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Singlet−Triplet Splittings and Ground- and Excited-State Electron Affinities of Selected Cyanosilylenes, XSiCN (X = H, F, Cl, CH_3, SiH_3, CN)[†,‡]

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Several cyanosilylenes, XSiCN, (X = H, F, Cl, CH_3, SiH_3, CN) have been investigated using the RHF-ACPF and CAS(2,2)-ACPF methods in conjunction with the aug-cc-pVTZ basis sets. All silylenes are found to have singlet ground states. The ground-state electron affinities are found to be rather high, i.e., 1.832, 1.497, 1.896, 1.492, 2.235, and 2.631 eV for HSiCN, FSiCN, ClSiCN, H_3CSiCN, $H_3SiSiCN$, and $Si(CN)_2$, respectively. The existence of bound excited negative ion states has been discovered for the first time within these silylenes. All these bound excited anion states belong to the totally symmetric irreducible representations and can be characterized as dipole-bound negative ion states. All triplet excited states have even larger dipole moments than the singlet states and are, therefore, "dressed" by dipole-bound negative ion states, which correspond to Feshbach resonances.

I. Introduction

In many thermal and photochemical processes, silylenes appear as transient species,[1] and even in the course of silane plasma reactions, silylenes seem to be important intermediates.[2] They are highly reactive species at higher temperatures and fairly unreactive at lower temperatures. This together with their similarities to the carbenes has raised essentially two threads of research during the recent decades. On one hand, the chemists tried to produce highly stable silylenes,[3,4] and on the other hand, there has been and there is still a hunt for silylenes with low-lying triplet states or even with triplet ground states.[5] Since there is a plethora of literature, these few key references should suffice, where many of the earlier references can be found. The versatility of silylenes seems to be enormous, since it has been described recently by the group of West[6] that "stable" silylenes can even be used as catalysts in olefin polymerization.

The situation is completely different for negatively charged silylenes in that there is not a great abundance of literature.[1,7−15]

In many spectroscopic investigations, however, negative ions are used as precursors and the neutral states are studied via photodetachment spectroscopy. Depending on their production history,[16] some anions can exist in excited states[17] or even in unexpected spin states.[18,19] It is, therefore, of vital interest to also have at least some information on the anion states of the corresponding silylenes.

This work represents a continuation of our computational studies on ground and excited negative ion states[20,21] of small molecules and is devoted to the singlet−triplet splittings and especially to the negative ion states of the title silylenes and addresses as well the question whether there might exist stable excited negative ion states. Such states have already been found earlier for certain silylenes,[8,9] and even recently for a special class of carbenes.[22] Since it has been established that several cyanocarbenes possess rather large ground-state electron affinities and even additional pronounced excited-state eletron affinities, we can make a direct comparison between the electron binding properties of cyanocarbenes and cyanosilylenes.

Because the silicon concentration in the interstellar gas[23] is only slightly lower than that of C, N, and O, astrophysicists have reasoned that molecules such as cyanosilylene on account of their high dipole moment might be ideally suited to study astrophysical processes. The intensive search for such silicon-containing molecules of astrophysical interest has in fact led to the discovery of HSiCN in discharge experiments in the laboratory by Sanz et al.[24]

II. Methodological Approach

The basis sets employed for this study are the augmented correlation consistent valence triple-ζ aug-cc-pVTZ (AVTZ) contracted sets of Dunning[25] and Woon and Dunning.[26]

The reference wave functions of the open-shell electronic states have been computed at the restricted open shell (RHF) level of theory, whereas the reference wave functions for the singlet ground states have been calculated with a CAS(2,2) ansatz,[27] although the improvement of this reference wave function over a single reference in silylenes has been questioned by Gordon[28] and Selmani and Salahub.[29] All these reference wave functions have been employed in conjunction with the averaged coupled pair functional,[30] ACPF, to evaluate the dynamical electron correlation. This approach will be abbreviated by the acronym ACPF in the following. This approach represents a size-extensive modification of the MR-CI(SD) method. An explicit discussion of the methodological details can be found in the original papers of Ahlrichs and Gdanitz.[30,31] Only the valence electrons have been taken into account in these procedures. The ACPF approach has been chosen for the computation of the correlation energy, since on one hand this approach can be used not only for single-determinant reference wave functions such as RHF, but also for multiconfiguration self-consistent field (SCF) reference wave functions, and on the other hand, it is almost perfectly size-extensive. This latter property is highly desirable, since it guarantees that our

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[‡] This paper is dedicated to Professor Jack Simons on the occasion of his 60th birthday.

