Preparation and properties of secondary amides of 1,1-dinitroalkanecarboxylic acids

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The previously unknown secondary amides of 1,1-dinitroalkanecarboxylic acids were prepared by the reaction of polynitroimidoyl fluorides with water in the presence of mineral acids. They are inert with respect to electrophiles, but react with nucleophiles with the cleavage of the C—C bond between the carbonyl C atom and the C atom of the dinitromethylene group. An X-ray structural study of the amides was carried out and their thermochemical characteristics were determined.

Key words: aldimines, amides of 1,1-dinitroalkanecarboxylic acids, conversions; bond cleavage; carbamates, ureas; orbital interactions; conformation; heat of combustion; the enthalpy of formation.

In a study of the chemical properties of the recently prepared[1] polynitroimidoyl fluorides (**1**) it has been found that they react with water in the presence of mineral acids. This reaction affords the previously unknown 1,1-dinitroalkanecarboxamides (**2**).

$$\underset{\mathbf{1a{-}c}}{X(NO_2)_2CCF{=}N(CH_2)_nC(NO_2)_2Y} + H_2O \xrightarrow[-HF]{}$$

$$\longrightarrow \underset{\mathbf{2a{-}c}}{X(NO_2)_2CCONH(CH_2)_nC(NO_2)_2Y}$$

a: $X = Y = Me$, $n = 1$
b: $X = Y = F$, $n = 2$
c: $X = F$, $Y = Me$, $n = 1$

Amides **2a,b** are most conveniently prepared in acetic acid with addition of water and mineral acid (HCl, H_2SO_4, HNO_3) at room temperature. The formation of amide **2c** under these conditions is extremely slow, therefore, in this case the reaction was carried out by heating in 70 % nitric acid.

The thus prepared amides **2a—c** are colorless crystalline substances. The main characteristic feature of their structure is the proximity of the carbamoyl group and the dinitromethylene group, a strong electron acceptor, which is clearly manifested in the chemical properties of these compounds.

Amides **2a—c** are inert with respect to electrophilic reagents: they are not hydrolyzed when heated with aqueous mineral acids, do not afford *N*-nitro derivatives through the action of nitrating systems based on nitric acid, and do not form *N*-fluoro and *N*-chloro derivatives through the action of fluorine and chlorine.

However, as was expected, these compounds react with nucleophiles and bases, which is apparently due to the presence of a noticeable positive charge at the C atom of the carbonyl group. However, the interaction with nucleophiles and bases results in cleavage of the C—C bond between the carbonyl C atom and the C atom of the dinitromethylene group, rather than in the cleavage of the C—N bond of the carbamoyl group typical of substituted carboxamides.

For example, all three of the amides studied react with methanol in the presence of an inorganic base to give the corresponding methyl carbamates (**3**). Compounds **2a** and **2c** yield the same ester **3a**.

$$\underset{\mathbf{2}}{X(NO_2)_2CCONH(CH_2)_nC(NO_2)_2Y} \xrightarrow{MeOH,\ KHCO_3}$$

$$\longrightarrow \underset{\mathbf{3a,b}}{MeOCONH(CH_2)_nC(NO_2)_2Y}$$

a: $Y = Me$, $n = 1$
b: $Y = F$, $n = 2$

In the case of amide **2a**, one more product, *viz.*, the potassium salt of 1,1-dinitroethane, was isolated from the reaction mixture.

$$\underset{\mathbf{2a}}{Me(NO_2)_2CCONHCH_2C(NO_2)_2Me} \xrightarrow{MeOH,\ KHCO_3}$$

$$\longrightarrow \underset{\mathbf{3a}}{MeOCONHCH_2C(NO_2)_2Me} + KC(NO_2)_2Me + H_2O + CO_2$$

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In the case of amides **2b** and **2c**, the fluorodinitromethane salt produced is unstable and decomposes in the course of the reaction.

