Cu(bidhp) in a solvent with a low dielectric constant.

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# Torsional Angles in Vinylarenes Determined by High-Field NMR Spectroscopy

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Abstract: High-resolution deuterium NMR spectra of styrene- $\alpha$ -d, styrene- $d_8$ , 1-vinylnaphthalene- $\alpha$ -d, and 2-vinylnaphthalene- $\alpha$ -d in hydrocarbon solvents were recorded at field strengths of 14.11 to 14.57 T. Quadrupolar splittings were observed as a consequence of magnetic field-induced alignment of the solute molecules. The magnitudes of the splittings were used to calculate the average value of  $\sin^2 \alpha$ , where  $\alpha$  is the dihedral angle between the vinyl and ring planes;  $\alpha_{\rm rms} = \sin^{-1} \langle \sin^2 \alpha \rangle^{1/2}$  was  $16.5 \pm 0.9^{\circ}$  for styrene,  $18.3 \pm 3.1^{\circ}$  for 2-vinylnaphthalene, and  $41.8 \pm 4.1^{\circ}$  for 1-vinylnaphthalene. The styrene value was used to deduce the magnitude of the twofold rotational barrier ( $4.0 \pm \frac{+0.4}{-0.3}$  kcal/mol) and the extent of steric destabilization of the planar form. The results are compared with available literature data.

The characterization of the conformation of and internal rotation in styrene (1) and substituted styrenes has been investigated by a large variety of techniques, including microwave,<sup>1</sup> infrared,<sup>2</sup> Raman,<sup>2,3</sup> ultraviolet,<sup>4</sup> fluorescence,<sup>3d,5</sup> photoelectron,<sup>6</sup> and NMR spectroscopy,7 molecular rotatory polarization,8 calorimetric9 and molecular refractometric<sup>10</sup> studies, molecular mechanics calculations,<sup>11</sup> and semiempirical<sup>12</sup> and ab initio molecular orbital calculations.<sup>13</sup> The consensus from these investigations is that

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Table I. Experimental and Theoretical Rotational Barriers and C1C7 Torsional Frequencies for Styrene

method	phase	rotational barri <b>e</b> r <sup>a</sup>	$\nu_{tor}^{b}$	ref
experimental				
statistical- thermodynamic	gas	2.2	~69	9, 3b
Raman	gas	$1.78 \pm 0.02$	127.7°	3Ъ
NMR	liquid	$1.6 \pm 0.3$		7a
NMR	liquid crystal		80	7b
fluorescence, Raman	gas	$3.06 \pm 0.02$	43	3d
NMR	liquid	$4.0 \pm 0.4_{0.3}$	76	this work
theoretical				
STO-3G		4.4		13a
MM2		1.5		11
(5,2/2) contracted		3.9		13b
$PPP/\sigma$ potential function			99	12c
CNDO/2		4.3		12d
INDO		3.0-3.1		12e
C-INDO		3.65		12f
6-31G		3.1		13c
4-31G	······································	2.8		13d

<sup>a</sup> In kcal mol<sup>-1</sup>. <sup>b</sup> Fundamental  $C_1C_7$  torsional frequency in cm<sup>-1</sup>. <sup>c</sup>Two-quantum transition; see also ref 5b.

the internal rotation in styrene is governed largely by a twofold barrier with the planar form being the most stable. However, the magnitude of the barrier is not very well determined, with values from 1.5 to 4.4 kcal mol<sup>-1</sup> being deduced or calculated (Table I). It is also not clear whether a steric destabilization of the planar form occurs,14 resulting in a shifting of the energy minimum from  $\alpha = 0^{\circ}$  ( $\alpha$  is the dihedral angle between the planes of the vinyl group and the phenyl ring) to  $\alpha = \pm 20$  to  $30^{\circ}$ .

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## Torsional Angles in Vinylarenes

In comparison to styrene (1), there is relatively little information available regarding the conformations of 1- and 2-vinylnaphthalene (2 and 3, respectively). Klemm et al. concluded on the basis of ultraviolet spectroscopy and inspection of molecular models that 2 exists in a nonplanar anti conformation (2-anti) whereas 3 exists predominantly in coplanar conformation 3-syn (as opposed to coplanar conformation 3-anti).15 We have reached similar conclusions on the basis of  ${}^{1}H$  NMR chemical shifts except that 3-syn was favored over 3-anti.<sup>16</sup> Recently it was concluded on the basis of proton-proton nuclear Overhauser effects that the minimum energy conformation for 2 is 2-anti with  $\alpha \approx 38^{\circ}$ .<sup>17</sup> A molecular mechanics (MMP2) calculation gave a calculated weighted mean minimum angle of 41°.17



The out-of-plane rotation in 2 was calculated to be 35° by C-INDO molecular orbital calculations.<sup>12f</sup> In contrast, 2-anti, 3-svn, and 3-anti were all calculated to be planar on the basis of a method utilizing empirical potential functions for the  $\sigma$  system coupled with semiempirical  $\pi$  (PPP) molecular orbital calculations.<sup>18</sup> Interestingly, the course of cationic cyclizations of a 1-vinylnaphthalene derivative could be satisfactorily rationalized on the basis of a **2**-anti conformation.<sup>19</sup> However, no experimental determinations of the value of  $\alpha$  in 1- and 2-vinylnaphthalene have been reported.

