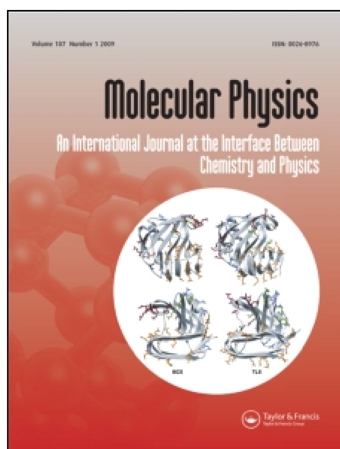
This article was downloaded by: *[Sjoblom, Rolf]*
On: *19 November 2010*
Access details: *Access Details: [subscription number 929883626]*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Physics
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713395160

Proton magnetic relaxation and molecular motion in polycrystalline amino acids

E. R. Andrew[a]; W. S. Hinshaw[a]; M. G. Hutchins[a]; R. O. I. Sjöblom[a]
[a] Department of Physics, University of Nottingham, Nottingham, England

To cite this Article Andrew, E. R. , Hinshaw, W. S. , Hutchins, M. G. and Sjöblom, R. O. I.(1977) 'Proton magnetic relaxation and molecular motion in polycrystalline amino acids', Molecular Physics, 34: 6, 1695 — 1706
To link to this Article: DOI: 10.1080/00268977700102891
URL: http://dx.doi.org/10.1080/00268977700102891

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

MOLECULAR PHYSICS, 1977, VOL. 34, NO. 6, 1695–1706

Proton magnetic relaxation and molecular motion in polycrystalline amino acids

III. Arginine, asparagine, cysteine, glutamine, phenylalanine and proline

by E. R. ANDREW, W. S. HINSHAW, M. G. HUTCHINS and R. O. I. SJÖBLOM

Department of Physics, University of Nottingham, University Park, Nottingham NG7 2RD, England

(*Received* 20 *June* 1977)

Downloaded By: [Sjoblom, Rolf] At: 21:53 19 November 2010

A proton magnetic relaxation investigation has been carried out on a further six polycrystalline amino acids from 130 to 500 K at 60·2 MHz and in two cases at 20·0 MHz also. Asparagine and glutamine with amide side chains exhibit closely similar relaxation minima well accounted for in terms of the Kubo–Tomita relaxation theory by NH_3 group reorientation in the zwitterion form of the molecules. Cysteine and phenylalanine exhibit two relaxation mechanisms, one at higher temperatures due to NH_3 group reorientation and a weaker mechanism at lower temperatures ascribed to motion of their side chains. The unusual relaxation behaviour of arginine arises from the protonation of the guadinium side group, so generating three reorienting amino groups in the molecule. The exceptionally long relaxation times of proline stem from the rigidity of its ring structure.

Relaxation constants, activation energies and time factors for all the amino acids studied in this series are tabulated and discussed. For 18 amino acids the relaxation constants for NH_3 group reorientation follow well an inverse dependence on the number of molecular protons being relaxed, and their absolute values agree well with those calculated using proton separations determined by neutron diffraction. Activation energies for NH_3 group reorientation range from 28 to 52 kJ/mole. Highest values are for amino acids with hydrocarbon side chains suggesting the formation of stronger hydrogen bonds by NH_3 groups in the crystal when in the absence of competition from polar interactions. Methyl rotors, unencumbered by hydrogen bonding, are characterized by lower activation energies in the range 7 to 22 kJ/mole.

1. INTRODUCTION

In a preceding paper [1] (to be referred to as I) an account was given of the proton spin-lattice relaxation and molecular motion in the solid state for seven amino acids commonly encountered in proteins, in all of which the mechanism of relaxation was ascribed to reorientation of the $-NH_3$ groups in the zwitterion structure $^{+}H_3N$–CHR–COO^{-}. In a second paper [2] (to be referred to as II) a further seven amino acids were considered, all of which included one or two methyl groups in the side chain R. The methyl groups provided independent sources of relaxation, efficient at lower temperatures. In the present paper a further six amino acids are discussed which have a variety of side groups R, and which exhibit a variety of types of relaxation behaviour.

