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NaSCN: Striking Differences between Its Gas-Phase and Crystal-Phase Structure: A Theoretical Study

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A detailed investigation of the gas-phase and crystal-phase structure of sodium thiocyanate has been presented. Using highly sophisticated ab initio calculations (MP2, QCISD, CCSD(T), CBS-Q), the existence of the four-membered ring monomer has been predicted. Three minima have been found on the PES of the NaSCN dimers using HF, B3LYP, and MP2 methods, and two of these have been identified as the main building blocks of the NaSCN crystal. The systematic enlargement of the clusters along the crystal axes at the HF level led to the convergence of the geometrical parameters and the interaction energy of the clusters. According to our results, the supermolecule model with one layer of molecules around the central molecule is not large enough to simulate the overall crystal structure of NaSCN, but the supermolecule model with a 17-member supermolecule (two layers of neighbors) has been successfully applied and found to be in excellent agreement with the experimental data, the principal findings, and point out major conclusions.

Introduction

Thiocyanates are important members of pseudohalides. Their applications are versatile; they cover the sequence analysis of proteins (Edman degradation),[1] semiconductor photoreceptors,[2] insecticides and fungicides.[3,4] They are used in the production of polyurethanes,[5] a wide range of copolymers and abrasion-resistant polymers,[6] solid polymer electrolytes,[7] etc. They are ubiquitously present in plants (e.g., beetroot and horseradish) and are produced in large quantities in damaged plant cells. Several known crown ether complexes contain thiocyanates. Together with the practical importance of thiocyanates, theoretical interest in them has grown, aiming at better understanding their structures.

Our work was inspired by the fundamental differences between the measured XRD structure of NaSCN and its predicted gas-phase structure. Although packing forces in the crystal may distort the gas-phase structure of molecules, such a difference is rarely conspicuous. Thiocyanate groups are almost always linear in their compounds due to the strong electron delocalization over the three atoms of the group. The crystal structure of several thiocyanates was already determined at the early stages of X-ray crystallography due to their simple structure: a ball-like cation and a rod-shaped anion. The NaSCN crystal belongs to the *Pnma* space group according to the X-ray[8a,b] and neutron diffraction[8b] studies. The atoms occur in the mirror planes at $y/b = (1/4), (3/4)$. The SCN ions are linear within the experimental error, and each Na^+ ion is surrounded by three S and three N atoms as shown in Figure 1.

Gas-phase ED and MW studies of some covalent pseudohalides are also well-known.[9] Although there has been much discussion about the bonding angle of the substituent to the pseudohalide group,[10] all of these studies indicated a linear structure for the pseudohalide unit in the gas phase.

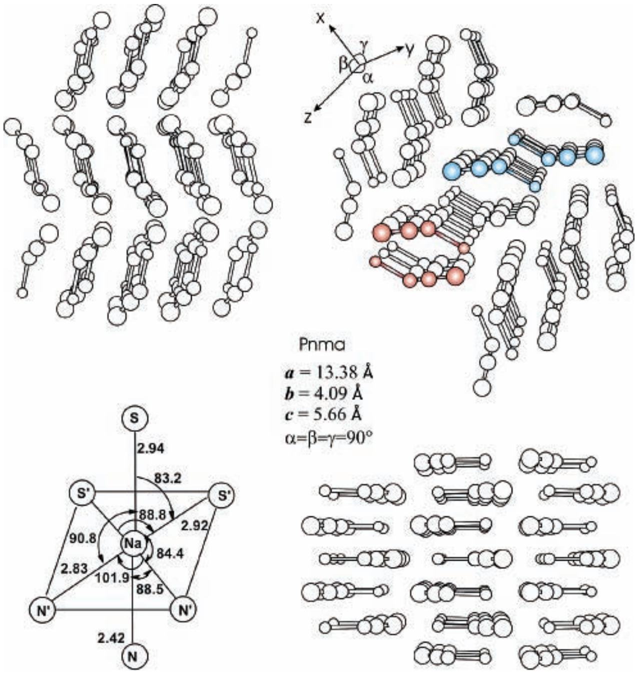

Figure 1. Measured X-ray structure [ref 8a] of NaSCN from three different angles and the coordination of the Na atoms.

