REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
	Technical Paper	

4. TITLE AND SUBTITLE

5a. CONTRACT NUMBER
F04611-99-C-0025

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

5d. PROJECT NUMBER
DARP

5e. TASK NUMBER
A205

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

ERC

8. PERFORMING ORGANIZATION REPORT

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory (AFMC)
AFRL/PRS
5 Pollux Drive
Edwards AFB CA 93524-7048

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
					Leilani Richardson
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER *(include area code)*
Unclassified	Unclassified	Unclassified	A		(661) 275-5015

1 item enclosed

FILE

MEMORANDUM FOR PRS (In-House/Contractor Publication)

25 Sept 2002

FROM: PROI (STINFO)

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-TP-2002-224**
Karl Christe (ERC) et al., "Tritylsulfinylamine: A New Member in the Family of Sulfinylamines"

55194

(Statement A)

Dr. C - 55881

Solid State Sciences
Deadline: 24 Oct 2002)

Tritylsulfinylamine: A New Member in the Family of Sulfinylamines

Karl O. Christe,*[† ‡] Michael Gerken,[†¶] Ralf Haiges,[†] Stefan Schneider,[†] Thorsten Schroer,[†] Fook S. Tham,[§] Ashwani Vij[‡]

Contribution from the Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, Los Angeles, California 90089, Propulsion Sciences and Advanced Concepts Division, Air Force Research Laboratory (AFRL/PRS), Edwards AFB, California 93524, and the University of California, Riverside, California 92521.

Dedicated to Prof. Neil Bartlett on the occasion of his 70th birthday.

* To whom correspondence should be sent. E-mail: karl.christe@edwards.af.mil.

† University of Southern California

‡ Air Force Research Laboratory

§ University of California at Riverside

¶ Present address: Department of Chemistry and Biochemistry, The University of Lethbridge, Alberta, T1K 3M4, Canada

---

Abstract

Triphenylmethyl N-sulfinylamine (trityl-NSO) was prepared from the reaction of trityl amine and $SOCl_2$. Trityl-NSO was characterized by ^{1}H, ^{13}C, and ^{14}N NMR spectroscopy in

CH_2Cl_2 solution and by Raman and infrared spectroscopy in the solid state. Crystals of trityl-NSO were grown from n-heptane and characterized by single crystal X-ray diffraction ($P\bar{1}$, a = 8.9642(9) Å, b = 9.2135(9) Å, c = 11.0645(11) Å, α = 93.578(2)°, β = 101.098(2)°, γ = 118.142°, Z = 2, and R_{int} = 0.0332 at 223 K). Trityl-NSO represents the first alkyl *N*-sulfinylamine that has been fully structurally characterized.

Keywords: Triphenylmethylsulfinylamine; Vibrational spectroscopy; NMR spectroscopy, Crystal structure

---

1. Introduction

There has been much recent interest in polynitrogen chemistry [1-9]. The successful synthesis of the N_5^+ cation [10, 11] and the recent experimental detection of the N_5^- [12] anion by cleavage of *p*-hydroxyphenylpentazole prompted us to search for methods to prepare N_5^- salts in bulk. Since alkylpentazoles might be cleaved more readily than arylpentazoles, and diazonium salts are the precursors required for the preparation of pentazoles [13] (eq 1),

$$N_3^- + {}^+N_2\text{-}R \longrightarrow N_5\text{-}R \qquad (1)$$

we became interested in the preparation of new alkyldiazonium salts. One of our targets in this area was the triphenylmethyldiazonium cation because of the exceptional stability of the triphenylmethyl (trityl) cation which would be formed as a by-product in the cleavage reaction of the C-N bond of the corresponding pentazole. Since the triphenylmethyldiazonium cation is unknown, methods for its synthesis were explored.

The synthesis of diazonium salts usually involves the reaction of nitrite with aryl amines in aqueous acids (eq 2).

$$RNH_2 + 2HX + NO_2^- \longrightarrow RN_2^+X^- + X^- + 2\,H_2O \quad (2)$$

(X = Cl, Br, NO_3, HSO_4, etc)

However, this method cannot be used for trityl amine because the highly electrophilic carbon center of the methyl group is readily attacked by HX. Therefore, alternate methods were sought for the preparation of trityl-N_2^+. One way to prepare diazonium salt under anhydrous, acid-free conditions employs the reaction of R-NSO with NO^+ [14] (eq. 3).

$$R\text{-}NSO + NO^+X^- \longrightarrow R\text{-}N_2^+X^- + SO_2 \quad (3)$$

(X = ClO_4, $SbCl_6$)

While more than 600 *N*-sulfinylamine compounds are known, trityl-NSO has not been reported. In the present paper, we report the preparation and full characterization of trityl-NSO.

