

# Conformational Studies by Dynamic NMR. 7.<sup>1</sup> Stereochemical Processes in 2,3-Dimethylbutane

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**Abstract:** The 90.5-MHz <sup>13</sup>C NMR spectrum of 2,3-dimethylbutane at -180 °C shows that the gauche and anti rotational isomers are present in the statistical ratio of 2:1. Line shape analysis of the methine signals gives a free energy of activation of 4.3 ± 0.2 kcal/mol for the anti-gauche interconversion. These results are supported by ab initio SCF-MO calculations which reproduce the anti-gauche rotational barrier and predict that the gauche-gauche barrier would be ca. 8 kcal/mol. Accordingly a direct gauche-gauche interconversion can be ruled out and the gauche rotamers must interchange via the anti rotamer.

Our interest in the preferred conformation and barriers to rotation of 1,1,2,2-tetraalkylethanes, R<sub>2</sub>CHCHR<sub>2</sub>, was stimulated by the discovery<sup>3</sup> that *sym*-tetra-*tert*-butylethane (R = (CH<sub>3</sub>)<sub>3</sub>C) adopts the gauche conformation and that rotation about the central bond is so hindered that it does not occur (on the NMR time scale) below the temperature of decomposition.

The conformation and barrier to rotation in the simplest *sym*-tetraalkylethane, 1,2-dimethylbutane (R = CH<sub>3</sub>), are obviously of interest. Raman spectra of the vapor suggest<sup>4</sup> that the gauche and anti conformations of this compound are present in about the statistical ratio of 2:1. (The gauche form may be obtained from the anti by two degenerate 120° rotations.) The intrinsic stability of the two rotamers must therefore be approximately equal. In fact, the Raman studies on the vapor<sup>4</sup> indicate that there is a small enthalpy difference between rotamers, the anti conformation being favored by 54 ± 30 cal/mol. An earlier study<sup>5</sup> of 2,3-dimethylbutane in the liquid phase by ultrasonic relaxation techniques had indicated an enthalpy difference (provided ΔS<sup>‡</sup> = 0) between rotamers of 950 cal/mol. However, recent theoretical studies of this molecule<sup>6</sup> have provided strong support for the view that, in the isolated molecule at least, the enthalpy difference between the two rotamers is not more than ca. 0.2 kcal/mol.

Only in the ultrasonic relaxation work have the barriers to internal motion been derived.<sup>5</sup> For the conversion of the more stable into the less stable rotamer<sup>7</sup> the free energy of activation (enthalpy if ΔS<sup>‡</sup> is zero) was found to be 3.75 ± 0.2 kcal/mol and for the reverse process 2.8 ± 0.15 kcal/mol.<sup>5</sup> If the difference in free energy between the two rotamers is as small in solution as is indicated by the Raman work on the vapor and solid,<sup>4</sup> then one or the other (or both) of these barriers must be in error.

The internal motions of 2,3-dimethylbutane are of particular interest because there are, in principle, two possible pathways for interconversion of the rotamers, viz., a gauche-anti-gauche process (GAG) and an anti-gauche-gauche process (AGG). In the present paper, we report a study of the conformational preference and barrier to rotation of 2,3-dimethylbutane in solution by low-temperature <sup>13</sup>C NMR spectroscopy.

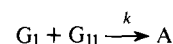
## Experimental Section

Spectra were run on a 360-MHz superconducting Bruker spectrometer which operates at 90.5 MHz for the <sup>13</sup>C frequency. The spectra were recorded in the FT mode with complete elimination of the hydrogen splittings at a pulse angle of about 90°. The repetition time was 3 s and 300 transients were usually collected at each temperature.

The sample was prepared by vacuum sealing into a 10-mm diameter tube 2,3-dimethylbutane and a mixture of CHF<sub>2</sub>Cl and CH<sub>2</sub>FCl, which is known<sup>8</sup> to remain liquid even at -190 °C. A small amount of C<sub>6</sub>D<sub>6</sub> was also added to provide a deuteron locking signal.

