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Comparable *ab initio* Calculated Energies of HCNS, CNSH, NCSH and HNCS. Optimized Geometries and Dipole Moments

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Dedicated to Professor K. A. Jensen on his 70th birthday

Energies of geometry optimized models of HCNS (−490.15344 hartrees), CNSH (−490.17332 hartrees), NCSH (−490.20453 hartrees), and HNCS (−490.21238 hartrees) have been calculated *ab initio* by LCAO-MO-SCF technique applying a 4*s*,1*p* (H); 7*s*,3*p* (N); 7*s*,3*p* (C); 10*s*,6*p*,1*d* (S) basis set. Within the framework of this basis the most stable species is HNCS while HCNS (0.05894 hartrees), CNSH (0.03906 hartrees), and NCSH (0.00785 hartrees) are of higher energy as quoted parenthetically. Only at *ca.* 2000 °C NCSH may coexist. At 700 °C HC=N−S−CO−O or 1,3,4-oxathiazol-2-one pyrolyzes to HNCS while a product in which the atomic sequence had been conserved would be HCNS, thiofulminic acid. Predicted dipole moments in Debye units are *ca.* 5 for HCNS and *ca.* 3 for the remaining structural isomers.

When the five-membered ring compound HC=N−S−CO−O, 1,3,4-oxathiazol-2-one (I)[1] is pyrolyzed on a quartz surface at 700 °C and $p \simeq 0.02$ mmHg for *ca.* 30 s it dissociates into HNCS (II) and CO_2. We have identified II by means of its well-known microwave spectrum [2,3] by pumping the products of pyrolysis continuously through a microwawe cell. Also, pyrolysis products were collected for 3−4 h on a cooled (liq. N_2) KBr-disc. An infrared spectrum was obtained verifying the presence of II [4] without, however, excluding the presence of hitherto unknown HCNS. A mass spectrum of the products showed dominating peaks for CO_2 and HCN. While work on necessary improvements of the experimental technique is in progress we have found it useful to produce *ab initio* estimates of the energies of the title compounds, simultaneously optimizing their structures. The energy calculations will determine relative stabilities. Optimized geometries and calculated dipole moments will assist in the search for spectra of HCNS, CNSH and NCSH whether of terrestrial or interstellar origin. These species have not yet been prepared, whereas infrared and microwave spectra of HNCS are known.[2—4] The difference between the experimental and the *ab initio* calculated structure of HNCS is informative as to the reliability of the calculated structures of the three remaining isomers (Fig. 1). Errors of ±0.02 Å may be implied due to basis set imperfection.

CALCULATIONS

All calculations were of conventional LCAO-MO-SCF type, the program system MOLECULE [5] being applied. Orbital exponents of the basis functions for C, N and S have been taken from Ref. 5. The orbital exponents for H were those of Huzinaga [6] multiplied by 1.25.

Fig. 1 summarizes energies and optimized structures. Data from $(CH_3)_2S$,[7] CH_3SH,[8] CH_3NCS,[9] and CH_3SCN [9] were used as start parameters. The changes necessary to produce minimum energy (='geometry optimization') were slight. In the case of HNCS differences between calculated and experimental geometry

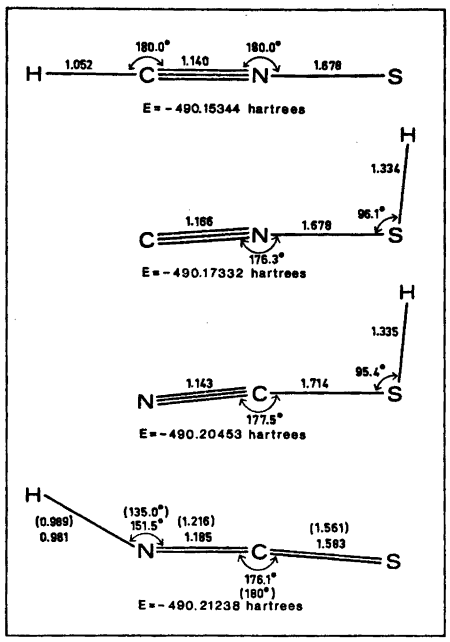

Fig. 1. Optimized structures (distances in Å) and energies of HCNS, CNSH, NCSH and HNCS. Experimental structure of HNCS in parentheses. 1 hartree = 627.5 kcal mol^{-1}.

may be seen from Fig. 1. They are probably of the same order of magnitude for all structural isomers.