2. Experimental Section

2.1. Materials and Apparatus

Reactions were carried out in Pyrex glass vessels closed by grease-free Kontes glass-Teflon valves. Volatile materials were handled on a Pyrex glass vacuum line equipped with the

same valves. Nonvolatile solids were handled in the dry argon atmosphere of a glove box. Infrared spectra were recorded on a Midac, M Series, FT-IR spectrometer using KBr pellets. The pellets were prepared inside the dry box using an Econo press (Barnes Engineering Co.). Raman spectra were recorded on a Bruker Equinox 55 FT-RA spectrometer using a Nd-Yag laser at 1064 nm and Pyrex melting point capillaries as sample containers. Nuclear magnetic resonance spectra were recorded unlocked on a Bruker AMX 500 NMR spectrometer at room temperature. The ^{1}H, ^{13}C (^{14}N) NMR spectra were referenced to external samples of neat TMS (neat nitromethane).

The starting materials, $(C_6H_5)_3CCl$ (Aldrich), NH_3 (Aldrich, anhydrous, 99,99%), $SOCl_2$ (Aldrich), Et_3N (Aldrich), were used without further purification. Tritylamine, $(C_6H_5)_3CNH_2$, was prepared by literature methods [15]. The CH_2Cl_2 (Mallinckrodt) and n-heptane (Aldrich, anhydrous 99%) were dried over molecular sieves.

2.2. Preparation of $(C_6H_5)_3CNSO$

In a typical experiment, a 15 mm diameter H-shaped Pyrex glass vessel with a frit, equipped with two concentric grease-free Teflon valves (Kontes) was loaded inside the glove box with $(C_6H_5)_3CNH_2$ (1.989 mmol). Approximately 3 mL of CH_2Cl_2 was condensed onto the solid at –196 °C, which dissolved completely upon warming to room temperature. At -196 °C, 0.403g (3.98 mmol) NEt_3 was distilled onto the frozen CH_2Cl_2 solution and allowed to warm to room temperature yielding a clear colorless solution. A stoichiometric amount of $SOCl_2$ (1.98 mmol) was added in three increments followed by stirring for ca. 1 h. After the first addition, white $HNEt_3^+Cl^-$ started to precipitate. The solution was stirred for further 18 h at room temperature resulting in a deep brown suspension. Removal of all volatile material under vacuum

was followed by repeated (20 times) extractions of the solid with a few mL n-heptane. Each time the n-heptane solution had been filtered through the frit, the n-heptane solvent was condensed back onto the solid at -196 °C in a static vacuum. The filtrate residue consisted of pale brown, solid $(C_6H_5)_3CNSO$ (0.5288g , 1.732mmol, 87% yield).

2.3. Crystal Growth of $(C_6H_5)_3CNSO$

Inside the dry box, 0.011g of $(C_6H_5)_3CNSO$ (0.036 mmol) was loaded into a Pyrex glass vessel closed by a grease-free Teflon valve. n-Heptane (0.75 mL) was distilled onto the solid and most of it dissolved upon warming to room temperature. The solution was placed in an ethanol bath at -20 °C resulting in crystal growth. The n-heptane was slowly removed between -20 and -10 °C in a dynamic vacuum, resulting in further crystal growth.

2.4. Crystal Structure Determination of $(C_6H_5)_3CNSO$

The single crystal x-ray diffraction data of Ph_3CNSO were collected on a Bruker 3-circle platform diffractometer equipped with a SMART CCD (charge coupled device) detector with the χ-axis fixed at 54.74° and using MoK_α radiation (λ = 0.71073 Å) from a fine-focus tube. This diffractometer was equipped with an LT-3 apparatus for low temperature data collection using controlled liquid nitrogen boil off. A few reasonably well-formed single crystals were selected in a glove-box, equipped with a CCD camera mounted microscope. The crystals were coated with epoxy grease and then mounted on a magnetic goniometer head. Cell constants were determined from 90 ten-second frames. A complete hemisphere of data was scanned on omega (0.3°) with a run time of thirty-second per frame at a detector resolution of 512 x 512 pixels using the SMART software [16]. A total of 1271 frames were collected in three sets and a final set of 50

frames, identical to the first 50 frames, were also collected to determine any crystal decay. The frames were then processed on a PC, running on Windows NT software, by using the SAINT software [17] to give the hkl file corrected for Lp/decay. The absorption correction was performed using the SADABS [18] program. The structure was solved by the direct method using the SHELX-90 program and refined by the least squares method on F^2, SHELXL-97 incorporated in SHELXTL Suite 5.10 for Windows NT [19]. All atoms were refined anisotropically. For the anisotropic displacement parameters, the U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor. The hydrogen atoms were located from difference electron density maps and refined in an isotropic manner.

