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# $^{13}$C-NMR Studies on Conformational Equilibria in Isopropyl Methyl Ether

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The energy difference between the two rotational isomers, *i.e.*, $C_S$ and $C_1$, of isopropyl methyl ether has been elucidated from the observed vicinal $^{13}$C-$^1$H coupling constant. The conventional Gutowsky method based on the simple rotational isomeric state model tends to give an underestimate, especially when the energy difference is large. A more elaborate treatment, which takes account of the overall profile of the torsional potential energy curve, has been attempted. Adoption of $J_T$=11.0—12.0 Hz for the trans coupling gave a value of 2.2± 0.2 kcal mol$^{-1}$ for the energy difference $E_{C_s}-E_{C_1}$. This result is consistent with the range (2.4±0.6 kcal mol$^{-1}$) estimated by the matrix-isolation method as reported by Nakata *et al.*

In the structural studies of polymeric chains, we occasionally encounter a stereochemical arrangement which bears some resemblance to isopropyl methyl ether. Poly[oxy(1-methylethylene)]$^{1)}$ $\{CH_2CH(CH_3)\text{-}O\}_n$ and poly(1-methoxyethylene)$^{2)}$ $\{CH_2CH(OCH_3)\}_n$ are the typical examples. The energy difference between the two rotational isomers (*i.e.*, $C_S$ and $C_1$) of isopropyl methyl ether is presumed to be large due to severe steric conflicts involved in the $C_S$ form. Any accurate value of the energy difference $\Delta E$ ($=E_{C_s}-E_{C_1}$) has not been determined experimentally. The corresponding value of $\Delta E$ for 2-methylbutane, a hydrocarbon analogue of isopropyl methyl ether, has been known$^{3)}$ to be 0.8 to 0.9 kcal mol$^{-1}$. Considering the fact that the C–O bond length is somewhat shorter than that of the C–C bond, $\Delta E$ for isopropyl methyl ether should be much larger than the value given above. Recently Nakata, Furukawa, Hamaguchi, and Tasumi$^{4)}$ applied the matrix-isolation technique to this compound: A gaseous mixture with argon was blown agaist a cold surface of CsI plate which was kept at 20 K. The characteristic Raman bands were used for detection of the two rotational isomers trapped in the argon matrix. The energy difference $\Delta E$ estimated in this manner amounts to 2.4±0.6 kcal mol$^{-1}$ over the temperature range 20—260 °C.

In this study, we have attempted to elucidate the same energy difference from the analysis of the $^{13}$C-$^1$H vicinal coupling constant determined on $^{13}CH_3OC^1H(CH_3)_2$. The information thus acquired regarding the conformation of isopropyl methyl ether will be used in the configurational studies on poly[oxy(1-methylethylene)], which is the subject of forthcoming paper.$^{5)}$

## Experimental

Isopropyl methyl ether was prepared by the Williamson synthesis from isopropyl alcohol and methyl iodide. Solvents used in the NMR measurements were commercially available and used without further purification.

Natural abundance proton-coupled $^{13}$C-NMR spectra were obtained at 25 MHz by using a JEOL FX-100 spectrometer equipped with FT and gated decoupling systems. In the measurements, 300 transients were accumulated with a 90° rf pulse of 13.5 μs duration. The pulse repetition time was 9 s. The Fourier-transformed spectra contain 8192 data points for a 500 Hz spectral width, yielding a resolution of 0.06 Hz. The temperature were maintained within ±1.0 °C during the measurements. A 10-mm NMR sample tube was used.

## Results

The spin system of the compound may be identified as $A_3BX$. The vicinal coupling constant $^3J_{CH}$ (identified as $J_{BX}$) can be easily obtained from the $^{13}$C-NMR spectrum of the methoxyl carbon. The results are summarized in Table 1. Observed values of $^3J_{CH}$ increase nearly linearly with temperature. The temperature coefficients, d ln $^3J_{CH}/dT$, estimated from these data are also included in the table. The coupling constant varies slightly with polarity of the medium as manifested by a change from 3.90 in cyclohexane-$d_{12}$ ($\varepsilon$=2.023) to 3.79 in dimethyl-$d_6$ sulfoxide ($\varepsilon$=46.68), both values being determined at 20 °C. Measurements were also carried out on the neat liquid. The following analysis will be mostly performed with resort to the experimental data obtained in cyclohexane-$d_{12}$.

