Barriers to Rotation and Conformer Populations of Two Substituted Butanes

By **J. Edgar Anderson** * and **Harry Pearson,** Ralph Forster Laboratory of Organic Chemistry, University College London, Gower Street, London WC1E 6BT

There is reported an n.m.r. study of 2-chloro-2,3-dimethylbutane (I) and 2,2-dichloro-3-methylbutane (II). In (I) the *trans*-conformation predominates while in (II) the *gauche* does. *gauche–gauche*, *gauche–trans*, and *trans–gauche* barriers are reported for both compounds.

THE determination and explanation of the conformational preferences of substituted ethanes and of the barriers to rotation in these compounds are subjects of continuing study.[1] In a molecule as simple as 1,2-dichloroethane the conformational preference varies dramatically from the vapour ($\Delta E_{g-t} = 1{\cdot}2$ cal mol^{-1}, *i.e. trans* favoured) to the neat liquid (ΔE_{g-t} *ca.* 0).[2]

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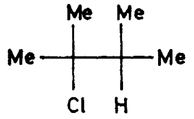
[1] A good impression of the present state of the study can be gained from papers presented at the symposium on the Energetics of Conformational Changes, held at the University of Salford, 1969, and recorded in a series of articles in *J. Mol. Struct.*, 1970, **6**, 1—84.

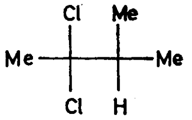
[2] Two convenient sources of early results are (*a*) N. Sheppard, *Adv. Spectroscopy*, 1959, **1**, 288; (*b*) J. P. Lowe, *Progr. Phys. Org. Chem.*, 1968, **6**, 1.

In this and in similar compounds, a considerable role is played by the interaction of the two carbon–chlorine bond dipoles and in the condensed phase by the interaction of these individual dipoles with solvent dipoles. Therefore, much might be gained by limiting such interactions by studying ethanes substituted principally with alkyl groups and with no polar substituents, or only one, or in the limit with two polar groups on the same carbon atom of the ethane.*

Dipole–dipole interactions along the ethane bond could then be discounted and the effect of other factors on the conformation might become apparent. This paper reports the first step in such an investigation, namely the determination of conformational populations and the various barriers to interconversion of the compounds (I) and (II), using the n.m.r. method in which separate signals for conformers are observed at low temperatures while an averaged signal is seen at high temperatures. This method has the advantage of giving a direct measure of conformer populations, a fairly direct measure of barriers to rotation, and of being generally quicker and unequivocal. As a consequence, a study of a series of compounds each slightly different from the others is feasible, and the effect of these slight differences can be deduced.



(I)



(II)

Both (I) and (II) are known compounds.[4,5] The i.r. spectrum (neat liquid) of (I) has been recorded and two carbon–chlorine stretch vibrations have been assigned[4,6] to the *gauche-* and to the *trans*-isomer respectively; these are of very similar intensities, that assigned to the *gauche*-isomer being slightly greater. There is no record of a spectroscopic study of (II), nor of information on its conformations.

RESULTS

The n.m.r. spectrum of (I) at room temperature comprises the expected doublet for the isopropyl methyl groups, a septet for the corresponding hydrogen, and a sharp singlet for the Me$_2$CCl groups (see Table 1). At *ca.* −135 °C the Me$_2$CCl signal (see Figure 1 and Table 1) comprises a singlet (fractional weight 0·59) and a doublet (fractional weight 0·41) corresponding respectively to the *trans*-isomer (III) where the two methyl groups are equivalent, and to the *gauche*-isomers (IV) and (V), in which the two methyl groups are different. The downfield signal of the latter doublet is assigned to the methyl staggered between methyl and hydrogen in (IV) and (V) on the basis of its proximity to the methyl signal of (III). The isopropyl methyl signal at −135 °C, should comprise a doublet from (III) and two equal doublets from (IV) and (V). In fact, there is overlapping and only four distinct signals are seen. Assuming the splitting of the doublets to be *ca.* 6·6 Hz as at room temperature, we assign these signals as in Table 1.† The signal of the isopropyl hydrogen is a

TABLE 1

Chemical shift and coupling constant data[a] for (I) and (II)

