$(CH_3)_2O$ and $(CH_3)_2S$ moieties indicates that the electrostatic effect of the complexed HF or HCl moiety is the dominant influence in increasing the monomer IPs on complexation. These calculations are described in more detail elsewhere.[21]

However, the π_F and π_{Cl} IP shifts are larger than any measured for $(CH_3)_2O$ and $(CH_3)_2S$ and the through-space dipole-induced potential-energy term only accounts for a fraction of the observed IP shifts in each case. The remaining amounts are accounted for by the effects of charge transfer and electronic relaxation. The decomposition scheme allows the calculation of the IP shift associated with charge transfer; the resulting values are labeled CT in Table II.

Molecular open-shell calculations are required to obtain theoretical estimates of electronic-relaxation effects associated with ionization. The data obtained for total ion energies of the appropriate valence-hole states of the monomer and complexed HF^+ and HCl^+ species allow the calculation of the differences in relaxation energies which represent the electronic-relaxation contribution to IP shift. The calculations which are described in more detail elsewhere[21] give the results labeled ER in Table II. These indicate that both charge-transfer and electronic-relaxation effects contribute comparable amounts to the π_F and π_{Cl} IP shifts on complexation. The calculated charge transfers involved are only small, being 0.06 e from $(CH_3)_2O$ to HF, 0.05 e from $(CH_3)_2S$ to HF, and 0.05 e from $(CH_3)_2O$ to HCl. The electronic-relaxation effect involves the highly polarizable $(CH_3)_2O$ or $(CH_3)_2S$ moieties in each complex, acting as a source of electron density which considerably stabilizes the localized valence hole in HF^+ or HCl^+. The calculations show that the movement of electron density is 0.13 e to HF^+ in $(CH_3)_2O{\cdot}HF^+$, 0.16 e to HF^+ in $(CH_3)_2S{\cdot}HF^+$, and 0.11 e to HCl^+ in $(CH_3)_2O{\cdot}HCl^+$.

Conclusion

On the basis of the He I photoelectron spectra measured for $(CH_3)_2O{\cdot}HF$ and $(CH_3)_2O{\cdot}HCl$, the much weaker gas-phase complex $(CH_3)_2S{\cdot}HF$ has been identified by its He I spectrum. The ionization-potential shifts associated with complexation are shown to arise from the electrostatic effect of the polar HF moiety on the $(CH_3)_2O$ and $(CH_3)_2S$ orbitals, but charge transfer accompanying complexation and electronic relaxation accompanying ionization are mainly responsible for the decreased IPs associated with its nonbonding π_F electrons. The neglect of electronic-relaxation effects is seen to have no influence on the spectral assignment based on the Koopmans approximation and the closed-shell wave functions.

This study provides a definitive spectroscopic identification of the $(CH_3)_2S{\cdot}HF$ species and indicates the considerable power of the photoelectron technique in the study of molecular systems of limited accessibility.

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Registry No. Dimethyl ether, 115-10-6; dimethyl sulfide, 75-18-3; hydrogen fluoride, 7664-39-3.

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Intermediates in the Sulfide Reduction of the 3,5-Diphenyl-1,2-dithiolylium Cation: A Resonance Raman Study

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Abstract: Resonance Raman spectra of two intermediates, absorbing at 545 and 473 nm, in the reaction between 3,5-diphenyl-1,2-dithiolylium perchlorate and excess sodium sulfide in ethanolic solution have been measured. Both chromophoric intermediates are assigned to anionic structures of the dithio-β-diketonate by using similar spectra of the disulfide cation and bis(dithiodibenzoylmethane)nickel(II) for comparison. The shorter lived transient is tentatively assigned to an open-chain disulfide anion or to the cis-*S*,*S* isomer of the dithio anion. The longer lived species is assigned to a trans isomer of the anion. Intense resonance Raman bands at 1140, 733, 550, and 380 cm^{-1} were assigned to $\nu(C{-}Ph) + \nu(C\underset{\cdots}{-}S)$, $\nu(C\underset{\cdots}{-}S)$, $\delta(CCC) + \delta(CCS)$, and $\delta(C\underset{\cdots}{-}S)$ vibrational modes in the intermediates. A medium-strong band at 600 cm^{-1} was linked with the open-chain $\nu(S{-}S)$ mode or $\delta(CCS)$ and $\delta(CCC)$ modes.

