Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2017, **27**, 31–34
Mendeleev Communications

Trifluoroacetyl nitrate

Victor P. Zelenov,*[a] Sergey S. Bukalov,[b] Larissa A. Leites,[b] Rinat R. Aysin,[b] Alexander N. Subbotin,[a] Marina I. Struchkova[a] and Ivan V. Fedyanin[b]

[a] *N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. E-mail: zelenov@ioc.ac.ru*
[b] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation. E-mail: buklei@ineos.ac.ru*

DOI: 10.1016/j.mencom.2017.01.009

Individual trifluoroacetyl nitrate (TFAN) was synthesized by the reaction of N_2O_5 with trifluoroacetic anhydride (TFAA) and was characterized by ^{13}C, ^{14}N, ^{15}N, and ^{19}F NMR and Raman spectroscopy. In the gas phase TFAN partially decomposes into N_2O_5 and TFAA, and in solutions the equilibrium is shifted to TFAN. Mono nitration of [2.2]paracyclophane with TFAN proceeds in good yields.

The mixtures of HNO_3 with trifluoroacetic anhydride (TFAA) were often employed for nitration and nitrolysis of organic compounds,[1,2] and trifluoroacetyl nitrate (TFAN) was supposed to be a nitrating agent [equation (1)]. There was also a supposition that N_2O_5 and TFAA were formed from these components.[1] An analysis of the peak areas in the ^{19}F NMR spectra of H_2O–HNO_3–TFAA mixtures showed[3] that 2 mol HNO_3 and 1 mol TFAA produced N_2O_5 [equation (3)], while TFAN was formed under the stoichiometric ratio of these components [equation (1)]. This was confirmed by the fact of heat emission maximum in the HNO_3 reaction with TFAA occurred at the component ratio 2 : 1.[4] As was alleged,[5] the TFAN solutions could be prepared by a reaction of any inorganic nitrate with excess TFAA, and the TFAN formation in the reaction of $^{15}NH_4{}^{15}NO_3$ with TFAA was later ascertained by ^{15}N NMR spectroscopy [equation (4)].[6] Significantly, in contrast to acetyl nitrate, which was isolated as a pure compound by distillation, individual TFAN was not still obtained (*e.g.*, due to 'extensive decomposition'[5]). No detailed investigations of TFAA reactions with nitric acid and its derivatives have been undertaken so far.

$$HNO_3 + (CF_3CO)_2O \longrightarrow CF_3COONO_2 + CF_3COOH \quad (1)$$

$$2\,HNO_3 + (CF_3CO)_2O \longrightarrow N_2O_5 + 2\,CF_3COOH \quad (2)$$

$$N_2O_5 + (CF_3CO)_2O \longrightarrow 2\,CF_3COONO_2 \quad (3)$$

$$MNO_3 + (CF_3CO)_2O \longrightarrow CF_3COONO_2 + M^+CF_3COO^- \quad (4)$$

Herein, identification of compounds prepared by these reactions was fulfilled using both literature[7–9] and own experimental ^{14}N, ^{19}F NMR and Raman spectra (Tables 1, 2, see also Online Supplementary Materials). For comparison, $AcONO_2$ was obtained by the reaction of Ac_2O with N_2O_5 or HNO_3 (see Online Supplementary Materials). Note that standard frequencies in the Raman spectra of individual compounds tend to noticeably shift depending on polarity of the medium, intermolecular interactions and complexing with other mixture components.

Table 1 ^{14}N and ^{19}F NMR spectra of the test compounds in different solvents at 22 °C.

Substance	^{14}N NMR, δ/ppm ($\Delta\nu_{1/2}$/Hz)				^{19}F NMR, δ/ppm			
	$CDCl_3$	EtOAc	TFAA	TFA	$CDCl_3$	EtOAc	TFAA	TFA
TFA	–	–	–	–	–76.6, –76.35,[10] –77.00[11]	–78.3	–79.5	–79.5
TFAA	–	–	–	–	–76.1, –75.69,[10] –76.05[11]	–77.5	–79.2	–79.1
CF_3COONH_4	–	–359 (m, *J* 49 Hz)	–	–363 (m, *J* 53 Hz)	–	–78.0	–	–79.4[a]
HNO_3	–45 (10)	–40 (12)	–47 (25),[b] –62 (32)[c,12]	–40 (16), –41 (17)[12]	–	–	–	–
N_2O_5[d]	–60 (35)	–60 (35)	–62 (25),[b] –62 (24)[12]	–62 (25),[b] –59 (40)[12]	–	–	–	–78.3[a]
$AcONO_2$[e]	–70 (30)	–	–	–	–	–	–	–
TFAN	–79 (35)	–80 (90)[f]	–80 (35)	–84 (35)	–73.8	–76.6	–76.7	–78.2[a]
$CF_3COO^{15}NO_2$[g]	–77.2[h]	–	–77.5[h]	–	–	–	–	–
N_2O[i]	–	–144, –229	–145, –230	–146, –231	–	–	–	–

