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# Conformation, Electronic Structure and Electronic Spectrum of the 1,2,3,4-Thiatriazole-5-thiolate ($CS_2N_3^-$) Anion and $HCS_2N_3$ Acid

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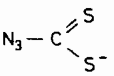
## Abstract

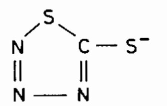
The MNDO method and a Hartree–Fock–Slater (HFS) routine are applied to the study of the $CS_2N_3^-$ anion. The MNDO geometry optimization indicates a 1,2,3,4-thiatriazole-5-thiolate structure. The UV transition at 340–350 nm calculated from the HFS wave function agrees with the experimental results. A Mulliken population analysis shows a very weakly bonded NNN segment in the $CS_2N_3^-$ cycle. The site of protonation in the $CS_2N_3H$ acid is studied with the MNDO method; the results indicate an equilibrium between the thiol and ketone forms, with slight predominance of the first. The calculated first electronic transition for the SH form of the acid agrees with the experimental results. The chemical properties of the $CS_2N_3^-$ anion are discussed.

## Introduction

The $CS_2N_3^-$ ion, formed by reaction of carbon disulphide with sodium azide [1], had been initially attributed to have the structure of an azidodithiocarbonate [2–4] (**I**). Later, on the basis of the chemistry and IR spectrum, the 1,2,3,4-thiatriazole-5-thiolate structure (**II**) was retained [5–7]. The 1,2,3,4-thiatriazole-5-thiolate ion is a member of the interesting family of pseudo-halides [2, 4] and is of some use in analytical chemistry [8] and as a complexing agent [9]; to our knowledge, a crystal structure determination is not available.



**I**



**II**

In this study we apply molecular orbital (MO) theory to:

(a) asses the geometrical structure of the $CS_2N_3^-$ ion;

(b) provide a description of its electronic structure and relate it to known properties;

(c) determine the probable site or sites of protonation of $CS_2N_3^-$.

For this purpose, we employ a two-level strategy in the choice of calculation methods. For the optimization of the geometry, we use the Modified Neglect of Differential Overlap (MNDO) method, which has been calibrated to reproduce geometries and some other properties by Dewar and co-workers [10]. For the analysis of the electronic structure, we employ the discrete variational solution of Baerends and co-workers [11] of the Hartree–Fock–Slater (HFS) equations [12]; the last procedure may be viewed as basically of an *ab initio* level, and it has been widely tested on heterocycles containing sulfur and nitrogen [13]; it has also more recently been applied to heterocycles containing phosphorus [14] or carbon [15], rather than sulfur and nitrogen. For a review of the results of the HFS method for binary SN ring systems and related heterocyclothiazenes, see ref. 16. The HFS calculations are performed at the double zeta level using the atomic STO basis set of Clementi and Roetti [17]. This basis set is further enlarged with 3d polarization orbitals on the sulfur atoms [18]. The atomic core orbitals are kept 'frozen' and orthogonal to the valence shell orbitals during the interaction process.

## II. The Geometry and Stability of the $CS_2N_3^-$ Anion

### *II.1. Geometry Optimizations*

In the order to ensure the determination of the absolute minimum energy conformation for the $CS_2N_3^-$ anion, the geometry search was started from various possible arrangements, and in each case a stepwise geometry optimization was performed. The criterion for stability was the standard heat of formation ($\Delta H_f^0$) as provided by the MNDO program. One such search is illustrated in Fig. 1, in which the initial geometry (Fig. 1, a) is the azidodithiocarbonate (**I**) structure leading, indeed, to the 1,2,3,4-thiatriazole-5-thiolate (Fig. 1, d) species **II**. Form **I** with standard bond distances and angles has $\Delta H_f^0 =$ 165.0 kcal/mol. In Fig. 1,a all bond distances and

