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Cyano-, Nitro- and Nitrosomethane Derivatives: Structures and Gas-Phase Acidities

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The structures and gas-phase acidities of resonance-stabilized methane/methanide derivatives ($H[CR^1R^2R^3]$/$[CR^1R^2R^3]^-$ with $R^{1,2,3}$ = H, NO_2, NO, and CN) have been studied through B3LYP/aug-cc-pvTZ computations. The gas-phase acidities lie in the range 1523–1459 for singly, 1365–1304 for doubly and 1274–1203 kJ mol^{-1} for triply substituted methane derivatives. In the NO-substituted methanides, protonation always occurs at the nitroso group, leading to the corresponding oxime. For the cyano- and nitromethane derivatives the C–H bonded isomer was found to be the more stable species. For mixed CN/NO_2-substituted methanides, protonation of the nitro group is energetically favourable except for the simplest cyanonitromethanide in which protonation occurred at the central carbon. Significant resonance effects occur in all three classes of methanides (NO_2-, NO- and CN-substituted). However, the magnitude of this effect differs significantly depending on the degree of substitution.

Introduction

We recently investigated the structure, bonding and resonance stabilization of methanides of the type $[CR^1R^2R^3]^-$ ($R^{1,2,3}$ = H, NO, NO_2 and CN).[1,2] This study revealed planar methanide anions with shortened C–NO, C–NO_2 and C–CN bond lengths, indicative of the presence of delocalized π bonds over the entire anion. MO and NBO[3] calculations displayed the existence of an $n\pi$-electron, m-centre bond unit in all of the methanides (with $n = 2 + 4x + 2y + 2z$ and $m = 1 + 3x + 2y + 2z$; x, y and z are equal to the number of NO_2, NO and CN groups, respectively). Such methanides can be regarded as resonance-stabilized pseudohalides.[2,4] The strongest resonance effect was found for the NO-substituted anions followed by the NO_2 species. For NO- and NO_2-substituted methanides, intramolecular hydrogen bonds stabilize the singly and doubly substituted methanides in the energetically favoured isomers, whereas the absence of such hydrogen bonds results in nonplanar anions of the trinitroso- and trinitromethanides due to electrostatic repulsion between lone pairs localized on the oxygen atom of the NO and NO_2 groups, respectively. Cyanomethanides are always planar. However, delocalization of the methanide lone pair onto the CN group is much less pronounced than with the NO and NO_2 analogues. Generally,[5–8] the synthesis of methanides starts from the free hydrogen acid, which often is only generated in situ.

Strong resonance effects have already been found by Vianello and Maksić to be the key to finding "ultrastrong Brønsted neutral organic superacids" based on the pentasubstituted cyclopentadiene framework [e.g., $(CN)_5C_5H$].[5] These authors successfully investigated other frameworks with accompanying percyanation in their search for enhanced acidity, including cyclononatetraene,[5c] indene,[5a] fluorine[5e] and other benzoannelated cyclopentadienes,[5a,5b] phenalene,[5b] "azatriquinanes"[6] and "Rees hydrocarbons".[5f] Moreover, it was found that polysubstituted methanes bearing a variety of strongly electron-withdrawing groups (F, Cl, Br, NC, CN and NO_2) exhibit significantly enhanced acidity. A detailed ("triadic") analysis reveals that the most important term influencing the ΔH_{acid} values is Koopmans' ionization energy of the final ions formed upon deprotonation. In other words, the negative charge is strongly stabilized in the conjugate bases.

Owing to the expected strong resonance effects in cyano-, nitro- and nitrosomethanides we decided to investigate the structures and gas-phase acidities of the corresponding acids, which then raises the question as to whether protonation occurs on the central methanide carbon atom or on one of the functional groups. Herein, we report on the potential energy surfaces of various cyano-, nitro- and nitrosomethane derivatives and their gas-phase acidities.

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Results and Discussion

We have used the following general abbreviations: N = nitroso, Nt = nitro, C = cyano and M = methanide, and the "numerals" D = di and T = tri. For example, HNtDCM represents protonated nitrodicyanomethanide.

Energetics and Structure

It is common knowledge that methane is tetrahedral and its deprotonated species trigonal pyramidal ($\Delta_{298}G_{\text{planar–nonplanar}}$ = 10.0 kJ mol^{-1}).[7] However, the question arises as to what is the structure of a methane derivative in which hydrogen atoms are substituted by functional groups such as CN, NO_2 and NO. Of special interest is the effect of delocalization in the structure and the energetics of the different possible tautomers. In principle, at least two different tautomers should be observed in cyano-, nitro- and nitrosomethanes because protonation of the corresponding resonance-stabilized methanides might occur at the central carbon atom, at the terminal nitrogen atom of the cyano group or at the oxygen atom of the nitro and nitroso groups (Figure 1). When protonation occurs on the functional group, the acid is customarily called the *aci* tautomer, in contrast to the C–H bound methane derivative.

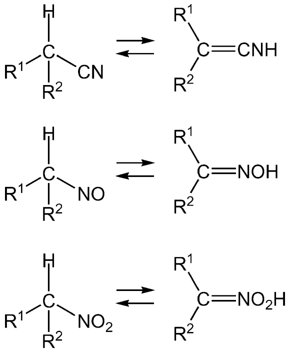

Figure 1. C–H bound versus *aci* tautomers of protonated cyano-, nitro- and nitrosomethane derivatives.

Cyanomethanes

Polycyanogen compounds [$H_{4-n}C(CN)_n$, with n = 1–3] are a class of molecules that exhibit both unusual chemical reactivity as well as peculiar physical properties and, therefore, have repeatedly attracted attention.[8]

Two isomers have been found for all three cyanomethanes: a C–H bound cyanomethane and an *aci* species (Figures 1 and 2), the latter always being the higher-lying isomer. (Other isomers such as isonitriles and azirines were ignored in the current study.)

Cyanomethane (HCM; acetonitrile) is energetically preferred over the *aci* compound (ketenimine, vinylideneamine) by $\Delta_{298}G$ = 92.4 kJ mol^{-1}. The energy difference between the two isomers decreases significantly with increasing cyano substitution (Figure 2). Although the difference is still fairly large at 48.5 kJ mol^{-1} for the dicyanomethane (HDCM, malononitrile) compared with the corresponding *aci* compound (cyanoketenimine, 3-iminoacrylonitrile), a difference of only 2.9 kJ mol^{-1} is computed in favour of tricyanomethane (HTCM, cyanoform, 2-cyanomalononitrile) compared with the *aci* acid (dicyanoketenimine, 2-iminomethylenemalononitrile). Delocalization of the methanide lone pair improves with increasing substitution[2] so that the basicity of the central carbon atom decreases ($CM^- > DCM^- > TCM^-$) and protonation at the terminal N atom of the cyano group relative to the central C atom is less expensive.