## Elucidation of the Torsional Potential Energy Curve and Interpretation of Results

According to the conventional Gutowsky method,$^{6)}$ $^3J_{CH}$ is given by

$$^3J_{CH} = J_T f_{C_s} + J_G(1-f_{C_s}). \qquad (1)$$

TABLE 1. TEMPERATURE DEPENDENCE OF THE VICINAL COUPLING CONSTANT $^3J_{CH}$ FOR THE MOIETY $^{13}$C-O-C-$^1$H IN ISOPROPYL METHYL ETHER

| $\frac{T}{\text{deg}}$ | $^3J_{CH}$/Hz in cyclo-hexane-$d_{12}$ | $^3J_{CH}$/Hz in dimethyl-$d_6$ sulfoxide | $^3J_{CH}$/Hz neat liquid |
|---|---|---|---|
| 20 | 3.90 | 3.76 | 3.88 |
| 40 | 3.94 | 3.81 | 3.89 |
| 60 | | 3.88 | 3.93 |
| 70 | 3.98 | 3.85 | 4.00 |
| 80 | 4.00 | | |
| 90 | | 3.93 | 4.00 |
| d ln$^3J_{CH}$/d$T$ × 10$^3$/K | 0.41 | 0.63 | 0.47 |

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Here $f_{C_s}$ denotes fraction of the Cs conformer:

$$f_{C_s} = \exp(-\Delta E/RT)/[2+\exp(-\Delta E/RT)], \qquad (2)$$

where $R$ is the gas constant and $T$ the temperature. The trans ($J_T$) and gauche couplings ($J_G$) are illustrated in Fig. 1. In this simple scheme, only the energy difference between the two preferred rotational isomeric states are considered. In principle, values of $J_T$, $J_G$, and $\Delta E$ can be determined by the least-squares method from the analysis of the observed temperature dependence of $^3J_{CH}$. The experimental data listed in Table 1 were however found to be reproducible by various combinations of $J_T$, $J_G$, and $\Delta E$. Calculations were therefore carried out for given values of $\Delta E$. The best-fit values of $J_T$ and $J_G$ derived from the analysis of the observed data in cyclohexane-$d_{12}$ are plotted against $\Delta E$ (solid curves) in Fig. 2. While $J_T$ increases markedly with $\Delta$E, $J_G$ stays nearly invariable over a wide range of $\Delta E$. It should be noted here that the assumption of discrete rotational isomeric states is, in principle, valid only when all the torsional potential energy minima are well-defined, and the energy differences among the minima are not too large.[7] Since one of the isomers (C1) is far more stable than the other (Cs) in isopropyl methyl ether, the aforementioned criteria may not be valid in this system. In such a case, the average of $^3J_{CH}$ should be desirably determined over the entire profile of the torsional potential energy curve.

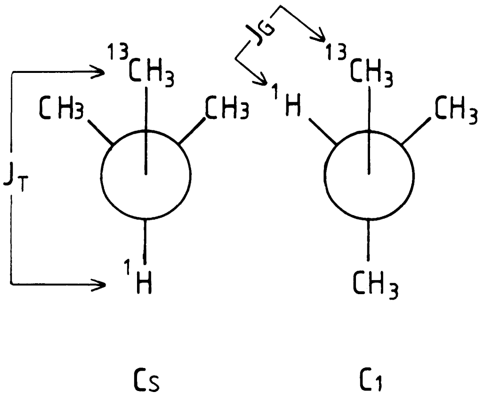

Fig. 1. Schematic representation of isomers and definition of the trans and gauche couplings.

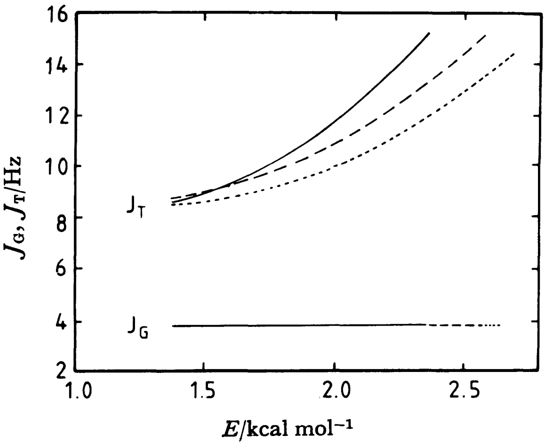

Fig. 2. Plot of best-fit values of $J_T$ and $J_G$ *vs.* $\Delta E$. The results obtained according to the simple Gutowsky treatment (Eq. 1) are indicated by the solid curves. The $J(0)$ and $J(140°)$ values derived from the more elaborate scheme (Eq. 5) are used for the other curves. The height of the cis barrier ($\phi = 180°$) is taken to be 1.2 and 1.8 kcal mol$^{-1}$, respectively, for the dotted and broken curves. The $J_G$ *vs.* $\Delta E$ curves are all very similar and practically indistinguishable with each other: they are all represented by a solid curve.

