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Molecular Structure and Conformation of Dimethyltrisulfane, CH$_3$SSSCH$_3$, As Determined by ab Initio Molecular Orbital Calculations and Gas-Phase Electron Diffraction

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Introduction

The gas-phase structure of dimethyltrisulfane,[1] CH$_3$SSSCH$_3$ (Figure 1) was first reported in 1948. The methyl groups were found to be ca. 106° out of the plane of the three sulfur atoms (74° away from the syn position), but it was not made clear if the methyl groups were on the same side or on opposite sides of the S−S−S plane. The reported uncertainties in the bond lengths (0.02−0.04 Å) and valence angles (5°) were fairly large, and this makes structural and conformational comparisons with related molecules impractical. In solid-phase both the G^+G^- or cis (substitutents on the same side of the S−S−S plane, C_s symmetry), and the G^+G^+ or trans[2] (substituents on opposite side of the plane, C_2 symmetry) conformers of trisulfanes have been observed depending on the substitutents.[3] The observed microwave rotational constants of trisulfane (HSSSH) were found to be consistent with the cis form.[4] A vibrational study assigned the IR and Raman spectra to the trans conformer,[5] however, and recently this trans form was identified using millimeter wave and Fourier transform infrared spectroscopy.[6] The observed conformational composition corresponded to only a small energy difference of about 1 kJ mol^{-1}, with the trans form lowest in energy. This was in agreement with results from ab initio molecular orbital calculations. For bis(trifluromethyl)-trisulfane[7] the gas-phase electron-diffraction data were interpreted as only the trans form being present and a larger ab initio energy difference between conformers of about 10 kJ mol^{-1} was calculated. The structure and conformation of trisulfanes therefore clearly depend on the substitutents at the ends of the sulfur chain. We feel that a reinvestigation of the gas-phase structure and conformation of dimethyltrisulfane, using electron diffraction, and with the aid of ab initio molecular orbital calculations, is in order and present the results in this article.

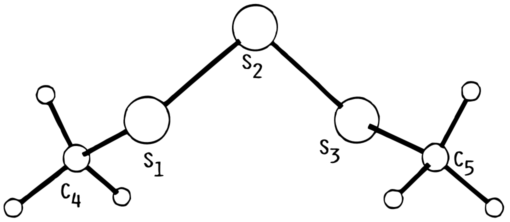

Figure 1. Model of *trans*-dimethyltrisulfane with atom numbering.

Experimental and Data Analysis

A sample of dimethyltrisulfane (98%) was obtained from Eastman Kodak Co. and was used without further purification. The diffraction data were collected using the Oregon State University apparatus at a nozzle-tip temperature of 383 K, using Kodak lantern slide photographic plates. Camera heights of 747.6 and 299.15 mm, respectively, for the long and middle camera experiments were used. Four photographic plates from each of the two camera distance experiments were selected for structural analyses. The usual data reduction procedures were followed. The intensity data were averaged and interpolated at integral q units ($q = 40\ \lambda^{-1} \sin \theta$, where λ is the wavelength of the electron beam and 2θ is the scattering angle) and covered the ranges $7 \leq q \leq 47$ (long camera) and $20 \leq q \leq 120$ (middle camera). These two average curves were used for least squares analyses following the procedures outlined by Gundersen and Hedberg.[8] The composite experimental intensity curve is shown in Figure 2, and the experimental radial distribution curve calculated from it is shown in Figure 3. Elastic scattering factors and phases tabulated by Schafer, Yates and Bonham[9] were used.