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TABLE 1: Structural Data, Dipole Moments, and Zero-Point Energies for the Various Electronic States of the Investigated XSiCN Species[a]

XCCN	state	E (h)	ZPE (h)	R_{XSi} (Å)	R_{SiC} (Å)	R_{CN} (Å)	Φ (°)	Ω (°)	μ (D)
HSiCN	X^1A'	−382.277978	0.014048	1.515	1.886	1.166	92.2	174.2	3.186
HSiCN	$^3A''$	−382.236404	0.014251	1.478	1.827	1.166	116.7	177.1	3.599
$HSiCN^-$	X^2A''	−382.344870	0.013620	1.537	1.928	1.172	91.7	174.7	
FSiCN	X^1A'	−481.498003	0.009900	1.609	1.913	1.165	97.1	171.8	2.864
FSiCN	$^3A''$	−481.421977	0.010242	1.601	1.815	1.167	116.0	177.0	3.134
$FSiCN^-$	X^2A''	−481.552525	0.009413	1.687	1.946	1.172	95.8	174.6	
ClSiCN	X^1A'	−841.479399	0.009107	2.078	1.901	1.165	97.0	172.3	2.776
ClSiCN	$^3A''$	−841.413875	0.009306	2.047	1.821	1.167	117.3	177.0	3.154
$ClSiCN^-$	X^2A''	−841.548665	0.008700	2.227	1.927	1.171	95.1	173.1	
H_3CSiCN	X^1A'	−421.481787	0.043257	1.902	1.906	1.172	95.4	175.5	3.685
H_3CSiCN	$^3A''$	−421.436982	0.044092	1.897	1.839	1.173	117.2	178.4	4.470
H_3CSiCN^-	X^2A''	−421.535883	0.043008	1.972	1.938	1.178	94.2	176.6	
$H_3SiSiCN$	X^1A'	−672.536380	0.032138	2.410	1.882	1.168	90.5	176.4	3.184
$H_3SiSiCN$	$^3A''$	−672.508442	0.032870	2.345	1.846	1.173	118.7	178.2	4.074
$H_3SiSiCN^-$	X^2A''	−672.618241	0.031853	2.382	1.919	1.172	91.4	175.2	
$Si(CN)_2$	X^1A_1	−474.377244	0.015678	1.881	1.881	1.165	94.1	172.0	3.267
$Si(CN)_2$	$^3B_1$	−474.326677	0.016090	1.818	1.818	1.165	116.6	176.1	3.191
$Si(CN)_2{}^-$	X^2B_1	−474.473921	0.015666	1.918	1.918	1.169	93.4	172.2	

[a] All data are obtained with the aug-cc-pVTZ basis set, employing the ACPF approach, except the zero-point energy contributions, ZPE, which have been calculated at the B3LYP level of theory. For details, see the text.

evaluated electron affinities are at least not biased by size extensivity errors, and it has turned out that this method provides rather reliable estimates for electron affinities.[13,22,32,33]

Each electronic state has been optimized numerically at the ACPF level of theoretical sophistication.

All RHF, CAS(2,2), and subsequent ACPF energy calculations and geometry optimizations have been performed with the MOLPRO-2000[34] suite of programs.

Since the numerical calulations of the harmonic vibrational frequencies would have been prohibitive, they have been calculated with the B3LYP hybrid functional, as implemented in the *Gaussian 98*[35] package, to assess the zero-point energies.

The paradigmatic isosurface pictures for the dipole-bound SOMOs have been generated with the program MOLDEN.[36]

Dipole-Bound Negative Ions. Fermi and Teller[37] found that there exists a critical dipole moment $\mu_{crit} = 1.625$ D within the pure dipole model such that any system with a permanent dipole moment μ in excess of μ_{crit} can bind an extra electron in its dipole field and give rise to dipole-bound negative ion states. The excess electron in these cases resides in a highly diffuse totally symmetric "orbital", which is largely located at the positive end of the dipole.

Any real molecule, which causes additional repulsion between the valence electron and the dipole-bound extra electron, has to have $\mu > \mu_{crit}$ to be able to support a dipole-bound negative ion state.

Nowadays, there is consensus[38−41] that a dipole moment of at least 2.5 D is necessary for a real molecule to be able to provide a dipole-bound negative ion state. Many research groups have essentially contributed to the understanding of such feebly bound anions. Especially noteworthy are the experimental contributions of the group of Desfrançois and Schermann[38,39,42−47] and the theoretical contributions provided by the group of Simons[48−58] as well as the group of Adamowicz.[59−62]

The reading of a recent review on dipole-bound anion states by Jordan and Wang[63] is highly recommended.

