The Microwave Spectrum of Silylisothiocyanate, SiH_3NCS
III. The Rotational Zeeman Effect

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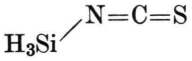
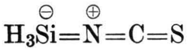
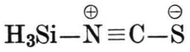
The rotational Zeeman effect has been investigated for four different isotopic species of SiH_3NCS. From the observed g-values we have determined the sign of the electric dipole-moment in SiH_3NCS to be $^{\oplus}H_3SiNCS^{\ominus}$. Thus the previous choice of sign which had been based on the results of a quantum chemical CNDO/2 calculation had to be revised. For the master isotope $g_{\perp}$, $g_{\|}$ and $(\chi_{\perp}-\chi_{\|})$ have been determined and were used to calculate the molecular electric quadrupole moment, the paramagnetic and diamagnetic susceptibilities and the second moments of the electronic charge distribution.

Introduction

In our previous papers on the microwave spectrum of SiH_3NCS we have discussed the low frequency bending mode, the r_s-structure, dipolemoment and the ^{14}N-quadrupole coupling constant of this molecule [1, 2]. The experimental information on this symmetric top molecule indicated a strong contribution of the mesomer forms (II) and (III) to the electronic ground state,


(I)


$H_3\overset{\ominus}{Si}=\overset{\oplus}{N}=C=S$ (II)


$H_3Si-\overset{\oplus}{N}\equiv C-\overset{\ominus}{S}$ (III)

but it remained impossible to decide on the direction of the electric dipolemoment (Si positive or negative). To settle this problem we undertook an investigation of the rotational Zeeman effect of four different isotopic species of SiH_3NCS. To improve the precision of our analysis and to demonstrate the quality of r_s-structure determinations we further reinvestigated the rotational spectra of three isotopic species of SiH_3NCS.

Experimental

The preparation of the samples has been described previously [1, 2]. The spectra were recorded with a conventional 33 kHz square wave Stark effect modulated microwave spectrometer equipped with an electromagnet. Details of the design of the Zeeman-microwave-spectrometer may be found elsewhere [3]. To improve the S/N ratio especially for the rare isotopes $^{28}SiH_3{}^{14}N^{12}C^{34}S$ and $^{30}SiD_3{}^{14}N^{12}C^{32}S$, which where observed in natural abundance ($\sim 4\%$), we used signal averaging [4].

r_s-Structure

The pure rotational spectra of $D_3{}^{28}Si^{14}N^{12}C^{32}S$, $D_3{}^{28}Si^{14}N^{12}C^{34}S$ and $D_3{}^{30}Si^{14}N^{12}C^{32}S$ are given in Table 1. The observed frequencies were fitted to the frequency formula [5]:

$$\nu_{J,K\to J+1,K} = 2B(J+1) - 4D_J(J+1)^3 - 2D_{JK}(J+1)K^2. \tag{1}$$

A complete list of rotational- and centrifugal distortion-constants for all isotopic species of SiH_3NCS, which have been investigated is given in Table 2.

The r_s-bond distances [6, 7], which were calculated from the rotational constants of Table 2, show a high consistency for different combinations of isotopes. The difference e.g. between the Si ... S distance determined for SiH_3NCS: $r(Si \ldots S) = 4.4678$ Å and the one determined for SiD_3NCS: $r(Si \ldots S) = 4.4683$ Å is only 0.0005 Å. It is found however, that the hydrogen coordinates are changed by deuterium substitution. If we calculate the z-coordinate of the hydrogen atoms relative to the centre of mass of the master isotope $H_3{}^{28}Si^{14}N^{12}C^{32}S$ for the different isotopic combinations, we obtain the following values (in Å units):

a) from $SiH_3 \to SiH_2D$: 2.7097 ± 0.0011,
b) from $SiH_3 \to SiD_3$: 2.7075 ± 0.0002,
c) from $SiHD_2 \to SiD_3$: 2.7041 ± 0.0016.

