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ENDOR Studies of the (*E*)-Stilbene Anion Radical and Its Methylated Derivatives

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Abstract: The ENDOR spectra of the anion radicals produced by reduction of (*E*)-stilbene and its methylated derivatives with potassium or sodium in 1,2-dimethoxyethane were measured. On the basis of the assumption that the most preferred conformation of (*E*)-2,2′-dimethyl- and (*E*)-2,2′,5,5′-tetramethylstilbene anion radicals is the *ap,ap* conformation, all the isotropic proton hyperfine coupling constants were unambiguously assigned. Especially, the hyperfine coupling constants of the nonequivalent ortho as well as the nonequivalent meta protons of the rotatable phenyl groups of the (*E*)-stilbene anion radical were separately assigned for the first time. From examination of the ENDOR spectrum, the most preferred conformation of the (*E*)-3,3′-dimethylstilbene anion radical was inferred to be the *sp,sp* conformation. The extraordinariness of the hyperfine coupling constants of the (*E*)-2,2′,4,4′,6,6′-hexamethylstilbene anion radical was found and attributed to nonplanarity of the conformation.

In the past 2 decades, many aromatic radical ions have been studied by ESR spectroscopy, and most of the well-resolved hyperfine splittings have been assigned to the corresponding protons without extreme difficulty, mainly by means of deuterium substitution or sometimes by the aid of molecular orbital calculation. However, when a phenyl group involved is rotatable around the bond which is not colinear with a C_2 axis of the radical ion, the origins of the hyperfine coupling constants (hfc's: *a*'s) of the nonequivalent ortho protons as well as the nonequivalent meta protons cannot be distinguished by ordinary methods.

We could, for the first time, unambiguously assign all the *a*'s of the (*E*)-stilbene anion radical ($S^{-}\cdot$) as a typical radical ion with such rotatable phenyl groups. In the present paper, we report the method and results of this assignment and a finding about the conformation of the (*E*)-3,3′-dimethylstilbene anion radical (3,3′-$DMS^{-}\cdot$).

In this paper, the numbering of carbon atoms shown in Figure 1 is used.

The preferred conformation of $S^{-}\cdot$ in fluid solutions is probably planar or nearly planar.[4]

ESR studies of $S^{-}\cdot$ have been repeatedly carried out.[5-7] In the ESR spectrum of a solution of $S^{-}\cdot$ and potassium ion in 1,2-dimethoxyethane (DME) at −60 °C, two values of $|a|$ (0.190 and 0.296 mT) were obtained for the ortho protons, and two values of $|a|$ (0.030 and 0.081 mT) were also obtained for the meta protons.[5,6] This implies that two nonequivalent sets of ortho protons and two nonequivalent sets of meta protons exist and therefore that the rotation around the C–Ph bonds is frozen on the ESR time scale. The assignment of $|a|$ values was made by referring them to the result of the calculation of spin densities by McLachlan's method[8] with use of the conventional Hückel MO's. However, the $|a|$ values of the nonequivalent ortho and the nonequivalent meta protons could not be separately assigned to protons at specified positions.

Deuterium substitution is useless for such an assignment. If one of the ortho protons, for example, of $S^{-}\cdot$ is substituted by a deuteron, the ESR spectrum of the *d*-substituted anion radical will be the spectrum of a mixture of planar or nearly planar 2-*d* and 6-*d* conformers (i.e., *ap* and *sp* conformers), which have approximately equal energies and therefore approximately equal populations. Therefore, the $|a|$ values of the protons at positions 2 and 6 cannot be distinguished.

