

Energetic Properties

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Solid-State and Gas-Phase Structures and Energetic Properties of the Dangerous Methyl and Fluoromethyl Nitrates

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 85th birthday

Abstract: An improved synthesis of the simplest nitric acid ester, methyl nitrate, and a new synthesis of fluoromethyl nitrate use the metathesis of the corresponding iodomethanes with silver nitrate. Both compounds were identified by spectroscopy and the structures determined for in situ grown crystals by X-ray diffraction as well as in the gas phase by electron diffraction. Fluorination leads to structures with shorter C–O and N–O bonds, has an energetically destabilizing effect and increases friction sensitivity, but decreases detonation performance.

Potential energetic materials are typically screened for density, performance, stability, and sensitivity towards friction and impact.^[1] In general, high density contributes to high performance.^[2] The influence of fluorine substituents on energetic materials is well documented, but almost nothing is known about the important parameter sensitivity towards impact and friction. These sensitivities were frequently rationalized with numerous and short inter- and intramolecular open-shell interactions.^[3] Understanding the mutual interactions between atoms and functional groups is crucial to develop safe-to-handle energetic materials. Small and simple, yet highly energetic molecules are particularly suitable for exploring the effect of H/F exchange on the sensitivities due to the limited number of intermolecular interactions.^[4] These molecules are often highly sensitive to

impact and friction. The challenge is to find suitable molecules whose sensitivities can be determined by conventional methods and to compare them with non- and polyfluorinated derivatives, as was recently demonstrated for perchloric acid esters.^[5]

Fluoromethyl nitrate (FCH₂ONO₂, FMN) is one of three fluorine-containing derivatives of methyl nitrate, CH₃ONO₂ (MN),^[6] besides F₂CHONO₂ (DFMN)^[8] and F₃CONO₂ (TFMN).^[9] Organic nitrates are important energetic compounds widely used in military and aviation industries, but so far FMN (and also DFMN) has been studied only by ab initio calculations.^[7,10] In contrast, TFMN (m.p. –163 °C, b.p. –18 °C) is isolable, but unstable even at low temperatures.^[8,9]

Methyl nitrate (MN, m.p. –82 °C, b.p. 65 °C), so-called *Schießwasser* (German for shooting water), was used as early as 1420, though then not recognized as this material.^[11a,b] Mysterious accidents were attributed to MN between 1933 and 1955 and again in the 1980s.^[11c–g] Despite its unflattering reputation, various synthetic protocols, properties, and applications have been reported.^[6,10,12] The first structure elucidation of this toxic and consciousness-altering substance dates back to 1937 with theoretical and initial gas-phase electron diffraction (GED) studies.^[13] Solid-state structures determined by single-crystal X-ray diffraction of MN and FMN have not been available so far, but could serve to compute electrostatic potentials, often used to explain changes in sensitivity, and for comparison with quantum-mechanical results.^[2,14]

The original synthesis of MN, the nitration of methanol with nitric acid, cannot be adopted for FMN. This would require starting from fluoromethanol, which is known to be unstable and readily decomposes into HF and formaldehyde under ambient conditions.^[6,15] However, the adaptation of an ethyl nitrate synthesis via silver-catalyzed heterolysis^[16] is successful: iodomethane or fluoroiodomethane is reacted with silver nitrate (Scheme 1). MN and FMN (m.p. –91 °C, b.p. 58 °C) were both isolated as strong-smelling, colorless, volatile liquids. They cause severe headache upon exposure.

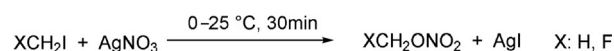
Identification and characterization is possible by NMR spectroscopy. In contrast to the ¹H NMR resonance of the methyl group in MN (4.10 ppm), the methylene group of

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Scheme 1. Synthesis of MN and FMN.

FMN gives rise to a doublet at 5.98 ppm ($^2J_{\text{FH}} = 52.0$ Hz); the downfield shift is due to the strong electron-withdrawing effect of fluorine. FMN shows a triplet at -155.9 ppm in its ^{19}F NMR spectrum, and a doublet of triplets at 99.1 ppm ($^1J_{\text{FC}} = 228.8$, $^1J_{\text{CH}} = 182.4$ Hz) in its ^{13}C NMR spectrum.

