of the protons of the methyl groups at positions 2, 2′, 4, and 4′ and those of the ring protons at positions 3 and 3′ are much larger and those of the protons at positions α and β are much smaller than those of the corresponding protons of the foregoing stilbene anion radicals (cf. Table I). The benzene rings of HMS⁻· cannot be coplanar with the central ethylenic part, mainly because of the steric interaction of the methyl groups at positions 6 and 6′ with the hydrogen atoms at positions β and α. Examination of the electronic absorption spectrum of this anion radical in frozen 2-methyltetrahydrofuran solution and of its change caused by controlled warming confirmed the nonplanarity of the preferred conformation.[4] The extraordinariness of the |*a*| values undoubtedly reflects the nonplanarity of the conformation.

The preferred conformation of the (*E*)-α,β-dimethylstilbene anion radical (α,β-DMS⁻·) was proved to deviate from planarity much more than does that of HMS⁻·.[4] No ENDOR signal of α,β-DMS⁻· could be detected, probably because of the strong tendency of this anion radical to become the dianion under reduction with alkali metal in fluid DME solution. The tendency possibly reflects the large nonplanarity of the conformation.[4]

Detection of ã³A₂ (n,π*) Selenoformaldehyde by Flash Pyrolysis

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Abstract: An absorption spectrum has been recorded in the near infrared, 822 nm, which has been attributed to the unstable species CH_2Se. It was detected in a flow system in which dimethyl selenide, $(CH_3)_2Se$, was flash pyrolyzed and then passed into a cell of 68-m path length. The spectrum was assigned to the spin-forbidden ã³A₂ ← X̃¹A₁, n → π* electronic transition. A single progression of bands at 707 cm⁻¹ was observed which was assigned to ν_3', the CSe stretching mode. Also appearing weakly in the spectrum was the double quantum addition $2\nu_4'$, the out-of-plane bending mode. It is believed that the structural changes which occur on excitation parallel those which have been observed for the corresponding transition in CH_2S. That is, the CSe bond increases slightly in length, and the planar configuration is retained in the upper state.

During the last few years, considerable attention[1] has been devoted to the spectroscopy of the thiocarbonyl compounds XYCS; X and Y are variously H, F, Cl, or R groups. Several methods have been used to produce this class of compound, all of which rely on the thermal instability of the thioether linkage which cleaves at moderate temperatures to form the thiocarbonyl bond. The starting material for these pyrolysis experiments has taken the form of cyclic trimers,[2] cyclic dimers,[3] cyclic sulfides,[4] alkyl sulfides,[5] and alkyl disulfides.[5]

The spectroscopy of the selenocarbonyl compounds is, to a large extent, unexplored. Recently the spectrum of F₂CSe has been recorded in the visible and ultraviolet[6] regions while CH₃CHSe (selenoacetaldehyde) has been observed in the microwave[7] region. Our experiences with thiocarbonyl molecules have shown that thioformaldehyde is the least stable compound. Accordingly, it was anticipated that while selenoformaldehyde would be highly unstable, it should be detectable under conditions of very fast flow and low pressures. The forbidden nature of the electronic transitions which lie in the near infrared would require that very long path lengths of the vapor be employed.

Experimental Section

Selenoformaldehyde was prepared by the flash pyrolysis of dimethyl selenide according to the reaction

$$CH_3SeCH_3 \xrightarrow[700\ °C]{\Delta} CH_2Se + CH_4$$
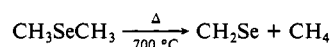
The dimethyl selenide was obtained from Alfa Products and was used without further purification. The pyrolysis chamber consisted of a dimpled fused silica tube, 2.5 cm in diameter and 20 cm in length, which had been heated to 700 °C by a pair of clam shell furnaces. The products of the reaction were quickly drawn into a 2-m White-type multiple reflection cell and then exhausted to a cold trap at −180 °C. The optimum pressure path was 1.5 torr (as measured by a pirani gauge) and 68 m.

Absorption within the region 7500–4000 Å was recorded on Kodak high-speed infrared film by using a Bausch and Lomb 1.5-m spectrograph with a dispersion of 15 nm/cm. Absorption spectra to lower frequencies were recorded by using a 2-m vacuum Ebert spectrograph with a first-order dispersion of 2.6 nm/cm. A 450-W Xe arc supplied the continuum for both experiments. Hollow cathode Fe/Ne lines served as calibration markers. Band heads were measured from negatives by using a traveling microscope or, in the case of weak indistinct bands, from photographic prints enlarged 10 times.