Calculated dipole moments and their corresponding μ_a-components ('a' being an inertial axis) are reported in Table 1 with rotationel constants A, B, C for all calculated structures.

Table 1. Calculated total dipole moments (μ) and components along inertial "a"-axis (μ_a) (in Debye units) for HCNS, CNSH, NCSH, and HNCS. Rotational constants A, B, C (in MHz).

	HCNS	CNSH	NCSH	HNCS
μ	5.38	3.05	3.41	3.14
μ_a	5.38	2.83	3.19	2.91[a]
A	–	259610	294591	2889304[b]
B	5857	6277	5765	5828[b]
C	5857	6147	5655	5816[b]

[a] Experimental $\mu_a = 1.72$ Debye.[12] [b] Necessarily different from experimental (ground state) value ($A = 1483000$, $B = 5883$, $C = 5846$).

DISCUSSION

As seen from Fig. 1. molecular energy decreases in the order HCNS, CNSH, NCSH and HNCS. This is in harmony with the fact that HNCS is the only hitherto available structural isomer. Also, the sequence $\mathscr{E}$(CNSH) > $\mathscr{E}$(NCSH) (energy $\mathscr{E}$) is expected. The energy relations suggest that primarily released HCNS, in which the atomic sequence of parental I has been conserved, reorganizes to HNCS. It is energetically possible that this happens step-wise through metastable CNSH and NCSH. Clearly, if species other than HNCS are wanted their formation must take place under non-equilibrium conditions. Such as low temperature, 'flash' heating *etc.*

Within the framework of the applied 4*s*, 1*p* (H); 7*s*, 3*p* (N); 7*s*, 3*p* (C); 10 *s*, 6*p*, 1*d* (S) Gaussian type basis set, hypothetical HCNS was found to be *linear*. The three remaining species possess slightly *bent* CNS or NCS groups in a conformation *trans* to H. However, it should be noted that these features have not been finally established until larger basis sets have been used. This general phenomenon is well illustrated in a recent publication[10] on HCNO, NCOH, and HNCO. So the calculated structures must be considered *preliminary* (Fig. 1).

From an *experimental* point of view the choice between a linear or a non-linear *NCS* group in HNCS is also difficult since the experimentally well-established difference between the rotational constants B and C may not entirely be due to off-line hydrogen (deuterium). Table 2 shows that a model in which NCS has been bent by 4° (as suggested by the *ab initio* treatment) can reproduce the experimental values for B and C if the angle HNC is changed by only 2°. This is not to suggest that this latter model is preferable for H(D)NCS considering, for example, that a large amplitude motion of H is involved.

In a series of calculations, S of HNCS (*ab initio* model) was moved from +4° (*trans*) through 0 to −4° while establishing hydrogen positions corresponding to minimum molecular energy as a function of the angle HNC and the H−N distance. It was found that H and S pass the N≡C axis simultaneously. The energy at linear conformation was calculated

Table 2. Experimental rotational constants B and C (a) in MHz of HNCS and DNCS and rotational constants of models b, c and d.

	a	b	c	d
B				
HNCS	5883	5870	5867	5875
DNCS	5501	5489	5479	5492
C				
HNCS	5846	5840	5839	5845
DNCS	5445	5440	5436	5445

[a] Experimental.[2,3] [b] Recalculated from exp. parameters in ( ), Fig. 1. [c] As for b, but NCS bent by 4° (*trans* to H). [d] As for c, but diminishing the angle HNC by 2°.

as being 86 cm^{-1} higher than for the "natural" bent molecule. The height of this barrier is of interest to spectroscopists. However, our calculated value only represents a crude estimate.

Parental HC=N–S–CO–O has also been a target in photolysis. Identified products were CO_2, HCN, OCS, and HNCO.[11] It is worth noting that the quanta of radiation involved in the present pyrolytic experiment are an order of magnitude smaller than quanta in the visible-ultraviolet region.

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