

Synthesis and Characterization of Tetramethylammonium Cyanosulfite, $(\text{CH}_3)_4\text{N}^+\text{SO}_2\text{CN}^-$

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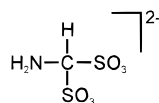
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Abstract: $(\text{CH}_3)_4\text{N}^+\text{SO}_2\text{CN}^-$ was prepared from $(\text{CH}_3)_4\text{N}^+\text{CN}^-$ and SO_2 and characterized by ^1H , ^{13}C , ^{14}N NMR, infrared, and Raman spectroscopy. The yellow salt is stable up to -10°C , but solutions in SO_2 decompose already at -50°C in 1 day. The structure of the anion was predicted by ab initio calculations, suggesting C_s symmetry with a pyramidal coordination at the central sulfur atom with the following geometry: $d(\text{SO}) = 146.7$ pm, $d(\text{SC}) = 190.8$ pm, $\angle(\text{OSO}) = 114.0^\circ$, $\angle(\text{OSC}) = 100.8^\circ$, and $\angle(\text{SCN}) = 173.6^\circ$. The bent SCN arrangement is explained by negative hyperconjugation.

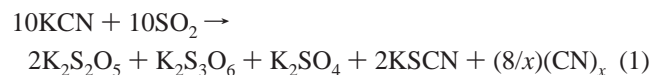
Introduction

More than half a century ago, Jander and Gruettner postulated the existence of cyanosulfurous acid in SO_2/HCN mixtures on the basis of electrochemical measurements.¹ More recently, $\text{NC}\text{SO}_2\text{H}$ was assumed to be a short-living intermediate in the lactoperoxidase-catalyzed oxidation of thiocyanate.^{2,3} Since then, the existence of free cyanosulfurous acid has not been proven by any other method.

Salts of cyanosulfurous acid were first mentioned by Etard in 1879.⁴ He obtained a crystalline product by passing sulfur dioxide through an aqueous solution of potassium cyanide. Subsequently, this product was proposed to be an amino-methanebissulfate salt.⁵

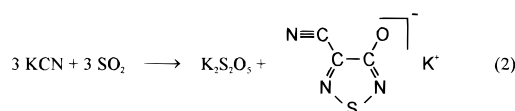


Seel and Mueller reinvestigated the reaction of KCN with SO_2 and showed that the precipitate formed from KCN and SO_2 in HCN solution at 0°C was $\text{K}_2\text{S}_2\text{O}_5$.⁶ They further examined KCN/ SO_2 mixtures at low temperatures and found a colorless 1:1 adduct, presumed to be cyanosulfite, which decomposed above -25°C . From the decomposition products they concluded an over-all reaction according to eq 1.



In contrast to these findings Ross and Smith reported in 1964 that KCN and SO_2 react in the absence of hydroxylic solvents with formation of potassium 3-cyanohydroxy-1,2,5-thiadiazolate (eq 2).⁷ The heterocyclic compound was characterized by

infrared spectroscopy and degradation reactions. Moreover, an independent synthesis from isonitrosocyanacetamide and sulfur dichloride yielded the same product.



Eller and Kubas discovered that large organic cations such as $[\text{PPh}_3\text{Bz}]^+$ and $[\text{K}(18\text{-crown-6})]^+$ render stable SO_2I^- salts, but the procedures failed to give well-defined isolable SO_2CN^- salts.⁸ No further attempts to isolate cyanosulfite salts have been reported in the literature.

In the course of our studies of halogenosulfite salts,^{9–11} the synthesis of the analogous pseudohalogenosulfite salts was interesting for the following reasons. Tetramethylammonium fluoride (naked fluoride) is known to be more soluble and, hence, more reactive than the alkali metal fluorides.¹² This difference in reactivity might apply to some extent to other small anions, such as chloride or cyanide. Following this assumption, we investigated the reaction of tetramethylammonium cyanide with SO_2 at low temperatures. We report herein the successful synthesis of tetramethylammonium cyanosulfite and its characterization by NMR and vibrational spectroscopy.