A new method of investigating this problem has become available, and we report here on its application. The method rests on the observation by Lohman and MacLean<sup>20</sup> that quadrupolar splittings become observable in the deuterium spectra of deuteriated aromatic molecules at very high fields. These splittings become observable because the molecules are slightly aligned as a result of the interaction of the strong magnetic field with the anisotropic magnetic susceptibilities of the molecules. The energy required to place a molecule in the field is

$$E = -\frac{1}{2}\vec{\mathbf{B}}_0 \cdot \boldsymbol{\chi} \cdot \vec{\mathbf{B}}_0 \tag{1}$$

where  $\vec{B}_0$  is the magnetic induction and  $\chi$  is the magnetic susceptibility tensor for the molecule. The alignment is counteracted by thermal motions of the molecule. The net alignment parameter  $S_{\rm v}$  for any chosen molecular axis is given by Boltzmann statistics as

$$S_{\mathbf{v}} = \left\langle \frac{3}{2} \cos^2 \theta_{\mathbf{v}} - \frac{1}{2} \right\rangle = \frac{\bar{B}_0^2}{15kT} \sum \left( \frac{3}{2} \cos^2 \theta_i - \frac{1}{2} \right) \chi_{ii} \quad (2)$$

In this expression  $\theta_{\rm v}$  is the angle between the chosen molecular axis and the static field direction, while  $\cos \theta_i$  is the direction cosine relating the chosen axis to the principal susceptibility axes, x, y, z, of the molecule.

The deuterium splitting is governed by the degree of orientation of the principal axes of the electric field gradient at the deuterium. Generally the largest field gradient is nearly colinear with the C-D bond, and this is taken as the "z" axis of the electric field-gradient tensor. The observed splitting is then given by<sup>21</sup>

$$\Delta \nu = \left(\frac{eQ}{h}\right) \mathbf{S}: \mathbf{V} \tag{3}$$

where S:V is the trace of the product of the ordering matrix S, and the electric field gradient (EFG) tensor, V, both represented in the same coordinate frame. Equations 2 and 3 can be combined to give the master equation

$$\Delta \nu = \left[\frac{eQ}{h}\right] \left[\frac{\vec{B}_0^2}{10kT}\right] V:\chi \tag{4}$$

where eQ is the nuclear quadrupole moment and V: $\chi$  is the trace of the product of the field gradient and susceptibility tensors represented in the same coordinate frame. The components of V may be transformed from the local frame specified by the C-D bond to the principal frame of the susceptibility tensor by the relations

$$V_{ii} = \exp\left\{ \left[ \frac{3}{2} \cos^2 \theta_{z''i} - \frac{1}{2} \right] + \frac{\eta}{2} \left[ \cos^2 \theta_{x''i} - \cos^2 \theta_{y''i} \right] \right\}$$
(5)

where  $\theta_{z''i}$  is the angle between the z'' axis of the EFG tensor and the *i*th axis of  $\chi$ , and  $\eta$  is the quadrupolar asymmetry parameter. Equation 4 is then expressible in the simpler form

$$\Delta \nu = \left(\frac{eQ}{h}\right) \left(\frac{\ddot{B}_0^2}{10kT}\right) \left\{ \Delta \chi V_{zz} + \frac{1}{2} \,\delta \chi (V_{xx} - V_{yy}) \right\} \quad (6)$$

where  $\Delta \chi = \chi_{zz} - \frac{1}{2}(\chi_{xx} + \chi_{yy})$  and  $\delta_{\chi} = \chi_{xx} - \chi_{yy}$ . Deuterium attached to different sites in a molecule will show

different splittings which reflect both geometry and internal motional averaging. The analysis of these differences yields information about the solution structure and dynamics. An analogous procedure has been demonstrated for the vinyl side chains of a porphyrin by using magnetic dipole-dipole splittings.<sup>22</sup>

### **Experimental Section**

Materials. Styrene- $\alpha$ -d. The general procedure of Shapiro was employed.<sup>23</sup> A solution of 8.61 g (50.0 mmol) of benzenesulfonohydrazide (Aldrich) and 6.00 g (50.0 mmol) of acetophenone in 100 mL of 1% hydrochloric acid/ethanol (w/w) was stirred for 10 min and then refluxed for 1 h. The mixture was cooled in ice and filtered, and the solid was washed with cold ethanol (25 mL) to give 12.30 g (45.0 mmol, 90%) of the hydrazone as a colorless solid.

