Theor Chim Acta (1994) 88: 1–12

Theoretica
Chimica Acta

A theoretical investigation of NC_3NC

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Received February 19, 1993/Accepted June 30, 1993

Summary. Various spectroscopic properties have been calculated by CEPA-1 for NC_3NC, a molecule of potential interest to astrochemistry. According to CCSD(T) calculations with a basis set of 168 cGTOs, it is less stable than dicyanoacetylene (NC_4N) by 108.5 kJ mol^{-1}. The equilibrium dipole moment is predicted to be 1.04 D (CCSD(T)/162 cGTO), with the negative end of the dipole at the terminal nitrogen site. The results of the present calculations are in excellent agreement with those of matrix-isolation IR spectroscopy carried out in the course of this work.

Key words: NC_3NC – CEPA-1 – Spectroscopy

1 Introduction

Dicyanoacetylene (NC_4N) is probably the source of the 478 cm^{-1} band found in the infrared emission spectrum of Saturn moon Titan during the Voyager IRIS mission [1–3]. Nothing was known from experiment about its less stable isomers until a few months ago. In the course of this work, however, Smith et al. [4] were able to produce the iso-nitrile NC_3NC through in-situ UV laser photolysis of matrix isolated dicyanoacetylene (NC_4N/Ar: 1/400–1/500, 1200 mbar). All five stretching fundamentals plus a number of combination tones and one overtone could be observed for the most abundant isotopomer by Fourier-Transform-Infrared Spectroscopy. The strongest stretching fundamentals were also observed for those six isotopomers resulting from single ^{13}C and ^{15}N substitution.

The scope of the present theoretical investigation consists in gaining a broader knowledge of the properties of NC_3NC, with particular emphasis on spectroscopic properties of interest to radioastronomy and IR astronomy. Since CN and C_3N are known constituents of interstellar clouds, NC_4N (not accessible through radioastronomy due to the lack of a permanent dipole moment) and NC_3NC are plausible candidates as well. The present paper may be regarded as an extension of our previous work on linear (or quasi-linear) molecules of astrochemical interest with four or more heavier atoms (see [5–10] for some recent work).

2 Details of calculations

Electronic structure calculations were mostly carried out by means of the coupled electron pair approximation [11–13], version 1 (CEPA-1), as introduced by W. Meyer. This method may be regarded as an approximation to coupled cluster theory with single and double substitution operators, CCSD [14]. In practical applications (see, e.g., [10]) it turned out that CEPA-1 almost always produces results which lie intermediate between those obtained by CCSD and CCSD(T) where the latter acronym stands for CCSD followed by a perturbative treatment of connected triple substitutions [15]. All calculations were carried out with the program system MOLPRO92[1]. The implementation of CCSD into this program system is due to Hampel et al. [16]; inclusion of the connected triples contributions has been carried out by M. Deegan and P. J. Knowles (unpublished work).

In most calculations, a basis set of 126 contracted Gaussian-type orbitals (cGTOs) was employed, where real spherical harmonics describe the angular parts of the *d*-functions. The same basis set (plus *f*-functions at C and N) was employed in our previous work on HC_2NC and HNC_3 [9]. It consists of Huzinaga's [17] 10*s*,5*p* set for carbon and nitrogen in contraction [7, 3] plus Dunning's [18] 2*d* sets which were contracted in the way described earlier [9] so that the contracted basis is of size [7, 3, 1] per atom. All valence electrons were correlated in the CEPA-1 and coupled cluster calculations and canonical molecular orbitals were employed.

3 Results and discussion

Using CEPA-1 and the basis set of 126 cGTO, 88 points of the potential energy surface with linear arrangement of the nuclei and 87 points with bent geometries have been calculated. These were least-squares fitted by a polynomial function in internal coordinates (five bond-stretching and four angle-bending ones). After transformation to equilibrium the analytical potential energy function (PEF) is given by the expression:

$$V - V_e = \sum_{ijklmnopq} C_{ijklmnopq} \Delta R_1^i \Delta R_2^j \Delta R_3^k \Delta R_4^l \Delta R_5^m \alpha^n \beta^o \gamma^p \delta^q \tag{1}$$

Here, ΔR_1, ΔR_2, ΔR_3, ΔR_4, and ΔR_5 are the changes in the $N_{(1)}C_{(1)}$, $C_{(1)}C_{(2)}$, $C_{(2)}C_{(3)}$, $C_{(3)}N_{(2)}$, and $N_{(2)}C_{(4)}$ internuclear separations with respect to the corresponding equilibrium values and α, β, γ, and δ are differences between 180° and the $N_{(1)}C_{(1)}C_{(2)}$, $C_{(1)}C_{(2)}C_{(3)}$, $C_{(2)}C_{(3)}N_{(2)}$, and $C_{(3)}N_{(2)}C_{(4)}$ angles, respectively. Two bending coordinates are defined to have the same sign for a *cis*-like distortion of the nuclear frame-work. The following equilibrium bond lengths were obtained: $R_{1e} = 1.1636$ Å, $R_{2e} = 1.3805$ Å, $R_{3e} = 1.2094$ Å, $R_{4e} = 1.3144$ Å and $R_{5e} = 1.1879$ Å. The corresponding total energy is $V_e = -261.173966$ au. The equilibrium rotational constant is calculated to be $B_e = 1396$ MHz, which is very likely an underestimate. Analogous calculations for NC_4N yielded 1324 MHz which differs from the experimental ground-state value of 1336.68 MHz [10] by 0.95%. We recommend B_0 (NC_3NC) = 1409 MHz by applying the scaling factor from NC_4N to the CEPA-1 B_e value for NC_3NC. Its uncertainty may be on the order of 5 MHz.