The normal case is that the extra electron is bound in the dipole field of the electronic ground state of the molecule M to yield a dipole-bound anion M_{DB}^-. If M also possesses, however, an excited state, M*, with a sufficiently large dipole moment to accommodate a dipole-bound anion state, M_{DB}^{*-}, this state will be called a Feshbach resonance, M_{FR}^{*-}, since its energy lies high above the neutral ground state, i.e., within the continuum of the neutral ground state. Since it is bound with respect to the excited neutral parent (NP) state M*, this binding energy can also be used to specify its energetics, as has been done in the sequela

$$EA_{FR} = E(M^*) - E(M_{FR}^{*-}) \qquad (1)$$

On account of the very diffuse structure of the surplus electron in a dipole-bound anion state, these systems cannot be tackled theoretically with standard basis sets, but instead need strong augmentations with highly diffuse s-type and p-type Gaussian basis functions.

For this purpose, we have decided to place a set of diffuse s-type and a set of diffuse p-type Gaussians with a 4 Å offset from that atom, which lies at the positive end of the dipole moment. The exponents α_n of these diffuse Gaussians have been chosen in an even-tempered manner, according to

$$\alpha_n = k^n \times \alpha_0$$

employing $\alpha_0 = 0.02$ and $k = \sqrt{1/10}$ for both the s-type and p-type functions. This leads to 10 even-tempered s-type as well as p-type functions with exponents in the range of 0.02 down to 1×10^{-6}, which seems sufficient for the present purpose, since the electron binding energies for all investigated dipole-bound states are in excess of 10 meV. These basis sets obtained as such will be denoted by dip-AVTZ in the following.

This procedure is very similar to that used by many other groups and practically identical to those made use of in previous studies on dipole-bound anion states of diatomic molecules.[32,33] To avoid any bias from the basis set, it is clear that all the neutral parent states listed in Table 1 have been recalculated with the dip-AVTZ basis sets, as given in Table 3.

III. Results and Discussion

Figure 1 provides a sketch of the structural features of a $H_3X{-}Si{-}C{\equiv}N$ molecule, as paradigm for $H_3C{-}Si{-}CN$ and $H_3Si{-}Si{-}CN$. The same sketch is valid for all investigated species, since in all other cases, where X corresponds to an atomic substituent, one just has to ignore the X−H bonds. All neutral and negatively charged species are planar. Thus, there are two important bond angles, denoted by Φ and Ω. Φ is the most important one, since it describes the bond angle at the

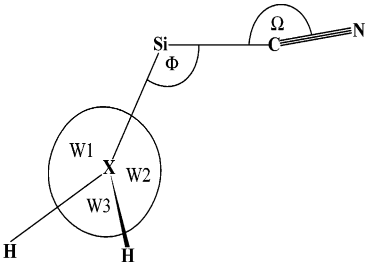

Figure 1. Structural sketch of the cyanosilylenes H_3XSiCN and definition of the bond angles Φ and Ω.

TABLE 2: Singlet−Triplet Splittings (ΔE_{ST}, eV), Ground-State Electron Affinities (EA, eV) , and Electron Affinities of the Dipole-Bound Negative Ion States (EA_d, ${}^2EA_{FR}$,[a] ${}^4EA_{FR}$,[a] all meV)′′

system	ΔE_{ST}	EA	EA_d	${}^2EA_{FR}$	${}^4EA_{FR}$
HSiCN	1.137	1.832	23.6	38.2	23.8
FSiCN	2.078	1.497	21.9	72.9	20.7
ClSiCN	1.791	1.896	22.7	68.8	23.0
H_3CSiCN	1.229	1.492	22.8	57.1	23.4
$H_3SiSiCN$	0.780	2.235	11.8	68.1	21.7
$Si(CN)_2$	1.387	2.631	28.1	105.7	28.1

[a] Electron affinities of the ${}^2A''$ and ${}^4A''$ Feshbach resonances.

