and 1F, $J = 58$ and ~16 Hz, 4,5-F), 10.8 and 8.3 (m, 1F and 1F, 6,7-F). δ_H ppm: 3.42. (**18***Z*) δ_F ppm: 41.7 (dd, 1F, $J = 66$ and ~16 Hz, 1-F), 23.4 (broadened peak, 1F, 3-F), 19.0 (dt, 1F, $J = 66$ and ~16 Hz, 8-F), 17.1 and 15.3 (dt, 1F, $J = 58$ and ~16 Hz, 4,5-F), 10.8 and 7.8 (m, 1F and 1F, 6,7-F); δ_H ppm: 4.25. Ratio of *E*/*Z* ~ 2.5/1. NMR spectra of other *N*-nitrosoamines are given in Table 2.

IR and UV spectral and analytical data for *N*-nitroso-*N*-alkylperfluoroarylamines, and physical characteristics are given in Table 3.

3.2. X-Ray analysis of N-nitroso-N-t-butylperfluoro-4-toluidine (27)

According to X-ray data (Fig. 1) nitrosoamine group is practically orthogonal to the benzene ring plane (dihedral angle is 89.4(2)°, Fig. 1). The atoms O1 and N2 have maximum deviations by 0.008(6) and −0.009(5) Å, respectively from the average plane of O1, N1, N2, C1, and C8 atoms. Bond lengths of the N–N=O fragment are close to the corresponding ones of 3.3-dibenzyl-1(*E*)-nitroso-1-(2-tolyl)urea [10], for example. No short intermolecular contacts were found in the crystal.

Monoclinic system, $a = 6.102(2)$ Å, $b = 21.340(5)$ Å, $c = 10.410(3)$ Å, $\beta = 97.95(2)°$, $V = 1342.4(6)$ Å^3, space group $P2_1/n$, $C_{11}H_9F_7N_2O$, $M = 318.20$, $Z = 4$, $D_c = 1.574$ g cm^{-3}, $\mu = 0.168$ mm^{-1}, F(0 0 0) = 640, crystal size 0.05 mm × 0.10 mm × 0.20 mm. Intensities of 1226 independent reflections were measured by $\theta/2\theta$-scans. No

Table 3
Elemental analyses, IR and UV data for *N*-nitroso-*N*-alkylperfluoroarylamines **2**, **5**, **6**, **8**, **11**–**14**, **17**, **21**–**23**, **27** and **28**

Compound number	C (%)		H (%)		F (%)		N (%)		Molecular weight		Molecular formula	Melting point (°C)(bp (°C), mmHg)	IR (cm^{-1}), Ar_f, –N–N =O	UV, λ_{max} (nm), (log ε)
	Found	Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found	Calculated				
2	37.62	37.17	1.32	1.33	42.10	42.03	12.57	12.39	226.01655	226.01698	$C_7H_3F_5N_2O$	(62.5/2)	1480–1540	224 (3.77), 245 (3.77), 374 (2.33)
5	34.92	34.78	1.05	1.09	47.90	48.19	9.73	10.14	276.01335	276.01342	$C_8H_3F_7N_2O$	42–43	1430–1510	210 (3.81), 250 (3.91), 374 (2.28)
6	33.36	33.13	0.84	0.92	52.60	52.45	8.61	8.59	326.01024	326.01016	$C_9H_3F_9N_2O$	40–40.5	1460–1520	240 (3.55), 280 (3.40), 370 (2.52)
8	35.43	35.50	0.90	0.89	50.36	50.59	7.66	8.29	308.01090[a]	308.01217	$C_{10}H_3F_9N_2O$	40–42	1480–1520	210 (4.13), 253 (3.97), 374 (2.30)
11	41.16	41.20	1.29	1.29	32.53	32.62	18.00	18.02	233.02153	233.02122	$C_8H_3F_4N_3O$	48.5–49	1480–1510	264 (3.86), 350 (2.00)
12	34.80	34.45	1.51	1.44	36.42	36.36	19.72	20.09	209.01991	209.02122	$C_6H_3F_4N_3O$	(63/2)	1450–1510	207 (3.85), 254 (3.97), 356 (2.20)
13	41.93	41.71	0.86	0.80	45.80	45.72	7.22	7.49	344.01137[a]	344.01217	$C_{13}H_3F_9N_2O$	108–109	1475–1550	250 (3.89), 375 (1.70)
14	40.58	40.58	1.46	1.45	36.75	36.71	13.41	13.53	384.03680[a]	384.03830	$C_{14}H_6F_8N_4O$	143–144	1460–1550	205 (4.27), 266 (4.42), 370 (2.60)
18	42.66	42.31	0.92	0.96	42.66	42.31	9.02	8.97	282.01550[a]	282.01536	$C_{11}H_3F_7N_2O$	60–61	1430–1510	215 (4.58), 243 (4.03), 372 (2.38)
21	44.74	44.78	3.37	3.36	35.50	35.44	10.47	10.45	238.06370[a]	238.06551	$C_{10}H_9F_5N_2O$	(70/2)	1470–1530	209 (4.02), 246 (3.90), 373 (2.20)
22	41.90	41.51	2.83	2.62	41.71	41.82	7.87	8.80	318.06016	318.06030	$C_{11}H_9F_7N_2O$	(73/2)	1470–1540	210 (3.88), 248 (3.85), 373 (2.23)
23	43.27	43.03	3.14	3.59	30.14	30.28	17.32	16.73	251.06869	251.06817	$C_9H_9F_4N_3O$	(70/2)	1450–1550	247 (3.60), 262 (3.62), 380 (1.70)
27	41.29	41.51	2.83	2.83	41.92	41.82	8.51	8.80	288.06226[a]	288.06231	$C_{11}H_9F_7N_2O$	21–28	1480–1520	211 (3.88), 238 (3.78), 372 (2.30)
28	42.86	43.03	3.49	3.59	30.91	30.23	17.31	16.73	221.06950[a]	221.07018	$C_9H_9F_4N_3O$	83–84	1450–1525	207 (3.72), 237 (3.75), 376 (2.08)

