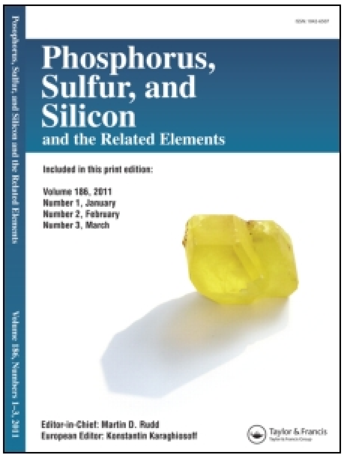

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A COMPREHENSIVE INVESTIGATION OF SODIUM AZIDODITHIOCARBONATE

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A COMPREHENSIVE INVESTIGATION OF SODIUM AZIDODITHIOCARBONATE

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A comprehensive theoretical and experimental study has been undertaken on the sodium azidodithiocarbonate salt, $[Na]^+[CS_2N_3]^-$. The IR and Raman spectra are reported and for the first time were assigned and compared to the quantum chemically calculated vibrational spectra with which they were found to be in excellent agreement. Investigation of the ^{14}N NMR spectrum and ^{13}C NMR spectrum results in the first report of the NMR spectra for the sodium salt of the $[CS_2N_3]^-$ anion. The structure of this compound was investigated quantum chemically to ascertain the likely reason for the experimentally observed ring structure being adopted rather than the chain structure. The results are in agreement with the experimentally deduced ring structure which was found to be energetically favorable over the chain structure by 8.3 kcal mol^{-1}. The ^{14}N NMR spectrum confirms the absence of a covalently bound azide unit as do the observed vibrational spectra.

Keywords: Sodium azidodithiocarbonate; Azides; Quantum chemical calculations; NMR spectroscopy; Vibrational spectroscopy

INTRODUCTION

The synthesis of sodium azidodithiocarbonate was first reported in 1915 by Sommer [1] from the cycloaddition reaction between carbon disulfide, CS_2 and sodium azide, NaN_3 (eq. 1).

$$CS_2 + NaN_3 \xrightarrow{H_2O,\ 40^\circ C} [Na]^+[CS_2N_3]^- \qquad (1)$$

In recent years, the investigation of the inorganic azides has been extensively studied [2–4] though the investigation of the pseudohalogenide $[CS_2N_3]^-$ has remained largely ignored, with only early reports in the liter-

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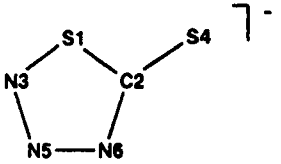
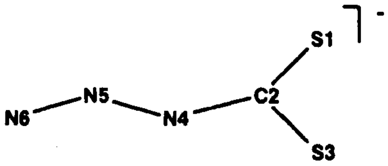
ature describing various derivatives, though without any experimental data for the assertions. [5–8] Further work has been reported on the reactions of transition metal azide complexes with CS_2 resulting in many compounds reported of varying low thermal stability [9–11]. However, despite the early synthesis of this compound, the structure which the anion adopted (ring structure, **I**; chain structure, **II**) was of great debate with the two structures considered to be most likely being the ring structure and the chain structure. Early IR spectra suggested the ring structure (**I**) to be the more expected structure [12–13] as did early semi empirical MNDO calculations. [14] However, it was not until 1991 that the structure of the $[CS_2N_3]^-$ anion was determined experimentally by X-ray diffraction techniques to be that of a 5-membered ring containing an N_3 unit with an exocyclic sulfur atom[15] and still remains the only reported example to our knowledge of an X-ray structure determination of this anion or of a main group derivative. However, we have found no reports with a comparison of the experimentally determined structural parameters with those of high level quantum chemical calculations, no ^{14}N NMR or ^{13}C NMR data and no assigned vibrational spectra. We therefore decided to investigate comprehensively this interesting pseudohalogenide to investigate the possibility of this anion being pseudoaromatic and to undertake a theoretical charge density study at semi empirical level of theory to ascertain if this $[CS_2N_3]^-$ anion represents the first reported cyclic pseudohalogenide.



I



II

EXPERIMENTAL

The preparation of the $[Na]^+[CS_2N_3]^-$ salt was achieved using the literature method.[1] Due to the thermal instability of this compound, storage in the freezer at –25°C is required, at which temperature it was stable for several weeks. The Raman spectra were recorded on a Perkin Elmer R2000 spectrophotometer as a neat solid as well as in aqueous solution, IR spectra on a Perkin-Elmer 980G spectrophotometer as Nujol mull and the ^{14}N NMR and ^{13}C NMR spectra were recorded on a Jeol 400 MHz machine in 10 mm glass NMR tubes using D_2O as a solvent.