TABLE 3: Energies for the Dipole-Bound (dip) and Feshbach Resonant (FR) Negative Ion $XSiCN^-$ States Together with the Energies for the Respective Neutral Parent (NP) States[a]

XCCN	state	type	E (h)	(NP) state	E_{NP} (h)
$HSiCN^-$	${}^2A'$	(dip)	−382.278882	X^1A'	−382.278014
$HSiCN^-$	${}^2A''$	(FR)	−382.237836	${}^3A''$	−382.236432
$HSiCN^-$	${}^4A''$	(FR)	−382.237306	${}^3A''$	−382.236432
$FSiCN^-$	${}^2A'$	(dip)	−481.498869	X^1A'	−481.498063
$FSiCN^-$	${}^2A''$	(FR)	−481.424703	${}^3A''$	−481.422023
$FSiCN^-$	${}^4A''$	(FR)	−481.422785	${}^3A''$	−481.422023
$ClSiCN^-$	${}^2A'$	(dip)	−841.480317	X^1A'	−841.479481
$ClSiCN^-$	${}^2A''$	(FR)	−841.416448	${}^3A''$	−841.413918
$ClSiCN^-$	${}^4A''$	(FR)	−841.414765	${}^3A''$	−841.413918
H_3CSiCN^-	${}^2A'$	(dip)	−421.533798	X^1A'	−421.532960
H_3CSiCN^-	${}^2A''$	(FR)	−421.439130	${}^3A''$	−421.437031
H_3CSiCN^-	${}^4A''$	(FR)	−421.437892	${}^3A''$	−421.437031
$H_3SiSiCN^-$	${}^2A'$	(dip)	−672.536853	X^1A'	−672.536419
$H_3SiSiCN^-$	${}^2A''$	(FR)	−672.510945	${}^3A''$	−672.508442
$H_3SiSiCN^-$	${}^4A''$	(FR)	−672.509240	${}^3A''$	−672.508442
$Si(CN)_2{}^-$	${}^2A_1$	(dip)	−474.379028	X^1A_1	−474.377995
$Si(CN)_2{}^-$	${}^2B_1$	(FR)	−474.330608	${}^3B_1$	−474.326723
$Si(CN)_2{}^-$	${}^4B_1$	(FR)	−474.327757	${}^3B_1$	−474.326723

[a] All data are obtained with the dip-AVTZ basis sets at the ACPF level of theory. The geometries are taken from the neutral parent states.

silylene center, and we will only consider this angle in the sequel. Ω defines only whether the −C≡N group is cis or trans with respect to the X−Si moiety. All values $\Omega < 180$ correspond to trans configurations.

Table 1 lists the geometry data optimized at the ACPF level of theory for the investigated species and electronic states together with the corresponding ACPF energies and the zero-point energies, which have been evaluated with the B3LYP approach. Table 2 collects the singlet−triplet splitting ΔE_{ST} together with the electron affinity values. Table 3 provides the ACPF energies for the dipole-bound negative ion states and the Feshbach resonant negative ion states obtained with the strongly augmented basis sets.

A. HSiCN and $HSiCN^-$. The X^1A' ground state of HSiCN is found to have an Si−C bond distance of 1.886 Å, an Si−H bond length of 1.515 Å, and a bond angle Φ of 92.2°within our ACPF approach. There is a good agreement with the

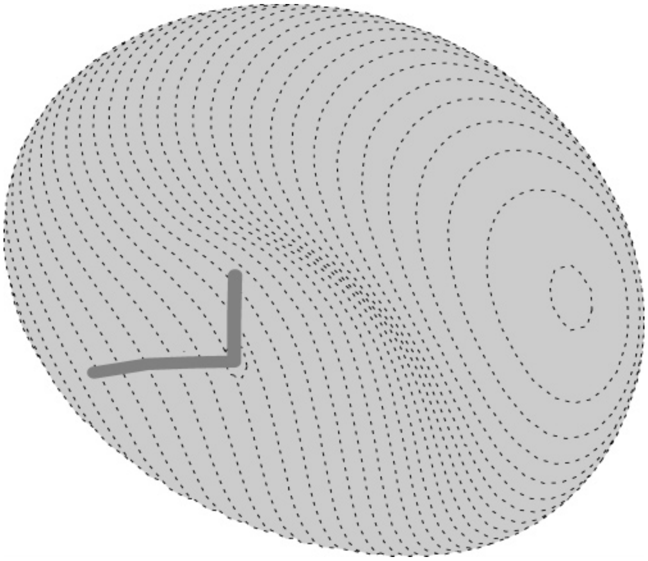

Figure 2. Contour surface with a value of 0.0007 for the SOMO in the ${}^2A'$ dipole-bound anion state of $HSiCN^-$.

corresponding aug-cc-pCVQZ CCSD(T) SiH_2 (${}^1A_1$) geometry parameters of Larkin et al.[15] The dipole moment of the ground state is as high as 3.184 D. This may be compared to an experimental estimate of around 3.5 D of Sanz et al.[24]

In going to the ${}^3A''$ state, it is interesting to note that, akin to triplet SiH_2, all bonds reaching out from the silicon atom are significantly shortened with respect to the X^1A' state, and we reach the usual, rather large angle Φ of some 116°, which is also rather similar to that found for $SiH_2({}^3B_1)$.[29] The dipole moment of the ${}^3A''$ state amounts to almost 3.6 D and, thus, is notably larger than that of the X^1A' ground state.