Three of these amino acids have side chains which include another amino group ; they are the amides asparagine and glutamine, together with arginine. Proline forms a heterocyclic ring, and being in zwitterion form this molecule also includes an NH_2 group. The other two amino acids, cysteine and β-phenylalanine, though not possessing an obvious rotor in their side chains, nevertheless show clear evidence of a second independent relaxation mechanism, additional to that generated by reorientation of the $-NH_3$ group.

In addition to the amino acids just mentioned there are two others which are found in the classical ' 20 ' encountered in proteins, namely glutamic acid and lysine. Several specimens of these two amino acids were prepared and some measurements were made. However, we were not satisfied that these specimens were completely free of moisture despite taking much trouble, and the results are therefore not presented. We shall hope to return to them at a later opportunity.

After discussing the results on the present six amino acids, some overall comparisons are made for the whole series.

Downloaded By: [Sjoblom, Rolf] At: 21:53 19 November 2010

2. Experimental details

All these six amino acids were in the L form. The preparation of specimens and the details of the nuclear magnetic resonance measurements were described in I.

The recovery of nuclear magnetization was found to be exponential within experimental error for all six amino acids, enabling a unique spin-lattice relaxation time T_1 to be specified at each temperature. Non-exponential behaviour of the type observed in some compounds and ascribed to correlated motion of the three-spin system and to coupling between the nuclear magnetization and the rotational polarization was not observed with these compounds [3, 4].

3. Results and analysis

The measured values of proton spin-lattice relaxation time T_1 are shown as a function of temperature in figures 1 to 4. All these amino acids were examined at 60·2 MHz ; arginine and phenylalanine were also examined at 20·0 MHz in view of their unusual behaviour. In each of the figures the full lines are calculated theoretical curves.

Asparagine and glutamine exhibited a single minimum of T_1 and were analysed using the well-known relaxation expression of Kubo and Tomita [5] :

$$T_1^{-1} = C[\tau_c(1+\omega^2\tau_c^2)^{-1} + 4\tau_c(1+4\omega^2\tau_c^2)^{-1}], \quad (1)$$

assuming the correlation time τ_c to follow a simple activation law

$$\tau_c = \tau_0 \exp E/kT. \quad (2)$$

As in I and II a computer programme minimized the r.m.s. percentage difference between observed and calculated values of T_1. As is seen from figure 1 the curves generated by these expressions fit the data very well, the best values of the relaxation constant C, the activation energy E and the time factor τ_0 being given in table 1. The accuracy of the values of C and E in table 1 are typically 5 per cent and of τ_0 typically 50 per cent.

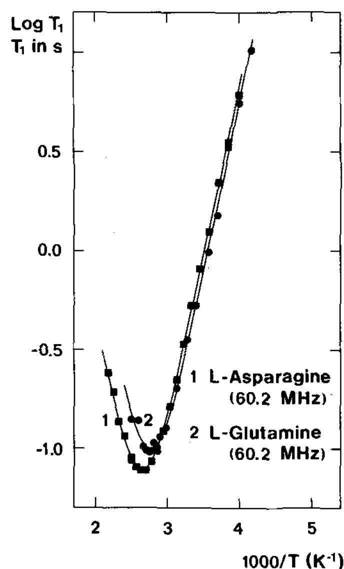


Figure 1. The variation of proton spin-lattice relaxation time T_1 with inverse temperature T^{-1} for polycrystalline amino acids at 60·2 MHz. Curve 1 : L-asparagine. Curve 2 : L-glutamine. The full lines are theoretical curves calculated in the manner described in the text.

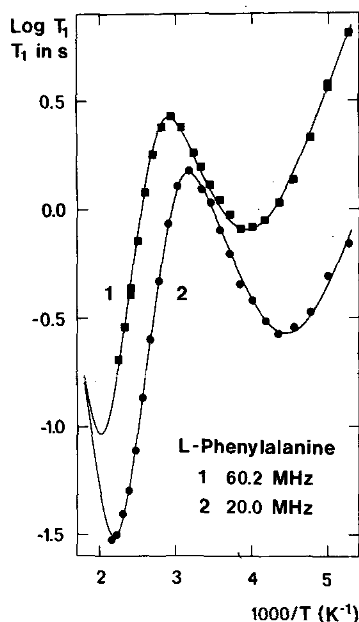


Figure 2. The variation of proton spin-lattice relaxation time T_1 with inverse temperature T^{-1} for polycrystalline L-phenylalanine. Curve 1 : 60·2 MHz. Curve 2 : 20·0 MHz. The full lines are theoretical curves calculated in the manner described in the text.

