TABLE II

COMPARISON BETWEEN CALCULATED AND OBSERVED BORON-11 CHEMICAL SHIFTS (PPM)

Compound[a]	Obsd shift[b]	Calcd shift	Diff
H_3BNH_3	23.8,[c] 24.0[d]	22.9	−0.97
$H_3BNH_2(t\text{-}C_4H_9)$	22.1[c]	23.2	1.12
$H_3BNH_2CH_3$	20.5,[c] 19.6[d]	19.9	−0.15
$H_3BNH(CH_3)_2$	14.7,[c] 15.0,[d] 15.4[e]	15.0	0.00
$H_3BN(C_2H_5)_3$	14.3[d]	12.9	−1.31
$(CH_3)_3BNH_3$	8.7[d]	9.5	0.79
$H_3BN(CH_3)_3$	8.5,[d] 8.1[f]	9.7	1.42
$(CH_3)_3BNH_2CH_3$	7.5[d]	6.7	−0.79
$H_3B^*N(CH_3)_2BH_2NH_3$	10.2[g]	10.8	0.61
$H_3B^*N(CH_3)_2BH_2NH_2CH_3$	12.1[g]	11.3	−0.79
$H_3B^*N(CH_3)_2BH_2NH(CH_3)_2$	12.4[g]	11.8	−0.59
$H_3B^*N(CH_3)_2BH_2N(CH_3)_3$	11.65[g]	12.3	0.66
$H_3BN(CH_3)_2B^*H_2NH_3$	2.9[g]	5.2	2.28
$H_3BN(CH_3)_2B^*H_2NH_2CH_3$	3.18[g]	2.21	−0.97
$H_3BN(CH_3)_2B^*H_2NH(CH_3)_2$	−3.0[g]	−3.0	0.00
$H_3BN(CH_3)_2B^*H_2N(CH_3)_3$	−3.45[g]	−3.58	−0.13
$(C_2H_5)_3BNH(CH_3)_2$	−4.0[c]	−3.7	0.26
$(CH_3)_3BNH(CH_3)_2$	4.9[d]	4.6	−0.26
$(CH_3)_3BN(CH_3)_3$	0.8[d]	0.8	0.00
$H_2B(NH_3)_2^+$	14.6[c]	13.9	−0.65
$H_2B[N(CH_3)_3]_2^+$	−2.9[h]	−3.6	−0.68
$H_2B[N(CH_3)_2C_2H_5]_2^+$	−1.4[h]	−1.4	0.00
$H_2B[N(CH_3)(C_2H_5)_2]_2^+$	0.6[h]	0.7	0.17

[a] B* indicates observed boron. [b] Boron-11 shifts are relative to $BF_3 \cdot (C_2H_5)_2O$. Where more than one value is reported the average was used. When necessary, values were converted by $\delta[BF_3 \cdot (C_2H_5)_2O] = \delta[B(OCH_3)_3] - 17.4$. See J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press Inc., New York, N. Y., 1966. [c] R. Schaeffer, "Progress in Boron Chemistry," Vol. 1, H. Steinberg and A. L. McCloskey, Ed., The Macmillan Co., New York, N. Y., 1964, p 417. [d] C. W. Heitsch, *Inorg. Chem.*, **4**, 1019 (1965). [e] W. D. Phillips, H. C. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **81**, 4496 (1959). [f] D. F. Gaines and R. Schaeffer, *ibid.*, **86**, 1505 (1964). [g] G. A. Hahn and R. Schaeffer, *ibid.*, **86**, 1503 (1964). [h] N. E. Miller and E. L. Muetterties, *ibid.*, **86**, 1036 (1964).

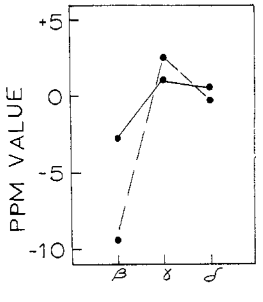

Figure 1.—Comparison of β, γ, and δ parameters for C^{13} (– – – –) and B^{11} (———) shifts.

coupled with the fact that indications exist[8] that the energy difference between the *gauche* and *trans* forms of amine boranes is similar to that for the corresponding alkanes, suggests that the positive γ-carbon effect observed in both the carbon-13 and the boron-11 systems arises from similar phenomena.