The singlet−triplet splitting between the X^1A' state and the lowest excited triplet state, ${}^3A''$, is computed as 1.137 eV. This is somewhat larger than the corresponding ΔE_{ST} value in SiH_2, which is estimated by Bauschlicher[64] to be close to 0.91 eV.

The ground-state electron affinity of HSiCN, to give the lowest X^2A'' negative ion state, amounts to 1.832 eV. This strongly exceeds that of SiH_2 and almost reaches $EA = 1.972$ eV of the homologous carbene,[22] HCCN. One has to recall, however, that the adiabatic electron affinity is always defined with respect to the neutral ground state, which is a triplet state for this carbene. Dissimilar to the HCCN, however, HSiCN shows no stable valence-bound excited negative ion state. Because of the large dipole moment of the X^1A' state, there is a dipole-bound ${}^2A'$ negative ion state with an EA value of 23.6 meV. Figure 2 provides an isosurface representation of the SOMO with a value of 0.0007 in the ${}^2A'$ dipole-bound negative ion state of $HSiCN^-$.

Since the positive end of the dipole in the X^1A' neutral ground state of HSiCN coincides with the hydrogen atom, it is no surprise that the extra electron in this loosely bound state resides essentially beyond the hydrogen atom, as can be seen in Figure 2.

Electron attachment to the ${}^3A''$ excited state gives rise to the dipole-bound Feshbach resonances ${}^4A''$ and ${}^2A''$ with associated electron affinity values of 23.8 and 38.2 meV, respectively.

B. FSiCN and $FSiCN^-$. The equilibrium bond angle Φ in the X^1A' ground state of FSiCN is 97.1°, which is some 5° larger than in the neutral ground state of HSiCN, and the angle Ω is rather small, i.e., only 171.8°. The dipole moment is no more than 2.864 D, and thus significantly smaller than that of cyanosilylene.

Apart from the Si−F bond, the $^3A''$ state of FSiCN shows strong structural similarity to the $^3A''$ state of HSiCN. The dipole moment of the triplet state is in excess of that of the singlet state by 0.270 D, as can be recognized from Table 1.

The singlet−triplet splitting between the X^1A' ground state and the $^3A''$ excited state in FSiCN amounts to 2.078 eV, which is the largest ΔE_{ST} value of all investigated cyanosilylene species, as can be seen in Table 2. This is a quite typical finding with fluorine substitution, not only for silylenes, but also for carbenes.[22]

Previous calculations on $SiHF^-$ and SiF_2 showed that fluorine substitution has a negative impact on the electron affinity.[15] We observe a very similar trend in that the FSiCN ground-state EA value is obtained as 1.497 eV, which is only 0.37 eV above the experimental EA value[10] of SiH_2, but it is 0.335 eV smaller than the EA value of HSiCN.

A valence-bound excited anion state could not be found, but again, there is a dipole-bound $^2A'$ negative ion state, with an electron affinity of 21.9 meV. The SOMO of this feebly bound state is now mainly centered beyond the silicon atom, since it constitutes the center with the highest positive partial charge in the neutral ground state.

Since the $^3A''$ state also has a dipole moment far in excess of the μ_{crit}, this state is "dressed" with Feshbach resonances, a $^4A''$ dipole-bound state and a $^2A''$ dipole-bound state, with 20.7 and 72.9 meV as $^4EA_{FR}$ and $^2EA_{FR}$, respectively. In conformity with the respective Feshbach resonances in $HSiCN^-$, in $FSiCN^-$ also the $^2A''$ resonance is more strongly bound than the $^4A''$, in disharmony with Hund's rule.

C. ClSiCN and $ClSiCN^-$. The structural features of the X^1A' ground state of ClSiCN are in close correspondence with those of the FSiCN singlet state, apart from the Si−X bond. The dipole moment is even smaller than for the fluoro-substituted species, i.e., 2.776 D.

The triplet state $^3A''$ lies 1.791 eV adiabatically higher in energy than the singlet ground state and has a notably larger dipole moment of 3.154 D.

