Eu(III) ions.[24]

A quite different situation is met for europium nitrate solutions. The fluorescence spectrum of the more dilute solutions (see Figures 1–3 and Table II) is similar to the spectra of $Eu(ClO_4)_3$ solutions, with minor changes: a weak band is always observed at 579.5 nm ($^5D_0 \rightarrow {}^7F_0$) and both the $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_4$ bands are differently shaped. When the salt concentration or the total NO_3^- concentration is increased above 0.01 M, all of the forced electric dipole transitions are enhanced.[25] The center of symmetry is removed because NO_3^- ions penetrate into the first coordination sphere. This results in a less effective quenching of the excited Eu(III) ions and the fluorescence lifetime increases from 108 μs to 140 μs for the more concentrated solution. The fluorescence lifetime of the mononitrato species $[Eu(NO_3)(H_2O)_n]^{2+}$ amounts to 159 μs,[26] and we can evaluate the association constant K for the inner-sphere process

$$[Eu(H_2O)_9]^{3+} + NO_3^- \rightleftarrows [Eu(NO_3)(H_2O)_n]^{2+} + (9 - n)H_2O$$

from the measured fluorescence lifetimes, if we make known assumptions.[18,26] K amounts to 0.3 ± 0.1 M^{-1} in a 0.1 M solution of $Eu(NO_3)_3$ and to 0.2 ± 0.1 in a 0.5 M solution. These values are in agreement with reported literature data for other inner-sphere $Ln(NO_3)^{2+}$ complexes: $K = 0.53$[4] and 0.54[8] for Ln = Dy; $K = 0.66$[9] for Ln = Pr. For comparison purposes, we should mention that the reported association constants which take into account both inner- and outer-sphere processes range between 2 and 4.[1,6,7]

Acknowledgment. This research is supported by the Swiss National Science Foundation (Project No. 2.978.0.77). We thank the Fondation Herbette for the gift of the dye laser, the transient recorder, and the signal averager.

Registry No. $Eu(NO_3)_3$, 10138-01-9; $Eu(ClO_4)_3$, 13537-22-9; $Eu(NO_3)^{2+}$, 15974-15-9.

