C$\overset{\cdots}{-}$N bond should be appreciably slower than rotation about the C—N single bonds, which accounts for the substantially higher barrier to isopropyl methyl group exchange in the *i*-Pr_2mtc complex. Finally, it is pleasing to see that the activation parameters for isopropyl methyl group exchange in [Ti(*i*-Pr_2mtc)$_4$] (Table III) are similar to those for rotation about the C$\overset{\cdots}{-}$N bond in [Ti(Me_2mtc)$_4$] (Table II).

Acknowledgment. The support of this research by National Science Foundation Grant GP-30691X is gratefully acknowledged. R.C.F. thanks Dr. M. L. H. Green for his generous hospitality during a period of sabbatical leave.

Registry No. Ti(Me_2mtc)$_4$, 66791-67-1; Zr(Me_2mtc)$_4$, 66791-68-2; Ti(*i*-Pr_2mtc)$_4$, 66758-38-1.

Contribution from the Departments of Chemistry, University of Calgary, Calgary, Alberta T2N 1N4, Canada,
and University of Arkansas, Fayetteville, Arkansas 72701

Crystal and Molecular Structures of $C_7H_8(S_3N)_2$: Substituent Effects on the S_3N Chromophore

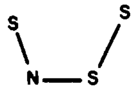
A. W. CORDES,[1a] H. KOENIG,[1b] M. C. NOBLE,[1a] and R. T. OAKLEY*[1b,c]

Received December 21, 1982

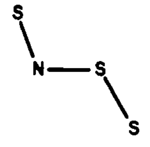
The isolation of $C_7H_8(S_3N)_2$ from the reaction of tetrasulfur dinitride with norbornadiene is reported. The crystal and molecular structures of the compound have been determined by X-ray crystallography; the crystals are monoclinic, space group $P2_1/c$, with $a = 9.216$ (1) Å, $b = 14.318$ (2) Å, $c = 10.229$ (1) Å, $\beta = 104.57$ (1)°, $V = 1306.3$ (5) Å^3, and $Z = 4$. The structure was solved by direct methods and refined by Fourier and full-matrix least-squares procedures to give a final $R = 0.037$ and $R_w = 0.053$ for 1627 observed reflections. The molecule consists of a norbornenyl unit with two S_3N groups attached in an exo fashion at the 2,3-positions. Both S_3N groups possess a cis formation with the following mean bond lengths: d(S–S) = 1.903 Å, d(SS–N) = 1.572 Å, d(CS–N) = 1.641 Å. The molecule exhibits a pair of strong visible absorptions at 433 and 408 nm, which are assigned to the excitonically coupled $\pi^* \rightarrow \pi^*$ transitions of the two S_3N chromophores. The effect of different substituents on the $\pi^* \rightarrow \pi^*$ transition energy of X–S_3N derivatives is described; π-donor ligands induce a large bathochromic shift.

Introduction

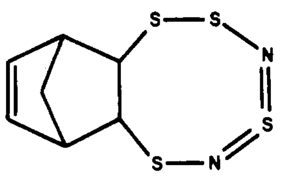
The preparation of the S_3N^- anion has recently been reported.[2] While the connectivity of the atoms, i.e. S–N–S–S, has been confirmed by the characterization of several metal complexes,[3] the conformation of the four-atom sequence in the free ion has not been unequivocally established. Ab initio Hartree–Fock–Slater (HFS) molecular orbital calculations have indicated a slight preference for the cis geometry **1** relative to the trans form **2**,[2] but our attempts to confirm this prediction by crystallographic methods have been unsuccessful.[4]



