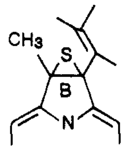
therefore C'_9 and C'_{10} originate from the 2-$H_{\beta\text{-c}}$ and 2-$H_{\beta\text{-t}}$ of an unmodified vinyl group.[11]

In contrast with the native hemin vinyls and the $S_C$hemin 2-vinyl, the three protons from the original 4-vinyl group do not exhibit the characteristic 11- and 17-Hz coupling constants.[11] Deconvolution (Figure 2E′) and spin-system simulation indicate for peak C'_{14} couplings of ~1 and 3.6 Hz. This latter coupling is removed upon on-acquisition irradiation of C'_7 (Figure 2G′). The remaining 15-Hz splitting of C'_6 and C'_7 disappears from either peak by irradiating the other (Figure 2F′,G′); this large coupling between the two 4-H_βs corresponds well to the geminal coupling of a saturated methylene pair.[12] C'_6, C'_7, and C'_{14} present no other detectable coupling (≥ 1 Hz) whether the reaction is carried out completely in H_2O or ^2H_2O. Consequently, the coupling pattern of the 4-substituent dictates that the $C_\alpha H{-}C_\beta H_2$ fragment no longer contains the double bond and did not undergo addition of any proton.

Since the ^{1}H NMR spectra of the three previously reported metSMbCN complexes are very similar, we expect that the same pyrrole is reduced in each derivative, with only differing substituent functionalities. The similar resonance positions of the original 4-H_α and 4-H_βs and of the resolved methyls in the extracted pigment (Figure 2A,B) and metS_CMbCN (Figure 1A) argue strongly for identical structures of the modified hemin. *Thus the saturated ring in sulfmyoglobin is pyrrole B.* This conclusion differs from the proposed site of attack presented in recent studies.[3,4]

This constitutes clear evidence for vinyl group participation in the formation of *one* of the forms of SMb, namely, S_CMb. On the other hand, since sulfmyoglobin complexes analogous to S_AMb and S_BMb have been detected by ^{1}H NMR for Mb reconstituted with deuteroheme[13] (2,4-vinyls replaced by hydrogens), it is obvious that *vinyls are not necessary to the formation of the initial SMb complex.* The direct participation of vinyl groups in SMb formation in one of the three forms may account for the difficulty in establishing the presence of intact vinyls in SMb preparations using resonance Raman spectroscopy.[3] The simple reaction of the 4-vinyl group to form an episulfide (or epoxide) can be discounted since such strained cyclic systems exhibit much smaller geminal couplings (5–7 Hz).[12]

The multiplet structure for the protons of the reacted 4-vinyl group, however, is completely consistent with the formation of a cyclic thioether, as depicted in III below; this is equivalent to the reduction of the buried B pyrrole, whereas others suggested reduction of ring A or less probably B,[3] or C or D.[4] The observed coupling constants are very close to those of the similarly structured 3-thiolenes.[12] The mechanism of formation of III (S_CMb) could involve the process I → III, with the presumed initially formed episulfide[2] (I) reacting with the 4-vinyl C_β. An alternate pathway would have II as the precursor, which, in turn, could be formed from I via attack of a protein-based or exogenous nucleophile. Thus we tentatively suggest the pathways $\text{I} \rightarrow \text{II} \rightarrow \text{III}$ as representing the reaction sequences $S_A\text{Mb} \rightarrow S_B\text{Mb} \rightarrow S_C\text{Mb}$.



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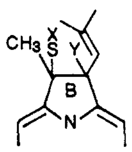

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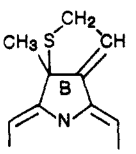

III

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Fourier Transform Infrared Vibrational Circular Dichroism of Matrix-Isolated Molecules

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Vibrational absorption measurements on matrix-isolated molecules have proved to be important with exciting applications[1] such as mode-selective excitation of reactions. Vibrational circular dichroism (VCD), which is a measure of differential absorption of left vs. right circularly polarized infrared radiation and was successfully measured,[2] has unique potential for revealing the three-dimensional structure of chiral molecules. Noting the numerous advantages in combining the VCD and matrix-isolation techniques, Schlosser et al.[3] demonstrated the feasibility of VCD measurements on α-pinene and β-pinene in Ar matrices at 4-cm^{-1} resolution in the 3100–2800-cm^{-1} region. For these measurements, a dispersive spectrometer and slow spray-on (SSO) procedure, with deposition times of 2–4 h, were used. Although FTIR instruments have been successfully used[4,5] for VCD measurements on neat liquids, their use for VCD measurements on matrix-isolated molecules remains to be established, especially since the procedures of and artifacts in FTIR and dispersive VCD techniques are different.

For several organic molecules, α-pinene for example, the absorptions of the bands in the 1600–800-cm^{-1} region are 1–2 orders of magnitude smaller than those of the intense bands in the 3100–2800-cm^{-1} region. Then for VCD measurements in the 1600–800-cm^{-1} region SSO deposition would require prohibitively long periods of time and introduce scattering and leak problems, there by questioning the feasibility of such measurements. In this paper, using pulsed matrix isolation[6] (PMI) we demonstrate that FTIR-VCD measurements are not only feasible in the 1600–800-cm^{-1} region but also obtainable at a higher resolution (1 cm^{-1}) than was achievable to date. FTIR-VCD of unusual molecules synthesized and (or) stable only at low temperatures may thus become feasible.

