Theoretical Study of NCNCO and Its Isomers

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Various cyanates, isocyanates, nitrile oxides, and fulminates substituted with CN− or NC− groups, as well as their sulfur and selenium analogues, were investigated by ab initio calculations at the MP2/6-31G* level. Equilibrium geometries were determined, and harmonic vibrational frequencies were calculated at these points. Relative stabilities of different isomers were compared. Transition states connecting the stable structures were also investigated, and possible isomerization pathways were suggested.

Introduction

It was shown by us recently[1-4] that ab initio calculations, carried out at the MP2 level, can be beneficial in understanding the structure of quasilinear pseudohalides and provide information complementary to microwave spectroscopy. There are usually two major difficulties in the derivation of molecular constants from the microwave spectra of larger molecules with large-amplitude bending motions. First, the choice of the bending potential is not unique but the derived structure usually strongly depends on this choice. Second, the number of independent parameters inferred from the spectrum is often smaller than the number of geometric parameters to be determined. A strong dependence of the determined parameters on the ones held fixed in the data fit may render the obtained constants unreliable, even though they were based on experiments. Ab initio calculations at a proper level are often useful in this situation, as they provide information on the shape of the bending potential[2] and the possible conformers.[3] In some cases they can assist in making a choice from conflicting structural data, determined by different estimates of the parameters which cannot be fitted.[4]

Pseudohalides are an interesting group of compounds because they often exhibit a low-frequency large-amplitude bending motion, which necessitates an entirely different approach in the microwave structure determination. CN-substituted pseudohalides can be viewed as containing similar functional groups at both ends, which may extend this large-amplitude motion to the entire molecule. The first aim of this work was to predict equilibrium structures for the possible isomers. By the calculation of harmonic vibrational frequencies, these structures can be verified as minimum-energy geometries and some information on the nature of the large-amplitude bends can be obtained. Also, these calculated frequencies may be useful in any future identification of the isomers that have not yet been observed.

The simplest analogous pseudohalides, where a hydrogen replaces the CN group, are important for this study because

state-of-the-art calculations are possible on them. Their structures have been the subject of detailed experimental[5] and theoretical[5-8] work. The stabilities of the four possible isomers are HNCO < HOCN ≪ HCNO < HONC,[5,6] as obtained from HF, MP2, and CCD calculations. Calculations performed at the MP2, MP4, and CCSD(T)/TZ2P levels of theory on HCNO[7] slightly favored a bent structure as opposed to a linear structure in calculations at the HF, MP3, CISD, and CCSD levels. Using MP2, MP3, MP4, and MP5 as well as CCSD and CCSD(T) calculations with large basis sets, Allen et al.[8] established the relative energetics of isocyanic, cyanic, fulminic, and isofulminic acids. It was also possible to derive a quartic force field, barrier to linearity, and fragmentation energies.

The experimental geometries of CN-substituted pseudohalides have not been studied extensively. The microwave spectrum of NCNCO[9-11] predicts a triangularly shaped structure, although the large number of vibrational satellite lines suggests possible quasilinear behavior for this molecule. The MW spectrum of NCNCS, on the other hand, has been analyzed in terms of a linear structure,[12] although the resulting model geometry from the fit of the experimental data was, to the contrary, bent. Due to quasilinearity, the exact value of the CNC angle could not be determined. This microwave spectrum was later reanalyzed using the semirigid bender model,[13] which partially allows for the interactions of other vibrations with the large-amplitude motion. The gas-phase Fourier-transform infrared spectrum of NCNCO[14] could not provide new information on the structure; thus, the simultaneous existence of two isomers at the measurement temperature could not be excluded.

From the microwave spectrum of NCSCN[15,16] a strongly bent frame with a CSC angle of 98° was deduced. However, this

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angle was obtained on the assumption that the CN bond length is the same as in a few other selected CN compounds: a variation in this bond length of about 0.03 Å would even allow the CSC angle to be linear. No further information on the geometry could be obtained from the infrared spectrum,[14,15] which was also used to obtain harmonic[17] and anharmonic[18] force fields for this molecule. The CSC angle was determined by electron diffraction to be 101°,[19] despite the strong dependence of this angle on the CN and CS bond lengths, as the smallest possible B value was in agreement with the experimental values. NCSeCN is also a stable compound; its infrared spectrum has been observed.[20] NCOCN is unstable, and it has only been detected in the flash photolysis of a $C_2N_2-O_3$ mixture.[21]

From the third set of isomers, only NCCNO has been synthesized. Its infrared spectrum was also recorded,[22] although only partially assigned. Nothing is known experimentally about the other four possible groups of isomers, CNNCX, CNXCN, CNXNC, and CNCNX, and about the oxazirines (RCXN, where R = NC or CN and X = O, S, or Se).

Until now, the geometries of only a few of these molecules have been studied by ab initio calculations, mostly with a minimum basis set, as for $(CN)_2S$,[23] $O(CN)_2$,[24-26] and NCNCO and NCOCN,[23,27] but also with a 4-31G basis.[27] The only larger basis set calculation including polarization functions was undertaken on $(CN)_2O$.[28] However, even though the importance of polarization functions and the allowance for the correlation energy in the description of the geometries of floppy molecules is well-known,[1-4,29-31] these have been mostly neglected in the past, apart from MP2/6-31G* calculations on NCOCN and NCSCN.[32] The calculations performed in this work on equilibrium structures allow for the above effects.