References and Notes

(1) G. R. Choppin and W. R. Strazik, *Inorg. Chem.*, **4**, 1250 (1965).
(2) G. R. Choppin, D. E. Henrie, and K. Buijs, *Inorg. Chem.*, **5**, 1743 (1966).
(3) I. Abrahamer and Y. Marcus, *Inorg. Chem.*, **6**, 2103 (1967).
(4) Z. Kollarik, *Collect. Czech. Chem. Commun.*, **32**, 435 (1967).
(5) I. Abrahamer and Y. Marcus, *J. Inorg. Nucl. Chem.*, **30**, 1563 (1968).
(6) T. G. Spiro, A. Revesz, and J. Lee, *J. Am. Chem. Soc.*, **90**, 4000 (1968).
(7) R. Garnsey and D. W. Ebdon, *J. Am. Chem. Soc.*, **91**, 50 (1969).
(8) J. Reuben and D. Fiat, *J. Chem. Phys.*, **51**, 4909 (1969).
(9) A. Anagnostopoulos and P. O. Sakellaridis, *J. Inorg. Nucl. Chem.*, **32**, 1740 (1970).
(10) D. I. Nelson and D. E. Irish, *J. Chem. Phys.*, **54**, 4479 (1971).
(11) A. Fratiello, V. Kubo, S. Peak, B. Sanchez, and R. E. Schuster, *Inorg. Chem.*, **10**, 2552 (1971).
(12) A. Fratiello, V. Kubo, and G. A. Vidulich, *Inorg. Chem.*, **12**, 2066 (1973).
(13) M. M. Jones, E. A. Jones, D. F. Harmon, and T. Semmes, *J. Am. Chem. Soc.*, **83**, 2038 (1961).
(14) H. B. Silber and A. Pezzica, *J. Inorg. Nucl. Chem.*, **38**, 2053 (1976).
(15) H. B. Silber, *J. Chem. Phys.*, **78**, 1940 (1974).
(16) J.-C. G. Bünzli and B. Klein, *Inst. Phys. Conf. Ser.*, No **37**, 115 (1978).
(17) J.-C. G. Bünzli, D. Wessner, and Huynh Thi Tham Oanh, *Inorg. Chim. Acta*, in press.
(18) J. F. Giuliani and T. Donohue, *Inorg. Chem.*, **17**, 1090 (1978).
(19) J.-C. G. Bünzli and J.-R. Yersin, *Helv. Chim. Acta*, **61**, 762 (1978).
(20) F. H. Spedding and S. Jaffe, *J. Am. Chem. Soc.*, **76**, 884 (1954).
(21) G. S. Ofelt, *J. Chem. Phys.*, **37**, 511–20 (1962).
(22) Since f–f transitions are Laporte forbidden, the only electronic transitions which may occur in a species possessing an inversion center are magnetic dipole in origin, with selection rule $\Delta J = 0, \pm 1$ (with j and j' not both equal to zero). When no inversion center is present, forced electric dipole (hypersensitive) transitions for which $\Delta J = 0, 2,$ or 4 may occur.[21]
(23) Apparent small changes are due to different resolutions with which the spectra were recorded (band-pass used: 3–8 Å).
(24) J. Chrysochoos and A. Evers, *J. Lumin.*, **6**, 335 (1973).
(25) P. K. Gallagher, *J. Chem. Phys.*, **41**, 3061 (1964).
(26) The lifetime of the aquo ion, containing 9 molecules of H_2O, $[Eu(H_2O)_9]^{3+}$,[27] is 108 μs and the lifetime of $[Eu(NO_3)_3(H_2O)_m]$ amounts to 257 μs, as measured in acetonitrile.[28] The lifetime of $[Eu(NO_3)(H_2O)_n]^{2+}$ is calculated using the linear relationship $\tau/\tau_0 = f([NO_3^-]/[Eu^{3+}])$.
(27) Y. Haas and G. Stein, *J. Phys. Chem.*, **75**, 3677 (1971).
(28) J.-C. G. Bünzli and J.-R. Yersin, to be submitted for publication.

Contribution from the Department of Chemistry,
University of Texas at Austin, Austin, Texas 78712

Carbon-13 Nuclear Magnetic Resonance Spectra of Trifluoromethyl Group 4 Compounds

LINDA A. HARMON, EDMUND K. S. LIU, and RICHARD J. LAGOW*

Received May 3, 1978

The carbon-13 chemical shifts and carbon–fluorine coupling constants for tetrakis(trifluoromethyl) compounds $(CF_3)_4M^{IV}$, where M = C, Ge, and Sn, and tris(trifluoromethyl)(difluoromethyl)methane are reported. The trends in the carbon-13 chemical shifts are the reverse of that expected on the basis of pure electronegativity effects. Correlations between carbon–fluorine coupling constants and both fluorine chemical shifts and the position in the periodic table of the substituents directly attached to the carbon atom are observed for trifluoromethyl derivatives of main-group elements.

Introduction

^{13}C NMR has proved to be a valuable technique for elucidating electronic and structural characteristics of numerous compounds.[1] However, a survey of the literature indicates that there is a paucity of carbon-13 spectral data for perfluorinated compounds and that the theoretical principles and molecular parameters affecting ^{13}C NMR coupling constants and chemical shifts of perfluorinated compounds are often not clearly understood. In an effort to provide new information we have recorded the ^{13}C spectra of the tetrakis(trifluoromethyl) derivatives of the group 4 elements and have compared their ^{13}C and ^{19}F NMR spectral data with that of other trifluoromethyl derivatives of main-group elements.