Empirical or semiempirical MO calculation is also useless for such a subtle problem, although it is useful as a limited guide for rough assignment of $|a|$'s of protons at positions with much different spin densities. If the spin densities are evaluated by McLachlan's method with use of the conventional Hückel MO's, the same value is obtained for the two nonequivalent sets of ortho positions (2 and 2′; 6 and 6′), for example, as a natural result of inclusion of only the nearest neighbor interactions. Such a situation is not much improved even by the use of the Pariser–Parr–Pople (PPP) method.[9] When the basis functions are constructed from the SCF-MO's of the neutral molecule or the dianion without an open shell, the spin densities at the nonequivalent ortho carbon atoms as well as those at the nonequivalent meta carbon atoms differ only slightly, and their relative magnitudes are changeable according to the selection of parameters used. Even if the SCF-MO's of the anion radical with an open shell are used, similar results are obtained from the restricted Hartree–Fock (RHF) calculation with configuration interaction (CI) and from the unrestricted Hartree–Fock (UHF) treatment with and without annihilation of the quartet spin component.[10] A similar result is also obtained from an INDO UHF calculation.[11] Thus, it is almost impossible to separately assign the $|a|$'s of the nonequivalent ortho protons as well as those of the nonequivalent meta protons by use of conventional empirical or semiempirical MO calculation.

In the present work, the assignment of all the $|a|$'s of $S^{-}\cdot$ was carried out by comparing the $|a|$'s of $S^{-}\cdot$ with those of some symmetrically methylated derivatives. Introduction of a methyl substituent to an ortho position of a phenyl group of $S^{-}\cdot$ destabilizes one of the two planar conformations by steric effect to a greater extent than the other and makes the less destabilized planar or nearly planar conformation the single most preferred conformation. It may be said that the *o*-methyl substitution nearly locks, in a sense, the phenyl group in a specifiable conformation. In the 2-methyl conformation (*ap* conformation), the methyl group in-

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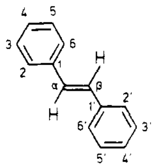

Figure 1. The numbering of carbon atoms in (*E*)-stilbene.

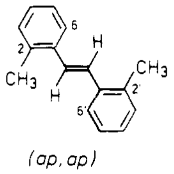

Figure 2. The 2,2′ conformation (*ap*,*ap* conformation) of (*E*)-2,2′-dimethylstilbene.