A further point of interest is the possible isomerization between the different equilibrium structures, of which only the NCSCN−NCNCS[33,34] and NCCNO−NCNCO[22] reactions have been observed experimentally. The only calculations on these reactions were a semiempirical one performed for the NCSCN−NCNCS isomerization[35] and a minimum basis set work on the CN− to NC− transition.[25] It was a further aim of the present work to make predictions for the structure of transition states.

Calculations

The calculations in this work were performed using the CADPAC[36] and GAMESS[37] quantum chemistry packages. Equilibrium molecular geometries were fully optimized with the gradient method. The

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optimization was terminated only when the largest Cartesian component of the gradient was less than 10^{-5} (in atomic units). Harmonic vibrational frequencies were then calculated at the minimum-energy geometry using analytic second derivatives. A standard 6-31G*[38,39] basis set was used on the lighter atoms and one of [6s4p2d] quality on selenium.[40] All polarization functions were defined as Cartesian d functions. Correlation energy was partially allowed for using second-order Møller−Plesset perturbation theory (MP2) with all electrons included (i.e. no "frozen-core").

Transition structures were optimized using eigenvalue following routines and a standard 6-31G* basis set. The starting points for these optimizations were semiempirical calculations,[41] where a linear synchronous transit path was calculated between the stable isomers. The total energies of the transition states were then obtained at the HF/6-31G* level, at which the stable structures were also recalculated for comparison (with the zero-point energies also considered). Single-point calculations on the HF-optimized structures were performed at the CCSD(T) level of theory for the stable structures and transition states to judge the reliability of the obtained transition structures. Vibrational frequencies were calculated for all of these states to ascertain whether the obtained structures are real saddle points (with one imaginary frequency).

Results and Discussion

The following stable isomers were initially studied in this work: isocyanates, cyanates, nitrile oxides (isofulminates), and fulminates, containing the respective pseudohalide groups −NCO, −OCN, −CNO, and −ONC, substituted with a cyano (NC−) or an isocyano (CN−) group. Also, related molecules with sulfur and selenium instead of oxygen were investigated, and the calculated equilibrium structures are collected in Table 1. All studied molecules are planar at equilibrium, and there are also some further similarities in their structures. The pseudohalide group (−NCX, −XCN, −CNX, or −XNC) and the CNY (NCY) unit at the opposite end of the molecule are in all cases linear or are nearly linear (i.e. α and $\gamma \sim 180°$ in Figure 1a). The middle bond angle (β in Figure 1a) is strongly dependent on the pseudohalide and varies between 96.2 and 180°. This angle is up to 15° different if polarization function and correlation energy are not included.[27] The cyanates and fulminates, as well as their thio and seleno derivatives, have a strongly bent frame with a decreasing β angle in the series O > S > Se. The iso derivatives, on the other hand, have a less bent frame and an increasing β angle in the O < S < Se series. This can be rationalized by the increasing localization of the HOMO π-system on the NC fragment of the XNC and XCN groups. This results in the N−C bond becoming more like a triple bond, which can also be seen from the decreased C−N bond lengths. A similar phenomenon was observed for methyl pseudohalides.[1] It is also important to consider the propensity for second- and third-row atoms to exhibit inert s pairs which participate little in hybridization within the valence shell. This effect is expected to be most important in the case of selenium derivatives, which further explains the increasing localization of the π-system and so the increasing β angle in the series O < S < Se of R−XCN and R−XNC. Also, the greater the β angle, the smaller the barrier to linearity, as shown in Table 2. This barrier height is a mere 7 cm^{-1} for NCCNO, and the molecule

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Table 1. Calculated and Experimental Equilibrium Structures of Different Isomers of NCNCX (X = O, S, Se)[a]