We know much less about the gas-phase structure of ionic thiocyanates, as in many cases it is difficult to evaporate them in appreciable amounts. In this case, quantum chemistry is the appropriate tool to obtain reliable information on the possible conformers in the gas phase. In 1994, a new cyclic isomer was discovered using high-level quantum chemical calculations.[11] In this isomer, the metal ion is positioned between the two ends of the thiocyanate anion and the anion is bent with an NCS

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angle around 165°. The structure of these π-complexes was explained by the overlap between the empty p-orbital of the substituent atom and the pseudohalide π-system. The larger the overlap, the more stable the π-complex compared to the linear pseudohalide conformations. It was observed that the cyclic isomer was the global minimum on the potential energy surface of several ionic pseudohalides such as LiNCS and NaNCS.[11] Further calculations on other pseudohalides led to the discovery of other π-complexes such as alkali-OCPs[12] and metal thionyl imides.[13]

So far, no studies have been published on the aggregates of NaSCN molecules. Our aim was to identify the most important interactions, which lead to the breakup of the four-membered ring structure and form the linear SCN ions, and to investigate how the crystal is built up from the individual NaSCN molecules.

Computational Strategy and Procedure

To check the reliability of methods used and the previous results,[11] several calculations have been performed for the NaSCN monomer at the HF, B3LYP, MP2, QCISD, CCSD(T), and the CBS-Q levels of theory using 6-31+G(d) and 6-311+G(2df) basis sets with the Gaussian 98[14] and Aces II[15] program packages. As the results proved that even moderate levels are appropriate for the description of the correct structure, the dimer structures were optimized only at the HF and B3LYP levels of theory with the 6-31+G(d) basis set. The inclusion of the diffuse functions in the basis set is thought to be important when long-range Coulomb interactions must be taken into account. In the calculation of interaction energy the basis set superposition error (BSSE) was estimated by the standard counterpoise method.[16] Harmonic frequency calculations were performed on all the optimized monomer and dimer structures in order to ensure that they are real minima on the potential energy surface.

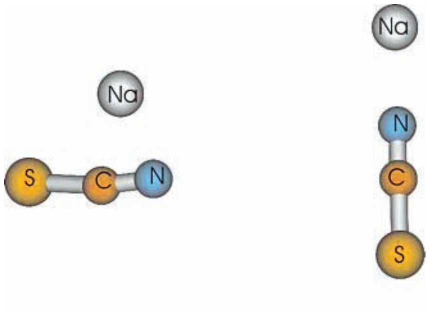
To simulate the crystal structure, two independent strategies were followed. First, aggregates up to seven molecules were considered along the crystal axes. These aggregates were fully optimized at the HF/6-31+G(d) level of theory with the Gaussian 98 program package.[14] The interaction energy, ΔE_{int}, was calculated as the energy difference of the following reaction:

$$n(\mathrm{NaSCN}) \rightarrow (\mathrm{NaSCN})_n \tag{1}$$

Since the interaction energy might be seriously influenced by the BSSE, an approximate method was used to estimate its value. The counterpoise correction was calculated for two molecules positioned in the center of the aggregate, and this correction has been used as the BSSE of one pair of molecules. This energy value was then multiplied by the number of pairs found in the aggregate. Using this procedure, the BSSE was found to be less than 1% of the interaction energy, thus thought to be negligible for this type of system.

Next, the point-charge (PC) and the supermolecule (SM) models were employed. The structure of the NaSCN crystal was completely optimized using the ab initio MIA method for the SCF calculation.[17] These calculations were performed with the BRABO program package[18] with the 6-31+G(d) basis set.

In the point-charge model the central molecule is surrounded by point charges placed on the atomic positions, which are generated using the symmetry operations of the respective point group (*Pnma*) and the experimental cell parameters. As the two XRD studies resulted in essentially the same parameters, we used the ones listed in ref 8a. In our calculations we used Stockholder charges[19] as point charges. In the supermolecule model (SM model) the nearest neighbors of the central molecule are included in the wave function of the system, while the neighbors farther away are replaced by point charges. The distance between the central molecule and its neighbors is defined by the smallest distance measured between any atom of the two selected molecules. In the calculations with the SM model both the internal and external coordinates were refined. The *y*-coordinate of the center of mass was kept fixed at the experimental value because in the space group *Pnma* the origin along the *y*-axis is not defined. In each step of the optimization procedure the forces were only calculated for the atoms of the central molecule, as this is the only molecule which is completely embedded in the supermolecular wave function and is therefore within our model the best representation of a molecule in the solid state. Structures were refined until all Cartesian forces were smaller than 0.0001 mdyn. At this level of refinement, structural parameters are thought to be converged to 0.0002 Å for bond length and to 0.1° for bond angles. A more complete description of the optimization procedure can be found in ref 20.



1b **1a**

Figure 2. Minimum-energy structures of NaSCN.