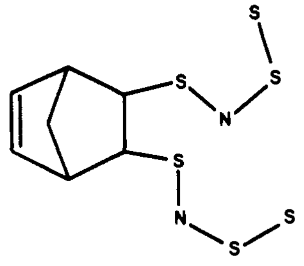
1



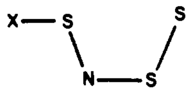
2



3



4



5

During our study of the reaction of tetrasulfur dinitride, S_4N_2, with norbornadiene, which yields $C_7H_8{\cdot}S_4N_2$ (**3**) as the major product,[5] we were able to isolate in trace quantities a second compound with the elemental composition, $C_7H_8{\cdot}S_6N_2$. The crystal and molecular structures of this material, which we report herein, reveal that it is an S-ester of the hypothetical acid HS_3N with two S_3N units per molecule, i.e. **4**. In addition to providing evidence in favor of the cis geometry for the S_3N^- anion itself, the compound **4** allows a comparison of the effects of inductive and conjugative interactions between the substituent and the S_3N chromophore in molecules of the type X–S_3N, e.g. **5**.[6-8] The effects of excitonic coupling between the two S_3N units of **4** are also reported.

Experimental Section

Materials and General Procedures. Tetrasulfur dinitride was prepared as recently described.[9] UV–vis spectra were recorded on

---

(1) (a) University of Arkansas. (b) University of Calgary. (c) Present address: Department of Chemistry, University of Guelph, Guelph, Ontario N1G 2W1, Canada.

(2) Bojes, J.; Chivers, T.; Laidlaw, W. G.; Trsic, M. *J. Am. Chem. Soc.* **1982**, *104*, 4837.

(3) (a) Bojes, J.; Chivers, T.; Codding, P. W. *J. Chem. Soc., Chem. Commun.* **1981**, 1171. (b) Weiss, J. *Angew Chem., Int. Ed. Engl.* **1982**, *21*, 705.

(4) Crystals with large cations such as $[Ph_3PNPPh_3]^+$ successfully prevent anion–anion interactions but also tend to create anion disorders which cannot be resolved: Cordes, A. W.; Swepston, A. N., unpublished work.

(5) Koenig, H.; Oakley, R. T.; Cordes, A. W.; Noble, M. C. *Can. J. Chem.* **1983**, *61*, 1185.

(6) (a) Chivers, R.; Laidlaw, W. G.; Oakley, R. T.; Trsic, M. *J. Am. Chem. Soc.* **1980**, *102*, 5773. (b) Burford, N.; Chivers, T.; Cordes, A. W.; Oakley, R. T.; Pennington, W. T.; Swepston, P. N. *Inorg. Chem.* **1981**, *20*, 4430.

(7) Chivers, T.; Cordes, A. W.; Oakley, R. T.; Swepston, P. N. *Inorg. Chem.* **1981**, *20*, 2376.

(8) Tamura, C.; Aibe, K.; Sato, S.; Hata, T.; Morimura, S.; Yoshioka, T. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1977**, *B33*, 3918.

0020-1669/83/1322-3375$01.50/0

a Cary 219 spectrophotometer. ^1H NMR spectra were recorded on a Varian XL-200 NMR spectrometer. Elemental analyses were performed by Lada Malek at the University of Calgary.

Preparation of $C_7H_8(S_3N)_2$ (4). The reaction of S_4N_2 and norbornadiene under conditions of high dilution has been described.[5] When an excess (ca. 10-fold molar) of norbornadiene is added rapidly to a solution of S_4N_2 in methylene chloride, the yield of **3** is drastically reduced (less than 1%) and small quantities of **4** (<1% based on S_4N_2) are formed. The two components can be separated by gel permeation chromatography on a BioBeads SX-8 column with toluene as eluting solvent; R_f values are 0.80 (**3**) and 0.85 (**4**). The latter can be recrystallized from diethyl ether at −20 °C as orange rectangular blocks, mp 72.5–73.5 °C. Anal. Calcd for $C_7H_8S_6N_2$: C, 26.90; H, 2.59; N, 8.96. Found: C, 27.45; H, 2.62; N, 9.02. UV–vis (CH_2Cl_2, λ_{max} (log ϵ)): 433 (4.2), 408 (4.3), 291 (3.7) nm. ^1H NMR ($CDCl_3$): δ 6.43 (2 H, t, $H_{5,6}$, J = 1.8 Hz), 4.23 (2 H, d, $H_{1,4}$, J = 2.1 Hz), 3.35 (2 H, t, $H_{2,3}$, J = 1.8 Hz), 1.98, 1.78 (2 H, AB, $H_{7,7'}$, $J_{7,7'}$ = 10.1 Hz).