The ^{15}N NMR signal of FMN at -52.4 ppm is a triplet of doublets ($^3J_{\text{NH}} = 6.7$, $^3J_{\text{FN}} = 1.7$ Hz; Figure 1); that is, substitution of MN (-39.4 ppm, quartet $^3J_{\text{NH}} = 3.9$ Hz) by one fluorine atom leads to an upfield shift. The ^{17}O resonance (obtained using highly concentrated solutions, Figure 1) of the FCH_2O unit in FMN at 363 ppm is shifted downfield relative to the methoxy resonance in MN at 310 ppm. In contrast, the NO_2 resonance at 446 ppm remains unaffected upon H/F exchange. The chemical shifts of both FMN and MN recorded in CD_3CN solution are similar to those of neat ethyl nitrate (340, 470 ppm).^[17]

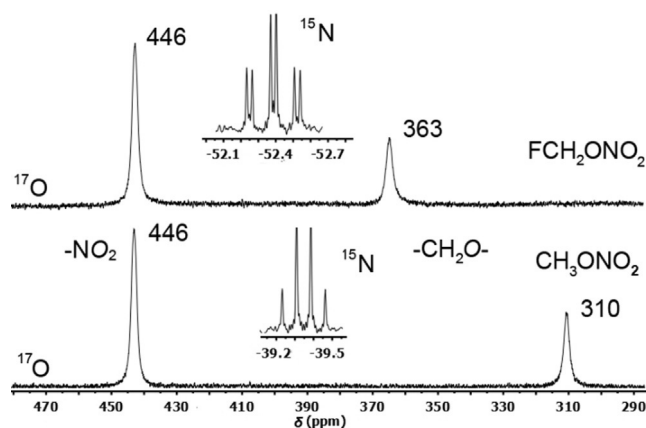


Figure 1. ^{15}N and ^{17}O NMR spectra of FMN (top) and MN (bottom) in CD_3CN (26 °C).

Selected vibrations of the IR and Raman spectra of MN and FMN are listed in Table 1. The IR stretching vibrations of the NO_2 group for FMN are found at 1670 cm^{-1} ($\nu_{\text{as}}\text{NO}_2$) and 1291 cm^{-1} ($\nu_{\text{s}}\text{NO}_2$). Compared to MN, these vibrational modes are shifted to higher wavenumbers due to the electro-negative F substituent. The lower values of the ν_{NO} stretching vibration of FMN (IR, 811 cm^{-1}) indicates a weaker $\text{N}-\text{O}(\text{CH}_2\text{F})$ bond upon F/H substitution. The experimental data differ in part from earlier calculated data, likely due to the liquid state.^[17]

MN and FMN were structurally characterized in the gas phase by electron diffraction (GED, Table 2) and in the case

Table 1: Selected IR/Raman vibrations of MN and FMN (liquids/25 °C, calcd B3LYP/6-311G(d,p), cm^{-1}).

	MN				FMN			
	IR		Raman		IR		Raman	
	expt.	calcd.	expt.	calcd.	expt.	calcd.	expt.	calcd.
$\nu_{\text{as}}\text{NO}_2$	1622 (s)	1714 (s)	1636 (w)	1714 (w)	1670 (s)	1767 (s)	1689 (w)	1767 (w)
$\nu_{\text{s}}\text{NO}_2$	1281 (s)	1324 (s)	1285 (m)	1324 (w)	1291 (s)	1340 (m)	1296 (m)	1340 (w)
ν_{CF}	–	–	–	–	1047 (m)	1032 (w)	1049 (w)	1032 (w)
ν_{CO}	989 (s)	1015 (m)	991 (m)	1015 (m)	996 (s)	1023 (s)	1005 (w)	1023 (w)
ν_{NO}	854 (s)	862 (s)	860 (m)	862 (m)	811 (s)	824 (s)	822 (m)	824 (m)
δNO_2	652 (m)	661 (m)	664 (w)	661 (m)	654 (m)	647 (w)	660 (w)	647 (m)