Reactions of amides **2a—c** with amines involve cleavage of the same C—C bond and afford ureas. Reactions of amides **2** with ammonia and 2,2-dinitro-2-fluoroethylamine[2] do not require the presence of an inorganic base. However, the large difference in the basicity of the amines chosen manifests itself in that the reaction with ammonia quickly proceeds at room temperature, whereas in the case of 2,2-dinitro-2-fluoroethylamine the reaction mixture must be heated for several hours. Only reactions with **2a** occur smoothly to yield the corresponding ureas (**4a** and **5a**).

$$\underset{\textbf{2a}}{Me(NO_2)_2CCONHCH_2C(NO_2)_2Me} + 2NH_3 \longrightarrow$$

$$\longrightarrow \underset{\textbf{4a}}{H_2NCONHCH_2C(NO_2)_2Me} + \overset{+}{N}H_4\overset{-}{C}(NO_2)_2Me$$

$$\underset{\textbf{2a}}{Me(NO_2)_2CCONHCH_2C(NO_2)_2Me} +$$

$$+ F(NO_2)_2CCH_2NH_2 \xrightarrow{MeOH}$$

$$\longrightarrow \underset{\textbf{5a}}{F(NO_2)_2CCH_2NHCONHCH_2C(NO_2)_2Me}$$

The other two amides afford essentially impure products, probably owing to decomposition of the ammonium salts of the dinitrofluoromethane formed. We did not manage to isolate pure ureas by recrystallization of the products from organic solvents, though their proportion in the products was no less than 75 % according to ^{1}H NMR data.

It should be noted that the methanol used as the medium is a weak competitor with 2,2-dinitro-2-fluoroethylamine in the reaction with amide **2a**, therefore, no substantial amount of carbamate **3a** is formed.

Amides **2** proved to be interesting objects for X-ray structural investigation. Using amides **2a,b** as examples we obtained information on various types of intramolecular orbital interactions involving orbitals of the nitro groups, the F atom, the O atom of the carbonyl group, and the N atom of the amino group.

It is actually the orbital interactions that determine the twist strained conformation of molecule **2b** (Fig. 1): first, the interaction of the unshared σ-type electron pair of the C(2)—O(1) carbonyl group with the vacant π-type MO of the two nitro groups, —N(3)O(4)O(5) and —N(5)O(8)O(9); second, the interaction between the π-type unshared electron pairs of the F(1), N(1), and F(2) atoms. The geometric parameters of the molecule attest to the σ—π* interaction: the C(1), C(2), O(1), N(1), and C(3) atoms are located in the same plane (within ±0.05 Å), which makes an angle of 75° with the C(1)N(3)O(4)O(5) plane. The O(1)—C(2)—C(5)—N(5) torsion angle is −11.7°; in addition, the O(1)···N(3) and O(1)···N(5) distances are 2.808 and 3.288 Å, respectively. Thus, the MO of the carbonyl-group unshared electron pair and the π*-MO of the two nitro groups are located fairly close to one another and are of the same symmetry. The strained conformation of the molecule found in the crystal is stabilized by electronic interactions, since the calculations of the optimal conformation of this molecule (by the MMX program of molecular mechanics) without regard for these interactions give another arrangement of the fragments in the molecule. The change in the conformation is associated with the rotation of the right (see Fig. 1) fluorodinitroethyl fragment of the molecule around the C(3)—C(4) bond and the left fragment around the C(1)—C(2) bond. The interaction of the unshared electron pairs of the F(1), N(1), and F(2) atoms is possible, since the F(1)—C(1)—C(2)—N(1) and N(1)—C(3)—C(5)—F(2) torsion angles are 15.15° and 3.0°, respectively, and the F(1)—N(1) and F(2)—N(1) distances are 2.629 and 3.028 Å, respectively.