Results and Discussion

Monomers. In accordance with the results of earlier calculations,[11] two stable NaSCN structures were found on the potential energy surface: the linear isothiocyanate **1a** and a four-membered ring monomer **1b** (see Figure 2). Selected geometrical parameters together with the relative energies of **1a** and **1b** calculated at different levels of theory are given in Table 1. As the calculated geometrical parameters do not change significantly with the level of theory, it suggests that the effect of electron correlation on the geometry of these compounds is small. A general trend can be observed: all the bond lengths are shortened by 0.01−0.08 Å if the 6-311+G(2df) basis set is used. The CN bond distance is almost the same in the two isomers at each level of theory, but the CS bond is much shorter in the linear isothiocyanate **1a**. This follows from the fact that in the isothiocyanate only nitrogen is connected to sodium, while in **1b** the sodium atom is in bridging position between nitrogen and sulfur.

Table 1 demonstrates that in the gas phase the most stable isomer of NaSCN is the four-membered ring monomer **1b**. This is proved by the increasing energy difference between the two conformers with increasing level of theory and with the size of the basis set. As a comparison, we calculated the energy difference with the highly sophisticated CBS-q method, and it also predicts the larger stability of **1b** compared to that of **1a** ($E_{\mathbf{1b}} - E_{\mathbf{1a}} = -1.84$ kcal/mol).

Dimers. To get comparable results to those of the calculations on higher aggregates, the calculations were performed at the HF and B3LYP levels with the 6-31+G(d) basis set and at the

TABLE 1: Total Energy (*E*, in au) and Geometrical Parameters (in Å and in deg) of the Linear Isothiocyanate (1a) and of the Four-Membered Ring Monomer (1b) at the Different Theoretical Levels with the 6-31+G(d) Basis Set (6-311+G(2df) Values in Parentheses)

	HF	B3LYP	MP2	QCISD	CCSD(T)
			Linear Isothiocyanate, **1a**		
E	−651.72636 (−651.78795)	−653.39058 (−653.45686)	−652.13942 (−652.30110)	−652.15055 (−652.30971)	−652.16892 (−652.33791)
NaN	2.133 (2.127)	2.106(2.103)	2.146(2.140)	2.143 (2.137)	2.145 (2.139)
NC	1.160 (1.152)	1.192 (1.181)	1.208 (1.197)	1.194 (1.180)	1.200 (1.189)
CS	1.638 (1.630)	1.624 (1.616)	1.616 (1.610)	1.631 (1.625)	1.630 (1.624)
			Four-Membered Ring Monomer, **1b**		
E	−651.72670 (−651.79011)	−653.38854 (−653.45697)	−652.14506 (−652.30508)	−652.15620 (−652.31319)	−652.175048 (−652.34257)
$E_{1b} - E_{1a}$[a]	−0.21 (−1.36)	1.28 (−0.07)	−3.54 (−2.50)	−3.55 (−2.19)	−3.84 (−2.92)
NaN	2.606 (2.559)	2.497 (2.470)	2.562 (2.487)	2.598 (2.521)	2.566 (2.541)
NaS	2.746 (2.749)	2.783 (2.777)	2.744 (2.807)	2.722 (2.757)	2.726 (2.770)
NC	1.151 (1.144)	1.185 (1.174)	1.205 (1.192)	1.187 (1.189)	1.193 (1.183)
CS	1.685 (1.673)	1.669 (1.659)	1.661 (1.652)	1.682 (1.678)	1.683 (1.668)
NCS	168.4 (169.0)	168.6 (169.0)	167.4 (169.4)	167.3 (164.9)	167.1 (169.1)

[a] Relative energy (in kcal/mol) of the four-membered ring monomer **1b** compared to the linear isothiocyanate **1a** ($E_{1b} - E_{1a}$).

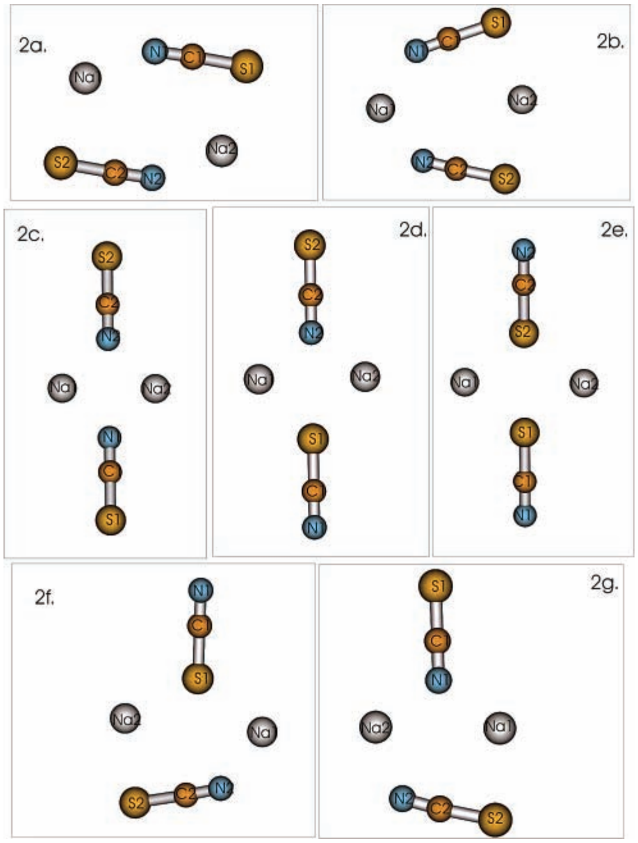


Figure 3. Possible dimer structures of NaSCN.

