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Ab Initio Study on the Equilibrium Structure and CCN Bending Energy Levels of Cyanofulminate (NCCNO)

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The molecular parameters of cyanofulminate, NCCNO, have been determined in large-scale ab initio calculations using the coupled-cluster method, CCSD(T), and basis sets of double- through quadruple-ζ quality. The equilibrium structure of the molecule was found to be linear, with a strongly anharmonic potential energy function of the CCN bending motion (ν_7 mode). The rotation−bending energy levels were then calculated using a semirigid-bender Hamiltonian. The vibrational energy levels and effective rotational constants determined for various ν_7 states were found to be in good agreement with the experimental data.

1. Introduction

Cyanofulminate, NCCNO, is a pseudohalide derivative of fulminic acid, HCNO. The parent species is a well-known example of a quasilinear molecule,[1] and it undergoes large-amplitude HCN bending motion. The two halofulminates ClCNO and BrCNO were recently shown both experimentally[2,3] and theoretically[4,5] to be also quasilinear. Both halofulminate molecules were found to be bent at equilibrium. However, the ClCN and BrCN bending potential energy functions were determined to be strongly anharmonic, with the barriers at linear configurations of 167[3]/156[4] and 131[3]/119[5] cm^{-1}, respectively. On the other hand, cyanofulminate is isoelectronic with carbon suboxide, OCCCO, another example of a quasilinear molecule.[1] The OCCCO molecule was found, refs 6 and 7 and references therein, to be nearly linear at equilibrium and to undergo a large-amplitude CCC bending motion. The CCC bending potential energy function is also strongly anharmonic, with a barrier to linearity of only ~30 cm^{-1}. Therefore, the immediate question arises about whether the equilibrium structure and nature of the CCN bending motion of the NCCNO molecule are similar to those of the halofulminates, those of OCCCO, or perhaps to those of neither set of molecules.

In a series of papers,[8−10] the photoelectron, microwave, infrared, and ultraviolet spectra of cyanofulminate were interpreted as those characteristic of a linear molecule. The experimental evidence was further supported by results of the ab initio calculations at the QCISD(T)/6-31G* level of theory.[8] The NCCNO molecule was computed to be linear at equilibrium, with the CCN bending potential energy function being wide and flat in the vicinity of a minimum. Additionally, the fundamental frequency of the CCN bending mode, ν_7, was determined from the analysis of infrared combinations bands[9] to be only 86 cm^{-1}. Pasinszki and Westwood[8] concluded that “the molecule is predicted to have a large amplitude deformation, suggesting possible quasi-linear behavior”. The definitive experimental evidence for such behavior came from the very recent study by Lichau et al.,[11] in which the high-resolution spectra of cyanofulminate in the millimeterwave and far-infrared range were investigated. Rotational transitions arising from NCCNO molecules in the excited ν_7 states were measured, and the spectrum was analyzed using a linear-molecule effective Hamiltonian. The changes in the rotational constants with excitation of the ν_7 mode were found to deviate significantly from those expected for a typical linear molecule. The spectroscopic data were further analyzed using a semirigid bender model.[12] In conjunction with the unpublished results of this theoretical study, the effective CCN bending potential energy function was determined by Lichau et al.[11] to be indeed strongly anharmonic, with a considerable quartic contribution.

The present study was undertaken with the aim of predicting the spectroscopic properties of cyanofulminate by the ab initio approach and of assisting the experimental study.[11] The extensively correlated electronic wave functions in conjunction with large one-particle basis sets were used to compute the equilibrium structure and CCN bending potential energy function of the NCCNO molecule. The associated rotation−bending energy levels were then determined by solving the four-dimensional rotation−vibration Schrödinger equation.

2. Method of Calculation

The molecular parameters of cyanofulminate were calculated using the coupled-cluster method including single and double excitations and a perturbational correction due to connected triple excitations, CCSD(T).[13−16] The one-particle basis sets used are the correlation-consistent polarized valence basis sets, cc-pV*n*Z.[17] The quality of the basis sets ranges from double-ζ (n = D), through triple-ζ (n = T), to quadruple-ζ (n = Q). The largest basis set employed, cc-pVQZ, consists of a (12*s*6*p*3*d*2*f*1*g*)/[5*s*4*p*3*d*2*f*1*g*] set for carbon, nitrogen, and oxygen. Only the spherical harmonic components of polarization *d* through *g* functions were used. In the correlation treatment involving only the valence electrons, the 1*s*-like core orbitals of the carbon, nitrogen, and oxygen atoms were excluded from the active space.