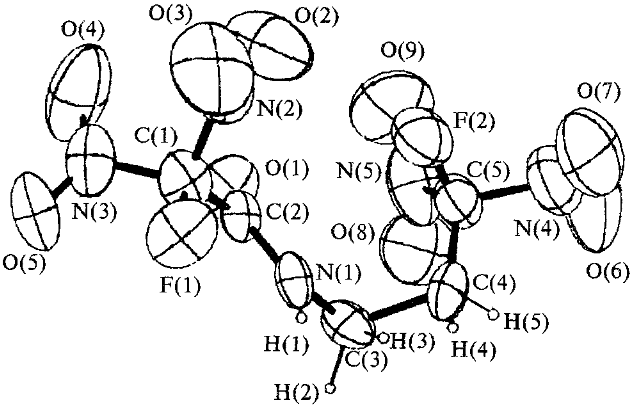

Fig. 1. The structure of the molecule of *N*-(3,3-dinitro-3-fluoropropyl)fluorodinitroacetamide (**2b**).

The conformation of molecule **2b** is favorable for overlap of the unshared electron pairs in the MO phase, and the antibonding combination will be stabilized in the case when it can act as a donor with respect to a vacant acceptor orbital having similar energy and suitable symmetry. The interaction with the vacant π-MO of the C(2)—O(1) bond would be the most efficient.

Thus, the comparison of the experimentally determined structural parameters with the qualitative consideration of orbital interactions in terms of two-electron stabilizing interaction[3] makes it possible to explain the strained conformation of molecule **2b**.

Molecule **2a** has no fluorine atoms (Fig. 2) and the interaction of the unshared electron pairs is missing, therefore, the methyl groups emerge from the plane of the amine atom N(5): the N(5)—C(3)—C(2)—C(1) and N(5)—C(4)—C(5)—C(6) torsion angles are equal to 51.1° and 39.5°, respectively. However, like in molecule **2b**, the σ—π* interaction between the unshared electron pair

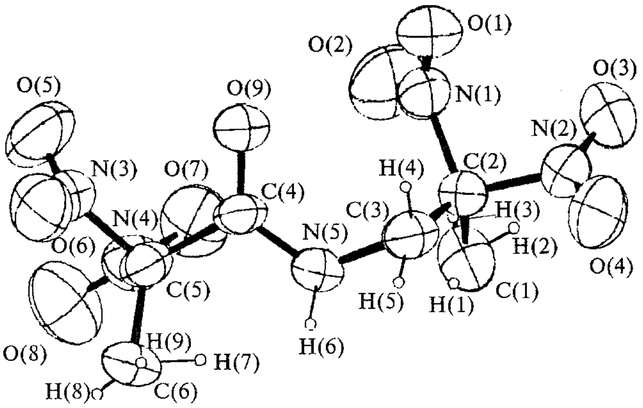

Fig. 2. The structure of the molecule of *N*-(2,2-dinitropropyl)-2,2-dinitropropionamide (**2a**).

of the C(4)—O(9) carbonyl group and the vacant π-MO of the two nitro groups, —N(3)O(5)O(6) and —N(1)O(1)O(2), may occur, since the O(9)···N(3) and O(9)···N(1) distances are 2.604 and 2.983 Å, respectively, the angle between the O(5)N(3)O(6)C(5) and C(3)N(5)C(4)O(9) planes is 92.4°, and the O(9)—C(4)—C(2)—N(1) torsion angle is 31.1°.

In addition to amides **2a,b**, we used secondary amides of 4,4,4-trinitrobutyric (**6**, **7**) and acetic (**8**) acids for the thermochemical study. This allowed us to make tentative estimates of the contribution of the carbamoyl group to the enthalpy of formation of the amides under study and of the interaction of this group with the fluorodinitromethyl, dinitromethylene, and methyl groups.

Table 1 presents the enthalpies of formation of amides calculated on the basis of the determined heats of combustion using the enthalpies of formation[5] of CO_2(g), H_2O(lq),[4] and $HF \cdot nH_2O$.

To calculate the contribution (*P*) of the carbamoyl group we used the previously[6] calculated values for contributions of the Me—(C), $-CH_2-(C_2)$, $-CH_2-(C)(N)$, $C(NO_2)_3-(C)$, $F(NO_2)_2C-(C)$, and $C(NO_2)_2-(C_2)$ groups, which are equal to −48.5, 25.5, −31.0, −38.7, −272.4, and −91.2 kJ (per one group), respectively. The contribution of the carbamoyl group itself was calculated from the enthalpy of formation of amide **6** in which the interactions of the carbamoyl group with the nitro-containing fragments of the molecule are substantially weakened due to two methylene groups and may be ignored in the calculations; the calculations gave *P*(—NHCO—) = −160.0 kJ.