Experimental Section

The tetrakis(trifluoromethyl) compounds $(CF_3)_4C$,[2] $(CF_3)_4Ge$,[3] and $(CF_3)_4Sn$[4] were prepared by methods developed in our laboratory. $(CF_3)_3CCF_2H$ was obtained from the direct fluorination of $(CH_3)_4C$ and purified by gas chromatography on a SE-30 column.

The natural-abundance carbon-13 spectra were obtained on a Bruker WH-90 (FT mode) spectrometer operating at a resonance frequency of 22.615 MHz. The spectrum of $(CF_3)_3CCF_2H$ was determined with proton noise decoupling. In order to obtain the chemical shift of the central carbon of $(CF_3)_4C$, a fluorine-decoupled carbon-13 spectrum was measured on a Thompson Packard TPV-XLFT-100 (FT mode) spectrometer operating at 25.2 MHz.

The $(CF_3)_4Sn$ and $(CF_3)_4Ge$ compounds were sealed in 5-mm tubes as neat liquids, and the tubes were placed coaxially in 10-mm tubes containing $CDCl_3$, which served as an external lock. (Chemical shifts were converted to the Me_4Si scale by $\delta(Me_4Si) = \delta(CDCl_3) + 77.7$.) The $(CF_3)_4Sn$ ^{13}C NMR spectrum was recorded at 0 °C to prevent decomposition of the sample. The spectrum of $(CF_3)_4Ge$ was recorded at 23 °C. Both $C(CF_3)_4C$ and $(CF_3)_3CCF_2H$ were sealed in 8-mm tubes containing cyclohexane as an internal reference. (Chemical shifts were converted to the Me_4Si scale by $\delta(Me_4Si) = \delta(C_6H_{12}) + 27.8$.) The 8-mm tubes were placed coaxially in 10-mm tubes

0020-1669/79/1318-0607$01.00/0 © 1979 American Chemical Society

Table I. Chemical Shifts and Coupling Constants for Trifluoromethyl Groups

compd	δ(C)[a]	δ(F)[b]	$\lvert J$(CF)$\rvert$[c]
(CF$_3$)$_4$C	120.9[d] 119[e] (63.4)[e,f] 119.9[g]	62.6[2]	289.9 292.7
(CF$_3$)$_3$CCF$_2$H	121.6 (110.9)[h]	66.01 (126.6)[h] [14]	288.3 (257.4)[h]
(CF$_3$)$_4$Ge	126.1	46[3]	330.7
(CF$_3$)$_4$Sn	132.7	43[4]	349.2
CF$_3$C(CH$_3$)$_3$[13]	129.2 (36.9)[f]	81	281
CF$_3$Ge(CH$_3$)$_3$[13]	132.6	61	338
CF$_3$Sn(CH$_3$)$_3$[13]	133.8	49.3	356
(CF$_3$)$_3$P[15]	126.4	50.8	
(CF$_3$)$_3$N[9]		58.6/59	269
(CF$_3$)$_2$O[2]	118.9	62	264
(CF$_3$)$_2$S[2]	127.6	38.64	309
(CF$_3$)$_2$Se[16]		31.92	331.3
CF$_4$[2]	119.9	62	260
CF$_3$Cl[2]	125.5	33	301
CF$_3$Br[2]	112.7	21	323
CF$_3$I	78.2	4.78	344

[a] Parts per million from δ(C)[(CH$_3$)$_4$Si]; positive values are low field. [b] Parts per million from δ(F)[CFCl$_3$]; positive values are high field. [c] In hertz. [d] From carbon-13; recorded on a Bruker WH-90 spectrometer. [e] From carbon-13; recorded on a Thompson Packard TPV-XLFT-100. [f] Central carbon. [g] Saturated solution of (CF$_3$)$_4$C in CDCl$_3$. [h] Difluoromethyl group.