Results and Discussion

The spectrum of selenoformaldehyde is illustrated in Figure 1. It is dominated by a band located at 12 169 cm⁻¹. As no further absorption was observed at lower frequencies, this band was immediately assigned as the electronic origin 0^0_0. Three other strong bands at 12 876, 13 573, and 14 266 cm⁻¹ can be grouped into a progression of 707 cm⁻¹. This is assigned to quanta of the CSe stretching mode, ν_3'. A closer examination of the 3^1_0 absorption band, 12 876 cm⁻¹, revealed the presence of a second band 19.9 cm⁻¹ to lower frequencies. It is assigned to two quanta of ν_4', the out-of-plane vibration. The value for $2\nu_4'$ of 687 cm⁻¹ compares favorably with that obtained for ã³A₂ (nπ*) thioformaldehyde,[8] 711 cm⁻¹. Very weak bands were observed at 13 481

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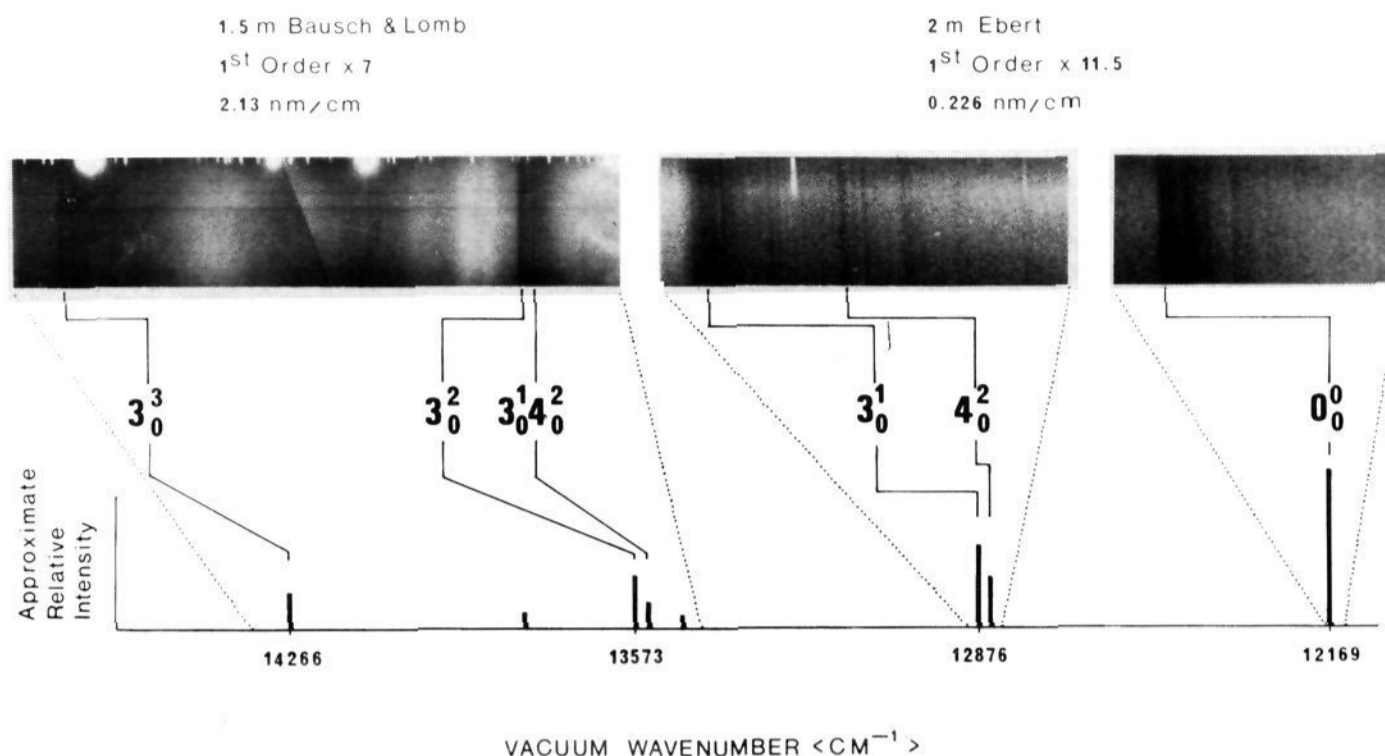(3) Downs, A. J. *Spectrochim. Acta* **1963,** *19,* 1165–1171.
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1.5 m Bausch & Lomb
1st Order x 7
2.13 nm/cm

2 m Ebert
1st Order x 11.5
0.226 nm/cm

3_0^3　　3_0^2　$3_0^1 4_0^2$　　3_0^1　4_0^2　　0_0^0

Approximate Relative Intensity

14266　　　　　　13573　　　　　12876　　　　12169

VACUUM WAVENUMBER <CM^{-1}>

Figure 1. Vibrational structure associated with the $\tilde{a}^3A_2 \leftarrow \tilde{X}^1A_1$ electronic transition in CH_2Se.

and 13 792 cm^{-1}. These bands cannot be fitted into this vibrational scheme, and it is believed that they are the result of a second electronic transition. Laser excitation spectra of this region[9] combined with H/D isotope shifts will be necessary for a more complete understanding.

