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Structure of thiocyanate dimer radical anion: An ab initio study

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Abstract

The various possible structures of thiocyanate dimer radical anion, $(SCN)_2^{\cdot-}$, have been optimized using Hartree–Fock (HF), density functional theory with B3LYP functional (DFT) and second order Moller–Plesset perturbation (MP2) methods. The most stable structure has been found to be the one where the two SCN subsystems are mutually out-of-plane with respect to each other involving a weak bonding between sulfur–sulfur atoms. The sulfur–sulfur bond length and dihedral angle have been calculated to be larger as compared to that of thiocyanogen, $(SCN)_2$. Binding energy for the global minimum of $(SCN)_2^{\cdot-}$ has been obtained as 53.7, 129.3 and 139.0 kJ/mol with the aid of HF, DFT and MP2 methods, respectively, suggesting a strong electron correlation effect. Similar to other dimer radical ion systems, the agreement in binding energy between DFT and MP2 results is quite satisfactory for $(SCN)_2^{\cdot-}$. However, the DFT calculated S···S bond distance is highly overestimated as compared to the corresponding MP2 value. Energy and geometry of these optimized structures have been discussed and compared with similar systems.

Keywords: Ab initio calculations; Thiocyante dimer radical anion

1. Introduction

The study of intermolecular interactions involving a neutral molecule and a molecular cation/anion, leading to the formation of a dimer radical cation/anion species, has been one of the active areas of research due to their importance in various chemical reactions such as proton transfer, electron transfer, molecular rearrangement, etc. [1–3]. In recent years there has been considerable interest [3–6] in assessing the performance of different exchange-correlation energy density functionals in predicting structure and stability of various dimer radical ion systems. The two subunits of dimer radical cation/anion are held together by a weak bond and so these systems are also termed as hemi-bonded systems. In this regard, sulfur-centered radicals are of importance in gas phase reactions, organic reactions in solutions and biological systems [1]. The sulfur-centered radical interacts with the parent cation or anion to produce a dimer radical cation and anion, respectively. One such species, viz. thiocyanate dimer radical anion $(SCN)_2^{\cdot-}$, is commonly used for the dosimetry [7] in pulse radiolysis experiments. This is formed by interaction of SCN radical with SCN anion (Eqs. (1) and (2)).

$$SCN^- + {}^{\cdot}OH \rightarrow SCN^{\cdot} + {}^{-}OH \quad (1)$$

$$SCN^- + SCN^{\cdot} \rightarrow (SCN)_2^{\cdot-} \quad (2)$$

$(SCN)_2^{\cdot-}$ can also be formed by addition of electron to thiocyanogen, $(SCN)_2$.

$$(SCN)_2 + e^- \rightarrow (SCN)_2^{\cdot-} \quad (3)$$

Thiocyanate anion (SCN^-) and its isomers are known to be present in interstellar ice and dust clouds [8]. It is interesting to note that the reaction between SCN^- and H_2O_2 produces hypothiocyanite anion $(OSCN)^-$, which is perhaps the first natural antimicrobial species [9]. A large number of theoretical studies have been carried out for the thiocyanate radical, $SCN^{\cdot}$ [10–15]. Recently, the structures and energies of the $SCN^{\cdot}$ radical, SCN cation [16], SCN anion [17], thiocyanogen and its cation [18,19] have been reported, however, there is very little literature on the structure of the dimer radical anion of this species, $(SCN)_2^{\cdot-}$. Using resonance Raman spectrum of $(SCN)_2^{\cdot-}$, Wilbrandt et al. [20] proposed a structure corresponding to electron addition on thiocyanogen $(SCN)_2$, thereby resulting in

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a structure with weak bonding between sulfur–sulfur atoms (S⋯S) and weakening of C≡N bond. Recently the structure of this dimer radical anion has been predicted through a combined experimental and theoretical study [21] involving thiocyanate photolysis at 77 K and density functional theory calculation, respectively. In another study, it has been reported that recombination reaction of $(SCN)_2^{\cdot-}$ in gelatin was not affected significantly by increase in macro-viscosity of the medium [22], which was ascribed to a compact structure of $(SCN)_2^{\cdot-}$. The above mentioned reports suggest contradictory structures of $(SCN)_2^{\cdot-}$. Further, it is well known that density functional methods sometimes fail [3–6] to predict correct structure of weakly bonded dimer radical species and also the relative stability of different isomers as compared to post-Hartree–Fock based methods. In this context it is to be noted that at least a moderate size basis set with polarization and diffuse functions is essential to obtain the structure and energies of weakly bonded anion species correctly. To the best of our knowledge neither Hartree–Fock based correlated methods nor a basis set containing diffuse functions have been adopted to study this system. Thus, it would be interesting to investigate various possible structures and binding energies of $(SCN)_2^{\cdot-}$ using different theoretical methods with extended basis set. Therefore, HF, DFT and MP2 methods have been applied to optimize the possible structures of $(SCN)_2^{\cdot-}$ and thus obtain the equilibrium geometry of the most stable structure, its binding energy and atomic spin density distribution. This most stable structure is also compared with the thiocyanogen structure.