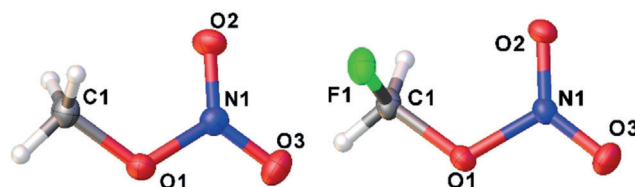


Figure 2. Molecular structures of MN (left) and FMN (right) in the solid state. Ellipsoids are set at the 50% probability level. Numbering holds for the gas-phase structures as well.

Table 2: Selected structural parameters for the solid-state (XRD) and the gas-phase structures (GED or GED + RotC) for methyl nitrate (MN) and fluoromethyl nitrate (FMN). Distances are given in Å and angles in degrees.

Parameter	MN		FMN	
	XRD	GED + RotC	XRD	GED
C-O	1.451(1)	1.425(3)	1.412(2)	1.385(3)
O1-N	1.388(1)	1.403(2)	1.433(2)	1.454(2)
N-O2	1.204(1)	1.205(1)	1.208(2)	1.190(2)
N-O3	1.212(1)	1.198(1)	1.200(2)	1.185(1)
C-F			1.379(2)	1.336(2)
C-O-N	113.3(1)	113.6(3)	113.3(1)	115.3(2)
O1-N-O2	118.5(1)	116.3(3)	118.1(1)	115.1(3)
O1-N-O3	112.9(1)	112.3(2)	111.9(1)	111.9(11)
O2-N-O3	128.6(1)	131.4(4)	130.1(1)	133.0(13)
F-C-O-N			79.7(1)	74.7(8)

of MN also by combining GED data with rotational constants (Table 3; details given in the Supporting Information). Figure 3 shows the radial distribution curves for the GED experiments. While MN adopts C_s symmetry with one of the hydrogen atoms in antiperiplanar position to the nitrogen atom, the fluorine atom in FMN resides *gauche* relative to the planar NO_2 unit ($\varphi(\text{F1C1O1N1}) = 74.7(8)^\circ$). Fluorination has severe effects on the structure parameters: in FMN the C–O1 and N–O2/O3 distances are shortened by 0.04 Å (MN 1.425(3), FMN 1.385(3) Å) and 0.01 Å (MN 1.205(1), 1.198(1) Å, FMN 1.190(2), 1.185(1) Å), respectively. In variance, the O1–N distance in FMN is about 0.05 Å longer than in MN (MN 1.403(2), FMN 1.454(2) Å). This is likely due to negative hyperconjugation of the oxygen lone pairs into the antibonding orbitals of the C–F and NO bonds. The C–O1–N angle in FMN (115.3°) is 2° greater than in MN.

The solid-state structures of both nitrates were determined by X-ray diffraction of in situ grown crystals (Figure 2). An unexpected small crystal of oxonium nitrate dihydrate obtained during crystallization of MN was also structurally characterized (details in the Supporting Information). MN crystallizes in the space group $Pbca$ and FMN in Cc . Both contain one molecule per asymmetric unit.^[18] In both molecules, the carbon, nitrogen, and oxygen atoms are almost coplanar; the root mean square deviation is 0.001 Å. The C_s symmetry of MN is broken by the torsion angles of the

Table 3: Theoretical and refined structural parameters (in Å, degrees) from GED intensities and rotational constants of MN.

Parameter	MP2(full)/cc-pwCVTZ	GED + RotC ^[a]	$w_{\text{GED}}^{[b]}$ [%]
C1–O1	1.426	1.425(3)	48
O1–N1	1.407	1.403(2)	40
N1–O2	1.207	1.205(1)	64
N1–O3	1.201	1.198(1)	64
average C–H	1.084	1.080(5)	49
C1–O1–N1	112.2	113.6(3)	14
O1N1O2	117.1	116.3(3)	17
O1N1O3	112.6	112.3(2)	7
O2N1O3	130.3	131.4(4)	8
wRMSD ^[c] [MHz]	15.9	2.7	
R-factor ^[d] [%]	7.0 ^[e]	4.8	