X-ray Analysis of $C_7H_8(S_3N)_2$. Crystals of **4** suitable for X-ray work were obtained as described above. The crystal used for data collection was mounted with epoxy on a glass fiber. All data were collected with an Enraf-Nonius CAD-4 diffractometer and graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation. A least-squares calculation using the diffractometer settings for 25 carefully centered reflections gave the following cell parameters (at 21 °C): a = 9.216 (1) Å, b = 14.318 (2) Å, c = 10.229 (1) Å, β = 104.57 (1)°, and V = 1306.3 (5) Å^3. For $C_7H_8S_6N_2$ with M_r = 312.54 and Z = 4, D_{calcd} = 1.59 g cm^{-3} and F_{000} = 640.

Systematic absences of $h0l$ for l odd and $0k0$ for k odd uniquely indicated the space group $P2_1/c$. A total of 2424 unique reflections were measured using θ–1.67θ scans for θ from 2 to 25° (h = 0 to 10, k = 0 to 17, l = −12 to 12). The scan range was (0.6 + 0.35 tan θ), and scan speeds varied from 4 to 20° min^{-1}. A total of 797 reflections had $I < 3\sigma(I)$ and were considered unobserved. The intensities of three reflections (1,4,−2, 0,0,2, −1,1,3) which were measured periodically during the data collection varied by less than 4.5% and thus indicated general crystal stability. An absorption correction (μ = 9.77 cm^{-1}) based on ψ scans gave correction factors that ranged from 0.80 to 1.00.

The structure was solved by direct methods (MULTAN78)[10] and refined by Fourier and least-squares techniques. The final full-matrix least-squares refinement based on F^2 included 136 parameters (positional and anisotropic thermal parameters for all non-hydrogen atoms) and had a final parameter:reflection ratio of 1:12.0. Hydrogen atoms were not refined but were included in the structure factor calculations at idealized positions and isotropic thermal parameters of 5.0 Å^2. The weighting scheme, based on counting statistics with an instability factor of 5%, gave no systematic variation of $\Delta F/\sigma(F)$ as a function of either F or sin θ. No secondary extinction correction was made. In the final cycle of refinement the maximum shift/error was 0.0008, R = 0.037, R_w = 0.053, and GOF = 1.43. The final difference map had a maximum value of 0.44 e Å^{-3}. Neutral-atom scattering factors corrected for real and imaginary anomalous dispersion corrections were used.[11] The computer programs used were those provided by the Enraf-Nonius SDP program package.

Results and Discussion

Formation of $C_7H_8(S_3N)_2$. The reaction of S_4N_2 with norbornadiene using high dilution addition techniques affords $C_7H_8{\cdot}S_4N_2$ (**3**) in 15% yield.[5] The importance of this method of mixing becomes apparent if the reagents are introduced rapidly and an excess of norbornadiene is used. Under these latter conditions, radical polymerization competes with simple addition, and the yield of **3** is limited to trace (<1%) quantities. At the same time another soluble compound is formed, albeit in low yield also (<1%). This second component has the empirical formula $C_7H_8{\cdot}S_6N_2$. While its ^1H NMR spectrum suggests a symmetrical substitution of the norbornenyl group by two sulfur atoms (the $H_{2,3}$ signal has a δ value of 3.35), the absolute elucidation of the molecular structure **4** has required the use of X-ray crystallography.

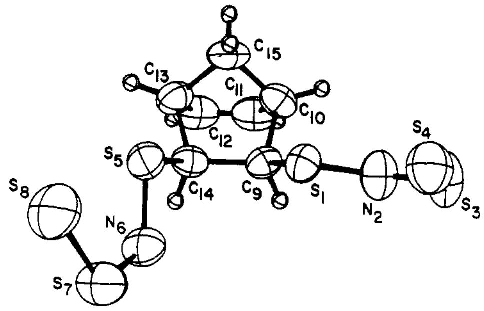


Figure 1. ORTEP drawing (50% probability ellipsoids) of $C_7H_8(S_3N)_2$ showing the atom-numbering scheme.