MP2 level with the 6-311+G(2d) basis set. The latter methods were used to investigate the effect of electron correlation on the energetics of dimer formation. Depending on the orientation of the SCN groups and the position of the Na atom, seven different dimer structures were tested (Figure 3). No structure resembling in any way the four-membered ring monomer **1b** could be located. This indicates that the ring structure is only feasible if no stronger interaction (e.g., Coulomb interactions) are present than the overlap between the empty p-orbital of the Na atom and the π-system of the SCN group, which was shown to stabilize the four-membered ring structure **1b**.[11] The harmonic frequency calculations revealed that only **2a**, **2b**, and **2c** are real minima on the potential energy hypersurface. (Note that Leung and Streitwieser found that in the case of LiOCN and NaOCN all the seven conformations were real minima.[21]) Table 2 summarizes some selected geometrical parameters of **2a**, **2b**, and **2c**. The relative energies, the interaction energies, and the CP corrections to the interaction energy are also presented. Although the dimerization energies do not take into account the entropy changes, they are largely negative, implying that the aggregation of the molecules is a highly favorable process. At both levels of theory an eight-membered ring dimer **2a**, with the two SCN groups in head-to-tail orientation, is the most stable conformer. The other eight-membered ring dimer **2b**, with the SCN groups in head-to-head orientation, is only 1.24 (1.87 at the B3LYP and 1.52 at the MP2 levels, respectively) kcal/mol higher in energy. In the third stable structure the nitrogen and sodium atoms form a four-membered ring. This conformer is 14.8 kcal/mol higher in energy; this energy difference is reduced to 5.82 kcal/mol at the B3LYP level and to 10.97 kcal/mol at the MP2 level, suggesting that the effect of electron correlation is important, in comparing the relative stabilities of the conformers. The value of the CP correction is only 1−2 kcal/mol, which is 2−4% of the interaction energy, so the 6-31+G(d) basis set is sufficiently large to study these kind of systems. The CP correction is, as expected, the largest in the MP2 calculations but still less than 10% of the interaction energy. In the case of LiSCN dimers, Squalli et al. found only two stable dimers, very similar to **2a** and **2c**.[22] The **2a**-type dimer was the more stable, but they stated the **2c**-type dimers are at least as important in aggregation in liquids as they are more accessible for solvent molecules. They showed that from the two dimers two classes of earlier experimentally detected aggregates[23] can be derived.

Compared to the geometrical parameters of the SCN group in the different dimers, it is interesting to note that the parameters of **2c** are similar to those of the linear isothiocyanate **1a**, while the parameters of **2a** and **2b** resemble those of the four-membered ring monomer **1b**. A possible explanation is that in both **2c** and **1a** mainly the nitrogen end of the SCN group interacts with the sodium atom, while in **2a**, **2b**, and **1b** both ends of the SCN group interact with a sodium atom.

A close look at the crystal structure (Figure 1) discerns two of the stable dimers **2a** and **2c** in the experimental crystal structure. This suggests that at the level of dimers the essential building blocks of the overall crystal structure can already be recognized. However, while the computed parameters of the SCN group agree well with the experimental data, the NaN and NaS distances are 0.2−0.3 Å shorter in the dimers than in the crystal.

TABLE 2: Optimized Geometrical Parameters (in Å and in deg) Relative Energies (E_{rel}) and Dimerization Energies without (E_{dim}) and with ($E_{dim,corr}$) the CP Correction (in kcal/mol) of the Possible Dimer Structures at the HF/6-31+G(d), B3LYP/6-31+G(d) (in Parentheses), and MP2/6-311+G(d,p) (in //) Levels

	2a	**2b**	**2c**
E_{rel}[a]	0.00 (0.00) /0.00/	1.24 (1.87) /1.52/	14.81 (5.82) /10.97/
E_{dim}	−50.90 (−51.36) /−49.34/	−49.66 (−49.49) /−47.82/	−36.09 (−45.54) /−38.37/
CP correction	0.38 (0.72) /3.55/	0.74 (0.78) /2.10/	1.46 (1.86) /1.97/
$E_{dim,corr}$	−50.52 (−50.63) /−45.79/	−48.91 (−48.70) /−45.72/	−34.62 (−43.67) /−36.40/
NC	1.149 (1.181) /1.189/	1.149 (1.181) /1.189/	1.166 (1.199) /1.204/
CS	1.673 (1.657) /1.640/	1.674 (1.659) /1.641/	1.627 (1.615) /1.601/
SNa	2.726 (2.714) /2.734/	2.723 (2.700) /2.723/	
NaN	2.258 (2.224) /2.269/	2.266 (2.236) /2.269/	2.297 (2.269) /2.307/

[a] Relative energy of the conformation compared to the most stable structure **2a** in kcal/mol.