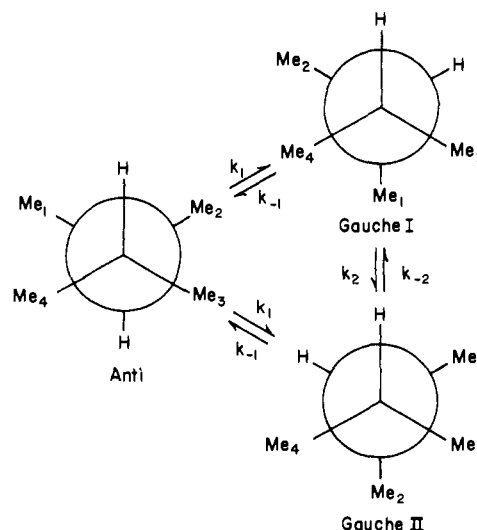
The temperature was monitored using the meter of the cooling device of the spectrometer. To calibrate these values, the line width of one of the solvent signals was taken at various temperatures. (The width of these lines is strongly dependent on the viscosity and hence on temperature in the -140 to -180 °C range.) These measurements were then repeated on the same sample in a 100-MHz spectrometer (Jeol PS 100, operating at 25.15 MHz for <sup>13</sup>C) where it was possible (in contrast to the 360-MHz spectrometer) to introduce a thermocouple inside the probe after each spectrum was recorded. The solvent line width was found to be linearly dependent on the temperature in both spectrometers. Extrapolation of the data obtained from the 100-MHz instrument (which could not reach temperatures below -165 °C) allowed us to check the temperature readings made on the 360-MHz spectrometer. Since the width of the <sup>13</sup>C solvent line should not be strongly dependent on the strength of the magnetic field, this method of temperature calibration should be fairly reliable under similar conditions of pulsing. In the event, the reading of the cooling device on the 360-MHz spectrometer was found to be off by only 3 °C.

The line shape analysis was carried out using the DNMR program.<sup>9</sup> Since the methine signal splits in a 2:1 ratio (see below) these signals were simulated by considering the forward process to be G(0.66) → A(0.33). It can be shown as follows that the calculated rate constant for this process, *k*, will be equal to the *k*<sub>1</sub> and *k*<sub>-1</sub> of Scheme I. Thus, for the process



the rate of formation of the anti rotamer is given by d[A]/dt = *k*[G<sub>I</sub> + G<sub>II</sub>], and from Scheme I it is given by d[A]/dt = *k*<sub>-1</sub>[G<sub>I</sub>] + *k*<sub>-1</sub>[G<sub>II</sub>], hence *k* = *k*<sub>-1</sub>. Since [A] = [G<sub>I</sub>] = [G<sub>II</sub>] it follows that *k*<sub>-1</sub> = *k*<sub>1</sub> (= *k*).

Scheme I



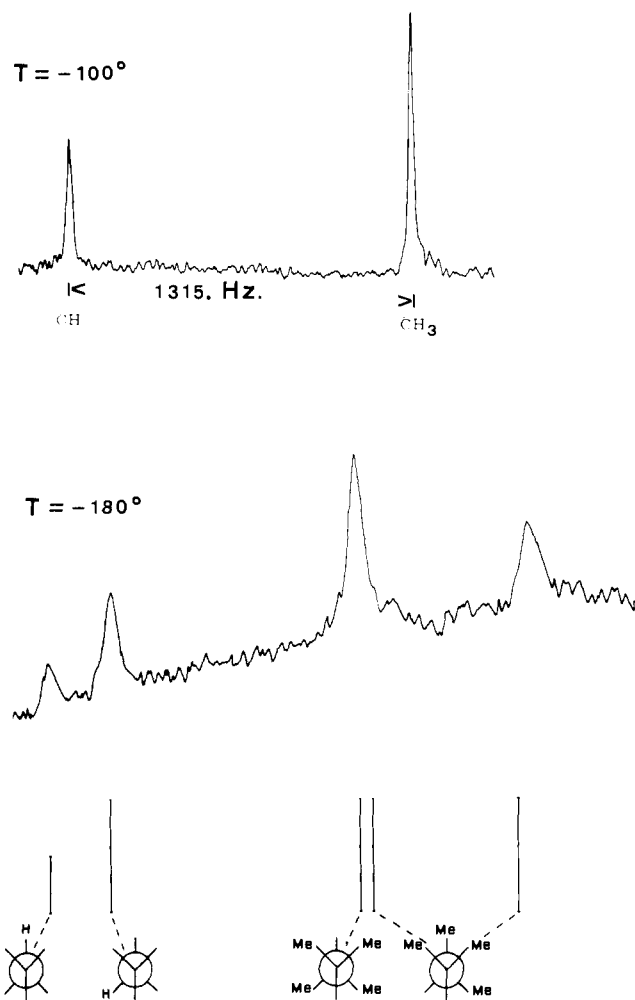


Figure 1.  $^{13}\text{C}$  NMR spectrum (90.5 MHz) of 2,3-dimethylbutane at  $-100^\circ\text{C}$  and  $-180^\circ\text{C}$ .