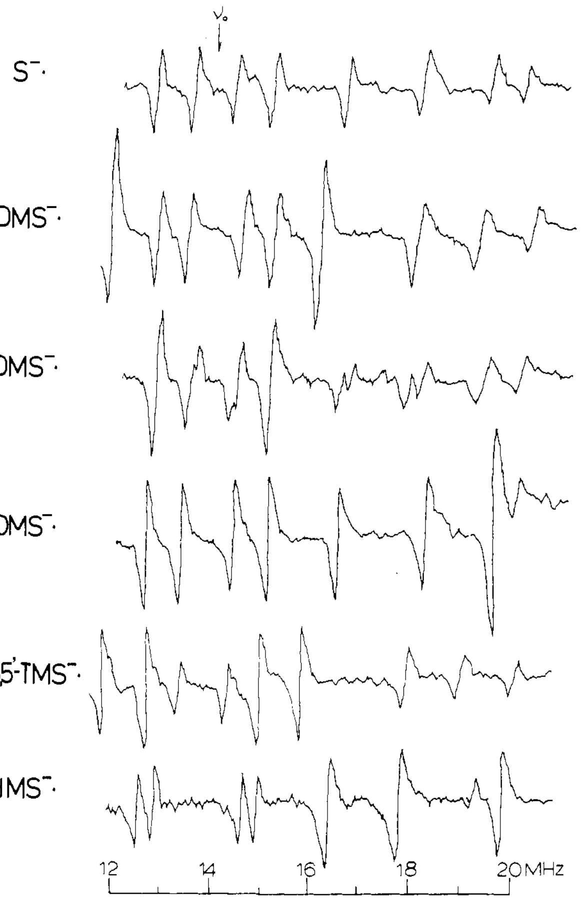

Figure 3. The high-frequency side of the ENDOR spectra recorded at −90 °C of the anion radicals of (*E*)-stilbene (S^{-}·), (*E*)-2,2′-dimethylstilbene (2,2′-DMS^{-}·), (*E*)-3,3′-dimethylstilbene (3,3′-DMS^{-}·), (*E*)-4,4′-dimethylstilbene (4,4′-DMS^{-}·), (*E*)-2,2′,5,5′-tetramethylstilbene (2,2′,5,5′-TMS^{-}·), and (*E*)-2,2′,4,4′,6,6′-hexamethylstilbene (HMS^{-}·), generated by reduction of the corresponding parent compounds with K in DME.

terferes sterically with the hydrogen atom at position α; in the 6-methyl conformation (*sp* conformation), the methyl group interferes sterically with the hydrogen atom at position β. The former interference is conceivably smaller than the latter.[12] Therefore, we assume that the most preferred conformation of the (*E*)-2,2′-dimethylstilbene anion radical (2,2′-DMS^{-}·), for example, is the nearly planar 2,2′-dimethyl conformation, that is, the *ap*,*ap* conformation, shown in Figure 2 (assumption 1).

The $|a|$'s were determined from the ENDOR spectra.[13] In addition to the nonequivalence of the ortho and the meta protons, the methylated derivatives of S^{-}· have a complication due to the presence of methyl groups. As a result, hyperfine structures observed in their ESR spectra are more complicated and almost impossible to analyze separately. Therefore, we used the ENDOR measurement as the most useful and adequate technique for determination of the $|a|$'s of these anion radicals.

In addition to assumption 1, the following assumptions are made. (2) The ENDOR signal of protons of a methyl group is appreciably stronger than that of a ring proton. (3) The difference between the $|a|$ value of protons of a methyl group and that of the ring proton at the corresponding position is small. (4) The effect of methyl substitution on the $|a|$'s of the ring protons at the other positions is small. That is, the difference between the $|a|$'s of a ring proton of a methylated anion radical and of the ring proton at the corresponding position of the unsubstituted anion radical is small, and it becomes smaller with increasing distance between the position of the proton under consideration and the substitution position. All these assumptions have already been validated in previous work[14] and, as shown below, are confirmed in the present work.

On the basis of these assumptions, the values of $|a|$ of 2,2′-DMS · and the (*E*)-2,2′,5,5′-tetramethylstilbene anion radical (2,2′,5,5′-TMS^{-}·) were assigned to the methyl and the ring protons at specified positions. Then, by comparison of the spectrum of S^{-}· with those of the methylated anion radicals, the $|a|$ values of the nonequivalent ortho and the nonequivalent meta ring protons of S^{-}· were separately assigned. The $|a|$ value of the para ring protons was definitely determined by comparing the spectrum of S^{-}· with that of the (*E*)-4,4′-dimethylstilbene anion radical (4,4′-DMS^{-}·). Thus, all the $|a|$ values in S^{-}· and its methylated derivatives were unambiguously assigned without any contradiction to results of previous assignments. The present treatment may also be applicable to similar problems in other chemical species with rotatable phenyl groups.

In the course of this study, we obtained an interesting finding that the most preferred conformation of 3,3′-DMS^{-}· is probably the planar or nearly planar 5,5′-dimethyl conformation (*sp*,*sp* conformation).

In addition, we found the extraordinariness of the $|a|$ values of the (*E*)-2,2′,4,4′,6,6′-hexamethylstilbene anion radical (HMS^{-}·) as compared with those of the other stilbene anion radicals, and we ascribed it to the nonplanarity of the preferred conformation.