	method	R_1	R_2	R_3	R_4	α	β	γ	tot. energy, au	rel energy, kJ/mol[b]	CCSD(T) energy[c]	rel energy, kJ/mol[c]
NCNCO	RHF/6-31G*	1.136	1.326	1.206	1.136	177.17	134.90	173.70	−259.471 642	0.00	−260.231 075	0.00
	MP2/6-31G*	1.184	1.330	1.228	1.177	176.10	135.83	171.64	−260.228 506	0.00		
	exp[9]	1.164*	1.343	1.218*	1.165*	172*	129.34	169*				
NCNCS	MP2/6-31G*	1.188	1.311	1.219	1.559	176.78	150.02	174.09	−582.821 320	0.00		
	exp[9]	1.164*	1.343*	1.218*	1.529	172*	140.983	173.8				
NCNCSe	MP2/6-31G*	1.191	1.294	1.207	1.696	180.00	180.00	180.00	−2582.89 307	0.00		
NCOCN	RHF/6-31G*	1.132	1.304	1.304	1.132	176.94	119.42	176.93	−259.401 487	184.2	−260.164 061	176.0
	MP2/6-31G*	1.182	1.328	1.328	1.182	175.71	115.51	175.71	−260.158 970	182.6		
NCSCN	MP2/6-31G*	1.184	1.704	1.704	1.184	175.45	98.01	175.45	−582.805 957	40.3		
	exp[11]	1.156	1.701	1.701	1.156	180*	98.37	180*				
NCSeCN	MP2/6-31G*	1.184	1.831	1.831	1.184	176.97	96.22	176.97	−2582.888 63	11.7		
NCCNO	RHF/6-31G*	1.136	1.383	1.134	1.184	179.89	179.96	179.90	−259.348 332	323.8	−260.135 287	251.5
	MP2/6-31G*	1.191	1.360	1.198	1.198	178.73	166.45	175.71	−260.143 832	222.4		
NCCNS	MP2/6-31G*	1.196	1.348	1.206	1.561	180.00	180.00	180.00	−582.788 344	86.6		
NCCNSe	MP2/6-31G*	1.197	1.348	1.203	1.705	180.00	180.00	180.00	−2582.866 42	70.0		
CNNCO	RHF/6-31G*	1.155	1.325	1.220	1.136	171.66	127.03	172.21	−259.390 639	212.7	−260.150 682	211.1
	MP2/6-31G*	1.195	1.328	1.242	1.176	172.48	125.97	168.59	−260.139 079	234.8		
CNNCS	MP2/6-31G*	1.198	1.315	1.236	1.555	172.74	131.56	170.50	−582.733 057	231.7		
CNNCSe	MP2/6-31G*	1.198	1.312	1.233	1.688	172.71	133.05	172.78	−2582.803 79	234.4		
CNOCN	RHF/6-31G*	1.155	1.318	1.305	1.132	170.42	117.71	176.68	−259.307 945	429.8	−260.071 816	418.2
	MP2/6-31G*	1.198	1.354	1.330	1.182	172.26	111.11	175.58	−260.057 112	450.1		
CNSCN	MP2/6-31G*	1.197	1.669	1.700	1.184	174.29	98.58	175.86	−582.751 267	184.0		
CNSeCN	MP2/6-31G*	1.196	1.800	1.827	1.184	175.32	96.54	177.36	−2582.837 01	147.2		
CNCNO	RHF/6-31G*	1.164	1.309	1.128	1.203	179.95	179.99	179.99	−259.309 237	426.5	−260.084 536	384.8
	MP2/6-31G*	1.197	1.321	1.205	1.200	175.39	149.20	167.43	−260.080 561	388.5		
CNCNS	MP2/6-31G*	1.201	1.310	1.204	1.569	175.96	155.82	173.71	−582.725 399	251.9		
CNCNSe	MP2/6-31G*	1.203	1.298	1.191	1.727	180.00	180.00	180.00	−2582.804 47	231.9		
CNONC	RHF/6-31G*	1.155	1.316	1.316	1.155	171.48	114.58	171.48	−259.219 490	662.1	−259.983 457	563.3
	MP2/6-31G*	1.199	1.351	1.351	1.199	173.00	108.88	173.00	−259.960 651	703.4		
CNSNC	MP2/6-31G*	1.198	1.660	1.660	1.198	175.32	99.27	175.33	−582.700 949	316.1		
CNSeNC	MP2/6-31G*	1.198	1.792	1.791	1.198	176.22	97.23	176.22	−2582.788 94	273.4		
(NO)CCN[d]	RHF/6-31G*								−259.303 403	441.8	−260.116 667	300.4
	MP2/6-31G*	1.728	1.343	1.418	1.183	46.36	133.53	179.52	−260.096 036	347.9		
(NS)CCN	MP2/6-31G*	1.991	1.741	1.411	1.184	39.07	140.50	178.47	−582.755 851	171.9		
(NO)CNC	RHF/6-31G*	2.255	1.180	1.395	1.164	28.42	127.35	179.98	−259.313 193	416.1	−260.053 872	465.3
	MP2/6-31G*	1.749	1.329	1.354	1.193	45.52	131.51	179.83	−260.055 105	455.3		
(NS)CNC	MP2/6-31G*	1.990	1.730	1.351	1.195	38.87	139.79	177.32	−582.712 751	285.1		

[a] The meaning of the different geometrical parameters is as shown in Figure 1. Bond lengths are in angstroms, and bond angles are in degrees. Asterisked values were kept constant in the fitting of the microwave data. [b] Energy relative to the lowest energy form of the molecule (i.e., NCNCO, NCNCS, and NCNCSe, respectively). [c] From a single-point calculation at the RHF/6-31G* geometry. [d] This isomer is no minimum at the RHF level of theory. The RHF energy is given at the optimized MP2 geometry.
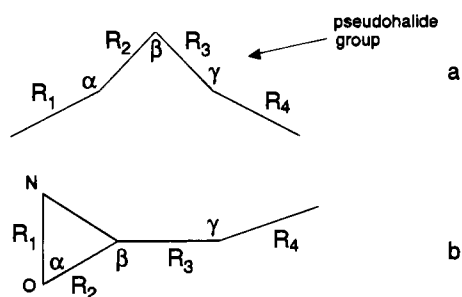

Figure 1. Geometric parameters used in the description of stable isomers of NCNCO in Table 1: (a) noncyclic isomers; (b) cyclic isomers.

