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Electron-withdrawing effect of α-substituents in acyl nitrates on the polarization of the O–NO_2 bond

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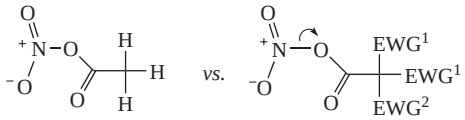
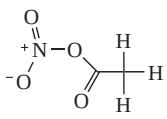
Regularities in the Raman ($\nu^s_{NO_2}$) and ^{14}N NMR spectra of acetyl nitrates containing various electron-withdrawing α-substituents were established by quantum chemical calculations. The experimental data on (poly)-α-haloacetyl nitrates (in solutions) revealed no reliable relationship between the halogen nature/number and the spectral characteristics, whereas the computed values of δ_N and O–NO_2 bond lengths disclose the substituent effect on the polarization of O–N bond and hence on the nitrating power of acyl nitrates.



Nitronium cation is the most efficient species in nitration reactions.[1] However, many covalent nitro compounds can also serve as nitrating reagents.[2,3] Polarization of the Y–NO_2 bond (Y = O for nitro esters) can be caused by polar solvent or by effect of electron-withdrawing groups (EWGs) in a molecule, which leads to elongation of the O–NO_2 bond and improves charge separation. The so called 'ionization' leading to nitronium cation can occur, for example, upon addition of Lewis acids to nitrate esters.[4–9] In the scope of step-by-step studies on the structure–property relationship in a series of O–NO_2 compounds,[9–12] in this work we performed quantum chemical calculations and studied spectroscopic properties of acetyl nitrate **1** and its some α-EWG-substituted derivatives **2**–**4**. Note that acyl nitrates are unstable and explosive compounds.[10] Parent $AcONO_2$ **1** is the first representative in a series of acyl nitrates, which was originally obtained from Ac_2O and HNO_3.[13] We compared characteristics of $AcONO_2$ **1** with those of nitrates **2**–**4**.

To date, the experimental values of nitration rates for aromatic substrates and the molar distribution of the resulting *ortho*-, *meta*-, and *para*-isomers are used as criteria of the nitrating efficiency of reagents.[3] These experiments are laborious and their results do not provide information on the nature of the nitrating particle in the reagent used. The nitronium cation, if it is present, can be detected only by spectral methods.[8,11]



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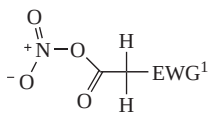
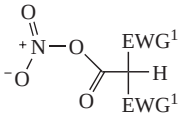
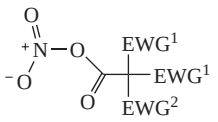


2a–d



3a–d

2, **3**: **a** EWG^1 = Br **c** EWG^1 = F
b EWG^1 = Cl **d** EWG^1 = CN



4a EWG^1 = EWG^2 = Br **4e** EWG^1 = F, EWG^2 = CF_3
4b EWG^1 = EWG^2 = Cl **4f** EWG^1 = CF_3, EWG^2 = F
4c EWG^1 = EWG^2 = F **4g** EWG^1 = EWG^2 = CF_3
4d EWG^1 = EWG^2 = CN

However, ^{14}N (^{15}N) NMR spectroscopy is not always suitable,[10–12] since nitric acid, often presenting, can mask nitronium ion.[9] The only good method for the quantitative determination of NO_2^+, being a linear particle, is Raman spectroscopy, since the increase in the relative intensity of the characteristic line of nitronium cation at 1400 cm^{-1} can be monitored.[14] However, this method cannot be used directly to evaluate the nitrating power of reagent since the concentration of N_2O_5, capable of nitration, is not taken into account.

One of the most expedient methods for estimating the nitrating ability of organic nitro compounds is based on the evaluation of the Y–NO_2 bond length (Y = C, N, O, *etc*.), which is correlated with degree of the bond ionicity. The comparison can be performed both by quantum chemical calculations and by the use of physicochemical characteristics. The Raman frequencies of symmetric vibrations for the O_2N–O group ($\nu^s_{NO_2}$) and the δ_N shift for the nitro moiety in ^{14}N or ^{15}N NMR spectra can be considered as these parameters.

