Nitration of hydrogen cyanide with nitryl tetrafluoroborate†

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The reaction of hydrogen cyanide at 0 °C in $CFCl_3$, purified nitrile-free nitromethane or tetrahydrothiophene 1,1-dioxide gave dinitrogen monoxide, N_2O and CO_n (n = 1 or 2). The same products were obtained in a solvent-free neat reaction of HCN(g) and $NO_2^+BF_4^-$(s). The experimental data are in accord with the intermediate formation of neutral CN–NO_2. This intermediate then undergoes cleavage–rearrangement to give N_2O and CO. In a subsequent reaction carbon monoxide is oxidized by unreacted $NO_2^+BF_4^-$ to give CO_2 and the corresponding nitrosyl salt, $NO^+BF_4^-$. The reaction was followed by low-temperature ^{14}N NMR spectroscopy and the identity of the products established by ^{14}N NMR and IR spectroscopy. The two isomers CN–NO_2 and NC–NO_2 were computed *ab initio* at the correlated MP2 level of theory and are discussed in terms of intramolecular stabilization by donor–acceptor interaction (negative hyperconjugation).

Several reports have appeared on the reaction behaviour of nitryl and nitrosyl salts towards covalently bound and ionic azides.[1-4] It was established that $ClNO_2$ reacts with $SiMe_3N_3$ initially to form $SiMe_3Cl$ and NO_2N_3 [equation (1)]; NO_2N_3 is thermodynamically unstable and decomposes to give N_2O [equation (2)].[3]

$$SiMe_3N_3 + ClNO_2 \longrightarrow SiMe_3Cl + NO_2N_3 \qquad (1)$$

$$NO_2N_3 \longrightarrow 2\ N_2O \qquad (2)$$

In contrast to the nitration of aromatics with $NO_2^+BF_4^-$,[5,6] early studies on the electrophilic nitration of non-aromatic compounds such as adamantane and related organic compounds with NO_2^+ salts gave only very moderate yields of organic nitrates.[7] However, in 1993 Olah *et al.*[8] reported on the nitration of adamantane with nitryl tetrafluoroborate obtaining 1-nitroadamantane in high yields.[8] It was further shown that the effect of impurity nitriles in the commercial nitromethane (solvent) used had a strong influence on the yield and the ratio of the products formed and that dry, nitrile-free nitromethane gave the best results.[8]

Following our earlier report on the reaction of nitryl salts with covalent azides,[3] in this paper we focus on the reaction behaviour of $NO_2^+BF_4^-$ with anhydrous hydrogen cyanide.

Experimental

All manipulations were performed under an inert atmosphere (dry-box, N_2 or under the vapour pressure of the corresponding solvent) in the following predried solvents which were distilled prior to use: $CFCl_3$ (Merck, P_4O_{10}), nitromethane (Aldrich, CaH_2), tetrahydrothiophene 1,1-dioxide[9] (Aldrich, P_4O_{10}). Hydrogen cyanide was prepared from KCN and H_2SO_4, dried over P_4O_{10} and distilled prior to use.[10] The salt $NO_2^+BF_4^-$ was either prepared from NO_2, F_2 and BF_3 (*cf.* ref. 11) or from HNO_3, BF_3 and HF.[12]

The ^{14}N NMR spectra were obtained in $CFCl_3$ solution using a Bruker SY 200 spectrometer operating at 14.462 MHz and are referred to external $MeNO_2$. Good spectra were usually obtained with a pulse width of 48 μs after 40 000 scans. Peak positions appearing upfield (low frequency) of nitromethane are reported as minus and those downfield (high frequency) as plus (δ scale), in agreement with the convention in proton NMR spectroscopy. Infrared spectra were recorded using a 10 cm gas-cell (2 Torr, KBr windows) on a Philips PU9800 FTIR instrument.

Method 1, NMR reaction

A 10 mm NMR tube was loaded in a dry-box with $NO_2^+BF_4^-$ (0.5 g, 3.76 mmol). On a calibrated stainless-steel vacuum line (SS 316), $CFCl_3$ (10 cm^{-3}) and HCN (0.09 g, 3.3 mmol) were condensed onto the nitronium salt at −196 °C. The NMR tube was then flame-sealed and warmed to −90 °C ($CFCl_3$, m.p. −111 °C). The reaction was monitored by ^{14}N NMR spectroscopy, spectra being recorded at −80, −50, 0 and 20 °C. A similar reaction was carried out in an NMR tube in nitromethane on the same scale. Spectra were recorded at 0 °C ($MeNO_2$, m.p. −29 °C) and at room temperature (20 °C). The reaction was also carried out on the same scale in tetrahydrothiophene 1,1-dioxide in an NMR tube at 30 °C (sulfolane, m.p. +27 °C). The ^{14}N NMR spectrum was recorded at 30 °C approximately 10 min after the HCN was added to the solution of the NO_2^- salt in tetrahydrothiophene 1,1-dioxide.