The hydrazone (2.74 g, 10 mmol) was dissolved in 20 mL of ether/ N, N, N', N'-tetramethylethylenediamine (TMEDA) (1/1) and cooled to -70 °C. A 1.6 M solution of methyllithium in ether (25 mL, 40 mmol, Aldrich) was added with a syringe over 30 min and the reaction mixture was warmed to 0 °C and stirred for 3 h. The mixture was again cooled to -70 °C and 1 mL of  $^{2}H_{2}O$  was added. The mixture was allowed to warm to room temperature, diluted with pentane (50 mL), washed with water and brine (20 mL each), dried over anhydrous sodium sulfate, passed through a small plug of neutral alumina, and evaporated under reduced pressure. The crude product was purified by  $GL\dot{C}$  on a 0.25 in. reduced pressure. The chube product was purified by GLC of 0.23 mi × 0.25 m column of 10% IGEPAL CO-880 on 100/120 mesh Chromo-sorb P AW/DMCS at 60 °C to give 334 mg (3.18 mmol, 32%) of styrene- $\alpha$ - $d_1^{24}$  as a colorless oil. <sup>2</sup>H NMR (30.71 MHz, cyclopentane):  $\delta$  (±0.01) 1.75 (C<sub>3</sub>H<sub>10</sub>), 6.90 (dd, J<sub>trans</sub> = 2.58 Hz, J<sub>cts</sub> = 1.70 Hz). **1-VinyInaphthalene-\alpha-d.** By the procedure described above, 1.86 g

(10.0 mmol) of p-toluenesulfonohydrazide (Aldrich) was caused to react

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**Figure 1.** Resolution-enhanced <sup>2</sup>H NMR spectrum of styrene- $\alpha$ - $d_1$  at 14.11 T. Sample concentration 2 vol % in cyclopentane (T = 296 K).

with 1.70 g (10.0 mmol) of methyl 1-naphthyl ketone (ICN pharmaceuticals) in 20 mL of solvent to afford 2.60 g (7.68 mmol, 77%) of the tosylhydrazone as a colorless solid.

A solution of lithium diisopropylamide (LDA) was generated at -70 °C by the addition of 4.1 mL of a 1.6 M solution (6.6 mmol) of *n*-butyllithium in hexane (Aldrich) to a solution of 0.84 mL (6.0 mmol) of diisopropylamine and 1.0 mL (6.6 mmol) of TMEDA in 2 mL of tetrahydrofuran. The solution was stirred for 30 min followed by the addition of 677 mg (2.0 mmol) of the tosylhydrazone in 10 mL of tetrahydrofuran. This mixture was stirred for 30 min at -70 °C and then for 48 h at room temperature, cooled to -70 °C and 1 mL of <sup>2</sup>H<sub>2</sub>O was added. The reaction was worked up as described above and the crude product was purified by GLC at 100 °C on the column described above to give 62 mg (0.40 mmol, 20%) of 1-vinylnaphthalene- $\alpha$ - $d^{25}$  as a colorless oil. <sup>2</sup>H NMR (30.71 MHz, cyclopentane):  $\delta$  (±0.01) 1.75 (C<sub>5</sub>H<sub>10</sub>), 7.68 (dd,  $J_{trans} = 2.57$  Hz,  $J_{cis} = 1.68$  Hz).

 $J_{\text{trans}} = 2.57 \text{ Hz}, J_{\text{cis}} = 1.68 \text{ Hz}.$ **2-Vinylnaphthalene-\alpha-d.** The procedure described above was followed by using 8.61 g (50.0 mmol) of benzenesulfonohydrazide and 8.51 g (50.0 mmol) of methyl 2-naphthyl ketone (Aldrich) in 100 mL of solvent to afford 13.70 g (42.2 mmol, 84%) of the corresponding hydrazone as a colorless solid.

This hydrazone (3.24 g, 10.0 mmol) was then treated as in the synthesis of styrene- $\alpha$ -d except that the reaction mixture was stirred at 0 °C for 4 h. The crude product was loaded on a column of Woelm neutral alumina (10 g) and eluted with pentane (300 mL). The pentane was removed under reduced pressure to give 0.78 g (5.0 mmol, 50%) of 2-vinylnaphthalene- $\alpha$ - $d_1$  as a colorless solid. <sup>2</sup>H NMR (30.71 MHz, cyclopentane):  $\delta$  (±0.01) 1.75 (C<sub>5</sub>H<sub>10</sub>), 7.07 (dd, J<sub>trans</sub> = 2.61 Hz, J<sub>cis</sub> = 1.63 Hz).

Styrene- $d_8$  (Chemical Dynamics Corp.) was purified by GLC on a 0.25 in. × 0.60 m column of 23% IGEPAL CO-880 on 100/120 mesh Chromosorb PAW/DMCS at 50 °C.

**NMR Samples.** The materials described above were dissolved at 5 mol % concentration in cyclopentane, cyclohexane, tetramethylsilane, or carbon disulfide. Samples were degassed by freezing and thawing under vacuum and then sealed in 5-mm precision NMR cells. Splittings measured in the presence of acetone were marginally larger, probably as a result of some association.

NMR Spectroscopy. Deuterium spectra were recorded in the FT mode at the NMR Facility for Biomedical Studies. During the course of this study the static magnetic field was increased from 14.11 to 14.57 T (600.6 to 620.17 MHz), which resulted in a shift of the deuterium observe frequency from 92.20 to 95.18 MHz. Splittings observed at different fields for the same sample were proportional to the square of the field within experimental error. All results are reported as though observed at 14.57 T.

In order to measure the doublet splittings accurately, spectra were recorded at the highest achievable resolution, which was limited by the natural line width of the deuterium resonances, and at high signal/noise ratios. Normally in excess of 1000 scans were accumulated. The doublets were then subjected to resolution enhancement, with care being taken to avoid the production of truncation wiggles that displace the peak maxima. Enhancement was applied to reduce the valley between the peaks to 5% or less of the peak maxima. The errors in the splittings obtained are estimated to be 0.01-0.02 Hz, depending on the signal studied.

