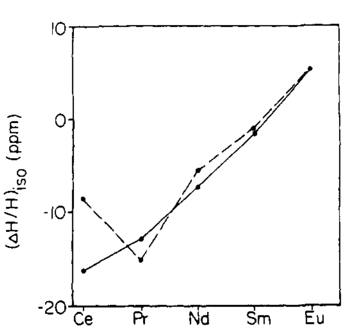

Figure 4. Plot of observed inner-ring meso ^1H isotropic shifts (293 K) for $Ln_2(OEP)_3$(- - -) and Bleaney's predicted dipolar shift values normalized for Eu (—) vs lanthanide.

II and compared to the observed ^{13}C isotropic shifts. As a general observation, there is very good agreement qualitatively, save for the α-carbon nuclei, between the observed isotropic shifts and those calculated on the basis of a metal-centered dipolar shift model. This is further confirmation that the solution geometry, proposed on the basis of the ^1H shifts and used herein, is indeed correct. The discrepency at α-carbon, the carbon atom closest to cerium, signals that some covalency must occur, whether from direct f orbital overlap or indirect spin polarization of the 6s or 6p orbitals. This is most manifest at the α-carbon of the outer ring, the ring which is closest to cerium.[20] There is no direct way to measure $(\Delta H/H)_{con}$ for the outer-ring carbon atoms; instead one must rely on indirect method—solution of simultaneous equations with numerous assumptions about spin delocalization—for separating $(\Delta H/H)_{con}$ from $(\Delta H/H)^{LC}_{dip}$. In the only complete study following this line of analysis, Goff[21] calculated $(\Delta H/H)_{con}$, $(\Delta H/H)^{LC}_{dip}$, and spin densities for the low-spin bis(1-methylimidazole) adduct of Fe(TPP)Cl. In this case the isotropic shife were as large as 100 ppm. Our attempts to separate ^{13}C contact from ligand-centered dipolar shifts for the outer-ring carbon atoms produced only nonsensical numerical results. This undoubtedly is due to the small isotropic shifts in $Ce_2(OEP)_3$ and the numerous assumptions necessary for a successful calculation.[22]

There is substantially less covalency, perhaps none, involving the inner OEP ring, the large shifts resulting from the metal-centered dipolar interaction with *two* equally distant cerium(III) ions. At an average Ce–N distance of 2.76 Å, it appears that the 4f orbitals are too contracted to interact covalently with the inner porphyrin ring.

Analysis of the ^{13}C isotropic shifts for $Pr_2(OEP)_3$ is problematic.[23] Were the shifts entirely metal-centered dipolar and the geometry—including disposition of the alkyl groups—identical, then the same pattern of shifts as seen for $Ce_2(OEP)_3$ would be expected. This is not observed. Because the ^{13}C and ^1H isotropic shifts are small and the term $(3\cos^2\theta - 1)/r^3$ is quite sensitive to changes in geometry, we chose not to proceed further with calculations. In summary, the ^{13}C $Pr_2(OEP)_3$ isotropic shifts appear irregular, particularly at the α- and β-positions, and may have sizeable contact and ligand-centered dipolar shift contributions.

Comparison of the isotropic shifts of $Ce_2(OEP)_3$ and $Pr_2(OEP)_3$, whether ^{13}C or ^1H, signals another difficulty: the relative magnitudes are not consistant with theory. According to the calculations of Bleaney,[16] metal-based dipolar shifts of Ce complexes should be approximately 60% less than those for Pr. This clearly is not the case if judged by the inner-ring CH_2, CH_3, and *meso*-carbon shifts, those most likely to be dipolar. This observation is reinforced in the ^1H NMR spectra where, with one exception, the $Ce_2(OEP)_3$ shifts are 25–35% greater than those of $Pr_2(OEP)_3$, although with the same general pattern of shifts. This irregularity is clearly evident in plots of the inner-ring meso and CH_2 isotropic shifts (assumed to dipolar) for ^1H (Ce, Pr, Nd, Sm, Eu) shown in Figure 4 along with a plot of Bleany's prediction[16,24] for the lanthanide series. In contrast the ^1H shifts from Pr through Eu qualitatively follow the pattern proposed by Bleaney.[14]

At this point it is unclear why the above irregularity occurs.[25] One possible cause could be a significant structural change distinguishing $Pr_2(OEP)_3$ from $Ce_2(OEP)_3$, although it is not obvious which geometry, if any, would be preferable for the former.

