Figure 3. Surface coil selectivity experiment on two capillary tubes, A and B, placed on axis at 2 and 4 mm from the surface coil. The first contained 3-μL saturated solution of a mixture of 50% 2-^{13}C- and 50% 3-^{13}C-enriched alanine; the second contained 2 μL of ethanol enriched to 25% at C_1 and C_2 on different molecules. (a) ^{13}C spectrum, with 10-ms proton presaturation and proton decoupling. (b) SHARP spectrum, pulse times intermediate between A and B. (c) SHARP spectrum, pulse times set for A. (d) SHARP spectrum, pulse times set for B.

a single resonance is obtained for each ^{13}C position, and the signal to noise is that of satellite protons. The approach is applicable to all pairs of coupled nuclei, provided that the coherence transfer time, τ, and the relative lengths of the t_1 subintervals are adjusted in accordance with the J coupling and the ratio of the magnetogyric constants, respectively.

We further note that SHARP spectroscopy inherently exhibits some spatial selectivity. This was demonstrated on two capillary tubes, containing alanine and ethanol, placed at different distances from the coil. Figure 3a shows the ^{13}C spectrum after a single pulse. It is nonselective and poorly resolved; resonances from both tubes appear, but the methyl groups on alanine and ethanol are not separated. Figure 3b–d are SHARP spectra. The spectrum in Figure 3b is nonselective and was obtained by setting the pulses in Figure 2 for a point halfway between the two tubes. The spectra in Figure 3c,d were obtained by setting the pulses for the first and second tubes, respectively; distinction of the contents of the two tubes illustrates a spatial separation of high resolution.

The technique described here yields high-resolution spectra that are easy to interpret and that can be combined with methods of accurate spatial selection designed for heteronuclear systems.[6,7,11] It should therefore prove a useful addition to topical NMR. Other pulse sequences have been designed which can retain or remove either heteronuclear or homonuclear couplings or both,[12] and this provides additional information and resolution. Background water does not interfere, since it has no heteronuclear coupling. The technique could be used for natural abundance studies of isotopes such as ^{13}C and ^{15}N or for following the metabolic pathway of specifically labeled compounds such as lactic acid, glucose, or drugs.

Structures and Raman Spectra of Two Crystalline Modifications of Dithiodiglycolic Acid

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Prompted by the observations of Lord and Yu[1] that the Raman spectra of lysozyme, ribonuclease, and α-chymotrypsin differed in the S–S stretching region near 500 cm^{-1}, there have been a number of attempts to establish how this frequency varies with the conformation proximate to the S–S bond in molecules containing CCSSCC fragments.[2] For almost a decade, however, an unresolved conflict over this question has persisted in the literature.

Sugeta, Go, and Miyazawa[3–5] proposed that bands having Raman shifts larger than the typical 505–510 cm^{-1} arise from disulfide conformations having one (525 cm^{-1}) or two (540 cm^{-1}) carbon atoms anti to distal sulfurs, i.e., one or two CCSS torsion angles of about 180°. Van Wart and Scheraga,[6–8] however, assigned these bands to conformations having either one (525 cm^{-1}) or two (540 cm^{-1}) quite small CCSS torsion angles, roughly in the range 20–50°.

Van Wart and Scheraga[6] rejected the Sugeta assignments because the spectrum they recorded for a solid sample of dithiodiglycolic acid, HOOCCH$_2$SSCH$_2$COOH, had a disulfide stretching frequency of 508 cm^{-1}, while an unpublished crystallographic study made by Frank[9] in Parthasarathy's laboratory gave a molecular structure having C_2 symmetry with CCSS torsion angles of 167°. This information, together with a survey of protein conformations that revealed significant numbers of CCSS torsion angles in the 20–40° range, then led Van Wart and Scheraga to propose their alternative correlation scheme.

We recently began a series of studies in which we have obtained both the Raman spectra and the structures of a number of mesocyclic disulfides. The results, which will be published in due course, have all supported the Sugeta, Go, and Miyazawa rather than the Van Wart and Scheraga correlations. For example, in the centrosymmetric molecule 1,2,6,7-tetrathiacyclodecane, the two CCSS torsion angles are 37° and −62°[10] and the disulfide stretching frequency is 502 cm^{-1} rather than the 525 cm^{-1} that the Van Wart and Scheraga correlations would have predicted. Findings such as this have caused us to question the experimental evidence on which the Van Wart and Scheraga correlations were based.

We now report that dithiogdiglycolic acid can be obtained in two different crystalline modifications, depending upon the method of crystallization. Form I, which is obtained uniquely only when an aqueous solution of the compound is allowed to evaporate through a small orfice for a matter of weeks, crystallizes in the

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space group *I2/a*. In this form the molecule has a C_2 axis with CCSS torsion angles of −167.4 (2)° and a CSSC torsion angle of −86.3 (1)°. Form II is obtained from a wide variety of organic solvents or when an aqueous solution of the compound is evaporated quickly. Mixtures of forms I and II are obtained when aqueous solutions are evaporated on the time scale of days.

Form II crystallizes in the space group *P*1, with no molecular symmetry elements. The CCSS torsion angles are −76.2 (5)° and −64.4 (6)°, and the CSSC torsion angle is −92.3 (4)°. Apart from the carboxyl groups, the bond distances and bond angles in the two forms are quite similar. Versus the corresponding dimensions in form I, one CS bond in form II is longer by 0.02 Å and the SSC angle involving that carbon is larger by 3.1°. The SCC angle on the other end of form II exceeds that in form I by 4°.