Table 2. Barriers to Linearity of Different Isomers of NCNCX (X = O, S, Se)[a]

	$X = O$	$X = S$	$X = Se$
NCCNX	7	0	0
NCNCX	662	112	0
NCXCN	7930	b	b
CNCNX	519	139	0
CNNCX	2734	1747	1252
CNXCN	14888	b	b
CNXNC	24543	b	b

[a] In cm⁻¹ (1 kJ/mol = 83.59 cm⁻¹), calculated at the MP2/6-31G* level of theory. [b] Barrier to linearity exceeds the dissociation energies of the S−N or S−C bonds and thus was not calculated.

is thus quasilinear. NCNCS and CNCNS also have reasonably low barriers (112 and 139 cm⁻¹, respectively). The NC− or CN− bond lengths (R_1) are virtually the same in all molecules, and the CN− derivatives of isocyanates and isofulminates have more bent frames than their NC− isomers. It must also be noted that the calculations on NCNCO give support to the bent microwave structure,[9,10] as opposed to the linear NCNCO frame from infrared spectroscopy.[42] The CN− and NC− groups are triple bonds in all stable isomers.

Two more structures for NC− substitution were found to be stable in ref 27 using STO-3G and 4-31G basis sets: the oxazirines and the carbonylnitrenes. The oxazirine was also found stable at the MP2/6-31G* level in this work. Addition-

ally, its isomer with isocyano substitution and the sulfur derivatives are also stable, as shown in Table 1. On the other hand, ab initio calculations showed that the cyanocarbonylnitrene does not correspond to any minimum on the potential energy surface. The possible reasons for the false identification of this molecule as a stable isomer in ref 27 are the lack of polarization functions and the omission of the correlation energy, as well as that only a partial geometry optimization was performed. Furthermore, the lack of frequency calculation in ref 27 may have concealed the fact that a true minimum was not found.

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Table 3. Harmonic Vibrational Frequencies (cm^{-1}) of Different NC- and CN-Substituted Pseudohalides[a]

	1	2	3	4	5	6	7	8	9[b]
NCNCO	2427	2244	1490	866	603	557	462	446	127
calc	(ν_{as}(NCO))	(ν_{as}(NCN))	(ν_s(NCO))	(ν_s(NCNC))	(δ(NCO))	(γ(NCO))	(δ(NCN))	(γ(NCN))	
exp	2272[42]	2233[14]	1430[42]	1074[14]	727[14]	610[14]	455[42]	365[42]	
NCNCS	2287	2102	1230	673	452	451	444	404	78
calc	(ν(NC))	(ν_{as}(NCS))	(ν_s(NCS))	(ν(NCNC))	(γ(NCN))	(δ(NCN))	(δ(NCS))	(γ(NCS))	
exp	2261[14]	2016[14]							
NCOCN	2255	2241	1162	897	607	431	419	399	148
calc	(ν_{as}(NCO))	(ν_{as}(OCN))	(ν_s(NCO))	(ν_s(OCN))	(δ(NCO))	(γ(NCO))	(γ(OCN))	(δ(OCN))	
exp	2205[17]								
NCSCN	2161	2160	714	704	502	334	327	321	123
calc	(ν_{as}(NCS))	(ν_{as}(SCN))	(ν_s(NCS))	(ν_s(SCN))	(δ(NCS))	(γ(NCS))	(γ(SCN))	(δ(SCN))	
exp	2190[11]	2180[11]	690[11]	672[11]	500[11]	378[11]	372[11]	329[11]	135[11]
NCCNO	2397	2124	1539	751	486	473	411	403	68
calc	(ν_{as}(CNO))	(ν(NC))	(ν(NCCN))	(ν_s(CNO))	(γ(NCC))	(δ(NCC))	(γ(CNO))	(δ(CNO))	
exp	2356[15]		1445[15]						
NCCNS	2143	2008	1169	592	426	425	388	382	53
calc	(ν(NCCN))	(ν(NCCN))	(ν(NCCN))	(ν_s(CNS))	(δ(NCC))	(γ(NCC))	(δ(CNS))	(γ(CNS))	
NCONC	2239	2105	1074	878	598	422	301	250	129
calc	(ν_{as}(NCO))	(ν_{as}(ONC))	(ν_s(NCO))	(ν_s(ONC))	(δ(NCO))	(γ(NCO))	(δ(ONC))	(γ(ONC))	
NCSNC	2170	2088	712	704	484	330	264	260	119
calc	(ν_{as}(NCS))	(ν_{as}(SNC))	(ν_s(NCS))	(ν_s(SNC))	(δ(NCS))	(γ(NCS))	(δ(SNC))	(γ(SNC))	
CNNCO	2350	2150	1422	882	642	531	358	309	146
calc	(ν_{as}(NCO))	(ν(CN))	(ν_s(NCO))	(ν(CNNC))	(δ(NCO))	(γ(NCO))	(δ(CNN))	(γ(CNN))	
CNNCS	2155	2013	1183	739	513	408	340	311	117
calc	(ν(CN))	(ν_{as}(NCS))	(ν_s(NCS))	(ν(CNNC))	(δ(NCS))	(γ(NCS))	(δ(CNN))	(γ(CNN))	
CNOCN	2239	2106	1074	878	598	422	301	250	129
calc	(ν_{as}(OCN))	(ν_{as}(ONC))	(ν_s(OCN))	(ν_s(ONC))	(γ(OCN))	(δ(OCN))	(δ(ONC))	(γ(ONC))	
CNSCN	2170	2087	712	704	483	330	264	259	119
calc	(ν_{as}(SCN))	(ν_{as}(SNC))	(ν_s(SCN))	(ν_s(SNC))	(δ(SCN))	(γ(SCN))	(δ(SNC))	(γ(SNC))	
CNCNO	2405	2124	1535	833	477	452	397	317	178
calc	(ν_{as}(CNO))	(ν(CN))	(ν(CNCN))	(ν_s(CNO))	(γ(CNO))	(δ(CNO))	(δ(CNC))	(γ(CNC))	
CNCNS	2235	2022	1162	644	399	382	344	319	127
calc	(ν(NCNC))	(ν(NCNC))	(ν(NCNC))	(ν_s(CNS))	(δ(CNS))	(γ(CNS))	(δ(CNC))	(γ(CNC))	
CNONC	2092	2077	961	887	556	247	237	217	111
calc	(ν_{as}(CNO))	(ν_{as}(ONC))	(ν_s(CNO))	(ν_s(ONC))	(γ(CNO))	(γ(ONC))	(δ(CNO))	(δ(ONC))	
CNSNC	2079	2065	713	706	440	267	262	226	115
calc	(ν_{as}(CNS))	(ν_{as}(SNC))	(ν_s(CNS))	(ν_s(SNC))	(δ(CNS))	(γ(CNS))	(γ(SNC))	(δ(SNC))	
(NO)CCN	2226	1912	1343	860	589	585	529	252	193
calc	(ν(NC))	(ν(NOC))	(ν(NOC))	(ν(NOC))	(δ(NOC))	(γ(NOCC))	(δ(NOCC))	(γ(CCN))	
(NS)CCN	2197	1714	1022	663	553	541	412	230	172
calc	(ν(CN))	(ν(NSC))	(ν(NSC))	(ν(NSC))	(δ(NSC))	(γ(NSCC))	(δ(NSCC))	(γ(CCN))	
(NO)CNC	2218	1953	1368	897	587	579	505	204	166
calc	(ν(NC))	(ν(NOC))	(ν(NOC))	(ν(NOC))	(δ(NOC))	(γ(NOCN))	(δ(NOCN))	(γ(CNC))	
(NS)CNC	2182	1795	1086	693	560	500	388	203	164
calc	(ν(NC))	(ν(NSC))	(ν(NSC))	(ν(NSC))	(δ(NSC))	(γ(NSCN))	(δ(NSCN))	(γ(CNC))	