#### Results

In the case of styrene, observations were made on both styrene- $\alpha$ -d and styrene- $d_8$ . The quadrupolar splitting for the  $\alpha$ deuterium in styrene-d is very clearly resolved (Figure 1). This



Figure 2. <sup>2</sup>H NMR spectrum of 5 mol % styrene- $d_8$  in cyclohexane (T = 296 K; B = 14.57 T). The ortho and para resonances were recorded with meta-deuterium decoupling; the *cis*- $\beta$ - and *trans*- $\beta$ -vinyl deuteriums with decoupling of the deuterium in the  $\alpha$ -position (not displayed); (a) normal spectrum; (b) resolution enhanced. Scale is 1 Hz/division.



**Figure 3.** Resolution-enhanced <sup>2</sup>H NMR spectrum of 2-vinylnaphthalene- $\alpha$ -*d* dissolved at 2 vol % in cyclopentane. The cis- $\beta$ -proton was decoupled (T = 296 K; B = 14.11 T).



**Figure 4.** Resolution-enhanced <sup>2</sup>H NMR spectrum of 1-vinylnaphthalene- $\alpha$ -*d* dissolved at 2 vol % in CS<sub>2</sub>/acetone-*d*<sub>6</sub> (80 vol %/20 vol %). The cis- $\beta$ -proton was decoupled (T = 296 K; B = 14.11 T).

splitting could not be observed in styrene- $d_8$  because of the coupling with the cis and trans deuteriums. However, by irradiation of the  $\alpha$ -deuterium in the latter compound, the quadrupolar splittings in the *cis*- and *trans*- $\beta$ -vinyl deuteriums could be displayed (Figure 2). The para and ortho splittings for the aromatic deuteriums were obtained under decoupling of the meta deuterium. This procedure is necessary to remove small scalar deuterium-deuterium couplings, which partially obscure the splitting.

For 2-vinylnaphthalene- $\alpha$ -d, the quadrupolar splittings in the deuterium spectrum were best observed by decoupling either the *cis*- or *trans*- $\beta$ -vinyl proton (Figure 3). In contrast, no quadrupolar splitting could be resolved for 1-vinylnaphthalene- $\alpha$ -d, even with decoupling of the *cis*- or *trans*- $\beta$ -vinyl protons (Figure 4). From the observed line width, we have deduced that the splitting must be less than 0.15 Hz. All observed deuterium splittings (corrected, if necessary, to a field strength of 14.57 T) are given in Table II.

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Table II. Deuterium Quadrupole Splittings in Deuteriated Vinylarenes Observed at (or Corrected to) 14.57 T (296 K)

compd and position	solvent	$\Delta \nu$ (Hz)	
styrene- $\alpha$ -d	cyclopentane + TMS	$0.49 \pm 0.02$	
cis- $\beta$		$0.565 \pm 0.010$ 0.443 ± 0.005	
ortho	cyclohexane	$0.572 \pm 0.010$ 0.557 ± 0.010	
1-vinylnaphthalene- $\alpha$ -d 2-vinylnaphthalene- $\alpha$ -d	cyclopentane 80% $CS_2/20\%$ acetone- $d_6$	< 0.15  0.76 ± 0.02	

### Discussion

Styrene. The first important observation from Table II is that the splittings for the ortho and para (o,p) deuteriums are identical within experimental error. As  $V_{xx}$  and  $V_{yy}$  differ for the two positions, it can be concluded that  $\delta \chi$  must be near zero. The possibility that the observed splittings for the o and p deuteriums are opposite in sign can be dismissed as it would require a completely unrealistic suspectibility tensor, with  $\chi_{xx} = 8\chi_{zz} + 9\chi_{yy}$ (eq 4). Thus the second term in brackets in eq 6 may be dropped. The equation for the quadrupolar splitting of any nucleus j in the molecule is now given by eq 7, which is derived from eq 5 and Thus if the quadrupolar coupling constant  $(e^2 q Q/h)$ , the 6.

$$\Delta \nu_{j} = \left[ \frac{e^{2} q Q}{h} \right]_{j} \frac{\Delta \chi \vec{B}_{0}^{2}}{10 k T} \left\{ \left( \frac{3}{2} \cos^{2} \theta_{z''z}^{j} - \frac{1}{2} \right) + \frac{1}{2} \eta_{j} [\cos^{2} \theta_{z''z}^{j} - \cos^{2} \theta_{y''z}^{j}] \right\}$$
(7)

asymmetry parameter  $(\eta)$ , and the angles  $\theta_{z'z}$ ,  $\theta_{z''y}$ , and  $\theta_{z'x}$  of a certain deuterium are known,  $\Delta \chi$  can be calculated from the splitting. If ratios of splittings are studied,  $\Delta \chi$ , which is a molecular parameter, drops out and unknown angles for some of the nuclei can be determined.