COMPUTATIONAL ASPECTS

The structures of all compounds considered were "*pre*"-optimized using semiempirical calculations. All semiempirical calculations as well as the theoretical charge density study were carried out with the program package HyperChem [16] at the semiempirical PM3 [17] level of theory using a VSTO-3G* basis set. The PM3 method (which differs from AM1 [18] only in the values of the parameters) was chosen since the parameters for PM3 were derived by comparing a much larger number and wider variety of experimental versus computed molecular properties.

The PM3 is a reparametrization of AM1, which is based on the neglect of diatomic differential overlap (NDDO) approximation. NDDO retains all one-center differential overlap terms when Coulomb and exchange integrals are computed. The PM3 method is within the unrestricted Hartree-Fock formalism. Finally, the structures, energies, vibrational frequencies and zero point energies were computed quantum chemically at various levels of theory (HF/6–31G* [19], MP2/6–31+G* [20,21], BLYP/6–311++G* [21,22], B3LYP/6–31+G* [21,22] and B3LYP/6–311++G* [21,22]) using the program package Gaussian 98 [23]. At the highest level of theory applied (B3LYP/6–311++G*) the agreement between the observed (IR and Raman) and computed vibrational frequencies was very good so that no scaling factor was applied.

An NBO analysis was carried out to elucidate the bond situation in the $[SCSN_3]^-$ anion. The NBO analysis transforms the input basis set into the localized basis sets:

$$\text{input basis set} \rightarrow \text{NAOs} \rightarrow \text{NHOs} \rightarrow \text{NBOs} \rightarrow \text{NLMOs}$$

(NHO, natural hybrid orital; NBO, natural bond orbital; NLMO, natural localized MO) [27a] The NBO (ϕ^{NBO}) for a localized bond between atoms A and B is formed from directed orthogonal hybrids h_A and h_B which correspond to the Lewis picture and are therefore well adapted to describing the covalency effects in molecules.

$$\phi_{AB}^{NBO} = c_A h_A + c_B h_B \tag{2}$$

The antibonding NBOs $(\phi^{*,NBO})$, which are unoccupied in the formal Lewis picture, may then be used to describe non-covalency effects.

$$\phi*_{AB}^{NBO} = c_A h_A + c_B h_B \tag{3}$$

It has been shown that the corrections due to small occupancies of these antibonds (non-covalent corrections) are usually so small that the energy lowering can well be approximated by simple second-order perturbative expressions (eq 4).[27a-c] The role of antibonds can be seen by transforming the occupied canonical MOs to localized molecular orbitals (LMOs) (eq 5) which then again are fully occupied with exactly two electrons. In other words, the LMO ϕ_{AB}^{LMO} represents the delocalization of a bond orbital ϕ_{AB}^{NBO} and, therefore, describes non-covalent interactions in terms of (negative) hyperconjugation.

$$E_{\phi\phi*}^{(2)} = 2\frac{\langle \phi | h^F | \phi* \rangle^2}{E_{\phi*} - E_{\phi}} \qquad (\mathbf{h}^F\text{, Fock operator}) \tag{4}$$

$$\phi_{AB}^{LMO} = \phi_{AB}^{NBO} + \lambda\phi*_{CD}^{NBO} + \ldots \tag{5}$$

RESULTS AND DISCUSSION

The ^{14}N NMR and ^{13}C NMR spectra of the $[Na]^+[CS_2N_3]^-$ salt were recorded in D_2O at room temperature. The ^{14}N NMR spectrum shows as expected three peaks corresponding to the 3 ring nitrogen's derived from the azide group (Fig. 1). However, also as would be expected, the peaks observed are far away from the position of covalently bound azides, thus eliminating the possibility of the chain isomer being formed which would necessitate the presence of a terminal, covalently bound azide moiety to be present [2–4]. The ^{13}C NMR spectrum shows only 1 peak which is again as would be expected and corresponds to the carbon atom derived from the CS_2 group.

^{14}N NMR (297 K, H_2O, $MeNO_2$, 28.904 MHz, δ in ppm): 68.7 (1), 4.1 (1), −25.2 (1) $[CS_2N_3]^-$); -133.1 (1), −281.8 (2) ($[Na]^+[N_3]^-$).