Polar solvents are known to facilitate nitration.[13] An increase in the O–N bond length in the homologous series of acyl nitrates (in the same solvent or in the gas phase) should imply an enhancement of their nitrating power. Previously,[10,12] we discovered some correlation between the frequency $\nu^s_{NO_2}$ in the Raman spectra of solutions of nitro compounds and the polarity of the solvent used. So, $\nu^s_{NO_2}$ for HNO_3 increases by ~10 cm^{-1} upon replacement of CCl_4 with CF_3COOH, while $\nu^s_{NO_2}$ for trifluoroacetyl nitrate **4c** increases by ~3 cm^{-1} upon replacement of CCl_4 with $MeNO_2$. For solutions of N_2O_5 in acids the following regularity has been found:[11] upon growing the strength of the acid used (AcOH < < CF_3COOH < HNO_3 < H_2SO_4), the $\nu^s_{NO_2}$ frequency of 1335±5 cm^{-1} of covalent bond O–NO_2 can disappear completely, while the ~1400 cm^{-1} frequency of NO_2^+ appears. The $\nu^s_{NO_2}$ frequency in the Raman spectra of nitronium salts is a characteristic frequency and it directly depends on the power of the anion-forming acid.[9]

Table 1 The calculated and experimental characteristics of acyl nitrates R–C(O)ONO_2.

Compound	R	^{14}N NMR, δ_N/ppm		Raman frequencies $\nu^s_{NO_2}$/cm^{-1}		Calc.[a] O–NO_2 bond length/Å
		Exp. (method), in $CDCl_3$	Calc. ($CDCl_3$)	Exp. (method, solvent)	Calc. [intensity, (a.u.)][a]	
1	Me	–70[10]	–70.00	1308 (CCl_4)[10]	1365.5 (0.63)	1.5257
2a	CH_2Br	–	–73.13	–	1369.5 (0.59)	1.5504
2b	CH_2Cl	–71.5 (1), –71.7 (3)	–73.31	1334 (1, 3, CCl_4)	1370.5 (0.66)	1.5531
2c	CH_2F	–	–73.25	–	1369.5 (0.73)	1.5609
2d	CH_2CN	–	–75.16	–	1370.5 (0.69)	1.5737
3a	$CHBr_2$	– (1)[b]	–75.34	– (1)[b]	1368.0 (0.38)	1.5733
3b	$CHCl_2$	–69.2 (1), –70.0 (2)	–75.85	1336 (3, CCl_4),[c] 1338 (2, CCl_4)	1369.0 (0.66)	1.5765
3c	CHF_2	–	–76.25	–	1362.5 (0.92)	1.5823
3d	$CH(CN)_2$	–	–79.77	–	1370.5 (1.20)	1.6130
4a	CBr_3	–	–76.42	–	1367.0 (0.65)	1.5796
4b	CCl_3	–67.0 (2)	–77.25	1333 (1, CCl_4)	1368.0 (0.78)	1.5869
4c	CF_3	–80[10]	–79.00	1340 (CCl_4, TFA)[10]	1371.0 (0.94), 1371[10]	1.6049, 1.604[10]
4d	$C(CN)_3$	–	–83.73	–	1371.0 (1.71)	1.6613
4e	CF_2CF_3	–79.9[12]	–79.19	1338 (CCl_4),[12] 1339 ($C_2F_5CO_2H$)[12]	1370.0 (0.97)	1.6104, 1.61[12]
4f	$CF(CF_3)_2$	–	–79.60	–	1373.0 (0.77)	1.6084
4g	$C(CF_3)_3$	–	–79.93	–	1373.0 (0.91)	1.6134

[a] For the gas phase.[15] [b] Decomposition of **3a** with Br_2 liberation was observed. [c] The acyl nitrate **3b** is present as an admixture, the main components of the mixture being HNO_3 (1309 cm^{-1})[10,16] and N_2O_4 (1377 cm^{-1}).[16]

A similar correlation is also observed for the $\nu^{as}_{NO_2}$ band that is active in IR spectra, however, this frequency is inactive in Raman spectra. Raman spectroscopy has a number of advantages over IR spectroscopy, and the use of frequency $\nu^{as}_{NO_2}$ as the analytical band is less convenient compared to that of $\nu^s_{NO_2}$.