Reprint requests to Prof. Dr. D. Sutter, Institut für Physikalische Chemie der Universität Kiel, Abt. Chemische Physik, Olshausenstraße 40–60, D-2300 Kiel. Please order a reprint rather than making your own copy.

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Table 1. Microwave spectra of three isotopic species of silylisothiocyanate (in MHz). The observed frequencies are compared to the values calculated from the molecular constants listed in Table 2 according to Equation (1).

D_3SiNCS

$J \rightarrow J'$	$9 \rightarrow 10$		$10 \rightarrow 11$		$11 \rightarrow 12$	
K	obs	obs-calc	obs	obs-calc	obs	obs-calc
0	28248.63	0.03	31073.41	0.01	33898.17	−0.01
1	28247.95	0.03	31072.65	0.00	33897.35	−0.01
2	28245.89	0.03	31070.39	0.01	33894.89	0.00
3	28242.44	0.01	31066.63	0.01	33890.79	0.01
4	28237.64	0.00	31061.34	0.00	33885.01	−0.01
5	28231.47	−0.00	31054.54	−0.01	33877.63	0.01
6	28223.91	−0.02	31046.25	−0.01	33868.56	−0.02
7	28215.01	−0.01	31036.44	−0.03	33857.87	−0.01
8	28204.70	−0.04	31025.11	−0.04	33845.52	−0.03
9	28193.07	−0.01	31012.33	0.00	33831.57	0.00
10	—	—	30998.03	0.01	33815.96	0.02
11	—	—	—	—	33798.75	0.07

$D_3{}^{30}SiNCS$

$J \rightarrow J'$	$9 \rightarrow 10$		$10 \rightarrow 11$		$11 \rightarrow 12$	
K	obs	obs-calc	obs	obs-calc	obs	obs-calc
0	27546.50	0.00	30301.08	0.00	33055.63	0.00
1	27545.85	0.00	30300.36	0.00	33054.86	0.01
2	27543.91	0.00	30298.21	−0.01	33052.50	−0.02
3	27540.67	0.00	30294.66	0.00	33048.62	−0.01
4	27536.16	0.02	30289.69	0.02	33043.18	0.00
5	27530.28	−0.02	30283.24	−0.02	33036.20	0.01
6	27523.18	0.00	30275.43	0.01	33027.64	0.00

$D_3SiNC^{34}S$

$J \rightarrow J'$	$9 \rightarrow 10$		$10 \rightarrow 11$	
K	obs	obs-calc	obs	obs-calc
0	27450.26	−0.01	30195.20	0.00
1	27449.65	0.02	—	—
2	27447.69	−0.01	—	—

Table 2. Rotational constants and centrifugal distortion constants of eleven isotopic species of SiH_3NCS. Except for the two partially deuterated compounds [16] all spectra have been reported in this series [1], [2]. Because D_J was not determined in Ref. [16] we have assumed a value of $D_J = 0.08$ kHz for the last two isotops.

Species	B_0/MHz	D_{JK}/kHz	D_J/kHz
(1) $H_3{}^{28}Si^{14}N^{12}C^{32}S$	1516.040 (1)	41.958 (6)	0.087 (4)
(2) $H_3{}^{29}Si^{14}N^{12}C^{32}S$	1493.640 (1)	40.50 (2)	0.089 (4)
(3) $H_3{}^{30}Si^{14}N^{12}C^{32}S$	1472.411 (3)	39.26 (3)	0.088 (9)
(4) $H_3{}^{28}Si^{15}N^{12}C^{32}S$	1514.552 (1)	42.30 (1)	0.086 (6)
(5) $H_3{}^{28}Si^{14}N^{13}C^{32}S$	1514.169 (1)	41.76 (1)	0.074 (6)
(6) $H_3{}^{28}Si^{14}N^{12}C^{34}S$	1473.556 (2)	40.01 (3)	0.089 (6)
(7) $D_3{}^{28}Si^{14}N^{12}C^{32}S$	1412.443 (1)	34.264 (5)	0.066 (5)
(8) $D_3{}^{30}Si^{14}N^{12}C^{32}S$	1377.342 (1)	32.39 (1)	0.083 (3)
(9) $D_3{}^{28}Si^{14}N^{12}C^{34}S$	1372.529	32.1	0.076
	B_0/MHz	C_0/MHz	D_{JK}/kHz
(10) $H_2D^{28}Si^{14}N^{12}C^{32}S$	1483.336 (25)	1474.854 (25)	40.5 (1)
(11) $HD_2{}^{28}Si^{14}N^{12}C^{32}S$	1448.957 (33)	1440.293 (33)	37.0 (1)

