Calculated Properties of $OCNS^-$ and Related Species

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The presumed, '$OSCN^-$' structure of the antibacterial agent hypothiocyanite is found to be unstable; the lowest-lying isomer is $OCNS^-$ while the $ONCS^-$ above it is also stable.

The hypothiocyanite ion, written as '$OSCN^-$',[1] has been identified to be an antibacterial agent against *Streptococcus* in both saliva and milk,[2–4] thus preventing the decay of both milk and teeth. This presumed species was found to be remarkably stable to heat in aqueous solutions near pH 7 at low concentration, up to about 0.1 mmol dm^{-3}.[2]

The structure and properties of the ion are, however, unknown. Chemical Abstracts classify it as 'cyanosulphoxylate,' $CNOS^-$.

We therefore extend our earlier study on the second row A=B=C=D systems[5] to the third row element sulphur. The Hartree–Fock- or Møller–Plesset-level 6-31G* calculations were performed using Gaussian 90. No stable structure was found for the $OSCN^-$ structure; the S–C bond breaks at the HF level. If the electronegative sulphur and oxygen atoms occupy the ends then short bonds and low energies are found. The structure $OCNS^-$ has the lowest energy at both HF and MP2 levels. The $ONCS^-$ one lies (186 kJ mol^{-1}) above it at the HF level. All vibrational frequencies for both structures were positive. Note that these two structures are the monothio analogues of the ion $OCNO^-$, considered in ref. 5 and observed in the gas phase by mass spectroscopy.[6] It is interesting to ask whether the inorganic[1] or enzymatic[2–4] reactions are able to isomerize thiocyanate to the lowest,

Table 1 Calculated total energies (au) and geometries (pm)

Species ABCD$^-$	Method	Energy	A–B	B–C	C–D
$OCNS^-$	HF	−564.70713	119.5	115.2	173.0
	MP2	−565.30752	122.5	118.9	170.7
$ONCS^-$	HF	−564.63619	126.4	113.6	168.9
	MP2	−565.25238	125.8	119.0	166.6
$SCNS^-$	HF	−887.37106	165.8	114.2	170.5
$SCCS^{2-}$	HF	−870.60970	173.4	120.6	173.4

Table 2 Calculated vibrational frequencies at HF level

Species	ν_1	ν_2	ν_3	ν_4	ν_5
$OCNS^-$	123	535	653	1496	2622[a]
$ONCS^-$	264	556	609	1152	2618[b]
$SCNS^-$	170	450	529	891	2506[a]
$SCCS^{2-}$	207	456	514	903	2363[a]

[a] π(u), σ(g), π(g), σ(u), σ(g). [b] π, π, σ, σ, σ.

$OCNS^-$ structure or just oxidize it to $ONCS^-$. The $OCSN^-$ structure lies much higher and develops a long S–N bond. The remaining eight isomers would have carbon at an end and/or oxygen in the middle and were neglected. We include in Tables 1 and 2 the dithio species $SCNS^-$ and $SCCS^{2-}$, the latter being the analogue of the known $OCCO^{2-}$.[5]

The present results support the existence of the uncharacterized hypothiocyanite ion, but suggest that its structure is OCNS– or, possibly, $ONCS^-$ while the traditional, '$OSCN^-$' structure is ruled out as entirely unstable.

The calculations were carried out on a Cray X-MP EA/432 computer at the Centre for Scientific Computing at Espoo, Finland. We are particularly grateful to Professor Alan L. Balch who brought refs. 1–4 to our attention.

Received, 4th January 1991; Com. 1/00061F

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