The line width in the absence of exchange ( $\omega_0 = 1/\pi T_2$ ) was measured at  $-180^\circ\text{C}$ . In order to allow for the effect of viscosity it was assumed that  $\omega_0$  changed with a trend equal to that of the solvent over the small temperature interval investigated ( $-180$  to  $-173^\circ\text{C}$ ).

Finally, it is worth noting that at 25.15 MHz the anti and gauche rotamers would not have given separated methine or methyl  $^{13}\text{C}$  signals at  $-180^\circ\text{C}$ , even if such a temperature could have been reached, on the 100-MHz spectrometer.

## Results and Discussion

**Interpretation of Spectra.** The 90.5-MHz  $^{13}\text{C}$  NMR spectrum of 2,3-dimethylbutane at temperatures from 25 to  $-100^\circ\text{C}$  contains two lines which have an intensity ratio of 1:2 and are separated by 1315 Hz ( $\sim 14.53$  ppm); these lines correspond to the two methine (downfield) and four methyl (upfield) carbons (see Figure 1). On further lowering the temperature the methyl signal broadens considerably and at about  $-177^\circ\text{C}$  splits into two lines separated by 710 Hz ( $\sim 7.84$  ppm) and having a relative intensity of about 2:1 (downfield vs. upfield). At even lower temperatures (ca.  $-180^\circ\text{C}$ ) the methine signal also splits into two lines with a 1:2 intensity ratio (downfield vs. upfield) and with a separation of 245 Hz ( $\sim 2.71$  ppm) (see Figure 1). Since the two methine carbons lie on the rotational axis their observed nonequivalence at  $-180^\circ\text{C}$  requires the presence of anti and gauche rotational isomers. The ratio of the peak areas due to the two methine signals was calculated by computer simulation at  $-180^\circ\text{C}$  with a negligible value for  $k$ .<sup>9</sup> There is possibly a 15% error in this method because the experimental line shapes are not precisely identical with the

calculated line shapes. The ratio of the methine signals was found to be  $2.0 \pm 0.3$  and this must correspond to the ratio of the concentrations of the two rotamers (see Scheme I). However, the methyl signals must be interpreted in order to determine which rotamer is which.

The anti rotamer must give a single methyl signal since all four methyls are equivalent. The gauche rotamer should give two methyl signals of equal intensity, each corresponding to two methyls. In this rotamer, the signal due to the two methyls that are gauche with respect to both a hydrogen and a methyl (i.e.,  $\text{Me}_2$  and  $\text{Me}_3$  in Gauche I and  $\text{Me}_1$  and  $\text{Me}_4$  in Gauche II of Scheme I) is expected to be very close to the signal due to the four methyls in the anti rotamer (each of which is also gauche to a hydrogen and a methyl). However, the signal due to the two methyls that are gauche with respect to two methyls (i.e.,  $\text{Me}_1$  and  $\text{Me}_4$  in Gauche I and  $\text{Me}_2$  and  $\text{Me}_3$  in Gauche II) should have quite a different chemical shift. This explains why the methyl groups produce only two methyl signals rather than the three that might have been anticipated.