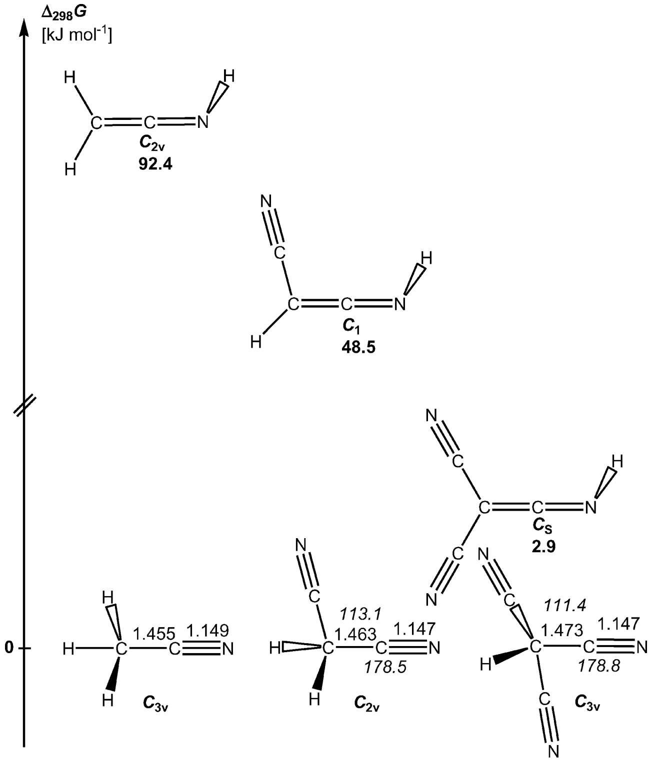

Figure 2. Isomers of cyanomethanes [bond lengths in Å, angles (italics) in degrees with the relative Gibbs energies and symmetries given in bold].[10]

Structures

Bond lengths and angles have only a small dependence on substitution. The C–C–N moiety remains essentially linear, whereas the C–C–C angle slightly decreases from 113.1 to 111.4° and the C–C distance increases slowly in the order HCM < HDCM < HTCM (1.455, 1.463 and 1.473 Å, respectively), which is in accord with experimental data.[8,9]

Nitromethanes

Nitromethanes, which are easily prepared by a range of reactions [e.g., CH_3NO_2 by nitration of ether or alcohol or the reaction of $NaNO_2$ with CH_3I[11] and $H_2C(NO_2)_2$ by protonation of $KHC(NO_2)_2$ with HF][12] and have been structurally characterized in the gas phase by means of microwave studies in the early 1970s.[13] Tetranitromethane and its "denitration" to nitroform [$HC(NO_2)_3$] were reported in 1899 by Hantzsch and Rinckenberger.[14]

Nitromethane (HNtM)

Three isomers of HNtM have been studied (Figure 3). The most stable isomer is the C–H bound nitromethane followed by *aci*-nitromethane, which is 59.8 kJ mol^{-1} less stable. In the highest-energy isomer both oxygen atoms of the nitro group are protonated and it is 221.5 kJ mol^{-1} less stable. The latter species can be formally regarded as a singlet carbene, that is, it is recognized as (*N*,*N*-dihydroxyamino)methylene.

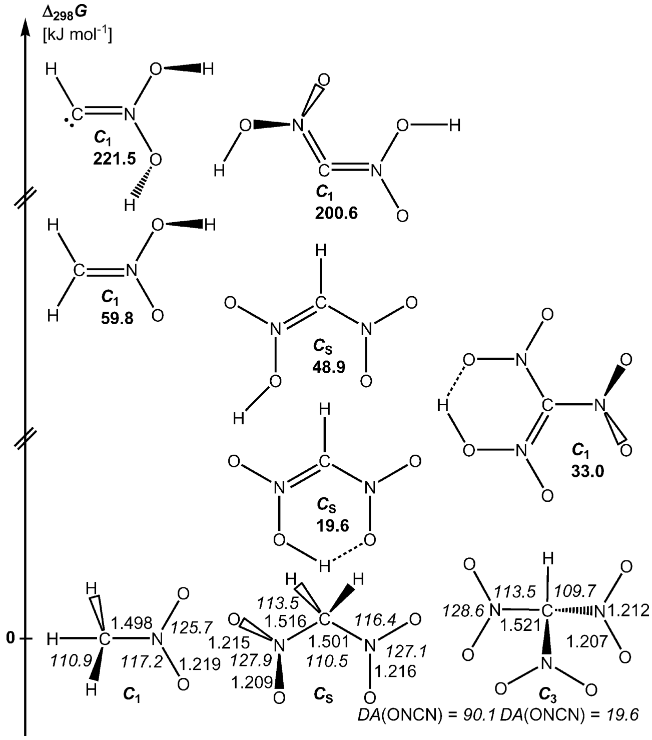

Figure 3. Isomers of the nitromethanes [bond lengths in Å, angles (italics) in ° with the relative energies and symmetries given in bold; DA = dihedral angle]. For simplification, we have not shown any double or partial bonds between the constituent atoms of the nitro groups.[10]

Dinitromethane (HDNtM)

For the C_s-symmetric HDNtM again the methane species was found to be the most stable isomer, energetically favoured by 19.6 kJ mol^{-1} over the planar C_s-symmetric nitro-*aci*-nitromethane (*aci*-HDNtM), which is stabilized by an intramolecular hydrogen bond (Figure 3). As displayed by the second *aci*-nitromethane isomer, in the absence of such a hydrogen bond, the energy rises to 48.9 kJ mol^{-1}. Moreover, one further high-energy isomer was found at 200.6 kJ mol^{-1} in which both nitro groups are protonated. One other isomer in which one of the nitro groups is doubly protonated, that is, $O_2N–C–N(OH)_2$, was ignored here, as it was assumed that it would be exceptionally high in energy, as shown for nitromethane and its corresponding isomer.

Trinitromethane (HTNtM)

In contrast to the series of cyanomethanes, the gap between the C–H bound and *aci*-nitromethanes increases from HDNtM to HTNtM (HDNtM: 19.6, HTNtM: 33.0 kJ mol^{-1}). *aci*-HDNtM is a planar molecule with three intramolecular hydrogen bonds (O···H···O and two C–H···O contacts), whereas only one (O···H···O) can be formed in HTNtM, which results in a nonplanar structure (Figure 3). Such intramolecular stabilization by hydrogen bonds is not possible in cyanomethanes, as the π bonds of the cyano groups are much poorer electron-pair donors than the oxygen atoms of the nitro groups.

Indeed, when taking into account the *aci*-dinitromethane that does not form an intramolecular hydrogen bond between the two NO_2 groups, a similar series is found with the energy gap decreasing along the series: 59.8 (HNtM) > 48.9 (HDNtM) > 33.0 kJ mol^{-1} (HTNtM).