Acknowledgment.—We wish to thank Professor C. N. Reilley and Mr. J. R. Layton of the University of North Carolina for the computer program.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA

The Reaction of Silicon Difluoride with Germane

BY D. SOLAN AND P. L. TIMMS[1]

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Gaseous silicon difluoride, prepared at high temperatures from silicon and silicon tetrafluoride, has been shown to react with many volatile compounds upon cocondensation at low temperatures.[2-4]

These reactions of silicon difluoride provide a convenient way of preparing types of compounds containing one or, more commonly, two or three $-SiF_2-$ groups, which are difficult to synthesize by other methods.[4] A reaction between germane and silicon difluoride thus suggested itself as a method of making compounds which would be analogs of the known silicon–germanium hydrides[5,6] but with $-SiH_2-$ groups replaced by $-SiF_2-$ groups. An attempt to make fully fluorinated germanium–silicon compounds from silicon difluoride and germanium tetrafluoride had led to the explosive formation of silicon tetrafluoride and germanium fluoride polymers instead of the desired products.[7]

Results

Condensation of a low-pressure gaseous mixture containing silicon difluoride, silicon tetrafluoride, and germane in a roughly 4:2:3 mole ratio, at −196°, gave an orange-yellow solid. When this solid was warmed under vacuum, unreacted silicon tetrafluoride and germane were pumped off first, followed by a mixture of reaction products. The solid became colorless as it warmed up, and at about 0° it melted and foamed vigorously. The residue at room temperature was an air-sensitive, viscous liquid, containing mainly silicon and fluorine with a little germanium and hydrogen. At least 80% of the silicon difluoride which had been condensed was retained in this residue, and the remainder was combined in the volatile products.

Reaction also occurred if a mixture of silicon difluoride and tetrafluoride in a 2:1 mole ratio was first condensed at −196°, and then germane was condensed on top of it. The behavior of the combined condensate on warming was similar to that observed when the components were cocondensed. However, the yield of volatile reaction products was lower than with cocondensation.

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(3) P. L. Timms, R. A. Kent, T. C. Ehlert, and J. L. Margrave, *J. Am. Chem. Soc.*, **87**, 2824 (1965).

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TABLE I

MASS SPECTRA OF THE GERMYLFLUOROSILANES AT 50 eV

		Intensity (relative to Ge–GeH_2 = 100)		
m/e	Assignment	GeH_3SiF_2H	$GeH_3Si_2F_4H$	$GeH_3Si_3F_6H$
47	SiF^+	40	83	12
66	SiF_2^+	20	7.5	...
67	SiF_2H^+	5	7.5	1.5
70–78[a]	Ge–GeH_2^+	100	100	100
85	SiF_3^+	20[b]	15	13
99–106[a]	GeSiH–$GeSiH_2^+$	...	5	68
113	SiF_3^+	...	...	3
114	$Si_2F_3H^+$	...	1.5	2
117–125[a]	GeSiF–$GeSiFH_2^+$	9	10	76
133	$Si_2F_4H^+$	...	1	...
136–145[a]	$GeSiF_2$–$GeSiF_2H_3^+$	33	22	66
145–153[a]	$GeSi_2F$–$GeSi_2FH_2^+$	...	...	63
155–163[a]	$GeSiF_3$–$GeSiF_3H_2^+$	3[b]	...	...
151	$Si_2F_5^+$	...	2[b]	...
183–192[a]	$GeSi_2F_3$–$GeSi_2F_3H_3^+$	...	7.5	53
203–211[a]	$GeSi_2F_4H$–$GeSi_2F_4H_3^+$	...	8	79
250–257[a]	$GeSi_3F_5H$–$GeSi_3F_5H_2^+$	...	...	48
269–277[a]	$GeSi_3F_6H$–$GeSi_3F_6H_3^+$	...	...	50

[a] The intensities are based on the sum of the heights of all of the peaks within the given mass range. [b] Peaks believed due to impurities in the germylfluorosilanes.