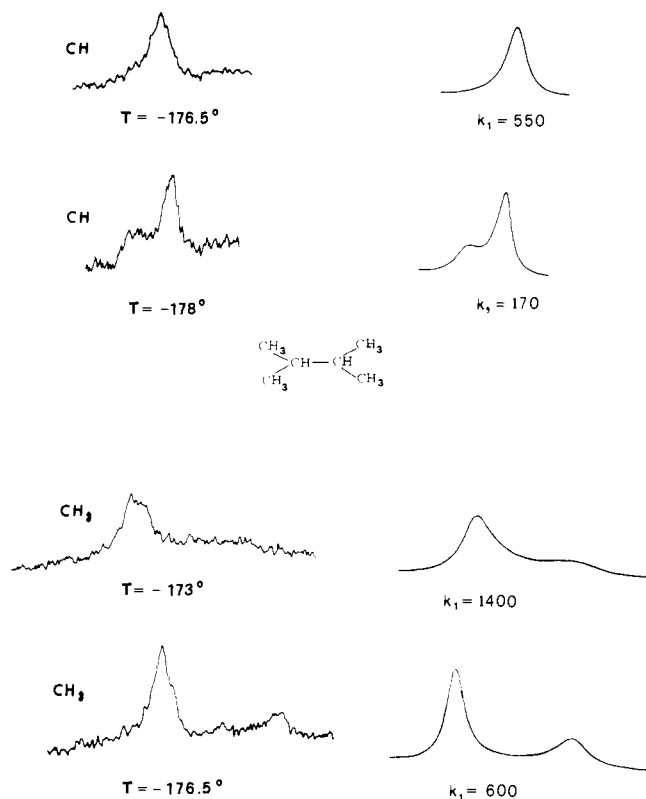
Since the methine signals indicate that the ratio of the rotamers is 2:1, the foregoing argument implies that if the anti rotamer were the more plentiful, the intensity ratio of the two methyl signals would have been  $(2 + 2 \times 4):2$ , i.e., 5:1. The actual experimental ratio of 2:1 for the methyl signals requires that the gauche concentration be twice that of the anti, i.e.,  $(4 + 2 \times 2):(2 \times 2)$ . Accordingly, the distribution of the rotamers in the liquid phase is statistically determined, just as it is in the vapor phase.<sup>4</sup> Furthermore, this statistical (within ca.  $\pm 15\%$ ) ratio of rotamers yields, via the Boltzmann equation, a free-energy difference,  $\Delta G^\circ (= RT \ln 2)$  equal to  $0.13 \pm 0.02$  kcal/mol at  $-180^\circ\text{C}$ . This value is essentially equal to the value of 0.12 kcal/mol obtained by extrapolation to this temperature of the vapor phase Raman data of Bernstein.<sup>4,10</sup> However, the fact that only the anti rotamer could be detected by Raman spectroscopy in the annealed solid at  $-196^\circ\text{C}$ <sup>4</sup> implies that the conformational preference of 2,3-dimethylbutane is not the same in the solid as it is in solution.

There are two potential pathways for interconversion of the rotamers that require consideration (see Scheme I). (i) A gauche-anti-gauche (GAG) process in which the gauche-gauche interconversion only occurs via the anti rotamer. In this case, only one barrier ( $\text{GA} \rightleftharpoons \text{AG}$ ) need be considered since rotation about the central bond is incomplete, i.e.,  $k_1 \gg k_2$ . (ii) An anti-gauche-gauche (AGG) process in which the gauche-gauche interconversion can occur both directly and by the indirect GAG route. In this case, two barriers must be considered (i.e., the GG and the AG) since there can be complete rotation about the central bond ( $k_1 \sim k_2$ ).

The fact that averaging of the anti and gauche signals is observed means that the AG interconversion occurs. It is less obvious whether there is a direct GG interconversion and therefore it is not clear whether the GAG or AGG sequence should be employed to interpret the spectra.<sup>11</sup>

The methine signals can be used to determine the rotational rate constant  $k_1$  because these signals will *only* be broadened by the AG interconversion. (They remain equivalent in the GG interconversion.) Experimental and computed methine signals at two temperatures are shown in Figure 2. The  $k_1$  values (Table I) yield an average  $\Delta G_1^\ddagger$  of  $4.3 \pm 0.2$  kcal/mol. No attempt has been made to evaluate the enthalpy and entropy of activation because of the small temperature range of the measurements and because of the experimental difficulties in determining the temperature and the  $T_2$  values.<sup>13,14</sup> However, since most rotational processes have negligible  $\Delta S^\ddagger$  values,<sup>15,16</sup> it seems likely that  $\Delta G_1^\ddagger$  will be almost temperature independent.