3. Results and Discussion

3.1. Synthesis and spectroscopic characterization of $(C_6H_5)_3CNSO$

Trityl-NSO was prepared following the method of Michaelis [20] which is based on the reaction of RNH_2 with $SOCl_2$. The product was isolated in 87% yield by repeated extractions with n-heptane, yielding a pale brown solid with a melting point of 89 to 89.5 °C. Its purity was ascertained by IR, Raman and NMR spectroscopy. The IR and Raman spectra of trityl-NSO are shown in Fig. 1, and the vibrational frequencies are listed in Table 1 together with assignments for selected vibrations. Since the trityl skeleton gives rise to a complex vibrational spectrum, Raman spectra of a series of trityl compounds were recorded (Table 1), leading to the unambiguous identification of the vibrational frequencies associated with the NSO group. A thorough study of N-sulfinyl-benzamine [21] showed that the N=S and the S=O stretching vibrations are strongly coupled and that the NSO group gives rise to an out-of-phase and an in-

phase stretching mode. In trityl-NSO, the ν_{as}(NSO) and the ν_s(NSO) vibrations are assigned to 1294 cm^{-1} and 1123 cm^{-1}, respectively. In addition, the deformation mode, δ(NSO), could be assigned to the band at 585 cm^{-1}.

The ^1H, ^{13}C and ^{14}N NMR spectroscopic data are listed in Table 2. The ^1H and ^{13}C NMR chemical shifts lie in the region expected for the triphenylmethyl group. The broad ^{14}N resonance for N-sulfinylamines at -39 ppm ($\Delta\nu_{1/2}$ = 700 Hz) is in the range observed for organic sulfinylamines [22].

3.2. Crystal Structure of $(C_6H_5)_3CNSO$

Details of the crystal data for $(C_6H_5)_3CNSO$ are provided in Table 3; the atomic coordinates and equivalent isotropic displacement parameters are listed in Table 4; and the observed bond lengths, angles, and contacts are listed in Table 5.

The tritylsulfinylamine crystallizes in the triclinic space group $P\bar{1}$ and is the first structurally characterized aliphatic derivative containing an NSO group. Three phenyl groups bonded to the tertiary carbon are oriented in a propeller-like fashion as shown in Fig. 2. The NSO group is oriented closest to the C(2)-C(7) phenyl ring as seen from the S(1)-N(1)-C(1)-C(2) torsion angle of 40.3(2)°. For the other two phenyl rings, this torsion angle increases to 82.1(2)° and 159.5(1)° for S(1)-N(1)-C(1)-C(8) and S(1)-N(1)-C(1)-C(14), respectively. The N=S=O angle of 122.61(8)° is also the largest known angle out of all the reported structures containing an uncoordinated terminal NSO group [23-30]. The next closest NSO angle reported is 121.87° for 2,4,6-tri-t-butyl-N-sulfinylaniline [25]. The CNSO fragment possesses the expected *syn* configuration [31] with respect to the SN double bond. The crystal lattice does not show any short-range intermolecular contacts, the closest one being H(12)···O(1)(-1+x,-1+y,z) 2.75(3) Å.

However, there are intramolecular hydrogen bonds [32] resulting from S(1), O(1) and N(1) i.e., S(1)···H(15) = 2.93(2), S(1)···H(3) = 3.00(2) Å, O(1)···H(15) = 2.57(2) Å and N(1)···H(13) = 2.35(2) Å. The NSO groups show dimer formation via the S(1)···O(1) (-x, 1-y, 1-z) contacts at 3.299(2) Å (Fig. 2) which is roughly equal to the sum of the van der Waal radii for sulfur (1.8) and oxygen (1.52 Å).

Conclusion

While more than 600 *N*-sulfinylamines are known, triphenylmethyl *N*-sulfinylamine represents only the 13th example of an organic sulfinylamine and the first example of an alkyl *N*-sulfinylamine that has been fully structurally characterized by single crystal X-ray diffraction. The N=S=O angle of 122.61(8)° is the largest known angle out of all the reported structures containing an uncoordinated terminal NSO group. In spite of the complexity of the vibrational spectra of trityl-NSO, the vibrational frequencies associated with the NSO group could be assigned.

Acknowledgements

The authors thank the National Science Foundation, the Defense Advanced Research Projects Agency, and the Air Force Office of Scientific Research for financial support. M. G. thanks the Natural Sciences and Engineering Research Council of Canada for a postdoctoral fellowship, and R. H., the Deutsche Forschungsgemeinschaft for a postdoctoral fellowship.

Supplementary material

Tables of structure determination summary, atomic coordinates, bond lengths and angles and anisotropic displacement parameters of $(C_6H_5)_3CNSO$ in CIF format has been sent to Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1 EZ, UK as supplementary material No. SUP NB1-22 (28 pages) and can be obtained by contacting the CCDC (quoting the article details and the corresponding SUP number).

References

[1] Bartlett R. J., Chem. Ind.(2000) 140, and references therein; a compilation of data for N_2 to N_{10} can be found at http://www.qtp.ufl.edu/~bartlett/polynitrogen.pdf.