Experimental Section

Materials. (*E*)-Stilbene (mp 123–124 °C) was purchased from Tokyo Kasei Co. and purified by recrystallization. (*E*)-4,4′-Dimethylstilbene (mp 177–178 °C) was prepared by reduction of *p*-toluoin with zinc amalgam and concentrated hydrochloric acid.[15] (*E*)-2,2′-Dimethylstilbene (mp 81–82 °C), (*E*)-3,3′-dimethylstilbene (mp 58.0–58.5 °C), and (*E*)-2,2′,5,5′-tetramethylstilbene (mp 161–162 °C) were prepared by reductive coupling of the suitably methylated benzaldehydes with titanium(IV) chloride and zinc powder in dioxane, according to the procedure of Mukaiyama et al.[16] (*E*)-2,2′,4,4′,6,6′-Hexamethylstilbene (mp 131–132 °C) was prepared by heating thiomesitaldehyde with copper powder.[15]

ENDOR Measurements. The anion radicals were prepared by reduction of the stilbenes with potassium or sodium metal in 1,2-dimethoxyethane (DME) at the temperature of dry ice and acetone. The ENDOR spectra were recorded on a JEOL-ES-EDX-1 spectrometer. The

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[12] For reference, a previous finding may be cited here that in methylated derivatives of styrene the methyl group at position α interferes with the phenyl group to a smaller extent than does the methyl group at position β-cis. (Suzuki, H. *Bull. Chem. Soc. Jpn.* **1960**, *33*, 619–628).

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Table I. Isotropic Proton Hyperfine Coupling Constants ($|a|$'s) of the (*E*)-Stilbene Anion Radical and Its Methylated Derivatives (in mT)[a]

anion radical	$\|a_3\|$	$\|a_5\|$	$\|a_2\|$	$\|a_6\|$	$\|a_4\|$	$\|a_\alpha\|$
S^{-}·	0.031	0.084	0.193	0.303	0.402	0.450
2,2'-DMS^{-}·	0.039	0.082	0.151*	0.294	0.383	0.460
3,3'-DMS^{-}·	0.034*	0.082	0.196	0.283	0.387	0.444
	0.034	0.082*	0.186	0.302	0.387	0.444
4,4'-DMS^{-}·	0.038	0.088	0.189	0.318	0.416*	0.450
2,2',5,5'-TMS^{-}·	0.035	0.081*	0.144*	0.294	0.371	0.451
HMS^{-}·	0.065	0.088	0.193*	0.297*	0.438*	0.398

[a] Hfc's of methyl protons are denoted by asterisks.

condition was as follows: magnetic field, 0.3250 T; magnetic field modulation, 80 Hz (ca. 1.0 mT); microwave, 9.15 GHz (5 mW); radiowave, ca. 11–22 MHz (ca. 150 W) (free proton frequency ν_0 13.8 MHz); radio-frequency modulation, 6.5 KHz; temperature, −65 to −90 °C. In this temperature range, temperature dependence of hyperfine coupling constants was not observed. No significant effect of the counter metal cations on the coupling constants was detected.

Results and Discussion

ENDOR Spectra. Figure 3 shows the high-frequency side of the ENDOR spectra of the stilbene anion radicals. Hereafter, discussions on the ENDOR spectra will be done for their high-frequency side. The $|a|$ values obtained from the ENDOR spectra are listed in Table I. All the present $|a|$ values of the (*E*)-stilbene anion radical (S^{-}·) are in essential agreement with the values obtained in previous ESR studies,[5-7] although each of the former is slightly larger than the corresponding one of the latter.

Validation of Assumptions 2–4 and Assignment of the hfc of the Para Protons. Each signal position of the (*E*)-4,4'-dimethylstilbene anion radical (4,4'-DMS^{-}·) is only slightly different from the corresponding one of S^{-}·. This fact validates assumption 4. The 4,4'-DMS^{-}· signal ($|a|$ = 0.416 mT) at frequency close to the S^{-}· signal ($|a|$ = 0.402 mT) assigned to the para ring protons is much more intense than the other signals, and it is reliably assigned to the *p*-methyl groups. This fact confirms the assignment of the S^{-}· signal to the para ring protons and validates assumptions 2 and 3.