Experimental Section

The triple-decker $Ce_2(OEP)_3$ and $Pr_2(OEP)_3$ sandwich compounds were prepared as reported previously.[3,5] The ^{13}C NMR spectra were run on Bruker AC 300 and AM 500 spectrometers operating at 75 and 125 MHz, respectively. Because of the limited solubility of these complexes, as many as 40000 transients (AC 300 spectrometer, 90° pulse) were needed to identify definitively the weakest resonance, that of the inner-ring *meso*-carbon.

Acknowledgment. Financial support from NATO (Grant 0034/85) is gratefully acknowledged. We also thank Drs. S. Braun and T. Pratum for their technical assistance.

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[20] The Ce–N distances taken from ref 3, are as follows: outer, 2.50 Å; inner, 2.76 Å.

[21] Goff, H. *J. Am. Chem. Soc.* **1981**, *103*, 3714.

[22] These calculations require four empirical polarization constants which are derived from ESR studies of simple π-radical systems. It is unclear whether these constants are meaningful for the nonplanar, saucer-shaped porphyrin rings of $Ce_2(OEP)_3$.

[23] The room-temperature magnetic moment of $Pr_2(OEP)_3$, 3.41 μ_B per Pr, is normal for a $4f^2$ system.

[24] Golding, R. M.; Pyykkö, P. *Mol. Phys.* **1973**, *26*, 1389.

[25] This irregularity has not been observed in other NMR studies of homologous Ce and Pr complexes: Peters, J. A.; Nieuwenhuizen, M. S.; Kieboom, A. P. G.; Raber, D. J. *J. Chem. Soc., Dalton Trans.* **1988**, 717. Arif, A. M.; Backer-Dirks, J. D. J.; Gray, C. J.; Hart, F. A.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1987**, 1665. Peters, J. A. *Inorg. Chem.* **1988**, *27*, 4686.

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A Linear Relationship between the Sulfur–Nitrogen Bond Enthalpy Term and Bond Length and an Assessment of the Reliability of Empirical Length–Strength Relationships in the Estimation of Thermochemical Properties of Sulfur–Nitrogen Compounds

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Although the kinetic aspects of sulfur–nitrogen chemistry have received much recent attention,[1] the thermodynamics of these systems has been relatively neglected. Part of the reason for this is the paucity of experimental data.[2] However, we have recently shown that many properties of homopolyatomic cations[3] and chalcogen–iodine cations[4] can be rationalized by reference to simple thermochemical estimates utilizing lattice energies obtained by the method of Bartlett[5a,b] (see below). We apply a similar

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[1] (a) Bestari, K. T.; Boeré, R. T.; Oakley, R. T. *J. Am. Chem. Soc.* **1989**, *111*, 1579. (b) Oakley, R. T. *Prog. Inorg. Chem.* **1988**, *36*, 299. (c) Maclean, G. K.; Parsons, S.; Passmore, J.; Sun, X.; White, P. S. *J. Chem. Soc., Chem. Commun.* **1991**, 369. Parsons, S.; Passmore, J.; Schriver, M. J.; Sun, X. *Inorg. Chem.* **1991**, *30*, 3342.

[2] Heal, H. G. *The Inorganic Chemistry of Sulfur, Nitrogen and Phosphorus*; Academic Press: London, 1980.

[3] Burford, N.; Passmore, J.; Sanders, J. C. P. In *Molecular Structure and Energetics. Atoms to Polymers, Isoelectronic Relationships*; Liebman, J., Greenburg, A. G., Eds.; Verlag Chemie: Deerfield Beach, FL, 1989; p 53.