[2] Fau S., Bartlett R. J., J. Phys. Chem. A 105 (2001) 4096.

[3] Tobita M., Bartlett R. J., J. Phys. Chem. A 105 (2001) 4107.

[4] Klapötke T. M., Angew. Chem. 111 (1999) 2694; Angew. Chem., Int. Ed. Engl. 38 (1999) 2536, and references therein.

[5] Glukhovtsev M. N., Jiao H., von R. Schleyer P., Inorg. Chem. 35 (1996) 7124.

[6] Michels H. H., Montgomery J. A., Jr., Christe K. O., Dixon D. A., J. Phys. Chem. 99 (1995) 187.

[7] Schmidt M. W., Gordon M. S., Boatz J. A., Int. J. Quantum Chem. 76 (2000) 434; Chung G., Schmidt M. W., Gordon M. S., J. Phys. Chem. A 104 (2000) 5647.

[8] Nguyen M. T., Ha T. K., Chem. Phys. Lett. 335 (2001) 311.

[9] Wang X., Hu H. R., Tian A., Wong N. B., Chien S. H., Li W. K., Chem. Phys. Lett. 329 (2000) 483.

[10] Christe K. O., Wilson W. W., Sheehy, Boatz J. A., Angew. Chem. 111 (1999) 2112; Angew. Chem., Int. Ed. Engl. 38 (1999) 2004.

[11] Vij A., Wilson W. W., Vij V., Tham F. S., Sheehy J. A., Christe K. O., J. Am. Chem. Soc. 123 (2001) 6308.

[12] Vij A., Pavlovich J. G., Wilson W. W., Vij V., Christe K. O., Angew. Chem. 114 (2002) 3177; Angew. Chem., Int. Ed. Engl. 41 (2002) 3051.

[13] (a) Huisgen R., Ugi I., Angew. Chem. 68 (1956) 705; (b) Huisgen R., Ugi I., Chem. Ber. 90 (1957) 2914.

[14] Bott K., Angew. Chem. 77 (1965) 132; Angew. Chem., Int. Ed. Engl. 4 (1965) 148.

[15] Dugat D., Just G., Sahoo S., Can. J. Chem. 65 (1987) 88.

[16] SMART V 4.045, Software for the CCD Detector System, Bruker AXS, Madison, WI, 1999.

[17] SAINT V 4.035, Software for the CCD Detector System, Bruker AXS, Madison, WI, 1999.

[18] SADABS, Program for absorption correction for area detectors, Version 2.01, Bruker AXS, Madison, WI (2000).

[19] Sheldrick, G. M. SHELXS-90, Program for the Solution of Crystal Structure, University of Göttingen, Germany, 1990; Sheldrick, G. M. SHELXL-97, program for the Refinement of Crystal Structure, University of Göttingen, Germany, 1997; SHELXTL 5.10 for Windows NT, Program library for Structure Solution and Molecular Graphics, Bruker AXS, Madison, WI (1997).

[20] Michaelis, R. Herz A., Ber. Deut. Chem. Ges. 23 (1890) 74.

[21] Romano R. M., Della Védova C. O., Hildebrandt P., J. Mol. Struct. 508 (1999) 5.

[22] (a) Armitage D. A., Mason J., Vinter J. G., Inorg. Chem. 17 (1978) 776; (b) Mason J., Multinuclear NMR, Plenum Press, New York, 1987, p. 350; (c) Berger, S., Braun, S., Kalinowski, H.-O., NMR Spectroscopy of the Non-Metallic Elements, John Wiley & Sons, Chichester, 1997, p. 206.

[23] Gieren A., Dederer B., Angew. Chem. 89 (1977) 190; Angew. Chem. Int. Ed. Engl.16 (1977) 179.

[24] Dederer B., Gieren A., Naturwissenschaften 66 (1979) 470.

[25] Iwasaki F., Acta Crystallogr. Sect. B B36 (1980) 1700.

[26] Roesky H. W., Weber K. L., Noltemeyer M., Sheldrick G. M., Z. Naturforsch. B 39B (1984).

[27] Butler R. N., Duffy J. P., McArdle P., Cunningham D., O'Halloran G.A., J. Chem. Soc., Chem. Commun. 17 (1989) 1210.

[28] Zibarev A. V., Lork E., Mews R., J. Chem. Soc., Chem. Commun. 9 (1998) 991.

[29] Romano R. M., Della Védova C. O., Boese R., J. Mol. Struct. 475 (1999) 1.

[30] Bagryanskaya I. Yu., Gatilov Yu. V., Makarov A. Yu., Shakirov M. M., Shuvaev K. V., Zibarev A. V., Russ. J. Gen. Chem. 71 (2001) 1050.

[31] Romano R. M., Della Védova C. O., J. Mol. Struct. 522 (2000) 1.