[a] Averaged δ_F due to fast exchange. [b] Immediately after dissolution. [c] The literature δ_N value was ill-defined since a rapid interaction of HNO_3 with TFAA was not considered. [d] In CCl_4: δ_N –58 ppm ($\Delta\nu_{1/2}$ 13 Hz); lit.,[13] –62 ppm. [e] Prepared from Ac_2O and N_2O_5 (1 : 1) in $CDCl_3$, 0.5 h, 20 °C. For $AcONO_2$ prepared from HNO_3–Ac_2O (1 : 1) δ_N –66 ppm ($\Delta\nu_{1/2}$ 30 Hz), with $MeNO_2$ as external standard; lit., δ_N –64 (neat),[13] –68 ppm (in the HNO_3–Ac_2O mixture)[14]. [f] The TFAN signal was broadened possibly due to the EtOAc nitrolysis. [g] ^{15}N NMR in $CDCl_3$–CD_3CN (8 : 2) δ_N 294.1 ppm[6] (–84.6 ppm, calc. from δ_N –378.7 ppm in recorded ^{14}N NMR spectrum of NH_3 in $CDCl_3$ solution). [h] ^{15}N NMR with $Me^{15}NO_2$ as external standard. [i] Lit., δ_N –147 and –231 ppm (MeCN),[15] –140 and –225 ppm,[16] –146.1 and –229.8 ppm (CH_2Cl_2, calc. from δ_N NH_3[g]).[17]

Table 2 Line frequencies of the $\nu^{s}_{NO_2}$ mode[a] in the Raman spectra of various nitro compounds and their solutions.

Substance	Solvent (molar ratio)	$\nu^{s}_{NO_2}$/cm^{-1}	
		Published data	Experimental
HNO_3	CCl_4 (2:1)	–	1296
	Neat[b]	1297,[18] 1299,[19] 1300[9]	–
	AcOH (4:1)	–	1303
	TFA (1:2)	–	1303
	TFA (1:1–4:1)	–	1306–1307
	HNO_3 (100%)	1294 (vs, HNO_3), 1400 (m, NO_2^+)[20]	–
$AcONO_2$[c]	CCl_4 (1:2)	–	1308
	Neat	1320[21]	1309
N_2O_5	CCl_4	1335[22]	1332
	$CHCl_3$	1335[23,24]	–
	$POCl_3$	1337[22]	–
	Gas	1338[24]	–
	Solid	1397 (NO_2^+)[25]	1395 (NO_2^+)
TFAN[d]	CCl_4 (3:1)	–	1340
	TFA (1:1–4:1)[e]	–	1339–1340
	$MeNO_2$ (2:1)	–	1343

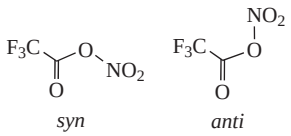
[a] The designation $\nu^{s}_{NO_2}$ is conventional because, according to the results of our NCA calculations, the eigenvectors of these normal modes and participation of the $\nu^{s}_{NO_2}$ coordinate in them substantially vary with a molecule (TFAN, HNO_3 and N_2O_5), *i.e.* the so called $\nu^{s}_{NO_2}$ vibration is not well-localized and is not characteristic by form. For N_2O_5, in-phase symmetric vibration frequencies for two NO_2 groups are given. [b] The H_2O content in HNO_3 was not established. [c] Prepared from Ac_2O and N_2O_5 (1:1, 1 day, 5 °C). [d] Prepared from TFAA and N_2O_5 (1.2:1, 1 day, 5 °C). [e] Equimolar mixture TFAN–TFA was prepared from HNO_3 and TFAA (Figure S9). The spectra were recorded 0.5 h (0–5 °C) after dissolution.