It is obvious, that the z-coordinate r_z decreases, as the number of deuterium bonds N in the isotopic combination used increases ($N = 1$ for a), $N = 3$ for b), and $N = 5$ for c)). Under the assumption of a linear dependence of r_z on N, we have calculated the z-coordinates of the hydrogen- and deuterium-atoms in the limiting cases of the SiH_3-group ($N = 0$) and the SiD_3-group ($N = 6$). This leads to slightly different effective bond distances and bond angles within the SiH_3- and SiD_3-groups (see Figure 1). The experimental uncertainties in the r_s-coordinates are $2 \cdot 10^{-4}$ Å for the heavy atoms and $1 \cdot 10^{-3}$ Å for the hydrogen atoms.

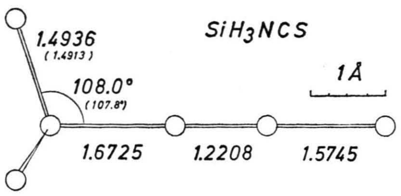

Fig. 1. r_s-structure of silylisothiocyanate, H_3SiNCS. The structural data for the deuterated compound D_3SiNCS only differ in the region of the silyl-group. The values for the D_3Si-group are given in bracketts. Since vibrational effects largely cancell in the equations used for the r_s-structure determination, differences between r_s- and r_e-values are believed to be smaller than $1 \cdot 10^{-3}$ Å.

Zeeman Effect

To analyze the rotational Zeeman effect we used the following Hamiltonian [8]:

$$\mathcal{H}_{\text{eff}} = \mathcal{H}_{\text{rot}} + \mathcal{H}_Q + \mathcal{H}_g^{\text{mol}} + \mathcal{H}_g^{\text{nucl}} + \mathcal{H}_\chi + \mathcal{H}_{\text{TS}}, \tag{2}$$

where the appropriate matrix elements in the uncoupled basis $|J, K, M_J, I, M_I\rangle$ are given in [8].

Because the splitting of the $J \to J+1$, $K=0$ transitions in the magnetic field is independent of J (at least in the rigid rotor limit), we used high J transitions between 26.5 and 38 GHz to determine $g_\perp$ (see Table 3). $g_\parallel$ and $(\chi_\perp - \chi_\parallel)$ of the master isotope $^{28}SiH_3{}^{14}N^{12}C^{32}S$ were obtained from an investigation of the $J \to J' = 3 \to 4$, $K=3$ transition at 12 GHz. The analysis of these splittings is