Table 1. Standard enthalpies of formation of amides

Compound	$-\Delta_f H°$/kJ mol^{-1}
$MeC(NO_2)_2CH_2NHCOC(NO_2)_2Me$ (**2a**)	454.8
$F(NO_2)_2CCH_2CH_2NHCOC(NO_2)_2F$ (**2b**)	752.3
$F(NO_2)_2CCH_2CH_2NHCOCH_2CH_2C(NO_2)_3$ (**6**)	578.6
$F(NO_2)_2CCH_2NHCOCH_2CH_2C(NO_2)_3$ (**7**)	622.6
$F(NO_2)_2CCH_2NHCOMe$ (**8**)	550.2

Using this value, we may similarly extract the contribution of the interaction of the carbamoyl group with the fluorodinitromethyl group located in the α-position with respect to the carbonyl group (E_1) from the enthalpy of formation of amide **2b**, and the contribution of the interaction with the fluorodinitromethyl group located in the β-position with respect to the amino group (E_2) may be derived from the enthalpy of formation of amide **7**. The calculation yields substantially distinct values, E_1 = +9.0 kJ and E_2 = −69.5 kJ, having opposite signs. This implies, first, that the interaction of the fluorodinitromethyl group with the amine fragment of the carbamoyl group is a decisive factor and, second, that it exerts a strong stabilizing effect on these amides.

The interactions of the dinitromethylene groups with the carbamoyl group are much weaker. We only managed to estimate them as a whole based on the enthalpy of formation of amide **2a**. So, the sum of the contributions of the interactions of the dinitromethylene groups in the amine fragment (E_3) and in the carbonyl fragment (E_4) amounts to +15.7 kJ.

The interaction of the carbamoyl group with the methyl group (E_5) (amide **8**) is characterized by a substantial repulsion effect whose contribution was evaluated to be +31.4 kJ.

Experimental

***N*-(2,2-Dinitropropyl)-2,2-dinitropropionamide (2a).** A solution of 2.97 g of compound **1a** and 4 mL of HCl (*d* = 1.17 g cm^{-3}) in 15 mL of AcOH was kept for 24 h at 20—22 °C and poured into 100 mL of ice water. The precipitate was filtered off, dried, and recrystallized from a $CHCl_3-CCl_4$ mixture to give 2.7 g (91 %) of amide **2a**, m.p. 90—91 °C, d_4^{20} 1.63. Found (%): C, 24.1; H, 3.3; N, 23.6. $C_6H_9N_5O_9$. Calculated (%): C, 24.42; H, 3.07; N, 23.27. ^1H NMR (CD_2Cl_2, TMS), δ: 7.4 (br. s, H, NH); 4.4 (d, 2 H, CH_2, *J* = 6.0 Hz); 2.4 (s, 3 H, CH_3); 2.2 (s, 3 H, CH_3).

***N*-(3,3-Dinitro-3-fluoropropyl)fluorodinitroacetamide (2b).** Treatment of 3.19 g of compound **1b** according to the above-described procedure afforded 2.8 g (88 %) of amide **2b**, m.p. 85—86 °C, d_4^{20} 1.78. Found (%): C, 19.2; H, 11.9; F, 12.2; N, 21.8. $C_5H_5F_2N_5O_9$. Calculated (%): C, 19.94; H, 1.59; F, 11.98; N, 22.08. ^1H NMR (CD_2Cl_2, TMS), δ: 7.3 (br. s, H, NH); 3.8 (m, 2 H, CH_2, J_1 = 6.5 Hz; J_2 = 6.0 Hz); 3.2 (dt, 2 H, CH_2, J_1 = 6.5 Hz, J_2 = 17.7 Hz).