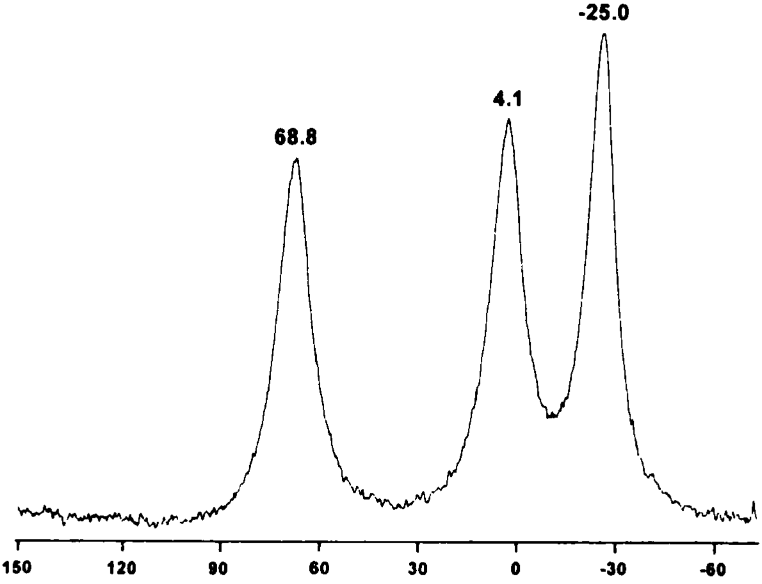


FIGURE 1 ^{14}N NMR spectrum of $[CS_2N_3]^-$ in $[Na]^+[CS_2N_3]^-$

^{13}C NMR (297 K, H_2O, TMS, 100.40 MHz, δ in ppm): 194.8 ($[CS_2N_3]^-$).

The vibrational spectra of the $[Na]^+[CS_2N_3]^-$ salt were recorded using room temperature IR and Raman spectroscopy (Fig. 2) with the vibrational spectrum also being calculated using high level quantum-chemical calculations. Both the ring and chain structures were calculated quantum chemically and both were found to possess true minima at all levels of theory applied. It could also be observed that at every level of theory applied, the observation of the ring isomer having a lower energy than the chain isomer was also consistent. The calculated vibrational spectra for the two isomers are shown in Tab.1. From comparison of the calculated vibrational spectrum with the experimentally observed vibrational spectra it is clearly observed that the $[CS_2N_3]^-$ anion in $[Na]^+[CS_2N_3]^-$ adopts a cyclic five-membered ring structure as in agreement with the X-ray structure determination [15]. A comparison of the experimental and calculated vibrational frequencies is shown in table II as well as an assignment, which has been carried out for the first time. In order to investigate the structural parameters as well as the vibrational spectra of this compound, repetition of the calculations for the five-membered ring structure were undertaken at various different levels of theory with each result showing *NIMAG* = 0 and the best fit between the theoretical and experimental data was observed from using B3LYP level of theory with the 6–311++G* basis set. From an NBO analysis, it can be observed that the thiolate rather than the ketonic form was shown to be more favorable with the calculated structural parameters being listed in table III for the chain isomer and table IV for the ring isomer. All structural parameters were shown to be reasonable and were found to agree very well with those determined experimentally from the X-ray structure determination [15] which was in contrast to the earlier semi- empirical MNDO calculations which inaccurately calculated the exocyclic sulfur-carbon bond length [14].

TABLE I Calculated vibrational spectra of $[CS_2N_3]^-$ for ring and chain form at B3LYP/6–311++G* level of theory (frequencies in cm^{-1}, IR intensities im parentheses in km mol^{-1})

B3LYP/6–311++G (ring isomer)*	*B3LYP/6–311++G* (chain isomer)*
215 (2)	78 (0.6)
272 (0.3)	153 (0.2)
445 (4)	309 (0.8)
550 (1)	369 (3)
579 (8)	498 (20)
631 (8)	535 (0)
652 (0)	546 (8)
904 (58)	677 (41)
1032 (62)	889 (271)
1120 (120)	1069 544)
1230 (573)	1283 (191)
1314 (4)	2206 (777)

TABLE II Computed energies and vibrational data of $[S\text{-}CSN_3]^-$ (*connectivity: S1-[C-N1-N2-N3-S2], frequeneies in cm^{-1}, IR intensities im parentheses in km mol^{-1})