The core-related correlation effects were investigated using the correlation-consistent polarized core-valence basis set of triple-ζ quality, cc-pCVTZ.[18] The basis set is obtained by augmenting the standard cc-pVTZ basis set with a (2*s*2*p*1*d*) set, and it consists thus of a (12*s*7*p*3*d*1*f*)/[6*s*5*p*3*d*1*f*] set for carbon, nitrogen, and oxygen. In the correlation treatment involving the

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TABLE 1: Equilibrium Molecular Parameters of NCCNO, Determined Using the CCSD(T) Method and Various cc-pV*n*Z Basis Sets

	cc-pVDZ	cc-pVTZ	cc-pVQZ
r(NC) (Å)	1.1842	1.1687	1.1651
r(CC) (Å)	1.3834	1.3685	1.3675
r(CN) (Å)	1.1864	1.1713	1.1678
r(NO) (Å)	1.1999	1.1946	1.1926
Energy + 260 (hartree)	−0.166288	−0.406295	−0.481067

TABLE 2: Equilibrium Structural Parameters of NCCNO, Determined at the CCSD(T)/cc-pCVTZ Level of Theory

	valence only (V)[a]	all electrons (A)[b]	A−V
r(NC) (Å)	1.1676	1.1657	−0.0019
r(CC) (Å)	1.3693	1.3675	−0.0018
r(CN) (Å)	1.1704	1.1687	−0.0017
r(NO) (Å)	1.1937	1.1920	−0.0017

[a] Correlating only the valence electrons. [b] Correlating all of the electrons.

TABLE 3: Experimental (r_s and r_{min}) and Calculated (r_e) Structural Parameters of NCCNO

	r_s[a]	r_{min}[b]	r_e[c]
r(NC) (Å)	1.1606	1.1616	1.161
r(CC) (Å)	1.3633	1.3669	1.366
r(CN) (Å)	1.1574	1.1652	1.164
r(NO) (Å)	1.1933	1.1947	1.190

[a] Reference 10. [b] Reference 11. [c] The estimated complete-basis-set limit at the CCSD(T) level of theory, including the core−electron correlation effects.

core and valence electrons, all of the molecular orbitals were included in the active space.

The ab initio calculations were performed using the MOLPRO-2000 package of ab initio programs.[19,20]

3. Results and Discussion

The calculated equilibrium molecular parameters of cyanofulminate are given in Table 1. For all of the basis sets employed, the equilibrium structure of the NCCNO molecule was found to be linear. The calculated total energy and structural parameters appear to converge to well-defined asymptotic limits with enlargement of the one-particle basis set.

The core-related correlation effects were investigated by comparing the results of calculations correlating only the valence electrons with those when all of the electrons were correlated. The bond lengths determined for the equilibrium configuration of cyanofulminate are listed in Table 2. Inclusion of the core-related effects decreases all of the bond lengths to nearly the same extent, by about 0.002 Å.

TABLE 4: Optimized Values of the Molecular Parameters of NCCNO, Determined for Various Assumed Values of the CCN Angle at the CCSD(T)/cc-pVQZ Level of Theory

∠(CCN)	180	170	160	150	140
r(NC) (Å)	1.1651	1.1651	1.1646	1.1640	1.1633
r(CC) (Å)	1.3675	1.3693	1.3728	1.3794	1.3885
r(CN) (Å)	1.1678	1.1691	1.1732	1.1798	1.1885
r(NO) (Å)	1.1926	1.1920	1.1903	1.1878	1.1847
∠(NCC) (deg)	180.	179.07	178.28	177.71	177.45
∠(CNO) (deg)	180.	177.38	174.86	172.55	170.53
energy/*hc* (cm^{-1})[a]	0.	17.6	89.5	273.5	667.9

[a] Relative to the energy of the linear configuration.

To estimate the complete basis set (CBS) limit for a molecular parameter, the exponential/Gaussian extrapolation formula[21] was applied. The other analogous extrapolation algorithms[22−25] were also applied, and the spread in the determined CBS limit values was used as an estimate for extrapolation accuracy. The total energy lowering from the cc-pVQZ to cc-pV5Z basis set computed in this way is ∼27 mhartrees, whereas that to the infinite basis set is estimated to be ∼42 mhartrees. The best estimate of the structural parameters of cyanofulminate can be determined by adding the changes in the parameters due to the core-related correlation effects to the CBS limits determined with the valence cc-pV*n*Z basis sets. The equilibrium bond lengths calculated in this way are given in Table 3. The calculated values compare favorably with the experimental data,[10,11] especially with the effective bond lengths, r_{min}, resulting from the semirigid-bender analysis. Except for the NO bond length, the calculated values agree with those derived from the latter analysis[11] to within the error bars (the experimental uncertainties are estimated to be about ± 0.001 Å).