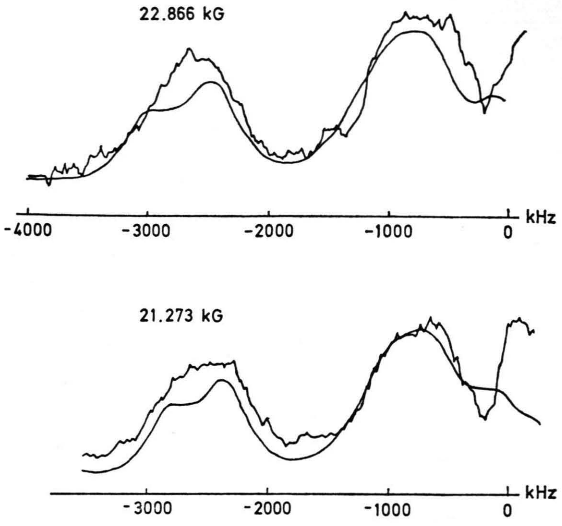

Fig. 2. Comparison between the experimental and calculated line profiles for the $J \to J' = 3 \to 4$, $K=3$ rotational transition and magnetic fields of 21.273 and 22.866 kG under the selection rule $\Delta M = \pm 1$. Because the $J \to J' = 3 \to 4$, $K = 2, 1, 0$ transitions are located only 1600, 2560 and 2880 kHz above the $K=3$ transition, they interfere with the upper part of the $K=3$ Zeeman pattern and only the low frequency half of the pattern is therefore given in the figure. The origin of the frequency scale is located at the position of the theoretical centre frequency $\nu^c = 8B - 256D_J - 72D_{JK} = 12125.277$ MHz of the $K=3$ transition. For the calculated line profile we used the value of the ^{14}N quadrupole coupling constant $eqQ = +0.75$ MHz [2], the electric dipole moment of $|\mu_{el}| = 2.38$ D, a cell temperature of -60 °C, a halfintensity halflinewidth of 60 KHz and the Zeeman parameters of Table 4.

Table 3. Zeeman splittings of the $J \to J+1$, $K=0$ rotational transitions of four different isotopic species of SiH_3NCS (in kHz) under the selection rule $\Delta M = \pm 1$. In the rigid rotor limit the observed doublett splittings are independent of J. The effect of the susceptibility anisotropy $\Delta\chi$ on the different $M_J \to M_J \pm 1$ components within the two Zeeman components of each transition can be neglected for the high J-transitions used here, and only the $g_\perp$-values were fitted to these splittings.

$J \to J'$	$8 \to 9$		$9 \to 10$		$10 \to 11$		$11 \to 12$	
	obs	obs-calc	obs	obs-calc	obs	obs-calc	obs	obs-calc
$H_3{}^{28}Si^{14}N^{12}C^{34}S$								
21.273 kG	454	−17	486	15	468	− 3	—	—
22.866 kG	506	0	514	8	506	0	—	—
$H_3{}^{28}Si^{14}N^{12}C^{32}S$								
21.273 kG	487	− 6	503	10	486	− 7	—	—
22.866 kG	532	2	543	13	520	−10	—	—
$D_3{}^{28}Si^{14}N^{12}C^{32}S$								
21.273 kG	—	—	481	12	450	−19	471	2
22.866 kG	—	—	514	10	498	− 6	502	− 2
$D_3{}^{30}Si^{14}N^{12}C^{32}S$								
21.273 kG	—	—	480	20	450	−10	459	− 1
22.866 kG	—	—	528	33	479	−16	467	−18

strongly impeded by a) the presence of a non-negligible ^{14}N-quadrupole coupling, b) the interference from nearby $K = 2, 1, 0$ lines and c) the mixing of different M_J-substates by the translational Stark-effect [9], which causes a smearing of the lines.

The resulting molecular Zeeman parameters are listed in Table 4. In Table 5 we present a listing of molecular quantities which may be derived from the Zeeman data given in Table 4, from the molecular structure, and from the bulk susceptibility, for which an approximate value was calculated from Pascals constants [17]. We note that — as expected — the paramagnetic susceptibilities $\chi_{\parallel}^{p}$ of SiH_3NCS and SiH_3Br turn out almost the same. Since they originate from those parts of the molecule where the electron configuration lacks cylindrical symmetry [10] they are largely determined by the structure of the silyl-group.

Table 4. Molecular Zeeman parameters of the master isotope $H_3{}^{28}Si^{14}N^{12}C^{32}S$. $g_{\perp}$ was calculated from the splittings listed in Table 3. $g_{\parallel}$ and $(\chi_{\perp} - \chi_{\parallel})$ were determined by comparing observed and calculated line profiles for the $J \to J' = 3 \to 4$, $K = 3$ transition (see Fig. 2 and 3). For comparison we also give the Zeeman parameters of silylbromide [8].