Exothermal effect of the reaction between HNO_3 (d^{20} = = 1.5 g cm^{-3}) and TFAA was observed at 0 °C approximately 5 min later [equation (1)]. Comparative kinetic NMR reaction monitoring showed that TFAA reacted with N_2O_5 [equation (3)] much slower (Tables S1, S3, Online Supplementary Materials), though the equilibrium shifted rightward and TFAN was synthesized in both cases. A new signal at *ca.* –76.6 ppm appeared in the ^{19}F NMR spectra of HNO_3–TFAA (1:1.2) solutions in EtOAc or TFAA (–73.8 ppm in $CDCl_3$), and the ^{14}N NMR spectra of solutions exhibited the only signal at *ca.* –80 ppm that significantly differed from δ_N of HNO_3 and N_2O_5 (Table 1).†

The most intensive lines of starting TFAA in the Raman spectrum of the stoichiometric TFAA–HNO_3 mixture (Figure S9, Online Supplementary Materials) were lacking, whereas the spectrum clearly displayed the lines intrinsic to TFA (256, 403, 416, 434, 813 and 1456 cm^{-1}). It is evident that the equimolar mixture TFAN–TFA has been obtained, and thus a set of pronounced Raman lines with frequencies 213, 314, 504, 599, 772, 891, 1279, and 1339 cm^{-1} could be assigned to the TFAN spectrum. Importantly, a similar set of lines with close frequencies and intensities was also observed in the spectrum of mixtures of TFAN prepared from N_2O_5 with aprotic TFAA [equation (3), Figure S10] and some of the lines showed up in the CCl_4 solution (Figure S11).

Thus, we can regard this 'ensemble' of lines as characteristics of the TFAN Raman spectrum in liquid mixtures.‡ To confirm that the designated set of frequencies belong to TFAN vibrations, a normal coordinate analysis (NCA, being the calculation of normal mode frequencies and eigenvectors as well as their intensities for an isolated TFAN molecule) was undertaken using the DFT method with different functionals and basis sets; a noticeable dependence of the resulting frequencies on the calculation level became apparent (Table S2, Figure S14).

It is worth noting that TFAN is a non-rigid molecule where the hindered internal rotation about ordinary bonds can take place, which could lead to conformational isomerism. According to earlier calculations[26] of the geometry and energy of TFAN *syn*- and *anti*-conformers around the C–O bond with the flat C–C(O)–O–N backbone, and for an isolated molecule the *syn*-conformer is more stable. As molecular conformations in gas and liquid phases, particularly in polar media, often disagree, we performed NCA calculations for both conformers. The geometry optimisation resulted in the NO_2 group located outside of the C–C(O)–O–N plane and turned perpendicular to it (Figure S13). The calculated spectra of TFAN *syn*- and *anti*-conformers differed significantly, and *syn*-conformer frequencies and Raman intensities appeared closer to the experiment.



syn *anti*

TFAN shifts (*ca.* –80 ppm) in the ^{14}N NMR spectra were close to those for covalent acetyl nitrate and N_2O_5 (–70 and –62 ppm, respectively, Table 1) and differed significantly from the signal of nitronium salts (*ca.* –130 ppm[27]). It can be concluded that TFAN in organic solutions has a covalent structure. This was confirmed by the comparison of the Raman spectra of TFAN with those of other nitro compounds (Table 2). The single TFAN line $\nu^{s}_{NO_2}$ (1340 cm^{-1}) was closer to respective frequencies of covalent nitro compounds ($AcONO_2$, N_2O_5) and substantially different from the diagnostic line of NO_2^+ (~1400 cm^{-1}).[28] The Raman spectra of TFAN in solvents (Table 2) did not reveal the presence of nitronium cation. Also, there was no NO_2^+ signal present in the ^{14}N NMR spectra of the TFAA–TFAN mixture

† *Trifluoroacetyl nitrate*. **Caution!** TFAN is explosive!

Method A. Ammonium nitrate (3.20 g, 40 mmol) was added to TFAA (6 ml) with stirring at 5 °C in a flask fitted with a Liebig condenser and condensate receiver containing a solvent (5 ml). The mixture was stirred and heated cautiously to 20–25 °C for ~0.5 h. The reaction proceeded exothermally. The liquid began to boil (bp 27–28 °C) and the reaction mass, at first, was thermostatted with a water bath (25–30 °C) and then heated, as may be required. Vapours were condensed and collected in a receiver cooled with ice. Distillation was terminated when the reaction mass temperature reached 45 °C. The mixture TFAN–TFAA (2.2 g, 3:2) in the organic solvent solution was obtained (yield 40%, calc. from the mass gain and from the TFAN–TFAA ratio in the ^{19}F NMR spectra).

