

$k$ , the full set of quadrupole interactions,  $\nu_Q^i$ , and an exchange-independent line width parameter,  $1/T_2$ . Examples of such best-fit spectra are shown in the right column of Figure 3. These were calculated by using the same  $\nu_Q^i$ 's used to derive the results of Figure 7 and the rate constants shown in the figure. The overall best-fit results for the interconversion rate are plotted in Figure 8 vs reciprocal absolute temperature. Also shown in this figure are the earlier results of Dalling et al.<sup>10</sup> obtained from <sup>13</sup>C NMR spectroscopy of neat liquid *cis*-decalin. It may be seen that within experimental accuracy, all data fall on the same Arrhenius plot, yielding an overall rate equation  $k = 3.9 \times 10^{14} \exp(-15.5/RT)$ . This corresponds to the activation parameters  $\Delta E = 15.5$  kcal mol<sup>-1</sup>,  $\Delta H = 14.9$  kcal mol<sup>-1</sup>, and (with  $\kappa = 0.5$ )  $\Delta S = 7.6$  eu, which are reasonably close to those determined for the <sup>13</sup>C results ( $\Delta H = 13.6$  kcal mol<sup>-1</sup>,  $\Delta S = 3.5$  eu). Thus there does not seem to be a significant effect of the solvent on the reaction rate, irrespective of its state, isotropic liquid, or a liquid crystal. A similar lack of solvent effects was noticed previously for other intramolecular rearrangement reactions.<sup>1,4</sup>

#### IV. Summary and Conclusions

We have used deuterium NMR spectroscopy to determine the ordering characteristics and the interconversion rate of *cis*-decalin in liquid-crystalline solutions. Combining the kinetic results of the present work with those obtained previously<sup>10</sup> in neat *cis*-decalin gives an overall dynamic range of six decades for the interconversion rate (see Figure 8). The large quadrupole splittings and consequently the large dynamic range over which the reaction

can be studied in liquid crystalline solution render this method most favorable. This is particularly so, also because the spectra are quite simple and readily lend themselves to quantitative analysis. We thus believe that when the problem of deuteration can be solved this method will find many more applications in studying dynamic processes.

We have also determined the full ordering matrix of the *cis*-decalin in two nematic solvents over the temperature range -5 to 160 °C. The results show that the actual values of the principal components depend not only on the temperature but also on their direction in the molecular frame. This is most likely due to solvation effects on the ordering matrix. The structure of the solvation complex, consisting of the solute and several closely associated solvent molecules, changes with temperature through association and dissociation equilibria, and consequently also its rotational diffusion properties are affected. Clearly such solvation effects must be included in any exact theory of solute ordering in liquid-crystal solutions.<sup>17</sup>

**Acknowledgment.** This work was supported by a grant from the U.S.-Israel Binational Science Foundation, Jerusalem. One of us (C.B.) thanks the Minerva Foundation for a visiting fellowship to the Weizmann Institute.

Registry No. *cis*-Decalin, 493-01-6.

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## Conformational *s*-Cis/*Trans* Isomerization in Free Radicals Observed by Muon Level Crossing Resonance Spectroscopy

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**Abstract:** A rare type of *cis*-*trans* isomerism arises from restricted rotation about a single C-C bond and has been seen here by level crossing resonance spectroscopy (LCR) in muonated free radicals. It is observed as a splitting of the proton's LCR when the C-atom adjacent to the unpaired electron density is an asymmetric sp<sup>2</sup> hybrid. Free radicals which contain C's with sp<sup>3</sup>, symmetric sp<sup>2</sup>, or sp hybrid bonds do not show this geometric isomerism. The  $\alpha$ -protons on these radicals show resolvable splitting less easily than the  $\beta$ -protons. The radicals observed are those resulting from formal addition of muonium to the C=C bonds of acrylates, and they occur regardless of whether the compounds are studied in dilute aqueous solution or as pure liquids.