For this purpose, the potential energy curve for the internal rotation around the $(CH_3)_2CH\ominus OCH_3$ bond was estimated by using the semiempirical energy expressions. Parameters adopted in these expressions for the three-fold torsional potentials and the 6-exp non-bonded interatomic interaction functions are identical with those used in our previous papers.[8,9] Bond lengths and bond angles used are as follows: $l_{CC}$=1.53 Å, $l_{CO}$=1.43 Å, and $l_{CH}$=1.10 Å; $\angle$CCC=$\angle$CCH=$\angle$OCH=109.5°. The bond angle $\angle$COC was adjusted somewhat when the highly hindered Cs conformer was treated. The deformation energy for the bond angle was estimated by[9,10]

$$E(\theta) = D(\pi/180)^2(\theta - 109.5)^2, \qquad (3)$$

where $\theta$ is expressed in degrees, and $D$ is set equal to 88 kcal mol$^{-1}$. As for the barriers situated on both sides of the Cs minimum, experimental results on *t*-butyl methyl ether $(CH_3)_3C\ominus OCH_3$ are suggestive. The barrier to the internal rotation of this compound was reported to be 3.57 kcal mol$^{-1}$ from IR studies in the gas phase.[11] Calculations were carried out so as to reproduce this value for the energy difference between the conformation at the top of the barrier ($\phi$=±60°) and that at the Cs minimum ($\phi$=0). Widening of the bond angle $\angle$COC was required besides adjustment of the rotation around the adjoining C–O and C–C bond. A set of values such as 116.4° and 113.0° for the bond angle $\angle$COC, respectively, at $\phi$=±60° and 0 was found to give an energy difference as stated above. The value of $\angle$COC=113.0° is comparable with those observed for ether linkages carrying bulky substituents (*e.g.*, glycoside linkages in polysaccharides[12]). At the Cs minimum, the methoxyl group is situated syn to both of the terminal methyl groups. To alleviate steric conflicts between these groups, rotation angles about the adjoining C–C bonds were displaced by *ca.* 15° from the regularly staggered position. In the C1 form, steric repulsions between the methoxyl and methyl groups can be largely reduced by the displacement ($\Delta\phi$) of the rotational minima from the regular position, *i.e.*, $\phi$=±120°. Locations and the energy of the C1 minima were calculated by assuming a bond angle $\angle$COC=111.5°, a similar value being adopted in the analysis of less hindered ethers.[8,9] The C1 minima were thus estimated to occur at $\phi$=±140°. A displacement of $\Delta\phi$=20° is in agreement with observations on compounds having a similar stereochemical arrangement.[13] The energy difference between the Cs and C1 minima obtained in this manner is *ca.* 2 kcal mol$^{-1}$. On the same basis, the height of the barrier separating two C1 minima was calculated to be *ca.* 1.2 kcal mol$^{-1}$ as expressed relative to these minima. Results of these considerations are all

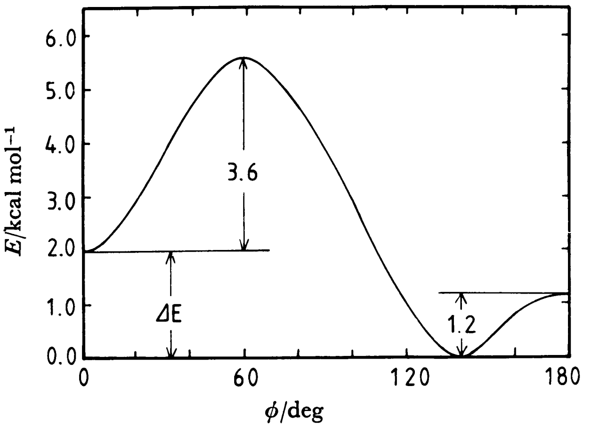

Fig. 3. Torsional potential energy curve for isopropyl methyl ether, $CH_3\not{O}CH(CH_3)_2$, estimated by using semiempirical energy calculations in consideration of experimental data on some relevant compounds. The slopes along the higher barrier are drawn by assuming trigonometric functions (see text). The value of $\Delta E$, representing the energy difference between the two minima, will be treated as a variable in the present analysis. Numerical values are given in kcal mol$^{-1}$.

put together in Fig. 3, where the potential energy curve is shown as a function of $\phi$. Since estimation of a reliable value of the energy is quite difficult for a highly strained conformation, trigonometric functions were assumed on both sides of the higher barrier at $\phi=\pm 60°$. The slope of the curve drawn from the $C_1$ minimum ($\phi=\pm 140°$) toward the lower barrier ($\phi=180°$) was estimated by the energy calculation.