In the mechanism of disulfide bond reduction of straight-chain organic disulfides with sulfide ion, it has been postulated[1] that 1 mol of thiolate and 1 mol of organic persulfide are formed with subsequent loss of sulfur in the persulfide, S_2^{2-}, ion form. In similar reactions of cyclic disulfide cations, it has been suggested[2] that persulfide formation is preceded by nucleophilic attack on the 3- or 5-ring-carbon position of the 3,5-diphenyl-1,2-dithiolylium cation, hereafter denoted by $3,5\text{-}Ph_2D^+$, to form an adduct between cation and anionic nucleophile. The electronic absorption spectra of several intermediates in the conversion of the 3,5-diphenyl-1,2-dithiolylium cation to monothiodibenzoylmethane have recently been measured.[3] The reaction between disulfide cation and sodium sulfide in aqueous or alcoholic media is of particular interest since an expected intermediate is the dithiodibenzoylmethane anion. The existence of the ligand[4] has been implied as a result of trapping its metal complexes and spectroelectrochemical studies[5] of the disulfide cation reduction. To identify

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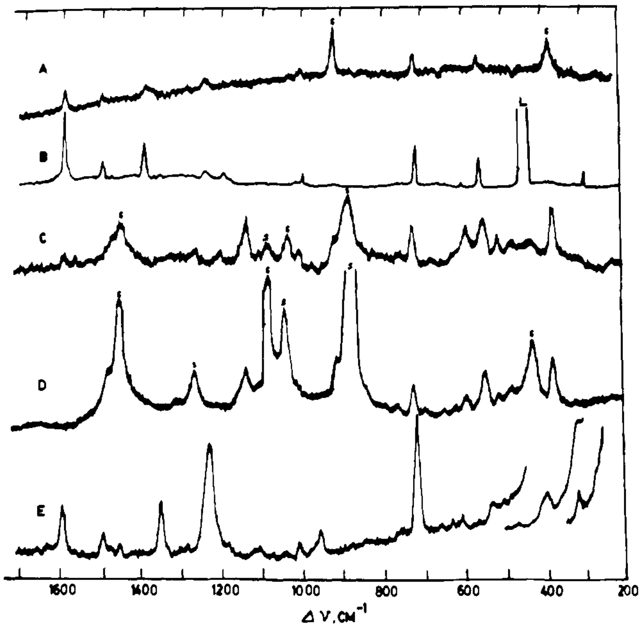

Figure 1. Raman spectra of (A) 647.1 nm, (B) 350.7 nm, 3,5-$Ph_2D^+ClO_4^-$ in acetonitrile; (C) 578.8 nm, (D) 476.5 nm, 1:1 mixture of 1.0 × 10^{-3} M 3,5-$Ph_2D^+ClO_4^-$ and 3.3 × 10^{-3} M Na_2S in ethanol; (E) 488.0 nm, bis(dithiodibenzoylmethane)nickel(II). (S) Solvent Raman bands; (L) laser line.

chromophoric intermediates in the reaction between 3,5-diphenyl-1,2-dithiolylium perchlorate and sodium sulfide and thus gain further insight into the mechanism of disulfide bond cleavage, we have measured the resonance Raman spectra of the disulfide cation, two transient species in the reaction with sulfide, and bis(dithiodibenzoylmethanato)nickel(II).

Experimental Section

The preparation and purification of 3,5-diphenyl-1,2-dithiolylium perchlorate have previously been described.[6,7] Solutions of 1.0 × 10^{-3} M 3,5-$Ph_2D^+ClO_4^-$ and 3.3 × 10^{-3} M anhydrous Na_2S in absolute ethanol were mixed 1:1 prior to passing through a quartz Raman cell. Anhydrous Na_2S was obtained by grinding reagent $Na_2S{\cdot}9H_2O$ into powdered form and drying it in vacuo over P_2O_5. A rapid flow rate (~3 mL/min) and short length of tubing between mixing chamber and Raman cell gave the violet species that absorbed maximally at 545 nm. A slow flow rate (~0.5 mL/min) and longer length of tubing gave the red species with λ_{max} 473 nm.