[32] Muchall H., J. Phys. Chem. A 105 (2001) 632.

Table 1
Vibrational Spectra of $(C_6H_5)_3CNSO$ Compared to the Raman Spectra of Related Trityl Compounds.[a]

$(C_6H_5)_3CNH_2$	$(C_6H_5)_3CCl$	$(C_6H_5)_3CN_3$	$(C_6H_5)_3COH$	$(C_6H_5)_3CNF_2$	$(C_6H_5)_3CNSO$ Raman	IR	
3367(2)							$\nu(NH_2)$
3301(4)							
3192(2)	3193(1)	3194(1)	3198(<0.5)	3195(2)	3189(1)		
3158(2)	3161(3)	3162(1)	3166(1)	3161(3)	3164(2)	3101(w)	
3072sh(40)						3084(m)	
3064(63)	3068(78)	3065(86)	3068(65)	3076(76)	3067(64)	3063(m)	
3045(42)	3056(52)sh			3065(56)sh	3058(42)sh	3056(sh)	
	3038(10)	3038(1)		3043(11)	3036(8)	3032(m)	
3023(9)	3023(8)	3024(1)		3026(7)	3023(7)	3021(m)	ν(CH)
3001(3)	3004(4)	3004(1)	3007(2)	3003(6)	3004(4)	3002(m)	
2971(3)	2971(4)	2973(2)	2986(2)	2978(4)	2977(3)		
	2924(1)		2937(10)	2914(2)	2936(1)		
	2897(1)	2906(1)			2905(1)		
				2894(1)	2890(1)		
2786(<0.5)	2769(1)	2772(<0.5)	2792(<0.5)		2774(<0.5)		
	2722(<0.5)						
2580(<0.5)	2576(1)	2569(1)	2585(1)	2568(1)	2570(<0.5)		
			2249(4)				
		2098(2)					ν_{as}(NNN)
	1639(1)sh						
					1609sh	1604(sh)	
1598(16)	1595(16)	1599(18)	1602(18)	1601(15)	1598(11)	1595(ms)	ν(CC)
1583(7)	1584(10)sh	1585(3)	1586(3)	1589(8)sh	1585(8)	1582(sh)	
		1490(1)	1499(<0.5)	1495(1)		1490(vs)	
1445(1)	1448(1)	1450(2)	1450(2)	1447(1)	1449(1)	1448(vs)	
						1445(vs)	
		1380(1)	1377(<0.5)			1393(m)	
	1321(1)	1326(1)	1345(1)	1338(1)	1328(1)	1325(ms)	
1302(<0.5)	1303(<0.5)		1300(<0.5)				
					1294(5)	1292(vs)	ν_{as}(NSO)
	1284(1)	1282(1)		1283(<0.5)		1283(vs)	
		1263(3)					ν_s(NNN)
1217(3)	1213(4)			1219(2)			
	1203(4)					1194(s)	
1186(13)	1187(11)	1188(8)	1199(7)	1193(10)	1189(10)	1188(s)	
						1180(s)	
1163(10)	1159(10)	1167(3)	1173(12)		1164(5)	1161(m)	
1159(11)	1149(23)	1157(12)		1152(13)	1152(7)	1150(m)	
					1123(23)	1124(vs)	ν_s(NSO)
1094(1)	1084(1)	1087(1)	1087(2)	1082(1)	1085(2)	1083(s)	
1078(1)							
1057(2)					1065(1)		
1029(17)	1034(20)	1033(19)	1039(18)	1036(17)	1034(17)	1037(ms)	
						1033(ms)	
1004(65)	1003(54)	1002(68)	1005(66)	1004(35)	1003(40)	1002(ms)	
	988sh			991(15)	995sh	991(w)	
						985(w)	
				965(3)	975(1)	976(w)	

Table 1(contd.)
Vibrational Spectra of $(C_6H_5)_3CNSO$ Compared to the Raman Spectra of Related Trityl Compounds.[a]