[4] (a) Klapötke, T.; Passmore, J. *Acc. Chem. Res.* **1989**, *22*, 234. (b) Johnson, J. P.; Murchie, M.; Passmore, J.; Tajik, M.; White, P. S.; Wong, C. M. *Can. J. Chem.* **1987**, *65*, 2744.

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Table I. Sulfur–Nitrogen Bond Lengths and Experimental and Calculated Bond Enthalpy Terms

species[a]	d(SN), Å	ref	BET(SN), kJ·mol^{-1}	ref	method of determn	BET(SN),[b] eq 2	BET(SN),[b] pol cov
$S_4N_4H_4$	1.674 (4)[c,d]	21	247 (4)	26	O_2 combustion[e]	249	233
S_4N_4	1.623 (4)[f]	22	301 (6)	26	thermal dec[g]	306	313
S_4N_2	1.561 (4)[c]	23	352	14	estd from $\Delta H_f[S_4N_2]$[h]	376	388
	1.676 (4)		247			246	233
$SN^•$	1.496 (7)[i]	25	463 (24)	13	electronic spectra	449	449
S_2N^+	1.510 (4)[c,j]	11	473 (30)	k	F_2 combustion	433	
SN^+	1.420[c,j]	17	511 (30)	13	electron impact	535	

[a] Other[2,14] authors have included the value of BET(S═N) in $S_3N_2O_2$ (335 kJ·mol^{-1}) given in ref 26 in their compilations of SN bond enthalpy terms. This was derived from assumed values for BET(S—N) and BET(S═O) of 248 and 538 kJ·mol^{-1}, respectively, applied to the structure O═S═N—S—N═S═O. This is seen to be unreasonable in terms of the two recent redeterminations of the X-ray crystal structure of $S_3N_2O_2$,[24] which both indicated strongly delocalized π-bonding in this system. For this reason, $S_3N_2O_2$ is not included in Table I. [b] The polar covalence method requires the use of fully weakened, partially weakened, or unweakened homonuclear bond energies (see refs 6 and 7). Fully weakened energies were used for nitrogen (163.0 kJ·mol^{-1}) in all cases and for singly bonded sulfur (230.6 kJ·mol^{-1}). The partially weakened energy was used for sulfur (253.7 kJ·mol^{-1}) involved in bonds with order greater than or equal to 2. Canonical bond orders[2] were used to calculate "bond multiplicity factors" using the equation $1.640^{b^{1/3}} - 0.578$ (see refs 6 and 7). [c] X-ray crystallography. [d] Neutron diffraction[27] gives d(SN) = 1.654 (18) Å, in agreement with the value from X-ray diffraction (1.674 (4) Å).[20] We use the latter, more precise, value. [e] Calculated from the experimental value of ΔH_{at}-$[S_4N_4H_4]$ assuming a sublimation enthalpy of 71 kJ·mol^{-1} (making allowance for hydrogen bonding) and a "standard" value for BET(NH). See ref 26. [f] Electron diffraction. [g] Calculated from $\Delta H_{at}[S_4N_4]$ assuming a sublimation enthalpy of 50 kJ·mol^{-1} and a S··S interaction energy of 50 kJ·mol^{-1}. Although $\Delta H_{sub}[S_4N_4]$ has been experimentally determined[28] (89 kJ·mol^{-1}), this value of BET(SN) is in good agreement those contained in refs 13 and 29. [h] These data, which were estimated on the basis of the linear relationship between SN bond energy and bond length, reproduce the enthalpy of formation to within 1 kJ·mol^{-1}.[14] No discussion of this point is given in ref 14, and the inclusion of more data in the derivation of eq 2 accounts for the small deviations between the calculated and "experimental" bond enthalpy terms. [i] From rotational analysis of the γ-band system of the electronic spectrum. [j] Corrected for thermal effects. [k] This work.