***N*-(2,2-Dinitropropyl)fluorodinitroacetamide (2c).** A mixture of 3.01 of compound **1c** and 15 mL of 70 % HNO_3 was heated to 60 °C with stirring, kept for 2 h at 60 °C, and cooled to 5 °C. 15 mL of ice water was added to the mixture and the precipitate was filtered off, dried, and recrystallized from a $CHCl_3-CCl_4$ mixture to give 2.45 g (82 %) of amide **2c**, m.p. 74—75 °C. Found (%): C, 20.1; H, 2.1; F, 6.7; N, 23.7. $C_5H_6FN_5O_9$. Calculated (%): C, 20.08; H, 2.02; F, 6.35; N, 23.41.

Methyl *N*-(2,2-dinitropropyl)carbamate (3a). *A.* A mixture of 1.5 g of amide **2a** and 0.5 g of $KHCO_3$ was stirred in 15 mL of MeOH for 1 h at 50 °C. The mixture was cooled to 5 °C and the yellow crystalline precipitate (0.76 g, 96 %) of the potassium salt of 1,1-dinitroethane was filtered off. The solvent from the methanolic filtrate was removed *in vacuo*. The oily residue crystallized in a refrigerator to give 1.0 g (97 %) of carbamate **3a**, m.p. 41—44 °C. Recrystallization from CCl_4 afforded 0.85 g (82 %) of **3a**, m.p. 44—45 °C. Found (%): C, 29.3; H, 4.2; N, 20.5. $C_5H_9N_3O_6$. Calculated (%): C, 28.99; H, 4.38; N, 20.29. ^1H NMR (CD_3CN, TMS), δ: 2.12 (s, 3 H, CH_3); 3.55 (s, 3 H, OCH_3); 4.20 (d, 2 H, CH_2, $J_{CH_2,\,NH}$ = 7.0 Hz); 6.14 (br. s, H, NH).

B. A mixture of 0.75 g of amide **2c** and 0.27 g of $KHCO_3$ was stirred in 15 mL of MeOH for 8 h at 20—22 °C. Most of the solvent was removed *in vacuo*, and the residue was dissolved in 20 mL of CH_2Cl_2. The solution was washed with water and poured onto a watch glass for evaporation. The paste-like residue was recrystallized from a CCl_4—$CHCl_3$ mixture to give 0.2 g (39 %) of carbamate **3a**, m.p. 44—45 °C; the melting point of a mixture with the sample prepared by procedure *A* was undepressed.

Methyl *N*-(3,3-dinitro-3-fluoropropyl)carbamate (3b). A mixture of 1.59 g of amide **2b** and 1.5 g of $KHCO_3$ was stirred in 30 mL of MeOH for 8 h at 20—22 °C, and the excess $KHCO_3$ was filtered off. Most of the solvent was removed *in vacuo*, the residue was dissolved in 30 mL of CH_2Cl_2, and the solution was washed with water and dried with $MgSO_4$. Removal of the solvent and vacuum distillation of the residue afforded 0.52 g (46 %) of carbamate **3c**, m.p. 100 °C (1 Torr), n_D^{20} 1.4516. Lit. data: b.p. 122 °C (2 Torr), n_D^{20} 1.4518. Found (%): C, 26.4; H, 3.7; F, 8.2; N, 19.1. $C_5H_8FN_3O_6$. Calculated (%): C, 26.67; H, 3.58; F, 8.44; N, 18.66.