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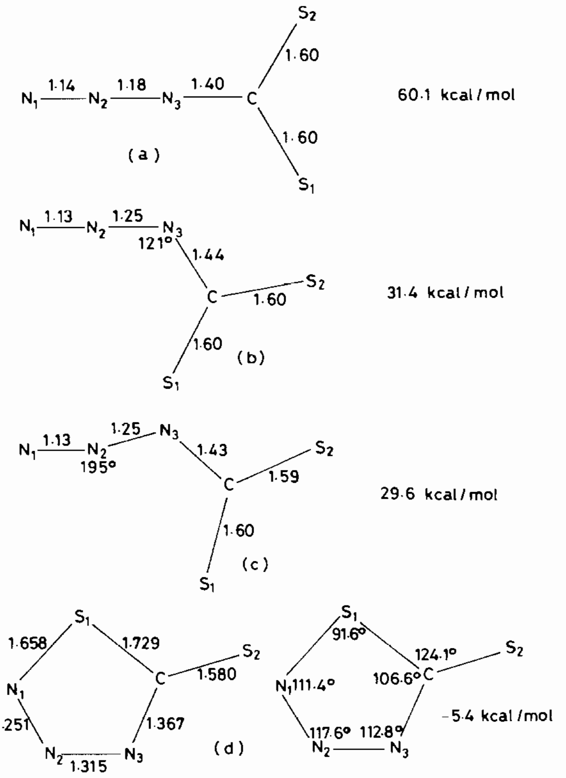


Fig. 1. MNDO geometry optimization of the $CS_2N_3^-$ anion. Distances in Å. (a) Azidodithiocarbonate form with bond lengths and SCS angle optimized. (b) Structure (a) with optimization of all bond lengths and angles. (c) Further optimization of all bond lengths and the NNN angle. (d) Bond lengths and angles for the minimum energy conformation. At the r–h–s of each structure the standard heat of formation, $\Delta H_f^0$, is indicated.

the SCS angle were optimized, while the $N_3S$ segment was maintained linear; this led to the lowering of $\Delta H_f^0$ to 60.1 kcal/mol. Allowing all angles and distances to vary leads to the structure of Fig. 1, b; the only noticeable change is in the NNC angle which bends to 121°, lowering $\Delta H_f^0$ to 31.4 kcal/mol. A further restart of the search, from a geometry close to that of Fig. 1, b, does not lead to the narrowing of the NNN angle, as one would hope; but the program is trapped in a local minimum with a slightly more open NNN angle (Fig. 1, c). Nonetheless, if the search is started from an NNN angle *ca.* 120°, the apparent minimum energy conformation of Fig. 1, d with $\Delta H_f^0 = -5.4$ kcal/mol is obtained; this pattern is reminiscent of the situation previously reported for the $S_2N_2$ molecule [19]. The same conformation of Fig. 1, d is obtained from other initial conformations.

The torsion angles were also optimized in this search. While the structure illustrated in Fig. 1, b is slightly non-planar, the structures 1,c and 1, d are strictly planar.

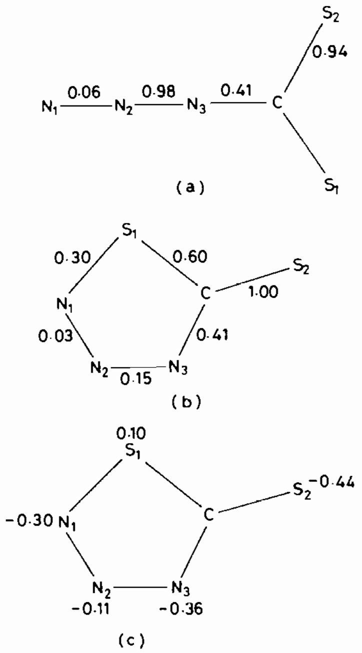


Fig. 2. HFS population analysis for the azidodithiocarbonate (structure **I**) and 1,2,3,4-thiatriazole-5-thiolate (structure **II**) forms of the $CS_2N_3^-$ anion. (a) Atom–atom overlap populations for structure **I**. (b) Atom–atom overlap populations for structure **II**. (c) Net atomic charges for structure **II**.

To the best of our knowledge, a crystal structure determination of the 1,2,3,4-thiatriazole-5-thiolate anion is not available in the literature. The closest structure with available crystal data is that of the 5-phenyl-1,2,3,4-thiatriazole [20] molecule. The coincidence between the MNDO optimized geometry of the anion and the 5-phenyl substituted ring is remarkable and gives support to the results of the present calculation.

### *II.2. Bonding in the 1,2,3,4-Thiatriazole-5-thiolate Anion*

Other than total energy, the degree of bonding between the atoms of a given structure is a further criterion for stability. To test this property for the 1,2,3,4-thiatriazole-5-thiolate anion, we performed a Mulliken type population analysis [21] for the optimized structure of the anion (Fig. 1, d) with the HFS wave function obtained for this geometry. The Mulliken total atom–atom overlap populations are shown in Fig. 2, for structure **I** (Fig. 2, a) and structure **II** (Fig. 2, b), both for MNDO optimized geometries. Figure 2, c shows atomic net charges for structure **II**.