containing D$_2$O. D$_2$O served as an external lock for the instrument. In order to record the spectra of (CF$_3$)$_4$C and (CF$_3$)$_3$CCF$_2$H as neat liquids, it was necessary to record the spectra at 80 °C. For the fluorine-decoupled spectra of (CF$_3$)$_4$C, the compound was sealed in a 8-mm tube and the tube was placed coaxially in a 12-mm tube which contained D$_2$O. The ^{13}C NMR of (CF$_3$)$_4$C was also recorded at 30 °C with a 10-mm tube containing a saturated solution of (CF$_3$)$_4$C in CDCl$_3$ (500 mg of (CF$_3$)$_4$C to 3 mL of CDCl$_3$).

Results

The carbon-13 chemical shifts and carbon–fluorine coupling constants for the compounds M(CF$_3$)$_4$, M = C, Ge, or Sn, are summarized in Table I. These are the first reports of carbon-13 chemical shifts and carbon–fluorine coupling constants for M^{IV}(CF$_3$)$_4$ compounds.

The temperature range of chemical shift and coupling constant data arises due to solubilities and concentrations of the compounds. Due to the low solubility of C(CF$_3$)$_4$, it was necessary to record the ^{13}C NMR spectrum at 80 °C. At 80 °C, C(CF$_3$)$_4$ is a liquid, thus facilitating spectral acquisition on the neat liquid. It was necessary to record the spectrum of Sn(CF$_3$)$_4$ at 0 °C to prevent decomposition of the compound during the long data collection. The signal-to-noise ratio was best for Ge(CF$_3$)$_4$ when the spectrum was recorded at room temperature. It is believed that the 80 °C spread should not affect the ordering of the chemical shifts in our case since large variations due to possible intermolecular interactions are not present.

Discussion

It has been previously reported that the ^{13}C resonances of trifluoromethyl derivatives of organic compounds occur in a surprisingly narrow spectral range.[5] A similar phenomenon is observed for the trifluoromethyl carbon of (CF$_3$)$_4$M^{IV} compounds. For the (CF$_3$)$_4$M^{IV} series, the total range of carbon-13 shielding is 13.9 ppm, which is less than half of that observed for the analogous tetramethyl derivatives. It appears that the three fluorines attached to carbon exert a greater influence on the carbon than the fourth substituent. However, the factors contributing to this effect are not totally obvious, as can be seen from examination of the trends in δ(C) of the (CF$_3$)$_4$M^{IV} compounds. As the atomic number of M^{IV} increases, the trifluoromethyl carbon of the (CF$_3$)$_4$M^{IV} resonance occurs at a lower field. In contrast, a high-field shift is observed as the atomic number of M^{IV} increases for (CH$_3$)$_4$M^{IV} compounds. The trend observed for the (CH$_3$)$_4$M^{IV} [1] compounds has been explained on the basis of both the electronegativity of M^{IV} and the estimated charge on the methyl carbon;[6] i.e., as the electronegativity of M^{IV} decreases with increasing atomic number, the electron charge density and shielding of the methyl carbon are increased. However, the shielding of the trifluoromethyl carbon with increasing electronegativity of M^{IV} observed for the (CF$_3$)$_4$M^{IV} compounds shows no simple dependence of the carbon-13 chemical shifts of the CF$_3$ groups with the expected charge distribution. The fact that the fluorine-19 resonances, as well as the carbon-13 resonances, are observed at lower fields as the atomic number of M^{IV} increases indicates that considerations of electronic charge are not necessarily preponderant in this series. It is expected that an inductive change in one part of a molecule, such as shielding of the carbon nucleus, would require balancing by an opposing effect, such as a relative deshielding of the fluorine nucleus. In fact, a plot of δ(C) as a function of δ(F) for the trifluoromethyl main-group compounds (Figure 1) indicates that, with the possible exception of the trifluoromethyl halides, there is no simple relationship between δ(F) and δ(C). It therefore appears that charge distribution is not the dominant factor which determines δ(C) for most trifluoromethyl main-group compounds, but instead anisotropic, inductive, steric, charge polarization, and multiple bonding effects or combinations of these effects may be important. However, it is not obvious how these factors affect the chemical shifts of the trifluoromethyl carbons.