Downloaded By: [Sjoblom, Rolf] At: 21:53 19 November 2010

These two amino acids are almost identical in their relaxation behaviour. Their activation energies (table 1) are 32·3 and 32·6 kJ/mole ; their time factors τ_0 are 5·5 and $3{\cdot}1 \times 10^{-14}$ s. The minimum relaxation time $T_{1\,\mathrm{min}}$ for asparagine lies lower because the molecule has only eight protons to be relaxed by the $-NH_3$ group reorientation, whereas glutamine has ten protons. The ratio of values of $T_{1\,\mathrm{min}}$, 0·79, is close to the ratio 8/10 expected if the source of relaxation is the same ; the ratio of relaxation constant C is also 0·79. The additional methylene group in the side chain R of glutamine evidently makes little difference to the constraints restricting the motion of the $-NH_3$ groups in these two solids.

β-phenylalanine exhibits two clearly resolved relaxation minima (figure 2). The results were analysed using the following expression which generalizes equation (1), each correlation time τ_i following an activation law of the form of equation (2) :

$$T_1^{-1} = \sum_i C_i[\tau_i(1+\omega^2\,\tau_i^2)^{-1} + 4\tau_i(1+4\omega^2\,\tau_i^2)^{-1}]. \qquad (3)$$

The computer programme minimized the r.m.s. percentage difference between the observed and calculated values of T_1 refining simultaneously the parameters characterizing each of the two processes ; moreover the programme refined together the data at both 60·2 MHz and 20·0 MHz. The two theoretical curves in figure 2 are based on the same optimized values of C, τ_0 and E, and it is seen

Table 1. Relaxation parameters for the forms of molecular motion.

Amino acid	Side chain	Number of protons n	R.M.S. (obs–calc) per cent	Reorienting group	$T_{1\,min}$ at 60 MHz ms	Temp. at $T_{1\,min}$ K	Relaxation constant C $10^8\ s^{-2}$	Activation energy E kJ/mole	Time factor τ_0 10^{-14} s
L-arginine	$-(CH_2)_3NHC(NH)NH_2$†	14	3·7	$-NH_2$	724	400	3·7	35·7	3·5
				$-NH_2$	990	331	2·7	25·2	17
L-asparagine	$-CH_2CONH_2$	8	4·0	$-NH_3$	79	377	33·7	32·3	5·5
L-cysteine	$-CH_2SH$	7	7·5	$-NH_3$	62	365	43·0	37·1	0·8
				$-SH$	909	224	2·9	10·6	535
L-glutamine	$-CH_2CH_2CONH_2$	10	7·0	$-NH_3$	100	361	26·5	32·6	3·1
L-β-phenylalanine	$-CH_2-C_6H_5$	11	4·7	$-NH_3$	93	497	28·5	51·2	0·7
				—	805	254	3·3	18·2	30

† Actually the arginine molecule occurs as $^+(NH_2)_2CNH(CH_2)_3CHNH_2COO^-$.

Downloaded By: [Sjoblom, Rolf] At: 21:53 19 November 2010

that they fit the data very well. The low temperature relaxation mechanism is considerably weaker than the high temperature mechanism, the values of $T_{1\,min}$ and C differing by almost a factor 10.