[a] Values correspond to equilibrium structure. In parentheses are total standard deviations obtained from Monte Carlo simulations as described earlier.^[19] [b] Contribution of GED data to refined value, estimated according to the W2 method.^[20] [c] Weighted root-mean-square deviation of model rotational constants from experimental. [d] Disagreement factor between model and experimental electron diffraction intensities. [e] Model refined against GED data with geometrical parameters fixed at ab initio values.

methyl group $\varphi(\text{NOCH})$: 175.6(7)°, 65.9(7)°, and 60.0(7)°. FMN adopts a *gauche* conformation with a torsion angle $\varphi(\text{NOCF})$ of 79.7(1)°; $\varphi(\text{NOCH})$ angles are 169(2)° and 40(2)°. As in the gas phase, structural changes upon fluorination result in a shorter C1–O1 bond (MN 1.451(1) Å; FMN 1.412(2) Å), a longer O1–N1 bond (MN 1.388(1) Å; FMN 1.433(2) Å) and slightly shorter N1–O2/O3 bonds (MN 1.204(1)/1.212(1) Å, FMN 1.208(2)/1.200(2) Å).

Solid MN and FMN contain N...O and N...F contacts shorter than or close to the van der Waals distances (3.07/3.02 Å) (Figure 4). Two independent N...O contacts in MN have lengths of 3.094(1) (N1...O3') and 3.042(1) Å (N1...O2'') and a corresponding angle O3'...N1...O2'' of 171.9(1)°. Comparable contacts in FMN are significantly shorter at 2.928(2) Å (N1...O2') and 2.895(2) Å (N1...F1'') and the angle O2'...N1...F1'' at 168.1(1)° is narrower. Thus, both crystal structures feature pseudo-trigonal-bipyramidally coordinated nitrogen atoms with intermolecular contacts in axial position.

The influence of H/F substitution on the energetic properties was determined and results for MN^[11e,f,21] and FMN are listed in Table 4. The sensitivity of MN and FMN towards friction and impact was determined experimentally according to the standards of the German Federal Institute for Material Research and Testing (BAM).^[22] The two nitrates show the same sensitivity to impact of 0.2 J. However, the friction sensitivity of FMN is significantly higher than that of MN. Thus, the UN recommendations on transport of dangerous goods require FMN to be classified as very sensitive towards impact and as sensitive towards friction.^[23]

In contrast to impact or shock sensitivity, friction sensitivity does not usually attract the attention of theoreticians, but there seems to be a correlation between friction sensitivity and electrostatic potential (ESP).^[24] The ESP of FMN differs significantly from that of MN, which may be related to the significantly greater impact sensitivity (Figure 5).^[2] For FMN the positive region (blue) is larger and the positive potential (max. +100 kJ mol⁻¹) is greater than for MN. The maximum