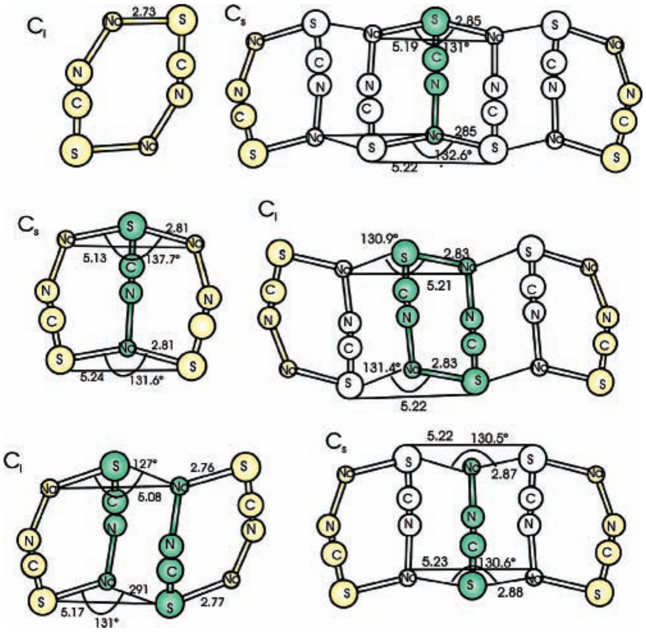


Figure 4. Optimized structures of the NaSCN clusters enlarged along the *y*-axis.

Clusters along the *y*-Axis. The structure of clusters up to seven molecules were completely optimized. Figure 4 depicts the calculated structure of the aggregates together with the intermolecular distances. The intermolecular distances within the clusters converged, but the SS and NaNa distances, which correspond to the *b*-cell constant, converge to 5.21 Å instead of the experimental 4.09 Å, while the S−Na−S (and the Na−S−Na) bond angle converges to 131° instead of the experimental 88° (compare it to Figure 1). These discrepancies are correlated and originate from the fact that in the crystal each sodium is surrounded by 6 neighboring atoms—3 sulfurs and 3 nitrogens—while in these clusters the sodium atoms have only 3 neighbors—2 sulfurs and 1 nitrogen. Therefore, the negatively charged SCN groups easily open up the S−Na−S angle, resulting in a large S−S distance, while the Na−S distance remains close to the experimental value (2.9 Å). Table 3 summarizes the changes of the geometrical parameters of the central molecule together with the experimental data. All the geometrical parameters of the central molecule converge to the experimental value; in the largest cluster most of them are within experimental error. The convergence of the N−Na distance is slowest, and even in the largest cluster it is shorter by 0.1 Å than the experimental one. This probably follows from the tricoordinations of the sodium in the clusters despite their hexacoordination in the crystal. In Table 4 the interaction energies of the clusters, the CP corrections to the interaction energies, and the interaction energies/molecules are collected. It can be concluded from the convergence of the geometrical parameters and that of the interaction energy/molecule that the important interactions have been taken into account, and addition of more molecules to the cluster along this axis would hardly change the results.

Clusters along the *z*-Axis. Clusters up to six molecules along the *z*-axis were completely optimized without geometrical constraints. In the beginning molecules were placed in two parallel planes according to the experimental X-ray structure (the distance between the two planes was 0.25*c*, where *c* is the cell constant), but during the optimization procedure all the clusters collapsed to one plane. The structures of the clusters together with the intramolecular distances are depicted in Figure 5. It is easy to observe that all the clusters are built up from four-membered and eight-membered "dimers" being very similar to **2a** and **2c**. Furthermore, the central dimer is always symmetric, while the "dimers" at the sides are always asymmetric due to the boundary effects. Therefore, the central dimer is the most representative for the crystal structure; the structural parameters of this molecule are shown in Table 5. The calculated parameters of the central molecule are in excellent agreement with the experimental data and hardly change with the size of the cluster. The NC and CS bond distances are between those calculated in the linear isothiocyanate **1a** and the four-membered ring monomer **1b**. Similarly, the values are between the bond distances calculated in **2a** and **2c** dimers. This is in accordance with the fact that the central molecule in every cluster is part of a four-membered ring and an eight-membered ring "dimer" at the same time. The NaN bond distance is the one most influenced by the size of the cluster, but the convergence of this parameter can be observed as well. However, the NaNa and SS distances, which correspond to the *c* cell constant, are about 1 Å longer than the experimental value, and the NNaS angle is about 145° despite the experimental 84°. These differences may be ascribed to similar reasons as in the case of the clusters along the *y*-axis: the sodium atoms are only tricoordinated instead of their original hexacoordination. The calculated interaction energies (with and without CP correction) and the interaction energies per molecule are collected in Table 6. Two dimers are presented as both **2a** and **2c** structures play a role. There are small deviations from an ideally smooth curve, which is due to the fact that addition of a new monomer to the cluster results in the formation of either a new four- or eight-membered ring, i.e., in different interactions.