#### Introduction

Free radicals of the type  $R_2\dot{C}-C(=X)-R_3$  have recently been found to exhibit conformational *s*-*cis*-*trans* isomerism, due to the partial double bond character of the (formal) single bond as a result of p- $\pi$  delocalization. The first example reported for this type of stereoisomerism seems to be the radical  $MuCH_2\dot{C}(CH_3)COOC_2H_5$ , which was observed by transverse-field muon spin rotation (TF- $\mu$ SR)<sup>1</sup> ( $Mu$  being a muonium atom, the hydrogen isotope with a positive muon as its nucleus). This radical showed two isotropic muon hyperfine coupling constants separated by 1.6 MHz and was assigned as a *cis*-*trans* pair when high-resolution ESR showed that the two methyl groups in  $(CH_3)_2\dot{C}COOC_2H_5$  were magnetically inequivalent.<sup>2</sup> Recently, Strub, Roduner, and Fischer<sup>3</sup> have determined the actual heights of the barriers to free rotation for five muonated free radicals (with

$\alpha$ -carbonyl,  $\alpha$ -carboxyl, or  $\alpha$ -carbamide groups). These authors again employed TF- $\mu$ SR to look directly at the muon hyperfine coupling constants from the pairs of precession frequencies formed in these compounds as pure liquids, as a function of temperature.

We report here a study using muon level crossing resonance spectroscopy to determine the extent of this *cis*-*trans* stereoisomerism. About half the compounds selected contained the structure sketched above and the others had C atoms in sp<sup>3</sup> or sp hybrid orbitals or were symmetric or ring sp<sup>2</sup> configurations. They were studied as solutes in dilute aqueous solution (or in micelles to solubilize them) and for comparison as pure liquids. In the former case, free thermalized muonium atoms are the free-radical precursors, whereas in the pure liquid state, "hot" muonium atom interactions, or ionic processes of  $\mu^+$ , are also possible precursors to the muonated radicals.

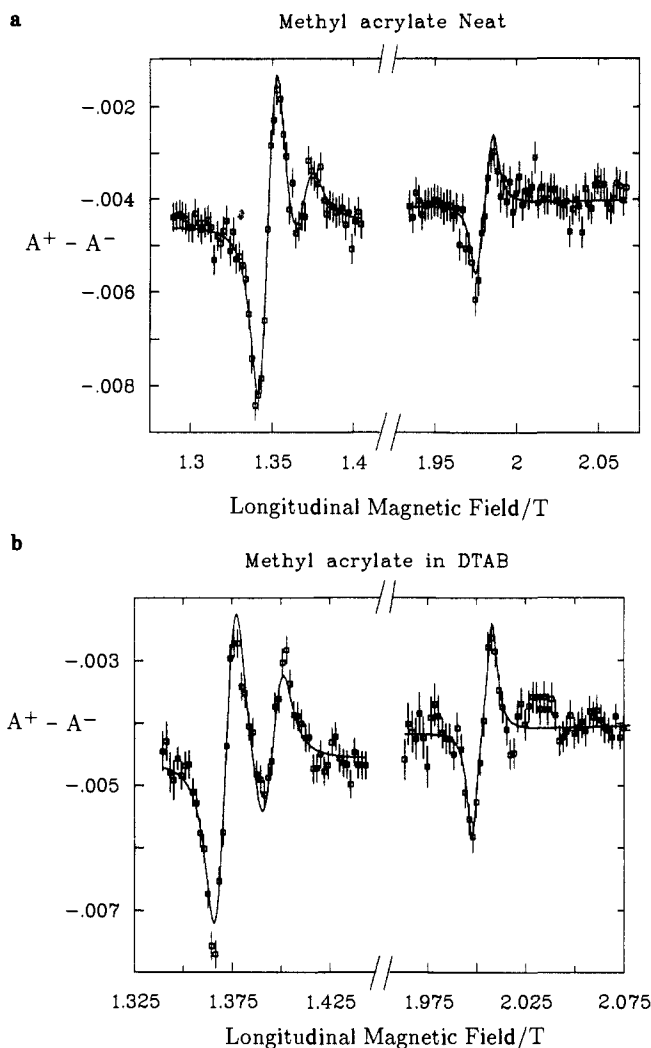
#### Experimental Section

The level crossing resonance technique (LCR) has been fully described previously.<sup>4-6</sup> It is based on the transfer of spin polarization from a muon to that of another nucleus of nonzero spin which is coupled to it through their mutual hyperfine interactions in a free radical. Resonant conditions

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**Figure 1.** LCR spectra—showing muon asymmetry differences against variable longitudinal magnetic field (T)—for methyl acrylate: (a) (neat) as a pure liquid and (b) (in DTAB) as a dilute solute in aqueous micelle solution. Spectrum on the left is for the  $H_{\beta}$  resonance, on the right  $H_{\alpha}$ .

occur at certain longitudinal magnetic fields ( $B_R$ ) where there is crossing of the split Zeeman levels. In the present cases, transfer occurs from a muon to an  $\alpha$ - or  $\beta$ -proton in free radicals formed by addition of muonium to an acrylic or allylic bond.