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[1] MOLPRO92 is a package of *ab initio* programs written by H.-J. Werner and P. J. Knowles, with contributions of J. Almlöf, R. Amos, M. Deegan, S. Elbert, C. Hampel, W. Meyer, K. A. Peterson, E. A. Reinsch, R. Pitzer, A. Stone and P. R. Taylor.

Table 1. Stretching part of analytical CEPA-1 potential energy function for NC_3NC[a]

PEF term						PEF term					
i	j	k	l	m	value	i	j	k	l	m	value
2	0	0	0	0	0.572994	2	0	0	1	0	0.000499
3	0	0	0	0	−0.685377	1	0	0	0	1	−0.003381
4	0	0	0	0	0.489911	1	0	0	0	2	−0.001474
5	0	0	0	0	−0.290795	2	0	0	0	1	−0.002184
6	0	0	0	0	0.124541	0	1	1	0	0	0.029057
0	2	0	0	0	0.228413	0	1	2	0	0	−0.000482
0	3	0	0	0	−0.218054	0	2	1	0	0	−0.040972
0	4	0	0	0	0.138076	0	1	0	1	0	−0.008546
0	5	0	0	0	−0.073227	0	1	0	2	0	0.007959
0	6	0	0	0	0.025084	0	2	0	1	0	0.005939
0	0	2	0	0	0.513572	0	1	0	0	1	0.004978
0	0	3	0	0	−0.536562	0	1	0	0	2	−0.000322
0	0	4	0	0	0.348515	0	2	0	0	1	−0.004564
0	0	5	0	0	−0.187442	0	0	1	1	0	0.036788
0	0	6	0	0	0.072503	0	0	1	2	0	−0.053232
0	0	0	2	0	0.269503	0	0	2	1	0	−0.007961
0	0	0	3	0	−0.281756	0	0	1	0	1	−0.028669
0	0	0	4	0	0.191181	0	0	1	0	2	−0.014372
0	0	0	5	0	−0.111283	0	0	2	0	1	−0.000044
0	0	0	6	0	0.039446	0	0	0	1	1	0.035696
0	0	0	0	2	0.493870	0	0	0	1	2	0.007039
0	0	0	0	3	−0.585384	0	0	0	2	1	−0.069264
0	0	0	0	4	0.411433	1	1	1	0	0	0.056124
0	0	0	0	5	−0.253154	1	1	0	1	0	−0.013539
0	0	0	0	6	0.116538	1	1	0	0	1	0.006048
1	1	0	0	0	0.030216	1	0	1	1	0	0.007500
1	2	0	0	0	−0.052714	1	0	1	0	1	−0.002133
2	1	0	0	0	0.004179	1	0	0	1	1	0.011023
1	0	1	0	0	−0.023189	0	1	1	1	0	0.000470
1	0	2	0	0	−0.007054	0	1	1	0	1	0.001737
2	0	1	0	0	−0.014492	0	1	0	1	1	−0.012626
1	0	0	1	0	0.005534	0	0	1	1	1	0.058833
1	0	0	2	0	−0.005054						

[a] PEF terms are given in au; see Eq. (1) for their definition

The quartic equilibrium centrifugal distortion constant is calculated to be $D_J^e = 312$ Hz. The corresponding ground-state value may be substantially larger as a consequence of the shallow CNC bending potential (see below).

The analytical PEF includes diagonal terms up to sextic ones while off-diagonal terms were considered up to the cubic ones. The coefficients $C_{ijklmnopq}$ are listed in Tables 1 and 2. The same sort of fit has been carried out for the electric dipole moment which was calculated as an energy derivative. The coefficients of the electric dipole moment function (EDMF) are given in Table 3. The variation of the dipole moment with the five stretching coordinates is shown in Fig. 1. The equilibrium dipole moment is $\mu_e = 1.069$ D (negative end at the terminal nitrogen site). From our experience with analogous calculations on similar molecules such as NCNC [5, 19] or HC_2NC [9, 10] we expect this value to be accurate to ca. 0.05 D.