	SiH_3NCS	SiH_3Br
$g_{\perp}$	−0.01521 (10)	−0.02185 (13)
$g_{\parallel}$	−0.315 (5)	−0.3185 (5)
$\dfrac{\chi_{\perp} - g_{\parallel}}{10^{-6}\,\mathrm{erg/(G^2 mol)}}$	28.0 (30)	2.7 (3)

Sign of the Electric Dipole Moment

The rotational g-values, when measured for two or more isotopic species of a molecule, can be used to calculate the direction and approximate magnitude of the electric dipole moment. For a substitution, which shifts the centre of mass along the symmetry axis z by Δz, so as to change all coordi-

Table 5. Molecular quantities derived from the experimental data given in Table 4. The values for SiH_3Br are taken from [8]. The bulk magnetic susceptibilities are calculated from the Pascal constants [17], with an assumed uncertainty of ± 10% for SiH_3Br and — because of the exceptional bonding situation — ± 20% for SiH_3NCS. The A-rotational constant has been calculated from the r_s-structure.

		SiH_3NCS	SiH_3Br
Molecular quadrupole moments in units of 10^{-26} esu cm^2			
$Q_{\parallel} = \frac{\lvert e\rvert}{2}\left\{\sum_{\varepsilon}^{\text{nuclei}} Z_n(2z_n^2 - x_n^2 - y_n^2) - \langle 0\rvert \sum_{n}^{\text{electrons}} (2z_\varepsilon^2 - x_\varepsilon^2 - y_\varepsilon^2)\lvert 0\rangle\right\}$ $= -\frac{\hbar\lvert e\rvert}{4\pi M_P}\left\{\frac{g_{\parallel}}{A} - \frac{g_{\perp}}{B}\right\} - \frac{4mc^2}{\lvert e\rvert}\{\chi_{\parallel} - \chi_{\perp}\}$	$Q_{\parallel}$	16.6 ± 3.7	−0.1 ± 0.4
Second moments of the nuclear charge distribution calculated from	$\sum_n Z_n z_n^2$	179.5 ± 0.2	61.5 ± 0.1
the geometry of the nuclear frame. The units are Å^2.	$\sum_n Z_n x_n^2$	3.018 ± 0.004	2.983 ± 0.004
Paramagnetic susceptibilities in units of 10^{-6} erg/(G^2 mol)			
$\chi_{\parallel}^{p} = -\frac{N_L e^2}{2m^2c^2}\sum_{\nu}^{\text{ex. states}}\frac{\lvert\langle 0\rvert L_z\lvert\nu\rangle\rvert^2}{E_0 - E_\nu}$	$\chi_{\parallel}^{p}$	33.61 ± 0.16	33.39 ± 0.05
$= -\frac{N_L e^2}{4mc^2}\left\{\frac{\hbar}{4\pi M_P}\frac{g_{\parallel}}{A} - \sum_{n}^{\text{nuclei}} Z_n(x_n^2 + y_n^2)\right\}$	$\chi_{\perp}^{p}$	796.1 ± 0.8	284.7 ± 0.5
Diamagnetic susceptibilities in units of 10^{-6} erg/(G^2 mol)			
$\chi_{\parallel}^{d} = -\frac{N_L e^2}{4mc^2}\langle 0\rvert \sum_{\varepsilon}^{\text{electrons}} x_\varepsilon^2 + y_\varepsilon^2\lvert 0\rangle$	$\chi_{\parallel}^{d}$	−92.5 ± 10.2	−87.6 ± 5.4
$= \chi_{\parallel} - \chi_{\parallel}^{p}$	$\chi_{\perp}^{d}$	−826.9 ± 9.9	−336.2 ± 5.8
Bulk susceptibility in units of 10^{-6} erg/(G^2 mol) $\chi = (\chi_{\parallel} + 2\chi_{\perp})/3$	χ	−40.2 ± 8.0	−52.4 ± 5.2
Second moments of the electronic charge distribution in Å^2			
$\langle 0\rvert \sum_{\varepsilon}^{\text{electrons}} z_\varepsilon^2\lvert 0\rangle = -\frac{2mc^2}{e^2}(2\chi_{\perp} - \chi_{\parallel})$	$\langle 0\rvert \sum_\varepsilon z_\varepsilon^2\lvert 0\rangle$	184.0 ± 3.7	68.9 ± 2.0
$-\frac{\hbar}{8\pi M}\left(\frac{2g_{\perp}}{B} - \frac{g_{\parallel}}{A}\right) + \sum_{n}^{\text{nuclei}} Z_n z_n^2$	$\langle 0\rvert \sum_\varepsilon x_\varepsilon^2\lvert 0\rangle$	10.9 ± 3.7	10.3 ± 2.0