2. Computational methods

Thirteen different possible structures of $(SCN)_2^{\cdot-}$ containing a weak bond between S⋯S, S⋯N and N⋯N have been attempted. Each of these structures has two SCN subsystems, which are arranged in linear, in-plane or out-of-plane fashion. Ab initio molecular orbital methods have been used to investigate the geometry of $(SCN)_2^{\cdot-}$ structures and its constituents, SCN anion and $SCN^{\cdot}$ radical. HF, DFT and MP2 methods have been used for the geometry optimizations. All the ab initio calculations have been performed using the GAMESS electronic structure program [23] along with 6-311++G(d,p) basis sets for carbon, nitrogen and sulfur atoms. Stable structures were characterized as either minima (no imaginary frequency) or transition states (one imaginary frequency) by vibrational analysis. The binding energy (ΔE) has been calculated as $\Delta E = E(SCN^{\cdot}) + E(SCN^{-}) - E(NCS\cdots SCN)^{\cdot -}$. Basis-set superposition error (BSSE) has been calculated for the stable species as found by MP2 method.

3. Results and discussion

Ab initio calculations performed for geometry optimization using HF method has predicted only four stable equilibrium structures, out of which three have a weak S⋯S bond (HF-I, II, III) and one has a weak S⋯N bond (HF-IV) (Table 1 and Fig. 1). The global minimum HF-I has been found to have S⋯S bond length of 2.825 Å and dihedral angle of 161.5°. Structures HF-I, HF-II and HF-III are symmetrical but HF-IV is asymmetric. The value of S–C and C–N bond lengths are calculated to be 1.683 and 1.142 Å for HF-I, 1.682 and 1.142 Å for HF-II and 1.679 and 1.143 Å for HF-III, respectively. Other structures of $(SCN)_2^{\cdot-}$ have been associated with either more than one imaginary frequency or same energy or negative binding energy of $(SCN)_2^{\cdot-}$. Stability order of the structures on the basis of binding energy of $(SCN)_2^{\cdot-}$ has been found to be: HF-I > HF-II > HF-III > HF-IV.

However, geometry optimization using DFT has predicted three stable structures out of which two have a weak S⋯S bond (DFT-I, II) and the third one has a weak S⋯N bond (DFT-IV) (Table 1 and Fig. 1). The global minimum DFT-I has S⋯S bond length and dihedral angle as 2.918 Å and 157.5°, respectively. The calculated structures DFT-I and DFT-II are symmetrical while DFT-IV is asymmetric. The S–C and C–N bond lengths are calculated to be 1.663

Table 1
Geometrical parameters and binding energy of various structures of $(SCN)_2^{\cdot-}$ by HF and DFT methods

Structure	Distance (Å)			Angle (degree)	Dihedral angle (degree)	ΔE^{a} (kJ/mol)	Type of structure
	S⋯S	S–C	C–N	S–C–N	NCS⋯S		
HF-I	2.825	1.683	1.142	178.5	161.5	53.71	Global minimum
HF-II	2.851	1.682	1.142	179.1	180.0	53.50	Local minimum
HF-III	2.880	1.679	1.143	178.1	180.0	43.16	Transition State
HF-IV[b]	2.902 (S⋯N)	1.657 (1.674)	1.151 (1.147)	178.3 (179.9)	180.0	34.32	Local minimum
DFT-I	2.918	1.663	1.171	178.8	157.5	129.35	Global minimum
DFT-II	2.851	1.665	1.171	179.4	180.0	129.22	Local minimum
DFT-IV[b]	2.716 (S⋯N)	1.658 (1.638)	1.173 (1.184)	178.8 (178.3)	180.0	98.54	Local minimum

[a] ΔE refers to the $[NCS\cdots SCN]^{\cdot -}$ binding energy.

[b] The two SCN subsystems with different bond lengths and bond angle.