Table 2. Bending and stretch-bend part of analytical CEPA-1 potential energy function for NC_3NC[a]

PEF term										PEF term									
i	j	k	l	m	n	o	p	q	value	i	j	k	l	m	n	o	p	q	value
0	0	0	0	0	2	0	0	0	0.041815	0	0	1	0	0	2	0	0	0	− 0.000840
0	0	0	0	0	0	2	0	0	0.028852	0	0	1	0	0	0	2	0	0	− 0.056832
0	0	0	0	0	0	0	2	0	0.039746	0	0	1	0	0	0	0	2	0	0.007248
0	0	0	0	0	0	0	0	2	0.001397	0	0	1	0	0	0	0	0	2	0.011923
0	0	0	0	0	1	1	0	0	− 0.001203	0	0	1	0	0	1	1	0	0	0.024162
0	0	0	0	0	1	0	1	0	− 0.004086	0	0	1	0	0	1	0	1	0	− 0.018489
0	0	0	0	0	1	0	0	1	0.000173	0	0	1	0	0	1	0	0	1	0.002626
0	0	0	0	0	0	1	1	0	0.028652	0	0	1	0	0	0	1	1	0	0.035612
0	0	0	0	0	0	1	0	1	− 0.000688	0	0	1	0	0	0	1	0	1	− 0.059248
0	0	0	0	0	0	0	1	1	0.005157	0	0	1	0	0	0	0	1	1	− 0.063450
1	0	0	0	0	2	0	0	0	− 0.083620	0	0	0	1	0	2	0	0	0	− 0.007248
1	0	0	0	0	0	2	0	0	0.000525	0	0	0	1	0	0	2	0	0	0.005988
1	0	0	0	0	0	0	2	0	− 0.027208	0	0	0	1	0	0	0	2	0	− 0.072379
1	0	0	0	0	0	0	0	2	− 0.020997	0	0	0	1	0	0	0	0	2	− 0.057679
1	0	0	0	0	1	1	0	0	0.040759	0	0	0	1	0	1	1	0	0	0.000840
1	0	0	0	0	1	0	1	0	0.038974	0	0	0	1	0	1	0	1	0	0.007564
1	0	0	0	0	1	0	0	1	− 0.054941	0	0	0	1	0	1	0	0	1	− 0.006224
1	0	0	0	0	0	1	1	0	0.003887	0	0	0	1	0	0	1	1	0	0.009560
1	0	0	0	0	0	1	0	1	0.000867	0	0	0	1	0	0	1	0	1	0.010951
1	0	0	0	0	0	0	1	1	− 0.003650	0	0	0	1	0	0	0	1	1	− 0.054416
0	1	0	0	0	2	0	0	0	− 0.032250	0	0	0	0	1	2	0	0	0	− 0.067495
0	1	0	0	0	0	2	0	0	− 0.029414	0	0	0	0	1	0	2	0	0	− 0.008929
0	1	0	0	0	0	0	2	0	− 0.002311	0	0	0	0	1	0	0	2	0	− 0.012291
0	1	0	0	0	0	0	0	2	0.003874	0	0	0	0	1	0	0	0	2	− 0.068781
0	1	0	0	0	1	1	0	0	0.001681	0	0	0	0	1	1	1	0	0	0.004097
0	1	0	0	0	1	0	1	0	0.004097	0	0	0	0	1	1	0	1	0	0.005778
0	1	0	0	0	1	0	0	1	− 0.030465	0	0	0	0	1	1	0	0	1	0.000919
0	1	0	0	0	0	1	1	0	0.011135	0	0	0	0	1	0	1	1	0	0.009980
0	1	0	0	0	0	1	0	1	− 0.021141	0	0	0	0	1	0	1	0	1	− 0.002889
0	1	0	0	0	0	0	1	1	0.003519	0	0	0	0	1	0	0	1	1	0.022770

[a] PEF terms are given in au; see Eq. (1) for their definition

Table 3. Parameters of the electric dipole moment function (EDMF)

		EDMF term[a]			CEPA-1(ED)
i	j	k	l	m	
0	0	0	0	0	0.42067
1	0	0	0	0	0.07877
2	0	0	0	0	– 0.09081
3	0	0	0	0	0.00501
4	0	0	0	0	– 0.05540
0	1	0	0	0	– 0.15283
0	2	0	0	0	– 0.04450
0	3	0	0	0	0.07040
0	4	0	0	0	– 0.07184
0	0	1	0	0	0.19700
0	0	2	0	0	– 0.07341
0	0	3	0	0	0.00712
0	0	4	0	0	0.00644
0	0	0	1	0	– 0.67632
0	0	0	2	0	0.07116
0	0	0	3	0	0.38637
0	0	0	4	0	– 0.02367
0	0	0	0	1	1.06752
0	0	0	0	2	– 0.20255
0	0	0	0	3	– 0.33992
0	0	0	0	4	0.11410
1	1	0	0	0	– 0.34783
1	0	1	0	0	0.00738
1	0	0	1	0	– 0.13462
1	0	0	0	1	0.10757
0	1	1	0	0	0.06216
0	1	0	1	0	0.04493
0	1	0	0	1	– 0.10618
0	0	1	1	0	– 0.16153
0	0	1	0	1	0.19958
0	0	0	1	1	0.41992