[a] These compounds did not give molecular ions in their MS spectra, so molecular weights were only determined for the fragment ions Ar_fNAlk (M–NO).

Table 4
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for *N*-nitroso-*N*-*t*-butylperfluoro-4-toluidine (**27**)

Atom	*x*	*y*	*z*	*U* (equivalents)
O1	7767(11)	2943(4)	6044(6)	114(2)
N1	5695(10)	3227(3)	4313(6)	67(2)
N2	6933(14)	3395(4)	5415(8)	100(3)
C1	5496(14)	2590(4)	3991(7)	60(2)
C2	3889(15)	2209(4)	4395(7)	71(2)
C3	3744(17)	1585(4)	4147(8)	79(3)
C4	5230(2)	1301(4)	3468(9)	90(3)
C5	6861(16)	1671(6)	3075(8)	88(3)
C6	6982(16)	2297(5)	3341(9)	76(2)
C7	5200(3)	624(6)	3134(13)	140(5)
C8	4581(15)	3745(4)	3511(8)	76(2)
C9	3490(3)	3501(6)	2266(13)	198(7)
C10	2770(3)	3989(8)	4127(16)	236(9)
C11	6130(2)	4216(7)	3290(2)	294(14)
F1	2396(8)	2471(2)	5087(5)	97(2)
F2	2131(10)	1257(3)	4589(5)	126(2)
F3	8379(10)	1412(3)	2408(5)	125(2)
F4	8646(8)	2619(3)	2931(5)	107(2)
F5	5332(15)	495(3)	1951(8)	175(3)
F6	6670(18)	304(3)	3834(9)	212(4)
F7	3330(2)	343(4)	3353(11)	228(5)

absorption corrections were applied. The structure was solved by direct methods using SHELXS-97 and then refined by least squares in full matrix anisotropic approximation to $wR_2 = 0.2179$, $S = 1.056$ ($R = 0.0750$ for $733F_o > 4\sigma(F)$) using SHELXL-97. Large atomic thermal parameters of *t*-butyl group and low crystal quality could be noted. The final atomic parameters are collected in Table 4. The crystal data have been deposited at the Cambridge Crystallographic Data Centre (deposition number CCDC 153993).

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References

[1] R.G. Coombes, in: I.O. Sutherland (Ed.), Comprehensive Organic Chemistry, Vol. 2, Pergamon Press, Oxford, 1979, p. 365.
[2] S. Hauptmann, J. Graefe, H. Remane, Lehrbuch der Organischen Chemie, VEB Deutscher Verlag für Grundstoffindustrie (Russian transl.), Leipzig, 1979, p. 489.
[3] H. Feuer (Ed.), The Chemistry of the Nitro and Nitroso Groups (Part 2; Russian transl.), Interscience Publishers, New York, 1970, p. 187.
[4] L.S. Kobrina, N.V. Popkova, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. 12 (1973) 99–104.
[5] V.E. Platonov, A. Haas, M. Schelvis, M. Lieb, K.V. Dvornikova, O.I. Osina, Yu.V. Gatilov, J. Fluorine Chem. 109 (2001) 131–139.
[6] H.W. Brown, D.P. Hollis, J. Mol. Spectrosc. 13 (1964) 305–312.
[7] J.H. Clark, D. Wails, T.W. Bastock, Aromatic Fluorination, CRC Press, Boca Raton, 1996, p. 4.
[8] J.G. Traynham, M.T. Yang, Tetrahedron Lett. 10 (1965) 575–577.
[9] R.D. Chambers, P.A. Martin, J.S. Waterhouse, D.L.H. Williams, J. Fluorine Chem. 20 (1982) 507–514.
[10] K. Yamaguchi, G. Matsumura, M. Tanno, S. Suayoshi, N. Miyata, Acta Crystallogr. Sect. C (Cr. Str. Commun.) 48 (1992) 1051–1054.