Structures

All three nitromethanes (HNtM, HDNtM and HTNtM) are nonplanar. In C_s-symmetric HDNtM both nitro groups are twisted by 90.1°, which still allows resonance stabilization along the two O_2NCN moieties. HTNtM is C_3 symmetric with a propeller-like structure (dihedral angle along ONCN 19.6°). With an increasing degree of substitution, the C–N bond lengths increase (HNtM: 1.498, HDNtM: 1.516, HTNtM: 1.521 Å), the N–O bond lengths decrease (HNtM: 1.219, HDNtM: 1.215/1.209, HTNtM: 1.212/1.207 Å), whereas the O–N–O angles are almost unaffected by a higher degree of substitution [cf. HNtM: $d_{\mathrm{exp}}(\mathrm{C–N}) = 1.489(5)$, $d_{\mathrm{exp}}(\mathrm{N–O}) = 1.224(5)$ Å;[13a] HTNtM: $d_{\mathrm{exp}}(\mathrm{C–N}) = 1.505(5)$, $d_{\mathrm{exp}}(\mathrm{N–O}) = 1.219(2)$ Å].[13b]

Nitrosomethanes

Nitrosomethane (HNM, $CH_3–NO$) was first isolated by Coe and Doumani[15] by photolysis of gaseous *tert*-butyl nitrite in 1948 [Equation (1)], whereas in 1936 Staveley and Hinshelwood[16] had found that addition of small quantities of nitric oxide to the reaction vessel during the pyrolytic decomposition of diethyl ether brought about a considerable reduction of the decomposition reaction rate (by the trapping of radicals with NO).

$$(CH_3)_3CONO \xrightarrow{h\nu} (CH_3)_2CO + CH_3NO \qquad (1)$$

HNM is known to be less stable than its isomer formaldoxime (*aci*-HNM) and early attempts to isolate this species failed owing to its facile isomerization to the oxime (*aci*-HNM). Bamberger and Seligman had already considered in 1903 that it would be difficult to isolate nitrosomethane after oxidation of methylamine due to its rapid isomerization to *aci*-HNM.[17] Hence, *aci*-HNM is always present in the synthesis of the nitrosomethane.

Batt et al. carried out a detailed study of the pyrolysis and photolysis of *tert*-butyl nitrite and established that dimeric nitrosomethane exists in two isomeric forms, *cis* and *trans*. Monomeric nitrosomethane could be generated by heating the dimer in the gas phase (the activation energy for dissociation of the dimer to form the monomer was found to be ca. 90 kJ mol^{-1}).[18]

Multiple isomers of HNM with different connectivities are known: the tautomers formaldehyde oxime (*aci*-HNM) with one hydrogen atom attached to the oxygen atom and formaldonitrone with one hydrogen atom attached to the nitrogen atom (Figure 4). Investigations of the potential energy surface showed two further high-energy isomers, CH_2–O–NH and the cyclic oxaziridine, which were calculated to be substantially less stable, and hence, they are not discussed here. The formamide isomer and its formamidic acid counterpart are much more stable but were not calculated as part of this work, as they are not relevant to our current study or the relative energy of the tautomers.

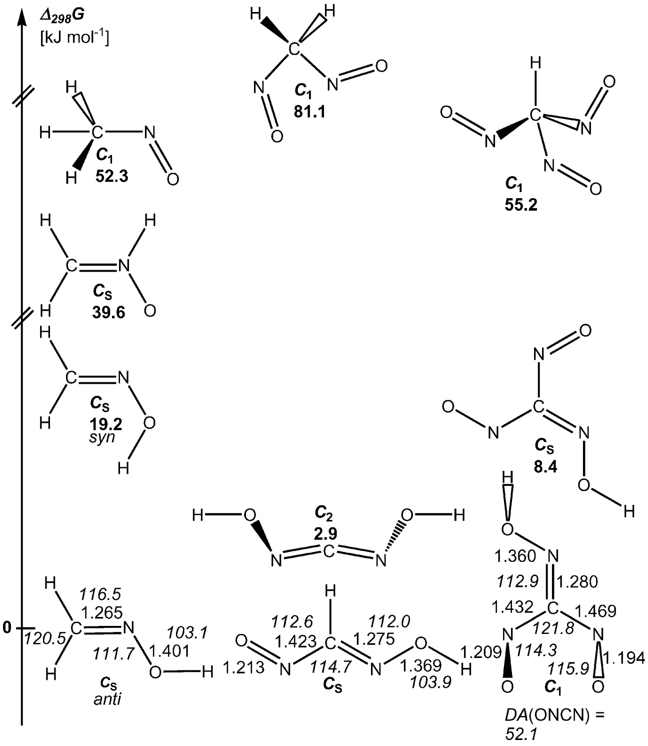

Figure 4. Selected isomers of nitrosomethanes [bond lengths in Å, angles (italics) in ° with the relative energies and symmetries given in bold; DA = dihedral angle].[10]

Based on a series of ab initio and DFT calculations and in accord with our B3LYP/aug-cc-pvTZ results,[19,20] *aci*-HNM (formaldoxime) represents the lowest-lying isomer ($\Delta_{298}G_{\text{HNM}-aci\text{-HNM}}$ = 52.3 kJ mol^{-1}) in an *anti* conformation followed by the *syn* structure ($\Delta_{298}G_{syn-anti}$ = 19.2 kJ mol^{-1}). This finding clearly demonstrates a high delocalization of the methanide lone pair onto the NO group, which results in the oxygen atom of the nitroso group being highly negatively charged and therefore most favourably protonated. Hence, protonation of the nitrosomethanides occurs at the O atom of the NO group, in contrast to the situation found for the cyano- and nitromethanides.

Exploration of the potential energy surface also showed that the formaldonitrone CH_2=N(H)–O is close in energy to HNM (Figure 4). However, experimental access to CH_2=N(H)–O is rather difficult, preventing an experimental structural analysis.[20] Some reports predicted the nitrone to be less stable than nitrosomethane, whereas recent papers have indicated that HNM and nitrone are comparable in energy with the nitrone slightly more stable, which is in accord with our findings ($\Delta_{298}G_{\text{HNM–nitrone}}$ = 12.7 kJ mol^{-1}).[19,20]

Although highly reactive formaldonitrone has been detected only recently,[20] both HNM and *aci*-HNM are also reactive compounds in the condensed phase; *aci*-HNM undergoes facile oligomerization,[21–23] whereas HNM forms a dimer[15] and isomerizes to *aci*-HNM.[23]

The "oldest" experimentally known isomer of HNM is formaldoxime (H_2C=NOH, *aci*-HNM, "formoxime"), the simplest member of the oxime family, which was first synthesized in 1891 by Scholl.[24] He succeeded in isolating *aci*-HNM in the condensation reaction of formaldehyde and hydroxylamine, leading to a white, amorphous polymeric solid $(H_2C{=}NOH)_n$. By gentle heating (100–134°C) of polymeric *aci*-HNM, Scholl obtained monomeric *aci*-HNM as a vapour and also in solution, whereas at high temperatures spontaneous dehydration, $H_2C{=}NOH \rightarrow H_2O + HCN$, took place.

The existence of monomeric *aci*-HNM has been proven unequivocally by microwave studies and vibrational spectroscopy.[25]

Dinitrosomethanes (HDNM)

Protonation of dinitrosomethanide $\{[HC(NO)_2]^-\}$ might lead to three different tautomers: (i) dinitrosomethane $[H_2C(NO)_2]$ when the protonation occurs at the carbon (HDNM),[26] (ii) methylnitrosolic acid (*aci*-HDNM, also formonitrosolic acid) when one of the oxygen atoms of the nitroso groups forms an oxime (enolic conformer) and (iii) the dioxime (HO–N=C=N–OH) of CO_2 (Figure 4).