Experimental Section

Apparatus and Materials. All synthetic work and sample handling were performed employing standard Schlenk techniques and a standard vacuum line. $\text{N}(\text{CH}_3)_4\text{CN}$ was prepared from an aqueous solution of $\text{N}(\text{CH}_3)_4\text{OH}$ and HCN by known literature methods.^{13,14} SO_2 was dried

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over CaH₂. (Caution! Cyanides and hydrocyanic acid are extremely toxic. Anhydrous hydrocyanic acid is easily absorbed by skin!)

Infrared spectra were recorded on a Bruker ifs 113v spectrophotometer. Spectra of dry powders were obtained with use of a CsBr plate coated with the neat sample. The Raman spectra were recorded on an ISA T64000, using an Ar⁺ laser tube (514.5 nm) from Spectra Physics. The spectra were recorded in a glass cell cooled with liquid nitrogen. The NMR spectra were recorded with a Bruker DPX 300 spectrometer.

Synthesis of (CH₃)₄N⁺SO₂CN⁻. A 130 mg (1.3 mmol) sample of carefully dried (CH₃)₄N⁺CN⁻ was placed in a dried glass vessel, and 2 g of SO₂ was condensed into the vessel at -196 °C. The glass vessel was warmed to -60 °C. The reaction proceeded upon thawing in a few minutes. The slightly yellow solution was frozen at -90 °C and excess SO₂ was pumped off. The weight of the resulting slightly yellow solid (220 mg) indicated quantitative yield. The salt is stable below -10 °C, but in SO₂ solution decomposes already in 1 day as the temperature is raised to -50 °C. Further characterization of the obtained compound was carried out by vibrational and NMR spectroscopy.

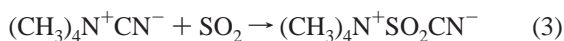
Computational Methods. The ab initio calculations for SO₂CN⁻ and SO₂NC⁻ were performed at the restricted Hartree-Fock level of theory with use of the Gaussian 94 program.¹⁵ All calculations were carried out at the 6-31+G* basis level, which augments the standard double- ζ plus polarization treatment (6-31G*) with a diffuse set of s,p functions (+) on each heavy atom and is known to describe anionic systems in an appropriate way. Harmonic vibrational frequencies were computed for the minimum-energy structures and scaled by the empirical factor 0.88 to maximize their fit with the experimentally observed frequencies.¹⁶⁻¹⁸

Chemical shielding calculations were performed using gauge-including atomic orbital (GIAO) as implemented in Gaussian 94. The isotropic chemical shieldings are obtained by averaging the three principal tensors: σ_{xx} , σ_{yy} , and σ_{zz} . The ab initio calculated isotropic chemical shieldings, σ_C (the values are the shifts relative to the bare nucleus), of the carbon in the optimized molecular structures are 71.1 ppm for SO₂CN⁻ and 45.0 ppm for SO₂NC⁻. To compare the theoretical shielding differences with experimental NMR shifts we have chosen tetramethylsilane (TMS, $\sigma_C = 201.8$ ppm) as reference. Both carbons are shifted to higher frequencies (downfield) by 130.7 (SO₂CN⁻) and 156.8 ppm (SO₂NC⁻), respectively.

For the optimized molecular structure, the wave functions were analyzed by the natural bond orbital (NBO) method,¹⁹⁻²¹ a standard program option of Gaussian 94.

Results and Discussion

Synthesis of (CH₃)₄N⁺SO₂CN⁻. The cyanosulfite salt is formed in quantitative yield by reacting an excess of SO₂ with (CH₃)₄N⁺CN⁻ at -60 °C according to eq 3.