Assignment of the hfc's of the Ortho Protons. In the ENDOR spectrum of the (*E*)-2,2'-dimethylstilbene anion radical (2,2'-DMS^{-}·), the intense signal due to the methyl group ($|a|$ = 0.151 mT) appears at a frequency lower than the lower frequency one of the two S^{-}· signals ($|a|$ = 0.193 and 0.303 mT) assigned to the ortho ring protons. As mentioned above, the steric effect due to the methyl groups probably makes the 6,6'-dimethyl conformation (*sp,sp* conformation) less stable than the 2,2'-dimethyl conformation (*ap,ap* conformation), and consequently it makes the latter the single most populated conformation of 2,2'-DMS^{-}·. Therefore, as shown in Table I, the $|a|$ value of 0.151 mT is assigned to the protons of the methyl groups at positions 2 and 2' and that of 0.294 mT to the ring protons at positions 6 and 6'. Accordingly, the lower ($|a|$ = 0.193 mT) of the two $|a|$ values of the ortho ring protons of S^{-}· is assigned to the protons at positions 2 and 2' and the higher ($|a|$ = 0.303 mT) to the protons at positions 6 and 6'. Thus, the "locking of conformation" by the *o*-methyl substitution permitted the assignment of the $|a|$'s of the nonequivalent ortho ring protons.

Assignment of the hfc's of the Meta Protons. The assignment of the $|a|$'s of the nonequivalent meta ring protons also necessitates the "locking of conformation". The (*E*)-2,2',5,5'-tetramethylstilbene anion radical (2,2',5,5'-TMS^{-}·) was used as the most suitable species for this purpose, while the (*E*)-2,2',3,3'-tetramethylstilbene anion radical may not be preferable because of the interaction between two adjacent methyl groups.

The most populated conformation of 2,2',5,5'-TMS^{-}· is probably the 2,2',5,5'-tetramethyl conformation (*ap,ap* conformation). In the ENDOR spectrum of this anion radical, there appear two intense signals. One of the $|a|$ values of these signals (0.144 mT) is close to the $|a|$ value of the protons of the methyl groups at positions 2 and 2' of 2,2'-DMS^{-}· (0.151 mT), and therefore it is assigned to the protons of the methyl groups at positions 2 and 2', in agreement with the above assumption of the most populated conformation of 2,2',5,5'-TMS^{-}·. Accordingly, the $|a|$ value of another intense signal ($|a|$ = 0.081 mT) is assigned to the protons of the methyl groups at positions 5 and 5'. The $|a|$ values of 0.294 and 0.035 mT of weak signals are assigned to the ring protons at positions 6 and 6' and those at positions 3 and 3', respectively. From these results, the S^{-}· $|a|$ values of 0.031 and 0.084 mT are assigned to the ring protons at positions 3 and 3' and those at positions 5 and 5', respectively. Thus, the $|a|$'s of the nonequivalent meta ring protons of S^{-}· were separately assigned.

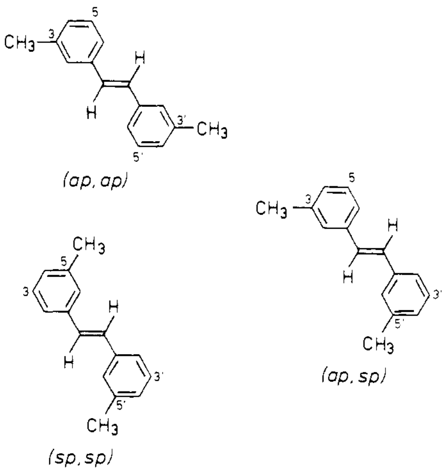

Figure 4. The 3,3' (*ap,ap*), 3,5' (*ap,sp*), and 5,5' (*sp,sp*) conformations of (*E*)-3,3'-dimethylstilbene.