Stationary points were found for all possible tautomers on the potential energy surface, which were characterized as minima by frequency analyses. Seven conformers of *aci*-HDNM and three for the dioxime were calculated (see Figure S2, of the Supporting Information). *aci*-HDNM turned out to be favoured over dinitrosomethane by 81.1 kJ mol^{-1} at the B3LYP/aug-cc-pvTZ level of theory. Hence, it can be concluded that protonation occurs exclusively on the oxygen atoms of the nitroso groups in dinitrosomethanide. Interestingly, the dioxime is only 2.9 kJ mol^{-1} less stable than *aci*-HDNM. However, the formation of the dioxime (in addition to *aci*-HDNM) in solution is rather unrealistic due to a very large activation barrier of around 200 kJ mol^{-1} for the obligatory hydrogen shift. Thus, preparation of the dioxime species needs a different synthetic approach.

Wieland first studied nitrosolic acids a century ago.[27] Nitrosolates can be obtained from unstable *N*,*N'*-dihydroxyamidines by disproportionation in ammonia or by oxidation (KIO_4) in basic solution.[28,29] A recently published new synthesis of dinitrosomethanide salts and the nitrosolic acid starts from formamidinium nitrate.[30] The monomeric *aci*-HDNM can be formed and extracted with diethyl ether, but evaporation of the nonpolar solvent results in a yellowish dimer.

Trinitrosomethanes (HTNM)

Similar to the synthesis of *aci*-HDNM, *aci*-HTNM should be formed upon protonation of trinitrosomethanides, $C(NO)_3^-$. However, trinitrosomethanides are not known.

In our computations six stationary points [five isomers of the *aci*-HTNM (oxime) species and HTNM] were found on the potential energy surface of HTNM (see Figure S2[31] and Figure 4). Protonation might occur at the central carbon atom, leading to the trinitrosomethane, or at one of the oxygen atoms of the NO groups, leading to oximes (Figure 4). The C_1-symmetric trinitrosomethane was calculated to be the less stable isomer, lying 55.2 kJ mol^{-1} above the most stable C_1-symmetric *aci*-HTNM, in accord with simple charge consideration (negative charge sits on the oxygen atoms). All the other minima represent planar C_s-symmetric oximes, which differ in the arrangement of the two nitroso groups and the position of the hydrogen atom attached to one oxygen atom (see Figure S2). The hydrogen atom can be directed towards a neighbouring O atom (*endo-w*), which stabilizes the conformation through the formation of an intramolecular hydrogen bond (formal formation of a six-membered ring), or towards a neighbouring N atom (*endo-s*). All five oxime isomers of HTNM lie within a range of 12.5 kJ mol^{-1}, which indicates a very flat potential energy surface.

Structures

Only two of the three *aci*-nitrosomethanes, HNM and HDNM, are planar with C_s symmetry (Figure 4) and stabilized by an intramolecular hydrogen bond. HTNM is nonplanar due to unfavourable electrostatic repulsion between lone pairs on the NO groups. Formaldoxime (*aci*-HNM) has been shown to have a planar structure with C_s symmetry (Figures 1 and 4). Experimental and theoretical studies found the *anti* conformer (*anti*-*aci*-HNM) to have the lower energy (with $\Delta_{syn-anti}E$ = 19–25 kJ mol^{-1}), which may reflect lone-pair–lone-pair repulsion between oxygen and nitrogen atoms. The *anti*–*syn* internal rotational barrier is about 38–42 kJ mol^{-1} depending on the level of theory applied.[32]

As formaldoxime (*aci*-HNM) is stable in the gas phase it is more easily studied experimentally than nitrosomethane. Experimental structural data are only available for formaldoxime *aci*-HDNM[25] and monomeric and dimeric nitrosomethane HDNM.[33]

The gas-phase structure was determined by Levine[25] by using microwave spectroscopy. In agreement with a double bond localized along the CN moiety, a short CN distance of 1.276 Å was determined, whereas the N–O distance of 1.408 Å is rather long, which shows a single bond with a small amount of π-bonding [cf. Σr_{cov}(N–O) = 1.45 Å vs. Σr_{cov}(N=O) = 1.17 Å].[34] In good agreement with these structural data, our computation gives 1.401 for the N–O and 1.276 Å for the C–N distance.

Experimental structural data for *aci*-HDNM or *aci*-HTNM or any other isomer of *aci*-HDNM and *aci*-HTNM, respectively, are not yet known. Computed structural data for *aci*-HDNM and the dioxime are given in Figure 4. The planar C_s-symmetric *aci*-HDNM displays two significantly different NO and CN bond lengths with alternating bonds with respect to the bond lengths [*d*(N=O) = 1.213, *d*(C–NOH) = 1.423, *d*(C=NOH) = 1.275, *d*(N–OH) = 1.369 Å]. For comparison, the calculated structural data obtained for the dioxime display a nonplanar C_2-symmetric species for the lowest-lying isomer (dihedral angles: HONC 180.0°, ONCN 135.1°) with two short CN bonds (1.231 Å) and two long NO bonds (1.413 Å), which is in contrast to the situation of *aci*-HDNM (Figure 4) with one longer NO and CN and one shorter NO and CN bond, respectively. Although there is a strong π-type bond along the NCN unit, the NCN angle at 167.3° is far away from the ideal angle of 180°.

In C_1-symmetric *aci*-HTNM, one nitroso group is twisted out of the molecular plane by 52.1°. Similar to the situation found in HDNM, two significantly different NO and CN distances are found [*d*(N–OH) = 1.360 vs. *d*(N–O) = 1.194/1.209 Å; *d*(C=NOH) = 1.280 Å vs. *d*(C–NO) = 1.469/1.432 Å], which indicates double bond character of the C=NOH bond and single bond character of the N–OH and C–NO bonds.

Mixed Substituted Methanes

In addition to multiple substitution with only one functional group (CN, NO_2 or NO), double and triple substitution are possible utilizing two and three different functional groups, respectively.

Nitrocyanomethane (HNtCM)

A convenient synthesis of nitroacetonitrile starts from nitromethane in basic solution and involves the extraction of the formed nitroacetaldoxime and subsequent dehydration, as described first by Steinkopf and Bohrmann a century ago.[35]

Four stationary points were computed for HNtCM (Figure 5), with the C–H bound isomer (nitroacetonitrile) the most stable isomer. Significantly less stable is *aci*-nitroacetonitrile (*aci*-HNtCM), 16.9 kJ mol^{-1} above HNtCM, followed by nitrovinylideneamine with a protonated cyano group ($\Delta_{298}G_{rel.}$ = 50.4 kJ mol^{-1}). The highest-lying isomer studied is *aci*-nitrovinylideneamine ($\Delta_{298}G_{rel.}$ =