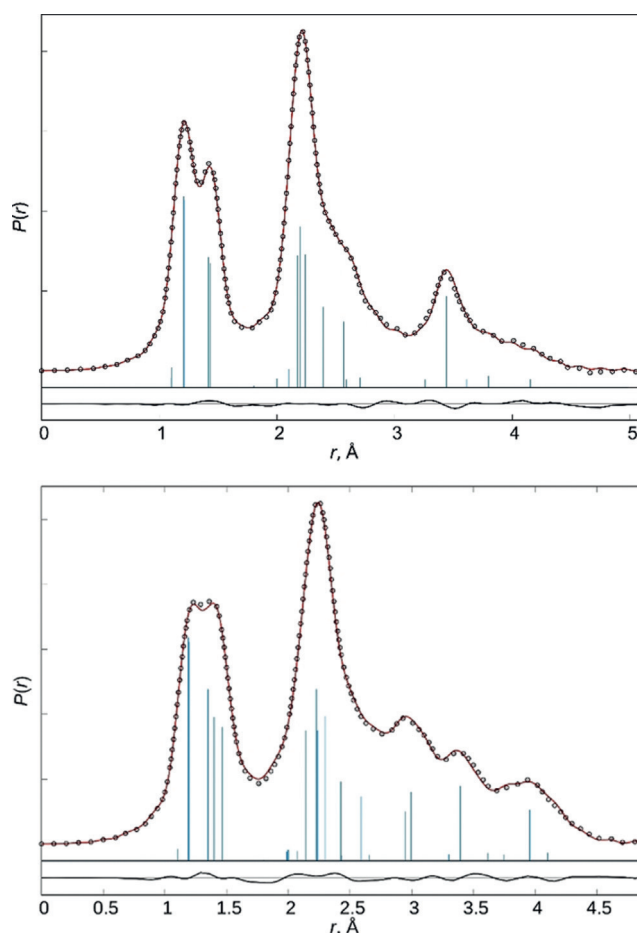


Figure 3. Experimental (circles) and model (line) radial distribution functions of MN (top) and FMN (bottom). The line below is the difference curve. Vertical bars indicate interatomic distances in the molecule.

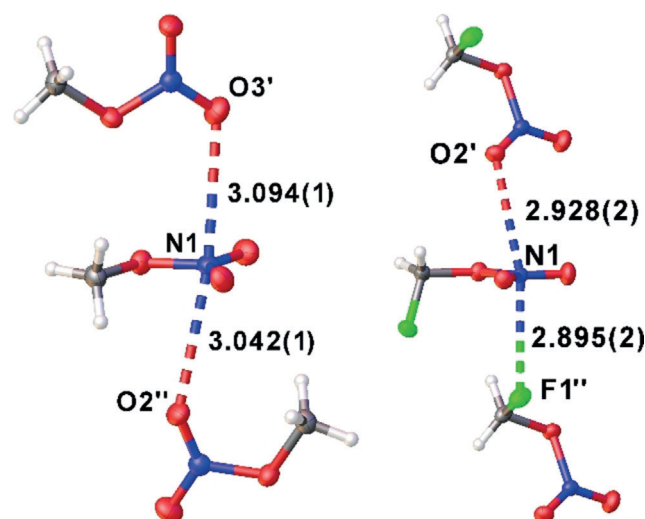
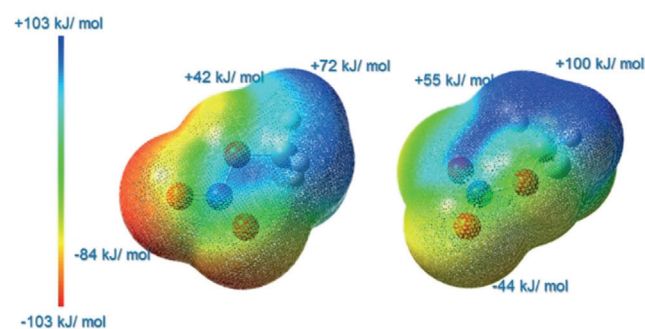


Figure 4. Molecular assembly of methyl nitrate and fluoromethyl nitrate in the solid state. Symmetry operations generating equivalent positions for MN: $(-1/2+x, y, 3/2-z)$ for (') and $(1/2+x, 1/2-y, 1-z)$ for (''), for FMN: $(+x, 1-y, 1/2+z)$ for (') and $(-1/2+x, 1/2-y, -1/2+z)$ for ('').

Table 4: Physical and thermodynamic properties of MN and FMN.

	MN	FMN
formula	CH ₃ NO ₃	CH ₂ FNO ₃
<i>M</i> [g mol ⁻¹]	77.04	95.03
<i>I</i> S ^[a] [J]	0.2	0.2
<i>F</i> S ^[b] [N]	353	108
<i>N</i> ^[c] [%]	18.18	14.74
<i>N</i> + <i>O</i> + <i>F</i> ^[d] [%]	80.48	85.24
<i>Ω</i> _{CO} ^[e] [%]	10.4	25.3
<i>Ω</i> _{CO₂} ^[e] [%]	-10.4	8.4
<i>T</i> _{melt} ^[f] [°C]	-83.0	-90
<i>T</i> _{boil} ^[g] [°C]	65.0	58.0
<i>ρ</i> _{100K} ^[h] [g cm ⁻³] (XRD)	1.579	1.838
<i>ρ</i> _{293K} ^[i] [g cm ⁻³]	1.21	1.28
<i>ΔH</i> _f ^[j] [kJ mol ⁻¹]	-162.3	-361.7
EXPLO5 V 6.03		
<i>ΔU</i> _f ^[k] [kJ kg ⁻¹]	-6021	-4450
<i>T</i> _{C-J} ^[l] [K]	4151	3827
<i>P</i> _{C-J} ^[m] [GPa]	14.2	12.3
<i>V</i> _{det} ^[n] [ms ⁻¹]	6653	6133
<i>V</i> _o ^[o] [dm ³ kg ⁻¹]	923.7	836.8

