

are clearly paratropic, since the inner olefinic protons resonate at considerably lower field than those of the atropic sulfones **8** and **19**, while the outer olefinic and methyl or allylic methylene protons resonate at higher field.<sup>13</sup> By comparison, the inner olefinic protons in the spectrum of the diatropic ketone **9** resonate at higher field than those of the sulfone **8**, while the outer methyl protons resonate at lower field.

The <sup>1</sup>H nmr spectrum of the mono-cis bisdehydrooxa[15]annulene **17** shows that it is atropic; models suggest that **17**, unlike the "all-trans" bisdehydrohetero[15]annulenes, cannot be planar.

The electronic spectra of carbocyclic annulenes and dehydroannulenes have been shown to alternate, the main maxima of (4n + 2) π-electron systems being at higher wavelength than those of 4n systems.<sup>14</sup> The electronic spectra of "all-trans" bisdehydrothiaannulenes appear to exhibit the same alternation, in both the dimethyl series ([13] 295 nm,<sup>1</sup> [15] 288 nm, [17] 322 nm<sup>12</sup>) and the biscyclohexene annelated series ([13] 300 nm,<sup>15</sup> [15] 290 nm, [17] 324 nm<sup>10,16</sup>).

It is also of interest that the dimethylbisdehydrothia[15]-annulene **7** is much less stable than either the "all-trans" 13-<sup>1</sup> or 17-membered<sup>12</sup> homolog, which may reflect the antiaromaticity of the 15-membered heterocycle.

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## Conformational Analysis by Spin Transmission into Rotating Alkyl Groups

Sir:

Unpaired spin density transmitted from a nickel atom into an organic ligand represents a very small electronic perturbation but may nevertheless be used as a sensitive tool to determine dihedral angles. We synthesized new

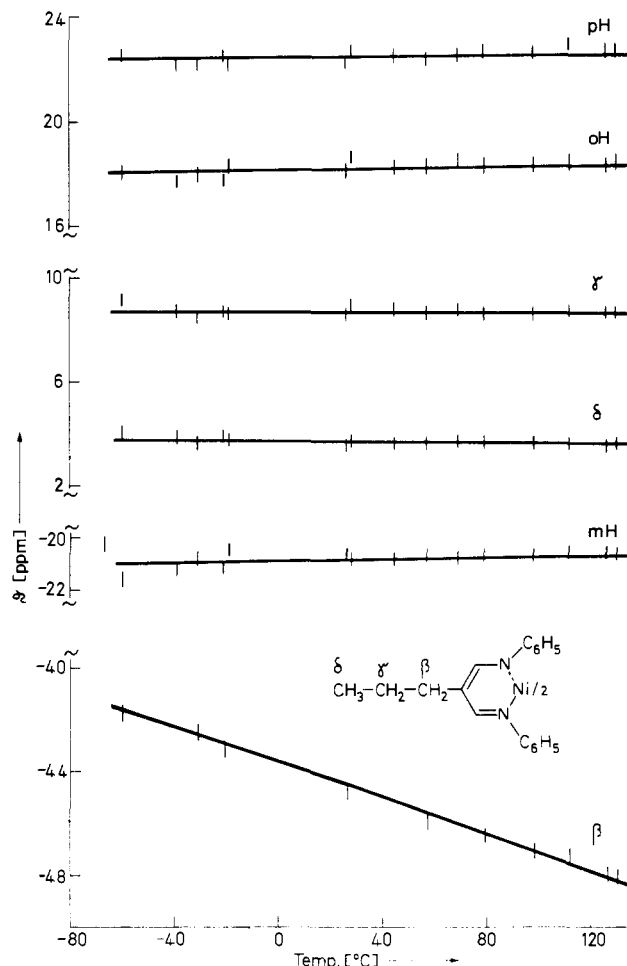
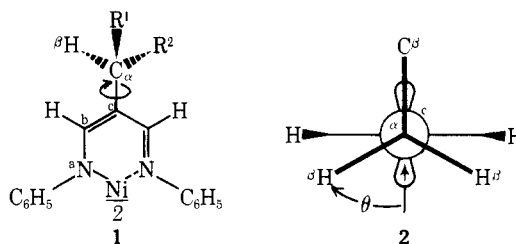