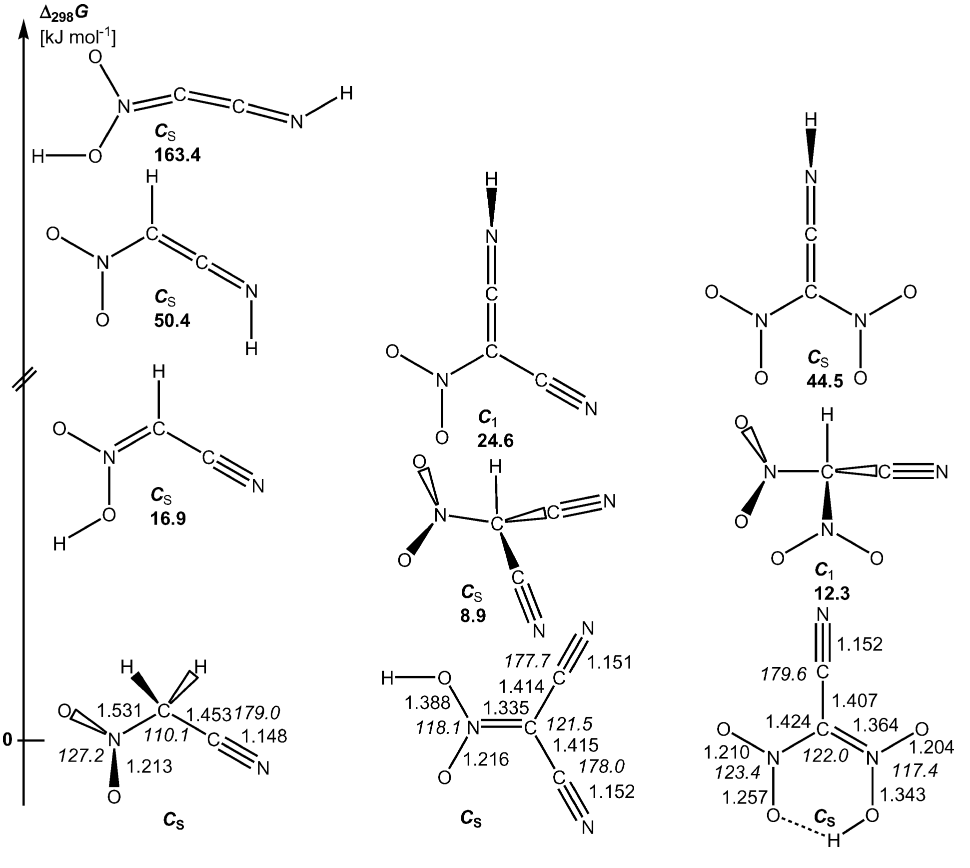

Figure 5. Isomers of nitrocyanomethanes [bond lengths in Å, angles (italics) in ° with the relative energies and symmetries given in bold].[10]

163.4 kJ mol^{-1}) with H atoms attached to both the nitro and cyano groups. The related carbene with two hydrogen atoms on the nitro group was ignored in our study.

Nitrodicyanomethane (HNtDCM, also Nitromalononitrile)

Although the anions (NtDCM and HDNtCM) have been intensively studied,[36,37] the free acids have not been structurally characterized yet.

In contrast to HNtCM, for HNtDCM the most stable isomer is 2-*aci*-nitromalononitrile (*aci*-HNtDCM). Introduction of a second cyano group improves the delocalization of the central carbon lone pair in the anion, decreasing the basicity of this carbon atom. Hence, protonation occurs at one of the O atoms of the nitro group. Slightly less stable at 8.9 kJ mol^{-1} is HNtDCM (2-nitromalononitrile) followed by 3-imino-2-nitroacrylonitrile at 24.6 kJ mol^{-1} above the *aci*-nitromalononitrile.

Dinitromonocyanomethane (HDNtCM)

Similarly to HNtDCM, better delocalization of the central carbon lone pair (in the anion, see above) by introduction of a second nitro group leads to nitro-*aci*-nitroacetonitrile (*aci*-HDNtCM) as the most stable isomer, lying 12.3 kJ mol^{-1} below dinitroacetonitrile, the C–H bound isomer. In addition, nitro-*aci*-nitroacetonitrile is stabilized by an intramolecular hydrogen bond. Dinitrovinylideneamine is a high-lying isomer at 44.5 kJ mol^{-1} above the nitro-*aci*-nitroacetonitrile.

Structures

Experimentally, the covalent (unionized) *aci* form $NCC(NO_2)NO_2H$ is found in aqueous solution at low temperatures.[38] C_s-symmetric HNtCM is nonplanar in contrast to the planar C_s-symmetric *aci*-HDNtCM and *aci*-HNtCM (Figure 5). Significant C–NO_2H double bond character is found in the *aci* compounds (*aci*-HNtDCM: 1.335, *aci*-HDNtDCM: 1.364 vs. HNtCM: 1.531 Å), which shows a favourable resonance stabilization of the π system.

Nitrosocyanomethane (HNCM)

aci-HNCM, cyanoformaldoxime, was first described by Grundmann and Fulton in the decarboxylation reaction of isonitrosocyanoacetic acid.[39] According to Grundmann, synthesis of cyanoformaldoxime results in the formation of a mixture of a *syn* and *anti* isomer ($\Delta_{298}G_{\text{syn-anti}}$ = 1.7 kJ mol^{-1}, see Figure S3 of the Supporting Information).[10,31] Another synthetic route to cyanoformaldoxime involves the decarboxylation of furazandicarboxylic acid;[40] in situ synthesized furazan can be treated with base to form[40] cyanonitrosomethanides. Formally, three tautomeric forms can be regarded as the corresponding acids of

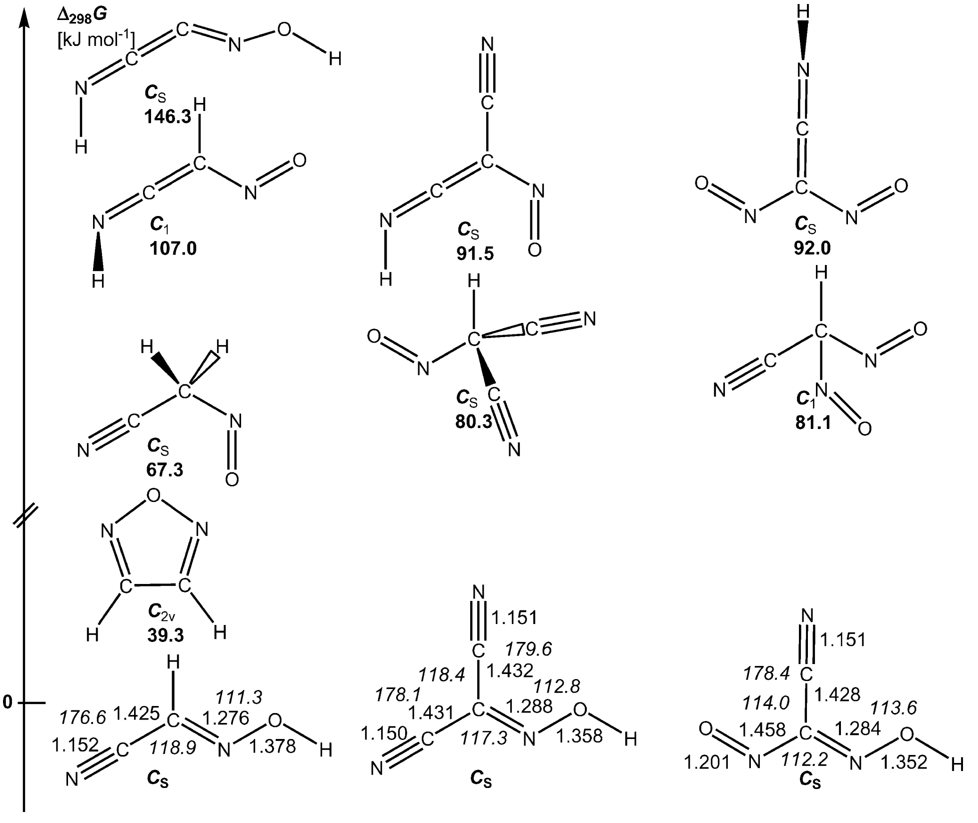

Figure 6. Isomers of nitrosocyanomethanes [bond lengths in Å, angles (italics) in ° with the relative energies and symmetries given in bold].[10]