***N*-(2,2-Dinitropropyl)urea (4a).** Gaseous ammonia (0.02 mol) was bubbled for 20 min through a solution of 1.5 g of amide **2a** in 15 mL of acetone with stirring and cooling to 15—18 °C. After a short period of storage, the yellow crystalline precipitate (0.45 g, 66 %) of the ammonium salt of 1,1-dinitroethane was filtered off. Most of the solvent was evaporated from the filtrate *in vacuo*. 30 mL of water was added to the residue and the mixture was allowed to stand at 0 to −5 °C for several hours. The precipitate was filtered off and dried to give 0.54 g (56 %) of urea **4a**, m.p. 154—155 °C (dec.). After recrystallization of **4a** from a dichloroethane—ethyl acetate mixture the m.p. was 155—156 °C (dec.). d_4^{20} 1.49. Found (%): C, 24.7; H, 4.6; N, 29.6. $C_4H_8N_4O_5$. Calculated (%): C, 25.01; H, 4.20; N, 29.16. ^1H NMR (CD_3CN, TMS), δ: 2.1 (s, 3 H, CH_3); 4.19 (d, 2 H, CH_2, $J_{CH_2,\,NH} \approx$ 7.0 Hz); 5.04 (br. s, 2 H, NH_2); 5.77 (br. s, H, NH).

***N*-(2,2-Dinitro-2-fluoroethyl)-*N'*-(2,2-dinitropropyl)urea (5a).** A solution of 1.5 g of amide **2a** and 3.06 g of 2,2-dinitro-2-fluoroethylamine in 15 mL of MeOH was stirred for 8 h at 45 °C and cooled to 5 °C. 10 mL of water was added dropwise. The precipitate was filtered off and dried to give 1.23 g (75 %) of urea **5a**, m.p. 200—201 °C (dec.). 30 mL of water and 10 mL of $CHCl_3$ were added to the filtrate and the mixture was allowed to stand for several hours at 0 to −5 °C. The precipitate was filtered off and dried to give an additional 0.15 g (9 %) of **5a**, m.p. 192—194 °C (dec.). The samples were combined and recrystallized from a dichloroethane—ethyl acetate mixture to yield 1.15 g (70 %) of urea **5a**, m.p. 202—203 °C (dec.). Found (%): C, 22.2; H, 2.6; F, 6.1; N, 25.4. $C_6H_9FN_6O_9$. Calculated (%): C, 21.96; H, 2.76; F, 5.79; N, 25.61. ^1H NMR (CD_3CN, TMS), δ: 2.09 (s, 3 H, CH_3); 4.20 (d, 2 H, CH_2, $J_{CH_2,\,NH}$ = 6.7 Hz); 4.52 (dd, 2 H, CH_2, $J_{CH_2,\,F}$ = 15.0 Hz, $J_{CH_2,\,NH}$ = 6.2 Hz); ~5.80 (br.t, H, NH); ~5.87 (br.t, H, NH).

Amides **6**, **7**, and **8** were prepared by the known procedures.[8,9]