A closed-cycle cryostat (Air products) was inserted into the sample compartment of an FTIR spectrometer (Nicolet 6000C) without physical contact between the two. Nitrogen–pinene mixtures premixed in a 2000-mL bulb (~600 torr of nitrogen was bled into the bulb saturated with pinene vapor at ~2 torr) are deposited on to KBr window at ~15 K through a 45° port in pulses, each pulse containing ~25 mL of mixture at about 600 torr. The open end of transfer line, which was made of copper with ~0.8-mm inner diameter, was located at about 2 cm from the deposition window. The deposition time is usually less than $^1/_2$ h. Transparent matrices with matching base lines for the enantiomers were obtained. Deposition of one or two pulses of matrix gas, prior to the mixture, significantly reduced the light scattering. Nitrogen matrices were found to be more transparent than argon matrices. An optical filter with 5% cut-on at 1650 cm^{-1}, BaF_2 polarizer, and ZnSe photoelastic modulator, with modulation frequency (ω_m) of 97 KHz, preceded the sample. A HgCdTe detector and lock-in amplifier were used[4,5] for signal processing. Six data files, each containing 1000 coadded ω_m interferograms and another six data files each containing 50 coadded transmission interferograms, were collected. For each interferogram 8192 data points were collected with one data point

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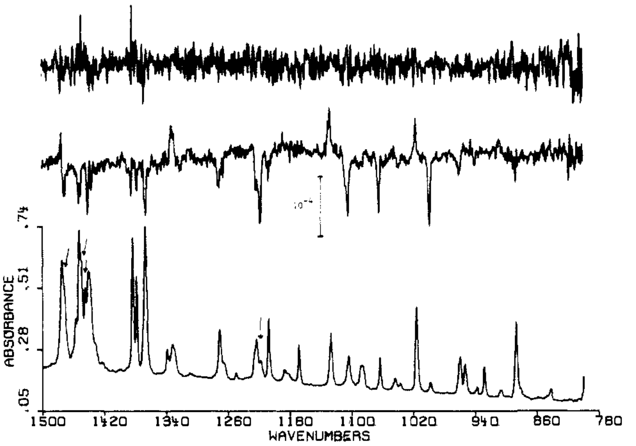

Figure 1. FTIR absorption (bottom) and VCD (middle) spectra of (+)-α-pinene in N_2 matrix at 1-cm^{-1} resolution. VCD is presented as, $\Delta A = A_L - A_R$, the difference in absorbance and its scale is displayed below the middle trace. The top most trace is the difference between the VCD obtained from the first and latter halves of the collected data and reflects spectral reproducibility and matrix stability. Matrix to sample ratio is estimated to be in the range 200:1–300:1, with the uncertainty resulting from the very low vapor pressure of α-pinene.

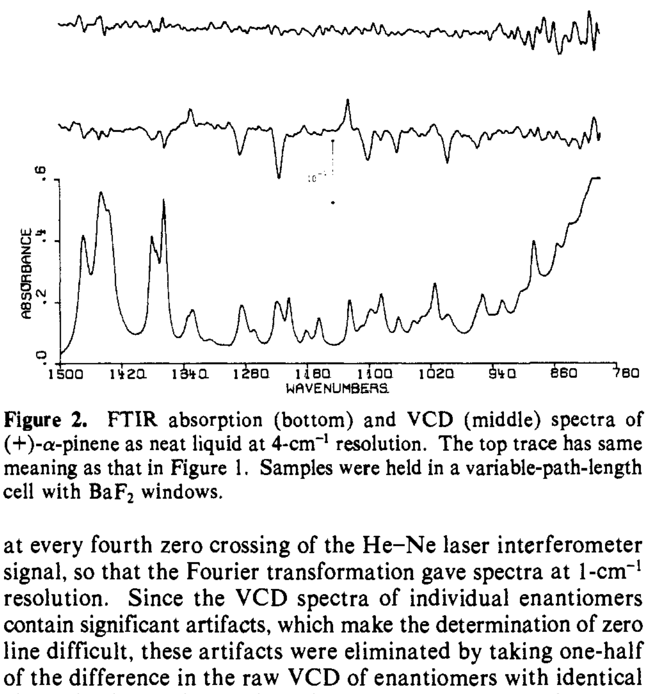

Figure 2. FTIR absorption (bottom) and VCD (middle) spectra of (+)-α-pinene as neat liquid at 4-cm^{-1} resolution. The top trace has same meaning as that in Figure 1. Samples were held in a variable-path-length cell with BaF$_2$ windows.