NCM upon protonation: (i) the cyanoformaldoxime when protonation occurs at the oxygen (*aci*-HNCM), (ii) nitrosocyanomethane (nitrosoacetonitrile, HNCM) if a proton is added to the central carbon and (iii) nitrosovinylideneamine upon addition of a proton to the nitrogen atom of the cyano group (Figure 6). Furthermore, if a 1,3-hydrogen shift follows protonation of the NO group an iminoethenone oxime could be formed. Three additional structural isomers of *ac*i-HNCM have been found, all of which lie within 24 kJ mol^{-1} (see Figure S3).

Nitrosodicyanomethane (HNDCM) and Dinitrosocyanomethane (HDNCM)

Although dinitrosocyanomethanides (DNCM) have not yet been synthesized, nitrosodicyanomethanides (NDCM) have been studied extensively.[41–43]

Comparison of all the isomers of HNCM, HDNCM and HNDCM illustrates that the oxime form is always the most stable tautomer (Figure 6).[44] Protonation at the central carbon of the methanide dramatically increases the total energy relative to the oxime species (NCM: 67.3, NDCM: 80.3, DNCM: 81.1 kJ mol^{-1}), and protonation at the cyano group is even less favoured (NCM: 107.0, NDCM: 91.5, DNCM: 92.0 kJ mol^{-1}). Hence, it can be concluded that protonation of NCM, DNCM and NDCM salts always occurs exclusively at the oxygen of the nitroso group, thereby generating an oxime.[45]

Structures

All three oximes (HNCM, HDNCM and HNDCM) are planar (C_s symmetry) and several isomers (e.g., the *syn* and *anti* isomers) have been localized at the potential energy surface (Figures S3, S4 and S5). Planar structures are favoured due to the presence of a highly delocalized π system. Selected structural data are given for all three oximes (*aci* species) in Figure 6. As expected, the NO distance (HNCM: 1.378, HNDCM: 1.358, HDNCM: 1.352 Å) decrease upon protonation, whereas the CN bond length remains almost unchanged (HNCM: 1.152, HNDCM: 1.150, HDNCM: 1.151 Å). The C–C≡N moiety reveals a slight deviation from linearity (HNCM: 176.6°, HNDCM: 178.1°, HDNCM: 178.4°).

Nitrosonitromethane (HNNtM)

Only the sodium and potassium salts of methylnitrolic acid [*aci*-HNNtM, HC(NO$_2$)=NOH] are known experimentally. These nitrosonitromethanides, however, were only generated in situ in aqueous solutions.[46] The class of nitrolic acids (nitro-oximes) was introduced by Meyer in 1873 with the simplest representative methylnitrolic acid.[47] Methylnitrolic acid and its salts can be prepared by the reaction of nitromethane and aqueous NO$_2^-$ followed by suitable extraction and separation.[48–50]

For the acids of nitrosonitromethanides, a similar situation is found with respect to the energetic energy order

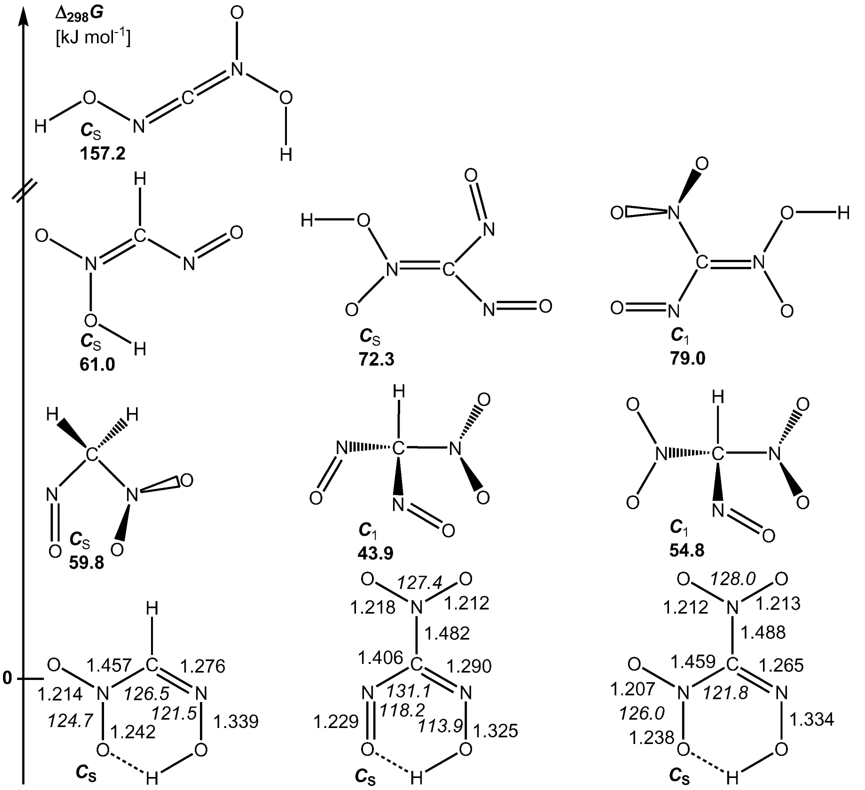

Figure 7. Isomers of nitrosonitromethanes [bond lengths in Å, angles (italics) in ° with the relative energies and symmetries given in bold].[10]

compared with the acids of nitroso- and nitrosocyanomethanides. For nitrosonitromethanide, protonation at the nitroso group leading to the oxime species is always energetically preferred (Figure 7). Less favourable by 59.8 and 61.0 kJ mol^{-1} is the formation of the C_s-symmetric nitrosonitromethane (protonation at the central carbon atom) and a species with a protonated nitro group (*aci*-nitronitrosomethane), respectively (Figure 7).

For DNNtM and NDNtM acids similar energy differences are found: 43.9 and 72.3, and 54.8 and 79.0 kJ mol^{-1}, respectively. Experimentally, neither the free acids dinitrosonitromethane (HDNNtM)/nitrosodinitromethane (HNDNtM) nor their anions are known.