Durig and Compton[14] deduced the profile of the potential energy curve for the internal rotation of ethyl methyl ether $CH_3O\not{}CH_2CH_3$ by the analysis of vibrational spectra in the low frequency region. The potential energy barrier, associated with the conformation in which C-O eclipses C-H, resembles the barrier at $\phi=180°$ in isopropyl methyl ether. A value of 1.8 kcal mol$^{-1}$ was estimated for the height of the barrier relative to the energy minimum in which $CH_3O\not{}CH_2CH_3$ is gauche.[14] Effect arising from the choice of this value will be examined later.

The vicinal coupling constant for the moiety $^{13}$C-O-C-$^1$H varies as a function of rotation angle $\phi$ defined for the C-O bond. The dihedral angle dependence of the coupling constant may be customarily represented by a conventional Karplus-type equation such as

$$J(\phi) = A\cos^2\phi + B\cos\phi + C. \tag{4}$$

In this expression, $B$ is responsible for the difference between the trans and cis couplings, *i.e.*, $J(0)-J(180°)=2B$. The parameter $C$, which determines the $J(90°)$ value, is usually quite small. In the present treatment, we adopt a simplified expression in which $C$ is set equal to zero. For given values of $A$ and $B$, an average of the coupling constant $\langle J\rangle$ can be obtained according to the formula specified by the equation

$$\langle J\rangle = \int_0^{2\pi} J(\phi)\exp[-E(\phi)/RT]\mathrm{d}\phi \Big/ \int_0^{2\pi}\exp[-E(\phi)/RT]\mathrm{d}\phi. \tag{5}$$

Numerical computations were carried out for discrete $\phi$ values taken at 5° intervals. The whole process of calculations was iteratively repeated until experimental values of $^3J_{CH}$ were reproduced within the limit of uncertainty. With values of $A$ and $B$ so determined, $J(0)$ and $J(140°)$ were calculated for $\phi=0$ (the $C_s$ minimum) and 140° (the $C_1$ minimum), respectively, from the Karplus relation (Eq. 4).

In order to elucidate a proper range of $\Delta E$, the energy of the $C_s$ minimum, $E(0)$, was tentatively raised or lowered in Fig. 3, the height of the barrier on both sides being kept constant (*i.e.*, $E(\pm 60°)-E(0)=3.6$ kcal mol$^{-1}$). For each potential energy curve, a set of $A$ and $B$, thus $J(0)$ and $J(140°)$, were determined. These results are indicated by the dotted curves in Fig. 2, where $J(0)$ and $J(140°)$ are adopted for $J_T$ and $J_G$, respectively, and $\Delta E$ is taken to be the difference between the minimum energies for the $C_s$ and $C_1$ forms. Values of $J_T$ calculated according to the simple Gutowsky treatment based on the discrete isomeric state scheme (upper solid curve) are consistent with the results derived from the more elaborate analysis (upper dotted curve) only for very low values of $\Delta E$ (<1.5 kcal mol$^{-1}$). On the other hand, the $J_G$ values are nearly unaffected by the procedure adopted in the analysis. Also shown by the broken curves in the figure are the results obtained on the basis of the torsional potential energy diagram in which the height of the barrier separating two $C_1$ minima is raised to 1.8 kcal mol$^{-1}$ as suggested by Durig and Compton.[14] In this revised scheme, locations of the $C_1$ minima were kept unchanged at $\phi=\pm 140°$, and the slope along the barrier was represented by a trigonometric function. An enhancement in the height of the torsional potential energy barrier causes some substantial upward shift in the $J_T$ *vs.* $\Delta E$ curve (compare two curves indicated by the broken and dotted drawings). The corresponding $J_G$ values are again indistinguishable with those derived from the other schemes.