The main complication to be resolved for styrene is the definition of the molecular frame (the frame in which the susceptibility tensor is diagonal). This definition will also depend on the angle that the vinyl group makes with the benzene ring. In general, the main susceptibility component in benzene derivatives can be chosen perpendicular to the ring. To test whether this is also a good choice for styrene,  $\Delta \chi$  for the molecule is first calculated based on this assumption. This value of  $\Delta \chi$  is then compared with the value deduced from group contributions and the measured expectation value,  $(\sin^2 \alpha)$ , which is obtained without any assumptions concerning the molecular frame directions. The deduced value is obtained from

$$(\Delta \chi)_{\text{molecule}} = (\Delta \chi)_{\text{ring}} + \langle 1 - \frac{3}{2} \sin^2 \alpha \rangle (\Delta \chi)_{\text{vinyl}}$$
(8)

Numerous measurements<sup>26-30</sup> have fixed the value of the anisotropic magnetic susceptibility for benzene at  $-(1.03 \pm 0.04) \times$  $10^{-28}$  cm<sup>3</sup>/molecule. The information on ethylene is much more sparse, but recent Cotton-Mouton measurements<sup>31</sup> give -0.127  $\times$  10<sup>-28</sup> cm<sup>3</sup>/molecule with the largest component oriented perpendicular to the plane of the molecule. Calculations from local susceptibilities<sup>32</sup> give  $-0.141 \times 10^{-28}$  cm<sup>3</sup>/molecule, in satisfactory agreement with the Cotton-Mouton measurements. Thus the dominant factor in the orientation of styrene in a magnetic field will be the benzene ring.

On the assumption that the z axis is perpendicular to the benzene ring, the formula for the splitting of the aromatic deuteriums ( $\theta_{z''z} = \theta_{x''z} = 90^\circ$ ;  $\theta_{y''z} = 0^\circ$ ) is given by

$$\Delta \nu(\mathbf{o},\mathbf{p}) = \left[ \frac{e^2 q Q}{n} \right]_{\mathbf{o},\mathbf{p}} \frac{\Delta \chi \vec{\mathbf{B}}_0^2}{10 k T} \left( -\frac{1}{2} - \frac{1}{2} \eta_{\mathbf{o},\mathbf{p}} \right)$$
(9)

For deuteriums attached to a benzene ring, the quadrupolar coupling constant<sup>33</sup> is well known to be  $186 \pm 6$  kHz, with a typical asymmetry parameter of  $0.05 \pm 0.02$ . Substitution of these constants into eq 8 yields  $\Delta \chi = -1.15 \pm 0.08 \text{ cm}^3/\text{molecule}$ , which agrees well with the sum of  $\Delta \chi$  for the benzene ring and vinyl group (-1.16  $\times$  10<sup>-28</sup> cm<sup>3</sup>/molecule<sup>-1</sup>) and suggests that the tensors simply add, i.e., that the groups are approximately coplanar. The latter point will be checked later with the determined dihedral angle.

The splittings of the  $\alpha$ - or trans- $\beta$  deuteriums in the vinyl group can be compared to that of the cis- $\beta$  deuterium (Figure 1 and 2) to obtain a precise measure of the expectation value of  $\langle \sin^2 \alpha \rangle$ . The values of these splittings are given by eq 7 and 9, but the quadrupolar coupling constants and asymmetry parameters of these vinyl deuteriums are about equal. A second assumption that we will make is that  $\eta_{vinyl} \approx 0$ , as determined by Emsley and Longeri for styrene in the nematic phase.<sup>7b</sup> This assumption is strengthened by comparing the splittings of the para aromatic deuterium and the  $cis-\beta$ -vinyl deuterium. The corresponding C–D bonds are nearly parallel,<sup>13c,d</sup> and, consequently, this orientation is unaffected by torsional motion. Thus the splittings should be in the ratio of the quadrupolar coupling constants (qcc) and the asymmetry parameter contributions.

Emsley and Longeri<sup>7b</sup> reported a qcc of  $180.5 \pm 9$  kHz and  $\eta = -0.01 \pm 0.03$  for the vinyl deuteriums in styrene-d<sub>8</sub> in the nematic phase. For the aromatic deuteriums they found qcc = 185.4  $\pm$  2 kHz and  $\eta = 0.03 \pm 0.03$ , which is close to the liquid phase value.<sup>33a</sup> Qcc's determined in liquid crystals may be in-fluenced by the environment,<sup>34</sup> but since the value for the aromatics fits with the generally accepted liquid phase value, we assume that taking a value of 180  $\pm$  6 kHz and  $\eta = 0.0 \pm 0.02$  will not cause more than a few percent error in the results. By assuming parallel bonds for the para and cis- $\beta$  deuteriums and z perpendicular to the aromatic ring, we expect a splitting ratio of  $1.05 \pm 0.04$ , which compares well with the experimental value of  $\Delta \nu(o,p)/\Delta \nu(cis) =$ 

1.00. Thus the assumption that  $\eta_{vinyl} \approx 0$  is reasonable. The C-D bonds in the  $\alpha$ - and trans- $\beta$ -positions are also expected to be almost parallel.<sup>13cd</sup> It is therefore expected that the observed quadrupolar splittings should be nearly identical. These values differ by an amount larger than the estimated error (Table II). This difference can probably be explained by slight differences in the bond angles, although differences in the qcc, the asymmetry parameters or the solvent may also contribute. To calculate the dihedral angle we take the more reliable value ( $\Delta \nu$ (trans)) and then obtain a splitting ratio (eq 9a) ( $\pm 0.784$ ) that is independent of the choice of the molecular frame on the assumption of a single vinyl qcc and  $\eta_{\text{vinyl}} = 0$ .