[a] EDMF terms are given in au. The dipole moment is defined to have positive sign when directed from the negative to the positive end in the direction of the positive z-axis

This view is substantiated by calculations at the CCSD(T) level which make use of a larger and more flexible basis set. The result is given in Table 4 which quotes also the equilibrium dipole moment values obtained by SCF, MP2, CCSD and CEPA-1 for the same basis set. Compared with CCSD(T), SCF overestimates μ_e by a factor of as much as 2.1. MP2 yields 71% of the CCSD(T) value. CEPA-1 lies intermediate between CCSD and CCSD(T), somewhat closer to the former. The contribution of connected triple substitutions amounts to – 0.1375 D. This is substantially larger than in other molecules we studied previously like CO, HCO^+, HCN, or HC_2NC [10]. Compared with isocyanogen, NCNC [5, 19], the dipole moment experiences an increase by 0.37 D. This may be compared with an increase in the ground-state dipole moment of 0.60(3) D found experimentally [20, 21] for NC_5H and NC_3H. With the analytical PEF and EDMF vibrational term energies and

Table 4. Dependence of the equilibrium dipole moment on the method of calculation[a]

Method	μ_e	Method	μ_e
SCF	2.2195	MP2	0.7375
CEPA-1	1.1254	CCSD	1.1793
CCSD(T)	1.0418		

[a] Basis: 162 contracted GTO (*s* and *p* functions from aug-cc-pVTZ basis of Kendall et al. [31]: *d* functions from cc-pVTZ basis of Dunning [18]). All calculations were carried out at the CEPA-1 equilibrium geometry (see text). For the methods including electron correlation effects the dipole moment has been calculated as an energy derivative

wavefunctions and absolute IR intensities have been calculated [22, 23]. The latter are obtained according to the formula:

$$A_{fi} \approx \frac{\pi N_0}{3\hbar c \varepsilon_0} \bar{\nu}_{fi} |\langle \Psi_f | \boldsymbol{\mu} | \Psi_i \rangle|^2 \tag{2}$$

In Eq. (2), N_0 is Avogadro's constant, $\hbar$ Planck's constant divided by 2π, c the vacuum velocity of light, ε_0 the permittivity of vacuum, and $\bar{\nu}_{fi}$ the wavenumber of the transition between states $|f\rangle$ and $|i\rangle$. The results are given in Table 5 where also comparison is made with the available experimental data [4]. The ν_3 band is calculated to be the strongest stretching vibrational band, with origin calculated at 2061.3 cm^{-1} and an absolute IR intensity of 186.0 $\mathrm{km\,mol}^{-1}$. The strongest band in the matrix IR spectrum appears at 2044.8 cm^{-1}, only 16.5 cm^{-1} off from our theoretical value. We calculate three further relatively strong bands at 2231.1, 2320.7 and 2388.5 cm^{-1}. The corresponding peaks in the matrix spectrum differ in position from the theoretical values by 27.5, 33.6 and 20.4 cm^{-1}. These peaks are assigned to ν_2, ν_1, and $2\nu_4$. According to our calculations, the latter gets most of its intensity through Fermi resonance interaction with ν_1. Expansion of the stretching vibrational wavefunctions into products of harmonic oscillator functions (denoted by Dirac brackets) yields the following results for the two components of the Fermi diade (I: upper component, II: lower component):

$$\Psi_I = -0.56\,|\nu_1\rangle + 0.75\,|2\nu_4\rangle + \cdots$$

$$\Psi_{II} = 0.77\,|\nu_1\rangle + 0.55\,|2\nu_4\rangle + \cdots$$

The ν_4 band, with calculated band origin at 1184.9 cm^{-1}, has very little intensity (0.7 $\mathrm{km\,mol}^{-1}$). This is in excellent agreement with the results from matrix IR spectroscopy [4]. NC_3NC is thus another example for a molecule where – due to anharmonic interaction – the intensity of an overtone is substantially larger than that of the corresponding fundamental (see [7] for a similar case). Compared with the matrix spectrum the present calculations exaggerate the degree of anharmonic interaction between ν_1 and $2\nu_4$. Therefore, the upper component of the Fermi diade gets too high an intensity in our calculations. The calculated sum of the intensities of both components, however, is in quite good agreement with experiment. Since the matrix absorptions may differ from the gas-phase values by a few cm^{-1} the

Table 5. Harmonic and anharmonic stretching vibrational wavenumbers and IR intensities for NC_3NC (CEPA-1/126 cGTO)[a]