Theoretical Calculations. Ab initio molecular orbital calculations were carried out at the HF/6-311+G(d), the MP2(fc)/6-311+G(d), and the B3LYP/6-31G(d) levels, using the Gaussian 94 program,[10] for the two conformations with starting ϕ(CSSS) values of (90, −90) and (90, 90). Optimized geometries were obtained for both the cis and the trans forms. The latter was found to be 7.78 kJ mol^{-1} (HF), 7.65 kJ mol^{-1} (MP2), or 6.15 kJ mol^{-1} (B3LYP) lower in energy than the former. A model where the starting values for the torsion angles were $\phi_1 = 180$, $\phi_2 = 90°$ was also tested, but when the geometry of this form was allowed to be fully optimized, it converged to the trans form suggesting that (180, 90) is not a minimum on the potential surface. The optimized geometry for the trans and cis forms obtained from the theoretical calculations are summarized in Table 1. Values for the zero-point energies (ZPE) and the entropies of both conformers were calculated at the HF/6-311+G(d) level. Frequencies and Cartesian force fields were also calculated for both the cis and the trans forms at the HF/6-31G(d) level. The absence of imaginary frequencies confirmed that these two conformers are true minima on the potential surface. The lowest frequency modes are from the C−S−S−S torsions (67 and 99 cm^{-1}), and the methyl torsions are calculated to be at 170 and 195 cm^{-1}. These theoretical force fields were used in the program

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(1) Donohue, J.; Schomaker, V. *J. Chem. Phys.* **1948**, *16*, 92.

(2) The terms cis and trans are normally used for geometrical isomers where breaking a bond is necessary to convert one form into the other. The use of these terms here for conformers is therefore strictly not correct, but we will use them for reason of convenience and because they have been used earlier in the literature for similar molecules.

(3) (a) Mott, A. W.; Barany, G. *J. Chem Soc., Perkin Trans. 1* **1984**, *11*, *2615. (b) Steudel, R.; Luger, P.; Bradaczek, H. *Chem. Ber.* **1977**, *110*, 3553.

(4) Maurer, D.; Winnewisser, G.; Yamada, K. M. T. *J. Mol. Spectrosc.* **1989**, *136*, 380.

(5) Wieser, H.; Krueger, P. J.; Muller, E.; Hyne, J. B. *Can. J. Chem.* **1969**, *47*, 1634.

(6) Liedke, M.; Saleck, A. H.; Yamada, K. M. T.; Winnewisser, G.; Cremer, D.; Kraka, K.; Dolgner, A.; Hahn, J.; Dobos, S. *J. Phys. Chem.* **1993**, *97*, 11204.

(7) Gaensslen, M.; Minkwitz, R.; Molzbeck, W.; Oberhammer, H. *Inorg. Chem.* **1992**, *31*, 4147.

(8) Gundersen, G.; Hedberg, K. *J. Chem. Phys.* **1969**, *51*, 2500.

(9) Schafer, L.; Yates, A. C.; Bonham, R. A. *J. Chem. Phys.* **1971**, *56*, 3056.

(10) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Peterson, G. A.; Montgomery, J. A.; Raghavachari, V.; Al-Laham, M. A.; Zakrzewski, V. G.; Oritz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, V.; Pople, J. A. *Gaussian 94*, Rev. D.4; Gaussian, Inc.: Pittsburgh, PA, 1995.

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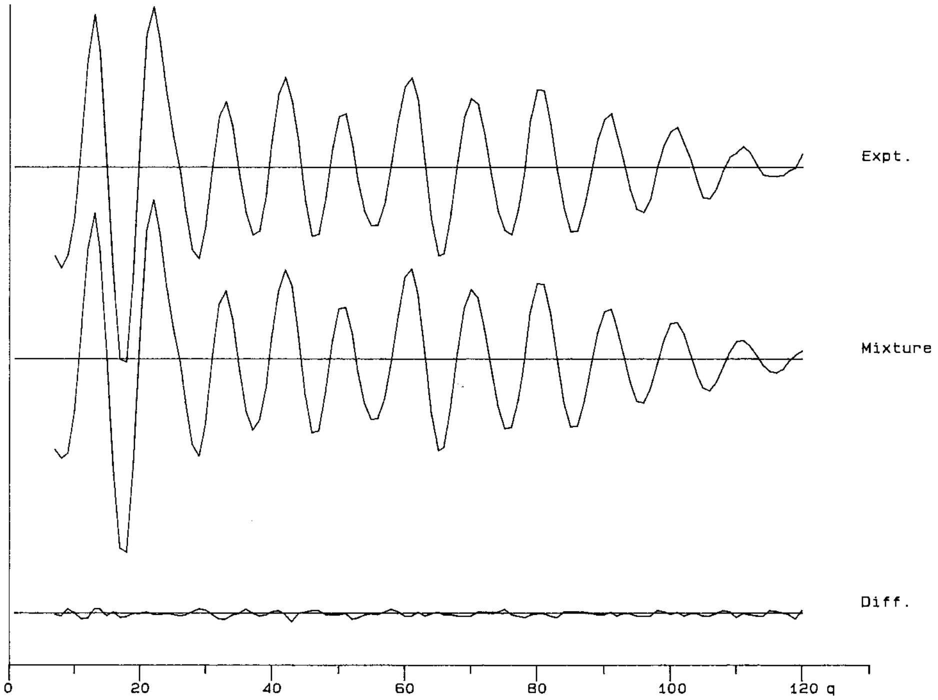