$$\frac{\Delta\nu(\text{trans})}{\Delta\nu(\text{cis})} = \frac{\left\langle \frac{3}{2}\cos^2\theta_z^{\alpha,1} - \frac{1}{2} \right\rangle}{\left\langle \frac{3}{2}\cos^2\theta_z^{\text{cis}} - \frac{1}{2} \right\rangle}$$
(9a)

with

$$\langle \cos^2 \theta_{z''z}^j \rangle = \langle \sin^2 \alpha \rangle \sin^2 \beta^j$$
 (9b)

Here  $\beta^{j}$  is the angle between the internal rotation axis and the  $(C-D)_i$  bond, and  $\alpha$  is the dihedral angle formed by the phenyl

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Table III.	Possible	Values of the Dih	edral Angle $\alpha_{\rm rm}$	$s = sin^{-1}$	$\langle \sin^2 \alpha \rangle^{1/2}$	<sup>2</sup> for Viny	'l-Substituted	Benzene and Naphthalene
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compd	$\Delta \nu (\text{vinyl}) > 0$		$\Delta \nu (\text{vinyl}) < 0$		literature
	$\langle \sin^2 \alpha \rangle$	$\alpha_{\rm rms}^{a}$	$\langle \sin^2 \alpha \rangle$	$\alpha_{\rm rms}^{b}$	$(\sin^2 \alpha)^b$
styrene	$0.081 \pm 0.009$	$16.5 \pm 0.9^{\circ}$	$0.666 \pm 0.009$	$54.7 \pm 0.6^{\circ}$	0.13-0.24
2-vinylnaphthalene	$0.099 \pm 0.030$	$18.3 \pm 3.1^{\circ}$	$0.811 \pm 0.032$	$64.2 \pm 2.5^{\circ}$	
1-vinylnaphthalene	$0.409 \pm 0.035$	$39.8 \pm 2.1^{\circ}$	$0.480 \pm 0.036$	$43.8 \pm 2.0^{\circ}$	

<sup>a</sup>Nonlinear error range; the maximum deviation is given. <sup>b</sup>Reference 13d.

and vinyl planes. The brackets  $\langle \rangle$  denote averaging.

A problem arises at this point as to the signs of the splittings. It can be concluded from susceptibility considerations ( $\Delta \chi < 0$ ) that the splittings for the ring deuteriums are positive.<sup>26</sup> The cis- $\beta$  C-D bond is almost parallel to the para C-D bond and its splitting will also be positive. However, the assignment of the signs for the trans- $\beta$  and  $\alpha$  deuteriums is less straightforward. In principle, two different angles may be obtained from eq 9, depending on the sign of the splitting ratio. The cis- $\beta$  deuterium-carbon bond is approximately parallel to the rotation axis ( $\beta^{cis} \approx 0^{\circ}$ ). Thus, if we take  $\beta^{rans} = 109.0^{\circ}$  (the average of the liquid crystal NMR and HF/6-31G ab initio<sup>13c</sup> values of  $\beta$  for the trans- $\beta$  deuteriums),  $\alpha_{rms} = \sin^{-1} (\sin^2 \alpha)^{1/2}$  values of 16.5  $\pm$  0.9° and 54.7  $\pm$  0.6° are found for positive and negative splitting ratios, respectively.

A decision on the correct angle can be made on physical grounds by means of eq 8. Using the values of  $\Delta \chi$  (benzene) = -1.03 ×  $10^{-28} \text{ cm}^3/\text{molecule}$  and  $\overline{\Delta}\chi(\text{vinyl}) = -0.13 \times 10^{-28} \text{ cm}^3/\text{molecule}$ , one obtains  $\Delta \chi$ (styrene) = -1.15 × 10<sup>-28</sup> and -1.02 × 10<sup>-28</sup> cm<sup>3</sup>/molecule for  $\alpha_{\rm rms} = 16.5$  and 54.7°, respectively. For smaller values of  $\Delta \chi$ , the ring deuteriums are expected to exhibit a smaller splitting; e.g.,  $\Delta \nu = 0.51$  Hz in benzene.<sup>26</sup> If the molecular frame is not oriented with its main axis perpendicular to the plane, the splitting is expected to decrease in magnitude (i.e.,  $|\langle^3/2 \cos^2 \theta_z\rangle$  $-\frac{1}{2}$  becomes smaller). As only small deviations from this picture are expected, a value of  $\Delta \chi = -1.02 \times 10^{-28} \text{ cm}^3/\text{molecule}$ cannot explain the large aromatic ring splittings of  $0.564 \pm 0.007$ Hz. Thus  $16.5 \pm 0.9^{\circ}$  is the correct angle. (Note that if  $\delta \chi$  is not zero the reasoning gets more complex, but fortunately this is not the case). Theoretical calculations<sup>13c,d</sup> also support a value of  $\alpha_{\rm rms}$  of this order of magnitude (Table III). Values of  $\beta$  in the range of 108.7-109.3° have been calculated<sup>13c,d</sup> or experimentally determined<sup>7d</sup> for the trans- $\beta$  deuterium. These give  $\alpha_{\rm rms}$ values within  $\pm 0.3^{\circ}$  of the determined value and therefore do not affect the result. Finally, it is clear from the above calculations that the molecular frame has an orientation very close to that with z perpendicular to the ring.