Method B. Dichloromethane (15 ml), TFAA (10 ml, 15 g, 71 mmol) and HNO_3 (2.5 ml, 3.75 g, 60 mmol) were placed with stirring to a 50 ml flask fitted with a fractional column, Liebig condenser and condensate receiver with a calcium chloride tube. The mixture was heated gradually to 32–34 °C until boiling (bp 29 °C). The bath temperature was 46–48 °C. Vapours were condensed and collected in the receiver cooled with ice. After the distillation completion (~1.5 h, bp 34–35 °C), the prepared TFAN solution in CH_2Cl_2 was utilized or stored in a freezer. The solution (25.90 g) with the ratio TFAN:TFAA = 100:9 (^{19}F NMR) was obtained. The TFAN concentration in solution (232 mg g^{-1}) was determined against internal standard $MeNO_2$ (in the ^{14}N NMR spectrum of the weighed sample in $CDCl_3$). TFAN yield was 6.01 g (64%).

Method C. The reaction was carried out under argon atmosphere. TFAA (1.37 g, 6.54 mmol) was added to N_2O_5 (0.70 g, 6.54 mmol), stirred at 0–5 °C until full dissolution and placed in a fridge for one week. TFAN concentration in the sample ⩾ 91 mol%, TFAA ⩽ 9 mol%. TFAN is able to overcool up to *ca.* –90 °C, mp –(33–30) °C. ^{13}C NMR ($CDCl_3$) δ: 154.90 (q, CO, *J* 45.5 Hz), 114.16 (q, CF_3, *J* 287.2 Hz).

‡ For safety reasons TFAN Raman spectra were recorded only in solutions.

obtained by careful distillation of the TFAA–NH_4NO_3 mixture. The spectra of TFA or EtOAc solutions of this mixture contained the only signal at *ca.* –80 ppm of TFAN. These data give reason to consider that in organic solvents the ionic structure $[NO_2]^+[CF_3COO]^-$ cannot arise from covalent TFAN, as supposed earlier.[3,5,12]

A clear TFAN signal at –84±2 ppm was observed in the ^{14}N NMR spectra of the solutions obtained by stirring of inorganic nitrates [KNO_3, $NaNO_3$, $AgNO_3$, $Ca(NO_3)_2{\cdot}4H_2O$, $Pb(NO_3)_2$, $Cu(NO_3)_2{\cdot}3H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, $Hg(NO_3)_2{\cdot}0.5H_2O$, and NH_4NO_3] in excess TFAA at 15–20 °C for 0.5–1 h [equation (4)]. This means that nitrate ester could be generated in an excess TFAA actually from any inorganic nitrate,[5] provided that the latter does not possess redox properties.§ Possibly, the reaction is an equilibrium because all anhydrous salts in TFAA changed their structures and were transformed into fine powders, whereas the concentration of TFAN in solutions was relatively low.

The synthesis of TFAN from the HNO_3–TFA mixture in the presence of $Na^{15}NO_3$ was reported;[29] however, this fact gave rise to doubt. In particular, the shift at 308.9 ppm¶ observed in the ^{15}N NMR spectrum of the mixture was markedly different from the signal at 294.1 ppm of $CF_3COO^{15}NO_2$ prepared from $NH_4{}^{15}NO_3$ and TFAA.[6] It is evident that to break the N–OH bond of nitric acid it is necessary to bond the formed water, *e.g.* as a hydroxonium cation by an excess of strong acid [equation (5), see. refs. 20, 30–32]. This result could also be achieved with the assistance of a dehydrating agent (*e.g.* P_2O_5,[33] TFAA[34]). Weak organic acids such as AcOH do not react with HNO_3 as it was reported.[30] That is why the synthetic route to $CF_3COO^{15}NO_2$ from HNO_3 and TFA in the $Na^{15}NO_3$ presence[29] should be verified.