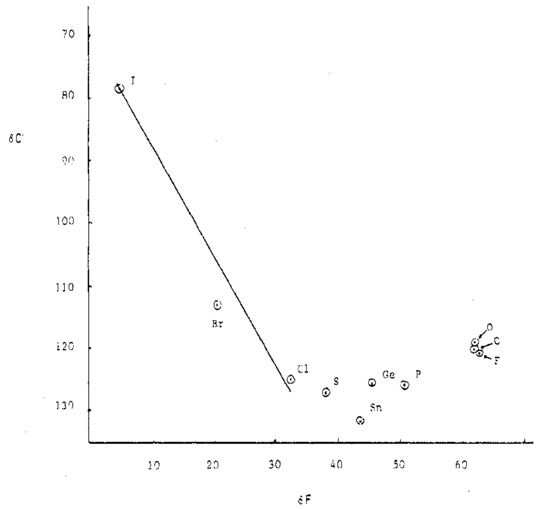

Figure 1. Plot of δ(C) (referenced to Me$_4$Si) vs. δ(F) (referenced to CFCl$_3$) for (CF$_3$)$_n$M compounds. The elements labeling the points identify M.

The values of $\lvert J$(CF)$\rvert$ for the (CF$_3$)$_n$M compounds (Table I) show a correlation with the position of M in the periodic table. The magnitude of the coupling constant $\lvert J$(CF)$\rvert$ generally decreases as the atomic number within a given row increases, and it increases as the atomic number of M within a given periodic group increases. The largest increase in $\lvert J$(CF)$\rvert$ within a given group for (CF$_3$)$_n$M compounds is observed with substitution of the first-row element by a second-row element for M. These periodic trends associated with increasing $\lvert J$(CF)$\rvert$ parallel expected increases in C–M bond lengths. Similar dependences of $\lvert J$(CH)$\rvert$[7] and $\lvert J$(CF)$\rvert$[8] on carbon–substituent bond lengths have been reported previously.

Muller and Carr observed linear relationships between $\lvert J$(CF)$\rvert$ and δ(F) for a series of structurally similar compounds.[9] The increases in $\lvert J$(CF)$\rvert$ with concomitant decreases in δ(F) reported by Muller and Carr for the tetrahalomethanes cannot be explained in terms of the expected changes in the

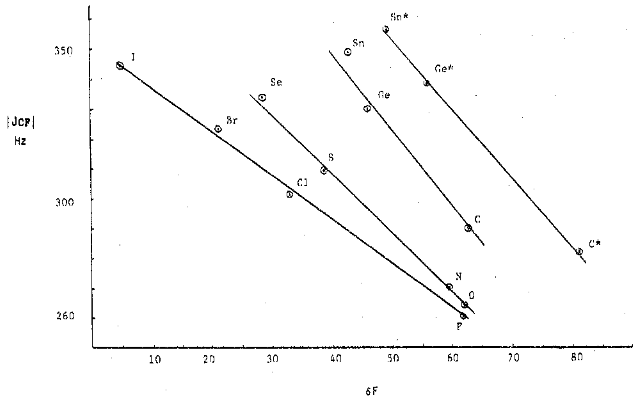

Figure 2. Plot of $|J(\mathrm{CF})|$ vs. $\delta(\mathrm{F})$ (referenced to $CFCl_3$) for $(CF_3)_nM$ and $CF_3M(CH_3)_3$ compounds. The elements labeling the points identify M. The asterisk designates compounds included in the $CF_3M(CH_3)_3$ series.