Bis(dithiodibenzoylmethanato)nickel(II) was prepared by mixing nickel(II) nitrate in water with 3,5-$Ph_2D^+ClO_4^-$ in ethanol and adding excess $NaBH_4$ in ethanol to the resulting solution. A dark red precipitate, which formed on addition of more water, was collected and dried in vacuo. Recrystallization of the crude product was performed in carbon disulfide. The melting point and infrared spectrum were compared with previously prepared material.[8]

Raman spectra obtained with Spectra-Physics Model 165 Ar^+ and Kr^+ laser and Coherent Model 590-03 dye (rhodamine 6G) laser excitation were measured on a Jarrell-Ash 25-500 double Ebert monochromator (*f*/6.5) by using a thermoelectrically cooled Hamamatsu R928 or R666S PM tube for detection. An EG&G PARC Model 1112 photon counter/processor was used in photon counting. Spectra of solid samples were obtained with a rotating cylindrical stainless steel cell that had a circular groove packed with powdered material. Incident laser light impinged on the groove at about 45° angle. Spectra in the ultraviolet region were recorded with a Spex 0.5-m double monochromator by using a Gencom picoammeter for DC detection and a Coherent Model 3000K laser for excitation. Solutions were recirculated with a peristaltic pump through quartz tubing (~1-mm diameter) arranged at 90° to the laser beam and monochromator slits. Scattered light was always collected at 90° to the incident beam.

Raman spectra are depicted in Figure 1 for A and B, saturated solution of 3,5-$Ph_2D^+ClO_4^-$ in acetonitrile; C and D, 1:1 mixture of 1.0 × 10^{-3} M 3,5-$Ph_2D^+ClO_4^-$ and 3.3 × 10^{-3} M anhydrous Na_2S in ethanol in flow cell; C, rapid flow rate; D, slow flow rate; E, bis(dithiodibenzoylmethane)nickel(II) solid. Experimental conditions [excitation wavelength (nm), laser power (mW), sensitivity, spectral slit width (cm^{-1}), scan speed (cm^{-1}/s)] are listed below: A, 647.1 Kr^+, 15, 3300 counts/s, 10.0, 1.0; B, 350.7 Kr^+, 100, 1 μA, 5.0, 0.75; C, 578.8 Ar^+ pumped dye, 60, 3300 counts/s, 10.0, 1.0; D, 476.5 Ar^+, 300, 5000 counts/s, 10.0, 1.0; E, 488.0 Ar^+, 120, 2500 counts/s, 10.0, 1.0. Solvent Raman bands, acetonitrile in A and ethanol in C and D, and the weak Kr^+ laser line in B are denoted by S and L, respectively.

Results and Discussion

The electronic absorption spectra of 3,5-$Ph_2D^+ClO_4^-$ and its reaction products with excess $Na_2S{\cdot}9H_2O$ in ethanol solution have been reported.[3] The lowest energy intense band[9] at 380 nm (log $\epsilon \sim 4.24$) of the disulfide ion collapsed on addition of sulfide. Well-defined absorption band maxima were observed at 545 nm ($\epsilon \geq 2800$) for a species of $t_{1/2} \simeq 1$ s and at 473 nm ($\epsilon \geq 2800$) for another species of $t_{1/2} \simeq 30$ min. Laser excitation at 350.7, 578.8, and 476.5 nm was used to irradiate into the 380-, 545-, and 473-nm absorption bands, respectively, of the three chromophoric species and obtain the resonance Raman spectra shown in Figure 1. The RR spectrum of the bis nickel(II) chelate shown in the same figure was obtained with 488.0-nm excitation into a 480-nm (ϵ 23 000) absorption band.[8]

The normal Raman spectrum (647.1-nm excitation) of 3,5-$Ph_2D^+ClO_4^-$ in acetonitrile or nitromethane solution (saturated) showed three bands assignable to the cation at 560, 719, and 1595 cm^{-1}. Very intense acetonitrile bands (Figure 1, spectrum A) are present at 378 and 920 cm^{-1}. The latter band may also contain some contribution from $\nu_1(ClO_4)$ at 928 cm^{-1}. In nitromethane solution the 378-cm^{-1} band is absent but a 920-cm^{-1} band from nitromethane also appears. Our previous Raman studies[10] of the 3,5-dimethyl-1,2-dithiolylium cation in aqueous solution showed that the most intense bands at 530 and 714 cm^{-1} were assignable to ν(S–S) and ν_s(C$\overset{..}{-}$S) modes in the cyclic disulfide ion. Therefore, bands at 560 and 719 cm^{-1} in 3,5-Ph_2D^+ are similarly assigned. The 1595-cm^{-1} band originates from a ring stretching mode of the phenyl groups. To obtain resonance Raman spectra (Figure 1, spectrum B) of 3,5-$Ph_2D^+ClO_4^-$ with 350.7-nm excitation into the 380-nm absorption band, we circulated a 5.0 × 10^{-3} M acetonitrile solution to prevent photodecomposition. Similar spectra were obtained in ethanolic solution, but the signal-to-noise ratio was much poorer (×10) due to lower solubility and photodecomposition and/or a chemical reaction to form ethoxide adduct.[2] RR band maxima in acetonitrile solution and suggested assignments are given in Table I. The spectrum with 350.7-nm excitation is free of interference from solvent and perchlorate bands—these are very weak if they occur at all; however, a *weak* Kr^+ laser line, <5-mW power, at 356.4 nm, which was not filtered out, gives an intense peak near 455 $cm^{-1} \simeq [(1/350.7) - (1/356.4)] \times 10^7$ cm^{-1}. No intense RR band is expected under the laser line since all observed RR bands have counterparts in the regular Raman spectrum in which no band appeared near 455 cm^{-1}. Clearly, the most intense Raman band is now the 1595-cm^{-1} phenyl group mode, indicating that the phenyl and dithiolylium ring systems are extensively electronically coupled, at least in producing the excited state that gives rise to the lowest energy parity-allowed transition, which is probably[11] $\pi \rightarrow \pi^*$. However, we note that the RR band at 1244 cm^{-1} that originates primarily from a stretching vibration of the phenyl–disulfide ring bond, ν(C–Ph), is very weakly enhanced. Its position is, though, 30 cm^{-1} higher than in the corresponding 3,5-dimethyl analogue.[10] Normal Raman spectra of the 3,5-dimethyl-1,2-dithiolylium cation in aqueous solutions obtained with 350.7- or 488.0-nm excitation, well removed from the lowest energy $\pi \rightarrow \pi^*$ band at 289 nm, showed an intense $\nu_s(C{-}CH_3)$ band at 1210 cm^{-1} with a peak height greater than that of the ν_s(C$\overset{..}{-}$C) band