Figure 2. Experimental and theoretical intensity curves for dimethyltrisulfane. The theoretical curve was calculate for a mixture of 28.5% cis and 71.5% trans conformers. The difference curve is experimental minus theoretical.

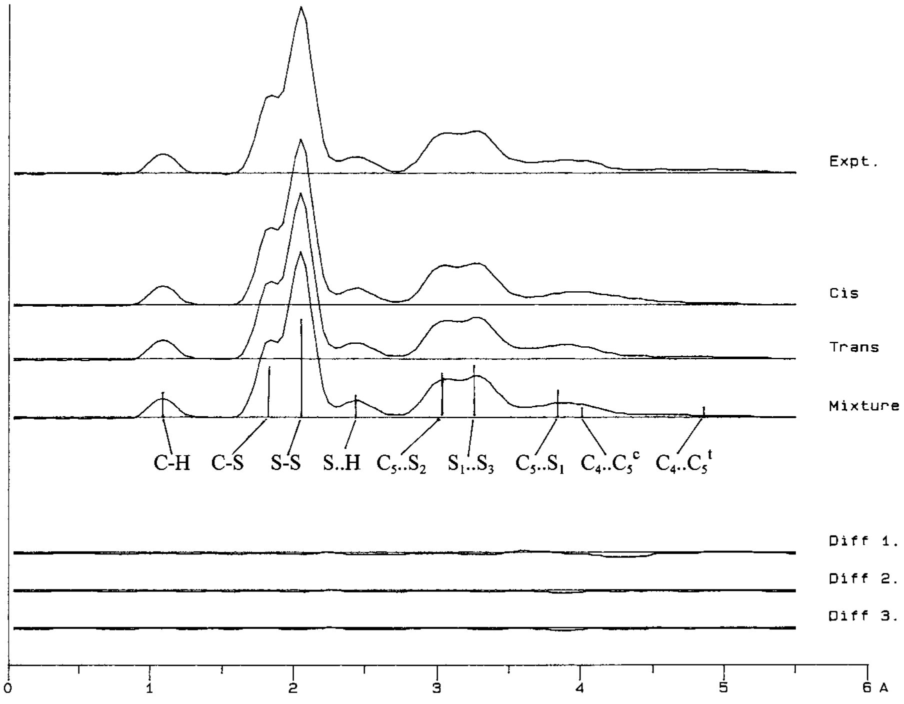

Figure 3. Experimental and theoretical radial distribution curves for dimethyltrisulfane. The theoretical curves are for cis and trans forms and for a mixture of both forms (28.5% cis, 71.5% trans). The difference curves are experimental minus theoretical.

ASYM40[11] to obtain valence force fields and to calculate theoretical values for the vibrational amplitudes *(l)*, the perpendicular amplitude corrections (*K*), and the centrifugal distortion constants (δr). Before the calculations of the vibrational quantities, the ab initio force constants (except the torsional force constants) were multiplied by a scale factor of 0.9. It is not uncommon for molecules such as dimethyl trisulfane to have large amplitude motions which make harmonic calculations inadequate. The force constant for the C−S−S−S torsion is, however, 0.123 mdyne Å^{-1} which is not very low and the refined vibrational amplitude of r(C···S) is very close to the calculated value, which lent support to the use of the harmonic approximation in the calculations.