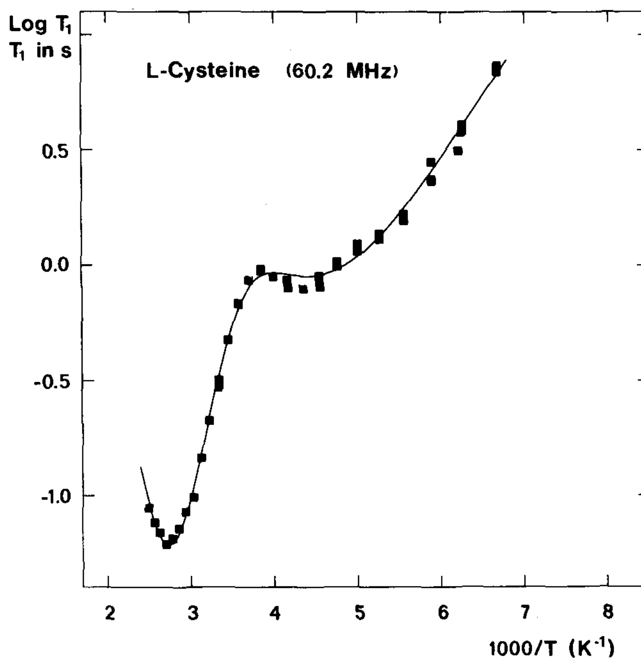


Figure 3. The variation of proton spin-lattice relaxation time T_1 with inverse temperature T^{-1} for polycrystalline L-cysteine at 60·2 MHz. The full line is a theoretical curve calculated in the manner described in the text.

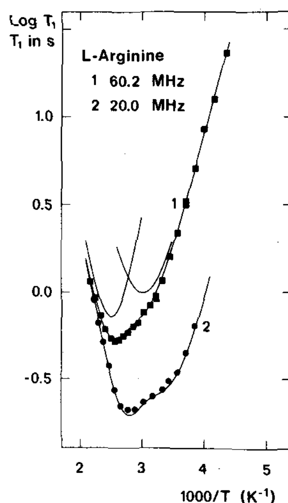


Figure 4. The variation of proton spin-lattice relaxation time T_1 with inverse temperature T^{-1} for polycrystalline L-arginine. Curve 1 : 60·2 MHz. Curve 2 : 20·0 MHz. The full lines are theoretical curves calculated in the manner described in the text.

Downloaded By: [Sjoblom, Rolf] At: 21:53 19 November 2010

Cysteine also exhibits two relaxation processes (figure 3). The data have been analysed in the same manner as for phenylalanine. Here the disparity between the strengths of the two relaxation processes is even larger, the values of $T_{1\,min}$ and C (table 1) differing by a factor 15.

The behaviour of arginine (figure 4) was quite different from any of the previous 18 amino acids studied in this series. The minimum value of T_1 at 60·2 MHz (table 1) was 724 ms, an order of magnitude longer than all the others. Moreover the points in figure 4 are unusually asymmetric about the minimum value at both measuring frequencies. The data have been analysed using equations (2) and (3) assuming two relaxation mechanisms, and it is seen that the theoretical relaxation curves generated by the best values of C, E and τ_0 for the two processes fit the experimental points well at both frequencies. The relaxation rates calculated for the two processes at 60·2 MHz are also shown separately to indicate their relative contributions. Since there are not two separately resolved minima of T_1 in this case we cannot be so sure that there are just two relaxation processes at work in arginine ; nevertheless this analysis is certainly the simplest which adequately fits the measurements at both frequencies.

The behaviour of proline was still further different from all the other amino acids. The spin-lattice relaxation time was found to be greater than 60 s at 200, 300 and 400 K. This is more than two orders of magnitude longer than $T_{1\,min}$ even for arginine, and more than three orders of magnitude longer than $T_{1\,min}$ for the others. Although this does not pretend to be a full investigation it is nevertheless a significant observation, indicating the absence in solid proline of any molecular motion comparable with that found in any of the other solid amino acids studied, capable of generating efficient spin-lattice relaxation of the protons.

Cysteine and phenylalanine have been examined by Zaripov [6] but no values of C, E, and τ_0 are given with which our values may be compared. The other amino acids investigated in this paper do not appear to have been studied previously.

Downloaded By: [Sjoblom, Rolf] At: 21:53 19 November 2010

4. Discussion

Neutron diffraction studies of *asparagine* and *glutamine* [7, 8] show the molecules to be in the zwitterion form in the solid state. Each therefore has an $-NH_3$ group. The product nC, where n is the number of protons in the molecule, is 27×10^9 s^{-2} for both solids, and falls in the range of values 25 to 32×10^{-9} s^{-2} found in I and II for $-NH_3$ group relaxation in the other amino acids. We conclude therefore that modulation of the magnetic dipolar interaction between the protons in the $-NH_3$ groups caused by their reorientation about the C–N bond provides the mechanism of spin-lattice relaxation in these two compounds, a common spin-temperature being maintained during the recovery of magnetization to its equilibrium value by means of the spin-exchange mechanism [9].