[a] Calculated at the MP2/6-31G* level of theory. All frequencies are unscaled. The symbols ν denote stretches, δ in-plane deformations, and γ out-of-plane deformations. [b] This deformation vibration (δ) extends over the entire molecule in all studied species; see text.

In order to ensure that the equilibrium structures in Table 1 all correspond to genuine minima on the potential energy surface, harmonic vibrational frequencies were calculated at the same (MP2/6-31G*) level of theory and are displayed in Table 3. These values can be compared with experiments for NCNCO,[14,42] NCNCS,[14] and NCSCN.[14,15] The stretching frequencies are overestimated due to the neglect of anharmonicity and the deficiencies of the applied electronic structure methods; a better agreement with experiments can be achieved with a simple scaling by 0.9.[43]

There has been some controversy in case of NCSCN: the vibrational frequencies and assignments are substantially different in Raman[44] and infrared[15] spectroscopy. Only some of the infrared bands were observed later from the reaction of Br$_2$ and AgSCN.[14] As can be seen from Table 3, the results of the

calculations support and provide the same assignment as the infrared work.[15] Also, the experimental infrared spectrum of NCCNO[19] can now be fully assigned as shown in Table 3. Some considerable discrepancies between the observed and calculated vibrational frequencies can be found in case of NCNCO. The ν_s(NCNC) and δ(NCO) modes are calculated at 866 and 603 cm^{-1}, respectively, significantly below their experimental counterparts at 1074 and 727 cm^{-1}. A possible explanation for this effect could be the deficiency of the used level of theory. However, in the analogous compounds CH$_3$NCO, SiH$_3$NCO, SiMe$_3$NCO, and GeH$_3$NCO, the δ(NCO) mode can be observed between 610 and 640 cm^{-1} and the ν(NC) mode between 807 and 852 cm^{-1}.[45–48] These are comparable with the values calculated in this work. Also these values are in good agreement

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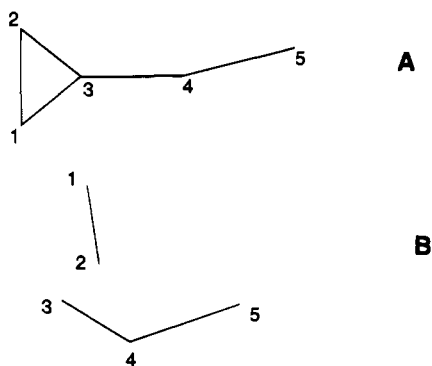(44) Long, D. A.; Steel, D. *Spectrochim. Acta* **1963**, *19*, 1731.