Table 2. Atomic coordinates $(\times 10^5)$ in the structure of compound **2b**

Atom	*x*	*y*	*z*
F(1)	27748(7)	53359(5)	23453(2)
F(2)	51183(6)	29824(5)	39982(3)
F(3)	25923(7)	81782(6)	35943(2)
O(1)	46148(6)	38541(7)	11780(3)
O(2)	46565(6)	50831(6)	35247(2)
O(3)	35537(7)	61538(5)	38521(3)
O(4)	42881(6)	58473(6)	6052(2)
O(5)	30258(7)	60165(6)	1314(2)
O(6)	60781(7)	6783(6)	44887(3)
O(7)	54424(6)	17311(7)	58327(2)
O(8)	57272(6)	12674(7)	17090(3)
O(9)	62984(7)	23127(6)	23712(3)
O(10)	35873(5)	89983(6)	43766(2)
O(11)	31230(6)	101676(7)	31014(2)
O(12)	32589(6)	77472(6)	12945(3)
O(13)	29772(7)	90749(5)	6379(3)
O(14)	20480(6)	91384(6)	63337(2)
O(15)*	18226(8)	22288(6)	36716(3)
O(16)*	3548(7)	23881(6)	36274(3)
O(17)*	6568(7)	41732(7)	9972(2)
O(18)*	18225(6)	25892(6)	18623(3)
O(19)*	100660(8)	28769(7)	34105(3)
O(20)*	99797(8)	92277(7)	69446(4)
N(1)	35969(5)	35391(5)	23050(2)
N(2)	39613(6)	55367(4)	32498(2)
N(3)	36308(5)	57113(4)	7945(3)
N(4)	56286(6)	14319(5)	47191(3)
N(5)	58008(5)	18706(4)	23812(2)
N(6)	31728(6)	93788(5)	35006(2)
N(7)	29918(5)	85235(4)	14528(2)
N(8)	10378(6)	93678(5)	47647(3)
N(9)*	9879(5)	25417(4)	41279(2)
N(10)*	12445(8)	34568(7)	14756(4)
N(11)*	1174(7)	39018(7)	32204(4)
C(1)	35589(6)	51235(4)	20248(2)
C(2)	39872(5)	40881(4)	18302(2)
C(3)	39038(5)	25344(4)	21270(3)
C(4)	43804(6)	19662(5)	33936(3)
C(5)	51805(6)	20913(5)	36371(2)
C(6)	25817(5)	88971(4)	28676(3)
C(7)	17472(5)	95687(5)	26697(3)
C(8)	63306(6)	50001(5)	10596(2)
C(9)	14350(6)	90416(5)	59448(3)
C(10)	9947(5)	83635(5)	66338(2)
H(1)	31563(55)	35390(45)	25224(35)
H(2)	35839(55)	22535(45)	14523(35)
H(3)	33717(55)	27367(45)	31833(35)
H(4)	45324(55)	13220(45)	26594(35)
H(5)	41782(55)	17103(45)	40305(35)
H(6)	6958(55)	42381(45)	54083(35)
H(7)	14956(55)	92267(45)	21088(35)
H(8)	19003(55)	99609(45)	18759(35)
H(9)	10044(55)	1.06034(45)	38853(35)
H(10)	14994(55)	1.03458(45)	46021(35)

* Coordinates of the atoms of lower multiplicities.

X-ray structural study. Unit cell parameters for crystals of **2b** and **2a** were determined on a DRON-1 diffractometer with a single crystal attachment.

Table 3. Atomic coordinates ($\times 10^5$) in the structure of compound **2a**

Atom	*x*	*y*	*z*
O(1)	26546(4)	10515(4)	38405(3)
O(2)	37184(4)	3580(5)	32428(2)
O(3)	19819(5)	−2846(6)	19664(3)
O(4)	15755(5)	9061(4)	8494(3)
O(5)	53464(3)	33993(6)	41009(2)
O(6)	47556(5)	45843(4)	32590(2)
O(7)	52330(4)	16447(5)	22167(3)
O(8)	60979(4)	26897(5)	17017(2)
O(9)	37538(5)	27014(6)	34079(3)
N(1)	31023(6)	7552(5)	30219(3)
N(2)	20632(5)	4920(5)	14629(3)
N(3)	49937(4)	37828(5)	32343(2)
N(4)	54358(5)	24469(6)	19667(3)
N(5)	36120(5)	24239(5)	12359(3)
C(1)	34179(4)	4080(5)	6389(2)
C(2)	28927(4)	9304(5)	15701(3)
C(3)	28393(5)	20011(4)	13234(2)
C(4)	40014(5)	27491(4)	22749(3)
C(5)	48032(6)	32072(5)	19870(3)
C(6)	48604(6)	38133(5)	7737(3)
H(1)	33401(35)	3395(25)	8038(20)
H(2)	40014(35)	6773(25)	5937(20)
H(3)	36200(35)	1240(25)	12094(20)
H(4)	25580(35)	22628(25)	20023(20)
H(5)	24963(35)	20726(25)	5447(20)
H(6)	38881(35)	23779(25)	5312(20)
H(7)	51976(35)	39698(25)	5007(20)
H(8)	45392(35)	32349(25)	5279(20)
H(9)	44025(35)	43323(25)	8161(20)

Crystals of $C_5H_5N_5O_9F_2$ (**2b**), M = 317.12, are monoclinic: *a* = 17.074(7) Å, *b* = 14.881(3) Å, *c* = 9.780(2) Å, β = 72.89(2)°; V = 2375.0 Å^3, d = 1.773 g cm^{-3}, λ = 0.711, space group *Bb*, *Z* = 8. 1647 nonzero nonequivalent reflections were measured on a KM-4 four-circle diffractometer with α-geometry (KUMA-DIFFRACTION, Poland) in the range $0.060 < \sin\theta/\lambda < 0.650$.