		Me_2CH	Me$_2$*CH*	Me$_2$CCl	MeCCl$_2$
	Room temp.	1·03 (d, *J* 6·6 Hz)	1·88 (sp, *J* 6·6 Hz)	1·52(s)	
(I)	−135 °C	1·05[b] (d, *J* 6·5 Hz) 0·97 and 1·13[c] (both d, *J* 6·6 Hz)	Broad signal at *ca.* 1·9	1·58(s)[b] 1·63(s) and 1·41(s)[c]	
	Room temp.	1·19 (d, *J* 6·6 Hz)	2·27 (sp, *J* 6·6 Hz)		2·09(s)
(II)	−137 °C	*d* 1·09(d) and 1·28(d)[c]	Broad signal at *ca.* 2·3		1·95(s)[b] 2·15(s)[c]

[a] Chemical shifts in δ (p.p.m.) for tetramethylsilane, sp = septet. [b] *trans*-Isomer. [c] *gauche*-Isomer. [d] Not observed as it underlies the signal for the *gauche*-isomer.

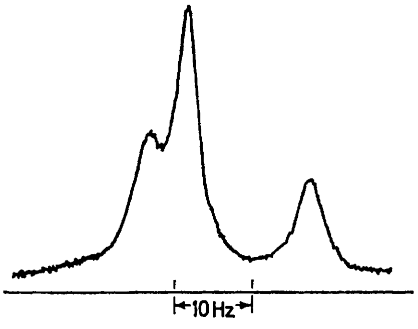
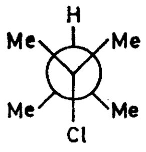
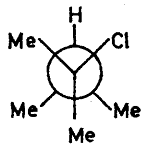


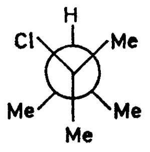
FIGURE 1 The Me$_2$CCl region of the spectrum of (I) at −138 °C



(III)



(IV)



(V)

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* In the latter case we are assuming that a $>C<^{X}_{Y}$ group can be treated as a single dipole like $\geqslant$C–Z. Even here, if there is distortion at the carbon atom in an eclipsed transition state the interaction of the polar groups X and Y will change and might affect the barrier a little. It is also assumed that carbon–carbon and carbon–hydrogen bonds are non-polar or rather, much less polar than bonds from carbon to what are normally considered to be polar groups. This is supported by a consideration of dipole moments. The contrast between the dipole moments of isobutane (Me$_3$CH; 0·13 D) and t-butyl chloride (Me$_3$CCl; 2·15 D)[3] and between propane (Me$_2$CH$_2$; 0·0 D) and methylene chloride (Cl$_2$CH$_2$; 1·63 D)[3] is striking.

† The assignment is not important to the present study since no quantitative use is made of this part of the spectrum, but its validity is supported by the appearance of the spectrum in vinyl chloride solution at −135 °C when five of the six expected peaks can be discerned.

[3] These values of dipole moments are for the gas phase, and are taken from A. L. McClellan, ' Tables of Experimental Dipole Moments,' Freeman, San Francisco, 1963.

[4] P. D. Bartlett, F. E. Condon, and A. Schneider, *J. Amer. Chem. Soc.*, 1944, **66**, 1531.

[5] A. G. Giunanini, *Boll. Chim. Farm.*, 1967, 106.

[6] J. J. Shipman, V. L. Folt, and S. Krimm, *Spectrochim. Acta*, 1962, **18**, 1603.

broad featureless hump of low intensity at low temperatures. On the basis of these results the free energy difference between the *gauche*- and *trans*-isomers is 0·29 kcal mol^{-1} (at −133 °C), the *trans*-form being of lower energy. The derivation of the three barriers in the potential diagram from n.m.r. spectra recorded at several temperatures is not straightforward, but since the problems involved have been discussed before,[7] details are relegated to the Experimental section. The result of this derivation is the barriers shown in Table 2 and in the potential diagram of Figure 2.

TABLE 2

Barriers to rotation (kcal mol^{-1})

Compound (I)		Compound (II)	
Rotation	Barrier	Rotation	Barrier
gauche–gauche		*gauche–gauche*	
(IV) $\rightleftharpoons$ (V)	8·2 ± 0·4	(VI) $\rightleftharpoons$ (VII)	8·4 ± 0·4
gauche–trans		*gauche–trans*	
(IV) $\longrightarrow$ (III) or (V) $\longrightarrow$ (III)	7·4 ± 0·4	(VI) $\longrightarrow$ (VIII) or (VII) $\longrightarrow$ (VIII)	8·3 ± 0·4
trans–gauche		*trans–gauche*	
(III) $\longrightarrow$ (IV) or (III) $\longrightarrow$ (V)	7·7 ± 0·4	(VIII) $\longrightarrow$ (VI) or (VIII) $\longrightarrow$ (VII)	7·75 ± 0·4