Spin polarized 4 MeV positive muon beams on the M20B channel of the TRIUMF cyclotron were used for these studies. Equation 1 corre-

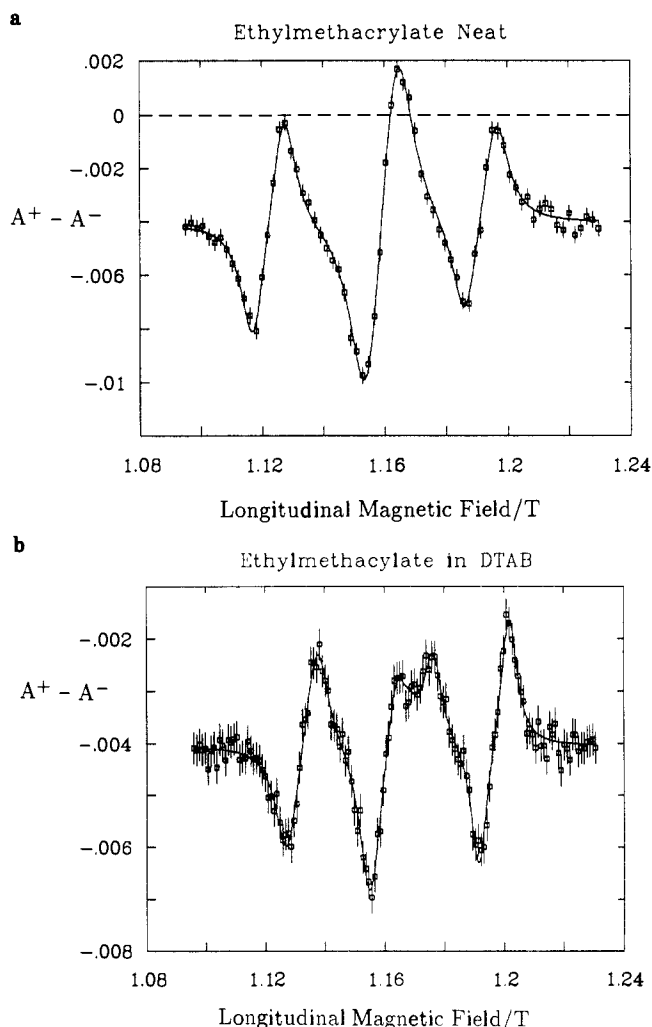
$$B_R = \frac{1}{2} \left( \frac{A_{\mu} - A_n}{\gamma_{\mu} - \gamma_n} - \frac{A_{\mu}^2 - 2MA_n^2}{\gamma_{\mu}(A_{\mu} - A_n)} \right) \quad (1)$$

lates the hyperfine coupling constants ( $A_{\mu}$ ,  $A_n$ , where  $A_n$  may be  $A_{H_{\alpha}}$  or  $A_{H_{\beta}}$ ). The  $\gamma$ 's are magnetogyric ratios, and  $M$  is the sum of the quantum numbers.  $B_R$  was obtained by  $\chi^2$ -minimization fitting to the spectra, as in the figures, which have a differential appearance due to the application of a small modulation field.<sup>4</sup> The yields of individual radicals were evaluated by use of eq 2<sup>7</sup>

$$P_R = \frac{\text{ampl}(\Delta B)^2(\gamma_{\mu} - \gamma_n)^2}{A_{\text{bf}}\nu_r^2} \quad (2)$$

where  $P_R$  is the fraction of incident muons forming that particular radical,  $A_{\text{bf}}$  is the experimental asymmetry,  $\nu_r$  is the LCR frequency, and  $\Delta B$  and  $\text{ampl}$  are the fitted LCR line width and amplitude.

The following substances were investigated as dilute solutes in water or solubilized by micelles and as pure liquids. They were all reagent grade quality and were used without further purification: acrylamide, acrylic acid, methyl acrylate, ethyl methacrylate, acrylonitrile, vinyl acetate, uracil, styrene, and allylbenzene. All solutions and liquids were



**Figure 2.** LCR spectra for ethyl methacrylate (a) (neat) for the pure liquid phase and (b) (in DTAB) for dilute aqueous micelle solution, showing two pairs of doublets for the two different  $\beta$ -H resonances.

thoroughly deoxygenated by bubbling with pure nitrogen before being pumped under nitrogen into the reaction vessel fixed between the counters in the center of a superconducting magnet. The water was purified to the point where Mu had a chemical lifetime of at least 4  $\mu\text{s}$  in the absence of added solutes (the muon lifetime being 2  $\mu\text{s}$ ). DTAB (decyltrimethylammonium bromide) was used as the micelle to solubilize those organic compounds of limited solubility in water.