methodology to S–N compounds and present a simple relationship for estimating SN bond enthalpy terms on the basis of bond lengths, and we compare our results to those obtained from Sanderson's method of polar covalence.[6,7] These methods allow the thermodynamic properties of simple, low coordinate sulfur-nitrogen compounds to be estimated in the absence of empirical data. Finally we illustrate their application and limitations.[8]

The recent determination[9] by O'Hare et al. of $\Delta H_f°[SNSAsF_6]$ (−1413.8 kJ·mol^{-1}) has enabled us to estimate the SN bond enthalpy term[10] in the SNS^+ cation. Construction of a Born–Haber cycle based on the formation of $SNSAsF_6$ from its elements, via the gas-phase reaction $SN^+ + S \rightarrow SNS^+$, gives

$$\Delta H_f[SNSAsF_6] = \Delta H_f[S(g)] + \Delta H_f[SN^+(g)] + \Delta H_f[AsF_6^-(g)] - BDE[SN\ in\ SNS^+] - U[SNSAsF_6] \quad (1)$$

in which the only experimentally unknown quantity is the lattice energy (U) of $SNSAsF_6$. This was calculated to be 509.4 kJ·mol^{-1} by an extended calculation utilizing X-ray structural data.[11] Calculational details have been described,[5a] and full details of the calculation of $U[SNSAsF_6]$ have been deposited as supplementary material and will be published later.[5c] The SN bond dissociation energy (BDE)[10] in SNS^+ (i.e. $\Delta H[SNS^+(g) \rightarrow SN^+(g) + S(g)]$) is therefore 441 ± 11 kJ·mol^{-1};[12] the average of this value and

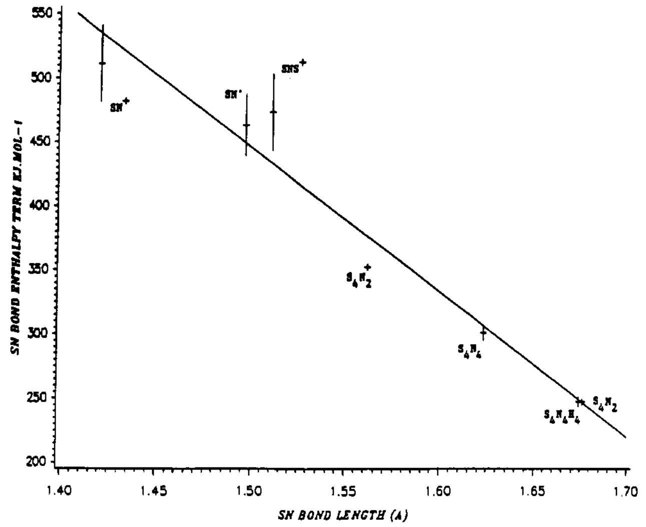

Figure 1. Linear relationship between sulfur–nitrogen bond length and the bond enthalpy term.[30] Data are given in Table I.

BDE[SN in SN^+] (511 kJ·mol^{-1})[13] gives 476 kJ·mol^{-1} for the SN bond enthalpy term in SNS^+.

Accepted values for sulfur–nitrogen bond enthalpy terms (BET(SN)) are compared with appropriate bond lengths (d(SN)) in Table I. These data lie on a straight line with a correlation coefficient of −0.98 and equation

$$BET(SN) = 2134.3 - 1126.4d(SN) \quad (2)$$

This is shown graphically in Figure 1, which demonstrates a surprising uniformity in the trend of the SN bond energy term with bond length in neutral, cationic, and radical species. Although the linear relationship between BET(SN) and d(SN) has been alluded to in the literature,[14] this is (so far as we are aware) the