## Estimation of the Energy Difference $\Delta E$

As is shown above, the Gutowsky analyses on the observed temperature dependence of the coupling constant $^3J_{CH}$ do not yield a unique solution for parameters $J_T$, $J_G$, and $\Delta E$ for the present compound. A reliable estimation of the $J_T$ value is therefore required. Hamer *et al.*[15] and more recently Yamada *et al.*[16] have studied the dihedral angle dependence of the coupling constants $^3J_{CH}$ for various compounds containing the $^{13}$C-O-C-$^1$H moiety. The former group deduced a value of $J(0)=6.0\pm 0.5$ Hz for a variety of carbohydrate compounds, while the latter found $J(0)=6.8\pm 0.7$ Hz from the analysis on cyclic compounds containing the acetal or ether linkages. These values are however apparently too low for the molecule under consideration. As is widely known, formation of a cyclic structure or introduction of electronegative substituents generally leads to a lower value of $J_T$.[17] For the present purpose, analyses on the observed coupling constants for the same moiety involved in some simple open-chain methyl ethers should provide more reliable information. The coupling constants associated with the methoxyl hydrogen are reported for dimethyl ether (5.7 Hz), methyl *n*-propyl ether (5.2 Hz), and isopropyl methyl ether (5.0 Hz).[18] Since hydrogens on the terminal methyl group are all equivalent, they should be equally populated among three rotational states. Then, from the relation

$$^3J_{\mathrm{CH}} = (1/3)(J_{\mathrm{T}}+2J_{\mathrm{G}}), \tag{6}$$

we estimate $J_{\mathrm{T}}$=13.1, 11.6, and 11.0 Hz for the aforementioned compounds, respectively, by adopting a value of $J_{\mathrm{G}}$=2.0 Hz, a standard value for an unstrained gauche coupling.[17] Adoption of an averaged value (12.0 Hz) for $J_{\mathrm{T}}$ in Fig. 2 yields $\Delta E$=2.0, 2.2, and 2.4 kcal mol$^{-1}$, respectively, for the solid, broken, and dotted curves. Use of a lower value (11.0 Hz), which may also be a probable choice, gives $\Delta E$=1.9, 2.0, and 2.2 kcal mol$^{-1}$, respectively. As is seen in Figure 2, the $J_{\mathrm{G}}$ value remains nearly invariable over a wide range of $\Delta E$. A value of $J_{\mathrm{G}}$=3.8±0.1 Hz is commonly applicable to all the models examined.

Plotted in Fig. 4 are the quantities $\langle J\rangle_{\mathrm{T}}$ and $\langle J\rangle_{\mathrm{G}}$ denoting respectively the averages of $J(\phi)$ over the range of $\phi$ associated with the $C_s$ and $C_1$ minima: *i.e.*,

$$\langle J\rangle = z^{-1}\int_{\mathrm{a}}^{\mathrm{b}} J(\phi)\exp[-E(\phi)/RT]\mathrm{d}\phi, \tag{7}$$

and

$$z = \int_{\mathrm{a}}^{\mathrm{b}} \exp[-E(\phi)/RT]\mathrm{d}\phi, \tag{8}$$

where the interval (a,b) is taken to be (−60°, 60°) for $\langle J\rangle_{\mathrm{T}}$ and (60°, 180°) for $\langle J\rangle_{\mathrm{G}}$. Correspondingly, the abscissa of the figure represents the difference between the energies $\langle E_{C_s}\rangle$ and $\langle E_{C_1}\rangle$ averaged over the respective energy minimum:

$$\langle E\rangle = z^{-1}\int_{\mathrm{a}}^{\mathrm{b}} E(\phi)\exp[-E(\phi)/RT]\mathrm{d}\phi. \tag{9}$$

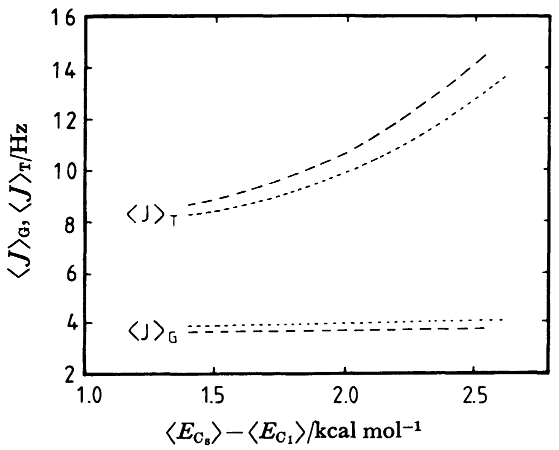

Fig. 4. The averages $\langle J\rangle_{\mathrm{T}}$ and $\langle J\rangle_{\mathrm{G}}$ plotted against $\langle E_{C_s}\rangle-\langle E_{C_1}\rangle$. The two curves differ with each other in the torsional potential energy curve used in the calculation. The dotted and broken curves are used to facilitate comparison with the corresponding plot in Fig. 2.