Table I. Positional Parameters (and their Standard Deviations) for the Non-Hydrogen Atoms of $C_7H_8(S_3N)_2$ [a]

atom	x	y	z	B, Å^2
S1	0.3569 (1)	0.39787 (6)	0.12722 (8)	4.18 (2)
S3	0.1734 (1)	0.25135 (9)	0.0107 (1)	6.63 (3)
S4	0.3462 (1)	0.21151 (8)	−0.0451 (1)	6.25 (3)
S5	0.6194 (1)	0.52437 (7)	0.25944 (9)	4.44 (2)
S7	0.8247 (1)	0.40151 (8)	0.4141 (1)	5.75 (2)
S8	0.9403 (1)	0.4326 (1)	0.2910 (1)	6.79 (3)
N2	0.1940 (3)	0.3450 (2)	0.0938 (4)	5.75 (8)
N6	0.6675 (3)	0.4508 (2)	0.3864 (3)	4.89 (7)
C9	0.3032 (4)	0.4961 (2)	0.2177 (3)	3.84 (7)
C10	0.1967 (4)	0.5656 (3)	0.1207 (4)	4.79 (9)
C11	0.1467 (4)	0.6336 (3)	0.2115 (4)	5.9 (1)
C12	0.2635 (5)	0.6863 (3)	0.2658 (4)	5.8 (1)
C13	0.3928 (4)	0.6547 (3)	0.2136 (4)	4.88 (9)
C14	0.4377 (4)	0.5589 (3)	0.2836 (3)	3.99 (7)
C15	0.3098 (5)	0.6240 (3)	0.0726 (3)	5.11 (9)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent parameter $B = {}^4/_3(a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ac\beta_{13} \cos \beta)$.

Table II. Selected Non-Hydrogen Distances (Å) and Angles (deg) for $C_7H_8(S_3N)_2$ [a]

S1–N2	1.639 (3)	C9–C10	1.564 (4)
S1–C9	1.819 (3)	C9–C14	1.542 (4)
S3–S4	1.910 (1)	C10–C11	1.496 (5)
S3–N2	1.573 (3)	C10–C15	1.513 (5)
S5–N6	1.644 (3)	C11–C12	1.318 (5)
S5–C14	1.821 (3)	C12–C13	1.493 (5)
S7–S8	1.896 (1)	C13–C14	1.555 (4)
S7–N6	1.571 (3)		
N2–S1–C9	96.4 (1)	C9–C10–C11	105.2 (2)
S4–S3–N2	114.8 (1)	C9–C10–C15	100.6 (3)
N6–S5–C14	98.1 (1)	C11–C10–C15	100.7 (3)
S8–S7–N6	114.9 (1)	C10–C11–C12	106.7 (3)
S1–N2–S3	119.1 (2)	C11–C12–C13	108.5 (3)
S5–N6–S7	118.9 (2)	C12–C13–C14	104.3 (3)
S1–C9–C10	112.1 (2)	C12–C13–C15	99.8 (3)
S1–C9–C14	112.4 (2)	C14–C13–C15	101.2 (2)
S5–C14–C9	116.6 (2)	C9–C14–C13	102.8 (2)
S5–C14–C13	108.9 (2)	C10–C15–C13	94.3 (2)
C10–C9–C14	102.4 (2)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Molecular Structure of $C_7H_8(S_3N)_2$. Crystals of the title compound consist of discrete molecules of **4**; there are no unusually short intermolecular contacts. An ORTEP drawing of the molecule illustrating the relative orientations of the two S_3N groups and indicating the atomic numbering scheme is shown in Figure 1. Atomic coordinates for the molecule are listed in Table I, and bond distance and angle information is

---

(9) Chivers, T.; Codding, P. W.; Laidlaw, W. G.; Liblong, S. W.; Oakley, R. T.; Trsic, M. *J. Am. Chem. Soc.* **1983**, *105*, 1186.