## Results

Figures 1–5 show the LCR spectra for five of the compounds studied in dilute solution and as pure liquids. They are presented here as  $A^+ - A^-$  against longitudinal magnetic field, where  $A^+$  is the difference of the forward to backward count rates, divided by their sum, when the modulation field ( $\sim 50$  G) was with the main field and  $A^-$  when it was opposed to it. Spectra for acrylamide,<sup>7</sup> styrene, and allylbenzene<sup>8</sup> have already been published, and uracil is due to be published elsewhere. Acrylamide shows a doublet with a splitting of 0.046 T; the other three show only singlets.

Table I records the values of  $B_R$  obtained for all the compounds studied. These resonances have been assigned to  $\alpha$ - or  $\beta$ -protons,

(5) Percival, P. W.; Kiefl, R. F.; Kreitzman, S. R.; Garner, D. M.; Cox, S. F. J.; Luke, G. M.; Brewer, J. H.; Nishiyama, K.; Venkateswaran, K. *Chem. Phys. Lett.* **1987**, *133*, 465.

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(4) Kiefl, R. F. *Hyperfine Interactions* **1986**, *32*, 707.

**Table I.**  $B_R$  Values (in T), Their Assignment as Cis or Trans, the Cis-Trans Splittings, and Ratios of Abundances All for  $\beta$ -H Resonances

compound <sup>a</sup>	assignments		$\Delta(B_R)$	ratio <sup>b</sup> trans:cis
	$B_R$ trans	$B_R$ cis		
methyl acrylate (neat)	1.3472	1.3692	0.022	4:1
methyl acrylate (in mic)	1.3716	1.3955	0.0239	3:1
ethyl methacrylate (neat)	1.1590	1.1221	0.0369	1:1
ethyl methacrylate (neat)	1.1912	1.1590	0.0322	1:1
ethyl methacrylate (in mic)	1.1603	1.1323	0.0280	1:1
ethyl methacrylate (in mic)	1.1966	1.1711	0.0255	1:1
acrylic acid (in water)	1.3756	1.4031	0.0275	3:1
acrylic acid (in water)( $\alpha^c$ )	2.0055	2.0272	0.0217	3:1
acrylamide (in water)	1.3189	1.3652	0.0463	1:10
vinyl acetate (neat)	1.2402	1.2115	0.0287	(1:3) <sup>d</sup>
vinyl acetate (in mic)	1.2443	1.2158	0.0285	1:>10
acrylonitrile (neat)	1.2049			
acrylonitrile (in mic)	1.2201			

<sup>a</sup> Neat means pure liquid phase; in mic means at  $\sim 2.5$  mM in DTAB aqueous micelle solutions; acrylic acid was at 6 mM in water and acrylamide at 0.6 M in water. <sup>b</sup> The ratio of abundances of the isotopes (trans/cis) were estimated from the fitted spectra based on the parameters of eq 2. Because of the overlap of spectra they are no better than  $\pm 30\%$ . <sup>c</sup> These are the only data referring to an  $\alpha$ -H resonance. <sup>d</sup> This may be inner C adduct rather than cis-trans pair, as in text.