Crystals of $C_6H_9N_5O_9$ (**2a**), M = 295.17, are rhombic: *a* = 16.969(6) Å, *b* = 14.097(4) Å, *c* = 10.082(3) Å; V = 2411.85 Å^3, d = 1.614 g cm^{-3}, λ = 1.5418, space group *Pbca*, *Z* = 8. 1645 of nonzero nonequivalent reflections ($I > 2.5(I)$) were measured on a DAR-UM diffractometer in the range $0.056 < \sin\theta/\lambda < 0.650$.

The structures of **2a** and **2b** were solved by the direct method using a personal computer and the SHELX-86 set of programs and refined in the full-matrix approximation to R = 0.065 (**2b**) and R = 0.045 (**2a**). The temperature parameters for nonhydrogen atoms were refined in the anisotropic approximation; those for H atoms were refined in the isotropic approximation. Atomic coordinates for structures **2b** and **2a** are listed in Tables 2 and 3, respectively. It should be noted that for compound **2b** at the multiplicity *Z* = 8 in space group *Bb* two independent molecules were determined; one of them was determined unambiguously, while the other molecule has a statistically disordered dinitrofluoroethyl fragment. In Table 2 the statistically disordered atoms whose multiplicities have been determined by the least-squares method are marked by an asterisk. Fig. 1 presents the structure of molecule **2b** unambiguously determined during the solution, and Fig. 2 shows the structure of molecule **2a**.

The thermochemical study. Heats of combustion for amides **2a**,**b**, **6**, **7**, and **8** were determined on a B-06-II calorimeter with a fixed platinum bomb in an oxygen atmosphere. Below we present the results of the study ($\Delta_c H°$/kJ mol^{-1} is the combustion enthalpy).

Compound	**2a**	**2b**	**6**	**7**	**8**
$\Delta_c H°$	3194.8± 1.7	2288.6± 1.3	3597.7± 2.7	2862.4± 2.3	2060.6± 4.2

The procedure of the experiments and the analytical procedures have been described previously.[6] The samples of the compounds under study were preliminarily recrystallized many times from organic solvents and then dried *in vacuo*. The purity of the substances was no less than 99.95 % (confirmed by the determination of CO_2 by the Rossini method).

References

1. A. G. Korepin, P. V. Galkin, N. I. Golovina, L. O. Atovmyan, and L. T. Eremenko, *Izv. Akad. Nauk, Ser. Khim.*, 1992, 742 [*Bull. Russ. Acad. Sci., Div. Chem. Sci.*, 1992, **41**, 582 (Engl. Transl.)].
2. H. G. Adolph and M. J. Kamlet, *J. Org. Chem.*, 1969, **34**, 45.
3. N. D. Epiotis, *J. Am. Chem. Soc.*, 1973, **75**, 3087.
4. *Termicheskie konstanty veshchestv* [*Thermal Constants of Compounds*], Ed. V. P. Glushko, Nauka, Moscow, 1968, No. 3, 460 (in Russian).
5. J. R. Lacher and H. A. Skinner, *J. Chem. Soc. A*, 1968, 1034.
6. L. V. Kustova, E. P. Kirpichev, Yu. I. Rubtsov, V. V. Avdonin, A. G. Korepin, and L. T. Eremenko, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 2232 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1981, **30**, 1830 (Engl. Transl.)].
7. A. G. Korepin, R. G. Gafurov, and L. T. Eremenko, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1969, 2565 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1969, **18**, No. 11 (Engl. Transl.)].
8. R. G. Gafurov, A. G. Korepin, and L. T. Eremenko, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1970, 442 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1970, **19**, 386 (Engl. Transl.)].
9. L. T. Eremenko, R. G. Gafurov, and A. N. Salakhova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1972, 662 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1972, **21**, 628 (Engl. Transl.)].

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