For either of the above reaction conditions, the products pumped off during warm-up proved to be a very complex mixture of compounds. The mixture could not be separated completely even using an efficient low-pressure distillation column. Attempts to use gas chromatography to separate the mixture, which had been very successful for the silicon–germanium hydrides,[6] caused complete decomposition of the products.

Five main fractions were collected, the compositions of which, judged by their mass spectra, were not appreciably changed by further distillation on the column. Two of the fractions were shown by their mass and infrared spectra to be nearly pure samples of the known perfluorosilanes Si_2F_6 and Si_3F_8.[3] The other three fractions were quite widely separated from one another in volatility. The amounts obtained of each decreased sharply from the most to the least volatile.

The mass spectra of the three fractions (Table I) showed that each contained the elements germanium, silicon, fluorine, and hydrogen. For all three, the most abundant group of ions was at *m/e* 70–78 corresponding to $^{70}Ge^+$–$^{76}GeH_2^+$. With the fractions considered in decreasing order of volatility, the most intense peaks at high *m/e* corresponded to $GeSiF_2H_3^+$, $GeSi_2F_4H_3^+$, and $GeSi_3F_6H_3^+$, respectively. The loss of at least one hydrogen atom on electron impact is known to occur frequently with the higher germanes and silanes.[8] Thus these ions suggested that the parent species were the saturated compounds containing one more hydrogen atom of molecular formula $GeSiF_2H_4$, $GeSi_2F_4H_4$, and $GeSi_3F_6H_4$, respectively.

The ions SiF_3^+ and $GeSiF_3H_2^+$ seen in the mass spectrum of the $GeSiF_2H_4$ fraction indicated a compound $GeSiF_3H_3$ as a possible impurity. Similarly, the small amount of the $Si_2F_5^+$ ion seen in the spectrum of the $GeSi_2F_4H_4$ fraction suggested that a compound containing an $-Si_2F_5$ group was present, but no more positive identification was possible.

Vapor density measurements on the $GeSiF_2H_4$ and $GeSi_2F_4H_4$ fractions gave values close to those expected for these formulas. Small amounts of impurities like $GeSiF_3H_3$, slightly richer in fluorine, would not have much effect on these measurements. Instability and low volatility prevented a vapor density determination on the $GeSi_3F_6H_4$ fraction.

The infrared spectra of the vapors of the three fractions each showed a strong absorption in the ranges 2190–2215, 2076–2150, and 774–778 cm^{-1}. These were assigned, respectively, by analogy with the silanes and germanes, to Si–H and Ge–H stretching frequencies and a GeH_3 symmetrical deformation frequency.[9] The group of strong absorptions in the 800–980-cm^{-1} range in all of the spectra could be assigned to Si–F stretching frequencies.[3]

On the basis of the infrared and mass spectra results, the structure of the main components of each fraction was indicated to be of the type $GeH_3Si_nF_{2n}H$. The position of the hydrogen atom attached to silicon in $GeH_3Si_2F_4H$ and $GeH_3Si_3F_6H$ was left uncertain by these results. Final confirmation of the structures of the components of the two most volatile fractions was obtained from their nmr spectra, but $GeH_3Si_3F_6H$ proved too unstable in the liquid phase to obtain reproducible nmr spectra.

The proton nmr spectra (Table II) showed resonances with chemical shifts similar to those of known fluorosilanes[10] and germanes.[11] The observed splittings corresponded to expected first-order interactions in the structures GeH_3SiF_2H and $GeH_3SiF_2SiF_2H$. In the spectrum of the GeH_3SiF_2H fraction, the ratio of the area of the Ge–H to Si–H resonances was 3.3:1.0. The ^{19}F nmr spectrum of the sample showed, in addi-