Method 2, IR reaction

A one-bulb vessel (volume 25 cm^3) was flame-dried under vacuum and loaded in a dry-box with $NO_2^+BF_4^-$ (0.5 g, 3.76 mmol). On the calibrated stainless-steel vacuum line (SS 316), HCN (0.09 g, 3.3 mmol) was condensed onto the NO_2^+ salt at −196 °C. The reaction mixture was allowed to warm to room temperature and shaken thoroughly for 15 min. The gas formed was condensed into an IR gas cell and the spectrum recorded at 20 °C and 2 Torr.

Results and Discussion

Spectroscopic results

The NMR monitoring of the reaction of $NO_2^+BF_4^-$ and HCN in $CFCl_3$ solution clearly indicated that there was no reaction at $\leqslant -50$ °C over period studied. However, allowing the components to react at 0 °C for several minutes resulted in the appearance of two new peaks at δ −62 and −170 (Table 1). These resonances appeared simultaneously after about 5 min and started disappearing simultaneously after the reaction mixture was held at 0 °C for more than 30 min. After 2 h of reaction at 0 °C they had completely disappeared while a new sharp resonance at δ −230 and a shoulder (at the broad HCN

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† *Non-SI unit employed:* Torr ≈ 133 Pa.

Table 1 Nitrogen-14 NMR data (δ scale)

Compound/reaction	Solvent	T/°C	δ	Assignment	Ref.
HCN	$\mathrm{CFCl_3}$	20	−122.5	HCN	*a*
KCN	Water	30	−102.5	$\mathrm{CN^-}$	13
$\mathrm{NO_2{}^+BF_4{}^-}$	Tetrahydrothiophene 1,1-dioxide	30	−129.8	$\mathrm{NO_2{}^+}$	*a*
$\mathrm{NO_2{}^+}$ ($\mathrm{HSO_4{}^-}$ salt)	$\mathrm{H_2SO_4}$	r.t.	−126	$\mathrm{NO_2{}^+}$	14
$\mathrm{NO_2{}^+}$ ($\mathrm{SO_3F^-}$ salt)	$\mathrm{HSO_3F}$	25	−129	$\mathrm{NO_2{}^+}$	15
$\mathrm{N_2O}$	Neat	20	−138	$\mathrm{N}N\mathrm{O}$	16
			−222	$N\mathrm{NO}$	
$\mathrm{HCN + NO_2{}^+BF_4{}^-}$	$\mathrm{CFCl_3}$	−80	—		*a*
		−50	−120[b]	HCN	*a*
		0	−120.2	HCN	*a*
		0, after 5 min	−62.2	$\mathrm{CN}N\mathrm{O_2}$	*a*
			−120.7	HCN	
			−171.4 (br)	$\mathrm{C}N\mathrm{NO_2}$	
		0, after 20 min	−62.2	$\mathrm{CN}N\mathrm{O_2}$	*a*
			−120.3	HCN	
			−169.9 (br)	$\mathrm{C}N\mathrm{NO_2}$	
		0, after 2 h	−121.6	HCN	*a*
			−135 (sh)	$\mathrm{N}N\mathrm{O}$	
			−229.9	$N\mathrm{NO}$	
	$\mathrm{MeNO_2}$	0	0[c]	$\mathrm{MeNO_2}$	*a*
	$\mathrm{MeNO_2}$	20	0[c]	$\mathrm{MeNO_2}$	*a*
			−122.0	HCN	
			−135 (sh)	$\mathrm{N}N\mathrm{O}$	
			−229.0	$N\mathrm{NO}$	
	Tetrahydrothiophene 1,1-dioxide	30	−122.0	HCN	*a*
			−135 (sh)	$\mathrm{N}N\mathrm{O}$	
			−228.0	$N\mathrm{NO}$	

r.t. = Room temperature, br = broad, sh = shoulder. [a] This work. [b] Very weak. [c] Very strong solvent signal.