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(5) (a) Mallouk, T. E.; Rosenthal, G. L.; Müller, G.; Brusasco, R.; Bartlett, N. *Inorg. Chem.* **1984**, *23*, 3167 and references therein. (b) Richardson, R. T.; Tanzella, F. L.; Bartlett, N. *J. Am. Chem. Soc.* **1986**, *108*, 4937. (c) Brooks, W. V. F.; Cameron, T. S.; Grein, F.; Parsons, S.; Passmore, J.; Schriver, M. J. Manuscript in preparation. Bartlett's elegant and important work has enabled the lattice energies of complex systems such as SF_3BF_4, $NOUF_6$, ClO_2BF_4, and $(SF_3)_2GeF_6$ to be calculated, and the reader is referred to ref 5a for full details. Although the calculation of $U(SNSAsF_6)$ requires several assumptions (e.g. atomic charges, polarizabilities, etc.; see supplementary material), ensuring that $\partial U/\partial r = 0$ reduces their importance, and in fact U is relatively insensitive to these assumptions, provided that this energy minimization criterion is met. Initial calculations using our programs on SF_3BF_4, KBF_4, and $(SF_3)_2GeF_6$ reproduced Bartlett's results.

(6) Sanderson, R. T. *Polar Covalence*; Academic Press: London, 1983.

(7) Sanderson, R. T. *Simple Inorganic Substances*; Robert Krieger: Malabar, FL, 1989.

(8) All data in this note are given in kJ·mol^{-1} (1 cal = 4.184 J).

(9) O'Hare, P. A. G.; Awere, E. G.; Parsons, S.; Passmore, J. *J. Chem. Thermodyn.* **1989**, *21*, 153.

(10) A bond enthalpy term (BET) is the enthalpy that a given bond contributes to the total atomization enthalpy; this is distinguished from a bond dissociation enthalpy (BDE), which is the enthalpy required to break one bond in a molecule. These two quantities are only rigorously equal in diatomics.

(11) Johnson, J. P.; Passmore, J.; White, P. S.; Banister, A. J.; Kendrick, A. G. *Acta Crystallogr., Sect C* **1987**, *43*, 1651.

(12) $\Delta H_f[S(g)] = 278.8$ kJ·mol^{-1}; $\Delta H_f[N_2(g)] = 472.7$ kJ·mol^{-1}; $\Delta H_f[F^-(g)] = 270.7$ kJ·mol^{-1}; $\Delta H_f[AsF_5(g)] = -1237.0 \pm 0.8$ kJ·mol^{-1}; $FA[AsF_5]$ (fluoride ion affinity) = 464.4 kJ·mol^{-1}; $\Delta H_f[AsF_6^-(g)] = \Delta H_f[AsF_5(g)] + \Delta H_f[F^-(g)] + FA[AsF_5] = -1972.1 \pm 0.8$ kJ·mol^{-1}; first IP of S = 1000 kJ·mol^{-1}; $\Delta H_f[SN^+(g)] = 1230 \pm 10$ kJ·mol^{-1}: Johnson, D. A. *Some Thermodynamic Aspects of Inorganic Chemistry*, 2nd ed.; Cambridge University Press: Cambridge, U.K., 1982. O'Hara, P. A. G.; Lewis, B. M.; Susman, S.; Volin, K. J. Unpublished data. See also refs 5 and 13. Woolf, A. A. *J. Fluorine Chem.* **1980**, *15*, 533.

(13) O'Hare, P. A. G. *J. Chem. Phys.* **1970**, *52*, 2992.

(14) Kudo, Y.; Hamada, S. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2627.

first occasion that it has been explicitly demonstrated.

Sanderson's method of polar covalence[6,7] has been shown to reproduce the atomization enthalpies of hundreds of neutral compounds with relatively few exceptions. Table I compares SN bond enthalpy terms derived from polar covalence calculations and from eq 2 with experimental data. The average deviation between calculated and experimental bond enthalpy terms is 23 kJ·mol^{-1}, which gives us confidence to apply this model to the calculation of the thermodynamic properties of neutral sulfur–nitrogen-containing systems.