Experimental and computed methyl signals at two temperatures are shown in Figure 2. Although the simplest hypothesis is that only the GAG sequence is operational, both the



**Figure 2.** Experimental (left) and computer simulated (right) 90.5-MHz  $^{13}\text{C}$  NMR spectra of the methine and methyl signals from 2,3-dimethylbutane at the temperatures indicated. The GAG model was used to obtain the computed methyl spectra.

**Table I.** Rate Constants Employed to Simulate the Methine Signals in the 90.5-MHz  $^{13}\text{C}$  NMR Spectra of 2,3-Dimethylbutane

Temp, $^{\circ}\text{C}$	$k_1, \text{s}^{-1}$	$\Delta G_1^{\ddagger}, \text{kcal/mol}^a$
-178	$170 \pm 10$	$4.38 \pm 0.10$
-176.5	$550 \pm 50$	$4.22 \pm 0.10$
-173	$(2000 \pm 500)$	$(4.13 \pm 0.15)$

<sup>a</sup> The errors in  $\Delta G_1^{\ddagger}$  include the uncertainty in the temperature (see text).

GAG and AGG sequences were employed to derive the computed spectra. Unfortunately, the differences between the two sets of spectra were much too small to discriminate between the two models. The derived rate constants are listed in Table II. It is apparent that the computed spectra are similar when the value of  $k_1$  in the GAG model and the sum  $k_1 + k_2$  in the AGG model are approximately the same. This result is not surprising because, with one gauche methyl resonance exactly overlapping the anti methyl resonance, the same net transfer of magnetization will be generated using adjusted rate constants in either model. Since the nature and quality of the experimental data did not allow the GAG and AGG sequences to be unequivocally distinguished,<sup>17</sup> ab-initio calculations were performed on 2,3-dimethylbutane to estimate the AG and GG barriers.

**Theoretical Calculations.** The SCF-MO ab-initio calculations were carried out on both rotamers and on the two possible transition states for rotation. In all computations a minimal STO-3G basis set<sup>18a</sup> with the Gaussian 70 series of programs<sup>18b</sup> was employed.

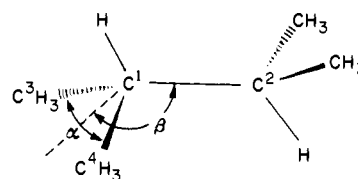
The anti isomer was investigated first. Since the number of independent geometrical parameters is too large to optimize

**Table II.** Rate Constants Employed to Simulate the Methyl Signals in the 90.5-MHz  $^{13}\text{C}$  NMR Spectra of 2,3-Dimethylbutane

Temp, $^{\circ}\text{C}$	Rotation sequence	$k_1, \text{s}^{-1}$	$k_2, \text{s}^{-1}$
-176.5	GAG	$600 \pm 50$	$0.1^a$
-173	GAG	$1400 \pm 100$	$0.1^a$
-176.5	AGG	$550 \pm 50$	$70 \pm 20$
-173	AGG	$1000 \pm 50$	$300 \pm 50$

<sup>a</sup> Assumed.

each of them, the energy for this rotamer was minimized with respect to  $\alpha$  (the  $\text{C}^3\text{C}^1\text{C}^4$  angle) and  $\beta$  (the angle between the  $\text{C}^1\text{C}^2$  bond axis and the bisector of the  $\text{C}^3\text{C}^1\text{C}^4$  angle).<sup>19</sup> This follows Allinger et al.'s<sup>20</sup> suggestion that valence angle distortions are of major importance in determining conformational stabilities.



The remaining geometrical parameters were fixed during optimization as follows: (i) The geometry of the isopropyl fragments was assumed to be the same as those found experimentally for 3-methyl-1-butene.<sup>21</sup> (ii) The methyl groups were assumed to be tetrahedral. (iii) The  $\text{C}^1\text{C}^2$  bond length was taken to be  $1.539 \text{ \AA}$ , the experimental value for the central bond in *n*-butane.<sup>22</sup>

Using the same geometrical data, the gauche rotamer was found to be intrinsically more stable than the anti by  $0.14 \text{ kcal/mol}$ , i.e.,  $\Delta H^{\circ} = 0.14 \text{ kcal/mol}$ . This result is not in significant disagreement with the present<sup>23</sup> and previous<sup>4</sup> experimental (and theoretical<sup>6</sup>) findings that, if the degeneracy is ignored, the two rotamers are of almost equal energy.