Conformations of the (*E*)-3,3'-Dimethylstilbene Anion Radical. For the (*E*)-3,3'-dimethylstilbene anion radical (3,3'-DMS^{-}·), there should be three types of planar or nearly planar conformation, which may be expressed as 3,3'-, 3,5'- (or 3',5-), and 5,5'-dimethyl conformations or as *ap,ap*, *ap,sp* (or *sp,ap*), and *sp,sp* conformations (see Figure 4). These conformations might be expected to have nearly equal energies and therefore nearly equal populations. The ENDOR spectrum of this anion radical is probably due to a mixture of the conformers corresponding to these conformations. Actually the spectrum is relatively complex, exhibiting two more signals than do the spectra of the other anion radicals. In the frequency region where signals due to meta ring protons are to be detected, two intense signals are observed. By referring to the results of the assignment of signals of 2,2',5,5'-TMS^{-}·, the higher frequency signal ($|a|$ = 0.082 mT) is assigned to the methyl groups at position 5 and 5' and the lower frequency one ($|a|$ = 0.034 mT) to the methyl groups at positions 3 and 3'. The fact that the former is stronger than the latter indicates that the conformations with the 5- or 5'-methyl group are more stable and therefore more populated than the conformations with the 3- or 3'-methyl group. This means that the sequence of stability of conformations is probably 5,5'-dimethyl > 3,5'-dimethyl (or 3',5-dimethyl) > 3,3'-dimethyl.

In the frequency region of the ortho ring protons, 3,3'-DMS^{-}· exhibits two sets of signals. The signals of the outer set ($|a|$ = 0.186 and 0.302 mT) are stronger than those of the inner set ($|a|$ = 0.196 and 0.283 mT). The former are ascribed to the more populated 5-methylphenyl group and the latter to the less populated 3-methylphenyl group. That is, the $|a|$ values of 0.186 and 0.302 mT are assigned to the ring protons at positions 2 and 6 of the 5-methylphenyl group, respectively, and those of 0.196 and 0.283 mT are assigned to the ring protons at positions 2 and 6 of the 3-methylphenyl group, respectively. The facts that the $|a|$ value of the 2-proton of the 3-methylphenyl group is larger than that of the 2-proton of the 5-methylphenyl group and that the $|a|$ value of the 6-proton of the 5-methylphenyl group is larger than that of the 6-proton of the 3-methylphenyl group are qualitatively in accordance with results of MO calculation and are attributed to the substituent effect of the adjacent methyl group.

Effect of Nonplanarity of Conformation. Lastly we refer to some other symmetrically methylated stilbene anion radicals.

The $|a|$ values of the (*E*)-2,2',4,4',6,6'-hexamethylstilbene anion radical (HMS^{-}·) are somewhat extraordinary. Thus, the $|a|$ values 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 $HMS^{-}\cdot$ 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-$DMS^{-}\cdot$) was proved to deviate from planarity much more than does that of $HMS^{-}\cdot$.[4] No ENDOR signal of α,β-$DMS^{-}\cdot$ 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]

Registry No. $S^{-}\cdot$, 34473-61-5; 2,2′-$DMS^{-}\cdot$, 91237-56-8; 3,3′-$DMS^{-}\cdot$, 91237-57-9; 4,4′-$DMS^{-}\cdot$, 38424-10-1; 2,2′,5,5′-$TMS^{-}\cdot$, 91237-58-0; $HMS^{-}\cdot$, 34473-63-7.

Detection of $\tilde{a}^3A_2$ (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 $\tilde{a}^3A_2 \leftarrow \tilde{X}^1A_1$, $n \rightarrow \pi^*$ 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 F_2CSe has been recorded in the visible and ultraviolet[6] regions while CH_3CHSe (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 $\tilde{a}^3A_2$ ($n\pi^*$) thioformaldehyde,[8] 711 cm^{-1}. Very weak bands were observed at 13 481

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