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Table I. Raman Band Frequencies (cm^{-1}) and Suggested Assignments

$3,5\text{-Ph}_2\text{D}^+\text{ClO}_4^-$ in CH_3CN			1:1 mixture of $3,5\text{-Ph}_2\text{D}^+\text{ClO}_4^-$ and Na_2S in abs ethanol			$\text{Ni}^{\text{II}}\text{L}_2$,[a] solid	
excitation, nm		assignment	excitation, nm		assignment	excitation, nm	assignment
647.1	*350.7*		*578.8*	*476.5*		*488.0*	
	294 m		380 s	380 s	$\delta(\mathrm{C}{\cdots}\mathrm{S})$	320 m	$\nu(\mathrm{Ni{-}S})$
560 m	560 ms	$\nu(\mathrm{S{-}S})$	487 w	487 w		405 m	
	617 w		520 w	520 w		715 vs	$\nu(\mathrm{C}{\cdots}\mathrm{S})$
719 s	719 s	$\nu(\mathrm{C}{\cdots}\mathrm{S})$	550 s	550 s	$\delta(\mathrm{CCC}) + \delta(\mathrm{CCS})$	955 mw	
	1002 m	$\nu(\mathrm{Ph})$	600 ms	600 mw	$\nu(\mathrm{S{-}S})$	1010 w	$\nu(\mathrm{Ph})$
	1197 w			655 vw		1233 vs	$\nu(\mathrm{C{-}Ph}) + \nu(\mathrm{C}{\cdots}\mathrm{S})$
	1244 w	$\nu(\mathrm{C{-}Ph})$	733 s	733 s	$\nu(\mathrm{C}{\cdots}\mathrm{S})$	1358 ms	$\nu(\mathrm{C}{\cdots}\mathrm{C})$
	1392 s	$\nu(\mathrm{C}{\cdots}\mathrm{C})$	1140 s	1140 s	$\nu(\mathrm{C{-}Ph}) + \nu(\mathrm{C}{\cdots}\mathrm{S})$	1502 mw	$\nu(\mathrm{Ph})$
	1503 m	$\nu(\mathrm{Ph})$				1595 ms	$\nu(\mathrm{Ph})$
1595 s	1595 vs	$\nu(\mathrm{Ph})$	1595 w		$\nu(\mathrm{Ph})$		

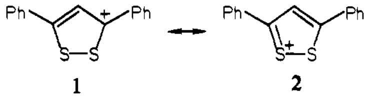
[a] L = dithiodibenzoylmethane anion.

at 1380 cm^{-1} but less than the peak heights of $\nu_s(\mathrm{C}{\cdots}\mathrm{S})$ and $\nu(\mathrm{S{-}S})$ bands at 724 and 525 cm^{-1}, respectively.