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Figure 2. Generalized shape of obtained transition structures. The numbers refer to the parameters in Table 4.

with the calculated frequencies at the same MP2/6-31G* level of theory.[1-3] This fact suggests that the experimental assignment in ref 14 may be in error.

The relative stabilities of the different isomers can be compared on the basis of their calculated total energies (Table 1). For all studied compounds, NCNCX (X = O, S, or Se) is thermodynamically the most stable isomer. The CN-substituted compounds are in excess of 100 kJ/mol more unstable than the NC-substituted ones, the difference decreases in the series O > S > Se. For X = O, the next most stable isomer, the cyanate lies near 180 kJ/mol; NCCNO is 220 kJ/mol above this energy. This situation is similar for X = S and Se: the thio and seleno cyanates are 40 and 12 kJ/mol less stable than the respective isothio or isoseleno cyanates, and even the nitrile sulfides and selenides are only 90 and 70 kJ/mol above the isothio and isoseleno cyanates. The sulfur and seleno fulminates are in all cases much less stable thermodynamically.

It is interesting to compare these stabilities with the corresponding compounds, where a hydrogen atom replaces the CN— group.[5-8] Similar to the trend in this work, HCNO is linear (or quasilinear, depending on the level of theory used) and the other isomers are trans-bent structures. Thus the CN or NC substitution does not have a strong influence on the structure and order of stabilities at first order. However, the situation is more complicated in the present case, as there are nine instead of four isomers.

As a lot of the higher energy isomers that are of possible interest for gas-phase spectroscopy lie at similar energies, the transition structures connecting them were also calculated in this work. These can be grouped into two categories: a three-membered ring at the end of a chain (structure **A** in Figure 2) and a diatomic fragment at an angle to the triatomic segment of the molecule (structure **B**). The geometries and total energies of all calculated transition structures are collected in Table 4. Three mechanisms can be distinguished, connecting the stable structures (denoted with α, β, and γ in Figure 3).

Path α is involved in the NC—R to CN—R rearrangement (R = pseudohalide group) and proceeds via a cyclic transition state. In process α, the CN—R distance increases, while the R_{45} bond length becomes shorter. This bond length is shorter in the transition states than the corresponding distances in HCN and CO (as obtained from 6-31G*/MP2 calculations). At the same time, the pseudohalide group, which keeps its near-linearity in the process, strongly moves out of the plane, defined by the rest of the molecule (δ_{1234}). This is, however, not the case for CNCNO, which remains planar throughout the isomerization process and the R_{34} bond, instead of the R_{45} bond,

becomes shorter in the process. The relative energetics of all these processes is displayed schematically in Figure 4.

Reaction β applies to four reactions, connecting the —NCO and —OCN as well as the —CNO and —ONC compounds via B-type transition states (Figure 2). In this process, the CN— or NC— group is transferred to the other end of the molecule, whereby the pseudohalide group becomes bent. Although this general description applies to all β reactions, these processes take place differently. In the NCONC—NCCNO and CNONC—CNCNO isomerizations, the pseudohalide group becomes bent and a π-type complex is formed between NC and ONC fragments in the process, which, however, is unstable, unlike in beryllium pseudohalides.[49] In the —NCO → —OCN transition, the NC bond of the pseudohalide group becomes longer and the CO bond much shorter (i.e., the CO group practically breaks off). However, this CO bond (R_{45}) is shorter than in an independent CO molecule proving that there remains a substantial interaction between the two parts. However, one must be cautious with these structures, as these structures are reached by partially dissociating the molecule, a process the RHF method cannot satisfactorily describe. Thus these two calculated structures may not even be proper zero-order approximations.

In contrast, reaction γ takes place via a cyclic (A-type) transition state with the pseudohalide forming the three-membered cycle. It connects groups of compounds, which cannot isomerize to each other in one step (e.g. those with —NCO and —CNO substitutions). The reaction takes place via the formation of a cyclic structure. The CN— or NC— group can then transfer to another site on this triangle, and the triangle subsequently opens up. Of these cyclic structures, (NO)CY (Y = CN, NC) are stable minima and (CO)NY are proper transition structures. Although no saddle point with the structure (CN)-OY was found in this work, it is likely from semiempirical reaction path calculations that the isomerization involves such a structure. The possible isomerization reactions are summarized in Figure 5, also showing the energetics of the processes. The energies in Figure 5 are shown relative to the lowest energy isomer, NCNCO, and from the several possible pathways, only the most favorable is given.

It is important to establish whether the calculated HF/6-31G* transition structures are good zero-order approximations. For this purpose, single-point CCSD(T) calculations were performed at the Hartree—Fock stationary points. These showed that, with the exception of two B-type complexes, (NC)ONC and (CN)-ONC, the correlated potential energy surface runs approximately parallel to the RHF surface, and thus the calculated structures should approximate the real structures well. It is likely, however, that the shapes of these two B-type complexes may be somewhat different if their geometries are optimized using a correlated method.