	ν^b	A^c		ν^b	A^c
ω_1	2373.0	111.1	$\nu_4 + 2\nu_5$	2397.0	2.6
ω_2	2259.1	79.2	$\nu_3 + \nu_5$	2672.7	0.4
ω_3	2088.2	188.2	$\nu_2 + \nu_5$	2842.1	0.6
ω_4	1196.4	0.9	$\nu_1 + \nu_5{}^d$	2927.8	0.9
ω_5	616.8	1.6	$2\nu_4 + \nu_5{}^d$	2992.4	0.6
ν_5	611.7	1.6	$\nu_3 + \nu_4$	3244.3	0.6
	(610.1)	(1.3)	$\nu_2 + \nu_4$	3410.9	1.0
ν_4	1184.9	0.7	$\nu_1 + \nu_4{}^d$	3478.2	0.03
	(1202.3)	(1.0)	$3\nu_4{}^d$	3589.9	0.16
$2\nu_5$	1222.2	0.02	$2\nu_3$	4104.8	2.8
$\nu_4 + \nu_5$	1791.2	0.3	$\nu_2 + \nu_3$	4282.9	0.4
ν_3	2061.3	186.0	$\nu_1 + \nu_3$	4376.0	0.04
	(2044.8)	(186)	$2\nu_2$	4450.3	0.2
ν_2	2231.1	78.0	$\nu_1 + \nu_2{}^d$	4536.1	0.04
	(2203.6)	(97)	$\nu_2 + 2\nu_4{}^d$	4602.3	0.02
$\nu_1{}^d$	2320.7	57.3	$\nu_1 + 2\nu_4{}^d$	4618.8	0.01
	(2287.1)	(100)	$2\nu_1{}^d$	4685.7	0.0005
$2\nu_4{}^d$	2388.5	42.6	$4\nu_4{}^d$	4795.6	0.0001
	(2408.9)	(25)			

[a] Experimental values [4] are given in parentheses. The measured relative intensity of the strongest band (ν_3) is normalized to the present *ab initio* value

[b] in cm^{-1}; [c] in $km\ mol^{-1}$

[d] These states undergo strong anharmonic interaction and the characterization with normal-mode quantum numbers is very approximative

strength of the Fermi resonance interaction in the (still unknown) gas-phase spectrum may be significantly different from the situation observed in an argon matrix. The stretching vibration with lowest wavenumber (ν_5) is calculated to occur at 611.7 cm^{-1}, very close to the matrix value of 610.1 cm^{-1}. Its intensity is calculated to be quite small, again in agreement with experiment.

According to our calculations the $\nu_4 + 2\nu_5$ band with calculated band origin at 2397.0 cm^{-1} is sufficiently intense ($A = 2.6\ km\ mol^{-1}$) to allow for its detection in the matrix spectrum. The position in the latter may be estimated in the following way:

$$\nu_4 + 2\nu_5(matrix) \approx \nu_4 + 2\nu_5(theor.) + \Delta\nu_4 + 2\Delta\nu_5 = 2411.2\ cm^{-1} \qquad (3)$$

where $\Delta\nu_4$ and $\Delta\nu_5$ are the differences between matrix values and *ab initio* values for the fundamentals. A. M. Smith (TU München) has reexamined the spectra at our notice and found a small peak at 2409.6 cm^{-1} which fits well our prediction. The experimental intensity ratio of the bands at 2408.9 cm^{-1} (upper component of $\nu_1/2\nu_4$ Fermi diade) and 2409.6 cm^{-1} is 17, in excellent agreement with the theoretical one of 16. In an analogous way we estimate the position of $2\nu_3$ (with 2.8 $km\ mol^{-1}$ absolute intensity) in the matrix spectrum to be 4071.8 cm^{-1}. A. M. Smith found a peak at 4073.0 cm^{-1} which nicely agrees with our prediction. Very good candidates for peaks in the matrix spectrum observed at 4395.9 and 4238.1 cm^{-1} are $2\nu_2$ and $\nu_2 + \nu_3$, with estimated positions of 4395.3 and 4238.9 cm^{-1}. We would also like to assign the observed peaks at 3404.4 and

3245.0 cm^{-1} to $\nu_2 + \nu_4$ and $\nu_3 + \nu_4$, respectively. Our estimated positions are 3404.4 and 3245.0 cm^{-1}. There are several more peaks in the matrix IR spectrum for which we cannot offer unambiguous assignments at present.

The wavenumbers and absolute IR intensities of the bending fundamentals were calculated within the harmonic approximation. The quadratric bending force constants are listed in Table 2 where also cubic stretch-bend coupling force constants are quoted. A very small value of 0.001397 au (0.0122 aJ) was calculated for the quadratic CNC bending force constant $f_{\delta\delta} = (\partial^2 V/\partial\delta^2)_e$. This is very likely an underestimate. CCSD(T) calculations with the same basis set yield $f_{\delta\delta} =$ 0.017481 au. This value may be too high since the effect of *f*-functions, investigated at the CEPA-1 level, consists in a flattening of the CNC bending potential. We presume that very large basis sets are required to obtain an accurate value for $f_{\delta\delta}$. Due to the shallow CNC bending potential anharmonicity effects are also expected to play a larger role for the bending vibration with lowest wavenumber; their explicit treatment is beyond the scope of the present paper.