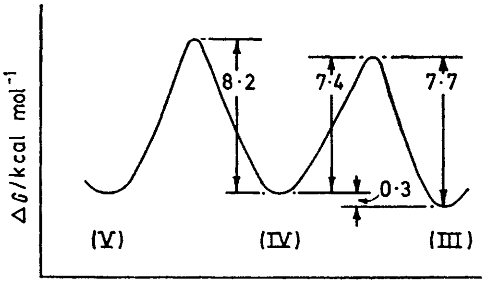


FIGURE 2 Potential energy diagram for rotation in (I). Small energy differences are exaggerated compared with the overall scale

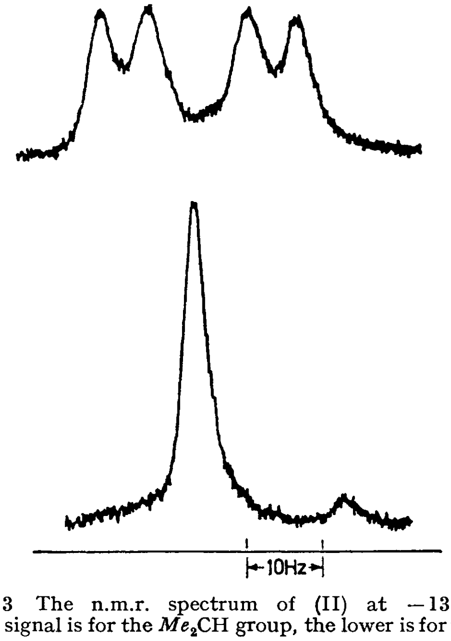
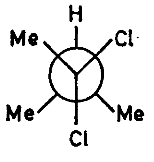
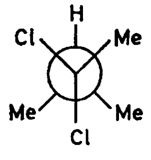


FIGURE 3 The n.m.r. spectrum of (II) at −136 °C. The upper signal is for the Me_2CH group, the lower is for the $MeCCl_2$ group

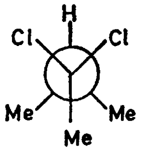
The spectrum of (II) at room temperature comprises a doublet for the isopropyl methyl groups, a septet for the isopropyl hydrogen, and a sharp singlet for the $MeCCl_2$ signal (see Table 1). At −136 °C (see Figure 3) the last signal appears as two single lines of relative intensity 93·8 : 6·2 representing the two rotational isomers. The isopropyl methyl signal at this temperature appears as two equal doublets, as in Figure 3. The signal for the conformation present to 6·2% is presumed to be hidden under this signal, so the predominant conformation is *gauche* [(VI) or (VII)] rather than *trans* (VIII) which would have only one doublet for the isopropyl methyl groups.



(VI)



(VII)



(VIII)

The free energy difference between the *trans*- and *gauche*-isomers is 0·55 kcal mol^{-1} at −136 °C the *gauche* being more stable. There are again three barriers in the potential diagram, and their derivation is described in the experimental section. The values resulting from this derivation are given in Table 2 and are shown in the potential energy diagram of Figure 4.

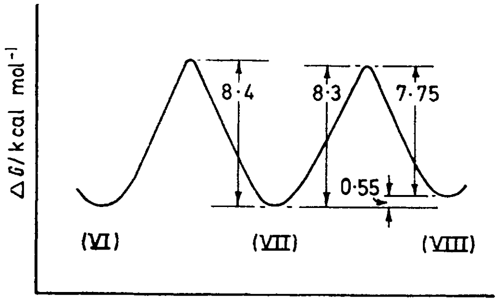


FIGURE 4 Potential energy diagram for rotation in (II). Small energy differences are exaggerated compared with the overall scale

We made a preliminary investigation of the effect of solvent on the *gauche–trans* equilibrium in (I) by the direct method indicated above. The selection of solvent available for use at −135 °C is limited, but it appears that the proportion of isomers in vinyl chloride solution is *ca.* 3 : 2 *trans–gauche* as in dichlorodifluoromethane, and *ca.* 65 : 35 in fluorodichloromethane. Among these three solvents therefore the *trans–gauche* energy difference varies between 290 and 360 cal mol^{-1} at −135°.