Structures

Four different isomers of *aci*-nitrosonitromethane (*aci*-HNNtM) have been found and all lie within an energy range of 25 kJ mol^{-1} and all are planar (see Figure S6 of the Supporting Information). Interestingly, for the energetically preferred *aci*-HNNtM, a stabilizing intramolecular hydrogen bond between the nitroso and nitro groups is formed, closing a six-membered ring. For the protonated nitro species, this kind of hydrogen-bonded species always results in proton transfer, leading to the most stable oxime species: –N=O··H–O–NO → –N=O–H··O–NO. Stabilization of the oxime species by formation of an intramolecular hydrogen bond is also found for *aci*-HDNNtM and *aci*-HNDNtM for the energetically preferred isomer, as shown in Figure 7.

Selected computed structural data for the three tautomeric forms of protonated NNtM, DNNtM and NDNtM are depicted in Figure 7. Only the most stable oxime isomers are presented. As long as only two functional groups are attached to the central methanide carbon, the entire molecule remains planar due to resonance stabilization, whereas introduction of a third group, either NO or preferably NO_2, results in rotation of at least one group. However, the CN_3 moiety in the nonplanar species remains planar as only the oxygen atom leaves the molecular plane (dihedral angles close to 90°). As already discussed above, the C–N distances display bond orders of between 1 and 2 for both the C–NO and C–NO_2 bonds. However, the C–NO bonds are always significantly shorter (HNNtM: 1.276 vs. 1.457, HDNNtM: 1.290/1.406 vs. 1.482, HNDNtM: 1.265 vs. 1.459/1.488 Å; Figure 7).

Nitrosonitrocyanomethane (HNNtCM)

Metastable *aci*-HNNtCM (also cyanomethylnitrolic acid) can easily be synthesized by nitrosation of nitroacetonitrile in water followed by a low-temperature extraction with ether.[51–53] The anion of *aci*-HNNtCM, nitrosonitrocyanomethanide, represents a methane derivative with three different functional groups all being capable of delocalizing the lone pair of the central carbon. The presence of a π system delocalized over the entire anion accounts for the remarkable stability of nitrosonitrocyanomethanide salts in contrast to the metastable free acid. In addition to protonation at the central methanide carbon atom, protonation of nitrosonitrocyanomethanide might also occur at all three functional groups. Indeed, as shown above, formation of the oxime species (*aci*-HNNtCM) is always energetically preferred, in this case separated by ca. 53.8 kJ mol^{-1} from *aci*-nitronitrosoacetonitrile, 69.0 kJ mol^{-1} from HNNtM and 92.9 kJ mol^{-1} from nitronitrosovinylideneamine (Figure 8).

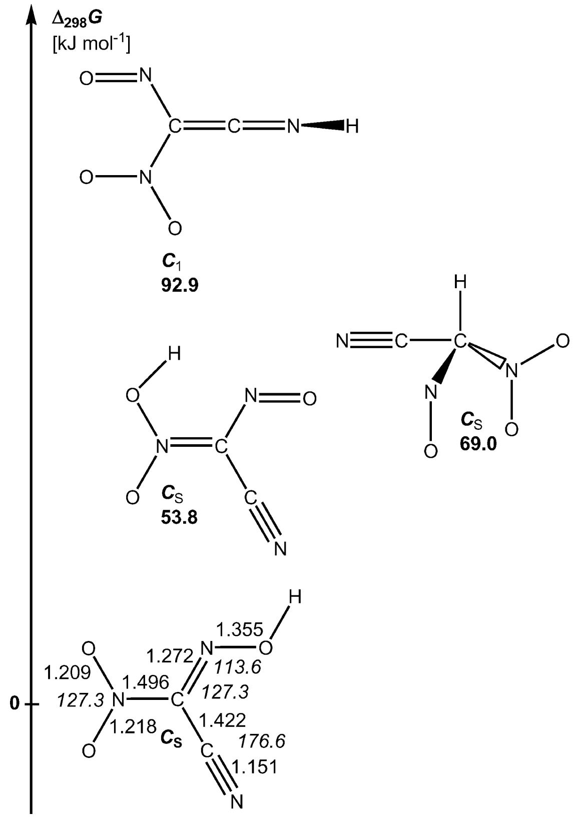

Figure 8. Isomers of nitrosonitrocyanomethanes [bond lengths in Å, angles (italics) in degrees with the relative energies and symmetries given in bold].[10]

Structure

Structural data for *aci*-HNNtCM are shown in Figure 8. As already discussed on several occasions before in this report, the presence of a delocalized π system results in a short C–NOH bond and a longer N–OH bond, a situation typically found in oximes.

Gas-Phase Acidities

Gas-phase acidities [$\Delta G_{(gas,298K)}$] describe the energetics of the deprotonation reaction of an acid in the gas phase at 298 K, and small gas-phase acidities in comparison with that of unsubstituted methane, $CH_4 \rightarrow CH_3^- + H^+$, can be regarded as a measure of the resonance stabilization in substituted methanides. Furthermore, with the help of gas-phase acidities it is possible to calculate absolute pK_a values if solvation can be estimated as illustrated in Figure 9 (pK_a = $\Delta G_{aq}/2.303RT$).[54–56] On the basis of DFT calculations at the B3LYP/aug-cc-pvTZ level of theory, gas-phase acidities are easily calculated with sufficient accuracy, whereas theoretical estimation of solvation effects with an acceptable accuracy (±6 kJ mol^{-1} corresponding to ΔpK_a = ±1) remains an unsolved problem. Hence, only gas-phase acidities have been calculated due to the lack of experimental data for most of the species considered. The gas-phase acidities listed in Table 1 refer to the most stable isomer of the considered methane derivative $H[CR^1R^2R^3]$ ($R^{1,2,3}$ = H, CN, NO_2 and NO). Stronger acids have smaller numerical values $\Delta G_{(gas,298K)}$, which imply easier release of the proton.

$$\begin{tikzcd}
AH_{(gas)} \arrow[r, "\Delta G_{(gas)}"] & A^-_{(gas)} \arrow[d, "\Delta G_{(solv)}(A^-)"'] & + & H^+_{(gas)} \arrow[d, "\Delta G_{(solv)}(H^+)"] \\
AH_{(aq)} \arrow[u, "-\Delta G_{(solv)}(AH)"] \arrow[r, "\Delta G_{(aq)}"] & A^-_{(aq)} & + & H^+_{(aq)}
\end{tikzcd}$$

Figure 9. Thermodynamic cycle for the estimation of pK_a values.