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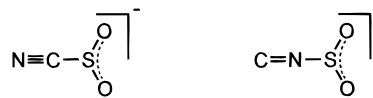
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The (CH₃)₄N⁺SO₂CN⁻ is a slightly yellow salt, stable below -10 °C. At room temperature it decomposes with formation of a brown product that contains the tetramethylammonium cation (identified by Raman spectroscopy) and various unidentified species. The (CH₃)₄N⁺SO₂CN⁻ is quite soluble in SO₂ at low temperatures. Solutions of the cyanosulfite salt are stable for a few hours at -60 °C, and decomposition takes place with a change in color from yellow via red to brown, resulting in a mixture similar to the decomposition products of the solid.

NMR Spectroscopy of (CH₃)₄N⁺SO₂CN⁻. The ¹³C NMR spectrum of freshly prepared (CH₃)₄N⁺SO₂CN⁻ dissolved in SO₂ at -50 °C shows a triplet at 55.8 ppm with a coupling constant (¹J(C,N)) of 4.1 Hz, which is typical for the (CH₃)₄N⁺ cation,²² and a singlet at 127.4 ppm, which is upfield-shifted in comparison to (CH₃)₄N⁺CN⁻ (161.2 ppm in D₂O). The chemical shift of the singlet is in the region of covalent C-bonded cyanide groups (118-135 ppm)²³ and in satisfactory agreement with the ab initio calculated value of 130.7 ppm. The alternative formation of isocyanosulfite can be excluded on the basis of this result, since the chemical shifts for isocyanosulfite are in the region between 157 and 169 ppm.²³ Ab initio calculation of the chemical shift of the energy minimized isocyanosulfite gave a value of 156.8 ppm.



The ¹H and ¹⁴N NMR spectra both display a singlet at 3.5 and 337 ppm, respectively, assigned to the (CH₃)₄N⁺ cation.²⁴⁻²⁶ The ¹⁴N signal for the SO₂CN⁻ anion was not observed for our dilute solutions. ¹⁴N NMR spectra of concentrated solutions of (CH₃)₄N⁺CN⁻ in water displayed a very weak peak at 112 ppm for the cyanide anion.

Vibrational Spectra. The infrared and Raman spectra of (CH₃)₄N⁺SO₂CN⁻ are shown in Figure 1 and the observed frequencies are summarized in Table 1. The vibrational data of the anion together with the frequencies of the isoelectronic cyanodifluorophosphine²⁷ and the ab initio calculated frequencies of cyanosulfite and isocyanosulfite are listed in Table 2. The assignments for SO₂CN⁻ were made by comparison with the isoelectronic F₂PCN. An ab initio investigation, which is discussed later, results, in accordance with the isoelectronic F₂PCN, in the expected structure of symmetry C_s. Consequently, nine fundamentals (6 A' + 3 A''), which should all be active in both the infrared and the Raman spectra, are expected for SO₂CN⁻. The assignments of the (CH₃)₄N⁺ cation were made according to well-known literature data.²⁸⁻³⁰

The carbon-nitrogen stretching mode of the SO₂CN⁻ anion is observed at 2133 cm⁻¹. The $\nu(\text{C}\equiv\text{N})$ is blue-shifted in comparison to the carbon-nitrogen stretching mode in (CH₃)₄N⁺CN⁻. This is a regular trend in the transition from ionic CN⁻ toward

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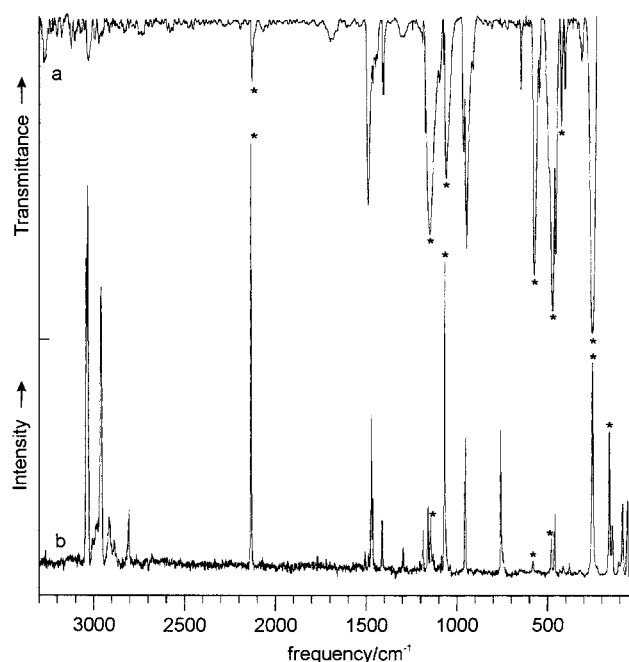