DISCUSSION

The *gauche*- and *trans*-conformations of (I) and (II) can be discussed in terms of several *gauche* interactions, *viz.* hydrogen–methyl, hydrogen–chlorine, methyl–methyl, and methyl–chlorine. While the first two of these should be comparatively small the latter two

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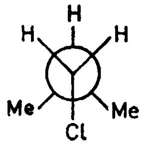
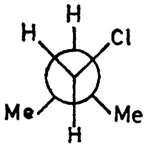
[7] R. A. Newmark and C. H. Sederholm, *J. Chem. Phys.*, 1965, **43**, 602.

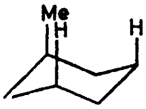
interactions are expected to dominate the conformational picture.

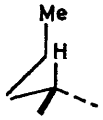
The *gauche*-conformation of n-propyl chloride is of lower internal energy than the *trans* by between 0·0 and 0·6 kcal mol^{-1}.[2a,8,9] Since there are no obvious destabilising influences in the *trans*-conformation, this suggests that there is an attractive methyl–chlorine interaction in the *gauche*-conformation.[10] That the attractive interaction is very small is suggested by the results for isobutyl chloride where by comparison with n-propyl chloride, conformation (IX) with two methyl–chlorine *gauche* interactions should be more stable than (X). In fact i.r. studies suggest that these conformations are of equal energy.[11]


(IX)


(X)

By contrast in butane, the *trans*-conformation is more stable than the *gauche* by *ca.* 0·7 kcal mol^{-1}.[12,13] This is reasonably attributed to a repulsive interaction between *gauche*-methyl groups in the *gauche*-conformation. There is an exact analogy for this interaction in the conformational analysis of methylcyclohexane, where the conformation with the methyl group axial (XI) is less stable than the equatorial one by *ca.* 1·7 kcal mol^{-1}.[14,15]


(XI)

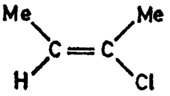

(XII)

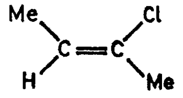
The conformational situation in *gauche*-butane is as in (XII) where the parallel [1,3] interaction[16] closely resembles these *syn*-diaxial interactions of axial methylcyclohexane. The parallel [1,3] interaction is additional to any [1,2] (Pitzer) interaction along the ethane bond, and a chlorine atom in propyl chloride does not have [1,3] interactions of this type.

Considering (I) and (II) in these terms it would seem that in each case, that conformation with more methyl–chlorine *gauche*-dispositions and fewer methyl–methyl *gauche*-dispositions of groups should be of lower internal energy. This is borne out by the results quoted and is sufficient explanation of the conformational preferences in these compounds.

In the transition state for rotation it is to be expected that methyl–methyl eclipsing interactions should be greater than methyl–chlorine ones. This is a reflection of a reasonable assumption that a methyl group occupies more space than a chlorine atom. More solid support is available in terms of the equilibrium of *cis*- and *trans*-2-chlorobut-2-ene (XIII) and (XIV). The *trans*-isomer (XIV) is of lower internal energy than (XIII) by *ca.* 0·8 cal mol^{-1}.[17] The *cis*-interactions in these molecules have a geometry which is very similar to that of the [1,2] interaction in an eclipsed ethane. In both cases the interaction should be principally steric but there may also be a small polar contribution.

For (I) the transition state with more methyl groups eclipsed (the *gauche–gauche* transition state) is of higher energy, but for (II) the two transition states are of very similar energies, although one has a methyl–methyl eclipsing interaction and the other does not. In all conformations there are many repulsive and attractive interactions which may be involved, and it seems that there is no obvious explanation of the relative energies of the transition states.


(XIII)


(XIV)

On the basis of the results for a series of ethanes with several halogen substituents, Roberts and his co-workers[18] have observed that the smallest of the three rotational barriers separates the two more stable isomers. They did not suggest that this is any more than a correlation which might be derived from the similarity of the nature of the non-bonded interactions in both the staggered and eclipsed conformations. In the present case, the correlation holds for (I) but not for (II).

This discussion is in terms of the ground and transition states being perfectly staggered and perfectly eclipsed respectively. We realise that there are likely to be distortions from these idealised geometries, and have already found evidence of bond angle distortion in the eclipsed state.[19] The various barriers found for (I)

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[8] Y. Morino and K. Kuchitsu, *J. Chem. Phys.*, 1958, **28**, 175.