The CEPA-1 harmonic bending wavenumbers (in cm^{-1}) and corresponding IR intensities (in km mol^{-1}; in parentheses) are $\omega_6 = 493$ (7), $\omega_7 = 395$ (12), $\omega_8 = 158$ (15) and $\omega_9 = 45$ (31). Making use of the CCSD(T) value for $f_{\delta\delta}$ yields $\omega_6 = 493$ (6), $\omega_7 = 404$ (25), $\omega_8 = 224$ (16) and $\omega_9 = 110$ (17). Three bending vibrations are thus fairly intense and might be suitable candidates for forthcoming experiments. They could not be observed by Smith et al. [4] due to the limited wavelength range accessible by the HgCdTe detector.

Vibration–rotation coupling constants α_r have been calculated from the cubic force field by standard second-order perturbation theory in normal co-ordinate space (see, e.g., [24, 25]). The results for various isotopomers are given in Table 6 which lists also the *l*-type doubling constants. According to our experience with other linear molecules with four and more atoms [5–9, 20], the α_s values for unperturbed (or deperturbed) stretching vibrations should be accurate to better than 10%. The α_6 and α_7 values are believed to be accurate to better than 20%. The uncertainties in the α_8 values are larger and may be of the order of 30%. The α_9 values depend very strongly on the chosen value for $f_{\delta\delta}$. We expect that the 'true' α_9 values lie in between those quoted in Table 6, but we are unable to give accurate estimates for them. A similar situation holds for the *l*-type doubling constants q_9. The q_t^J values are calculated to be very small throughout. Their determination by means of high-resolution microwave or infrared spectroscopy will thus present a very difficult task.

A comparison of the CN and NC equilibrium bond lengths and stretching force constants (quadratric, cubic and quartic) of NC_3NC with those of other molecules is made in Table 7. Throughout, the same basis set and method have been employed. We find almost monotonic behaviour when drawing the force constants as a function of R_e (see Figs. 2–4). The molecules dealt with in Table 7 are divided into 4 classes: RCN, RNC, $RCNH^+$, and $RNCH^+$. $HCNH^+$, which is a joint member of the last two classes, has the shortest CN (or NC) equilibrium bond length and the largest force constants. Compared with an accurate R_e value of 1.1341 Å [26] which we have determined by a combined experimental/theoretical approach (see, e.g., [6]) the present CEPA-1 calculations overestimate R_e by 0.0047 Å. CCSD(T) calculations with a large basis set of 156 cGTOs in which all electrons were correlated yield $R_e = 1.1349$Å [26]. The present CEPA-1 calculations overestimate R_e (HCN) by 0.0043 Å compared to the recent accurate value of Carter, Mills, and Handy [27]. Similar errors are observed for the CN equilibrium bond lengths of NCCN, NCNC, and HC_3N. The CEPA-1 calculations with

Table 6. CEPA-1 vibration–rotation coupling and *l*-type doubling constants for NC_3NC (α_v and q_t values in MHz; q_t^J values in Hz)[a]

	NC_3NC	$^{15}N_{(1)}$	$^{13}C_{(1)}$	$^{13}C_{(2)}$	$^{13}C_{(3)}$	$^{15}N_{(2)}$	$^{13}C_{(4)}$
α_1	5.06	5.03	5.16	4.76	4.72	4.98	4.90
α_2	3.58	3.47	3.29	3.75	3.77	3.53	3.47
α_3	2.71	2.59	2.63	2.71	2.72	2.59	2.73
α_4	3.57	3.44	3.55	3.51	3.51	3.56	3.42
α_5	1.34	1.28	1.32	1.33	1.33	1.32	1.28
	(1.33)	(1.28)	(1.32)	(1.33)	(1.33)	(1.32)	(1.27)
α_6	−1.24	−1.24	−1.23	−1.19	−1.23	−1.23	−1.18
	(−1.26)	(−1.26)	(−1.28)	(−1.21)	(−1.24)	(−1.26)	(−1.21)
α_7	−2.51	−2.43	−2.46	−2.53	−2.45	−2.48	−2.44
	(−2.23)	(−2.15)	(−2.17)	(−2.25)	(−2.19)	(−2.20)	(−2.18)
α_8	−3.87	−3.78	−3.80	−3.81	−3.87	−3.75	−3.76
	(−2.80)	(−2.72)	(−2.76)	(−2.77)	(−2.81)	(−2.72)	(−2.76)
α_9	−8.30	−7.98	−8.21	−8.28	−8.22	−7.94	−8.28
	(−2.75)	(−2.68)	(−2.71)	(−2.71)	(−2.71)	(−2.70)	(−2.68)
q_6	0.34	0.33	0.34	0.34	0.34	0.33	0.32
	(0.34)	(0.33)	(0.34)	(0.34)	(0.34)	(0.33)	(0.32)
q_7	0.38	0.39	0.40	0.41	0.42	0.40	0.39
	(0.41)	(0.36)	(0.37)	(0.38)	(0.39)	(0.37)	(0.36)
q_8	0.86	0.83	0.85	0.87	0.86	0.85	0.82
	(0.61)	(0.58)	(0.60)	(0.62)	(0.61)	(0.61)	(0.58)
q_9	2.87	2.73	2.81	2.87	2.87	2.83	2.77
	(1.22)	(1.17)	(1.19)	(1.23)	(1.22)	(1.19)	(1.18)
q_6^J	−0.02	−0.02	−0.02	−0.02	−0.02	−0.02	−0.02
	(−0.02)	(−0.02)	(−0.02)	(−0.02)	(−0.02)	(−0.02)	(−0.02)
q_7^J	−0.10	−0.09	−0.09	−0.10	−0.10	−0.10	−0.09
	(−0.07)	(−0.06)	(−0.06)	(−0.07)	(−0.07)	(−0.07)	(−0.06)
q_8^J	−0.7	−0.7	−0.7	−0.7	−0.7	−0.7	−0.7
	(−0.3)	(−0.3)	(−0.3)	(−0.3)	(−0.3)	(−0.3)	(−0.3)
q_9^J	−1.8	−1.6	−1.7	−1.8	−1.8	−1.7	−1.7
	(−1.1)	(−1.0)	(−1.0)	(−1.1)	(−1.1)	(−1.0)	(−1.0)