	*PM3/ VSTO-3G**	*HF/6–31G* (S: LANL2DZ)*	*MP26–31+G* (S: LANL2DZ)*	*BLYP/ 6–311++G**	*B3LYP/ 6–31+G**	*B3LYP/ 6–311++G**	*exptl. IR (powder)*	*exptl. Ra. (solid)*	*exptl. Ra. (H_2O sol.)*	*tentative assignme*
symmetry	C_s	C_s	C_s	C_s	C_s	C_s				
-*E*/a.u.	614.9 kcal mol^{-1}	220.954136	221.710666	998.820442	998.776618	998.872175				
NIMAG	0	0	0	0	0	0				
zpe/ kcal mol^{-1}		14.3	12.6	11.9	12.8	12.76	12.6	12.6	12.6	
ν_1 (A")	210 (2)	242 (4)	208 (1)	200 (2)	216 (2)	215 (2)	---	184 (1)	184 (2)	τ(ring)oop
ν_2 (A')	266 (1)	288 (0.6)	283 (0.5)	258 (1)	273 (0.2)	272 (0.3)	278 w	280 (5)	279 (6)	δ(CSC)ip
ν_3 (A')	448 (12)	454 (10)	433 (2)	392 (3)	448 (4)	445 (4)	---	457 (2)	456 (2)	ν(ring-S1)
ν_4 (A")	510 (1)	609 (0.6)	547 (4)	523 (2)	549 (1)	550 (1)	524 m	---	---	δ(ring)oop
ν_5 (A')	593 (5)	637 (14)	563 (10)	509 (12)	589 (7)	579 (8)	590 w	---	---	ν(C-S2)
ν_6 (A')	615 (8)	686 (10)	619 (9)	568 (14)	638 (7)	631 (8)	639 sh	---	---	δ(CNN)oop
ν_7 (A")	740 (13)	706 (6)	633 (1)	617 (0)	651 (0)	652 (0)	653 m	658 (10)	651 (10)	δ(ring)ip
ν_8 (A')	952 (55)	966 (87)	897 (63)	855 (56)	902 (57)	904 (58)	927 m	927 (1)	914 (1)	ν(ring)sym
ν_9 (A')	968 (12)	1119 (53)	1028 (147)	966 (70)	1034 (73)	1032 (62)	1047 sh	---	---	ν(C-S1)
ν_{10} (A')	1168 (501)	1169 (202)	1116 (39)	1031 (77)	1117 (97)	1102 (120)	1077/ 1063s	1082 (5)/ 1062 (5)	1079 (2)/ 1054 (3)	ν(ring)as
ν_{11} (A')	1315 (126)	1458 (490)	1220 (83)	1159 (531)	1237 (577)	1230 (573)	1197/ 1209 s	1194 (6)/ 1211 (4)	1212 (9)	ν(N1-C)
ν_{12} (A')	1599 (52)	1688 (41)	1290 (492)	1219 (1)	1322 (5)	1316 (4)	1282 s	1286 (4)	1282 (2)	ν(N2-N3)

TABLE III Calculated structural parameters for ring isomer of $[CS_2N_3]^-$ anion at B3LYP/6–311++G* level of theory

Symmetry = C_s			
-E/a.u. = 998.872175			
Bond	*d/Å*	*Angle*	*∠/°*
C2-S1	1.77	C2-S1-N3	90.5
N3-S1	1.74	S1-C2-S4	124.4
S4-C2	1.70	S1-N3-N5	109.1
N3-N5	1.28	S1-C2-N6	108.0
N6-C2	1.35	S4-C2-N6	127.6
N6-N5	1.34	N3-N5-N6	118.8
		C2-N6-N5	113.6

TABLE IV Calculated structural parameters for chainisomer of $[CS_2N_3]^-$ anion at B3LYP/6–311++G* level of theory

Symmetry = C_s			
-E/a.u. = 998.859003			
Bond	*d/Å*	*Angle*	*∠/°*
N5-N6	1.14	N4-N5-N6	172.6
N4-N5	1.29	C2-N4-N5	119.7
C2-N4	1.46	S3-C2-N4	112.5
S1-C2	1.69	S1-C2-N4	118.6
S3-C2	1.70	S1-C2-S3	128.9

The theoretical charge density structure computed semi empirically at PM3 level of theory using the VSTO-3G* basis set was found to yield the probable structure as being a five-membered ring which is planar with C_s symmetry. The electron density was also observed to lie above and below the plane of the ring as would be expected for a pseudoaromatic species (Fig. 5) thus raising the interesting question as to whether this pseudohalogenide, $[CS_2N_3]^-$ does indeed represent an example of a cyclic pseudohal-