at every fourth zero crossing of the He–Ne laser interferometer signal, so that the Fourier transformation gave spectra at 1-cm^{-1} resolution. Since the VCD spectra of individual enantiomers contain significant artifacts, which make the determination of zero line difficult, these artifacts were eliminated by taking one-half of the difference in the raw VCD of enantiomers with identical absorption intensities and base lines. Matrix stability and spectral reproducibility were verified by comparing the VCD obtained from the first and latter halves of the collected data. Total time involved in obtaining the final VCD spectra, including the time for evacuating the cryostat during sample changeover from one enantiomer to the other, was about 12 h. Since the amount of sample used for VCD measurements on matrix-isolated α-pinene (Figure 1) is much less than that used for those on neat liquid (Figure 2) and the spectral resolution in the former is 1 cm^{-1} while that in the latter is 4 cm^{-1}, slightly higher noise is apparent in the VCD of matrix-isolated α-pinene. However, the significant points are the following: (a) Signs of VCD bands in the neat liquid VCD spectrum match with those in the VCD spectrum of matrix-isolated α-pinene, as would be expected for rigid molecules and for good quality matrices; this suggests that in the matrix, aggregates were either absent or, if present, did not influence VCD. (b) Some closely spaced bands, for which there is no indication in the neat liquid spectrum, are nicely resolved (marked by arrows in Figure 1) in the spectrum of matrix-isolated α-pinene; although we do not expect the fine spectral features to be originating from aggregates (see above), further experiments would be needed to verify this. (c) For closely spaced bands associated with bisignate VCD, the dissymmetry factors and hence signal quality in the VCD spectrum of matrix-isolated α-pinene are clearly superior. Similar observations are noted for (+)-3(R)-methylcyclohenanone and (+)-3(R)-methylcyclopentanone in nitrogen matrices.

Further improvements to these FTIR–VCD measurements on matrix-isolated molecules can be incorporated. For example, by inclusion of two remotely rotatable and mutually orthogonal deposition windows with shutters[7] to prevent gas movement to adjacent window and deposition of one enantiomer on each window, the dead time in evacuating the cryostat can be eliminated. This time savings can inturn be used to further improve the FTIR-VCD spectral resolution.

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Registry No. (+)-α-Pinene, 7785-70-8.

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Models for Reactions of Acetylene on Platinum(111): The Vinylidene Intermediate

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One of the most studied surface reactions is that of acetylene on platinum(111). A μ_3-η^2-acetylene complex is formed at low temperature but this rearranges on warming to a μ_3-η^2-vinylidene, Pt$_3$(μ_3-η^2-C=CH$_2$), which then reacts with surface-bound hydrogen to give a μ_3-ethylidyne, Pt$_3$(μ_3-CMe).[1,2] Since the cluster [Pt$_3$(μ_3-H)(μ-dppm)$_3$]$^+$ (**1**, dppm = Ph$_2$PCH$_2$PPh$_2$) acts as a useful model for the triply bridging sites on a Pt(111) surface,[3] a study of its reaction with acetylene was initiated with the aim of isolating complexes having the above functional groups, none of which appears to be known. This article reports the formation of a stable μ_3-η^2-C=CH$_2$ complex.

Reaction of acetylene with **1**, as the PF$_6^-$ salt, at −80 °C gave an unstable acetylene complex, characterized as [Pt$_3$(μ_2-H)(HCCH)(μ-dppm)$_3$]$^+$ (**2**). The hydride was clearly characterized as μ_2 rather than μ_3 by the ^{1}H and ^{195}Pt NMR spectra[4] but the

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(4) NMR for at −80 °C in CD$_2$Cl$_2$: ^{1}H δ −8.2 [*m*, ^1J(Pt(B)H) = 625, ^2J(PH) = 14 Hz, Pt$_2$(μ-*H*)]; ^{31}P 21.21 [m, ^1J(Pt(A)P) = 4200, ^{2}J(Pt(B)P) = 210, ^{3}J(P(A)P(C) = 80 Hz, P(A)], 34.76 [m, ^1J(Pt(B)P) = 1970, ^3J(P(B)P(B) = 135 Hz, p(B)], 27.29 ppm [m, ^1J(Pt(B)P) = 4440, ^2J(Pt(B)P) = 640, ^3J(P(A)p(C) = 80 Hz, Pt(C)]; ^{195}Pt −3138 [m, Pt(A)], −3394 ppm [*m* ^1J(Pt(B)H) = 625 Hz, Pt(B)]. Note the coupling of the hydride to Pt(B) but not Pt (A). No ^{195}Pt couplings to the coordinated acetylene was resolved in the ^{13}C{^{1}H} or ^{195}Pt{^{1}H} NMR spectra of **2***, but the ^{13}C atoms and P(B) atoms gave rise to an AA′XX′ spin system for which the inner four lines were resolved in the ^{31}P NMR spectrum and gave J(P(B)C) + J(P(B)C′) = 92 Hz. This shows that the acetylene is aligned parallel to the P(B)Pt(B)Pt(B)P(B) axis, but it could lie along the Pt(B)Pt(B) bond or lie above one Pt(B) atom but flip rapidly between Pt(B) atoms. If the acetylene were freely rotating, a triplet resonance for P(B) due to ^{13}C coupling would be observed. The ^{13}C{^{1}H} NMR spectrum of 2* at −90 °C gave only a broad singlet at 256.5.

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