The adiabatic electron affinity of the X^1A' state to yield the X^2A'' negative ion state ground state is no larger than 1.896 eV, which is rather close to the EA value of HSiCN. So, one can state that a Cl substituent also is not prone to increase the electron affinity of a silylene. This is in marked contrast to the respective carbenes.[22]

It is not unexpected that no valence-bound stable excited negative ion state could be found, but because of the dipole moment of more than 2.7 D in the X^1A' state, there is a dipole-bound $^2A'$ negative ion state, which has a stability of 22.7 meV against the loss of the extra electron.

On account of the dipole moment of more than 3 D for the $^3A''$ state, there are two Feshbach resonances $^4A''$ and $^2A''$ with $^4EA_{FR} = 23.0$ meV and $^2EA_{FR} = 68.8$ meV, respectively.

D. H_3CSiCN and H_3CSiCN^-. Methylcyanosilylene shows almost equidistant Si−C bond lengths in its X^1A' neutral ground state. Its ground-state dipole moment surmounts the ground-state dipole moment of any investigated system.

The energetic separation between the X^1A' ground state and the excited $^3A''$ state, i.e., the ΔE_{ST} value, is found to be 1.229 eV, which does not deviate strongly from the corresponding singlet−triplet splitting in cyanosilylene.

Inspection of Table 2 reveals that the adiabatic electron affinity of the $H_3CSiCCN$ X^1A' ground state is only 1.492 eV, which is the smallest EA value of all investigated cyanosilylenes, since it falls even somewhat below that of HSiCN. Such an unfavorable effect of the CH_3 substituent on the silylene electron affinity has been found long ago by Kalcher and Sax[8] and is also in conformity with recent findings of Larkin et al.[15] for mixed halo- and methyl-substituted silylenes.

There is no valence-bound excited anion state, but like in all other cases, there exists a dipole-bound $^2A'$ negative ion state on account of the large dipole moment of the neutral ground state, which is almost as large as 3.7 D and, thus, constitutes the largest ground-state dipole moment within the investigated cyanosilylene series. The calculated electron affinity for this dipole-bound state is, however, no larger than 22.8 meV, which means it is even 0.6 meV smaller than that of the corresponding $^2A'$ state in $HSiCN^-$. In this electronic state, the extra electron resides opposite the methyl group. The reason for this can be found in the charge distribution of the X^1A' neutral ground state, where the hydrogen atoms altogether bear a positive charge of approximately +0.5, whereas the silylene center hosts only very little charge.

The two Feshbach resonances $^4A''$ and $^2A''$ are stable by 23.4 and 57.1 meV, respectively, with respect to the $^3A''$ state, as may be seen from Table 2. The electron affinities for these Feshbach resonances appear to be surprisingly small in relation to the sizable dipole moment of their $^3A''$ parent state.

E. $H_3SiSiCN$ and $H_3SiSiCN^-$. Substituting the hydrogen atom in HSiCN by an SiH_3 group leads to silycyanosilylene. The X^1A' ground state of $H_3SiSiCN$ exhibits a high structural similarity with the ground state of HSiCN. The only differences are that Φ is some 2° smaller and Ω is approximately 2° larger than the correponding bond angles in HSiCN. Interestingly, even the dipole moments are highly comparable, i.e., 3.184 D vs 3.186 D, which means they are virtually identical.

The singlet−triplet splitting amounts to only 0.780 eV, which is the smallest calculated ΔE_{ST} value of all the investigated cyanosilylenes. This finding corroborates the previously found trend that a silyl substituent decreases the singlet triplet gap in silylene.[8] In conformity with all the above-mentioned triplet states of HSiCN, FSiCN, ClSiCN, and H_3SiCN, $H_3SiSiCN$ also has a much larger dipole moment of 4.07 D in its $^3A''$ triplet excited state than in its singlet ground state.

We compute an adiabatic electron affinity of 2.235 eV for $H_3SiSiCN$, which is 0.4 eV larger than the EA value of HSiCN. More than a decade ago, Kalcher and Sax[8] found that a silyl group has a positive impact on the silylene electron affinity, which has been reconfirmed quite recently by Larkin et al.[15]

Because of the previous findings that $Si(SiH_3)_2^{-8}$ as well as $HCCN^{-22}$ possess valence-type bound excited negative ion states, we suspected that this might also be the case for H_3SiCN^-. Therefore, we started a search for a valence-bound excited anion state, but we did not succeed. The only excited negative ion state of which we could ascertain the existence is the $^2A'$ dipole-bound state. This corresponds to attaching the extra electron to the dipole field of the $^1A'$ ground state of the molecule. The extra electron resides over the silyl group, since the Si atom of the SiH_3 group is strongly positively charged, albeit the negative charges on the hydrogen atoms partially shield this attraction. This is the reason the electron binding energy is no larger than 11.8 meV. Despite the fact that the dipole moment is virtually the same as that in HSiCN, the dipole-bound state of $HSiCN^-$ has an electron binding energy twice as large.