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TABLE II

NMR SPECTRA OF THE GERMYLFLUOROSILANES

Compound	Assignment	Chemical shift, ppm	$J_{\text{F-Si-H}}$, Hz	$J_{\text{F-Si-Ge-H}}$, Hz	$J_{\text{H-Si-Ge-H}}$, Hz	$J_{\text{F-Si-Si-H}}$, Hz	Remarks
		A. ^{1}H Spectra, $Si(CH_3)_4$ Reference					
GeH_3SiF_2H	Si–H	−4.96	53		3		Triplet of quartets
	Ge–H	−2.72		9	3		Triplet of doublets
$GeH_3SiF_2SiF_2H$	Si–H	−4.74	55			5	Triplet of triplets
	Ge–H	−3.00		7.5			Triplet
		B. ^{19}F Spectra, external CCl_3F Reference					
GeH_3SiF_2H	Si–F	+126.6	54.5	8			Doublet of quartets
		$J_{^{29}\text{Si–F}}$ = 344 Hz					Doublet of doublets of quartets
GeH_3SiF_3?	Si–F	+106		8			Quartet
		$J_{^{29}\text{Si–F}}$ = 343 Hz					Doublet of quartets

tion to the doublet of quartets expected for GeH_3SiF_2H, another quartet at lower field. The area of this was approximately one-tenth the area of the doublet of quartets. Similar coupling constants were found for these two sets of resonances with both the F–Si–Ge–H and the F–^{29}Si interactions. These results were consistent with the presence of the molecule GeH_3SiF_3 together with GeH_3SiF_2H. This had already been indicated in the mass spectrum of the fraction, and the two compounds would be expected to be of very similar volatility and thus difficult to separate.

The main components of the three fractions can be called germylfluorosilanes. Only the fraction containing GeH_3SiF_2H and GeH_3SiF_3, which was gaseous, was stable at room temperature. The other two fractions, particularly the $GeH_3Si_3F_6H$ fraction, decomposed readily above 0°. The fractions were pyrophoric and extremely sensitive to moisture. They all evolved germane on treatment with 10% KOH solution.

Discussion

There is much evidence that the normal pattern of reaction of silicon difluoride with another compound at −196° is as follows.[12,13] Two or more molecules of silicon difluoride come together upon condensation on the cold surface to form a short-lived diradical species. This can either interact immediately with other molecules cocondensed with the silicon difluoride to give products containing two or more silicon atoms or form a less reactive silicon difluoride polymer.

The reaction of silicon difluoride and germane does not fit this pattern. Reaction occurred both when the two compounds were cocondensed and when they were condensed one after the other. The major product containing germanium and silicon was GeH_3SiF_2H and not the disilicon compound. This suggests that germane attacked the silicon chain in a $(SiF_2)_n$ polymer, breaking off units containing one, two, or more silicon atoms. The diminishing stability of the germylfluorosilanes with increasing numbers of $-SiF_2-$ groups illustrates the large effect a germyl group has on an $-SiF_2-$ chain. The fraction containing $GeH_3Si_3F_6H$ gave polymers and lower germylfluorosilanes on decomposition.

Apart from their unexpected low stability, the spectroscopic and other physical properties of the germylfluorosilanes indicate they have some characteristics of both the silicon–germanium hydrides[5] and the perfluorosilanes.[3]

Experimental Section

Silicon difluoride was prepared as previously described[2] at the rate of about 0.8 mmol/min, at a pressure not exceeding 200 μ. It contained unreacted silicon tetrafluoride, the $SiF_2:SiF_4$ ratio being about 2:1. Germane was made by hydrolysis of magnesium germanide and was carefully distilled before use. It was added to the low-pressure silicon difluoride stream at the rate of about 0.6 mmol/min. The gas mixture was condensed on being pumped through a trap at −196°.

A few millimoles of volatile reaction products were pumped off on warming the above condensate. These were fractionated on a 3 ft long distillation column. The column was of an unpublished design used in the laboratories of R. Schaeffer at Indiana University, in which the volatiles moved under vacuum up the annular space between two vertical, concentric, glass tubes. Cold nitrogen gas, passing into the inner tube from the top, was warmed in passage down the column establishing an axial temperature gradient. The fractions collected off the column were handled in a grease-free vacuum line employing Viton O-ring stopcocks and joints.