We illustrate this approach with the estimation of $\Delta H_f°$[NSF] and the thermochemical properties of some related species. Polar covalence calculations on thiazyl fluoride using the experimentally determined bond lengths (SF, 1.643 Å; SN, 1.448 Å[15]) give bond enthalpy terms for the SF and SN bonds of 323 and 502 kJ·mol^{-1} (cf. 503 kJ·mol^{-1} from eq 2), respectively. These data, when combined with atomization enthalpies,[12] give $\Delta H_f°$[NSF] = 5 kJ·mol^{-1}, in reasonable agreement with the experimental value of −20.9 ± 3.8 kJ·mol^{-1}.[16] Combination of these data with the estimated SN BET in SN$^•$ (449 kJ·mol^{-1}) yields a SF bond dissociation enthalpy in NSF of 376 kJ·mol^{-1}, in agreement with the experimental value of 382 ± 25 kJ·mol^{-1}.[16] $\Delta H_f°$[SN$^+$(g)] may be calculated from ΔH_f[S(g)], ΔH_f[N(g)], IP[S],[12] and BET[SN] from eq 2 to be +1217 kJ·mol^{-1} (cf. experimental +1230 ± 10 kJ·mol^{-1} [13]). When the latter is combined with an estimation of the lattice energy of SNAsF$_6$[17] using Bartlett's equation[5b] (eq 3) (556 kJ·mol^{-1}), $\Delta H_f°$[SNAsF$_6$] (which has not been empirically determined) is estimated to be −1300 kJ·mol^{-1}.

$$U = 2336.5V^{-1/3} + 110.5 \qquad (3)$$

The errors incurred in the estimation of enthalpies of formation from calculated BETs increase rapidly with the number of bonds in the species under investigation. For example, $\Delta H_f°$[CF$_3$NSF$_2$] is calculated[18] to be −871 kJ·mol^{-1}, which, although in only moderate agreement with the experimental value (−815 ± 8 kJ·mol^{-1} [16]), corresponds to an error of only 8 kJ·mol^{-1} in the estimated BETs for each of the seven bonds, which is well within the error of most experimental determinations of bond energies.

There are several cases for which this method yields particularly inaccurate estimates. A calculation on thiazyl trifluoride,[15] NSF$_3$, gives apparently reasonable BETs of 514.5 (SN) and 339.4 kJ·mol^{-1} (SF) but gives a $\Delta H_f°$[NSF$_3$] of −462 kJ·mol^{-1}, in poor agreement with the experimental value of −357.8 ± 2.1 kJ·mol^{-1}.[16] Similarly, the calculated enthalpy of the detrimerization of (NSCl)$_3$[19] is 401 kJ·mol^{-1}, in very poor agreement with the experimental value (92 ± 13 kJ·mol^{-1}).[20]

The method of polar covalence reliably estimates bond enthalpy terms for a wide range of low-coordination sulfur–nitrogen compounds, although small errors in individual BETs can accumulate rapidly in calculations of enthalpies of formation. The success of the methods depends upon the surprising uniformity of the dissociation potential for many S–N compounds, which is implied by the linearity of Figure 1. The poor performance of the polar covalence model in the cases of NSF$_3$ and S$_3$N$_3$Cl$_3$ is consistent with results obtained for ΔH_f[SF$_6$] (calcd −1349, exptl −1209 kJ·mol^{-1}), which Sanderson has ascribed[7] to destabilizing repulsions between the fluorine atoms. Similar interactions may lead to a distortion in the dissociation potential of NSF$_3$ and S$_3$N$_3$Cl$_3$, accounting for the poor agreement between calculated and experimental enthalpies of formation. Increased ligand–ligand repulsion is likely the cause for the breakdown of these simple methods, and therefore both eq 2 and polar covalence calculations are best applied only to low-coordination S–N compounds. In addition, although eq 2 adequately reproduces BETs for a variety of "conventional" SN bonds, BET(SN) becomes infinite as d(SN) → 0 and approaches zero at large d(SN). Thus, eq 2 should only be applied to SN bonds of lengths between 1.4 and 1.7 Å and not to weak SN interactions such as secondary bonds or interionic contacts.