Electron Diffraction. The geometrical parameters chosen to describe each of the two forms of dimethyltrisulfane are as follows: $\langle r(\mathrm{C{-}H})\rangle_{\mathrm{av}}$, r(S−C), r(S−S), ∠HCS, ∠CSS, ∠SSS, and ϕ(CSSS). Preliminary theoretical radial distribution curves for the trans form showed very good agreement with curves calculated from the experimental data. Refinements of the molecular structure based on the electron diffraction data were made by the least-squares method, adjusting a theoretical intensity curve simultaneously to the two average

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[11] Hedberg, L.; Mills, I. M. *J. Mol. Spectrosc.* **1993**, *160*, 117.

Table 1. Calculated Geometrical Parameter Values and Energy Differences between Conformers for Dimethyltrisulfane[a]

	HF/6-311+G(d)		MP2/6-311+G(d)		B3LYP/6-311+G(d)	
	cis	trans	cis	trans	cis	trans
$r(C_4-H_6)$	1.0826	1.0824	1.0924	1.0921	1.0921	1.0919
$r(C_4-H_7)$	1.0798	1.0797	1.0893	1.0898	1.0892	1.0892
$r(C_4-H_8)$	1.0796	1.0799	1.0900	1.0904	1.0892	1.0896
$r(C-S)$	1.8144	1.8132	1.8097	1.8072	1.8319	1.8299
$r(S-S)$	2.0682	2.0687	2.0695	2.0714	2.1018	2.1028
$\angle S-C_4-H_6$	106.06	106.40	106.76	107.26	106.04	106.36
$\angle S-C_4-H_7$	110.83	110.68	110.90	110.89	110.89	110.87
$\angle S-C_4-H_8$	111.43	110.61	110.57	110.34	110.39	110.57
$\angle C-S-S$	103.19	102.26	101.74	100.33	103.30	102.30
$\angle S-S-S$	107.98	106.54	108.48	106.22	109.82	108.33
$\phi(C-S-S-S)$	91.90	80.31	89.52	78.26	90.43	81.39
ΔE^b	7.78		7.65		6.15	

[a] Distances (r) in angstroms, angles ($\angle$) in degrees, energies in kJ mol^{-1}. [b] Cis − trans.

Table 2. Experimental and Calculated Parameter Values for the Trans Form of MeSSSMe[a]

	MP2/6-311+G(d)	ED			
	r_e	$r_g/\angle_\alpha$	r_α	l_{calcd}	l_{exp}
$r(C-H)_{average}$	1.091	1.084(7)	1.058	0.077	0.068(6)
$r(S-C)$	1.807	1.817(2)	1.812	0.053	0.052(2)
$r(S-S)$	2.071	2.046(2)	2.044	0.053	0.058(1)
$\angle(C-S-S)$	100.3	103.1(5)			
$\angle(S-S-S)$	106.2	107.3(5)			
$\angle(H-C-S)_{average}$	109.5	112(2)			
$\phi(C-S-S-S)$	78.3	79(5)			
dependent distances					
$r(S\cdots S)$	3.313	3.283(10)	3.280	0.098	0.104(6)
$r(S2\cdots C4)$	2.983	3.011(10)	3.006	0.100	0.090(6)
$r(S3\cdots C4)$	3.811	3.856(80)	3.850	0.233	0.230(50)
$r(C4\cdots C5)$	4.865	4.893(170)	4.887	0.311	
$r(S\cdots H_{gem})$	2.402	2.426(15)	2.411	0.109	0.106(12)

[a] Distances (r) and vibrational amplitudes (l) are in angstroms and angles ($\angle$) in degrees; the uncertainties quoted are 2σ values where the effects of correlation in the experimental data and uncertainty in the voltage and camera heights are included.

intensity curves, one from each of the two camera distances, using a unit weight matrix.

A second model with the presence of only the cis form was introduced and tested. When the value of ϕ(CSSS) was allowed to refine simultaneously with other geometrical parameters, the agreement with the experimental data for the cis conformer was almost as good as for the trans form, and ϕ(CSSS) converged to a value of 79.5°. The geometrical parameters obtained are indistinguishable from those of the pure trans model. When the dihedral angles were fixed at the MP2-calculated values of 89.5° (cis) and 78.3° (trans), the agreement for the cis model ($R = 6.8\%$) was, however, slightly worse than for the trans model ($R = 6.0\%$).