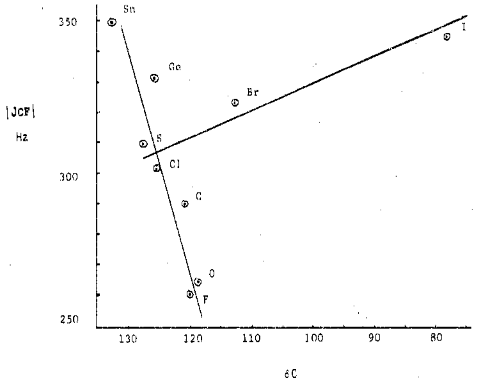

Figure 3. Plot of $|J(\mathrm{CF})|$ vs. $\delta(\mathrm{C})$ (referenced to Me_4Si) for $(CF_3)_nM$ compounds. The elements labeling the points identify M.

ionic character of the C–F bond. Instead, it was concluded that the multiple-bonding character of the C–F bond has the most important influence on $\delta(\mathrm{F})$ and $|J(\mathrm{CF})|$ for these compounds. Muller and Carr have suggested that with increasing polarity or decreasing multiple-bonding character of the C–F bond, $\delta(\mathrm{F})$ increases whereas $|J(\mathrm{CF})|$ decreases. To determine if these same factors are important for $(CF_3)_nM$ compounds, $|J(\mathrm{CF})|$ has been plotted as a function of $\delta(\mathrm{F})$ and $\delta(\mathrm{C})$. From Figure 2 a roughly linear relationship is seen between $|J(\mathrm{CF})|$ and $\delta(\mathrm{F})$ in $(CF_3)_nM$ compounds in which the elements bonded to the CF_3 groups are from the same group in the periodic table. Since $|J(\mathrm{CF})|$ increases as $\delta(\mathrm{F})$ decreases with increasing atomic numbers within a given group, it appears that the multiple-bonding character of the C–F bond influences $\delta(\mathrm{F})$ and $|J(\mathrm{CF})|$ in $(CF_3)_nM$ compounds. The different slopes of the lines characteristic of each periodic group may in part reflect differences in the number of lone pairs associated with elements of a given group.

The plot of $|J(\mathrm{CF})|$ as a function of $\delta(\mathrm{C})$ (Figure 3) indicates that the no single parameter can be invoked to explain the relationship between carbon–fluorine coupling constants and carbon-13 chemical shifts. As DeMarco and co-workers have noted for trifluoromethyl halides, $|J(\mathrm{CF})|$ increases as $\delta(\mathrm{C})$ decreases.[5] This trend is in accord with that predicted in multiple-bonding effects. However, comparison of the carbon–fluorine coupling constant and the carbon-13 chemical shift for other $(CF_3)_nM$ compounds indicates that as $|J(\mathrm{CF})|$ increases $\delta(\mathrm{C})$ also increases. There is at the present time no rationalization for this reversal in these trends.

The resonance of the central carbon of $(CF_3)_4$ occurs at a surprisingly high field. Since the carbon–carbon bond distance in neopentane is 1.562 Å,[10] whereas the carbon–halide bond distances for CF_4, CCl_4, and CBr_4 are 1.323, 1.766, and 1.942 Å,[11] respectively, one would expect, based on structural considerations, the central carbon to resonate to lower field. (The $\delta(\mathrm{C})$ observed for CF_4, CCl_4, and CBr_4 are 119.9,[5] 96.7,[1] and −28.5,[1] respectively.) However, comparison of the chemical shift of the central carbon with that of neopentane and trimethyl(trifluoromethyl)methane indicates that the shielding of the central carbon of neopentane decreases in a regular manner with successive substitution of CF_3 groups for CH_3 groups. Since the chemical shifts of the central carbons of neopentane, trimethyl(trifluoromethyl)methane, and perfluoroneopentane are 28.1,[12] 36.9,[13] and 63.4, respectively, it appears that the replacement of a CH_3 group in neopentane by a CF_3 group produces a deshielding of 8.8 ppm.