With this in mind, we prepared the HNO_3 solution in TFA with the $NaNO_3$ additive using the reported[29] ratio and with $MeNO_2$ as a solvent. In the ^{14}N NMR spectrum of the prepared solution, δ_N –45 ppm ($\Delta\nu_{1/2}$ 12 Hz) was only observed, which is typical of HNO_3 solutions *per se*. In the Raman spectra of the HNO_3 mixtures in TFA, $\nu^s_{NO_2}$ frequencies were found at 1303–1307 cm^{-1} (Table 2), which was another evidence of the TFAN (1340 cm^{-1}) absence. TFA (pK_a = 0.23) is a weaker acid than HNO_3 (pK_a = –1.44) or other mineral acids, consequently, the equilibrium was shifted towards the starting compounds [equation (6)].

$$HNO_3 + 2\,H^+X^- \longrightarrow NO_2^+\,X^- + H_3O^+\,X^- \quad (5)$$

$$X^- = NO_3^-,\ F^-,\ HSO_4^-,\ CF_3SO_3^-,\ ClO_4^-$$

$$HNO_3 + 2\,CF_3COOH \not\rightarrow CF_3COONO_2 + H_3O^+CF_3COO^- \quad (6)$$

Nitration in aprotic medium is often used where nitro compounds are sensitive to strong acids. TFAN is well suitable for such syntheses due to its strong nitration power and low medium acidity. As described above, a few methods exist to prepare the TFAN solution from TFAA.

A shortcoming of the TFAA–NH_4NO_3 mixture is by-production of CF_3COONH_2[6] whose nitration consumes TFAN partially. We managed to obtain amide-free solutions containing TFAN by careful distillation of reaction mixture. That was the pathway to prepare TFAN–TFAA (~3:2, ^{19}F NMR data) solutions (Table S1). Note that dinitrogen pentoxide is present in the CCl_4 solution (11 mol%, ^{14}N NMR), but in polar solvents ^{14}N NMR spectra contained only broadened signal of TFAN.

Quantum chemical calculations of the equilibrium constant of the TFAN decomposition in the gas phase under normal conditions (298 K, 0.1 MPa) showed that it was close to 1 [equation (7)]. Theoretically, up to 15 mol% of N_2O_5 could be found in vapours.

$$2\,CF_3COONO_2 \overset{\text{gas}}{\rightleftharpoons} N_2O_5 + (CF_3CO)_2O \quad (7)$$

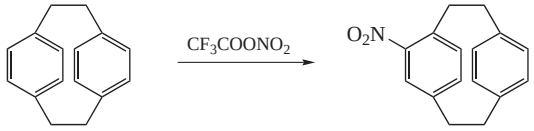
Meanwhile, NMR studies made it possible to establish that in solutions the equilibrium was shifted toward TFAN [equation (3)]. It is exactly a low rate of TFAN formation in the CCl_4 solution, which enabled to detect N_2O_5 as result of the thermally induced partial decomposition of TFAN in the course of distillation.

Obviously, it is impossible to obtain a spectrum of individual TFAN as gas under normal conditions. For this reason, the assignment of the photoelectron spectrum obtained for gaseous products of the CF_3COOAg reaction with NO_2Cl to TFAN[26] seems unfounded.

Recently we have shown that the TFAA–HNO_3 mixture together with strong acid could be a source of solid nitronium salt (*e.g.* $NO_2CF_3SO_3$ yields 71–83%).[34] Formed in this reaction TFA is distinguished by a good dissolving capacity. An additional inert solvent (CH_2Cl_2) to reduce nitronium salt solubility is needed. The TFA-free TFAN solution in CCl_4 obtained from the TFAA–NH_4NO_3 mixture by distillation allowed us to obtain $NO_2CF_3SO_3$ in quantitative yield.

TFAN is stable when stored in an inert aprotic media at ⩽5 °C, whereas in the presence of acids it is decomposed to N_2O_4 (also see ref. 3). Main disadvantages of the TFAN preparation by distillation from TFAA–NH_4NO_3 mixture are low yield (40%) and explosion risk. The best method to prepare a TFA-free solution of TFAN is azeotropic distillation of the TFAN–CH_2Cl_2 mixture from the TFAA–HNO_3–CH_2Cl_2 composition with TFAN yield up to 64%. The most facile synthetic route to TFAN solutions is stirring of inorganic nitrate with excess TFAA. The $CF_3COO^{15}NO_2$ solution was prepared from $K^{15}NO_3$ in this manner. The concentration of TFAN obtained from KNO_3 and TFAA was rather low though sufficient for successful nitration.