[9] T. N. Sarachman, *J. Chem. Phys.*, 1963, **39**, 469.

[10] It may be useful to consider the nett stabilising interaction in terms of a repulsive steric interaction and stabilising hydrogen–chlorine polar interactions, R. J. Abraham and K. Parry, *J. Chem. Soc.* (*B*), 1970, 539.

[11] (*a*) H. F. Hallam and T. C. Ray, *J. Chem. Soc.*, 1964, 318 gives an equilibrium ratio of 2 : 1 for (X) : (IX). A statistical factor of 2 favouring (X) means that (IX) and (X) are of equal energy; (*b*) P. N. Gates, E. F. Mooney, and H. A. Willis, *Spectrochim. Acta*, 1969, **23***A*, 2043 report that in the i.r. spectrum of isobutyl chloride the C–Cl stretch region is the same at room and liquid nitrogen temperatures confirming the conclusions of ref. 11*a*; (*c*) G. H. Pauli, F. A. Momamy, and R. A. Benham, *J. Amer. Chem. Soc.*, 1964, **86**, 1286 suggest a ratio of *ca.* 4 : 1 (X) : (IX) from electron diffraction data.

[12] G. J. Szasz, N. Sheppard, and D. H. Rank, *J. Chem. Phys.*, 1948, **16**, 1704.

[13] P. B. Woller and E. W. Garbisch, jun., *J. Amer. Chem. Soc.*, 1972, **94**, 5310 and references therein.

[14] A recent review quoting the original references for such values is given by F. R. Jensen and C. H. Bushweller, *Adv. Alicyclic Chem.*, 1971, **3**, 139.

[15] J. A. Hirsch, *Topics Stereochem.*, 1967, **1**, 199.

[16] A. B. Dempster, K. Price, and N. Sheppard, *Spectrochim. Acta*, 1969, **25A**, 1381.

[17] R. P. Neureiter and F. G. Bordwell, *J. Amer. Chem. Soc.*, 1960, **82**, 5354.

[18] F. J. Weigert, M. B. Winstead, J. I. Garrels, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1970, **92**, 7359.

[19] J. E. Anderson and H. Pearson, *J.C.S. Chem. Comm.*, 1972, 908.

and (II) are within the range of those expected for ethanes with five substituents [19-21] where barriers range from *ca.* 6·0 kcal mol^{-1} for t-butylcyclopentane,[20] to 8·9 kcal mol^{-1} for 1,1-dichloro-2,2-dimethylpropane.[19]

It is assumed that the free energy of activation is temperature independent, *i.e.* that the entropy of activation is zero. It is reasonable that this is small, so that any error arising from this over the temperature range used is much less than errors from other sources. These uncertainties are reflected in the error limits quoted in Table 2. The relative values of the various barriers for either compound are rather more certain. Thus for (I) the *gauche–trans* barrier is less than the *gauche–gauche* and *trans–gauche* barriers by 0·8 ± 0·2 and by 0·28 ± 0·06 kcal mol^{-1} respectively. This greater precision reflects the fact that these relative values are determined rather more directly from primary data than the barrier heights.

EXPERIMENTAL

Compound (I) was prepared by stirring concentrated hydrochloric acid and an ether solution of 2,3-dimethylbut-2-ene at 0 °C and was purified by fractional distillation which gave a liquid, b.p. 66 °C at 176 mmHg (lit.,[4] 68 °C at 185 mmHg), $\nu_{max.}$ (neat liquid) 742, 612, 568, and 506 cm^{-1} (lit.,[6] 743, 611, 569, and 508 cm^{-1}).

Compound (II) was prepared by stirring 3-methylbutan-2-one with phosphorus pentachloride in ether at 0 °C for 5 h. G.l.c. (20 ft × ¾ in silicon oil at 60 °C) gave a liquid, n_D^{25} 1·4373 (lit.,[5] n_D^{20} 1·4420), $\nu_{max.}$ 701s and 553 cm^{-1}.

Calculation of Rate Constants.—The problems involved in calculating rate constants for rotation of asymmetric ethanes from changes in n.m.r. spectra have been discussed before.[7] Some of this discussion must be repeated to show the methods adopted for the present two molecules.