Structural arguments given here lead to a logical conclusion, consistent with the data. However, it should not be inferred that only structural considerations are important in considering ^{13}C chemical shifts and coupling constants.[17] In considering group 4 trifluoromethyl compounds, the central atom increases in size from carbon to germanium to tin; thus the trifluoromethyl groups are necessarily farther apart as one goes down the periodic table. Therefore, structural considerations lead to a logical conclusion to explain the downfield chemical shifts as we observe. Possible steric crowding in $C(CF_3)_4$ would cause an upfield chemical shift if one can infer a "gauche" effect.[18] This is one possible explanation since intuitively the CF_3 groups should be less "crowded" in going from C to Ge to Sn.

Conclusion

The many factors involved in simple correlations between shifts and coupling constants can be quite complex in fluorine-containing compounds, as in the completely substituted trifluoromethyl compounds presented here. In an effort to further elucidate the factors which might affect both carbon-13 and fluorine-19 nuclear magnetic resonance of compounds containing trifluoromethyl groups, we are preparing and examining other trifluoromethyl-containing compounds.

Acknowledgment. Support of this work by the National Science Foundation (Grant No. CHE-76-20866-A01) is gratefully acknowledged. We especially thank Dr. J. D. Odom for measuring the fluorine-decoupled carbon-13 spectrum of perfluoroneopentane.

Registry No. $(CF_3)_4C$, 374-51-6; $(CF_3)_4Ge$, 55642-43-8; $(CF_3)_4Sn$, 41268-44-4; $(CF_3)_3CCF_2H$, 2993-15-9.

References and Notes

(1) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, 1972.
(2) N. J. Maraschin and R. J. Lagow, *Inorg. Chem.*, **12**, 1458 (1973).
(3) E. Liu and R. J. Lagow, *J. Chem. Soc., Chem. Commun.*, 450 (1977).
(4) R. J. Lagow, L. L. Gerchman, R. A. Jacobs, and J. A. Morrison, *J. Am. Chem. Soc.*, **97**, 518 (1975).
(5) R. A. DeMarco, W. B. Fox, W. B. Moniz, and S. A. Sojka, *J. Magn. Reson.*, **18**, 522 (1975).
(6) J. M. Sichel and M. A. Whitehead, *Theor. Chim. Acta*, **5**, 35 (1966).
(7) N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 1471 (1959); A. W. Douglas, *ibid.*, **45**, 3465 (1966).
(8) I. Love, *J. Mol. Phys.*, **15**, 93 (1968).
(9) N. Muller and D. T. Carr, *J. Phys. Chem.*, **67**, 112 (1963).
(10) H. Oberhammer, private communication.
(11) I. Náray-Szabó, "Inorganic Crystal Chemistry", Akadémiai Kiadó, Budapest, 1969, p 156.
(12) F. J. Weigert, M. Winakur, and J. D. Roberts, *J. Am. Chem. Soc.*, **90**, 1566 (1968).
(13) R. Eujen and H. Burger, *J. Organomet. Chem.*, **88**, 165 (1975).
(14) J. L. Adcock, B. D. Catsikis, J. W. Thompson, and R. J. Lagow, *J. Fluorine Chem.*, **7**, 197 (1976).
(15) R. G. Cavell, J. A. Gibson, and K. I. The, *J. Am. Chem. Soc.*, **99**, 7841 (1977).
(16) R. K. Harris, *J. Mol. Spectrosc.*, **10**, 309 (1963).
(17) Theoretical calculations for carbon–fluorine coupling constants have not been very successful. The complexity has been shown in a recent review. See J. W. Emsley, L. Phillips, and V. Wray, "Fluorine Coupling Constants", Pergamon Press, Ltd., Oxford, 1977, pp 111–113.
(18) D. G. Gorenstein, *J. Am. Chem. Soc.*, **99**, 2254 (1977).