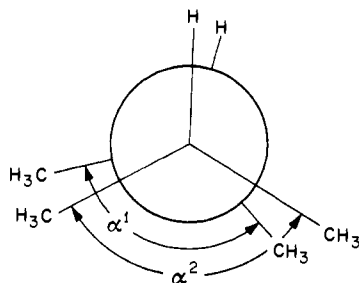
The energies of the transition states were computed within the framework of a rigid rotor model. For the anti-gauche rotation the difference in the energies of the transition and ground states yielded a rotational barrier of  $4.6 \text{ kcal/mol}$  in excellent agreement with the experimental  $4.3 \pm 0.2 \text{ kcal/mol}$ . For the gauche-gauche rotation the barrier was found to be  $8.9 \text{ kcal/mol}$ .

In order to assess whether the parameters used in the computations may have affected to any significant extent the value found for the GG barrier, a series of more sophisticated calculations were carried out.

(i) Optimization of the  $\alpha$  and  $\beta$  angles<sup>24</sup> for the gauche conformation gave a GG barrier of  $10.8 \text{ kcal/mol}$  within the rigid rotor framework.

(ii) A subsequent optimization of the  $\text{C}^1\text{-C}^2$  bond length in the transition state<sup>25</sup> reduced the preceding GG barrier to  $8.4 \text{ kcal/mol}$ .

(iii) Finally, we investigated a modified GG transition state in which the two isopropyl groups had different geometries. In the preceding models, the two isopropyl groups have been assumed to have identical geometries which leads to a GG transition state in which there are two pairs of fully eclipsed methyls. In the new model the two isopropyl groups are slightly distorted so that only one pair of methyls is fully eclipsed in the transition state. Computations were carried out with an  $\alpha$  angle at  $\text{C}^1$ ,  $\alpha^1 = 107.42^{\circ}$ ,<sup>19</sup> and with an  $\alpha$  angle at  $\text{C}^2$ ,  $\alpha^2 = 110.05^{\circ}$ .<sup>24</sup> The  $\text{C}^1\text{-C}^2$  bond length was reoptimized<sup>26</sup> and the GG barrier was found to be  $7.9 \text{ kcal/mol}$ .



We conclude from the calculations described above that the GG barrier is probably ca. 8 kcal/mol and that it is undoubtedly appreciably larger than the 4.3 kcal/mol found for the AG barrier.<sup>27</sup> As a consequence, the direct GG interconversion is of negligible importance and the GAG process is the only significant path by which the rotamers of 2,3-dimethylbutane are interconverted.

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## References and Notes

- (1) Part 6: F. Bernardi, L. Lunazzi, P. Zanirato, and G. Cerioni, *Tetrahedron*, in press.
- (2) (a) Laboratorio CNR, Ozzano E., Italy; (b) Division of Chemistry, National Research Council, Ottawa, Canada.
- (3) S. Brownstein, J. Dunogues, D. Lindsay, and K. U. Ingold, *J. Am. Chem. Soc.*, **99**, 2073 (1977).
- (4) A. L. Verma, W. F. Murphy, and H. J. Bernstein, *J. Chem. Phys.*, **60**, 1540 (1974).
- (5) J. H. Chen and A. A. Petrauskas, *J. Chem. Phys.*, **30**, 304 (1959).
- (6) R. H. Boyd, *J. Am. Chem. Soc.*, **97**, 5353 (1975).
- (7) In ref 5 it was assumed that the anti rotamer was the more plentiful (i.e., stable). Since we show that the gauche:anti ratio in solution is ca. 2:1, the 3.75 kcal/mol barrier of ref 5 would actually correspond to the gauche  $\rightarrow$  anti transformation.
- (8) F. A. L. Anet, G. N. Chmurny, and J. Kraw, *J. Am. Chem. Soc.*, **95**, 4423 (1973).
- (9) G. Binsch and D. A. Kleier, Program No. 140, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind.