**Table II**

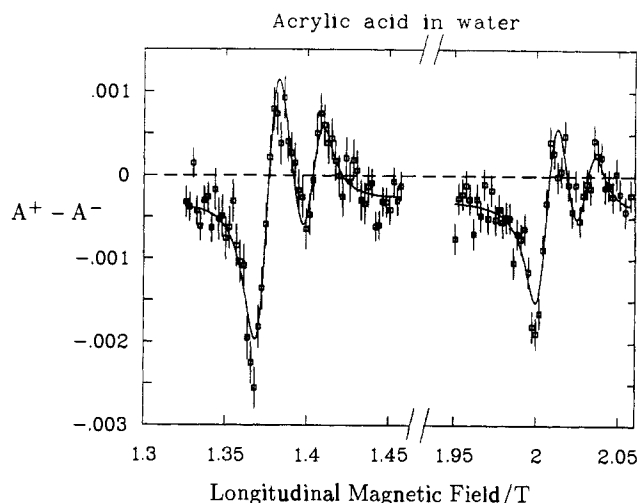
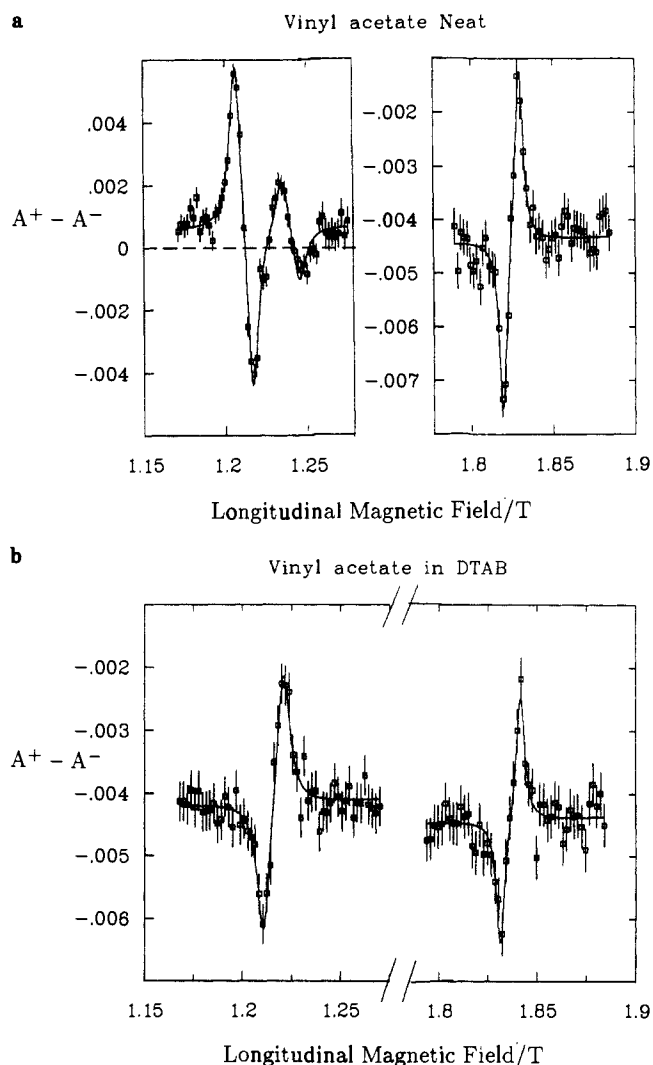
compound	structure of radical	$H_\alpha$	$H_\beta$
methyl acrylate		singlet	doublet
ethyl methacrylate		NA	doublet
acrylic acid		doublet	doublet
acrylamide		singlet	doublet
vinyl acetate		singlet	(doublet in neat) (singlet in mic)
acrylonitrile		singlet	singlet
styrene		singlet	singlet
allylbenzene		singlet	singlet
uracil		singlet	singlet

based on our unresolved measured values of  $A_\mu$  by TF- $\mu$ SR and correlations with ESR data of related radicals. In general the value of  $A(\alpha\text{-H})$  is  $\sim -50$  and of  $A(\beta\text{-H}) \sim +60$  MHz. For the cases of allylbenzene and styrene, these data have already been published with full details on the reasons for the assignments.<sup>8</sup> Neither of these aromatics show the doublets characteristic of cis-trans isomerism, but they are particularly valuable examples to the present study because of this, as will be seen.