It seems very likely that *phenylalanine* is in zwitterion form, but direct confirmation awaits diffraction studies. The product nC is 31×10^9 s^{-2} (table 1) for the high temperature relaxation process, which certainly supports the view that reorientation of the $-NH_3$ groups provides the mechanism for this process. The low temperature relaxation process, which is an order of magnitude weaker

($nC = 3{\cdot}6 \times 10^{-9}\ s^{-2}$) is more difficult to identify positively. We note that it is absent in L-tyrosine [1] which differs in having a hydroxyl group on the end of the side chain. This hydroxyl group is hydrogen-bonded to a neighbouring molecule [10], tying the side chain down. It therefore seems very probable that in phenylalanine where this hydrogen-bonded group is absent, the low temperature mechanism arises from motion of its more free side chain.

Diffraction studies of *L-cysteine* in both monoclinic and orthorhombic forms [11–13] show the molecules to be in zwitterion form. The product nC is $30 \times 10^9\ s^{-2}$ (table 1) confirming that the main relaxation process is due to reorientation of the $-NH_3$ groups. The much weaker low temperature process ($nC = 2 \times 10^9\ s^{-2}$) is probably associated with mobility of the $-CH_2SH$ side chain. Certainly in serine, where the $-CH_2OH$ side chain is strongly hydrogen-bonded [14] this second relaxation process is absent [1]. It is, moreover, absent in cystine [1] where two molecular units form a disulphide bridge. In both serine and cystine the side group is therefore tied down, in contrast with cysteine in which it has greater freedom to move. Such motion is consistent with the apparent disorder of the side group observed in the neutron diffraction investigation of cysteine [13].

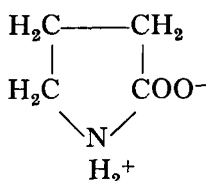
Downloaded By: [Sjoblom, Rolf] At: 21:53 19 November 2010

A neutron diffraction study of crystalline *arginine* dihydrate [15] shows that the molecules are in zwitterion form, but not the usual zwitterion $^{+}NH_3CHRCOO^{-}$ assumed by the other amino acids. The proton detached from the acidic group does not reside on the usual α amino group but instead lodges in the guanidinium group, giving the following molecular structure :

$$^{+}(H_2N)_2CNH(CH_2)_3CHNH_2COO^{-}.$$

The molecule thus has three $-NH_2$ groups, but unlike the other amino acids has no $-NH_3$ group. We thus have an immediate suggestion for the unusually long relaxation times in the anhydrous solid arginine studied here. Two-fold reorientation of $-NH_2$ groups about axes normal to their inter-proton vectors generates little relaxation, since their intra-group proton–proton contributions to the dipolar hamiltonian of the system are unchanged by these transpositions. However, the two-fold reorientations do modulate the dipolar interaction between the protons in the $-NH_2$ groups and other protons in their environment, and between the protons and the nitrogen nuclei, giving a weaker relaxation mechanism. If the decomposition of the observed relaxation behaviour (figure 4) into two relaxation processes is correct, we may tentatively identify the stronger one with reorientation of the two closely similar guanidinium $-NH_2$ groups and the weaker with the α amino group. The guanidinium $-NH_2$ groups may be expected to form stronger hydrogen bonds than the uncharged α amino group, and this could explain why the relaxation minimum of the α amino group occurs at a lower temperature, and its value of activation energy is lower (table 1). The plausibility of this explanation of the unusual relaxation behaviour of anhydrous L-arginine suggests that in this compound the molecule is in the same zwitterion form, shown above, that was found in the dihydrate by neutron diffraction [15].

The molecular structure of *proline* provides an explanation for its exceptionally long solid-state proton relaxation times. Proline forms the heterocyclic zwitterion ring confirmed in detail in crystalline hydroxylproline by neutron diffraction [16]. The molecule possesses no triangular rotors of the kind



responsible for relaxation in almost all the other solid amino acids. Even the $-CH_2$ and $-NH_2$ groups are integral parts of the ring structure and have no degree of freedom.