Both ethanolic and aqueous solutions of $3,5\text{-Ph}_2\text{D}^+\text{ClO}_4^-$ mixed with excess sodium sulfide show an initial absorption band maximum at 545 or 540 nm. Figure 1, spectrum C, shows the resonance Raman spectrum of this species, obtained with 578.8-nm excitation, well removed from the absorption peak of the subsequent absorbing species at 473 nm. The comparable intensification of $\nu(\mathrm{C}{\cdots}\mathrm{S})$ at 733 and $\nu(\mathrm{C{-}Ph}) + \nu(\mathrm{C}{\cdots}\mathrm{S})$ at 1140 cm^{-1} is similar to RR spectra[12] of bis(dithioacetylacetonato)nickel(II), which showed intense bands at 708 and 1165 cm^{-1}, and of the diphenyl analogue, Figure 1, spectrum E, which exhibits intense bands at 715 and 1233 cm^{-1}. The absence of any notable RR enhancement of $\nu(\mathrm{C}{\cdots}\mathrm{C})$ or $\nu(\mathrm{Ph})$ as observed in the nickel(II) complex in spectrum E at 1358 and 1595 cm^{-1} suggests that predominantly the $\mathrm{S}{\cdots}\mathrm{C}{\cdots}\mathrm{C}_{\mathrm{Ph}}$ groups are linked to the excited state and, therefore, to the vibrational modes that were observed. Very nearly the same Raman spectrum (D) is observed for the sulfide reaction intermediate that absorbs at 473 nm. A 476.5-nm excitation was used in this case, and the resonance enhancement of Raman bands is not as great as in spectrum C. The large increase in relative intensity of solvent Raman bands at 430, 890, 1055, 1100, 1280, and 1458 cm^{-1} shows that the enhancement factor is smaller. One notable change is the relative decrease in intensitification by more than a factor of 2 of a resonance Raman band at 600 cm^{-1}. Since excitation at 476.5 nm does enter part of the broad absorption band of the first species at 545 nm (absorbance of this band has dropped to one-fifth or less of its peak absorbance), it is possible for part of the RR spectrum of this initial species to be observed in spectrum D and thus show some intensity in the 600-cm^{-1} band.

The deep red two-electron reduced species from electrochemical reduction[5] of $3,5\text{-PhD}^+\text{ClO}_4^-$ in acetonitrile showed an absorption band at 483 nm that was assigned to the dithio-β-diketonate anion. The chemically generated red species ($\lambda_{\max} = 473$ nm) that is the second intermediate in the sulfide reduction of $3,5\text{-Ph}_2\text{D}^+$ in ethanol is also identified with the dithio anion. The same red species is obtained by sodium borohydride reduction of $3,5\text{-Ph}_2\text{D}^+$ in aqueous ($\lambda_{\max}$ 460 nm, $t_{1/2} = 15$ min) and ethanolic ($\lambda_{\max}$ 473 nm, $t_{1/2} = 3$ h) solutions. No shorter lived intermediate was detected in the borohydride reductions.

Reactions between a variety of nucleophiles and 1,2-dithiolylium cations have previously[2] been examined. In these studies evidence was cited to propose the initial formation of an adduct between the cation and nucleophile. For the bisulfide ion in aqueous and ethanolic solution, the dominant species from equilibrium constant data is the hydrosulfide ion, ^-SH. The principal resonance hybrids of $3,5\text{-Ph}_2\text{D}^+$ are the carbonium (**1**) and sulfonium (**2**) forms.



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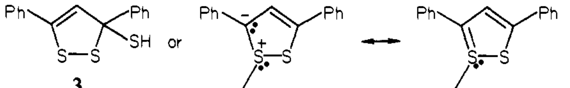
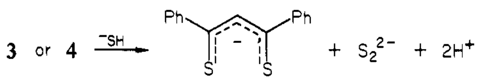
Thus the most likely adduct structures that would result from nucleophilic attack by ^-SH are