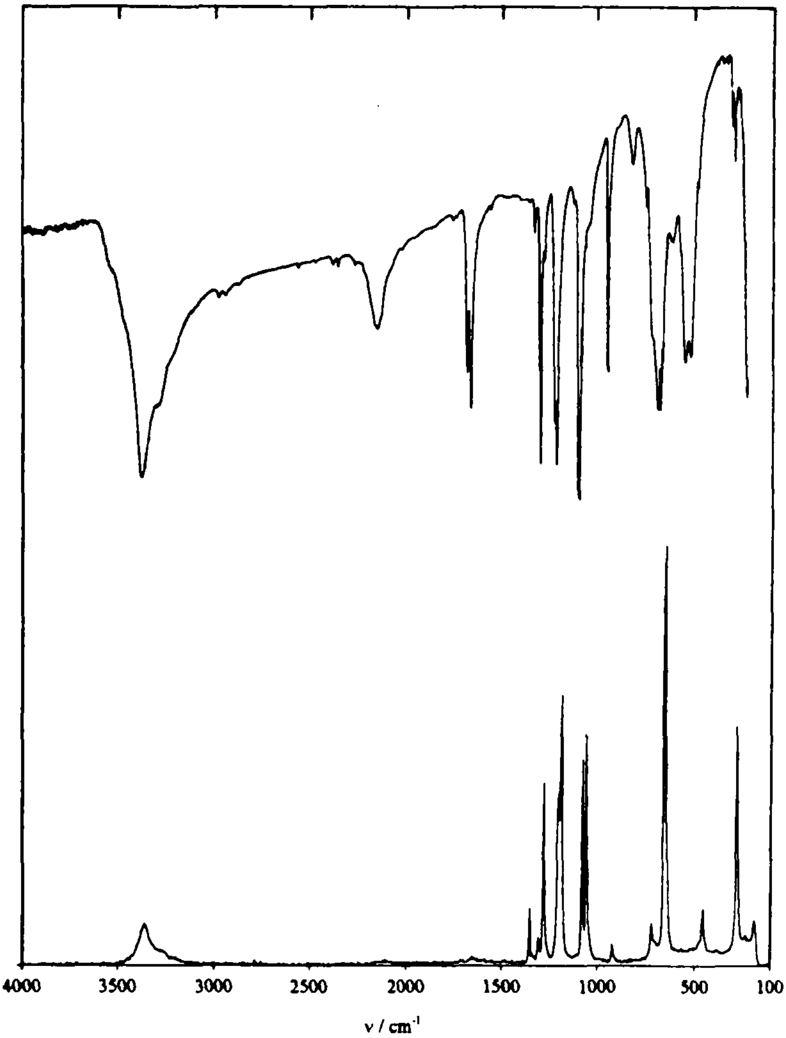


FIGURE 2 IR (top) and Raman (bottom) spectra of $[CS_2N_3]^-$ in $[Na]^+[CS_2N_3]^-$

ogenide which is also pseudoaromatic. The Hückel minimum requirements for a compound to be classed as being pseudoaromatic are as follows: 1. homocyclic system, 2. conjugated π system which has no node in the lowest occupied π orbital (*Note*: although $(PNCl_2)_3$ is monocyclic, has 6 π electrons and is planar the lowest π MO has nodes in the lowest π orbital [24–26]), 3. planar system, 4. (4n + 2)π electrons (n = 0, 1, 2....). Therefore, this pseudohalogenide does indeed represent a pseudoaromatic system fulfilling all of the requirements listed above. Now that the structure and spectroscopic characteristics of this interesting pseudohalogenide have been thoroughly investigated both theoretically and experimentally the area of this anion has now been elucidated and opened up.