Figure 1. Isotropic reduced shifts  $\vartheta$  of **1c** as a function of temperature.

pseudo-tetrahedral<sup>1</sup> complexes, **1**, and measured their isotropic shifts,<sup>2</sup>  $\Delta H_i/H$ , in 1,2-dideuterio-1,1,2,2-tetrachloroethane relative to the free ligands. We find it more practical to use a differently defined isotropic shift,  $\vartheta_i$  in eq 1,

$$\vartheta_i = \frac{\Delta H_i}{H} \frac{T}{298^\circ\text{K}} = -\rho_i^{\text{H}} 60,400 \text{ ppm} \quad (1)$$



which is reduced to 298°K.  $\vartheta_i$  will depend exclusively on the spin population  $\rho_i^{\text{H}}$  transferred to a proton *i* if the Bloembergen-McConnell equation<sup>2</sup> applies to **1**.<sup>3</sup> Curie-



type (1/T) behavior is expected<sup>1</sup> for  $\Delta H_i$  of **1**.<sup>4</sup> Therefore,  $\vartheta_i$  should not depend on the temperature. Figure 1 demonstrates this for five types of protons in a typical example, **1c**. Only  $\vartheta_i$  of the two equivalent  $\beta$ -hydrogens drifts strongly downfield with increasing temperature. We assume that this "abnormal" temperature dependence originates in modulation of the spin density by rotation about the C<sup>c</sup>C<sup>c</sup> bond of **1**.

The 2p orbital at C<sup>c</sup> carries positive spin density.<sup>1a,d,5</sup> Spin transmission into the C<sup>c</sup>H<sup>β</sup> bond depends on the cos<sup>2</sup> of the dihedral angle  $\theta$  between this bond and the axis of the

**Table I.** Angular Independent Shift Contributions  $\vartheta_0(\beta)$ , Rotational Barriers  $V_2$ , and Equilibrium Conformations  $\theta_0$  of complexes **1a-j** from  $-60$  to  $+130^\circ$

Compound	-CHR <sup>2</sup> R <sup>2</sup>	$\vartheta_0(\beta)$ , ppm	$V_2$ , kcal/mol	$\theta_0$ , deg
<b>1a</b>	-CH <sub>3</sub>	15.5	0	60 ± 2
<b>1b</b>	-CH <sub>2</sub> CH <sub>3</sub>	17 ± 3	2.5 ± 0.3	60 ± 2
<b>1c</b>	-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	14.5 ± 4	3.7 ± 0.5	60 ± 2
<b>1d</b>	-CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	13.5 ± 2	3.2 ± 0.3	60 ± 2
<b>1e</b>	-CH <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	20 ± 2	3.2 ± 0.3	60 ± 2
<b>1f</b>	-CH(CH <sub>3</sub> ) <sub>2</sub>	15.5 ± 5	4.1 ± 0.3	68 ± 3
<b>1g</b>		12.5 ± 4	2.3 ± 0.2	69 ± 3
<b>1h</b>		11 ± 5	3.7 ± 0.2	72 ± 2
<b>1i</b>	-CH(CH <sub>3</sub> )C <sub>2</sub> H <sub>5</sub>	13.5 ± 3	4.2 ± 0.2	76 ± 2
<b>1j</b>	-CH(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	13.5 ± 2	4.5 ± 0.3	83 ± 3