The final step in the analysis is to use  $\langle \sin^2 \alpha \rangle$  to obtain an indication of the torsional energy for rotation around the phenyl-vinyl bond. Since styrene is studied here in the liquid phase, it is reasonable to suppose that the frequency of molecular collisions is sufficient to cause the torsional population to obey classical Boltzmann statistics. We assume a twofold barrier, with the form  $E = V_2 \sin^2 \alpha$ , and calculate the expectation value,  $\langle \sin^2 \alpha \rangle$ ), from

$$\langle \sin^2 \alpha \rangle = \frac{\int \sin^2 \alpha e^{-E/kT} \, d\alpha}{\int e^{-E/kT} \, d\alpha}$$
 (10)

The expression was evaluated numerically for a range of values of  $V_2$  at 296 K. A value of  $\alpha_{\rm rms}$  of 16.5° corresponds to a torsional barrier of 4.0 kcal mol<sup>-1</sup>. Furthermore, we calculate this barrier to be >3.5 kcal mol<sup>-1</sup> when account is taken of the range (15.6–17.3°) obtained for  $\alpha_{\rm rms}$ . If one then employs the analysis suggested by Guillory,<sup>35</sup> this barrier corresponds to a ground-state torsional frequency of 76 cm<sup>-1</sup>.

As seen in Table I, our values of the torsional barrier and the ground-state torsional frequency are at the high end of the range of previously determined values. This is not unreasonable since the theoretical values and many of the experimental values correspond to the gas phase and the barrier is expected to increase in solution. Note that our value of the tosional frequency is very similar to that obtained by a  $^{1}H$  and  $^{2}H$  NMR study of a nematic solution of 1.<sup>7b</sup>

The form of the barrier may well deviate from that assumed above. Admixture of higher terms, such as fourfold or sixfold barriers, cannot be excluded and would change somewhat the value deduced for  $V_2$ . A trial potential energy curve of the type  $E = V_2 \sin^2 \alpha + E_s \cos^{12} \alpha$  was employed in order to assess the importance of steric destabilization in the planar form. In this equation  $E_s$  represents the increase in energy of the planar form arising from steric interference. A high exponent was used to simulate rapid relief of strain on rotation out of the plane, in analogy with the Lennard-Jones potential. From curves of  $\alpha_{\rm rms}$ versus  $V_2$  calculated for trial values of  $E_s$ , it is clear that  $E_s$  must be quite small (<1 kcal mol<sup>-1</sup>), as otherwise  $V_2$  becomes unrealistically large.

**Vinylnaphthalenes.** For 2-vinylnaphthalene- $\alpha$ -d the magnetic anisotropy is dominated by the contribution of the naphthalene ring, for which a value of  $\Delta \chi = -1.99 \pm 0.06 \times 10^{-28} \text{ cm}^3/\text{molecule}$ has been very firmly established.<sup>21,36</sup> The asymmetry  $\chi_{xx} - \chi_{yy}$ is 0.04 to  $0.05 \times 10^{-28}$  cm<sup>3</sup>/molecule.<sup>21</sup> Thus the deviation of the naphthalene ring susceptibility from axiality may be ignored, and an analysis paralleling that used for styrene may be employed. If we add the contribution from the vinyl group, then parallel vinyl and naphthalene planes are calculated to give  $\Delta \chi = -2.12 \times 10^{-28}$ cm<sup>3</sup> molecule. As only one splitting is known, eq 7 has to be used, together with the qcc and  $\eta$ -values for the vinyl group mentioned in the previous paragraph for styrene. Calculation of  $\alpha_{\rm rms}$  and insertion in eq 8 to check  $\Delta \chi$  of the *total* compound provides a simple iterative procedure to obtain  $\alpha_{\rm rms}$  and  $\Delta \chi$ . We find  $\alpha_{\rm rms} = 18.3 \pm 3.1^{\circ}$  and  $\Delta \chi = -2.09 \times 10^{-28} \,{\rm cm}^3/{\rm molecule}$ . The alternative solution  $\alpha_{\rm rms} = 64.2^{\circ}$  is excluded on the basis of the arguments made for styrene. The torsional energy curve is similar to that of styrene.