(10) Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J.-P.; Woolfson, M. M. "MULTAN78—A system of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data"; 1978, University of York: York, England, and University of Louvain: Louvain, Belgium, 1978.

(11) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

Table III. Bond Lengths (Å), Valence Angles (deg), and $\lambda_{max}(\pi^* \rightarrow \pi^*)$ Values (nm) for X-S_3N Derivatives

compd	*d*(S-S)	*d*(SS-N)	*d*(XS-N)	∠NSS	∠SNS	∠XSN	λ_{max}	ref
$C_7H_8(S_3N)_2$ [a]	1.903	1.572	1.641	114.9	119.0	97.2	433, 408	this work
$Ph_4As^+S_4N^-$ [b]	1.93	1.56	1.62	114.0	120.1	111.5	582	6a
$[(Ph_3P)_2N]^+S_4N^-$ [b]	1.91	1.62	1.57	111.0	120.5	110.5	582	6b
Ph_3PN-S_3N	1.908	1.592	1.587	111.4	120.9	107.7	491	7
$C_{11}H_{20}O_2N$-S_3N	1.912	1.569	1.657	114.9	119.2	105.7	*c*	8

[a] Mean values from two S_3N groups. [b] Mean values from two disorder models. [c] Not reported.

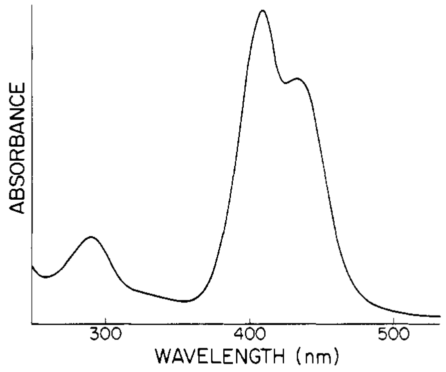


Figure 2. UV-visible spectrum (in CH_2Cl_2) of $C_7H_8(S_3N)_2$.

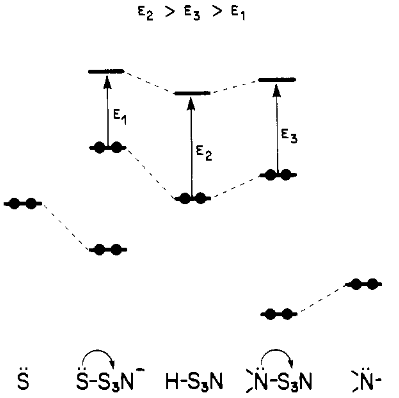


Figure 3. Qualitative MO diagram illustrating the effect of soft (e.g. S) and hard (e.g. N) π-donors and nonconjugating (e.g. H) ligands on the frontier π^* levels and the $\pi^* \rightarrow \pi^*$ excitation energies of X–S_3N derivatives.

provided in Table II. The molecule consists of a norbornenyl group with two S_3N residues bound in an exo fashion at the 2,3-positions. Both S_3N units are planar (to within 0.006 and 0.007 Å), and their mean planes intersect with a dihedral angle of 82.4°. While complete freedom of rotation about the S1–C9 and S5–C14 bonds is not expected (because of steric crowding), the observed disposition of the two S_3N groups has no simple interpretation. The bond lengths and angles within the two S_3N groups are remarkably similar; their mean values are presented in Table III, along with the corresponding parametes observed in other X–S_3N structures. For this series of compounds the S–S distances remain relatively constant at 1.89–1.93 Å, a value in keeping with their multiple-bond character.[2,6a] By contrast, the S–N bond lengths fluctuate in a seemingly random fashion. This observation is consistent with the results of ab initio HFS calculations on the S_4N^- anion,[6a] which showed that the total energy of the anion was insensitive to variations in the two S–N distances.