The carboxyl groups in form I are unexceptional, with their planes essentially coincident with the SCC planes. The carboxyl group on the end of form II having the longer CS bond has reasonably normal dimensions, but it is twisted, with an SCCO torsion angle of −79.1 (9)° to the carbonyl oxygen atom. The other end of form II displays a statistical disordering of the oxygen atoms that is best interpreted as two alternative orientations for the carboxyl group: one that is coplanar with SCC and one that is rotated away from coplanarity by 64 (2)°. Such a disordering avoids several short O–O contacts that would otherwise occur if the molecules were to adopt one or the other orientation exclusively. Because of the disorder, however, the bond distances and angles in this group are less reliable.

The Raman spectra of authentic samples of crystalline forms I and II show significant differences, particularly in the 200–800-cm⁻¹ region. For form I we find such spectral lines (with subjective intensities) at 194 (s), 250 (m), 292 (w), 402 (vs), 422 (m), 536 (vs), 563 (w), 651 (w), and 799 (vs) cm⁻¹. The corresponding portion of the spectrum of form II has lines at 182 (sh), 235 (w), 269 (m), 290 (w), 422 (w), 434 (w), 510 (vs), 550 (w), 570 (w), 582 (m), 664 (s), 766 (w), and 786 (w) cm⁻¹.

In their original article Van Wart and Scheraga[6] report Raman lines for their sample of dithiodiglycolic acid as follows: 270 (m), 293 (w), 419 (w), 431 (w), 481 (w), 508 (vs), 549 (w), 569 (w), 581 (m) cm⁻¹. A comparison of these results with ours leaves little doubt that the unspecified recrystallization procedure to which they subjected their commercial sample of this compound gave a form II product. Since their interpretation of the conformational dependence of the disulfide stretching frequency was predicated on the assumption that they had studied form I, we must now conclude that the Van Wart and Scheraga model is no longer credible. The actual disulfide stretching frequency in form I does, however, closely approximate the 540-cm⁻¹ value predicted by the Sugeta, Go, and Miyazawa correlation scheme.

Normal coordinate calculations were then used to establish that the spectral differences between forms I and II indeed have a conformational origin. With the realization that the results cannot be strictly correct, owing to the fact that in both crystals the carboxyl groups form hydrogen-bonded dimers, the spectrum of crystalline form I was fitted with a Fletcher–Powell[11] optimized Urey–Bradley force field. The starting force constants were taken from Sugeta[5] for the CH₂SSCH₂ portion of the molecule and from Nakamoto and Kishida[12] for the in-plane motions of the carboxyl group. The out-of-plane bending force constant was estimated from the results of Brooks and Haas.[13] No force constant changed by more than 15% upon optimization of the force field.

When the optimized force field was used to calculate the spectrum of an isolated molecule having the form I geometry, the calculated disulfide stretching frequency was 532 cm⁻¹. The same force field than gave a calculated disulfide stretching frequency of 510 cm⁻¹ for an isolated molecule having the geometry of either of the form II rotamers. These results strongly support the validity of the Sugeta, Go, and Miyazawa model of the conformational dependence of the disulfide stretching frequency.

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Synthesis and Characterization of Dirhodium Complexes with Four *N*,*N*′-Diphenylbenzamidine Bridging Ligands. Electrochemical Generation and ESR Properties of [Rh₂(N₂R₂CR)₄]ⁿ Where R = Phenyl and n = 1 and −1

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The syntheses and characterizations of a large number of dirhodium(II) complexes have been reported. Studies include the well-characterized dirhodium carboxylates, $Rh_2(O_2CR)_4$,[1,2] as well as dirhodium complexes with mixed bridging ligands such as $Rh_2(O_2CR)_n(R'NOCR)_{4-n}$[3-7] and $[LRh_2(O_2CR)_3]^+$ where L is a neutral bridging ligand which binds through two nitrogen donors.[8]

Dirhodium complexes with carboxylate bridging ligands undergo only a single oxidation, but complexes containing the more basic amidate bridging ions may undergo two reversible oxidations corresponding to the formation of a formal Rh(II,III) and Rh(III,III) species.[3-7] The reversible formation of a formal Rh(II,I) species has not been observed for the reduction of any neutral dirhodium(II) complexes. This oxidation state appears to be accessible[8] during electrochemical reduction of the positively charged $[LRh_2(O_2CCH_3)_3]^+$ and may also be observed as a transient intermediate during the irreversible reduction of $Rh_2(O_2CR)_4$.[9] However, no spectral characterization of dirhodium(II,I) complexes has been reported.

Numerous theoretical studies on dirhodium(II) complexes have been published (see ref 1, 2) but no experimental data exist on the LUMO of these complexes. Thus, the synthesis of a neutral dirhodium(II) complex which may be reversibly reduced to $Rh_2(II,I)$ is of some interest. We have now synthesized such a complex using N,N'-diphenylbenzamidine. This dirhodium(II) complex is represented by the formula $Rh_2(N_2R_2CR)_4$ where R = phenyl. This is the first reported dirhodium(II) complex with this class of bridging groups. The complex is oxidized and reduced by reversible one-electron transfer processes and a characterization of the products is possible by ESR spectroscopy.

Tetrakis(benzamidinato)dirhodium(II) was the major product obtained from the reaction of $Rh_2(O_2CCH_3)_4$ with benzamidine. The general procedure has previously been described in the literature for substitution reactions involving amide ligands.[7] The

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