The CCN bending potential energy function has been determined by optimizing the structural parameters of cyanofulminate for various assumed values of the valence angle CCN. Results of the calculations are presented in Table 4. The bent NCCNO molecule is predicted to have a W-shaped overall structure, with the trans conformation of the NCCN and CCNO moieties. All of the structural parameters are found to vary significantly with the CCN angle. For the CC and CN bond lengths, the differences amount to more than 0.02 Å when the CCN angle ranges from 180° to 140°. The calculated structural parameters of cyanofulminate can be expanded as polynomials in the coordinate ρ, defined as the supplement of the valence angle CCN. The expansions may be given as

$$\begin{aligned} r(\mathrm{NC}) &= 1.1651 - 0.0047\rho^2 + 0.0018\rho^4 \\ r(\mathrm{CC}) &= 1.3675 + 0.0426\rho^2 + 0.0001\rho^4 \\ r(\mathrm{CN}) &= 1.1678 + 0.0455\rho^2 - 0.0060\rho^4 \\ r(\mathrm{NO}) &= 1.1926 - 0.0193\rho^2 + 0.0064\rho^4 \\ \sigma &= 5.35\rho - 3.50\rho^3 \\ \tau &= 15.10\rho - 3.16\rho^3 \end{aligned} \tag{1}$$

where ρ is given in radians, the bond lengths are given in angstroms, and the supplements of the valence angles NCC and CNO, σ and τ, respectively, are given in degrees.

To represent the calculated total energies in the form of a CCN bending potential energy function $V(\rho)$, the ab initio data were fitted with an analytical function. As in the experimental study,[11] a simple two-term polynomial expansion was found to satisfactory represent the calculated function:

$$V(\rho) = f_2\rho^2 + f_4\rho^4 \tag{2}$$

The expansion coefficients f_2 and f_4 were adjusted in a least-squares fit of formula 2 to the calculated total energies (Table 4). The root-mean-square deviation of the fit is 0.2 cm^{-1}, and the adjusted parameters are $f_2 = 520.2\ \mathrm{cm}^{-1}$ and $f_4 = 1744.2\ \mathrm{cm}^{-1}$. This potential energy function is referred to hereafter as function I.

The core-related corrections to the CCN bending potential energy function are given in Table 5. Inclusion of the corrections results in a slightly steeper function. The core-related corrections were added to the total energies obtained with the cc-pVQZ basis set, and the corrected CCN bending potential energy function was fitted with formula 2. The parameters f_2 and f_4 were calculated to be 637.2 and 1730.4 cm^{-1}, respectively. This potential energy function is referred to hereafter as function II.

TABLE 5: Total Energy[a] of NCCNO (in cm^{-1}) as a Function of the CCN Angle, Determined at the CCSD(T)/cc-pCVTZ Level of Theory

∠(CCN)	180	170	160	150	140
valence only (V)[b]	0.	9.2	60.1	216.2	582.5
all electrons (A)[c]	0.	13.2	74.2	247.1	636.3
A−V	0.	4.0	14.1	30.9	53.8

[a] Relative to the energy of the linear configuration, calculated with the structural parameters given in Table 4. [b] Correlating only the valence electrons. [c] Correlating all of the electrons.

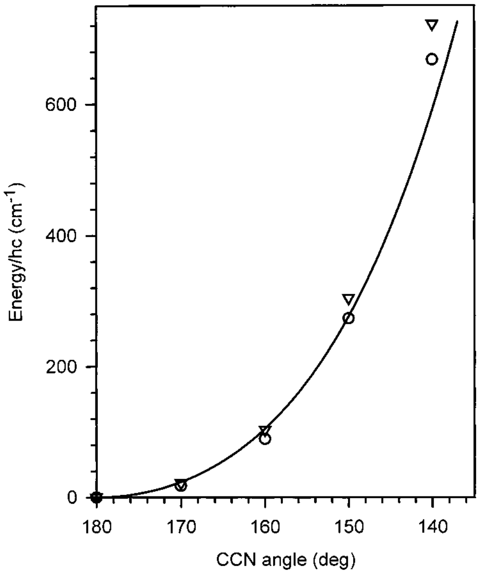

Figure 1. Experimentally determined[11] (solid line) and ab initio calculated CCN bending potential energy function of NCCNO. The theoretical points were determined at the CCSD(T)/cc-pVQZ level of theory, without (circles, "function I") and with (triangles, "function II") the core−electron correlation effects.