It is interesting to note that such dipole-bound electrons respond to many molecular contingencies and acquire a high degree of individuality, where one would expect great uniformity.

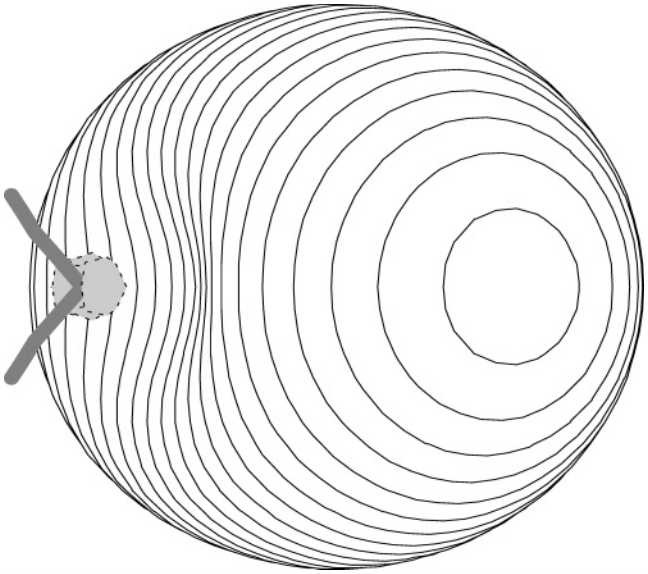

Figure 3. Contour surface with a value of 0.001 for the SOMO in the $^2A_1$ dipole-bound anion state of $Si(CN)_2^-$.

The $^3A''$ state of $H_3SiSiCN$ has a dipole moment of 4.074 D and gives rise to two dipole-bound Feshbach resonances $^4A''$ and $^2A''$ with $^4EA_{FR} = 21.7$ meV and $^2EA_{FR} = 68.1$ meV, respectively.

F. $Si(CN)_2$ and $Si(CN)_2^-$. The X^1A_1 ground state of $Si(CN)_2$ has an Si−C bond distance of 1.818 Å, which is the shortest of all the investigated cyanosilylene bond lengths. The angle Φ is obtained as 94.1°, which does not support unusually narrow bond angles as advocated by Shogo and Satoshi,[65] according to their MP2 and MP4 investigations.

The adiabatic energy separation between the singlet ground state and the triplet excited state, ΔE_{ST}, amounts to 1.387 eV. It is noteworthy that $^3B_1$ $Si(CN)_2$ represents the only triplet state, which has a dipole moment smaller than its pertaining singlet ground state.

We calculate an EA value of 2.631 eV for $Si(CN)_2$, to give the X^2A'' ground state of $Si(CN)_2^-$, which represents the largest electron affinity within the whole investigated cyanosilylene series. This is in full compliance with the homologous dicyanocarbene, which also exhibits the largest electron affinity of all the homologous carbenes.[22]

Akin to all the other cyanosilylene anions, the dicyanosilylene anion does not yield a valence-bound excited negative ion state either. There exists only a $^2A_1$ dipole-bound negative ion state with an electron binding energy of 28.1 meV. This binding energy is larger than in the corresponding dipole-bound negative ion state of $HSiCN^-$, where the dipole moment of the neutral parent is comparable to that of $Si(CN)_2$, and even larger than in the dipole-bound anion state of H_3CSiCN^-, where the dipole moment of the neutral parent is in strong excess of that of $Si(CN)_2$. An isocontour surface for the SOMO of this dipole-bound negative ion state is displayed in Figure 3.

The existence of Feshbach resonances due to the dipole moment of more than 3 D of the $^3B_1$ state is not a surprise. It is really surprising, however, that the enormously large electron binding energy in the $^2A''$ negative ion state, $^2EA_{FR}$, is 105.7 meV, while the electron binding energy for the $^4A''$ negative ion state is 28.1 meV and, thus, significantly larger than expected, but in principle comparable to the other $^4EA_{FR}$ values.