TFAN solutions have been often used for nitration.[5,6,29,35] Our successful nitration of [2.2]paracyclophane **1** is a bright example of its application (Scheme 1). Up to now, mono nitration of compound **1** has been a challenge because, first, this molecule possesses several reaction sites and, second, its polycyclic system can be easily broken by acids. The previously used HNO_3–AcOH mixtures lead to polysubstitution of this molecule, its partial decomposition and, as a consequence, to a low yield of 4-nitro-[2.2]paracyclophane **2** (23–49%).[36,37] Nitration in the presence of H_2SO_4 was accompanied by significant resinification.[37] An unusual nitration method was elaborated for the high-yield synthesis of compound **2**, by ion-exchange resin impregnated with nitric acid.[38] However, incorrect values of ν_{NO_2} frequencies in the IR spectrum for the aromatic nitro group of the product (1196 and 1519 cm^{-1}; lit.,[36(a),(b),39] $\nu^{as}_{NO_2}$ 1340–1342 and $\nu^s_{NO_2}$ 1512–1515 cm^{-1}), difference from the known ^1H, ^{13}C NMR data,[36(c),40] and lacking melting point, ^{14}N (^{15}N) NMR and X-ray analysis data for this compound prevent from considering these results[38] credible.



1 **2**

Scheme 1

§ Nitrates $Mn(NO_3)_2{\cdot}6H_2O$ and $CrO_2(NO_3)_2$ participated in redox reactions; colour changes of solutions and TFAN signal absence were observed.

¶ With $^{15}NH_3$ as external standard.

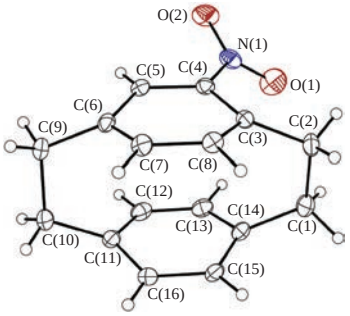


Figure 1 Molecular structure of 4-nitro[2.2]paracyclophane **2**.

Nitration of compound **1** with TFAN *in situ* generated from anhydrous nitrate (KNO_3, $AgNO_3$) and TFAA made it possible to obtain nitro compound **2** under normal conditions (25–35 °C, 2–3 h) in 62–77% yield.†† Where crystalline hydrates of nitrates were used, TFA generated from TFAA accelerated the occurrence of TFAN and subsequent nitration of compound **1**; however, the increase in acidity led to the molecule skeleton destruction. For instance, 0.5 mol $Hg(NO_3)_2 \cdot 0.5H_2O$ enabled accomplishing the synthesis within 10 min, though the yield of compound **2** dropped to 39%. With $Zn(NO_3)_2 \cdot 6H_2O$ the resinification proceeded faster than nitration. The structure of compound **2** (block-shaped slightly yellow crystals) was established by a single-crystal X-ray diffraction analysis (Figure 1). The conformation, bond lengths and angles observed for the arene **2** moiety were typical of similar compounds. The nitro group rotated by 39.47(17)° relative to the average plane of four central carbon atoms of the substituted ring.‡‡

In conclusion, TFAN is a convenient reagent to prepare nitronium salts and nitro compounds, also it may be suitable for creating new organic nitrogen–oxygen systems.[41]

This work was supported by the Russian Foundation for Basic Research (project nos. 16-03-00713 and 16-29-01042-ofi_m).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2017.01.009.

References

1 J. H. Robson and J. Reinhart, *J. Am. Chem. Soc.*, 1955, **77**, 2453.
2 (*a*) J. H. Robson, *J. Am. Chem. Soc.*, 1955, **77**, 107; (*b*) R. Reed, *J. Org. Chem.*, 1958, **23**, 775; (*c*) J. A. Young, S. N. Tsoukalas and R. D. Dresdner, *J. Am. Chem. Soc.*, 1958, **80**, 3604; (*d*) M. D. Coburn and H. E. Ungnade, *J. Heterocycl. Chem.*, 1965, **2**, 308; (*e*) M. Shin, T.-H. Ha, K.-H. Chung, J. S. Kim and Y. G. Kim, *Appl. Chem. Eng.*, 2014, **25**, 188.
3 M. G. Harriss and J. B. Milne, *Can. J. Chem.*, 1971, **49**, 2937.
4 V. G. Tsvetkov, V. A. Shmakov, V. F. Sopin, A. V. Ivanov, A. A. Ikonnikov and G. N. Marchenko, *J. Gen. Chem. USSR (Engl. Transl.)*, 1989, **59**, 1220 (*Zh. Obshch. Khim.*, 1989, **59**, 1376).