The reasons for the favoring of the cis conformation of S_3N^- and S_4N^- have been examined by both ab initio and MNDO methods.[2,6,12] We have carried out MNDO calculations on H–S_3N (as a model for 4) and find again a slight preference for the cis geometry relative to the trans (by about 5 kcal/mol) and an increase in the rotational barrier in comparison to that for S_3N^- itself. However, the numerical results probably underestimate the true energy differences; the restricted MNDO basis set sulfur (3s and 3p)[13] leads to a rather poor assessment of long-range sulfur–sulfur interactions.

Electronic Spectra of X–S_3N Derivatives. Ab initio HFS MO calculations on the cis conformation of the S_3N^- anion indicate that the ground state corresponds to a six-π-electron system and that the strong 470-nm absorption band in the visible spectrum of S_3N^- salts represents a $\pi^* \rightarrow \pi^*$ excitation.[2] Other molecules of the type X–S_3N also exhibit intense visible absorption bands (see Table III), and similar $\pi^* \rightarrow \pi^*$ transitions are likely to be responsible (this has been confirmed theoretically in the case of S_4N^-[6a]). In 4 the absorption appears as a pair of overlapping bands with maxima at 408 and 433 nm (Figure 2). This effect is, we believe, the result of an excitonic coupling[14] of the two S_3N chromophores. Such interactions between strong electric dipole allowed transitions are commonly observed in organic systems[15] but have not hitherto been reported for sulfur nitride derivatives. While strong $\pi^* \rightarrow \pi^*$ transitions are characteristic of these compounds,[9,16–19] the occurrence of two closely spaced chromophores in the same molecule, as in 4, is novel.[20] The weak higher energy band at 291 nm is probably a $\sigma \rightarrow \sigma^*$ transition. Such a band is predicted to occur in S_3N^- near 300 nm with an intensity of one-tenth of the $\pi^* \rightarrow \pi^*$ band.[21] Its observation in S_3N^- and S_4N^- salts has so far been prevented because of overlapping cation (e.g. $[Ph_3PNPPh_3]^+$) absorptions. However, it is observed in Ph_3PN–S_3N (at 314 nm).[7]

The isolation of 4 extends the series of known X–S_3N derivatives and provides an opportunity to evaluate qualitatively the separate influences of σ- and π-interactions between the ligand X and the six-π-electron four-orbital manifold of the S_3N unit. Covalent attachment of a group X onto a terminal atom of S_3N^- to form X–S_3N will affect the π-system in two ways. First, the formation of a σ-bond from a lone-pair orbital on sulfur will draw σ-electron density away from this atom. In response to this migration of σ-charge, there will be compensating back-polarization of π-charge toward the substituted atom. Secondly, in those cases where the ligand has orbitals which can interact conjugatively with the π-system, a more

---

(12) Gleiter, R.; Bartetzko, R. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1981**, *36B*, 492.

(13) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4399.

(14) Davydov, A. S. "Theory of Molecular Excitons"; Kasha, M., Oppenheimer, M., translators (Engl.); McGraw-Hill: New York, 1962.

(15) For example, see: (a) Harada, N.; Nakanishi, K. *Acc. Chem. Res.* **1972**, *5*, 257. (b) Schellman, J. A. *Ibid.* **1968**, *1*, 144. (c) Gouterman, M.; Holten, D.; Liberman, E. *Chem. Phys.* **1977**, *25*, 139.

(16) (a) Bojes, J.; Chivers, T.; Laidlaw, W. G.; Trsic, M. *J. Am. Chem. Soc.* **1979**, *101*, 4517. (b) Waluk, J. W.; Michl, J. *Inorg. Chem.* **1981**, *20*, 963.

(17) Waluk, J. W.; Michl, J. *Inorg. Chem.* **1982**, *21*, 556.

(18) Trsic, M.; Laidlaw, W. G.; Oakley, R. T. *Can. J. Chem.* **1982**, *60*, 2281.

(19) Burford, N.; Chivers, T.; Cordes, A. W.; Laidlaw, W. G.; Noble, M. C.; Oakley, R. T.; Swepston, P. N. *J. Am. Chem. Soc.* **1982**, *104*, 1282.