3 4a 4b

Species **4** is an ylide in which the central sulfur atom requires an expanded valence shell to have a pπ–dπ carbon–sulfur bond. Alternatively, the carbanion **4a** may be stabilized by polarization[12] at sulfur. Both adduct species retain the ring disulfide bond and have a ring pπ–pπ bond order of 1. This contrasts with the parent dithiolylium cation, which has a ring pπ–pπ bond order between 1 and 2. Crystallographic data and normal-mode analyses indicated[4] considerable π character in the ring C–C, C–S, and S–S bonds. Both adduct structures, though, no longer possess the plane of symmetry that is perpendicular to the ring, contains the central C–H bond, and bisects the S–S bond. Thus the ring C–S bonds are not equivalent. Directly bonded to one C–S moiety is a sulfhydryl group while the other C–S group is unchanged. The above adduct properties are inconsistent with the resonance Raman spectra shown in Figure 1, C and D, for the two intermediates. The asymmetry in the ring C–S bonds of the adducts should give two $\nu(\mathrm{CS})$ bands, albeit, one at lower frequency to reflect the weaker ylide bonding or the ring single bond C–S about a tetrahedral carbon atom. Additional nonring C–S(H) or S–S(H) stretching-mode bands should also be observed. A single RR band is observed for both intermediates at 733 cm^{-1}, which represents an increase from 719 cm^{-1} for the $\nu(\mathrm{C}{\cdots}\mathrm{S})$ band of the symmetrical cation, $3,5\text{-Ph}_2\text{D}^+$. Bands that might be assigned to two $\nu(\mathrm{S{-}S})$ modes in **4** or to a single-bond $\nu(\mathrm{C{-}S})$ mode and a $\nu(\mathrm{S{-}S})$ mode in **3** are observed at 600 and 550 cm^{-1}, respectively. Both sets of bands should disappear when the adduct collapses to give the second intermediate ($\lambda_{\max}$ 473 nm), the dithiodibenzoylmethanato anion, **5**. The 600-cm^{-1} band decreases in intensity



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from medium-strong to medium-weak while the 550-cm^{-1} band intensity remains the same relative to the 733-cm^{-1} $\nu(\mathrm{C}{\cdots}\mathrm{S})$ band. This implies that the ring disulfide bond has not been cleaved in the second intermediate and thus contradicts the electronic absorption band assignments. Since the assignment of the red species to the dithio anion **5** is on firm ground, we conclude that the violet chromophore ($\lambda_{\max}$ 545 nm) is not an adduct. The very similar resonance Raman spectra of the two intermediates in the sulfide reaction, Figure 1, spectra C and D, suggest that the first species ($\lambda_{\max}$ 545 nm) can also be assigned to an anionic one whose composition and structure are closely related to **5** or its isomers.

Furthermore, the position of a $\nu(\mathrm{C{-}Ph}) + \nu(\mathrm{C}{\cdots}\mathrm{S})$ band at 1140 cm^{-1} in the intermediates is found at considerably lower frequency

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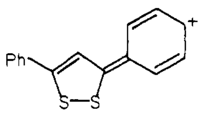
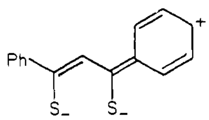
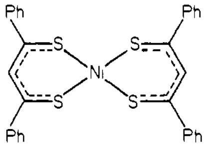
than that of its counterparts at 1244 cm^{-1} in 3,5-Ph$_2$D$^+$ and 1233 cm^{-1} in the Ni(II) chelate[13] of the dithio anion. Structural and electronic differences (vide infra) between the intermediates and the necessarily cis-*S,S* configurations of the cyclic disulfide cation and the chelating anion, **5**, are expected to affect ν(C–Ph) frequencies. An extended resonance hybrid of 3,5-Ph$_2$D$^+$ such as



gives the C–Ph bond partial-double-bond character. An analogous hybrid for the anion

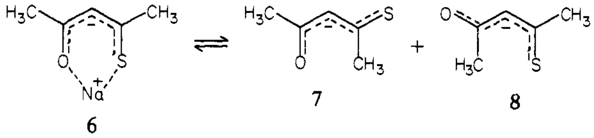


would not be favorable due to the further separation of charges. The latter form can contribute significantly when the ligand chelates to an electropositive Ni^{2+} ion that can accept the negative charge. This can account for the relatively low position of the ν(C–Ph) + ν(C$\cdots$S) band in the anionic intermediates. The degree of resonance enhancement of this band, however, depends on the nature of the electronic excited state that is involved. Intensification of this Raman band in both intermediate species and the Ni(II) chelate but not in the dithiolylium ion suggests that the excited states of the intermediates and chelate are similar in origin. Thus the electronic structure of the intermediates is more closely related to the dithio ligand in



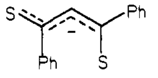
than to the cyclic disulfide cation or its derivatives.