Clusters along the *y*- and *z*-Axes. Since the a cell constant (*x* direction in Figure 1) is much longer ($a = 13.66$ Å) than the other two, and our efforts to optimize clusters along the *x*-axis resulted in the destruction of the original cluster, we began to optimize clusters enlarged along the *y*- and *z*-axes. Still, although the *a* cell constant is much larger than *b* or *c*, the clusters constructed in this way disintegrated during the optimization procedure. This may have been a consequence of too large boundary effects. This effect could be reduced only by consider-

TABLE 3: Geometrical Parameters (in Å and in deg) of the Central Molecule in the Different Clusters along the *y*-Axis at the HF/6-31+G(d) Level

	no. of molecules in the cluster						
	2[a]	**3**	**4**	**5**	**6**	**7**	expt 1975[8a]
SC	1.675	1.694	1.689	1.681	1.684	1.686	1.663(9)
CN	1.148	1.143	1.145	1.147	1.146	1.145	1.168(18)
NNa	2.257	2.402	2.352	2.307	2.322	2.336	2.42
CNNa	148.0	146.7	143.1	141.9	142.8	144.2	144.0
N′CS′	177.9	177.0	177.7	178.6	178.3	178.0	179.0(8)
NaNa[b]		5.13	5.08	5.23	5.21	5.19	4.09
S′S′ [b]		5.24	5.17	5.22	5.22	5.22	4.09
NaS′	2.72	2.81	2.91	2.87	2.83	2.85	2.92
NaS′Na		137.7	127	130.6	133.1	131.0	88.8

[a] Eight-membered dimer, **2a**. [b] These values refer to the distance along the *y*-axis; i.e., they correspond to the *b* cell constant.

TABLE 4: Interaction Energies (E_{int}), Interaction Energies Corrected with the CP Correction ($E_{\mathrm{int,corr}}$), Interaction Energies per Molecule ($E_{\mathrm{int/molecule}}$), and Corrected Interaction Energies per Molecule ($E_{\mathrm{int,corr/molecule}}$) (in kcal/mol) for the Different Clusters along the *y*-Axis Calculated at the HF/6-31+G(d) Level

no. of molecules	**2**[a]	**3**	**4**	**5**	**6**	**7**
E_{int}	−50.90	−80.51	−117.92	−152.01	−187.51	−222.30
$E_{\mathrm{int,corr}}$	−50.15	−79.88	−116.97	−150.75	−185.94	−220.41
$E_{\mathrm{int/molecule}}$	−25.45	−26.84	−29.48	−30.40	−31.25	−31.76
$E_{\mathrm{int,corr/molecule}}$	−25.07	−26.62	−29.24	−30.15	−30.99	−31.49

[a] Eight-membered dimer, **2a**.

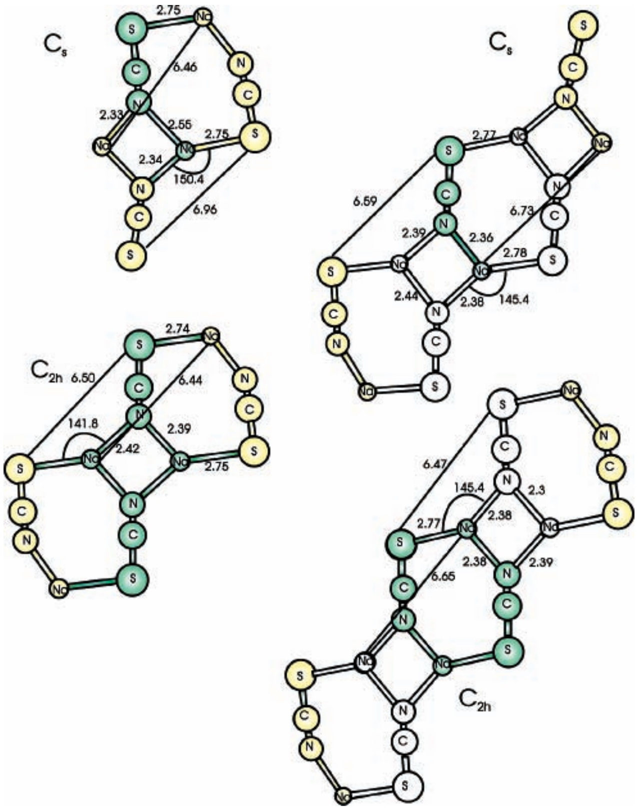


Figure 5. Optimized structures of the NaSCN clusters enlarged along the *z*-axis.