(20) The observed Davydov splitting (~1400 cm^{-1}) can be reproduced approximately in a model calculation in which the transition dipoles are assumed to lie on lines parallel to the C–S bonds and to originate from the carbon-bonded sulfurs. For transition dipoles of 3.0 D, a dipole–dipole interaction on the order of 10^3 cm^{-1} is expected.

(21) This corresponds to a 9a′ → 10a′ excitation: Laidlaw, W. G., personal communication.

direct and larger perturbation will occur. From a conceptual viewpoint the outcome of the latter conjugative interaction is more easily anticipated. The extension of the π-system of S_3N^- to include the X group will naturally lead to a decrease in the energy gap between the occupied and unoccupied orbitals. Thus the red shift observed for S_4N^- and Ph_3PN-S_3N relative to S_3N^- is as expected. The smaller shift for Ph_3PN-S_3N probably reflects the higher electronegativity of a nitrogen vs. a sulfur lone pair; its mixing with the frontier π orbitals of the S_3N chromophore will be less extensive (see Figure 3). Similar trends are observed in the $\pi^* \rightarrow \pi^*$ transition energies of carbonyl[22] and thiocarbonyl[23] groups possessing π-donor ligands.

In the present molecule **4** the absence of such conjugative effects allows an assessment of the first type of perturbation. While the result would be difficult to predict on an a priori basis, it is apparent that the conversion of a lone-pair orbital of S_3N^- into a C–S σ-bond in **4** leads to an increase in the $\pi^* \rightarrow \pi^*$ transition energy. In the light of this result the true magnitude of the conjugative effects in $X-S_3N$ derivatives becomes apparent. Relative to nonconjugating ligands (such as the norbornenyl group in **4**) soft π-donor ligands (such as sulfur) cause a bathochromic shift of up to 150 nm, while harder donors (e.g. nitrogen) produce somewhat smaller shifts (ca. 70 nm in Ph_3PN-S_3N).

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada, Research Corp., the National Science Foundation (EPSCOR Grant ISP 8011447), and the State of Arkansas for financial support. We also thank the NSERCC for a University Research Fellowship (to R.T.O.) and a Summer Undergraduate Scholarship (to H.K.). We are grateful to Professor W. G. Laidlaw for unpublished information on the calculated transition moments of the S_3N^- anion.

Registry No. **4**, 87191-27-3.

Supplementary Material Available: Tables of anisotropic thermal parameters (Table S1), structural parameters relating to hydrogen atoms (Table S2), and structure factor amplitudes for $C_7H_8(S_3N)_2$ (19 pages). Ordering information is given on any current masthead page.

---

[22] Porter, G.; Suppan, P. *Trans. Faraday Soc.* **1965**, *61*, 1664.

[23] (a) Fabian, J.; Viola, H.; Mayer, R. *Tetrahedron* **1967**, *23*, 4323. (b) Hui, M. H.; de Mayo, P.; Suau, R.; Ware, W. R. *Chem. Phys. Lett.* **1975**, *31*, 257.

Contribution from the Department of Chemistry,
National Tsing Hua University, Hsinchu, Taiwan 300

Interactions of *triangulo*-(μ-Carbonyl)decacarbonyl(μ-hydro)triferrate(1−), $HFe_3(CO)_{11}^-$, with Its Countercation and Solvent