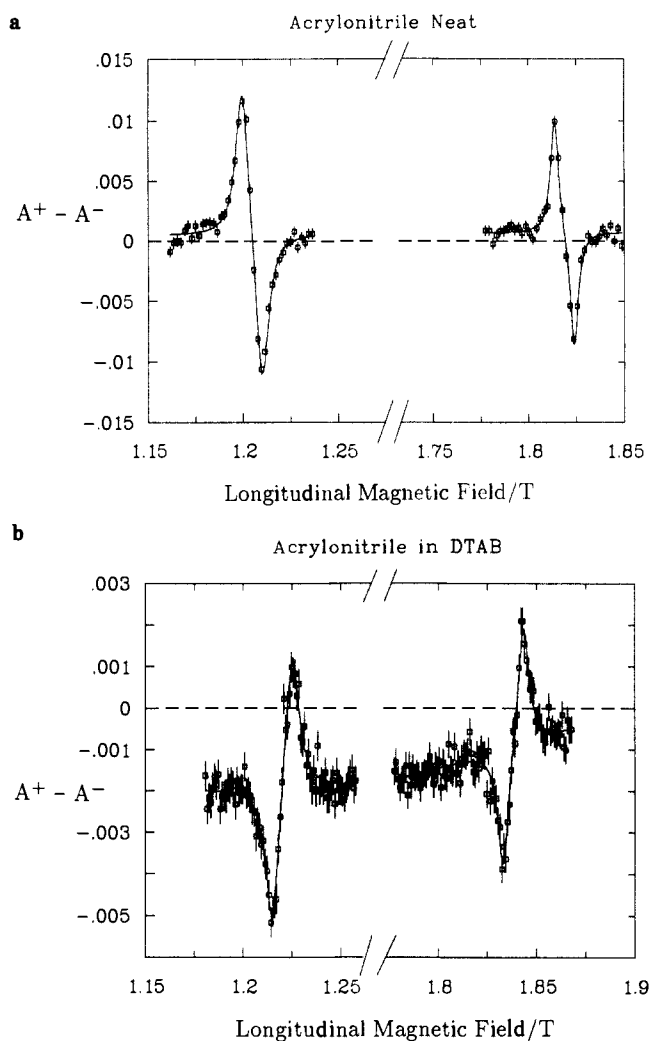
These figures show both pure liquid phases (neat) and solutions where both could be studied. The differences are given in Table I. Some differences are evident in all cases with respect to relative yields and values of  $B_R$ , but the same doublets appear, or do not appear, for a given radical regardless of whether they were formed in the pure organic liquid or in a dilute aqueous environment. Table I contains estimates of the relative abundances of the cis and trans isomers.

### Discussion

It is evident from visual inspection of Figures 1-5 that some solutes show doublets for their  $\beta$ -proton LCRs and some do not.

**Figure 3.** LCR spectra of acrylic acid at 6 mM concentration in water: for the  $\beta$ -H (lower field) and  $\alpha$ -H (the only  $\alpha$  to show a doublet).**Figure 4.** LCR spectra of vinyl acetate (a) (neat) as a pure liquid (no significance in one going up first and other down first) and (b) (in DTAB) in dilute aqueous micelle solution. Spectrum on the left is for the  $H_\beta$  resonance, on the right  $H_\alpha$ .

They are summarized in Table II together with the radical structures. Their actual positions and relative amplitudes were determined by a MINUIT  $\chi^2$ -minimization fitting program which, by subtracting pairs of Lorentzian curves, is free to fit the data to any number of overlapping bands. The lines given in the figures are the best computer fits.



**Figure 5.** LCR spectra of acrylonitrile (a) (neat) as a pure liquid and (b) (in DTAB) in dilute aqueous micelle solution. Spectrum on the left is for the  $H_\beta$  resonance, on the right  $H_\alpha$ .

In about half the compounds studied the  $\beta$ -protons give doublets and the rest give only singlets. Ethyl methacrylate shows doublets for both types of  $\beta$ -protons. For the  $\alpha$ -protons the situation is not quite as clear cut. Acrylic acid shows a resolvable doublet for its  $\alpha$ -proton, but acrylamide and methyl acrylate do not show doublets for their  $\alpha$ -protons. Vinyl acetate is somewhat ambiguous since it shows no splitting in micelle solutions, where Mu is the precursor, though its  $\beta$ -proton (but not the  $\alpha$ ) shows splitting when the pure liquid phase is studied. Several separate conclusions can be drawn from these data, as follows.

1. The first four entries in Tables I and II show that protons which are  $\beta$ - to the  $C^*$  can discern two geometric structures in the rest of the molecule. As the C to the right of  $C^*$  in the Table II structures has  $sp^2$ -hybrid orbitals (in simple valence bond terms) and is involved in  $\pi$ -bonding to O, it is evident that this part of the molecule is *planar*—with the half-filled atomic p on  $C^*$  and the  $C=O$   $\pi$  above and below this plane. These orbitals can mix, resulting in delocalization and partial double-bond character for the central C—C. This allows for cis–trans isomers by restriction of rotation. [Let us take the cis form to be that in which the  $CH_2Mu$  group is on the same side of the C—C as the  $C=O$  (cis drawn in Table II except uracil).]