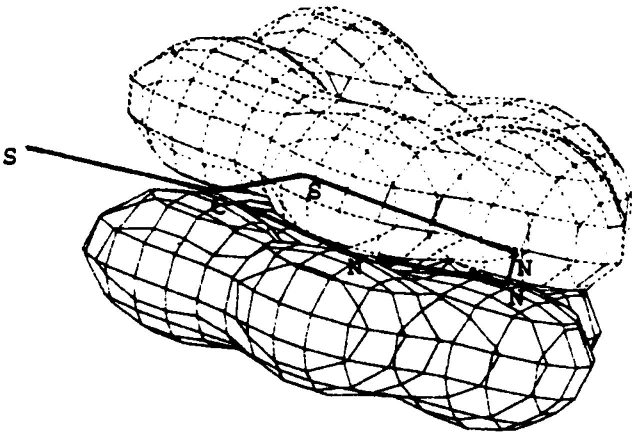


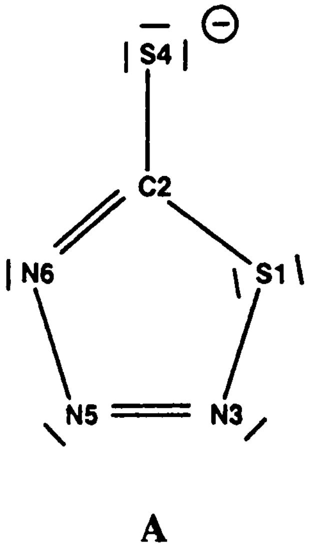
FIGURE 3 Lowest occupied π MO of $[CS_2N_3]^-$, calculated at PM3/VSTO-3G* level of theory

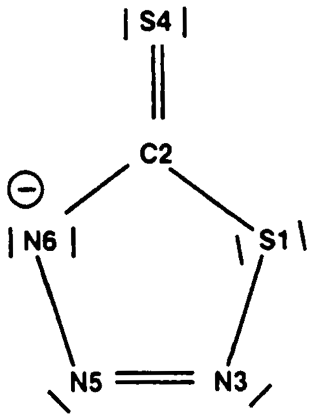
NBO Analysis

The bonding situation in the cyclic $[SCSN_3]^-$ anion **I** was also investigated with the help of a NBO analysis. The calculated Mulliken and NBO charges are summarized in table V. The *RESONANCE* keyword was activated to permit strongly delocalized structures. The structure to which the NBO analysis corresponds is shown in Figure 4 (**A**). This resonance structure (**A**) has reasonably well localized σ NBOs (1.975 – 1.985 electrons), but one severely depleted π bond (C2-N6,1.795 electrons) and corresponding high occupancy in two π* antibonds (C2-N6 and N3-N5; 0.515 and 0.418 electrons, respectively). Figure 4 also presents the other two most likely Lewis structures **B** and **C**.

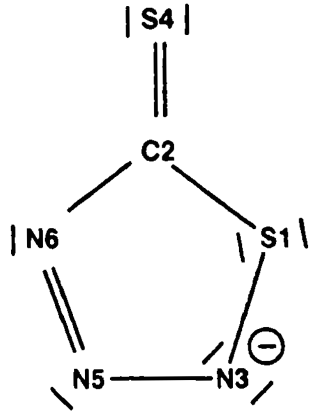
TABLE V Calculated Mulliken and NBO charges for the $[SCSN_3]^-$ anion (for atomic labeling see Figure 4)

atom	*Mulliken charge / e*	*NBO charge /e*
S1	0.02	0.38
C2	−0.14	−0.18
N3	−0.09	−0.42
S4	−0.65	−0.33
N5	−0.15	−0.05
N6	0.01	−0.40





B



C

FIGURE 4 Lewis structures for the $[SCSN_3]^-$ anion according to a NBO analysis

Proton Affinity of $[SCSN_3]^-$

Of particular interest is the gas-phase acidity of the neutral Brønsted acid $HSCSN_3$ (the corresponding acid to the $[CS_2N_3]^-$ anion under investigation). The calculated total energies of $[SCSN_3]^-$ and $HSCSN_3$ (B3LYP/6–311++G*: –998.872175 and –999.378663 a.u.) can be used to predict theoretically the acidity. The dissociation energy of reaction (6) was calculated, which, after correction for zero-point energies ($[CS_2N_3]^-$, 12.8 and CS_2N_3H, 18.45 kcal mol^{-1}), differences in rotational (0 RT) and translational (3/2 RT) degrees of freedom, and the work term (RT), was converted into the gas-phase acidity at room temperature (enthalpy value) $\Delta H_{acid}[HSCSN_3(g) \rightarrow [SCSN_3]^-(g) + H^+(g)] = 310.9$ kcal mol^{-1}. This value compares nicely with the acidity (*i.e.* the proton affinity) of other related and relatively strong S-H acids. The acidity of CF_3-COSH, for example, was reported to be 312.5 kcal mol^{-1}.[28]

$$HSCSN_3(g) \rightarrow [SCSN_3]^- + H^+(g) \qquad (5)$$

Acknowledgements

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