C. K. CHEN and C. H. CHENG*

Received April 7, 1983

A series of $MHFe_3(CO)_{11}$ complexes (M = Li, Na, K, Rb, Cs) have been synthesized, and their ion-pairing phenomena in solutions and solid state have been studied by IR spectroscopy. In ether or dioxane, all the $MHFe_3(CO)_{11}$ salts exist as contact ion pairs. The ν value of the bridging CO of $HFe_3(CO)_{11}^-$ increases in the order $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$. In THF, $MHFe_3(CO)_{11}$ exists as less associated forms and contact ion pairs. The nature of these two forms was characterized by the crown ether titration of a representative member of the series, $KHFe_3(CO)_{11}$. The ratio of the less associated forms to the contact ion pairs was determined and found to decrease in the order $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$. In Me_2SO, CH_3CN, CH_3NO_2, or diglyme, only the less associated forms were observed for all $MHFe_3(CO)_{11}$ salts. The difference in the ν values of the bridging CO of the less associated forms in different solvents is explained in terms of hydrogen bonding between the oxygen of the bridging CO and the acidic protons of the solvent molecule. The interaction between solvent and μ-CO is best seen in alcohol solutions. $MHFe_3(CO)_{11}$ also exists in two forms in alcohol. One is the "less associated form" at 1745 cm^{-1}, while the other is the "solvated form" at 1699 cm^{-1} arising from the interaction of the bridging CO and the hydroxyl group in alcohol. The nature of the solvated form is different from that of the contact ion pair, and methods for distinguishing between the two species were described. In the solid state, besides the cation–bridging CO interaction, a cation–terminal CO interaction for the potassium and rubidium salts was also inferred from the similarity of the IR spectra at the lower frequency end of the terminal CO region of these salts and $[(i\text{-}Pr)_2NH_2][HFe_3(CO)_{11}]$ and the X-ray structure determination study of the latter complex.

Introduction

There has been considerable interest in the ion-pairing phenomena of the transition-metal carbonylates[1-14] due to the close relationships of the ion-pairing behaviors to the reactivities of the carbonylates. To date, the majority of the investigations were focused on mononuclear metal carbonylates.[1-12] Only two works are related to the ion pairings of dinuclear and trinuclear metal carbonyl anions. In the dinuclear system $MHFe_2(CO)_8$, with M = Li or Na, Collman et al.[13] have shown that the countercation formed a contact ion pair with the bridging carbonyl group of $HFe_2(CO)_8^-$ in THF, while in the trinuclear system $(Et_3NH)[HFe_3(CO)_{11}]$, Pribula and co-workers[3] had revealed that the proton in the tri-

---

(1) (a) Edgell, W. F.; Lyford, J., IV; Barbetta, A.; Jose, C. I. *J. Am. Chem. Soc.* **1971**, *93*, 6403. (b) Edgell, W. F.; Lyford, J., IV. *Ibid.* **1971**, *93*, 6407. (c) Edgell, W. F.; Yang, M. T.; Koizumi, N. *Ibid.* **1965**, *87*, 2563.

(2) Darensbourg, M. Y.; Darensbourg, D. J.; Burns, D.; Drew, D. A. *J. Am. Chem. Soc.* **1976**, *98*, 3127.

(3) Pribula, C. D.; Brown, T. L. *J. Organomet. Chem.* **1974**, *71*, 415.

(4) Collman, J. P.; Cawse, J. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1972**, *94*, 5905.

(5) Darensbourg, M. Y.; Burns, D. *Inorg. Chem.* **1974**, *13*, 2970.

(6) Darensbourg, M. Y.; Barros, H.; Borman, C. *J. Am. Chem. Soc.* **1977**, *99*, 1647.

(7) Darensbourg, M. Y.; Barros, H. *Inorg. Chem.* **1979**, *18*, 3286.

(8) Pannell, K. H.; Jackson, D. *J. Am. Chem. Soc.* **1976**, *98*, 4443.

(9) Darensbourg, M. Y.; Borman, C. *Inorg. Chem.* **1976**, *15*, 3121.

(10) Pannell, K. H.; Chen, Y.-S.; Belknap, K. L. *J. Chem. Soc., Chem. Commun.* **1977**, 362.

(11) Collman, J. P.; Finke, R. G.; Cawse, J. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1978**, *100*, 4766.

(12) Collman, J. P.; Finke, R. G.; Cawse, J. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 2516.

(13) Collman, J. P.; Finke, R. G.; Matlock, P. L.; Wahren, R.; Komoto, R. G.; Brauman, J. I. *J. Am. Chem. Soc.* **1978**, *100*, 1119.

(14) Wilkinson, J. R.; Todd, L. J. *J. Organomet. Chem.* **1976**, *118*, 199.

0020-1669/83/1322-3378$01.50/0 © 1983 American Chemical Society