ing many more parallel planes, but even in that case the surface would grow too quickly. Therefore, we decided to use point-charge and the supermolecular models in order to simulate the overall crystal structure.

Point-Charge (PC) and Supermolecule (SM) Model Calculations. First, we applied the point-charge model to simulate the crystal structure. In this model all the molecules surrounding the central molecule were replaced by stockholder charges (Figure 6). The poor agreement of the results with the experimental parameters (NNa = 2.72 Å, NaNC = 103°) indicates that the interactions between the molecules within the crystal are not only of electrostatic nature. Therefore, we constructed a supermolecule from the central molecule and its six nearest neighbors (Figure 6). In this model, one layer of neighbors surrounded our central molecule. After choosing the nearest neighbors that were included in the supermolecular wave function, we simulated the farther layers of molecules being within a 20 Å radius sphere around the central molecule by stockholder charges. The geometry of this supermolecule could not be optimized; the sodium atoms moved too far away from their SCN counterions.

As it was obvious from the previous model that one layer of molecules around the central molecule is not enough to simulate

TABLE 5: Comparison of Optimized Parameters (in Å and in deg) of the Central Molecule in the Different Clusters along the *z*-Axis at the HF/6-31+G(d) Level

	no. of molecules in the cluster				
	3	**4**	**5**	**6**	expt values 1975[8a]
SC	1.663	1.663	1.656	1.658	1.663(9)
CN	1.154	1.154	1.155	1.155	1.168(18)
NNa	2.555	2.419	2.364	2.375	2.42
CNNa	139.3	139.3	137.3	137.2	144.0
NCS	178.7	179.3	179.0	179.3	179.0(8)
NaNa[a]	6.458	6.434	6.728	6.656	5.66
SS[a]	6.968	6.503	6.593	6.475	5.66
N′NaS′	150.4	141.8	145.4	145.4	84.4

[a] These values refer to the distance along the *z*-axis; i.e., they correspond to the *c* cell constant.

TABLE 6: Interaction Energies (E_{int}), Interaction Energies Corrected with the CP Correction ($E_{\mathrm{int,corr}}$), Interaction Energies per Molecule ($E_{\mathrm{int/molecule}}$), and Corrected Interaction Energies per Molecule ($E_{\mathrm{int,corr/molecule}}$) (in kcal/mol) for the Different Clusters along the *z*-Axis Calculated at the HF/6-31+G(d) Level

no. of molecules	**2**[a]	**2**[b]	**3**	**4**	**5**	**6**
E_{int}	−50.9	−36.1	−80.8	−123.8	−155.4	−198.1
$E_{\mathrm{int,corr}}$	−50.51	−34.62	−78.93	−121.66	−151.76	−194.07
$E_{\mathrm{int/molecule}}$	−25.4	−18.0	−26.9	−30.9	−31.0	−33.0
$E_{\mathrm{int,corr/molecule}}$	−25.26	−17.31	−26.31	−30.42	−30.35	−32.34

[a] Eight-membered dimer, **2a**. [b] Four-membered dimer, **2c**.