Many of the studied molecules, the isocyanates, the isofulminates, and their sulfur and selenium derivatives, are known to possess a bending mode with large-amplitude motion. The cyanates, fulminates, and their thio and seleno derivatives, on the other hand, are molecules with a rigid frame. This question can be exemplified with NCCNO and CNONC, where the potential energy function of the lowest energy bending mode was obtained (see Figure 6). It can be seen in this figure that whereas NCCNO indeed has a large-amplitude deformation, CNONC is rather rigid.

The microwave spectrum of NCNCS was first analyzed in terms of a linear structure.[12] Although a term for the dependence of the reduced mass on the bending angle was included
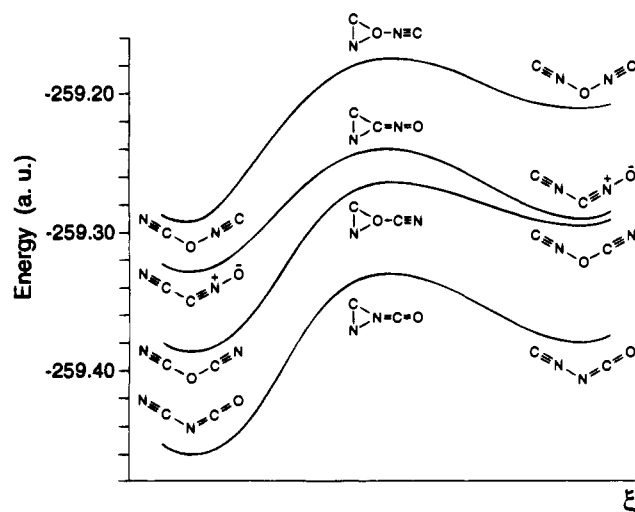
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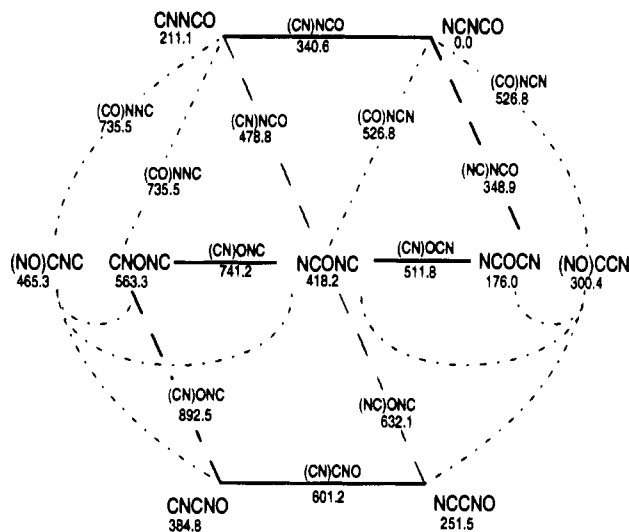(49) Pasinszki, T.; Veszprémi, T.; Fehér, M. *Chem. Phys. Lett.* **1993**, *215*, 395.
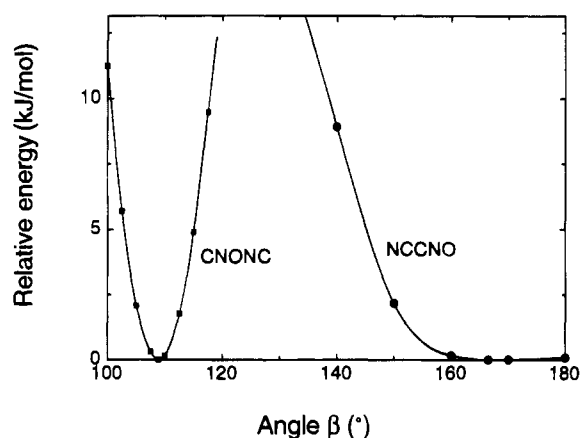
Table 4. Total Energies and Geometries of Transition Structures Connecting the Structural Isomers of NCNCO[a]

	type[b]	R_{12}	R_{23}	R_{34}	R_{45}	α_{123}	α_{234}	α_{345}	δ_{1234}	δ_{2345}	tot. energy, au	rel energy, kJ/mol[c]	CCSD(T) energy[d]	rel energy, kJ/mol[e]
(CN)OCN	A	1.223	1.749	1.295	1.134	61.21	114.34	177.86	88.9	155.5	−259.264 795	543.2	−260.036 162	511.8
(CN)NCO	A	1.211	1.767	1.222	1.136	59.98	108.68	173.51	122.9	179.5	−259.333 558	362.6	−260.101 374	340.6
(CN)CNO	A	1.192	1.732	1.134	1.193	59.93	146.71	179.86	180.0	180.0	−259.240 289	607.5	−260.002 143	601.2
(CN)ONC	A	1.219	1.791	1.304	1.155	58.66	113.86	177.07	86.3	174.0	−259.175 042	778.8	−259.948 827	741.2
(CO)NNC	A	1.498	1.416	1.282	1.160	50.68	133.13	176.15	180.0	0.0	−259.181 550	761.8	−259.950 979	735.5
(CO)NCN	A	1.366	1.445	1.308	1.138	54.91	131.93	179.23	180.0	180.0	−259.256 993	563.6	−260.030 457	526.8
(NC)NCO	B	1.160	1.287	2.091	1.109	174.64	106.37	155.35	180.0	180.0	−259.343 744	335.8	−260.098 222	348.9
(CN)NCO	B	1.172	1.273	1.890	1.110	173.90	110.17	149.25	180.0	180.0	−259.292 271	471.0	−260.048 746	478.8
(NC)ONC	B	1.151	1.590	1.524	1.203	141.56	99.44	104.85	180.0	0.0	−259.178 263	770.4	−259.990 359	632.1
(CN)ONC	B	1.222	1.395	1.783	1.255	132.46	76.93	89.37	180.0	0.0	−259.106 075	959.9	−259.891 199	892.5