Like CH_2O and CH_2S, the $\tilde{X}$ ground state of CH_2Se is expected to be planar and belongs to the C_{2v} point group. Electronic transitions would then be directed along the x, y, and z axes and be of b_1, b_2, and a_1 species, respectively. CH_2Se will behave like a near prolate symmetric top with the x, y, and z axes corresponding to the c, b, and a principal axes. Consequently, type A transitions will be directed along the top axis (parallel-type bands) while type B or C transition will be perpendicular to the top axis (perpendicular-type bands). For a near prolate symmetric type, type A bands are governed by the selection rule $\Delta K = 0$ and generally give rise to bands with a single sharp band head. For example, the type A bands of CH_2S and CH_2O are single headed and red degraded. By contrast, type B and C bands of a near prolate rotor follow the selection rule $\Delta K = \pm 1$ and give rise to absorption bands which contain multiple band heads. The strong bands at 12 169 and 12 876 cm^{-1} are clearly single headed. They are assigned as parallel, type A, bands.

Type A bands appear in the lower electronic transitions of CH_2O and CH_2S by one of three mechanisms: (a) as a magnetic dipole transition between the $\tilde{A}^1A_2$ and $\tilde{X}^1A_1$ states, (b) as vibronically allowed transitions between the higher vibrational levels of the $\tilde{A}^1A_2$ state and the ground state, or (c) as the R(z) component of the spin forbidden $\tilde{a}^3A_2 \leftarrow \tilde{X}^1A_1$ transition. The rotational contour of the bands made allowed by mechanisms (a) and (b) are similar and are governed by the rotational selection rule $\Delta K = 0$, $\Delta J = 0, \pm 1$. The singlet–triplet bands of case (c) are characterized by S, Q, and O form branches, $\Delta N = 0, \pm 2$ and $\Delta K = 0$, and are generally more conjested and more extensive than those of the singlet–singlet bands (a) and (b).

Under the resolution of the 2-m instrument, the individual rotational lines of CH_2Se are not resolved. This is a consequence of the modest resolving power of this instrument and the presence of the five isotopes of selenium, $^{76}Se/^{77}Se/^{78}Se/^{80}Se/^{82}Se$, with percent abundance of 10/8/24/50/9. It was not immediately apparent whether these bands were from the S–S or T–S systems. This difficulty was resolved by turning to thee S–S and T–S systems of CH_2S. The 6000-Å region of CH_2S was rephotographed under the first-order resolving power of the 2-m Ebert

instrument, and the type A bands corresponding to cases (a), (b), and (c) were identified in the spectrum. A comparison of the structure and the widths of the rotational contours of the bands of CH_2S with those of CH_2Se clearly show that the spectrum of selenoformaldehyde is the result of a triplet–singlet transition, $\tilde{a}^3A_2 \leftarrow \tilde{X}^1A_1$.

It is somewhat surprising that the spin allowed companion transition $\tilde{A}^1A_2 \leftarrow \tilde{X}^1A_1$ does not appear strongly in the spectrum. This we believe is not due to an inherent weakness of the S–S system but rather to the relative strength of the T–S system. The oscillator strength of the T–S transition in CH_2S has been estimated[8] to be at least three times greater in CH_2S than it is in CH_2O. This can be attributed to the higher spin orbit coupling constant for sulfur, $\xi(O)/\xi(S) = 382/152$, and to the smaller perturbation gap between the $\tilde{a}^3A_2$ and $\tilde{B}^1A_1$ states. Since the atomic spin orbit coupling factor contains the factor Z^4 it would be anticipated that the *f* value of CH_2Se should be about an order of magnitude greater than CH_2S. It follows that if the T–S bands of CH_2Se were observed with good contrast in the spectrum, then the bands of the S–S system would be at, or below, the level of photographic detection.

Vibronic-spin–orbit selection rules allow only for the activity of the a_1 totally symmetric vibrational modes. Thus, any analysis of the "cold" band structure would involve quanta of ν_1(CH), ν_2(HCH), ν_3(CSe), and even quanta of ν_4 (out of plane), ν_5, and ν_6. The intensities of these transitions depend on Franck–Condon factors which in turn depend on the changes in the internal coordinates which occur in the molecule on electronic excitation. Structural changes accompanying n $\rightarrow \pi^*$ electron promotion can be reduced to two contributions: (a) those resulting from the loss of the nonbonding electron and (b) those resulting from the addition of that electron to the antibonding π^* orbital. While the removal of the n electron only indirectly affects the molecular structure, the presence of the electron in the π^* orbital reduces the order of the CSe bond from 2 to 1.5. Thus, it would be expected on Franck–Condon grounds that a progression in the ν_3'(CSe) stretching mode would dominate the spectrum. A quantitative determination of Δr(CSe) from Franck–Condon considerations will have to await the vibrational data[9] from the lower $\tilde{X}$ state. The lack of activity in the ν_1' and ν_2' modes can be related to the absence of structural changes in the CH or HCH internal coordinates. The weakness of the 4_0^2 band relative to the 0_0^0 origin band is an indicator that the molecule, like CH_2S, is floppy planar in the $\tilde{a}^3A_2$ state.

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