$(C_6H_5)CNH_2$	$(C_6H_5)CCl$	$(C_6H_5)CN_3$	$(C_6H_5)COH$	$(C_6H_5)CNF_2$	$(C_6H_5)CNSO$ Raman	IR	
954(1)				952(3)	945(2)	942(w)	
920(1)	932(1)	949(2)	927(3)	927(2)	936(3)	933(w)	
910(1)	896(3)	900(3)		914(2)	906(2)	904(s)	
					898(4)	898(vs)	
			877(3)	881(1)			
867(2)				858(4)	861(<0.5)		
849(1)	849(2)	844(1)		848(3)sh		850(m)	
						847(m)	
	820(5)						
						763(vs)	
767(2)	766(1)	762(1)	766(2)	771(1)	755(2)	758(vs)	
754(1)	741(1)	741(1)		748(<0.5)		747(vs)	
				711(4)		703(vs)	
700(14)	703(1)	704(3)	701(12)	703(5)	689(10)	687(s)	
	669(12)	670(4)		660(3)	653(2)	652(s)	
					640(2)	639(vs)	
629(3)	629(3)						
620(9)	619(6)	619(7)	621(9)	620(7)	621(7)	618(m)	
585(1)				596(3)			
					585(2)	582(m)	δ(NSO)
				541(5)			
533(2)		531(1)			533(2)	531(m)	
	511(1)sh	508(1)		517(1)	509(1)	502(s)	
	497(7)						
445(2)		455(2)	450(1)				
416(<0.5)	406(1)	411(4)			416(2)	416(s)	
						413(s)	
						412(s)	
376(1)		386(<0.5)	384(2)		389(3)		
342(1)	350(23)	334(2)	354(<0.5)	362(4)			
311(3)	319(6)	316(1)	319(<0.5)	312(8)	324(2)		
		307(1)			304(2)		
281(8)	281(13)	280(9)	285(9)	286(12)	281(9)		
250(9)	245(5)		249(7)	263(10)	253(3)		
234(2)		238(9)		239(3)	243(2)		
208(4)	183(13)	214(5)		188(2)	209(9)		
				140(15)sh	160(8)		
				129(27)sh			
111(90)				117(35)sh	116sh		
99(100)	102(100)	103(100)	94(100)	95(100)	105(100)		

w = weak; m= medium; ms = medium strong; s = strong; vs = very strong; sh = shoulder. [a] All data from this study.

Table 2

^{1}H, ^{13}C and ^{14}N NMR Spectroscopic Data for $(C_6H_5)_3CNSO$ in CH_2Cl_2.

		δ (ppm)	$\Delta\nu_{1/2}$ (Hz)
^{1}H		6.75 (m)	
^{13}C	o/m $(C_6H_5)_3$	128.19/128.62	
	p $(C_6H_5)_3$	127.64	
	ipso $(C_6H_5)_3$	144.50	
	$C(C_6H_5)_3$	80.98	
^{14}N		-39	700

Table 3

Crystal Data for $(C_6H_5)_3CNSO$.

chemical formula	$C_{19}\ H_{15}\ N\ S\ O$
fw	305.38
T, K	223(2)K
space group	triclinic $P\bar{1}$ (No. 2)
a, Å	8.9642(9)
b, Å	9.2135(9)
c, Å	11.0645(11)
α, deg	93.578(2)
β, deg	101.098(2)
γ, deg	118.142(2)
V, Å^3	778.24(13)
Z	2
ρ_{calc}, g cm^{-3}	1.303
μ, mm^{-1}	0.209
R_1,[a] wR_2[b] [I > 2σ(I)]	$R_1 = 0.0345$, $wR_2 = 0.0910$
R_1,[a] wR_2[b] (all data)	$R_1 = 0.0409$, $wR_2 = 0.0962$

[a] $R1 = (\Sigma(F_0-F_c)/F_0)$. [b] $wR2 = [\Sigma(w(F_0-F_c)^2)w/F_0^2)]^{1/2}$.

Table 4

Atomic Coordinates (x 10^4) and Equivalent Isotropic Displacement Parameters ($Å^2$x 10^3) for $(C_6H_5)_3CNSO$.

	x	y	z	U(eq)[a]
O(1)	2025(2)	5053(2)	5284(1)	51(1)
S(1)	601(1)	3352(1)	4857(1)	35(1)
N(1)	83(2)	2101(2)	5706(1)	29(1)
C(1)	678(2)	2061(2)	7047(1)	24(1)
C(2)	1161(2)	3684(2)	7898(1)	26(1)
C(3)	132(2)	4433(2)	7655(2)	33(1)
C(4)	501(3)	5854(2)	8438(2)	43(1)
C(5)	1899(3)	6541(2)	9483(2)	45(1)
C(6)	2910(3)	5794(2)	9747(2)	44(1)
C(7)	2548(2)	4370(2)	8960(2)	34(1)
C(8)	-884(2)	573(2)	7349(1)	25(1)
C(9)	-1029(2)	490(2)	8571(2)	32(1)
C(10)	-2418(2)	-865(2)	8844(2)	41(1)
C(11)	-3677(3)	-2151(2)	7898(2)	46(1)
C(12)	-3543(2)	-2081(2)	6683(2)	46(1)
C(13)	-2158(2)	-734(2)	6406(2)	35(1)
C(14)	2246(2)	1761(2)	7130(1)	25(1)
C(15)	3739(2)	2953(2)	6824(2)	31(1)
C(16)	5132(2)	2689(2)	6826(2)	39(1)
C(17)	5072(2)	1239(2)	7143(2)	43(1)
C(18)	3622(2)	68(3)	7469(2)	45(1)
C(19)	2210(2)	322(2)	7463(2)	34(1)

[a] U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

Table 5

Experimental Bond Lengths [Å] and Angles [°] for $(C_6H_5)_3CNSO$.