[a] Geometries obtained at the HF/6-31G* level. Bond lengths are in angstroms, and bond angles are in degrees. [b] See Figure 2 and text for explanation. [c] Energy relative to that of the molecule NCNCO, calculated at the same level of theory (Table 1). [d] From a single-point CCSD(T) calculation at the RHF optimum.
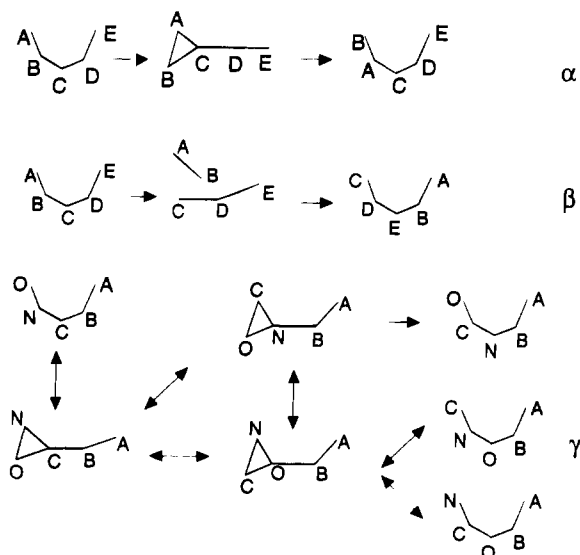
Figure 3. Isomerization pathways between different isomers of NCNCO. Double arrows depict strongly reversible processes.

Figure 5. Lowest energy isomerization pathways between different stable isomers of NCNCO. Energies are given in kJ/mol relative to NCNCO (at the CCSD(T)/6-31G* level of theory for HF-optimized structures). Pathway: (−) α; (− −) β; (− · −) γ.

Figure 4. Potential energy curves for the α isomerization pathways. The energies given are from HF/6-31G* calculations (1 au = 2625.9 kJ/mol).

Figure 6. Potential energy curves for the lowest frequency bending modes NCCNO and CNONC. All other bond lengths and bond angles were optimized at each point of the curve. Total energy is given relative to the minimum of the potential.

in the Hamiltonian, this motion could not be treated directly. It was proved that the molecule is not linear at the central nitrogen atom but the CNC angle could not be determined. The determined ν_7 bending frequency, 97 cm^{-1},[12] is to be compared with the MP2/6-31G* value here of 78 cm^{-1}. The reanalysis of the microwave spectrum with the semirigid bender model[13] resulted in a geometry more similar to the ab initio structure.

The relatively large difference of 10° in the CNC angle is due to the difference in the optimized ab initio values and the parameters, which were kept fixed in the microwave analysis. For the slightly less floppy molecule, NCNCO, the difference between theory and experiment in the bending frequency is a mere 6 cm^{-1}. These examples provide further indications that calculations at the MP2/6-31G* level are capable of describing the geometry of systems with large-amplitude bends.

Another molecule, accounted as floppy in the literature, is NCSCN.[15-19] It has, however, a very high barrier to linearity (see Table 2), and thus it cannot be treated as floppy. Although the agreement between the experimental and theoretical structures is seemingly very good (the equilibrium CSC angle is 98.37° from microwave spectroscopy[15] and 98.01° from calculations), this agreement may be fortuitous, as there were large uncertainties in the determined structures both in microwave spectroscopy[15] and in electron diffraction.[19] These uncertainties arose because of the very strong coupling of the C−S and C−N stretches to the bending mode. Again the calculated harmonic bending frequency (123 cm^{-1}) is in good agreement with the infrared value (135 cm^{-1} [15]).

A common feature of the lowest energy bending mode of the studied molecules is that the vibration extends to the entire molecule, as can be observed from the eigenvectors of the calculated force matrix. This can be explained by the relatively symmetric nature of the molecules (i.e. similar masses at both ends). In contrast, in a normal-coordinate analysis of NCSCN,[15] the lowest frequency bending mode was assigned exclusively to the totally symmetric SCN deformations. However, it was also pointed out that small changes in the force field give this motion principally as a CSC deformation. In the view of the present ab initio calculations, neither of the extreme descriptions is accurate and the two deformations will mix strongly. Thus the lowest energy deformations in Table 3 can all be assigned to this mode.

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