Indeed, structure **I** (Fig. 2, a) is unlikely to be stable since there is almost no bonding between nitrogen atoms 1 and 2 (we consider an atom–atom overlap population of *ca.* 0.5 as indication of a single bond [22]). What is distressing is that the MNDO optimized form of structure **II** shows only a residual bond between N(1) and N(2) and a very weak bond between N(2) and N(3). This suggests the case of the $S_5N_6$ molecule, for which a HFS calculation [23] indicates only a residual bonding between the NSN 'handle' and the $S_4N_4$ unit; this species is extremely unstable and even explosive, although under appropriate conditions it can be preserved for some time [24]. Similar behaviour appears in the 1,2,3,4-thiatriazole-5-thiolate chemistry. The $NaCS_2N_3$ solutions slowly decompose even in the absence of air and light at 4 °C [25]; the Cd(II), Zn(II) and Pb(II) salts are explosive even in solution [26]. The alkaline salts are stable at 4 °C in respect to decomposition into $S^0$, $N_2$ and $SCN^-$ but are quite shock-detonant, mainly when dried [25].

It is interesting to note that the weakness of the NNN bond originates solely from the $\sigma$ framework. As a matter of fact, there is 30–40% of a full single $\pi$ bond along the whole $CS_2N_3^-$ cycle (the extracyclic CS double bond is 75% $\sigma$ and 25% $\pi$ in character) which originates from the four occupied $\pi$ (a″) orbitals. That is, the 8$\pi$ electrons provide a substantial bonding to the cycle. The N(3)–N(4) nonbonding behaviour is thus caused by a strong antibonding character of the $\sigma$ framework; the N(4)–N(5) linkage is also weakened through the $\sigma$ contribution. This situation is reminiscent of the NSN fragment [27] in which, depending on geometry, the $\pi$ electrons are responsible for most or all of the bonding.

## III. The Electronic Spectrum of the $CS_2N_3^-$ Anion

According to the ordering of the orbitals as provided by the HFS calculation, the two lowest electronic transitions of $CS_2N_3^-$ are the HOMO–LUMO 12a′ → 5a″ and 4a″ → 5a″. The second is of a $\pi \rightarrow \pi^*$ character. The 12a′ orbital is an in-plane lone pair on the extracyclic sulfur atom, *i.e.*, $n_\sigma$–S(2). The wavelengths of these transitions, as calculated by Slater's transition state method [12], are 350 nm for 12a′ → 5a″ and 340 nm for 4a″ → 5a″. This is in remarkable agreement with the findings of Neves and Franco [28]. Indeed, they measure a band with $\lambda_{max}$ at 310–320 nm, which they attribute to an overlap of $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions.

## IV. The $HCS_2N_3$ Acid and the Reactivity of the $CS_2N_3^-$ Anion

The electron density on N(3) and on the extracyclic sulfur atom is another point of interest. The charge delocalization in the $CS_2N_3^-$ anion should enhance its stability as compared to the $HCS_2N_3$ acid and lead to a sulfur atom slightly more electron-rich than N(3) in the anion. Thus, in principle, the anion has at least two active centres, *i.e.*, N(3) and S(2). In order to assess the position of the proton, we performed MNDO calculations for the acid. The positions of the proton in the regions of S(2) and N(3) were optimized, with the results shown in Fig. 3. In the first case (Fig. 3, a) the CSH angle and SH distance were optimized; in the second case (Fig. 3, b) the CNH angle and NH distance were optimized. In both cases the proton was found to lead to an energy minimum when located in the molecular plane. Comparison of the $\Delta H_f^0$ values shows that both forms of the acid are unstable as compared to the $CS_2N_3^-$ anion (see Fig. 1, d), by 27.1 kcal/mol for the SH form and by 29.5 kcal/mol for the NH form; therefore, it seems reasonable to assume the equilibrium **III** for the anion, with the thiolate form more abundant and reactive. The thiol form of the acid should also predominate over the ketone structure.