†† For details of procedure and analytical data for compound **2**, see Online Supplementary Materials.

‡‡ *Crystallographic data for* **2**. Block-shaped slightly yellow crystals, monoclinic, space group *Cc*, at 120 K: a = 14.3470(3), b = 7.3942(2) and c = 11.5916(2) Å, β = 91.3430(10)°, V = 1229.35(5) Å^3, Z = 4 (Z' = 1), d_{calc} = 1.369 g cm^{-3}. Intensity data of 36041 reflections were collected on a Bruker APEX DUO diffractometer [λ(MoKα) = 0.71073 Å, $2\theta < 80.0°$] and 7474 independent reflections (R_{int} = 0.0382) were used in the calculations. The structure was solved by direct methods and refined by the full-matrix least-squares technique against F^2 in the anisotropic approximation. Hydrogen atoms were placed in calculated positions and refined in the riding model. The refinement converged to R_1 = 0.0446 [for 6484 reflections with $I > 2\sigma(I)$], wR_2 = 0.1190 and GOF = 1.023. All calculations were performed with a SHELX software package.[42]

CCDC 1456828 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

5 J. V. Crivello, *J. Org. Chem.*, 1981, **46**, 3056.
6 P. Romea, M. Aragones, J. Garcia and J. Vilarrasa, *J. Org. Chem.*, 1991, **56**, 7038.
7 V. A. Shlyapochnikov, *Kolebatel'nye spektry alifaticheskikh nitrosoedinenii (Vibrational Spectra of Aliphatic Nitro Compounds)*, Nauka, Moscow, 1989 (in Russian).
8 B. Schrader, *Raman/Infrared Atlas of Organic Compounds*, 2nd edn., VCH, Weinheim, 1989.
9 C. K. Ingold and D. J. Millen, *J. Chem. Soc.*, 1950, 2612, and references cited therein.
10 M. C. Davis and T. J. Groshens, *Synth. Commun.*, 2011, **41**, 255.
11 T. P. Smith and B. W. Corby, *J. Org. Chem.*, 1998, **63**, 8946.
12 M. I. Khalil, *Inorg. Chem.*, 1990, **29**, 5131.
13 K. F. Chew, M. A. Healy, M. I. Khalil, N. Logan and W. Derbyshire, *J. Chem. Soc., Dalton Trans.*, 1975, 1315.
14 M. Haouas, S. Bernasconi, A. Kogelbauer and R. Prins, *Phys. Chem. Chem. Phys.*, 2001, **3**, 5067.
15 Yu. A. Strelenko and N. M. Sergeyev, *J. Mol. Struct.*, 1996, **378**, 6.
16 B. Wrackmeyer, *Z. Naturforsch.*, 2011, **66b**, 1079.
17 G. A. Olah, R. Herges, K. Laali and G. A. Segal, *J. Am. Chem. Soc.*, 1986, **108**, 2054.
18 B. Susz and E. Briner, *Helv. Chim. Acta*, 1935, **18**, 378.
19 J. E. Harrar and R. K. Pearson, *J. Electrochem. Soc.*, 1983, **130**, 108.
20 J. E. Harrar, L. P. Rigdon and S. F. Rice, *J. Raman Spectrosc.*, 1997, **28**, 891.
21 J. Chédin and S. Fénéant, *Compt. Rend.*, 1949, **229**, 115.
22 J. Chedin and J. C. Pradier, *Compt. Rend.*, 1936, **203**, 722.
23 J. Chedin, *Compt. Rend.*, 1935, **201**, 552.
24 I. C. Hisatsune, P. Devlin and Y. Wada, *Spectrochim. Acta*, 1962, **18**, 1641.
25 W. W. Wilson and K. O. Christe, *Inorg. Chem.*, 1987, **26**, 1631.
26 X. Zeng, L. Yao, W. Wang, F. Liu, Q. Sun, M. Ge, Z. Sun, J. Zhang and D. Wang, *Spectrochim. Acta, Part A*, 2006, **64**, 949.