Using calculated values for the differences (cis − trans) in entropies ($\Delta S = 11.05$ J mol^{-1} K^{-1}), zero-point energies ($\Delta ZPE = -0.5$ kJ mol^{-1}) and the MP2 electronic energies of these two conformers, a conformational mixture of 71.5% trans and 28.5% cis was obtained at the temperature of our experiment, 383 K. It is therefore likely that both conformers are present in the gas-phase simultaneously. A model with a mixture of trans and cis conformers was tested (the differences in the geometrical parameters between the two forms calculated by ab initio were imposed as constraints), and using the calculated composition the fit ($R = 6.0\%$) to the experimental data was excellent. The uncertainty in the experimental value for the conformational mixture is of the order of at least 15%. The theoretical radial distribution curves calculated for this mixture, for 100% of the trans, and for 100% of the cis conformers are included in Figure 3. The final least-squares results and the intensity curves are shown in Table 2 and Figure 2, respectively. The vibrational amplitudes which could not be refined in the least-squares analysis were kept constant at the calculated values from the valence force field. The correlation matrix for the refined parameters is presented in Table 3. The small numbers clearly showed how low the correlation between the refined parameters are.

Discussion

In order for the conformer of dimethyltrisulfane to be consistent with the electron diffraction data, a dihedral angle ϕ(CSSS) of ca. 80° is required. Both pure cis and pure trans models with refined dihedral angles of ca. 80° fit the ED data almost equally well. The theoretical RD curves showed that the experimental peak at 3.8 Å is derived from the nonbonded C···S distances with a 80° dihedral angle. The corresponding distance from a 90° dihedral angle would be at 4.1 Å. The ab initio calculated dihedral angle for the cis form (90°) is 10° larger than the ED preferred value. We therefore believe the trans form to be the dominant conformer in the gas phase. Ab initio calculations also show that the trans form is lower in energy than the cis conformer by 8 kJ mol^{-1}, both at the HF and the MP2 level, and by 6 kJ mol^{-1} from the DFT calculations (B3LYP). However, these energy differences are small enough to make it likely that some of the cis conformer is present at 383 K, especially since the cis form was calculated to have higher entropy, and we used this model with a mixture of both forms as our final one. Both the experimental studies and the theoretical calculations have indicated that of the three trisulfanes, X−S−S−S−X (X = H, CH_3, CF_3), the amount of cis conformer is decreasing with increasing size (and electronegativity) of X.

Table 4 summarizes the major geometrical parameters of dimethyltrisulfane and some related methyl substituted sulfur compounds. The major differences between the two electron diffraction studies of dimethyltrisulfane are the values of r(S−C) [1.817(2) vs 1.78(4) Å] and the values of ∠SSS [107.2(5) vs 104(5)°]. The two investigations are in agreement within

Table 3. Correlation Matrix (×100) for Parameters of Dimethyltrisulfane

		$\sigma_{LS}{}^{a} \times 100$	r_1	$\angle_2$	r_3	$\angle_4$	ϕ_5	r_6	$\angle_7$	l_8	l_9	l_{10}	l_{11}	l_{12}	l_{13}	l_{14}
1.	r(S−S)	0.03	100													
2.	∠SSS	17.2	−14	100												
3.	r(C−S)	0.07	8	−2	100											
4.	∠SSC	17.0	−8	54	−16	100										
5.	ϕ(CSSS)	199	2	−25	1	−26	100									
6.	r(C−H)	0.29	1	−1	4	−1	−4	100								
7.	∠SCH	51.2	−5	−2	−21	−12	0	−38	100							
8.	l(S−S)	0.03	−6	2	−16	2	0	−3	18	100						
9.	l(S···S)	0.22	−2	−10	2	−32	15	−1	3	0	100					
10.	l(C−S)	0.06	16	−3	4	1	0	5	−14	−26	−1	100				
11.	$l(C_4S_2)$	0.22	1	28	−1	1	−1	1	1	0	23	1	100			
12.	$l(C_4S_3)$	1.88	−1	−20	0	−5	3	−3	0	0	13	0	−7	100		
13.	l(S···H)	0.42	−18	0	9	−12	1	0	−4	−7	5	−2	−8	−3	100	
14.	l(C−H)	0.23	1	0	−2	−1	1	−8	4	−1	−1	2	0	0	−2	100

[a] σ_{LS} is the standard deviation from least squares. Distances (r_g) and vibrational amplitudes (l) are in angstroms, angles ($\angle_\alpha$) are in degrees.