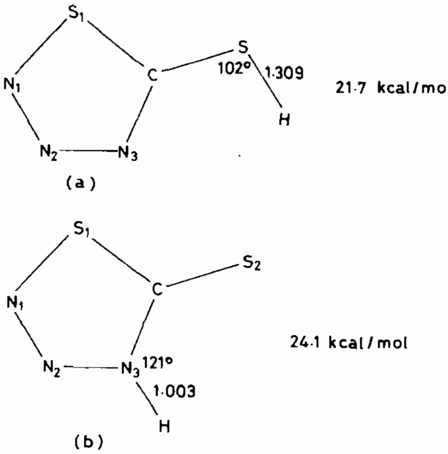
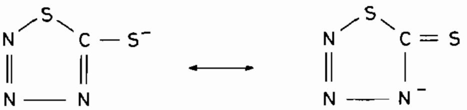


Fig. 3. NMDO geometry optimization for two sites for the proton in the $HCS_2N_3$ acid. The values of $\Delta H_f^0$ are also indicated.



**III**

Neves and Franco [28] found that when increasing the H ion concentration the 310–320 nm band of the anion remained basically unchanged, while a new band appeared at 272 nm. Since the $n_\sigma$–S(2) → $\pi^*$ (12a′ → 5a″) band is likely to be more affected by protonation, we calculated this transition for the acid with Slater's transition state method. The result of 287 nm is again in remarkable agreement with the experimental data. As for the $\pi \rightarrow \pi^*$ (4a″ → 5a″) transition for the acid, an estimate employing the procedure described in ref. 29 indicates that it should appear at 304 nm. Thus, for the acid, we can attribute the band at 310 nm to a $\pi \rightarrow \pi^*$ transition, and the one at 272 nm to a n → π* transition. The increase in energy of the last transition may be attributed to the stabilization of the $n_\sigma$–S(2) electrons by protonation.

The higher negative charge on S(2) as compared to N(3) and the fact that $\Delta H_f^0$ values favour the thiolate form in the equilibrium **III** provide a better understanding of the chemistry of the $CS_2N_3^-$ anion. One of the most important characteristics of this ion is its suceptibility to oxidation. The reaction of this pseudo-halide with $H_2O_2$, Au(III), Cu(II) or $I_2$ always results in the formation of the disulphide $N_3CS_2S_2CN_3$ [30]. Another example of the reactivity of the extracyclic sulfur atom is the formation of $N_3CS_2$–R–$S_2CN_3$ compounds by reaction with organic halides X–R–X [31].

The data on the association of the $CS_2N_3^-$ anion with labile cations suggests that this pseudo-halide behaves as a monodentate ligand [26, 32]. The $CS_2N_3^-$ ion associates strongly with soft acids (Au(I), Ag(I), Hg(I) and Cu(I)), but weakly with hard or borderline acids (Cr(III), Co(II), Ni(II), Mn(II), Zn(II)); therefore, it exhibits a soft base character.

The shift in the maximum electrocapillarity observed in $NaCS_2N_3$ solutions strongly suggests that the ion is absorbed at the mercury electrode as a sulphide [9]. It could be argued that the $HCS_2N_3$ acid, $pK_a = 1.51$, is too strong for a mercapton [28]. Nevertheless, since the extracyclic CS bond is 75% σ in character, the electron-withdrawing effect of the thiatriazol ring on the C–S–H moiety may be responsible for an increase in the acidity of the proton. Of course, this effect will be less evident on N(3), where σ electron contributions are not as relevant.

## V. Conclusions

Both the geometry optimization, as originated by the MNDO method, and the calculated electronic spectrum with the unique band with $\lambda_{max}$ at 340–350 nm, as provided by Slater's transiton state method and the HFS wave function, give support to the cyclic form of the $CS_2N_3^-$ anion accepted in the more recent literature. The lack of bonding in the NNN segment of the cyclic form of $CS_2N_3^-$, as indicated by a Mulliken-type population analysis and the HFS wave function, may be viewed as consistent with the unstable character of $CS_2N_3^-$. The excess of negative charge on the extracyclic S(2) atom as compared to the carbon-bonded N(3) atom, as calculated with the HFS routine, is in accord with the chemistry of the $CS_2N_3^-$ ion. The MNDO method indicates that the S(2)H form of the acid is favored by some 2.5 kcal/mol over the N(3)H form. This suggests an equilibrium between thiolate and ketone structures for the $CS_2N_3^-$ anion, with a possible preponderance of the first form.

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