5. $-NH_3$ group reorientation

The values of C, E and τ_0 for $-NH_3$ group reorientation found in the 18 solid amino acids which exhibit this motion are collected together in table 2. As shown in I, if the geometry of the $-NH_3$ groups were the same in all the amino acids, and if the three protons in this reorienting group are responsible for relaxing all the n protons in the molecule, we expect C to be inversely proportional to n. The values of C^{-1} for all 18 amino acids are plotted against n in figure 5 and it is seen that the proportionality is rather well borne out, bearing in mind approximations involved in the assumptions. The median line drawn in figure 5 yields the value for C of $1 \cdot 0 \times 10^{10}\ s^{-2}$ for $n=3$, appropriate to reorienting $-NH_3$ groups which have no other protons to relax. Assuming the

Table 2. Relaxation parameters for $-NH_3$ group reorientation in amino acids.

Amino acid	Number of protons	Relaxation constant C $10^8\ s^{-2}$	Activation energy E kJ/mole	Time factor τ_0 10^{-14} s
Leucine	13	22·2	51·7	0·2
Phenylalanine	11	28·5	51·2	0·7
Isoleucine	13	22·8	44·8	0·6
Norleucine	13	23·2	41·7	0·25
Serine	7	42·6	40·0	0·45
Methionine	11	25·2	39·4	0·5
Alanine	7	43·5	38·6	1·6
Valine	11	24·5	37·4	3·8
Cysteine	7	43·0	37·1	0·8
Tyrosine	11	27·5	37·0	2·3
Glutamine	10	26·5	32·6	3·1
Threonine	9	34·2	32·5	3·3
Asparagine	8	33·7	32·3	5·5
Cystine	6	48·1	31·5	3·6
Histidine	9	33·6	31·4	2·8
Aspartic acid	7	35·6	29·8	19·0
Glycine	5	62·9	28·6	0·7
Tryptophan	12	20·6	27·8	7·2

Downloaded By: [Sjoblom, Rolf] At: 21:53 19 November 2010

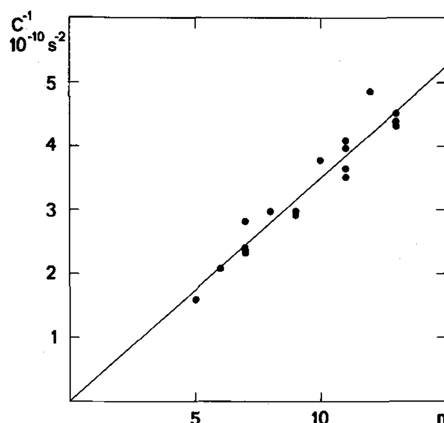


Figure 5. The variation of the inverse relaxation constant C^{-1} with the number of protons in each amino acid molecule for relaxation by $-NH_3$ group reorientation.

Downloaded By: [Sjoblom, Rolf] At: 21:53 19 November 2010

three protons are at the vertices of an equilateral triangle of side b, we expect [17]

$$C=\frac{9}{20}\frac{\gamma^4\hbar^2}{b^6}. \quad (4)$$

Insertion of the value of C just found for $n=3$ in equation (4) yields a value of 1·717 Å for b, which corresponds to an N–H bond length of 1·051 Å in a tetrahedral NH_3 group. From figure 5 the uncertainty in C for $n=3$ is of order 10 per cent, yielding a corresponding uncertainty in N–H of order 0·02 Å. Koetzle and Lehmann [18] have summarized 55 observations of the N–H bond length determined by neutron diffraction on α amino acids and find a range 1·007 to 1·083 Å with mean value 1·039 Å; the mean HNH angle from 53 observations is close to tetrahedral, 108·3° (range 105·0° to 111·9°). The agreement of the N.M.R. value of b is thus very good and we may feel we understand the origin and strength of this relaxation mechanism in the solid amino acids fairly well. (A discussion of some of the factors affecting the precise measured and calculated values of C was given in I.)