2p orbital, eq 2.<sup>6</sup> Formula 2 illustrates the structural situation, looking from C<sup>α</sup> toward C<sup>c</sup> and the nickel. The expect-

$$\vartheta(\beta) = \vartheta_0(\beta) + \vartheta_2(\beta)\langle \cos^2 \theta \rangle \quad (2)$$

$$\langle \cos^2 \theta \rangle = \int \cos^2 \theta \cdot e^{-V(\theta)/RT} d\theta / \int e^{-V(\theta)/RT} d\theta \quad (3)$$

$$V(\theta) = V_2 \sin^2 (\theta - \theta_0) \quad (4)$$

tation value  $\langle \cos^2 \theta \rangle$  may be computed classically by eq 3 yielding the same result as the quantum mechanical procedure.<sup>7</sup> Assuming the  $\sin^2$  potential energy function<sup>8</sup> of eq 4, we compute a theoretical temperature dependence which is shown as the heavy trace through the  $\beta$ -shifts in Figure 1. The parameters used in these calculations have been collected in Table I; additionally,  $\vartheta_2(\beta)$  in eq 2 equals  $-200$  ( $\pm 20$ ) ppm for all complexes. The specified error limits indicate which variations of one parameter may be canceled by suitable changes of the others.

One of the two conformations of lowest energy for **1a-e** is depicted in formula 2 with each C<sup>α</sup>H<sup>β</sup> bond at  $\theta_0 = 60^\circ$ . Rotations by  $\pm 90^\circ$  will produce the energy maxima with C<sup>β</sup> in the chelate plane. This picture agrees perfectly with an *ab initio* calculation<sup>10</sup> for ethylbenzene which should be a good model for **1b**. The computed<sup>10</sup> barrier of 2.2 kcal/mol compares well with **1b** in Table I. Conformation 2 is also supported by dibenzyl<sup>11</sup> as a model for **1e** as well as by esr<sup>12</sup> and vibration spectroscopy.<sup>13</sup> The vanishing barrier to methyl rotation<sup>14</sup> in **1a** shows up as a totally temperature-invariant shift  $\vartheta(\beta)$ .

The parameters for *sec*-alkyl groups in **1f-j** were derived by assuming two barriers at  $\theta = 0$  or  $180^\circ$ , *i.e.*, when the single  $\beta$ -hydrogen eclipses the 2p orbital. The equilibrium angles  $\theta_0$  in Table I, resulting from a slight modification of eq 4, compare well with esr results<sup>12b</sup> on isopropylbenzene ( $64^\circ$ ), cyclopentylbenzene ( $66^\circ$ ), and cyclohexylbenzene ( $74^\circ$ ). The barrier of 3.9 kcal/mol computed for cyclohexylbenzene<sup>15</sup> agrees with that of **1h**. It is also evident from Table I that cyclopentyl<sup>16</sup> and ethyl<sup>17</sup> groups rotate much easier than isopropyl<sup>16,17</sup> and cyclohexyl.<sup>16</sup>

Our  $\vartheta_0/\vartheta_2$  ratio of  $-0.08$  is to be compared with theoretical ratios of  $-0.03^{6b,d,e}$  or  $+0.03^{6c}$  or  $+0.055^{6f}$ . A recent experimental estimation<sup>18</sup> was between  $-0.02$  and  $-0.06$ .

Dipolar shifts<sup>2</sup> will not contribute to the overwhelming part ( $\vartheta_2$ ) of our  $\beta$ -shifts if the rotation axis C<sup>α</sup>C<sup>c</sup> of the  $\beta$ -hydrogens coincides with the magnetic axis of **1**.

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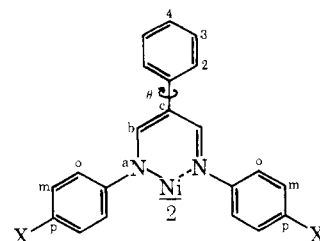
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## Conformational Analysis by Spin Transmission into Rotating and Rigid Phenyl Groups

Sir:

The Curie law is generally valid for nickel complexes of the chelate type **1**.<sup>1</sup> Therefore, the previously<sup>1</sup> defined re-



- 1a**, X = H  
**b**, X = C<sub>2</sub>H<sub>5</sub>  
**c**, X = *n*-C<sub>3</sub>H<sub>7</sub>  
**d**, X = OC<sub>2</sub>H<sub>5</sub>