Unlike nitronium salts, the symmetric vibration of the O_2N–O moiety in covalent acyl nitrates is not characteristic since it is influenced by vibration of the whole molecule. According to quantum chemical calculations performed for CF_3COONO_2 **4c**[10] and $C_2F_5COONO_2$ **4e**,[12] their experimental Raman spectra agree with the calculated spectra of *syn*-conformers. It can be assumed that other EWGs in α-substituted acyl nitrates will not change their most energetically favorable *syn*-conformation. Replacement of hydrogen atoms in acetyl nitrate with EWGs should cause elongation of the O–NO_2 bond and modification of the spectral properties of compounds **2**–**4**. In view of this, we tried to use the changes in the Raman frequencies $\nu^s_{NO_2}$ for evaluation of the polarization of O–NO_2 bonds. One should take into account that the changes in the Raman frequency $\nu^s_{NO_2}$ can be somewhat neutralized by the remoteness of the electron-withdrawing substituents affecting the O_2N–O moiety through three bonds.[12]

The ^{14}N NMR shift δ_N of the nitro group also correlates with the electron-withdrawing properties of the substituent R in $RC(O)ONO_2$: it changes from –70 (R = Me)[10] to *ca.* –80 ppm (R = C_nF_{2n+1}),[10,12] *i.e.*, an upfield shift occurs towards values where the nitronium cation signals are observed (*ca.* –130 ppm). In all cases the accuracy of δ_N measurement was improved using $MeNO_2$ as the internal standard.

In view of the aforesaid, the search for a fine structure–spectral properties relationship as a possible criterion for estimating the nitrating power of a compound with a comparative estimation of the EWG effect on the change in the O_2N–O bond length in acyl nitrates† seems topical. The quantum chemical methods were used to calculate the O–NO_2 bond lengths and to simulate the Raman spectra in the acyl nitrates (gas phase), as well as ^{14}N NMR spectra in $CDCl_3$.

The experimental results obtained (Table 1) revealed no unambiguous correlations between the spectral characteristics (δ_N and $\nu^s_{NO_2}$) of halogen-substituted acyl nitrates and the number of substituents. The experimental values of $\nu^s_{NO_2}$ frequencies for all substituted acyl nitrates **2**–**4** are located in rather a narrow range of 1333–1340 cm^{-1} and are little dependent on the nature and number of EWGs but considerably exceed the value of 1308 cm^{-1} that

† Nitric acid (d_{20} = 1.5 g cm^{-3}) was purified by distillation over sulfuric acid; the colourless fraction was used in the syntheses. Dinitrogen pentoxide was prepared from HNO_3 and P_2O_5[23] and subjected to extra purification over P_2O_5 *in vacuo* (680 Torr). A receiver with N_2O_5 was cooled to –40±5 °C. ^{14}N NMR spectra (21.69 MHz) were recorded on a Bruker AM300 spectrometer with $MeNO_2$ as the internal standard. Raman spectra were recorded on an Acton Research spectrometer with 500 mm focus distance, on a 1200 lines mm^{-1} grid. A CCD from Princeton Instruments cooled with liquid nitrogen was used as the light-sensitive detector for the optical signal. The spectra were measured on the 641.7 nm line of a krypton laser with up to 2 mW power, in the 180° Raman line scattering configuration (back scattering). The spectral resolution was 1.5 cm^{-1}. The optical path of the instrument was designed by the confocal microscope scheme with a spatial resolution of 2 μm. The spectra were recorded for the solutions in sealed glass ampules.

Structure optimizations were computed on the basis of the hybrid density functional B3LYP and 6-311++G(d,p) basis set by Gaussian 09 program package.[15] The positions of stationary points were determined using Hessian matrix analysis based on the absence of imaginary frequencies for the minima. For calculations of ^{14}N NMR chemical shifts, molecules **1**–**4** were localized by PBE0/cc-pVTZ and after that the chemical shifts were calculated by PBE0/6-311+G** using Gauge-Independent Atomic Orbital. Two last steps were performed with $CDCl_3$ as the solvent.

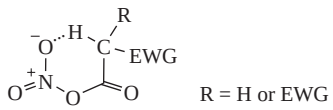
Method 1. Synthesis of acyl nitrates **2b**, **3a**,**b**, **4b** *from acid chlorides and* N_2O_5. Stoichiometric amounts of N_2O_5, a carboxylic acid chloride (0.5 mmol each) and $CDCl_3$ (or CCl_4, 0.4 ml) were mixed in an ampule and then kept at 0–5 °C for 1 day. In the Raman spectra of liquid NO_2Cl and its solutions, the $\nu^s_{NO_2}$ (ν_1) is located at 1291–1293 cm^{-1} (refs. 24, 25) (or 1259 cm^{-1}),[26] while no bands were observed in the region of 1320–1360 cm^{-1}.