[a] Impact sensitivity (BAM drop-hammer, method 1 of 6). [b] Friction sensitivity (BAM friction tester, method 1 of 6). [c] Nitrogen content. [d] Combined nitrogen, oxygen, and fluorine content. [e] Absolute oxygen balance assuming the formation of CO or CO₂ and HF. [f] Melting point. [g] Boiling point determined by the Siwoloboff method. [h] Density determined by X-ray diffraction at 100 K. [i] Experimentally determined density at 293 K. [j] Heat of formation calculated at the CBS-4M level of theory. [k] Detonation energy. [l] Detonation temperature. [m] Detonation pressure. [n] Detonation velocity. [o] Volume of detonation gases at standard temperature and pressure conditions.

**Figure 5.** ESP of MN (left) and FMN (right), isovalue = 0.02.

negative potentials at the NO₂ unit (-44 kJ mol⁻¹) and the F atom (-52 kJ mol⁻¹) in FMN are much less negative than in MN. This is in contrast to the situation in MN, which has a more strongly negative (max. -84 kJ mol⁻¹) than positive region. This and the fact that there is a higher positive potential in the molecular center indicate FMN to be more friction sensitive.^[2,14b] The weaker negative potential (maximum: -44/-52 vs. -84 kJ mol⁻¹) is probably the main reason for the increased friction sensitivity.^[24] A destabilizing effect of fluorine substitution was already evoked to explain the high instability of trifluoromethyl nitrate (TFMN).^[9] Initial results on methylene dinitrate CH₂(ONO₂)₂,^[25] prepared in analogy to FMN, confirm this increased instability (see the Supporting Information).^[26] Consequently, it is not surprising

that attempts to synthesize the multiply fluorine/nitrate-substituted FCH(ONO₂)₂ from FCHI₂ were not successful. An immediate decomposition into N₂O₅ (hydrolyzing to HNO₃) and “FCHO” was proven by NMR spectroscopy.^[27]

Quantum-chemical calculations were carried out for MN and FMN. Heats of formation were computed using optimized structures^[28] and are considerably more negative for FMN than for MN (Table 4). Based on these values and the corresponding densities at ambient temperature, detonation parameters of MN and FMN were calculated using the EXPLO5 V6.03 code^[30] (Table 4). Calculations at the Chapman–Jouguet (C-J) point applied a stationary detonation model with a modified Becker–Kistiakowski–Wilson state equation. The C-J point was located using the first derivative of the Hugoniot curve of the system.^[31] The calculated detonation parameters are comparable with those of glycerine trinitrate (*ΔU*_f⁰ -6099 kJ kg⁻¹, *T*_{C-J} 4316 K, *P*_{C-J} 23.7 GPa, *V*_{det} 7850 ms⁻¹, *V*_o 781 dm³ kg⁻¹). The heat of detonation, detonation pressure, velocity, and temperature of glycerine trinitrate are all higher than those of MN and FMN, but the gas volumes released from MN and FMN are smaller.

In essence we have synthesized and characterized fluoromethyl nitrate for comparison with methyl nitrate in order to learn about the effect of fluorine substitution on various structural and energetic parameters. We find shorter C–O and N–O bonds and a wider C–O–N angle in the fluorinated species. Fluorine substitution has a destabilizing effect: it increases friction sensitivity but decreases detonation performance.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: energetic properties · fluoromethyl nitrate · gas electron diffraction · methyl nitrate · X-ray diffraction

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