G. Additive Electron Affinity Increment System. If we adopting the experimental EA value of 1.12 eV for silylene,[10] it is possible to propose an additive increment system of the substituents on the ground-state electron affinities of the cyanosilylenes. The increment values for the substituents are listed in Table 4. These increment values are highly transferable and are in conformity with those obtained by Larkin et al.,[15] who have studied $SiXY^-$ systems with (X, Y = F, Cl, CH_3, SiH_3), but did not provide increment values. It is, however, possible to reproduce their calculated electron affinities *cum grano salis* by just employing our appropriate EA increments. It can be recognized that the fluorine atom and the methyl substituent have an almost equal attenuation effect on the electron affinity by −0.33 and −0.34 eV, respectively. The CN group enhances the electron affinity by 0.71 eV, and the silyl group still provides an EA boost of 0.40 eV.

TABLE 4: Additive Electron Affinity Increments ΔEA_{inc} for the Presently Investigated Substituents

substituent	ΔEA_{inc} (eV)
F	−0.33
Cl	+0.07
H_3C	−0.34
H_3Si	+0.40
CN	+0.71

H. Survey of Excited Negative Ion States. Unlike in the cyanocarbene anions, there are no valence-bound excited negative ion states in the cyanosilylene systems. Instead, the lowest excited negative ion states are of dipole-bound character. In conformity with the dipole moments of 2.7−3.7 D of their neutral ground-state parent states, these excited negative ion states belong to the totally symmetric irreducible representations, A′ and A_1, in the present cases. Interestingly, the corresponding electron affinities, EA_d, are rather uniform, 23.6, 21.9, 22.7, and 22.8 meV for HSiCN, FSiCN, ClSiCN, and $Si(CN)_2$, respectively, despite the differences in their ground-state dipole moments. The only exception is $H_3SiSiCN$, which exhibits an EA_d value of only 11.8 meV, although the dipole moment is almost as large as in HSiCN. We attribute this to the fact that the dipole-bound electron is efficiently shielded by the negatively charged hydrogen atoms from the strongly positively charged silicon atom of the silyl group. Therefore, we observe a “side-on” instead of the “head-on” binding, as in H_3CSiCN^-, where the hydrogen atoms are positively charged, since in this arrangement, the shielding effect can be outweighed most efficiently.

According to the fact that the triplet excited states of the investigated cyanosilylenes exhibit dipole moments in excess of the corresponding singlet ground states, similar to CNa and SiNa,[33] each excited state is “dressed” by dipole-bound Feshbach resonances. Moreover, we have shown that both conceivable states with doublet and quartet multiplicity do exist.

Interestingly, the doublet states have quite notable electron binding energies, all of them larger than 65 meV, and even 105 meV for $Si(CN)_2^-$, except for HSiCN and $H_3SiSiCN$, which have electron affinities of only 38.2 and 57.1 meV. The electron affinities of the quartet Feshbach resonances turn out to be considerably smaller, and they are in good agreement with the electron affinities of the corresponding lowest-lying dipole-bound states.

Previous studies on dipole-bound negative ion states of CNa^- and $SiNa^-$ showed[33] that the energetic splitting between neighboring states with different spin multiplicity amounts to some 20 cm^{-1}. Perusing the data in Table 2 makes clear that this does not hold for the double quartet splittings of the cyanosilylene anions. The value of 14.4 meV for $HSiCN^-$ can be considered abnormally low within the cyanosilylene series.

The other values are 52.2, 45.8, 33.7, 46.7, and 77.6 meV for $FSiCN^-$, $ClSiCN^-$, $H_3SiSiCN^-$, and $Si(CN)_2{}^-$, respectively.

IV. Conclusions

All cyanosilylenes have a singlet ground state. All cyanosilylenes have larger singlet−triplet splittings than SiH_2, except $H_3SiSiCN$. The ground-state electron affinities can be understood within a substituent additive incremental scheme to SiH_2, where SiH_3 and especially CN represent EA-increasing substituents and F and CH_3 represent EA-decreasing substituents. Cl acts almost neutral with a slight bias toward an increase. All cyanosilylenes have electron affinities in excess of SiH_2. The largest EA value of 2.63 eV is found for $Si(CN)_2$. The electron affinities of all XSiCN systems are smaller than those of the comparable XCCN carbene species, except for X = H, where the electron affinities are of a comparable size. In contrast to these carbene species, none of the investigated cyanosilylenes possesses a valence-bound excited negative ion state. All excited negative ion states can be characterized as dipole-bound states.

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