Method 2. Synthesis of acyl nitrates **3b**, **4b** *from acid anhydrides and* HNO_3. An acid anhydride (0.7–0.8 mmol), $CDCl_3$ (or CCl_4, 0.4 ml) and HNO_3 (0.60±0.05 mmol) were placed in an ampule at 10–15 °C and stored at 0–5 °C. Spectra were recorded in 1–6 h. The acids formed have no bands in the region 1320–1360 cm^{-1}. The syntheses were carried out with a small excess of acid anhydrides in order to trap nitric acid completely, because the δ_N shift in ^{14}N NMR spectra can be affected by the presence of strong acid.[9]

Method 3. Synthesis of acyl nitrates **2b**, **3b** *from acid anhydrides and* N_2O_5. Dinitrogen pentoxide (0.5 mmol), an acid anhydride (1.5 mmol) and $CDCl_3$ (or CCl_4, 0.4 ml) were mixed in an ampule and kept in a refrigerator for 4 days. A threefold molar excess of a carboxylic acid anhydride was used, since at equimolar ratio this reaction can be reversible and require a long time.

observed for acetyl nitrate **1**. Obviously, the electron-withdrawing action of α-substituents is most likely neutralized both by the remoteness of the substituent and by the involvement of the whole molecule skeleton in the vibrations of the nitro moiety. However, the calculated values of vibration frequencies show the trend of a minor increase, up to 3 cm^{-1}, in the $\nu^{s}_{NO_2}$ frequency of the nitro moiety from mono-substituted nitrate esters **2a**–**d** to trisubstituted ones **4a**–**g**, with simultaneous increase in intensity of the band from ~0.6–0.7 to ~0.8–1.7 a.u. Note that the calculated δ_N values of all acyl nitrates **1**–**4** manifest a trend of an upfield shift with an increase in the number of EWGs.

Apparently, in CH-acidic $Hal_2CHC(O)ONO_2$ compounds acidic proton is readily replaced by a nitro group. This assumption is confirmed by the appearance of a new signal typical[17–20] of the shifts of the C–NO_2 group δ_N –8.5 ppm in the ^{14}N NMR spectra of solutions of $Cl_2CHC(O)ONO_2$. However, the main signal at δ_N –59 ppm, which becomes predominant after storage for 1–3 days, is close to that of N_2O_5 (lit.,[10] –60 ppm). It is known that N_2O_5 can be obtained from 2 equiv. of HNO_3 and 1 equiv. of a carboxylic acid anhydride,[10,21,22] hence N_2O_5 can be formed under the reaction conditions. What is more, we believe that *anti*-conformers of the form $EWGCH(R)C(O)ONO_2$ can be stabilized as cyclic structures **A**, which would inevitably affect spectral characteristics of mono- and disubstituted acyl nitrates in comparison with trisubstituted ones.



R = H or EWG

A

The observed changes in the calculated O–NO_2 bond lengths in the series of halo-substituted acyl nitrates from 1.55–1.56 (monosubstituted compounds **2a**–**c**) to 1.58–1.61 Å (trisubstituted compounds **4a**–**c**) unambiguously indicate that polarization of the O–N bond occurs. Comparison between calculated values for pairs of compounds **4c** and **4g**, **4c** and **4f** (O–N bond lengths, $\nu^{s}_{NO_2}$ and δ_N) agrees with the earlier conclusion[10,12] that the electron-withdrawing effect of the CF_3 group is slightly greater than that of the fluorine substituent. According to calculations (see Table 1), the electron-withdrawing effect of the nitrile group is markedly higher than those of the halogen and trifluoromethyl groups.

In conclusion, studying the effect of α-EWGs on the polarization of the O–NO_2 bond and on the changes in the spectral characteristics in a series of acyl nitrates revealed that their calculated values of $\nu^{s}_{NO_2}$ (gas phase) and δ_N agree well with EWG nature and their number. The experimental values of $\nu^{s}_{NO_2}$ and δ_N for mono- and disubstituted acyl nitrates **2**, **3** (in solutions) lack an unambiguous correlation due to the influence of acidic protons. The results obtained allow one to predict the spectral properties changes of trisubstituted acyl nitrates depending on the type of substituents. A comparative evaluation of the α-substituents of acyl nitrates **1**–**4** showed that the nitrile moiety has the largest electron-withdrawing effect.

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