2. Table I shows the relative distribution of these s-cis–trans conformational isomers in the Mu radicals. If cis and trans isomers were to interchange rapidly (within the LCR time scale of  $10^{-6}$  s), then two spectra would not be resolved, so we can infer that the barrier to rotation does not allow such fast mixing. Furthermore, following Strub et al.,<sup>3</sup> the cis–trans distribution found in the radical can be taken to represent the average cis–trans distribution that the parent molecule takes on, because muonium

reacts with these molecules on first collision ( $k_M$  is known to be at the diffusion-controlled limit of  $\sim 10^{10} M^{-1} s^{-1}$  for these acrylates<sup>9</sup>). The distributions of s-cis–trans isomers in Table I should thus represent the mean distribution of conformers occurring in the parent molecules.

3. Our shifts in  $B_R$  are typically two to three times as large as the changes reported by Strub et al. for  $A_\mu$ ,<sup>3</sup> which implies that changes in  $A_H$  also contribute to  $\Delta(B_R)$ . Since  $\alpha$ -protons have  $A_H$  values of the opposite sign to  $\beta$ -proton couplings, we suggest that shifts in  $A_{H\alpha}$  subtract from changes in  $A_\mu$ , whereas changes in  $A_{H\beta}$  add to the net shift. We suggest this may be the reason that two of the three compounds with  $\alpha$ -protons (acrylamide and methyl acrylate) which show s-cis–trans isomerism in their  $\beta$ -protons do not give resolvable bands on their  $\alpha$ -protons. In the case of acrylic acid, a small splitting is seen for its  $\alpha$ -proton band as if the two counteracting shifts did not cancel out sufficiently in this case. If this is correct, it implies that cis–trans shifts occur in  $A_H$  as well as in  $A_\mu$  and that the shifts have opposite signs for  $\alpha$ - and  $\beta$ -protons. [Perhaps it is somewhat surprising, however, that  $A_\mu$  does not change much more than  $A_H$  in view of Mu having a significantly larger zero point vibrational energy and excluded volume than H.]

4. Acrylonitrile shows no doublets—consistent with the linearity of C—C $\equiv$ N arising from its formal  $sp$  hybridization. The absence of doublets in this case, where s-cis–trans isomerism is impossible, adds credence to this interpretation for the origin of these splittings in LCR spectra.

5. In allylbenzene neither pair of  $\beta$ -protons shows doublets. In this case the C to the right of  $C^*$  (as in Table II) has  $sp^3$  hybridization, so no strong conformational preference would be expected, and there are no  $\pi$  electrons on the adjacent C for partial delocalization.

6. Styrene also shows no doublets. Here the C to the right of  $C^*$  is  $sp^2$ , and part of the molecule will be planar, with full delocalization, as in the acrylic examples. But the benzene ring is symmetrical about the  $C^*$ -ring axis. This symmetry breaks the possibility for cis–trans isomerism in the side-chain radical. Perhaps ortho- or meta-substituted styrenes would show doublets.

7. When muonium adds across the  $C(5)=C(6)$  double bond of uracil (or thymine<sup>10</sup>), all the  $\beta$ -proton LCRs are found to be singlets, even though the C adjacent to  $C^*$  has  $\pi$  orbitals from  $sp^2$  hybridization. However, this result will be a natural consequence of the *fixed* ring structure of uracil which allows only the trans isomer to exist, as drawn in Table II.

8. This cis–trans isomerism is evident in the free radicals regardless of whether they are formed by reaction of the parent molecule with muonium, as a dilute solute in solution, or formed by muon irradiation of the pure liquid state. One explanation is that, even in the pure liquids, muons predominantly react as muonium atoms rather than as ions.<sup>11</sup>

Vinyl acetate seems to be an exception here, in that it gives a doublet—though just for its  $\beta$ -proton's resonance and just in the pure liquid phase. There is the possibility that this is not a doublet but a new nearby resonance from a different radical, specifically, from the radical formed by addition of Mu to the inner C, as seen for allylbenzene,<sup>8</sup> in which case vinyl acetate would not be at all spurious in the context of cis–trans isomerism. [We have disregarded the possibility of there being enough restricted rotation about the  $C^*-O$  bond to give cis–trans isomers, even for a microsecond. It would require mixing of the half-filled p on  $C^*$  with the  $\pi$  of  $C=O$  through the lone pairs on the central O.]

## Summary

Conformational cis–trans isomers are detected by the resolved splitting of the LCR spectra of free radicals formed by formal addition of muonium to acrylic compounds. The isomerism is the same as that postulated by Strub et al.<sup>3</sup> It arises because of partial

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double bond character being granted to a formal single bond by mixing through delocalization of a radical's unpaired electron with a molecule's  $\pi$  bond one C atom away. It is seen for radicals which can be described in VBT hybridization terms as asymmetric  $sp^2$  hybrids on C. It is absent from symmetrical  $sp^2$ 's, from  $sp^3$ 's, and  $sp$  hybrid structures. Acrylamide, methyl acrylate, ethyl methacrylate, and acrylic acid show the effect, whereas acrylonitrile, styrene, allylbenzene, and uracil do not. Since muonium reacts

with these molecules on its first encounter, it implies that the cis-trans distribution found in the radical represents that present in the parent molecule.