Several RR bands in the intermediates remain to be identified. Infrared, Raman, and proton magnetic resonance spectra of the monothioacetylacetonate anion (TAA$^-$) have previously been reported.[14] An increased ν(C$\cdots$S) Raman frequency, 753 cm^{-1}, in TAA$^-$ as opposed to the sodium(I)–TAA$^-$ ion pair, 686 cm^{-1}, or solid NaTAA, 708 cm^{-1}, also implies that the higher 733-cm^{-1} frequency observed for the intermediate species (Figure 1, spectra C and D) stems from ionized thiolate groups. In dilute aqueous solutions of NaTAA the 753-cm^{-1} ν(C$\cdots$S) Raman band of the free anion dominated. ^{1}H NMR spectra[14] of NaTAA solutions in water, Me$_2$SO, or methanol showed two sets of methyl- and γ-proton resonances, the relative intensities of which were dependent on concentration. One set that dominated in concentrated solutions was assigned to a cis structure, **6**, of the Na$^+$TAA$^-$ ion pair. The other set that occurred in dilute solutions was assigned to trans structures, **7** and **8**, of the free anion. Thus the following equilibrium was proposed:



6 7 8

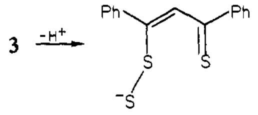
From infrared and Raman spectral analyses, the keto tutomer of **7** and **8** was found to make a larger contribution than the thioketo one. Such isomerism has also more recently been proposed[15] for monothioacetylacetone itself. As in NaTAA aqueous solution Raman specra,[14] the bands in spectra C and D between 300 and 650 cm^{-1} can be associated with various skeletal bending modes. Five Raman bands were observed at 607, 510, 450, 360, and 330 cm^{-1} in NaTAA; four or five bands (380, 487, 520, 550, and 600 cm^{-1}) are also observed here in spectra C and D. Several of these bands also have nearby counterparts at 405 and 525 cm^{-1} in the nickel(II) chelate spectrum (E). The intense RR band at 380 cm^{-1} is absent in the 3,5-Ph$_2$D$^+$ spectrum. In fact the RR spectrum of 3,5-Ph$_2$D$^+$ shows no intense bending-vibrational-mode band in the low-frequency region. Bands at 294 and 617 cm^{-1} are more than a factor of 2 less intense as the 560-cm^{-1} ν(S–S) or 719-cm^{-1} ν(C$\cdots$S) bands. For the dilute solution (1.0 × 10^{-3} M) of 3,5-Ph$_2$D$^+$ClO$_4$$^-$ that was mixed in a 1:1 ratio with sodium sulfide solution, the concentration of products in the Raman cell must be 5.0 × 10^{-4} M or less. By analogy to the monothioacetylacetonate anion, the observed dithiodibenzoylmethane anion (λ_{max} = 473 nm) may also have a trans structure in dilute solution,



9

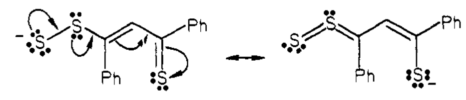
Unfavorable Ph–Ph steric hindrance in the cis-Ph–Ph isomer is expected to make its contribution small. The cis-*S,S* isomer, which can form a 1:1 chelate with the sodium ion, should begin to appear only in concentrated sodium salt solutions (>0.1 M).

In the Robertson mechanism,[2] the intermediate species that followed adduct formation was the organic persulfide, e.g.,



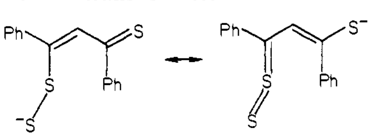
10

Hydroxide and ethoxide ions are better bases than thiolates; thus, **10** is represented as an anionic structure. Assignment of the short-lived (λ_{max} 545 nm) intermediate to the persulfide ion **10** rather than **3** or **4** is our preferred assignment. In dilute solution, the cis isomer, **10**, is expected to convert rapidly to a trans isomer, **11a**, which may be written in delocalized form to account for the presence of another resonance hybrid, **11b**, as follows.



11a 11b

The ylide in **11b** requires the participation of d orbitals of the central sulfur atom to give a dπ–pπ sulfur–sulfur bond or the presence of a carbanion that is stabilized by polarization in the $>^-$C–$\ddot{\mathrm{S}}^+$= bond. Resonance structures for **9** require conventional pπ–pπ bonding only. The structural asymmetry of the persulfide allows an additional trans isomer:



12a 12b

The 600-cm^{-1} RR band in spectrum C can be assigned to the open-chain disulfide bond stretching mode in **11** or **12** that would be absent in **9**. The persulfide ion product, S$_2$$^{2-}$, from reaction of another mole of $^-$SH with **11** or **12** does not absorb in the visible region as does its supersulfide ion counterpart, S$_2$$^-$. The latter gives a ν(S–S) resonance Raman band[16] at 594 cm^{-1}. The pale yellow iron pyrite, for example, contains the S$_2$$^{2-}$ ion. Since the concentration of disulfide cation is ~0.50 mM, we do not expect to observe the normal Raman spectrum of an S$_2$$^{2-}$ product of the

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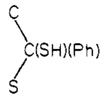
same concentration. With delocalization of the negative charge in the organic persulfide anion, the disulfide bond can acquire multiple-bond character as in the supersulfide ion where the bond order is formally 1.5. Thus, ν(S–S) frequencies should be similar.