Acknowledgment. We thank the NSERC (Canada) and the University of New Brunswick for funding, the Canadian Commonwealth Scholarship and Fellowship Committee for a graduate fellowship (S.P.), and Prof. N. Bartlett for a computer program to calculate the electrostatic contributions to lattice energies.

Registry No. S$_4$N$_4$H$_4$, 293-40-3; S$_4$N$_4$, 28950-34-7; S$_4$N$_2$, 79796-31-9; SN$^•$, 12033-56-6; S$_2$N$^+$, 38263-99-9; SN$^+$, 27954-72-9; SNSA$_2$F$_6$, 80485-40-1; SNSbF$_6$, 34770-46-2.

Supplementary Material Available: Table S1, listing contributing terms to the lattice energies of SNSAsF$_6$ and SNSbF$_6$ (5 pages). Ordering information is given on any current masthead page.

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(15) Glemser, O.; Mews, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 883.

(16) Larson, J. W.; Johnson, G. K.; O'Hare, P. A. G.; Hubbard, W. N.; Glemser, O. *J. Chem. Thermodyn.* **1973**, *5*, 689.

(17) Although the crystal structure of SNAsF$_6$ has not been determined, its molar volume can be estimated from that of SNSbF$_6$ (153.8 Å^3) by assuming that AsF$_6^-$ and SbF$_6^-$ differ in volume by 10 Å^3. See: Clegg, W.; Glemser, O.; Harms, K.; Hartmann, G.; Mews, R.; Noltemeyer, M.; Sheldrick, G. M. *Acta Crystallogr., Sect B* **1981**, *37*, 548. Equation 3 gives a lattice energy for SNSbF$_6$ of 542.4 kJ·mol^{-1}, in good agreement with 541.3 kJ·mol^{-1} obtained from an extended calculation (see supplementary material). This gives us confidence to apply this equation to SNAsF$_6$.

(18) Karl, R. R.; Bauer, S. H. *Inorg. Chem.* **1975**, *14*, 1859. Fully weakened homonuclear bond energies[6,7] were used throughout, except for the S═N bond, for which a partially weakened value was used for sulfur. These data give the following bond enthalpy terms (in kJ·mol^{-1}): CF, 443; CN, 312; SN, 423; SF, 335.

(19) Hargittai, I. *The Structure of Inorganic Sulphur Compounds*; Reidel: Dordrecht, The Netherlands, 1985. Wiegers, G. A.; Voss, A. *Proc. R. Soc. London* **1962**, 387. Sanderson's fully weakened homonuclear bond energies[6,7] were used for S$_3$N$_3$Cl$_3$, giving BET(SN) = 317 kJ·mol^{-1} and BET(SCl) = 286 kJ·mol^{-1}. Similarly, fully weakened energies were also used for the S—Cl bond in NSCl, but a partially weakened S—S homonuclear energy was used for the S≡N bond (see Table I, footnote *b*), giving BET(SN) = 504 kJ·mol^{-1} and BET(SCl) = 285 kJ·mol^{-1}.

(20) Patton, R. L.; Jolly, W. L. *Inorg. Chem.* **1970**, *5*, 1079.

(21) Sass, R. L.; Donahue, J. *Acta Crystallogr.* **1958**, *11*, 497.

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(26) Fleig, H.; Becke-Goehring, M. *Z. Anorg. Allg. Chem.* **1970**, *375*, 8.

(27) Sabine, T. M.; Cox, G. W. *Acta. Crystallogr.* **1976**, *23*, 574.

(28) Hamada, S. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 3598.

(29) Barker, C. K.; Cordes, A. W.; Margrave, J. L. *J. Phys. Chem.* **1965**, *69*, 334.

(30) One reviewer suggested that the data in Figure 1 may represent two curves: one corresponding to the radical and ions; the other, to the molecules. In our view, the paucity of available experimental data does not permit a definitive case to be made either way, although our treatment is justified by the performance of eq 2 between 1.4 and 1.7 Å (see Table I).