resonance, δ −120) at δ −135 had appeared. The species causing these final resonances at *ca.* δ −135 and −230 was found to be indefinitely stable in a sealed NMR tube at room temperature and was, in comparison with reported chemical shift data, identified to be dinitrogen monoxide, $\mathrm{N_2O}$ (Table 1). Therefore, it is reasonable to conclude that the intermediate species is the direct reaction product of HCN (or $\mathrm{CN^-}$) and $\mathrm{NO_2{}^+BF_4{}^-}$. Since the intermediate species is very soluble in $\mathrm{CFCl_3}$ we can assume that the NMR-active intermediate species is the neutral molecule $\{\mathrm{CN{-}NO_2}\}$ (*cf.* due to the poor solubility in $\mathrm{CFCl_3}$ nitronium salts do not show $^{14}\mathrm{N}$ NMR spectra under the experimental conditions applied in this study). (N.B. In agreement with this, no formyl fluoride, HCOF,[17] was detected in the IR spectrum of the products from a neat reaction of HCN and $\mathrm{NO_2{}^+BF_4{}^-}$, see below.) Since the resonance at δ −62 is very sharp and appears relatively close to that of the reference compound ($\mathrm{MeNO_2}$) and other covalently bound organonitro compounds we assign it to the nitro group, *i.e.* $\{\mathrm{CN{-}}N\mathrm{O_2}\}$ (Fig. 1). The high-field resonance at δ −171 is very similar in shape (linewidth) and chemical shift to that of free hydrogen cyanide, therefore we assign it to the nitrile nitrogen atom, *i.e.* $\{\mathrm{C}N\mathrm{{-}NO_2}\}$ (Fig. 1). It should be noted that the relative linewidths in the $^{14}\mathrm{N}$ NMR spectra are related to the local symmetry around the nitrogen, with highly symmetric N atoms (*i.e.* the $\mathrm{CN{-}}N\mathrm{O_2}$) having sharper lines, whilst the more asymmetric nitrogen atoms ($\mathrm{C}N\mathrm{{-}NO_2}$) have broader lines.

The initially formed species $\{\mathrm{CN{-}NO_2}\}$ is unstable in solution at 0 °C and decomposes to give $\mathrm{N_2O}$ (Tables 1 and 2). Therefore, N–N connectivity in the intermediate product (structure **A**) is much more likely than C–N (structure **B**) in solution. Moreover, this is consistent with the higher electronegativity of nitrogen (*i.e.* in $\mathrm{CN^-}$ the larger part of the negative charge is localized at the nitrogen atom).[27]

The formation of $\mathrm{N_2O}$ naturally led to the assumption that CO could be another likely decomposition product. However, when we looked at the gas-phase IR spectrum following an equimolar reaction only traces of CO, but a large amount of $\mathrm{CO_2}$, was found (Table 2). This is consistent with the fact that at the end of the equimolar NMR reaction there was always a considerable amount of unreacted HCN left (*cf.* Table 1) which was not the case when we treated HCN with a two- to three-fold excess of $\mathrm{NO_2{}^+BF_4{}^-}$. In agreement with this, after the neat reaction of a three-fold excess of $\mathrm{NO_2{}^+}$ salt with HCN only traces of HCN and no CO (but $\mathrm{CO_2}$) were identified from their IR data. This indicated that the CO initially formed upon decomposition of $\{\mathrm{CN{-}NO_2}\}$ [equation (3)] is further oxidized by unreacted $\mathrm{NO_2{}^+}$ salt to give $\mathrm{CO_2}$ and $\mathrm{NO^+}$ [equation (4)].

$$\{\mathrm{CN{-}NO_2}\} \longrightarrow \mathrm{N_2O + CO} \qquad (3)$$

$$\mathrm{CO + NO_2{}^+} \longrightarrow \mathrm{CO_2 + NO^+} \qquad (4)$$

Thermodynamics and mechanism

Simple thermodynamic considerations clearly indicate that a reaction according to equation (4) should be favourable by 301 kJ mol^{-1} (−72 kcal mol^{-1}) (Table 3).