On the other hand, 1-vinylnaphthalene- $\alpha$ -d gave no detectable splitting. The absolute magnitude of the splitting was judged to be less than 0.15 Hz based on the line width after resolution enhancement. However, either positive or negative splittings are possible; thus the resulting angle must include both options. By using the same iterative procedure with eq 7 and 8 mentioned for the previous example, it can be calculated that  $\alpha_{\rm rms} = 41.8 \pm 4.1^{\circ}$ and  $\Delta \chi = -2.03 \times 10^{-28} \text{ cm}^3/\text{molecule}$ . Such a torsional angle is easily explained by repulsion between  $H_8$  on the naphthalene ring and the  $\alpha$ - or trans- $\beta$  deuteriums on the vinyl group. The  $H_8$  to  $\alpha$ -d distance in a planar molecule with normal bond angles and distances would be approximately 1.76 Å, considerably less than the sum of the van der Waals radii. A large distortion of the three intervening bond angles would be required to relieve this strain. On the other hand, the principal repulsion in styrene is between the trans- $\beta$  hydrogen of the vinyl group and the ortho proton, which would be separated by approximately 1.82 Å in a standard geometry. The strain is relieved by the deformation of four bond angles, and much less severe departures from 120° are required<sup>14</sup> than in 1-vinylnaphthalene to bring the H-H separation to 2.0 Å.

The agreement between our value of  $\alpha_{\rm rms}$  and the dihedral angle deduced from NOE measurements<sup>17</sup> is excellent, but it should be

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born in mind that the averaging applied in the two methods is quite different, ours yielding directly  $(\sin^2 \alpha)$ , whereas the NOE method yields  $\langle r^3_{\rm HH} \rangle^{-2}$  which is related to  $\alpha$  by complex trigonometric relations. The NOE method weights small HH distances (in this case the planar arrangement) strongly, so that a somewhat smaller angle should be predicted.

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# Electrocatalysis at a Novel Electrode Coating of Nonstoichiometric Tungsten(VI,V) Oxide Aggregates

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Abstract: Cycling the potential between 0.8 and -0.4 V vs. SCE in the colloidal mixture of WO<sub>3</sub>·2H<sub>2</sub>O/WO<sub>3</sub>·H<sub>2</sub>O existing in 2 M H<sub>2</sub>SO<sub>4</sub> at 35 °C causes the electrodeposition of stable, mixed-valent W(VI,V) oxide aggregates on common electrode substrates. Infrared spectroscopy confirmed the presence of H<sub>2</sub>O in the deposit and showed that the extent of hydration is lower than in WO3.2H2O. Well-defined redox transitions have been attributed to the reductive formation and oxidative elimination of hydrogen W oxide bronzes in dihydrate portions of the film. Reduction of monohydrate semirigid microstructures in the film is more irreversible and apparently leads to lower substoichiometric W oxides. Depth profiles were determined by Auger electron spectrometry and secondary ion mass spectrometry. The coating is easily permeable to ions, and the dynamics of charge propagation and electrochromism are comparable to those of dihydrate films. The W(VI,V) oxide film catalyzes the electroreduction of bromate to bromide in H<sub>2</sub>SO<sub>4</sub>. At bare carbon, BrO<sub>3</sub><sup>-</sup> is not reduced prior to the onset of hydrogen evolution at about -0.7 V. At the modified surface, a bromate reduction peak appears at about -0.1 V vs SCE. The peak is linear with concentration from 10<sup>-5</sup> to 10<sup>-3</sup> M and is nearly diffusion-controlled. Cyclic and rotating disk voltammetry have been employed to characterize the catalytic reaction between BrO<sub>3</sub><sup>-</sup> and reduced centers in the film. For typical quantities of the W(VI,V) oxide film ((1-4)  $\times$  10<sup>-7</sup> mol cm<sup>-2</sup>), a moderate apparent rate constant of the heterogeneous reaction (2  $\times$  10<sup>-4</sup> cm s<sup>-1</sup>) was found.

Considerable recent effort has been devoted to the preparation and characterization of organic polymers as materials for coating electrode surfaces.<sup>1-3</sup> Potential applications based on the catalysis of electrochemical reactions have provided much of the incentive for this development.<sup>2-8</sup> The attractiveness of such systems is in the combination of advantages from heterogeneous catalysis (particularly those of a catalyst attached to insoluble matrix) together with benefits of a three-dimensional distribution of catalytic centers, normally characteristic of homogeneous catalysis.8

One of the important conflicts in these systems concerns the need to distribute electrons rapidly in the microstructure vs the need for the structure to engage in fast redox chemistry with substrate molecules in solution. Almost all catalytic modified electrodes have been developed by immobilizing good redox mediators into the microstructures.<sup>2</sup> Normally, these are simple, coordinatively saturated, and substitutionally inert redox couples, e.g.,  $Fe(CN)_{6}^{3-/4-}$ ,  $Mo(CN)_{8}^{3-/4-}$ , and  $Ru(NH_{3})_{3}^{3+/2+}$ . They are effective as distributors of charge, because they interchange electrons readily among themselves, but they are unpromising in practical terms, because they are not potent catalysts.<sup>8</sup> In one of the most advanced illustrations of electrocatalysis at chemically modified electrodes, Buttry and Anson<sup>5</sup> separated the mediator and catalyst roles in a three-component system, wherein a redox mediator carried electrons rapidly to and from the immobilized, efficient catalyst sites.

Other problems with modified electrodes arise from the lack of chemical stability among the parts of the microstructure.

A reasonable approach is devising novel electrocatalytic surfaces is to consider inorganic matrices,<sup>9-16</sup> through which one could exploit the available information on heterogeneous catalysts and the electronic concepts of solids.<sup>17-20</sup> Inorganic polymeric oxides

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