[a] Values in parentheses were calculated with the CCSD(T) value for $f_{\delta\delta}$. The vibration–rotation coupling constants for stretching vibrations remain practically unchanged by this modification

the standard basis set of this work perform somewhat worse for the NC (isocyanide) bonds. The error in R_e amounts to 0.0054 Å for HC_2NC and NCNC and to 0.0069 Å for HNC. Accurate equilibrium geometries for these three species are taken from [9, 6, 28], respectively.

The dependence of the quadratic force constant $f_{RR} \equiv (\partial^2 V/\partial R^2)_e$ on the equilibrium bond length R_e is represented well in the range $1.13\ \text{Å} \leqslant R_e \leqslant 1.19\ \text{Å}$ by a parabola in the variable $x = R_e - 1.13$:

$$f_{RR}(x) = 23.04 - 181.72x + 870.59x^2 \tag{4}$$

Here, f_{RR} and x are quoted in aJ Å^{-2} and Å, respectively. Likewise, the cubic and quartic force constants (in aJ Å^{-3} and aJ Å^{-4}, respectively) may be represented by the straight lines:

$$f_{RRR}(x) = -143.4 + 689.6x \tag{5}$$

Table 7. CEPA-1 CN and NC equilibrium bond lengths and force constants for various linear molecules[a]

Molecule		R_e (Å)	f_{RR} (aJ Å^{-2})	f_{RRR} (aJ Å^{-3})	f_{RRRR} (aJ Å^{-4})
$HCNH^+$		1.1388	21.43	−137	747
HC_3NH^+		1.1490	20.05	−129	693
HNC_4N^+	CNH	1.1493	19.94	−129	694
HC_2NCH^+		1.1498	19.63	−129	695
HC_5NH^+		1.1531	19.47	−127	678
HCN		1.1575	18.84	−125	673
		(1.1532)[b]	(18.67)[c]	(−126)[c]	(699)[c]
NCCN		1.1613	18.16	−123	661
		(1.1578)[d]			
NCNC	CN	1.1620	17.91	−122	657
		(1.1581)[d]			
HC_3N		1.1631	17.93	−121	655
		(1.1605)[e]			
NC_3NC	CN	1.1636	17.87	−121	654
NC_4N		1.1636	17.84	−121	651
HC_5N		1.1645	17.73	−120	642
HNC_4N^+	CN	1.1657	17.54	−120	645
HNC		1.1754	16.93	−110	595
		(1.1685)[f]	(16.91)[f]	(−110)[f]	(592)[f]
HC_2NC		1.1848	15.68	−105	562
		(1.1794)[g]			
NCNC	NC	1.1867	15.59	−104	552
		(1.1813)[d]			
HC_4NC		1.1867	15.45	−104	557
NC_3NC	NC	1.1879	15.38	−103	549

[a] Experimental values or accurate values from a combined experimental/theoretical approach are given in parentheses

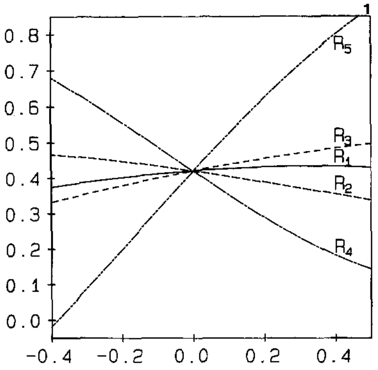
[b] Ref. [27]; [c] Ref. [29]; [d] Ref. [6]; [e] Ref. [32]; [f] Ref. [28]; [g] Ref. [9]