As an alternative to the persulfide assignment, we associate the 545-nm absorbing species with the cis isomer of the dithio anion **5**. This may be the preferred form on initial cleavage of the dithiolylium ring, although a mechanism that postulates formation of an intermediate adduct can produce either cis or trans isomers upon collapse of the tetrahedral carbon center,



In dilute solutions the cis isomer is expected to be unstable and, thus, rapidly rearrange to give a trans form such as **9**. The very similar RR spectra that were obtained with excitation into the 545-nm band of the parent chromophore, Figure 1, spectrum C, and into the 473-nm band of the daughter, Figure 1, spectrum D, attest to the conclusion that the two species possess very similar structures. Geometrical isomerism is anticipated to have a minimum effect on the positions of most vibrational modes, stretching and bending, in the dithio anion, except, perhaps, on the energies of bending modes in the immediate vicinity of the geometrical change. In the low-symmetry molecules (C_{2v} for cis isomer, C_s for trans), local bonding properties dominate in their influence on vibrational spectra. The 600-cm^{-1} RR band that is noticeably affected lies in the region of CCS and CCC angle bending mode frequencies.

Conclusions

The present RR study shows the high potential of this technique in obtaining information on the mechanisms of disulfide bond cleavage reactions. When parity-allowed bands of the $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ type are present in the chromophoric molecule, such as the cyclic disulfides of the 1,2-dithiolylium cation and its reaction products, excited states and chromophore-linked vibrations and therefore intermediate reaction species can be identified. In nucleophilic reactions of this cation, intermediates and products that retain at least one sulfur atom absorb either in the 340–400-nm range or to longer wavelengths and thus serve as resonance Raman probes of the reaction pathway.

In the present study of the reaction between 3,5-diphenyl-1,2-dithiolylium perchlorate and excess sodium sulfide in ethanol, we prefer to assign the shorter lived transient that absorbs maximally at 545 nm to the open-chain disulfide anion. Therefore, the open-chain aliphatic disulfides and the cyclic disulfide cation appear to have a common persulfide intermediate in their nucleophilic reaction with hydrosulfide ion. The possible existence of a shorter lived cation–hydrosulfide adduct species remains to be proved. The presence of a fleeting perthiolate ligand suggests that it may be trapped in chelate form with an appropriate metal ion. Perthiolate functional groups have reportedly been obtained by addition of elemental sulfur to a copper(I) cluster complex, $Cu_8L_6^{4-}$, where L = 1,1-dicarbobutoxyethylenedithiolate,[17] and in nickel(II) dithiocarboxylate complexes.[18] The longer lived red species, λ_{max} 473 nm, has been assigned to the trans isomer of the dithioacetylacetonate anion, which results from reaction of the open-chain disulfide anion with another mole of hydrosulfide. Again, this is similar to the reaction mechanism that was suggested for the reaction of open-chain organic disulfides with hydrosulfide ion.

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Registry No. 1 perchlorate, 1270-66-2; bis(1,3-diphenyl-1,3-propanedithionato-*S,S'*)nickel, 21609-14-3; sodium sulfide, 1313-82-2.

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Natural-Abundance One-Bond ^{13}C–^{13}C Coupling Constants in Monosaccharide Derivatives and in Sucrose

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Abstract: Natural-abundance one-bond ^{13}C–^{13}C coupling constants have been measured (at 25.16 MHz) for monosaccharide derivatives and for sucrose in the presence of the strong signals due to species containing only one ^{13}C isotope. In the case of strong AB systems the measurement of the carbon–carbon couplings was carried out also at 50.31 MHz via double quantum coherence. Equations are established for the calculation of coupling constants for situations where all four lines of an AB or AX system cannot be observed. The measured one-bond coupling constants have been correlated with the stereochemical changes in the carbohydrates studied.

Introduction

Since the advent of carbon-13 nuclear magnetic resonance spectroscopy in the late 1960's, a vast amount of research has been directed with this technique toward the structural elucidation and conformational analysis of complex molecules.[2] Application of ^{13}C NMR spectroscopy has been focused on the chemical shift of this nucleus or on ^{13}C–^{1}H coupling constants. However, recent advances in instrumentation and the availability of high-field spectrometers have increased greatly the scope and utility of ^{13}C–^{13}C coupling constants at natural abundance in structural and

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