Figure 1. Infrared spectrum (trace A) and Raman spectrum (trace B) of $(\text{CH}_3)_4\text{N}^+\text{SO}_2\text{CN}^-$. Vibrations of the SO_2CN^- anion are marked by asterisk.

Table 1. Vibrational Frequencies (cm^{-1}) of Tetramethylammonium Cyanosulfite

obsd freq		calc freq ^a	assignment	
IR	Raman		$(\text{CH}_3)_4\text{N}^+$ (T_d)	SO_2CN^- (C_s)
3029 w	3041 (73) 3034 (92) 2961 (67) 2914 (13) 2806 (15)		} $\nu(\text{CH}_3)$	
2133 w	2136 (100)	2196		
1493 s	1507 (6) 1472 (37) 1465 (17)		} $\delta_{\text{as}}(\text{CH}_3)$	
1415 w	1412 (13)			} $\delta_{\text{s}}(\text{CH}_3)$
1409 w			} $\rho(\text{CH}_3)$	
1313 vw	1298 (6) 1186 (10) 1160 (16)			
1152 s	1145 (13)	1120		$\nu_{\text{as}}(\text{SO}_2)$
1065 m	1069 (72)	1017		$\nu_{\text{s}}(\text{SO}_2)$
970 m			} $\nu_{\text{as}}(\text{C}_4\text{N})$	
952 s	957 (32)			} $2\delta_{\text{as}}(\text{C}_4\text{N})$ $\nu_{\text{s}}(\text{C}_4\text{N})$
918 w	759 (33)			
579 vs	581 (3)	581		$\nu(\text{SC})$
479 vs	481 (9)	472		$\delta(\text{SO}_2)$
462 s	459 (14)		$\delta_{\text{as}}(\text{C}_4\text{N})$	
432 m		440		$\delta(\text{SO}_2)$
411 w	415 (2) 380 (3)			$\delta(\text{CSO}) + \tau$
261 vs	252 (49) 158 (33) 142 (12) 85 (17) 57 (17)	269 158	$\delta_{\text{s}}(\text{C}_4\text{N})$	$\delta(\text{CSO})$ τ
			} lattice	

^a RHF/6-31+G*, frequencies scaled by an empirical factor of 0.88. covalently bonded CN ligands ($\nu(\text{C}\equiv\text{N}) = 2076 \text{ cm}^{-1}$ for KCN, 2097 cm^{-1} for HCN, and 2206 cm^{-1} for ClCN).³¹

The two oxygen–sulfur stretching modes of the SO_2CN^- occur at 1152 and 1065 cm^{-1} , respectively. These values are

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Table 2. Comparison of Observed and Calculated Frequencies (cm^{-1}) of SO_2CN^- , SO_2NC^- , and Isoelectronic F_2PCN

IR	obsd freq		calcd freq ^a			assignment
	Raman	SO_2CN^-	SO_2NC^-	F_2PCN^b		
2133	2136	2196	2054	2195	$\nu_1(\text{A}')$	
1152	1145	1120	1268	861	$\nu_7(\text{A}'')$	
1065	1069	1017	1142	869	$\nu_2(\text{A}')$	
579	581	581	536	628	$\nu_3(\text{A}')$	
479	481	472	339	460	$\nu_4(\text{A}')$	
432		440	218	412	$\nu_8(\text{A}'')$	
261	252	269	91	344	$\nu_5(\text{A}')$	
		205	75	185	$\nu_6(\text{A}')$	
	158	158	72	145	$\nu_9(\text{A}'')$	