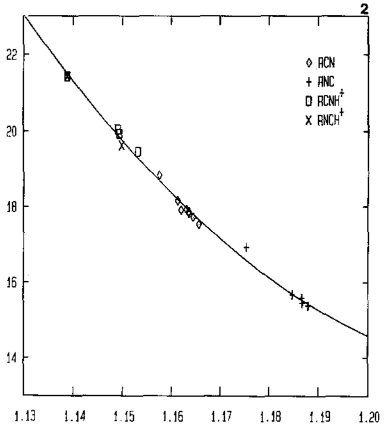
and

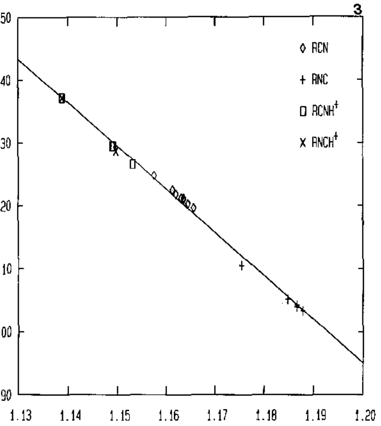
$$f_{RRRR}(x) = 776.5 - 3880x \tag{6}$$

Use of Eq. (4) should allow for force constants predictions with an accuracy of 1–3%. It may be checked for HCN and HNC where accurate values of f_{RR} and R_e are available [27, 28]. Inserting the R_e values (values in parentheses in Table 7) into Eq. (4) yields f_{RR} values of 19.29 (HCN) and 17.33 aJ Å^{-2} (HNC), to be compared with the accurate values of 18.67 and 16.91 aJ Å^{-2}, respectively. For comparison, all-electron CCSD(T) calculations with a basis set of 133 cGTOs (Dunning's [18] cc-pVQZ exclusive of *f*-functions) yield 18.83 and 17.15 aJ Å^{-2} for HCN and HNC, respectively.

The equilibrium geometry of NC_4N has been calculated by CEPA-1/126 cGTO: $R_{1e}(C{\equiv}N) = 1.1636$ Å, $R_{2e}(C{-}C) = 1.3811$ Å, and $R_{3e}(C{\equiv}C) = 1.2119$ Å. This species lies 110.2 kJ mol^{-1} deeper in energy than NC_3NC. Augmenting the basis set by *f*-functions yields a slightly smaller value of 105.9 kJ mol^{-1}. The corresponding values obtained by SCF, MP2, CCSD, and CCSD(T) are listed in Table 8. The CCSD(T)/168 cGTO results of 108.5 kJ mol^{-1} should be the most







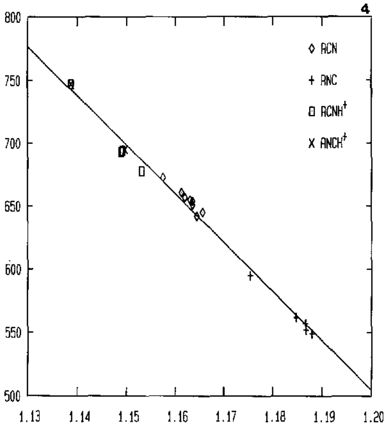


Fig. 1. Variation of the electric dipole moment with stretching coordinates ΔR_i for NC_3NC (μ and ΔR_i in a.u.)

Fig. 2. Dependence of quadratic CN (or NC) stretching force constant f_{RR} (in aJ Å^{-2}) on R_e (in Å)

Fig. 3. Dependence of cubic CN (or NC) stretching force constant f_{RRR} (in aJ Å^{-3}) on R_e (in Å)

Fig. 4. Dependence of quartic CN (or NC) stretching force constant f_{RRRR} (in aJ Å^{-4}) on R_e) (in Å)

Table 8. Dependence of the NC_3NC/NC_4N isomerization energy on the method of the calculation and basis set[a]

Method	126 cGTO	168 cGTO[b]
SCF	81.3	76.3
MP2	135.4	129.6
CEPA-1	110.2	105.9
CCSD	110.2	105.7
CCSD(T)	113.0	108.5

[a] in kJ mol^{-1}

[b] basis set of 126 contracted GTOs plus *f*-functions of Dunning [18]

reliable one. The difference in zero-point vibrational and mean internal energy at room temperature between NC_4N and NC_3NC is smaller than 2 kJ mol^{-1}. We therefore recommend an isomerization energy (or enthalpy) at 298 K (or below) of 109 kJ mol^{-1}, with an uncertainty of ca. 5 kJ mol^{-1}. This is very similar to the isomerization energy calculated earlier for NCCN/CNCN [30].

Acknowledgments. We thank Prof. H.-J. Werner (Universität Bielefeld) for providing us with a copy of MOLPRO92. The electronic structure calculations were mainly carried out on an IBM RISC/6000 workstation model 320H purchased with support from the Fonds der Chemischen Industrie. Computation time provided by the Gesellschaft für wissenschaftliche Datenverarbeitung Göttingen (GWDG) and the Regionales Rechenzentrum für Niedersachsen (RRZN) at Hannover is gratefully acknowledged. Thanks are due to the Deutsche Forschungsgemeinschaft for financial support. We thank Prof. V. E. Bondybey and Dr. A. M. Smith (TU München) for providing us with their experimental results prior to publication and several fruitful discussions.

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