In the experimental study,[11] the expansion coefficients of the effective CCN bending potential energy function were determined to be $f_2 = 747.4$ cm^{-1} and $f_4 = 959.2$ cm^{-1}. The ab initio calculated values, especially that for f_4, seem to be somewhat different. However, as shown in Figure 1, agreement between the calculated and experimental function is quite satisfactory. It must be pointed out that the calculated function represents a minimum-energy (equilibrium) path along the CCN bending coordinate, whereas the experimental function is an effective (mass-dependent) function. It incorporates contributions from all of the small-amplitude vibrations of the NCCNO molecule (the zero-point averaging effect).

The accuracy of the computed molecular parameters can be assessed by comparing the calculated and observed rotation−bending energy levels of cyanofulminate. The energy levels and wave functions were calculated using an approximate, semirigid-bender Hamiltonian,[12] similar to that used to fit the experimental data.[11] The four-dimensional Hamiltonian describes the NCCNO molecule bending at the CCN angle and rotating in space. Interaction of the CCN bending motion with the other vibrational degrees of freedom is accounted for by varying the corresponding structural parameters along the minimum-energy CCN bending path.

The calculated $J = |l_7|$ rotation−bending energy levels of the NCCNO molecule are listed in Table 6. The energy levels are labeled by the rotational quantum number J and, as is customary in the experimental studies on cyanofulminate, by the vibrational quantum numbers v_7 and l_7. The quantum numbers v_7 and l_7 describe the doubly degenerate CCN bending vibration of a semirigid linear molecule. In comparison with the experimental data,[11] the energy levels determined using the potential energy function II are systematically overestimated, whereas for the function I, this is the case only for the higher-excited states. The root-mean-square deviation between the experimental and calculated energy levels is determined to be about 5 and 18 cm^{-1} for the functions I and II, respectively. Bearing in mind that the experimental energy levels span 5 excited vibrational states of the ν_7 mode, the agreement can be called good. However, it is less satisfactory than in the case of halofulminates[4,5] or carbon suboxide.[7] This may be the indirect evidence that the CCN bending motion for cyanofulminate is more strongly coupled with the small-amplitude vibrations than the corresponding bending motions for the ClCNO, BrCNO, and OCCCO molecules. In fact, as shown by the harmonic potential energy distribution for the NCCNO molecule,[8] the ν_7 normal mode consists of 78% of the CCN bending vibration and of 21% of the CNO bending vibration.

TABLE 6: $J = |l_7|$ Rotation−Bending Energy Levels (in cm^{-1}) and Changes in the Effective Rotational Constant B (in MHz) Due to Excitation of the CCN Bending Mode, ν_7, of NCCNO

	energy/hc (calc.)[a]		energy/hc	ΔB (calcd)[b]		ΔB
$v_7^{l_7}$	I	II	(exp.)[c]	I	II	(exp.)[b,c]
0^0	0.0	0.0	0.00	0.0	0.0	0.000
1^1	77.9	82.6	80.60	11.3	11.0	10.758
1^1	77.9	82.6	80.60	15.6	15.1	15.093
2^2	161.3	170.3	164.76	25.8	25.0	25.002
2^0	164.8	173.3	166.12	24.3	23.8	24.037
3^3	249.4	262.4	252.04	37.2	36.3	36.440
3^1	255.0	267.2	254.11	31.2	30.6	30.878
3^1	255.0	267.2	254.11	38.8	38.1	38.988
4^4	341.7	358.4	341.86	48.1	46.9	47.382
4^2	348.5	364.2	344.34	45.5	44.7	45.561
4^0	350.8	366.1	345.06	44.5	43.9	44.919
5^5	437.6	457.9	434.25	58.4	57.2	57.927
5^3	445.1	464.1	436.68	55.6	54.7	55.925
5^1	448.9	467.4	437.82	48.7	48.1	49.001
5^1	448.9	467.4	437.82	59.5	58.6	60.693
6^6	537.0	560.5		68.3	67.0	68.145
6^4	544.6	566.9		65.5	64.5	66.041
6^2	549.4	570.9		63.6	62.8	64.664
6^0	550.9	572.2		63.0	62.2	64.185

[a] Calculated using the CCN bending potential energy functions I and II, respectively. The ground-state energy level is found to lie 70.4 (I) and 75.9 (II) cm^{-1} above the minimum of the potential energy function. [b] Calculated and experimental ground-state effective rotational constants B are 2308.5(I), 2314.3 (II), and 2310.9983 MHz, respectively. [c] Determined using the spectroscopic constants from ref 11.