**Acknowledgment.** We greatly appreciate the collaboration of John M. Stadlbauer, Zhennan Wu, and Alicia Gonzalez in these studies and the continued help from Curtis Ballard and Keith Hoyle. NSERC of Canada provided some of the funds needed.

## Theoretical Study of Pseudorotation of Pentacoordinated Silicon Anions: The Prototypical $SiH_5^-$

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**Abstract:** Ab initio and semiempirical calculations are used to analyze the minimum energy path for the pseudorotation of  $SiH_5^-$ . Both AM1 and MP2/6-31++G(d,p) predict pseudorotation barriers of 2.4 kcal/mol. A decomposition of the projected vibrational frequencies along the path is used to assist in the interpretation of the process.

### Introduction

Pentacoordinated silicon compounds preferentially bond in trigonal-bipyramidal (tbp) shapes rather than square-pyramidal (spy) or other geometries.<sup>1</sup> In the tbp geometry, the substituents can assume either one of the two axial positions or one of the three equatorial positions. Depending on the nature of the substituents, any or all of the possible permutations of the ligands may or may not be stable structures. For example, in the model compound  $SiX_4Y^-$ , two distinguishable isomers are predicted, one with Y axial and the other with Y equatorial. With a larger variety of substituents, there are a proportionately larger number of possible isomers of the pentacoordinated structure.

These stereoisomers of simple pentacoordinated silicon compounds are not experimentally separable at room temperature; rapid ligand exchange occurs between the axial and equatorial positions.<sup>2</sup> There has been a large body of work devoted to understanding these processes in the analogous pentacoordinated phosphorus compounds,<sup>3-7</sup> and studies of pentacoordinated silicon make use of this body of work as a base. Differences between the two systems will be strongly dictated by the more electropositive nature of the silicon atom as compared with phosphorus<sup>8</sup> and to the presence of a formal negative charge on silicon.

One possible mode for rapid ligand exchange is the process of pseudorotation. Strauss defines pseudorotation as an intramolecular motion of nuclei in a molecule in which conformers interchange to equivalent structures differing only by the number of the atoms.<sup>9</sup> In a broader sense, pseudorotation can also include the exchange of nonequivalent nuclei to produce a trigonal-bipyramidal stereoisomer of the original structure. Berry proposed a specific type of pseudorotation, now widely known as Berry pseudorotation, to explain fluxional behavior of phosphoranes.<sup>10</sup> This Berry pseudorotation process is now widely used to explain isomerization phenomena in 10-electron systems.<sup>11</sup> In this mechanism, shown in Figure 1, a single equatorial substituent (the pivot group) is held stationary, while the two axial ligands become equatorial and the two equatorial ligands become axial. At some intermediate point in the process, a square-pyramidal structure is formed with the four interconverting ligands forming basal

positions in the pyramid and the pivot ligand occupying an apical position in the pyramid (see Figure 1). If all ligands are equivalent, the trigonal-bipyramidal structures have  $D_{3h}$  symmetry while the square-pyramidal structure has  $C_{4v}$  symmetry. In this case, the path joining the  $C_{4v}$  and  $D_{3h}$  structures will have  $C_{2v}$  symmetry. There are a number of other types of pseudorotations that are possible: see either Musher<sup>12</sup> or Gillespie et al.<sup>13</sup> for discussion of all possible rearrangements of these systems.

The prototypical pentacoordinated silicon compound,  $SiH_5^-$ , anion has recently been observed in the gas phase.<sup>14</sup> A number of calculations have been done on this and related systems at both the semiempirical and ab initio levels of theory, as recently reviewed by Burggraf, Davis, and Gordon.<sup>15</sup> Predictions at all levels of theory confirm that the  $D_{3h}$  pentacoordinated trigonal-bipyramidal structure is a minimum on the potential surface and the  $C_{4v}$  tetragonal pyramid is higher in energy, but only a few studies have addressed the nature of the tetragonal structure as a transition state for Berry pseudorotation. Reed and Schleyer have done the most extensive characterization of the  $SiH_5^-$  system to date,

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