Table 4. Comparison of Geometrical Parameter Values Obtained for Dimethyl Trisulfane and Related Molecules[a]

	HSMe	MeSMe	MeSSMe	CF_3SSCF_3	MeSSSMe	MeSSSMe	$F_3CSSSCF_3$
r(S−C)	1.814(5)	1.807(2)	1.816(3)	1.835(5)	1.78(4)	1.817(2)	1.820(5)
r(S−S)	−		2.029(3)	2.030(5)	2.04(2)	2.046(1)	2.040(4)
∠XSC	96.5(5)	99.05(4)	−				
∠CSS		−	103.2(2)	101.6(6)	104(5)	103.1(5)	101.0(7)
∠SSS		−	−		104(5)	107.3(5)	105.3(6)
ϕ(CSSS)						79(5)	89(3)
ϕ(CSSC)		−	85.3(37)	104.4(40)	−	−	−
methods	MW	ED/MW	ED	ED	ED	ED	ED
ref	12	13	14	16	1	this work	7

[a] Angles in degrees and distances in angstroms. Parenthesized values are estimates of uncertainties and are those reported in the original papers. MW = microwave spectroscopy; ED = gas-phase electron diffraction; ED/MW = combined microwave and electron diffraction analysis

uncertainties, but the estimated uncertainties have been improved by an order of magnitude in our study, compared with the old investigation which used the visual method.

Comparing the geometrical parameters obtained for dimethyltrisulfane with those in related molecules, we find that the S−S bond length in dimethyltrisulfane is nearly the same as the one in solid elemental S_8 [2.048(2) Å],[15] but there appears to be an increase in the S−S bond length from dimethyldisulfane[14] to dimethyltrisulfane. The S−C bonds in dimethyldisulfane [1.816(3) Å] and dimethyltrisulfane [1.817(2) Å] are indistinguishable and they are both longer than the S−C bond length in dimethyl sulfide[13] [1.807(2) Å], suggesting a decrease in the S−C bond length when two methyl groups are attached to the central sulfur atom. The S−C bond length in methanethiol[12] was found to be 1.814(5) Å.

The valence angle of the central sulfur atom is increasing as the size of the group attached to it increases. The observed values for the valence angle ∠CSH, ∠CSC, ∠CSS, and ∠SSS are 96, 99, 103, and 107°, respectively.

The S−C and S−S bonds in dimethyltrisulfane and bis(trifluoromethyl)trisulfane[7] are nearly identical to within uncertainties. The fluorine substitutions, however, are shown to decrease both the ∠CSS and the ∠SSS valence angles values. A similar stability in the S−S bond distance and a decrease in ∠CSS is also seen when comparing the results for dimethyldisulfane[14] and bis(trifluoromethyl)disulfane.[16] Here there is, however, a significant increase in the S−C bond when H is substituted with F. The dihedral angles (ϕ(CSSS) or ϕ(CSSC)) are larger in the fluorinated compounds, perhaps because of steric reasons since the trifluoromethyl group is larger than the methyl group.

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(12) Kojima, T. *J. Phys. Soc.* **1960**, *15*, 1284.
(13) Iijima, T.; Tsuchiya, S.; Kimura, M. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2564.
(14) Yokozeki, A.; Bauer, S. H. *J. Phys. Chem.* **1976,** *80*, 618.
(15) Slack, G. A. *Phys. Rev.* **1965**, *139A*, 511.
(16) Marsden, C. J.; Beagley, B. *J. Chem. Soc., Faraday Trans 2* **1981**, *77*, 2213.