Table 1. Gas-phase acidities for methane derivatives of the type $H[CR^1R^2R^3]$ ($R^{1,2,3}$ = H, CN, NO_2 and NO) at the B3LYP/aug-cc-pvTZ level of theory.[10]

Acid[a]	Abbreviation	Gas-phase acidity[b] [kJ mol^{-1}]	Figure
H_4C	–	1704.4	
$H_3C(CN)$	HCM	1523.61	2
$H_2C(CN)_2$	HDCM	1351.85	2
$HC(CN)_3$	HTCM	1209.08	2
$H_3C(NO_2)$	HNtM	1459.12	3
$H_2C(NO_2)_2$	HDNtM	1304.31	3
$HC(NO_2)_3$	HTNtM	1247.69	3
$H_2C(NOH)$	*aci*-HNM	1479.92	4
$HC(NOH)(NO)$	*aci*-HDNM	1333.39	4
$C(NOH)(NO)_2$	*aci*-HTNM	1272.22	4
Mixed substituted			
$H_2C(CN)(NO_2)$	HNtCM	1307.11	5
$HC(CN)(NOH)$	*aci*-HNCM	1365.06	6
$HC(NO_2)(NOH)$	*aci*-HNNtM	1333.67	7
$C(CN)_2(NO_2H)$	*aci*-HNtDCM	1202.95	5
$C(CN)(NO_2H)(NO_2)$	*aci*-HDNtCM	1214.49	5
$C(CN)_2(NOH)$	*aci*-HNDCM	1273.95	6
$C(CN)(NOH)(NO)$	*aci*-HDNCM	1260.44	6
$C(NO_2)_2(NOH)$	*aci*-HNDNtM	1261.56	7
$C(NO_2)(NOH)(NO)$	*aci*-HDNNtM	1236.64	7
$C(CN)(NO_2)(NOH)$	*aci*-HNNtCM	1253.92	8

[a] Only the lowest-lying isomer is listed (see the figures indicated in the last column). [b] Gas-phase acidity = $\Delta G_{(gas,298K)}$ for the reaction $HR^1R^1R^3 \rightarrow [CR^1R^2R^3]^- + H^+$.

The calculated gas-phase acidity of methane is 1704.4 kJ mol^{-1}, which is in good agreement with the experimental value of 1709.0 ± 3.3 kJ mol^{-1}.[57] Substitution of one hydrogen atom in H_4C by one functional group dramatically increases the acid strength as shown by the decrease in $\Delta G_{(gas,298K)}$ ($\Delta G_{H4C–HCM}$ = 180.8, $\Delta G_{H4C–HNtM}$ = 245.3 and $\Delta G_{H4C–HNM}$ = 224.5 kJ mol^{-1}) to 1523.6 (HCM), 1459.1 (HNtM) and 1479.9 kJ mol^{-1} (HNM). Double and triple substitution further increases the acid strength significantly (Table 1), however, the differences in the gas-phase acidity between single, double and triple substitution are much smaller ($\Delta G_{\text{HCM–HDCM}}$ = 171.8, $\Delta G_{\text{HDCM–HTCM}}$ = 142.8; $\Delta G_{\text{HNtM–HDNtM}}$ = 154.8, $\Delta G_{\text{HDNtM–HTNtM}}$ = 56.6; $\Delta G_{\text{HNM–HDNM}}$ = 146.5, $\Delta G_{\text{HDNM–HTNM}}$ = 61.2 kJ mol^{-1}). Interestingly, for the cyanomethanes the decrease in the ΔG values upon higher substitution is much less pronounced.

Furthermore, the gas-phase acidities of mixed substituted methane derivatives do not depend much on the combination of functional groups. The same holds true for the triply substituted methane derivative. Nevertheless, three distinct ranges can be established: (i) the gas-phase acidities for singly substituted methane derivatives lie between 1523 (HCM) and 1459 kJ mol^{-1} (HNtM), (ii) for the doubly substituted methane derivatives between 1365 (*aci*-HNCM) and 1304 kJ mol^{-1} (HDNtM) and (iii) for triple substitution between 1274 (*aci*-HNDCM) and 1203 kJ mol^{-1} (*aci*-HNtDCM). In contrast, the unsubstituted species, that is, $CH_4 \rightarrow CH_3^- + H^+$, has $\Delta_{\text{calcd.}}G_{(\text{gas},298\text{K})}$ = 1704.4 kJ mol^{-1}. The calculated gas-phase acidity of cyanomethylnitrolic acid (*aci*-HNNtCM) with one apiece of our acidifying substituents CN, NO and NO_2 is sensibly 1254 kJ mol^{-1}.

Computational Details

Our goal was to compare the structures and energetics of differently substituted methane isomers and related methanide anions. Structural and vibrational data of all the considered species were calculated by using the hybrid density functional theory (B3LYP) with the Gaussian 98 program package.[58] Three different types of basis sets were used: (i) 6-31G(d,p), (ii) aug-cc-pvDZ and (iii) aug-cc-pvTZ. All stationary points were characterized by a frequency analysis at the B3LYP level: no imaginary frequencies were found. Further details are presented in the Supporting Information. Unless otherwise stated, all the discussed computational data refer to the B3LYP/aug-cc-pvTZ level of theory. Comparison of these data sets using different basis sets exhibit differences in bond lengths no larger than 0.01–0.02 Å. The bond angles in all these molecules are also independent of the choice of basis sets.[59]

Ervin and DeTuri[60] have calculated and provided benchmark figures of the gas-phase acidities at 0 K at several levels of theory. Excellent performance at the CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ level was found, with a mean error of –0.2 kJ mol^{-1} and a mean absolute error of 1.5 kJ mol^{-1}. Since post-Hartree–Fock, ab initio CCSD(T)/aug-cc-pVTZ quantum chemical calculations are still very expensive, we have changed from the CCSD(T) to the less expensive, but still highly reliable, B3LYP DFT method, as tested by Alcamí et al.[61] To limit the data, only $\Delta G_{(\text{gas},298\text{K})}$ values obtained at the B3LYP/aug-cc-pVTZ level are discussed throughout the paper. All further information can be found in the Supporting Information, such as $\Delta E^{\text{tot}}{}_{(\text{gas},0\text{K})}$ and $\Delta H_{(\text{gas},298\text{K})}$ values for the reaction $HCR^1R^1R^3 \rightarrow [CR^1R^2R^3]^- + H^+$, and the temperature correction at all three levels of theory applied [B3LYP/6-31G(d,p), B3LYP/aug-cc-pvDZ and B3LYP/aug-cc-pvTZ]. The computed $\Delta H_{(\text{gas},298\text{K})}$ values are in good agreement (deviation less than 6 kJ mol^{-1}) with those obtained by Vianello et al. at the B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) level {cf. H_3C–CN: 1553.7 vs. 1552.3 kJ mol^{-1} [this work: $H_2C(CN)_2$: 1378.6 vs. 1381.2 kJ mol^{-1}; $HC(CN)_3$: 1231.8 vs. 1234.9 kJ mol^{-1}]}.[5d] Likewise, Koppel and Taft and their co-workers reported $\Delta G_{(\text{gas},298\text{K})}$ values for a series of acids (including nitro- and cyanomethane) derived from $\delta\Delta G$ values for the proton-transfer equilibria and from computations at the MP2/6-311++G(d,p), G2, G2(MP2) and B3LYP/6-311+G** levels.[62]

It should be emphasized that the computations were carried out on single isolated (gas-phase) anions. There may well be significant differences between gas-phase, solution and solid-state results and the conclusions derived from these.

Supporting Information (see footnote on the first page of this article): A full list of $\Delta E_{\text{tot}(\text{gas},0\text{K})}$, $\Delta H_{(\text{gas},298\text{K})}$ and $\Delta G_{(\text{gas},298\text{K})}$ values at different levels of theory, including data for all the isomers considered and additional graphical material. Refs.[10,31,44] also refer to material in the Supporting Information.

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