The fact that the gas-phase IR spectrum indicates the presence of both $\mathrm{BF_3}$ and HCN is in agreement with earlier work which established the very weak nature of the $\mathrm{HCN{\cdot}BF_3}$ Lewis acid–Lewis base complex which readily dissociates in the gas phase to give free HCN and $\mathrm{BF_3}$.[32–35]

In earlier studies it was established that the intermediate products formed in the reaction of azide compounds with $\mathrm{NO^+}$ and $\mathrm{NO_2{}^+}$ salts (*i.e.* $\mathrm{ON{-}N_3}$ and $\mathrm{O_2N{-}N_3}$) decompose according to equations (2) and (5) in an unimolecular process

$$\mathrm{N_4O} \longrightarrow \mathrm{N_2O + N_2} \qquad (5)$$

via cyclic intermediates.[2,3,36,37] Therefore, we propose a reaction mechanism for the formation and decomposition of $\mathrm{CNNO_2}$ as shown in Scheme 1. It is stressed that the formal charges in structures **A** and **B** as well as in Scheme 1 are to satisfy the Lewis representations and are of no relevance for the discussion of the partial charges.[27]

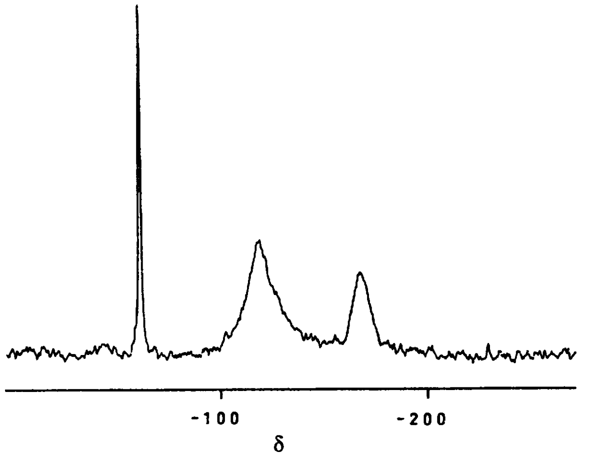
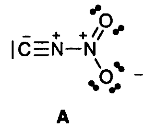


Fig. 1 The ^{14}N NMR spectrum of an equimolar reaction mixture of $NO_2^+BF_4^-$ and HCN in CFC_3 after 20 min of reaction at 0 °C



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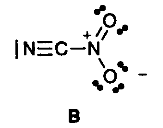

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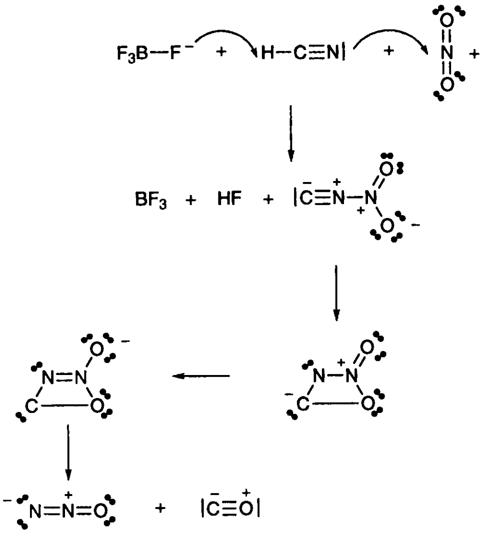
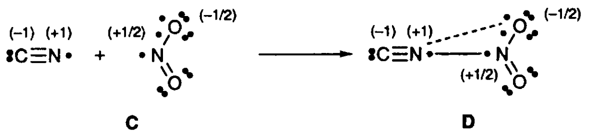


Scheme 1 Proposed reaction mechanism for the formation and decomposition of $CNNO_2$

Theoretical aspects

From the increased valence point of view[38,39] the $CNNO_2$ molecule can formally be described as the product of the reaction of NO_2 and NC radicals [equation (6)]. The 'best'



(6)

C **D**

representation for an NO_2 radical summarizing several possible Lewis structures is shown in **C**)[40–42] by using the Pauling three-electron bond structure (in resonance with its mirror image), which has (fractional) odd-electron charge located in both the nitrogen and oxygen atomic orbitals. The recombination with isocyanide radicals subsequently gives a $CNNO_2$ molecule which has both a (fractional) N–N bond (—) and a (fractional) 'long' N–O bond (- - -). Comparison of the increased valence-bond structure **D** (in resonance with its mirror image) with the most common Lewis structure **A** reveals that there are two additional bonding electrons in **D**. Therefore, this structure can be designated as an *increased valence* structure[38,39] and must be more stable than any of the component Lewis structures.