In these calculations, the integrations were again replaced by summations with discrete $\phi$ values taken at 5° intervals. The temperature was taken to be 20 °C. In principle, $\langle J\rangle_{\mathrm{T}}$ and $\langle J\rangle_{\mathrm{G}}$ evaluated in this manner should be more closely related to the parameters representing the trans and gauche couplings in the two-parameter expression. The curves drawn in Fig. 4 vary, however, very little from those given for $J(0)$ and $J(140°)$ in Fig. 2: For the ease of comparison, the broken and dotted drawings are used in common. These results arise from the fact that a small decrease in $\langle J\rangle_{\mathrm{T}}$ from $J(0)$ is nearly exactly compensated by a concerted decrease in the energy term. In Fig. 4, two $\langle J\rangle_{\mathrm{G}}$ curves are distinguishable with each other, but the difference is very small. Adoption of $\langle J\rangle_{\mathrm{T}}$=11.0—12.0 Hz should therefore yield the same energy differences for $\langle E_{C_s}\rangle-\langle E_{C_1}\rangle$ as those ($\Delta E$) derived above.

We finally conclude that the energy difference between the two conformers is in the range 2.2±0.2 kcal mol$^{-1}$. Values obtained from the simple Gutowsky treatment (1.9—2.0 kcal mol$^{-1}$) are a little too low. The present result is consistent with the range estimated by Nakata *et al.*[4] employing the matrix isolation technique.

## Concluding Remarks

In the above treatment, the parameter $C$ in the Karplus equation (Eq. 4) was taken to be zero. However, $C$ is empirically known to be variable within the range ±1.0 Hz. Trial calculations indicate that use of a nonzero value for $C$ causes only some minor modifications on the results: For the range of $C$ given above, $J_{\mathrm{T}}$ and $\Delta E$ vary by an amount less than 0.3 Hz and 0.05 kcal mol$^{-1}$, respectively.

As is shown in Fig. 2, the discrepancy between the solid and either of the other two curves for $J_{\mathrm{T}}$ tends to be more enhanced as $\Delta E$ increases. At $J_{\mathrm{T}}$=12.0 Hz, the difference amounts to 0.2 to 0.4 kcal mol$^{-1}$ in the $\Delta E$ value. Assumption of discrete rotational isomeric states leads to a lower estimate of $\Delta E$. In this regard, we should note some characteristic features of the torsional potential energy curve for this compound: 1) The energy difference between the $C_s$ and $C_1$ minima is considerably high (>2 kcal mol$^{-1}$), 2) the height of the barrier separating the two $C_1$ minima is relatively low, and accordingly, 3) the shape of the potential well for the $C_1$ minimum is somewhat skewed. The effect arising from the latter factors is illustrated by the difference between the broken and dotted curves in Figs. 2 and 4.

Following the conventional rotational isomeric state treatment,[19] we may assign a statistical weight $\tau$ to the $C_s$ form, the weight of unity being given to the $C_1$ state:

$$\tau = \tau_0\exp(-\Delta\langle E\rangle/RT) \tag{10}$$

where $\tau_0$ reflects the shape of the energy minima, and $\Delta\langle E\rangle=\langle E_{C_s}\rangle-\langle E_{C_1}\rangle$. By definition, $\tau=z_{C_s}/z_{C_1}$. The partition functions $z_{C_s}$ and $z_{C_1}$ associated with the $C_s$ and $C_1$ isomers, respectively, can be obtained by Eq. 8. We thus have

$$\tau = 0.88\exp(-2200/RT) \tag{11}$$

for the potential energy curve shown in Fig. 3: The temperature is taken to be 20 °C, and $RT$ is expressed in kcal mol$^{-1}$. Use of the relation $f_{Cs}=\tau/(2+\tau)$ in place of Eq. 2 yields calculated values of $^{3}J_{CH}=3.88$ Hz and $d \ln {^{3}J_{CH}}/dT=0.30\times10^{-3}$ K$^{-1}$ for the temperature of 20 °C, values of $J_T$ and $J_G$ being set equal to 12.0 and 3.8 Hz, respectively. Experimental results obtained in cyclohexane-$d_{12}$. (*cf.* Table 1) are reasonably reproduced.

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