nates $z_k' = z_k - \Delta z$, and which changes $I_\perp$ and $g_\perp$ to $I_\perp'$ and $g_\perp'$ we have [8]:

$$g_\perp' I_\perp' - g_\perp I_\perp = -\frac{2 M_p}{|e|} \Delta z \, \mu_{el} \,. \tag{3}$$

We measured the $g_\perp$-values for four isotopic species of SiH_3NCS and obtained the following results:

Isotope No.		$g_\perp$	$g_\perp I_\perp$/ amu Å^2
(1)	$H_3{}^{28}Si^{14}N^{12}C^{34}S$	$-0.01453(15)$	-4.983
(2)	$H_3{}^{28}Si^{14}N^{12}C^{32}S$	$-0.01521(10)$	-5.070
(3)	$D_3{}^{28}Si^{14}N^{12}C^{32}S$	$-0.01445(15)$	-5.170
(4)	$D_3{}^{30}Si^{14}N^{12}C^{32}S$	$-0.01419(25)$	-5.207

Combination	$(g_\perp' I_\perp' - g_\perp I_\perp)$/[amuÅ^2]	Δz/Å	$\mu_{el} = \sum_i q_i r_i$/D
(3)−(1)	-0.187 ± 0.102	-0.1376	-3.24 ± 1.77
(4)−(1)	-0.224 ± 0.142	-0.1868	-2.86 ± 1.81
(3)−(2)	-0.100 ± 0.085	-0.0887	-2.69 ± 2.28
(4)−(2)	-0.137 ± 0.125	-0.1379	-2.37 ± 2.16
Weighted average:			$\bar{\mu}_{el}/D = -2.85 \pm 0.99$

The results show unequivocally, that the silicon atom is situated at the positive end and that the sulfur atom is situated at the negative end of the molecular dipole:

$$^{\oplus}H_3Si-N-C-S^{\ominus} \,.$$

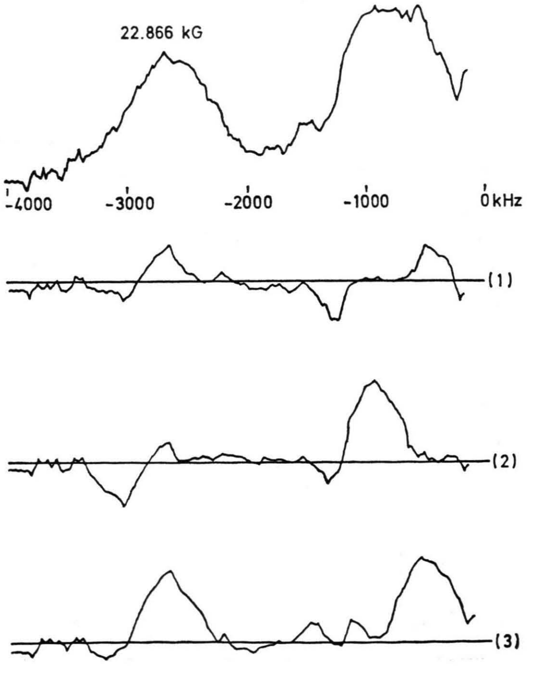

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Fig. 3. Comparison of the observed $J \rightarrow J' = 3 \rightarrow 4$, $K = 3$, $M_J \rightarrow M_J \pm 1$ transition at 22.866 kG with calculated Zeeman patterns (observed minus calculated). To demonstrate the accuracy of the analysis shown in Fig. 2, we have successively varied $g_{\|}$ and $\Delta\chi$ by two standard deviations and plotted the difference between observed and calculated intensities. The best values for $g_{\|}$ and $\Delta\chi$ ($g_{\|} = -0.315$ and $\Delta\chi = 28.0$) which were obtained in a fit to the observed spectra shown in Fig. 2, were used in the first calculation (1). For the second calculation (2) we have varied $\Delta\chi$ ($g_{\|} = -0.315$, $\Delta\chi = 22.0$) and for the third one (3) we have varied $g_{\|}$ ($g_{\|} = -0.325$, $\Delta\chi = 28.0$).

The absolute value of $|\mu_{el}| = 2.8 \pm 1.8$ D determined here is in agreement with the value of $|\mu_{el}| = 2.38 \pm 0.02$ D determined from the molecular Stark effect [2]. The result indicates, that in a simplified picture the electronic ground state of SiH_3NCS may be described by a 65% to 35% mixture of the mesomer forms (II) and (III) [2], which is in good agreement with the observed bond distance of the Si-N bond [2].

Discussion

The result of the experimental determination of the direction of the electric dipole moment (Si at positive end) came as a surprise to us, since an earlier semiempirical quantum chemical calculation with Poples CNDO/2 program [11, 2] had given the opposite sign. The CNDO/2 value for the dipole moment is +0.8 D (Si at negative end) and includes a +3.2 D contribution from p-d orbital overlap in the region of the Si-N bond. Apparently the CNDO/2 program overestimates this effect by far and the question may be raised whether at all the silicon 3d orbitals are involved to a significant extent in the electron configuration of SiH_3NCS. The doubts as to the significance of the Si-3d orbitals for the bonding may be further aggrevated by the results of a quantum chemical STO-3G calculation on SiH_3NCS carried out at the University of Bielefeld by Engelbrecht and Schöller [12]. The STO-3G program which does not explicitly include 3d-type orbitals at the silicon atom not only did predict the stability of the linear arrangement of the SiNCS chain, but also calculated the electric dipole moment as $\mu_{STO\text{-}3G} = -3.5$ D (Si at positive end), i.e. it predicted the correct sign of the dipole moment, although the calculated value is about 1.1 D off the experimental value determined from the Stark effect. However, we doubt, that the results of the STO-3G program may be used to entirely discard the idea of $p\pi$-$d\pi$ bonding in SiH_3NCS, since the same program gave comparatively poor results when applied to disilylether, an other molecule in which $p\pi$-$d\pi$ bonding is thought to be important [13, 14]. In $H_3Si-O-SiH_3$ the Si—O—Si bond angle calculated with the STO-3G program turns out much smaller than the observed value ($\sphericalangle \mathrm{SiOSi}_{\mathrm{STO-3G}} = 124.2°$ [12] as compared to $\sphericalangle \mathrm{SiOSi}_{\mathrm{exp}} = 145°$ [14]) and the potential barrier for the Si—O—Si bending vibration at the linear configuration is calculated much too high ($V_{\mathrm{STO-3G}} = 3.5 \cdot 10^3\ \mathrm{cm}^{-1}$ [12] versus $V_{\mathrm{exp}} = 0.112 \cdot 10^3\ \mathrm{cm}^{-1}$ [15]). In view of the comparatively short Si-N bond distance [2] we therefore still believe, that inclusion of Si-3d type orbitals will be necessary, if one wants to describe the bonding in SiH_3NCS correctly. Certainly silylisothiocyanate should be an interesting candidate for a refined ab initio quantum chemical calculation.

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