Vapor Densities.—The vapor densities of the GeH_3SiF_2H and $GeH_3SiF_2SiF_2H$ fractions were measured on 10-mg samples in a calibrated constant-volume system, using a mercury manometer to determine pressure. The molecular weights were found to be 144 ± 4 (correct for GeH_3SiF_2H, 140; for GeH_3SiF_2H + 10% GeH_3SiF_3, 142) and 208 ± 6 (correct for $GeH_3SiF_2SiF_2H$, 209), respectively.

Mass Spectra.—Samples were evaporated directly from a condensed phase into the ion-source region of a Bendix Model 1400 time-of-flight mass spectrometer equipped with an all-glass input system. This method was well suited to getting reliable spectra for the less stable germylfluorosilanes.

Infrared Spectra.—All spectra were taken in the vapor phase at 5–20 mm in 6-cm glass cells with KBr or NaCl windows using an Infracord spectrometer. Quite rapid decomposition of $GeH_3Si_3F_6H$ was noticed. The observed frequencies (cm^{-1}) for the three germylfluorosilane fractions were as follows (intensities in parentheses): GeH_3SiF_2H: 2198 (s), 2090 (s), 980 (m), 960 (s), 885 (s), 870 (s), 774 (vs); $GeH_3Si_2F_4H$: 2190 (s), 2076 (s), 981 (m), 957 (s), 932 (vs), 884 (m), 844 (s), 807 (s), 778 (vs), 546 (m); $GeH_3Si_3F_6H$: 2215 (m), 2105 (m), 968 (vs), 945 (s), 870 (s), 850 (vs), 826 (m), 809 (m), 779 (s).

Nmr Spectra.—Proton nmr spectra were run on a Varian A-60 spectrometer using neat liquid samples containing about 2% tetramethylsilane, contained in 3-mm bore, thick-walled tubes.

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Spectra were run at −30° for GeH_3SiF_2H and at 0° for $GeH_3Si_2F_4H$. The ^{19}F spectrum of GeH_3SiF_2H was obtained on a Varian HR-100 spectrometer at 94.1 Mc.

Physical Properties.—The melting points of the GeH_3SiF_2H and $GeH_3Si_2F_4H$ fractions were measured by the Stock ring method at −77 and −4°, respectively. Vapor pressure measurements on the GeH_3SiF_2H fraction over the temperature range −70 to −10° and on the $GeH_3Si_2F_4H$ fraction over the temperature range −40 to −4° gave log p *vs.* $1/T$ plots which could be fitted approximately to the equations $\log p_{mm} = 6.93 - (1162/T)$ and $\log p_{mm} = 10.10 - (2365/T)$. From the vapor pressure equation of the liquid GeH_3SiF_2H fraction, the boiling point of the compound is estimated to be 13°.

The Reaction with KOH.—A sample of the GeH_3SiF_2H fraction, corresponding to 0.30 mmol, was condensed on top of 5 ml of 10% KOH solution frozen in an ampoule. The ampoule was sealed, warmed to room temperature to allow reaction to occur, and then reopened on the vacuum line. The gas pumped out contained 0.28 mmol of germane, 94% of the theoretical yield.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF SOUTHERN CALIFORNIA,
LOS ANGELES, CALIFORNIA 90007

Further Knowledge of Ligand–Nickel Sesquicarbonyls[1]

BY ROBERT A. SINCLAIR AND ANTON B. BURG

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An earlier publication described new binuclear nickel–carbonyl derivatives of the type $L_2Ni_2(CO)_3$, where L is a bis-phosphine ligand.[2] The synthesis of another compound in this class, namely, $Lhn_2Ni_2(CO)_3$, where $Lhn = (CF_3)_2P(NH)P(CF_3)_2$,[3] permits a fuller comparison of properties; for example, an infrared comparison with the compound previously designated as "$Ln_2Ni_2(CO)_3$," namely $[(CF_3)_2P(NCH_3)P(CF_3)_2]_2Ni_2(CO)_3$, leads to a possible explanation of the greater stability of $Lhn_2Ni_2(CO)_3$.