- (10) Extrapolation of the data contained in Figure 4 of ref 4 yields a gauche:anti ratio of 1.9 at  $-180^\circ\text{C}$ , from which  $\Delta G^\circ = R \times 93 \times \ln 1.9 = 0.12 \text{ kcal/mol}$ .
- (11) A rough estimate of the energy difference between the AG and GG transition states can be obtained by comparing the (supposed) contribution of two eclipsed HMe (1.44 kcal/mol)<sup>12</sup> plus one eclipsed MeMe (2.76 kcal/mol)<sup>12</sup> in AG with that due to two eclipsed MeMe plus one eclipsed HH (0.98 kcal/mol)<sup>12</sup> in GG. Accordingly, the AG barrier should be lower than the GG barrier by 0.86 kcal/mol, which is small enough that the GG process cannot just be ignored.
- (12) See, e.g., (a) S. Weiss and G. E. Lerol, *J. Chem. Phys.*, **48**, 962 (1968); (b) J. P. Lowe, *Prog. Phys. Org. Chem.*, **6**, 1 (1968); (c) J. A. Hirsch, "Concepts in Theoretical Organic Chemistry", Allyn and Bacon, Boston, 1974; (d) J. E. Anderson, C. W. Doecke, and H. Pearson, *J. Chem. Soc., Perkin Trans. 2*, 336 (1976).
- (13) G. Binsch, "Dynamic Nuclear Magnetic Resonance Spectroscopy," M. Jackman and F. A. Cotton, Ed., Academic Press, New York, N.Y., 1975, Chapter 3, p 45.
- (14) M. Eisenuth, H. L. Mitchell, D. D. Traficante, R. J. Kaufman, J. M. Deutch, and G. M. Whitesides, *J. Am. Chem. Soc.*, **96**, 5385 (1974); R. E. Carter, T. Drakenberg, and C. Roussel, *J. Chem. Soc., Perkin Trans. 2*, 1690 (1975).
- (15) I. O. Sutherland, "Annual Reports on NMR Spectroscopy", Vol. 4, E. F. Mooney, Ed., Academic Press, New York, N.Y., 1971, p 71; F. A. L. Anet and R. Anet, "Determination of Organic Structures by Physical Methods", Vol. 3, F. C. Nachod and J. J. Zuckermann, Ed., Academic Press, New York, N.Y., 1971, p 344.
- (16) L. Lunazzi, D. Macciantelli, and A. Boicelli, *Tetrahedron Lett.*, 1205 (1975); L. Lunazzi, A. Ticca, D. Macciantelli, and G. Spunta, *J. Chem. Soc., Perkin Trans. 2*, 1121 (1976); L. Lunazzi, D. Macciantelli, and G. Cerioni, *ibid.*, in press.
- (17) At  $-173^\circ\text{C}$  they do, however, tend to favor the GAG sequence (cf. Tables I and II).
- (18) (a) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969); (b) W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, Program No. 236, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind.
- (19) The computed values of  $\alpha$  and  $\beta$  are:  $\alpha = 107.42^\circ$ ,  $\beta = 132.31^\circ$ .
- (20) N. L. Allinger, J. A. Hirsch, M. A. Miller, I. J. Tyminski, and F. A. Van-Cattledge, *J. Am. Chem. Soc.*, **90**, 1199 (1968).
- (21) A. R. Mochel, A. Bjorseth, C. O. Britt, and J. E. Boggs, *J. Mol. Spectrosc.*, **48**, 107 (1973).
- (22) K. Kuchitsu, *Bull. Chem. Soc. Jpn.*, **32**, 748 (1959).
- (23) The experimentally determined gauche:anti statistical ratio of 2:1 means that a single molecule in the gauche conformation is as stable as a single molecule in the anti conformation at  $-180^\circ\text{C}$ . That is,  $\Delta H^\circ = 0$  if the reasonable assumption is made that  $\Delta S^\circ = 0$ . With this assumption the difference between experiment (in solution) and calculation (for an isolated molecule) is merely 0.14 kcal/mol.
- (24) The computed values of  $\alpha$  and  $\beta$  are:  $\alpha = 110.05^\circ$ ,  $\beta = 133.97^\circ$ .
- (25) The corresponding computed value of the  $\text{C}^1\text{--C}^2$  bond length is 1.6117 Å.
- (26) The corresponding computed value of the  $\text{C}^1\text{--C}^2$  bond length is 1.6068 Å.
- (27) These calculations also indicate that simple additivity methods for estimating rotational barriers can be very misleading since such techniques suggested that the GG barrier would be larger than the AG barrier by only 0.86 kcal/mol.<sup>11</sup>