The calculated rotation−bending energy levels were then used to determine the effective rotational constant B for each vibrational $v_7^{l_7}$ state. These values were obtained by fitting an odd power series in $(J + 1)$ to the calculated rotational transition frequencies. The effective rotational constant B for the ground vibrational state of the NCCNO main isotopomer is determined in this way to be 2308.5 and 2314.3 MHz for the potential energy functions I and II, respectively. The predicted values are in remarkably good agreement with the experimental value of 2310.9983 MHz.[11] The predicted and observed changes in the rotational constant B due to excitation of the ν_7 mode are listed in Table 6. For the 18 excited states quoted, the root-mean-square deviation is determined to be 0.6 and 1.1 MHz for the functions I and II, respectively.

As in the case of halofulminates[4,5] and carbon suboxide,[7] it is interesting to investigate the effect of electron correlation on the shape of the CCN bending potential energy function for cyanofulminate. The calculations were performed at various

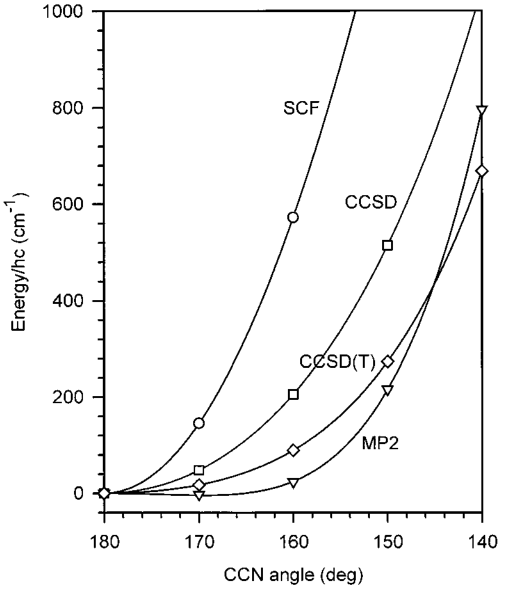

Figure 2. Total energy (relative) of NCCNO as a function of the CCN angle, determined using the cc-pVQZ basis set at the SCF, MP2, CCSD, and CCSD(T) levels of theory. The functions are drawn to a common scale.

TABLE 7: Total Energy[a] of NCCNO (in cm^{-1}) as a Function of the CCN Angle, Determined Using the cc-pVQZ Basis Set at Various Levels of Theory

∠(CCN)	180	170	160	150	140
SCF	0.	145.7	572.0	1256.1	2172.4
MP2	0.	−2.4	23.9	216.0	796.0
CCSD	0.	47.8	206.1	514.4	1044.5

[a] Relative to the energy of the linear configuration, calculated with the structural parameters given in Table 4. The energies at the CCSD(T) level of theory are those listed in Table 4.

levels of theory, namely, self-consistent field,[26] second-order Møller−Plesset[27], and coupled-cluster,[13−16] using the cc-pVQZ basis set and the structural parameters given in Table 4. The potential energy functions thus determined are shown in Figure 2 and are also given in Table 7. As was found previously, the primary shape of the CCN bending potential energy function is due to a balance between different electron correlation effects. Changes in the shape of the potential energy function upon inclusion of the correlation effects are similar, however, not as spectacular, as those observed for the ClCNO and BrCNO molecules.[4,5]

In conclusion, the electronic structure and vibrational dynamics of cyanofulminate were reliably predicted at the CCSD(T)/*spdfg* level of theory. Remarkably good predictions of the effective rotational constant *B* and of the CCN bending vibrational dependence of that constant were obtained. In conjunction with the very recent experimental study by Lichau et al.,[11] the reported results of the ab initio calculations confirm that the NCCNO molecule is linear at equilibrium, with the CCN bending potential energy function being strongly anharmonic.

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