Compound (I). The isopropyl signal of this compound at low temperature does not show much detail, so we concentrated on the spectrum of the methyl groups on the carbon bearing the chlorine atom and calculated four series of spectra, in which (a) the *trans–gauche* transition state is of energy 1·0 kcal mol^{-1} less than *gauche–gauche* transition state *i.e.* $\Delta G_{t.s.} = +1{\cdot}0$; (b) $\Delta G_{t.s.} = +0{\cdot}5$; (*c*) $\Delta G_{t.s.} = 0{\cdot}0$; and (d) $\Delta G_{t.s.} = -0{\cdot}5$ kcal mol^{-1}. Within each series, the *gauche–gauche* barrier was varied in steps of 0·2 kcal mol^{-1} over a range of *ca.* 1·0 kcal mol^{-1} around the estimated barrier. This immediately fixed all other energies for each case within each series and so, using a computer programme already described,[22] a set of spectra was obtained for each series. A comparison of these four sets with a set of experimentally recorded spectra noting the manner in which the signals broadened and coalesced suggested that in reality $\Delta G_{t.s.}$ should be *ca.* +0·8 kcal mol^{-1}. Thenceforward this value was used.

A series of absolute values for $\Delta G^{\ddagger}_{g\text{-}g}$ the *gauche–gauche* barrier, were next chosen and the corresponding rate constants $k_{g\text{-}g}$, $k_{g\text{-}t}$, and $k_{t\text{-}g}$ at −129·6 °C were calculated. Using this information a series of spectra was computed. Visual matching of these calculated spectra with the experimental spectrum at this temperature allowed the determination of the optimum value of $\Delta G^{\ddagger}_{g\text{-}g}$. This and the already determined $\Delta G_{t.s.}$ and $\Delta G_{g\text{-}t}$ are sufficient to determine the conformational potential energy diagram. This was repeated at a second temperature, −126·4 °C. The mean of the two values of $\Delta G_{g\text{-}g}$ thus obtained was used to give the results in Table 2 and Figure 2. We assumed that the proportion of the two isomers and free energies of activation do not change between −135 and −126 °C, which is certainly true within the limits of accuracy of the results quoted in Table 2.

Compound (II). For this compound, both signals were used to calculate barriers. The two signals observed for the $MeCCl_2$ group corresponded to the *gauche* and *trans* isomers, and interconversion of these signals is achieved only by passage through the *gauche–trans* transition state, so that the *gauche–trans* and *trans–gauche* barriers can be obtained in a straightforward manner from the temperature dependence of the $MeCCl_2$ signal. These barriers were obtained by matching specta recorded at −121·4 and −125·4 °C. Assuming that $\Delta G_{g\text{-}t}$ is temperature independent, the relative amounts of the two conformations at these two temperatures were calculated. Spectra were then derived for a range of barriers $\Delta G_{g\text{-}t}$ using a computer programme similar to that already described.[22] It was concluded that the *gauche–trans* barrier is 8·3 kcal mol^{-1} whence the *trans–gauche* barrier is 7·75 kcal mol^{-1}. The barrier to interconversion of *gauche*-conformations, was then measured from changes in the spectrum of the isopropyl methyl groups. It will be recalled (see Figure 3) that these appear as two doublets at low temperatures, corresponding to the two methyl group environments in the *gauche*-conformation which is preferred by 93·8% of molecules. There should be another weak doublet arising from the 6·2% of the molecules in the *trans*-conformation. There is no asymmetry in the appearance of the low-temperature spectrum to suggest where this low intensity doublet should be, relative to the two doublets arising from the *gauche*-isomers, so it was assumed to occur at the mean chemical shift of these two doublets, for the purpose of calculating spectra. Several values of the *gauche–gauche* barrier were postulated and a series of spectra at various temperatures based on each of these postulations was calculated. Each series was compared visually with the experimental series of spectra at different temperatures to find the best *gauche–gauche* barrier. The potential energy diagram for rotation in (II) was then drawn (see Figure 4).

N.m.r. spectra and temperatures were measured, and calibrated as described previously.[22,23] The relative amounts of isomers were measured from several experimental spectra using a planimeter. The free energy differences between conformational isomers were estimated to be accurate to ±60 cal mol^{-1} at the temperature stated. The error values quoted in Table 2 reflect the uncertainties in absolute values of barriers. It is considered that relative to each other the barriers are accurate to ±200 cal mol^{-1}.

An S.R.C. studentship (to H. P.) is gratefully acknowledged.

[2/2424 *Received, 24th October,* 1972]

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