^a RHF/6-31+G*, frequencies scaled by an empirical factor of 0.88.
^b Experimental data from ref 27.

somewhat lower than those observed for fluorosulfites (1180 and 1105 cm^{-1}), but still in a region typical for sulfite derivatives.¹⁰ The assignments to the symmetric and antisymmetric modes are based on their infrared and Raman intensities. In comparison to F_2PCN , whose corresponding frequencies appear at lower wavenumbers, the order of symmetric and antisymmetric modes is reversed.

The sulfur–carbon stretching mode occurs at 580 cm^{-1} at a somewhat lower wavenumber than for F_2PCN (628 cm^{-1}). This represents the expected trend comparing isoelectronic species with different charges and atomic masses.³¹

The five deformation modes, of which four are observed, occur below 500 cm^{-1} . A comparison of the observed frequencies with those from the ab initio calculations for SO_2CN^- (in Table 2) shows a satisfactory agreement. The deviations from the frequencies calculated for the isomer SO_2NC^- exclude the alternate isocyanate formulation, as already made on the basis of the ^{13}C NMR spectrum.

Ab Initio Calculations. The ab initio RHF/6-31+G* calculated geometry for SO_2CN^- and SO_2NC^- together with literature data for sulfite derivatives and F_2PCN are presented in Table 3.^{10,32–34} The energy minimum is found for a pyramidal arrangement of C_s symmetry.

The calculated S–O and C–N bond lengths of both cyanosulfite isomers are in the range of regular double and triple bonds, respectively.³⁵ The O–S–O bond angles are similar to other sulfite derivatives (Table 3). The S–C bond length of SO_2CN^- (190.8 pm) is slightly longer than regular S–C single bonds (178 – 186 pm),³⁵ whereas the SO_2NC^- isomer possesses a S–N distance of 229.9 pm that is far beyond that of regular S–N single bonds (165 – 171 pm).³⁵ Even the calculations of Sakaki et al.,³² which yielded a remarkably shorter S–N distance of 194.8 pm , are outside the region for regular S–N single bonds. However, both calculations indicate that the isocyanosulfite can be described rather as a weak complex between SO_2 and CN^- .

The outstanding feature of the cyanosulfite isomer is the bent arrangement of the sulfur atom with the cyanide group, since nonlinear coordination at a formally sp-hybridized carbon violates a fundamental rule of elementary valence theory.

Nonlinear Coordination of sp-Carbon Atoms. A bent arrangement at formally sp-hybridized carbon atoms, which is not forced by obvious steric effects, has been observed for a

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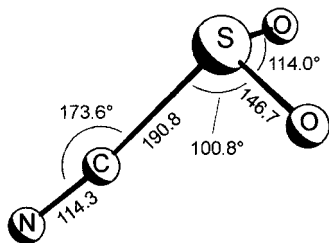
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Table 3. Calculated Geometry of SO_2CN^- and SO_2NC^- Compared to Those of Halogenosulfite Ions SO_2X^- ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) and F_2PCN

	SO_2CN^-	SO_2CN^-^b	SO_2NC^-^c	SO_2NC^-^b	SO_2F^-^d	SO_2F^-^e	SO_2Cl^-^e	SO_2Br^-^e	SO_2I^-^e	F_2PCN^-^f
$r(\text{SO})$ [pm]	146.7	146	143.1	145	145.8	143.7	143.3	142.8	142.4	156.7
$r(\text{SX})^a$ [pm]	190.8	192.3	229.9	194.8	169.8	166.4	260.0	294.9	336.6	181.1
$r(\text{CN})$ [pm]	114.2	115	116.0	117						115.8
$\angle(\text{OSO})$ [deg]	114.0	114	114.9	114	113.2	112.9	114.8	115.4	116.0	99.1
$\angle(\text{OSX})^a$ [deg]	100.8	111	100.6	109	100.6	100.5	102.4	103.4	104.9	97.1
$\angle(\text{SCN})$ [deg]	173.6	174	161.4	174						171.5