O(1)-S(1)	1.450(1)	O(1)-S(1)-N(1)	122.61(8)
S(1)-N(1)	1.492(1)	C(1)-N(1)-S(1)	136.8(1)
N(1)-C(1)	1.486(2)	N(1)-C(1)-C(2)	111.8(1)
C(1)-C(2)	1.538(2)	N(1)-C(1)-C(8)	105.5(1)
C(1)-C(8)	1.542(2)	N(1)-C(1)-C(14)	105.3(1)
C(1)-C(14)	1.544(2)	C(2)-C(1)-C(8)	109.7(1)
C(4)-C(5)	1.382(3)	C(2)-C(1)-C(14)	112.5(1)
C(11)-C(12)	1.375(2)	C(8)-C(1)-C(14)	111.8(1)
C(16)-C(17)	1.382(2)	C(5)-C(4)-C(3)	120.2(2)

Figure Captions

Fig. 1. Infrared and Raman Spectra of $(C_6H_5)_3CNSO$.

Fig. 2. Structure of the $(C_6H_5)_3CNSO$ Molecule showing the Dimer Formation via S···O Contacts. Thermal Ellipsoids are shown at the 50% Probability Level.

Figure 1

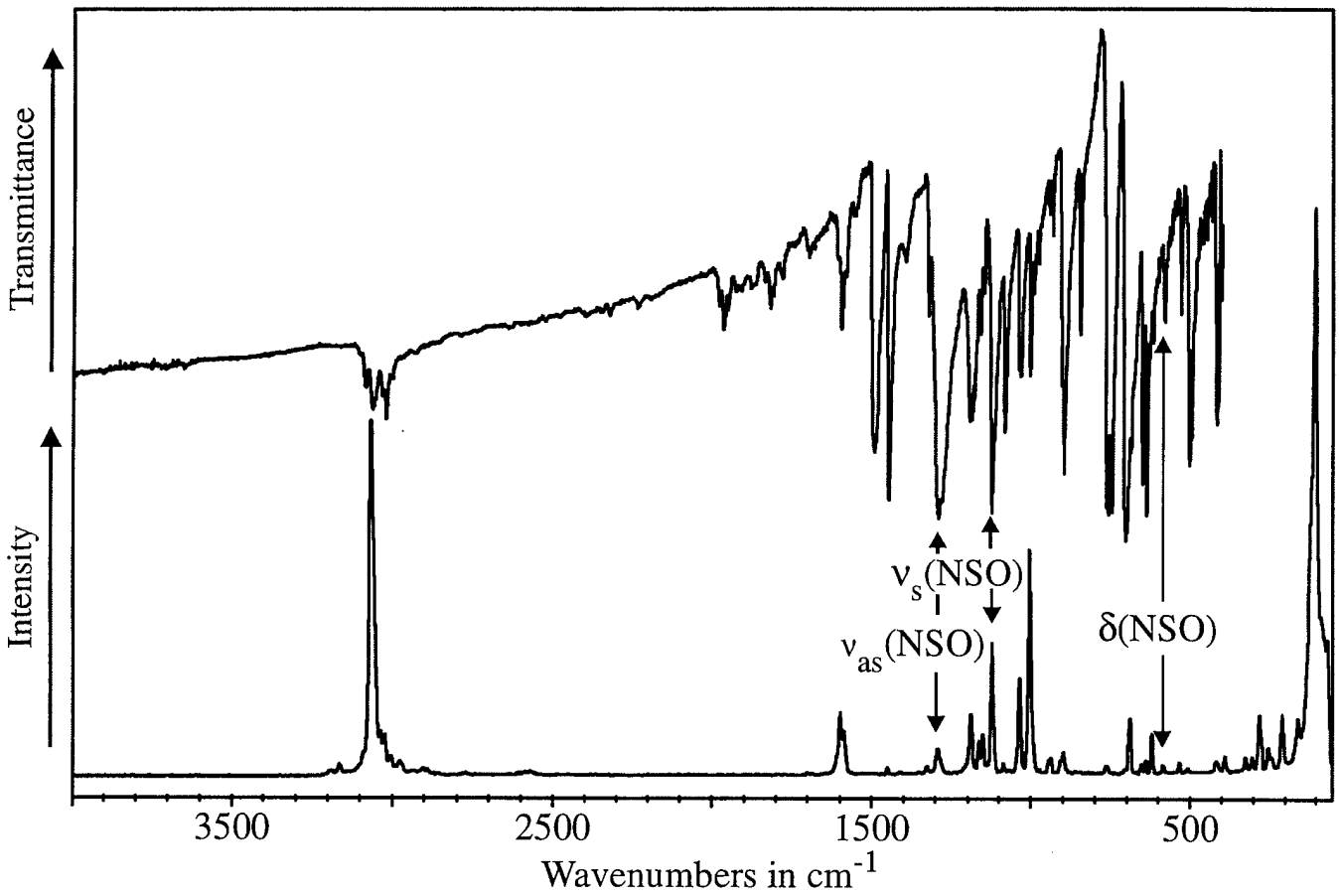
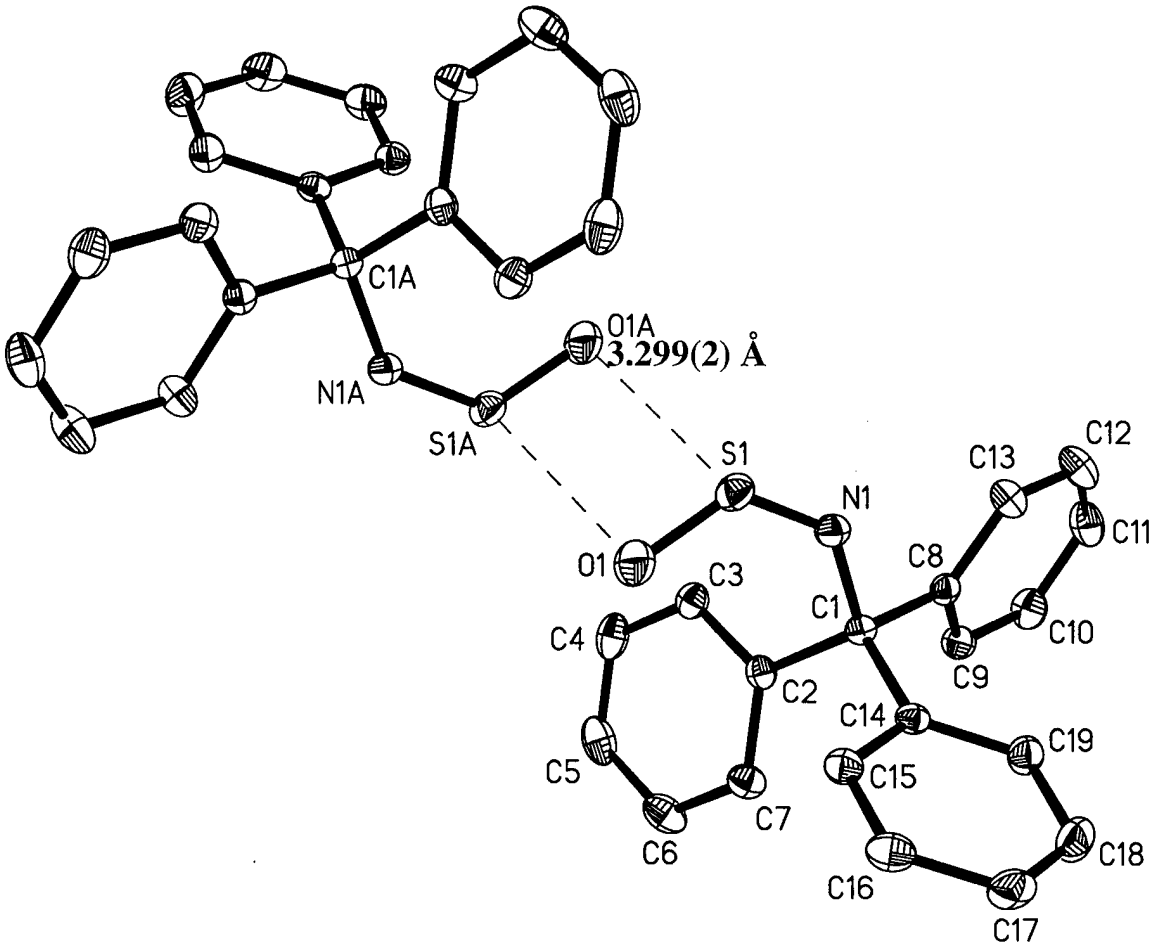

Transmittance
Intensity
ν_s(NSO)
ν_{as}(NSO)
δ(NSO)
3500
2500
1500
500
Wavenumbers in cm^{-1}

Figure 2


C1A
O1A
3.299(2) Å
N1A
S1A
S1
N1
C13
C12
C11
O1
C3
C8
C1
C10
C4
C9
C2
C14
C19
C5
C15
C7
C6
C18
C16
C17

Tritylsulfinylamine: A New Member in the Family of Sulfinylamines

Karl O. Christe, Michael Gerken, Ralf Haiges, Stefan Schneider, Thorsten Schroer, Fook S. Tham, and Ashwani Vij

Contribution from the Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, Los Angeles, California 90089, Propulsion Sciences and Advanced Concepts Division, Air Force Research Laboratory (AFRL/PRS), Edwards AFB, California 93524, and the University of California, Riverside, California 92521.