Synthesis and Formula.—A solution of the ligand Lhn and $Ni(CO)_4$ in isohexane (a clean mixture of 2- and 3-methylpentanes) was formed under high-vacuum conditions in a stopcocked filtering Λ tube, which then stood at 25° with frequent pump-off of the evolved CO. During the first 3 hr it developed a pale yellow tinge, and after 6 hr (1.387 CO evolved per Ni) yellow crystals appeared. After 81 hr the yellow solid was collected on the filter, leaving only an unweighable trace in the yellow solution.

The quantitative results now could be expressed by the following equation with millimolar stoichiometry.

$$\begin{array}{ccccc} 2Ni(CO)_4 & + 2Lhn & \longrightarrow & 5CO & + Lhn_2Ni_2(CO)_3 \\ 1.768 & 2.105 & & 4.164 & 0.878 \\ & & & (>94\%) & (99.2\% \text{ of Ni}) \end{array}$$

Although the measured CO was nearly 6% deficient, its further evolution during the subsequent work-up of the mixture would account for the difference. Also, although the amount of unused Lhn was not accurately determined, a rough estimate would agree well enough with the exact equation.

At 80–90° under high vacuum, the yellow solid $Lhn_2Ni_2(CO)_3$ sublimed completely except for a 0.36% residue (not included in the reported 0.878-mmol yield). Its volatility over a range of temperatures conformed well to the equation $\log P = 12.502 - (4820/T)$ (examples: 0.31 mm at 97.3°, 0.55 mm at 105.1°, 0.97 mm at 112.0°, and 1.36 mm at 116.5°), indicating a pure substance having a 22.07-kcal molar heat of sublimation. The molecular weight was determined tensiometrically in ether: 907 at 25° or 956 at 0° (calcd, 907.5). The virtually quantitative synthesis left no doubt of the identity of the new compound as a close analog of the earlier $Ln_2Ni_2(CO)_3$,[2] differing only in having NH rather than NCH_3 groups connecting P to P. The infrared spectra also confirmed the analogy.

Solubility and Stability Comparisons.—Many tests showed that the N-connected sesquicarbonyls dissolve only in media which might solvate them by electron-donor bonding. For example, $Ln_2Ni_2(CO)_3$ is not soluble enough in hexane to show color, while $Lhn_2Ni_2(CO)_3$ shows only the faintest yellow; but both dissolve fairly well in acetone. The solubility of $Lhn_2Ni_2(CO)_3$ in diethyl ether at 25° is at least 20%; that of $Ln_2Ni_2(CO)_3$ at 36°, about 8%. The far stronger base $(CH_3)_3N$ was absorbed (10 days at 25°) to form $Ln_2Ni_2(CO)_3 \cdot 2(CH_3)_3N$ without loss of CO. The purple, solid product in a Nujol mull showed infrared peaks at 2047, 2032, and 1832 cm^{-1}, *vs.* 2075, 2052, and 1913 cm^{-1} for the original $Ln_2Ni_2(CO)_3$.

The ostensibly analogous $[(CF_3)_2PSP(CF_3)_2]_2Ni_2(CO)_3$, which we have written as $Ls_2Ni_2(CO)_3$,[2] decomposes promptly in any medium capable of dissolving it. In ethers it turned brown, with liberation of volatiles showing C–F infrared spectra; and the original compound could not be recovered. The $(CH_3)_2O$ solution at 25° became permanently violet during 24 hr. The effects of methanol, acetone, acetylacetone, monoglyme, or acetonitrile were much like those of the ethers. The amines $(CH_3)_3N$ and $(C_2H_5)_3N$ liberated CO and $P_2(CF_3)_4$, and the infrared spectrum of the residue showed no CO-bridge mode.

This S-connected compound is very unstable in the vapor phase (so that only its strongest infrared peaks could be recorded, at 65°), whereas $Lhn_2Ni_2(CO)_3$ vapor remained stable during long infrared scans at 102°. Solid $Lhn_2Ni_2(CO)_3$ survived a 10-min heating at 157° but melted at 180° with loss of CO and Lhn. The de-

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(1) It is a pleasure to acknowledge the generous support of this research through Grants GP-3812 and GP-6751X from the National Science Foundation, which aided also toward making available the Beckman IR7 infrared spectrophotometer through Grant No. 14665.

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