^a $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{CN}^-$. ^b SCF-MO (6-31G(d)) calculations from ref 32. ^c The huge deviations found for $r(\text{SX})$ and $\angle(\text{SCN})$ compared to the calculated data of Sakaki et al.³² are caused by using a better 6-31+G* basis level that augments the standard double- ζ plus polarization treatment (6-31G*) with a diffuse set of s,p functions (+) on each heavy atom. ^d HF/6-31+G* calculated data from ref 10. ^e HF/6-31G(d) calculated data from ref 33. ^f Experimental data from ref 34.

**Figure 2.** Calculated structure of the SO_2CN^- anion. Bond lengths in pm.

few cumulated double bonds in molecules such as propadienone and allene derivatives.^{36–38} Seppelt et al. found a bent $\text{C}\equiv\text{S}$ arrangement in $\text{F}_3\text{C}-\text{C}\equiv\text{SF}_3$, and Emerson et al. and Lee et al. measured bent $\text{P}-\text{C}\equiv\text{N}$ angles in $\text{P}(\text{CN})_3$ and F_2PCN .^{34,39–41} In prior X-ray studies it has been suggested that the nonlinearity is due to the close packing in the crystal lattice.⁴¹ Later, gas-phase studies have revealed that the bent arrangement is not caused by crystal effects but rather a matter of the molecule.^{34,42}

An NBO analysis of the SO_2CN^- ion shows that the nonlinear arrangement of the $\text{S}-\text{C}\equiv\text{N}$ fragment can be explained by negative hyperconjugation. The charge delocalization from a filled lone pair n_S of the donor S into an adjacent unfilled antibonding orbital σ_{CN}^* of the acceptor C–N leads to an energy stabilization that can be estimated from simple perturbation theory considerations.⁴³ The contour plot of the $n_S \rightarrow \sigma_{\text{CN}}^*$ interaction is shown in Figure 3. The stabilization energy $\Delta E^{(2)}(n_S \rightarrow \sigma_{\text{CN}}^*)$ is about 10.8 kcal/mol.

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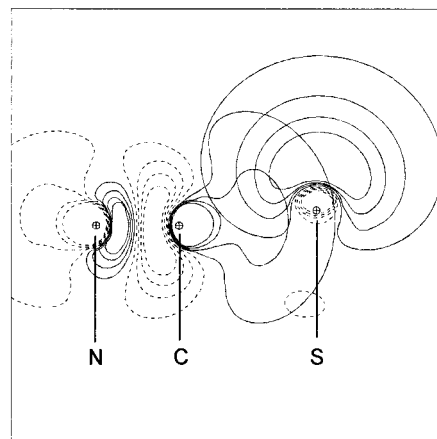
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**Figure 3.** Contour plot of canonical NBOs for the unfilled antibond orbital σ_{CN}^* of the acceptor C–N and the filled lone pair orbital n_S of the donor S.

Conclusion

This study has confirmed that cyanosulfite salt can be synthesized with appropriate counterions, such as tetramethylammonium. The $(\text{CH}_3)_4\text{N}^+\text{SO}_2\text{CN}^-$ salt possesses moderate stability in the solid state, but in solution a rapid decomposition occurs. Compared to the stability of halogenosulfite salts,^{10,44–46} its stability is similar to that of $(\text{CH}_3)_4\text{N}^+\text{SO}_2\text{Cl}^-$. The synthesis of both the SO_2Cl^- and SO_2CN^- ions succeeds starting from $(\text{CH}_3)_4\text{N}^+$ salts, but not from the corresponding alkali salts. This suggests enhanced reactivity of the $(\text{CH}_3)_4\text{N}^+$ salts compared to alkali metal salts.

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