27 (*a*) J. Mason and K. Christe, *Inorg. Chem.*, 1983, **22**, 1849; (*b*) Th. M. Klapötke, G. McIntyre and A. Schulz, *J. Chem. Soc., Dalton Trans.*, 1996, 3237; (*c*) G. A. Olah, B. G. B. Gupta and S. C. Narang, *J. Am. Chem. Soc.*, 1979, **101**, 5317.
28 G. A. Olah, G. K. Surya Prakash, Á. Molnár and J. Sommer, *Superacid Chemistry*, 2nd edn., John Wiley & Sons, Hoboken, 2009, ch. 4.
29 G. A. Olah, V. P. Reddy and G. K. S. Prakash, *Synthesis*, 1992, 1087.
30 C. C. Addison, *Chem. Rev.*, 1980, **80**, 21.
31 S. S. Odokienko, N. V. Latypov, I. N. Shokhor, Yu. A. Fedorov and E. N. Vishnevskii, *Zh. Prikl. Khim.*, 1978, **51**, 683 (in Russian).
32 F. P. Del Greco and J. W. Gryder, *J. Phys. Chem.*, 1961, **65**, 922.
33 C. W. Schoenfelder and M. S. Cohen, *Patent US 3244474*, 1966.
34 V. P. Zelenov, V. A. Tartakovsky and S. S. Bukalov, *Patent RU 2558115 C1*, 2015.
35 (*a*) R. D. Bach, T. H. Taaffee and J. W. Holubka, *J. Org. Chem.*, 1980, **45**, 3439; (*b*) P. Dampawan and W. W. Zajac, Jr., *Synthesis*, 1983, 545; (*c*) A. G. Anderson, Jr., E. R. Davidson, E. D. Daugs, L. G. Kao, R. L. Lindquist and K. A. Quenemoen, *J. Am. Chem. Soc.*, 1985, **107**, 1896; (*d*) B. Masci, *J. Org. Chem.*, 1985, **50**, 4081; (*e*) S. C. Suri and R. D. Chapman, *Synthesis*, 1988, 743; (*f*) E. Carvalho, J. Iley, F. Norberto and E. Rosa, *J. Chem. Res. (S)*, 1989, 260; (*g*) W. Rank, *Tetrahedron Lett.*, 1991, **32**, 5353; (*h*) D. Korakas and G. Varvounis, *J. Heterocycl. Chem.*, 1996, **33**, 611; (*i*) C. Serra, C. Aragones, J. Bessa, J. Farras and J. Vilarrasa, *Tetrahedron Lett.*, 1998, **39**, 7575; (*j*) Y. Miki, M. Umemoto, H. Maruyama, M. Kuromatsu and H. Hamamoto, *Heterocycles*, 2007, **71**, 2457; (*k*) A. R. Katritzky, A. V. Vakulenko, J. Sivapackiam, B. Draghici and R. Damavarapu, *Synthesis*, 2008, 699; (*l*) K. Smith, M. D. Ajarim and G. A. El-Hiti, *Catal. Lett.*, 2010, **134**, 270; (*m*) G. Aridoss and K. K. Laali, *J. Org. Chem.*, 2011, **76**, 8088; (*n*) D. A. Skladchikov, A. A. Fatykhov and R. R. Gataullin, *Russ. J. Org. Chem.*, 2014, **50**, 48 (*Zh. Org. Khim.*, 2014, **50**, 55); (*o*) G. G. Mazgarova and R. R. Gataullin, *Russ. J. Gen. Chem.*, 2014, **84**, 672 (*Zh. Obshch. Khim.*, 2014, **84**, 592).
36 (*a*) D. J. Cram and N. L. Allinger, *J. Am. Chem. Soc.*, 1955, **77**, 6289; (*b*) B. E. Norcross, D. Becker, R. I. Cukier and R. M. Schultz, *J. Org. Chem.*, 1967, **32**, 220; (*c*) M. Draĉinsky, P. Jansa and P. Bouř, *Chem. Eur. J.*, 2012, **18**, 981.
37 H. J. Reich and D. J. Cram, *J. Am. Chem. Soc.*, 1969, **91**, 3527.
38 J. Lahann, H. Höcker and R. Langer, *Angew. Chem. Int. Ed.*, 2001, **40**, 726.
39 H. J. Reich and D. J. Cram, *J. Am. Chem. Soc.*, 1969, **91**, 3534.
40 L. Ernst, *Liebigs Ann. Chem.*, 1995, 13.
41 S. G. Zlotin, A. M. Churakov, O. A. Luk'yanov, N. N. Makhova, A. Yu. Sukhorukov and V. A. Tartakovsky, *Mendeleev Commun.*, 2015, **25**, 399.
42 G. M. Sheldrick, *Acta Crystallogr., Sect. C*, 2015, **71**, 3.

Received: 7th July 2016; Com. 16/4988