Table 2 Gas-phase IR data obtained from an equimolar reaction mixture of $NO_2^+BF^-_4$ and HCN (conditions see Experimental section)

Wavenumber (cm^{-1})	Intensity[a]	Assignment	Ref.
3308	10	ν(C–H), HCN	3311[8]
2355	9	ν_{asym}(OCO), CO_2	2349[19,20]
2250	9	ν_1(NNO), N_2O	2224, matrix;[21] 2277,[22a] 2242[22b]
1878	1	ν(NO), NO	1880[23]
1580	br	ν_3(ONO), NO_2[b]	1610[24]
1508	1	ν_3, BF_3	1505[25,26]
1300	9	δ(NNO), N_2O	1285, matrix;[21] 1300[22a]
740	sh	ν_3(ONO), NO_2[b]	749[24]
717	8	δ(HCN), HCN + ν_2, BF_3	721[18] 718[25,26]
670	sh	δ(OCO), CO_2	667[19,20]

[a] Intensity scale 1 (very weak)–10 (very strong). [b] NO and NO_2 are impurities due to the presence of NO^+ and NO_2^+ salts.

Table 3 Heats of formation ($\Delta H°_f$ values) for the reactants according to equation (4)*

Gas-phase species	$\Delta H°_f$/kcal mol^{-1}	Ref.
CO	−26.6 (−111)	28
CO_2	−94.3 (−394)	28
NO_2^+	240.7 (1006)	28-31
NO^+	236.6 (989)	28

* Values in parentheses are in kJ mol^{-1}.

We were surprised to find that CN–NO_2 and not NC–NO_2 was formed from the reaction of HCN and NO_2^+ (N.B. NC–NO is an unstable, though well characterized compound[43]). However, to our knowledge so far there is no experimental proof for the existence of a compound of type NC–NO_2. The structure of NC–NO_2 was calculated *ab initio* at the Hartree-Fock (HF) level of theory using the proton affinities of substituted cyanides.[44] The structures of both molecules CN–NO_2 and NC–NO_2 were computed at the correlated MP2 level of theory using a 6-31G(d,p) basis set and the program package GAUSSIAN 92[45] (Fig. 2). We also calculated the reaction enthalpies according to equations (7) and (8) and

$$NO_2^+ + CN^- \longrightarrow CN\text{–}NO_2; \quad \Delta H(9, \text{MP2}) = -696 \text{ kJ mol}^{-1} \tag{7}$$

$$NO_2^+ + CN^- \longrightarrow NC\text{–}NO_2; \quad \Delta H(10, \text{MP2}) = -856 \text{ kJ mol}^{-1} \tag{8}$$

established that the NC–NO_2 isomer is favoured by 156 (MP2 level) or 107 kJ mol^{-1} (HF level), respectively (Fig. 3). Since the thermodynamically slightly less favourable isomer CN–NO_2 was formed we conclude that this has to be for kinetic reasons which is also consistent with the nearly identical energies of a weakly bound $\{X^-\cdots NO_2^+\}$ adduct (X = CN or NC) for medium and long interionic distances ($d > 2.5$ Å, *cf.* Fig. 3).

The (experimentally observed) decomposition of the CN–NO_2 molecule formed as an intermediate in the reaction of HCN and NO_2^+ (see above) was calculated to be thermodynamically highly favourable [equation (9)].

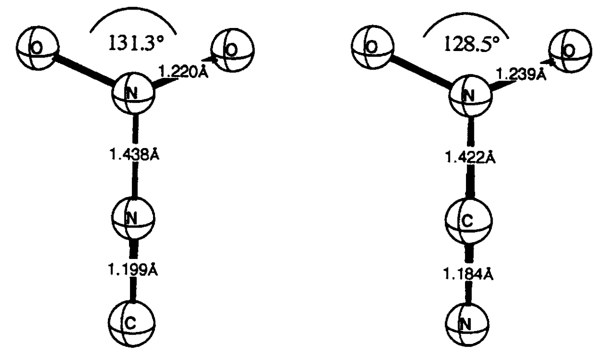


Fig. 2 Computed structures of CN-NO_2 (left) and NC-NO_2 (right)