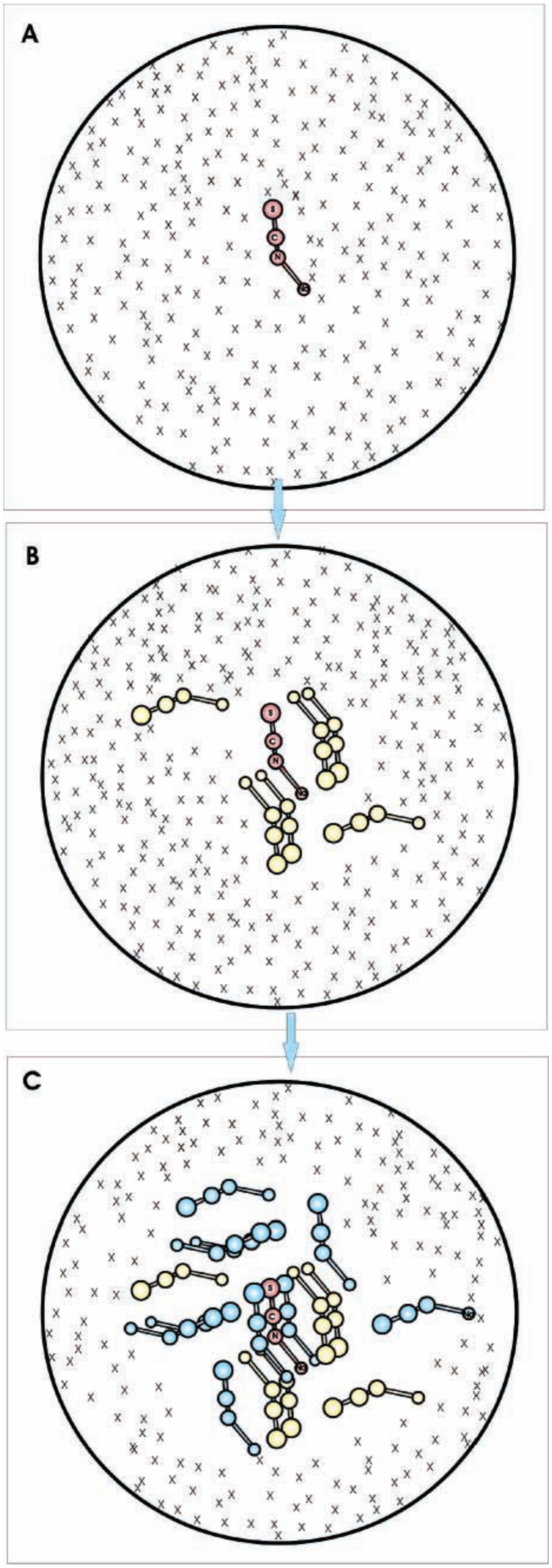


Figure 6. Point-charge and supermolecule model calculations.

the crystal structure, we included two layers of surrounding molecules in the supermoleculer wave function. This supermolecule contained the 17 nearest neighbors of the central molecule (see Figure 6) and was surrounded by stockholder charges in a 20 Å radius imaginary sphere. This supermolecule

TABLE 7: Optimized Geometrical Parameters of the Central Molecule 17-Member SM Calculation (in Å and in deg)

(HF/6-31+G(d))	calculations 17-member supermolecule	exptl data XRD[8a]
NaN	2.440	2.42
NaNC	142.6	144.0
NC	1.150	1.168(18)
CS	1.663	1.663(9)
SCN	179.2	179.0(8)
NaN′	2.630	2.63
NaS	2.965	2.94
NaS′	2.899	2.92
N′NaS′	83.9	84.4
N′NaN′	102.0	101.9
SNaS′	84.0	83.2
NNaN′	88.0	88.5
SNaN′	90.9	90.8
NaS′Na	89.7	88.8

was the next step to find the smallest supermolecule, which may be large enough to give relevant results on the structure of the crystal phase. The optimized parameters of the crystal structure are collected in Table 7. All the bond distances and bond angles are in very good agreement with the experimental results.

The calculated stockholder charges (Na, 0.436; S, −0.265; C, 0.119; N, −0.290) for the central molecule, which were used in the point-charge sphere, show a similar pattern as in the SCN anion.[24] The carbon atom has a low positive charge, and the negative charge is equally distributed between the N and S atoms in accordance with earlier calculations. The charge on sodium is slightly higher than the value obtained by the numerical integration of the experimental electron density (0.27(6) *e*),[8b] but still a relatively low value. This low value is not a sign of less ionic (electrostatic) bonding in the crystal phase, as was stated by Dannöhl et al.[25] We investigated the effect of the point-charge sphere on the structure of the supermolecule, optimizing its structure without point charges and with a 35 Å radius imaginary sphere, but the effect was negligible. This may be ascribed to the fact that interaction of the central molecule with the two layer of neighbors is much stronger than with molecules farther away, so the farther lying point charges do not affect the geometrical parameters considerably.

Conclusions

A detailed investigation of the gas-phase and crystal-phase structure of sodium thiocyanate has been presented. Using sophisticated ab initio calculations, the existence of the four-membered ring monomer has been predicted. Three minima have been found on the PES of the NaSCN dimers; two of these (**2a** and **2c** in Figure 3) have been identified as the main building blocks of the NaSCN crystal. The systematic enlargement of the clusters along the crystal axes lead to the convergence of the geometrical parameters and the interaction energy of the clusters. According to our results, the supermolecule model with one layer of molecules around the central molecule is not large enough to simulate the overall crystal structure of NaSCN, but a 17-member supermolecule model (two layers of neighbors) has been successfully applied and found to be in excellent agreement with the experimental data.

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