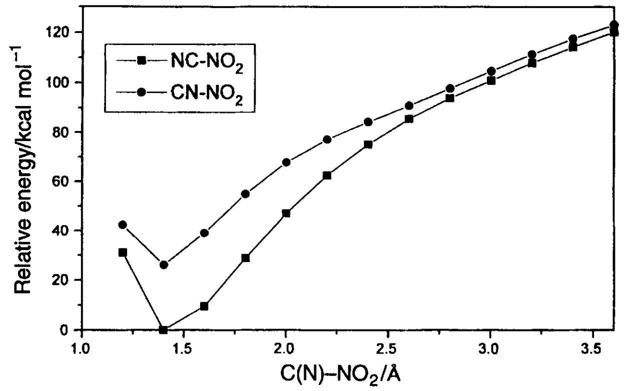


Fig. 3 Approach of the CN^- and the NO_2^+ ions to give CN-NO_2 or NC-NO_2, respectively (energies relative to the more stable NC-NO_2 isomer) (1 kcal mol^{-1} = 4.184 kJ mol^{-1})

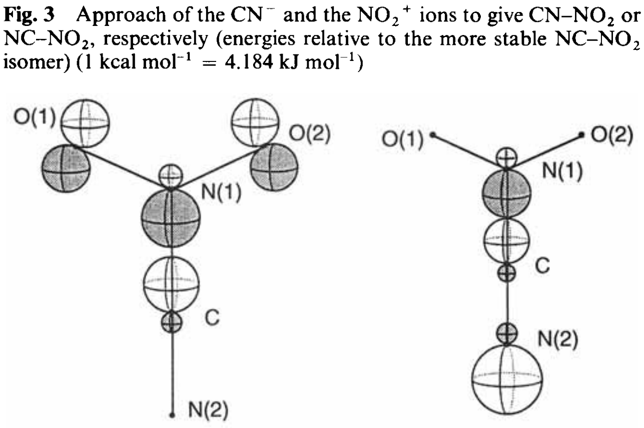


Fig. 4 Intramolecular donor–acceptor interaction (negative hyperconjugation) in NC-NO_2. Left: lone pair (O) to σ*[N(1)–C]. Right: lone pair (N) to σ*[N(1)–C]

$$\text{CN-NO}_2 \longrightarrow \text{CO} + \text{N}_2\text{O}; \qquad \Delta H(11, \text{MP2}) = -1007 \text{ kJ mol}^{-1} \quad (9)$$

Natural bond orbital (NBO) analysis revealed that both molecules, NC-NO_2 and CN-NO_2, possess two strong intramolecular donor–acceptor interactions (negative hyperconjugation) which both weaken the C–N or the N–N bond, respectively.*,[46] In the case of NC-NO_2, electron density is transferred (*i*) from the oxygen lone pairs to the σ*[N(1)–C] bond (2 × 77 kJ mol^{-1}) and (*ii*) from the sp lone pair at the terminal nitrogen atom to the σ*[N(1)–C] bond (79 kJ mol^{-1}) (Fig. 4). The molecule CN-NO_2 also shows two types of hyperconjugative interactions: (*i*) lone pair (O) to σ*[N(1)–N(2)] (2 × 161 kJ mol^{-1}) and (*ii*) lone pair (C) to σ*[N(1)–N(2)] (93 kJ mol^{-1}) (Fig. 5).

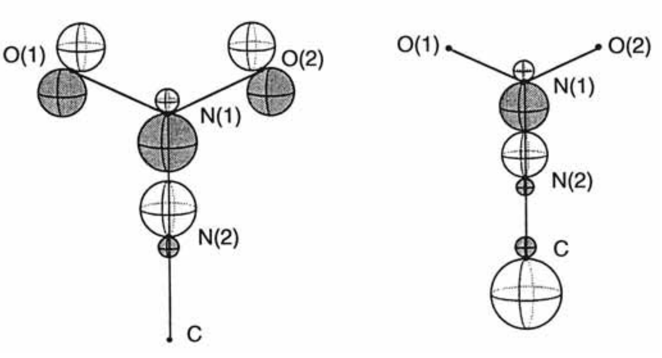


Fig. 5 Intramolecular donor–acceptor interaction (negative hyperconjugation) in CN-NO_2. Left: lone pair (O) to σ*[N(1)–N(2)]. Right: lone pair (C) to σ*[N(1)–N(2)]

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* In the quantum-mechanical computation (subjecting the HF density matrix as represented in the localized NBOs to a second-order perturbative analysis) the energy was computed according to $E^{(2)}_{\varphi\varphi^*} = -2\langle\varphi|h^F|\varphi^*\rangle^2/(E_{\varphi^*} - E_\varphi)$ where h^F is the Fock operator φ and φ* are the filled and unfilled NBO orbitals respectively and $\Delta E_{\varphi\varphi^*}$ the energy lowering due to the donor–acceptor interaction.

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