The values of activation energy fall in the range 28 to 52 kJ/mole, with mean and median value of 37 kJ/mole. This wide variation in the barriers to reorientation of the NH_3 groups from one solid amino acid to another suggests that they are to a large extent intermolecular in origin, and depend on the details of the packing, the hydrogen bonding and the electrostatic interactions. It should be noted that the barriers are rather higher for amino acids with hydrocarbon side chains than for those whose side chains contain other atoms as well (or contain no carbon atom at all). This may be explained as follows. Hydrogen-bond interactions are stronger than electrostatic interactions between other polar groups which in turn are stronger than van der Waals interactions. If a hydrogen bond in a crystal structure only competes with the much weaker van der Waals interactions, one may expect an optimization of the hydrogen bond. The bond will be stronger and perhaps straighter, and the barrier to NH_3 reorientation will be higher. If, on the other hand, a hydrogen bond must compete with several electrostatic interactions, one may expect that a compromise

Downloaded By: [Sjoblom, Rolf] At: 21:53 19 November 2010

is achieved so that the hydrogen bond becomes less well optimized, and perhaps less linear, than in the former case, with correspondingly lower barriers to NH_3 group reorientations.

The simple activation law, equation (2), is essentially an empirical law with some justification in statistical mechanics (see for example Glasstone, Laidler and Eyring [19]), and it is remarkable that it works as well as it does over many orders of magnitude of τ_c. Clearly the measured value of activation energy E is at least a qualitative measure of the constraints hindering the rotational motion of the molecular group, but its particular value must depend on the precise shape of the potential barrier describing the motion, insofar as it can be so described, and on the eigenvalues of energy of the rotor in the well and above the barrier. Until the factors determining E are better understood it is perhaps not too fruitful to attempt a more quantitative understanding of their differences at present.

The theory of rate reactions to which we have just made reference [19] leads to the expectation that the time factors τ_0 should be of the order $\hbar/kT$. Taking for T the median value of the temperature at $T_{1\,\mathrm{min}}$ for $-NH_3$ group reorientation in the solid amino acids, namely 375 K, the value of $\hbar/kT$ is 2×10^{-14} s. The values in table 2 are all of this order, ranging on either side by a factor 10. The difference between this and the value derived from the measurements is often ascribed to an entropy of activation indicative of a greater or lesser degree of order required of the excited state for the motion to take place. On this interpretation the variations of τ_0 in table 2 represent small entropy differences. However, it must be remembered that there can be other causes of the differences. Thus a small change in E requires a large change in τ_0 to give the same value of τ_c. Moreover as the temperature is raised under isobaric conditions the lattice expands and the potential barrier may be expected to decline ; any linear term in that decrease will appear as an apparent reduction in τ_0 as Brot [20] points out. In this connection it is to be noticed that those solids in table 2 with higher values of E tend to have lower values of τ_0 and vice versa. Brot further points out that there are alternative interpretations of τ_0 with comparable claims to validity. It is therefore perhaps most productive to draw the general conclusion from the values of τ_0 in table 2 that they are all of the order of magnitude one should expect.

6. Methyl group reorientation

The values of C, E and τ_0 for methyl group reorientation are gathered together in table 3. With the same simplifying assumptions as in the previous section we expect the relaxation constant C to be inversely proportional to the number of protons each methyl group relaxes. This is tested in figure 6 where C^{-1} is plotted against the number of protons in the molecule for alanine, norleucine, threonine and valine, for each of which one methyl group per molecule is responsible for relaxation. The scatter from the straight line is similar to that in figure 5 where there were many more points. Leucine has two methyl groups per molecule, and its value of C does not fit. Its anomalous behaviour was discussed in II.

The value of C one reads from the straight line in figure 6 for $n=3$, appropriate to reorienting methyl groups which have no other protons to relax,

Table 3. Relaxation parameters for methyl group reorientation in amino acids.

Amino acid	Number of protons	Relaxation constant C 10^8 s^{-2}	Activation energy E kJ/mole	Time factor τ_0 10^{-14} s
Alanine	7	35·0	22·4	15
Isoleucine	13		13·0	
Leucine	13	27·4	13·2	59
Methionine	11		6·7	
Norleucine	13	17·8	12·6	16
Threonine	9	24·4	12·0	50
Valine	11	24·0	11·3	189

Downloaded By: [Sjoblom, Rolf] At: 21:53 19 November 2010

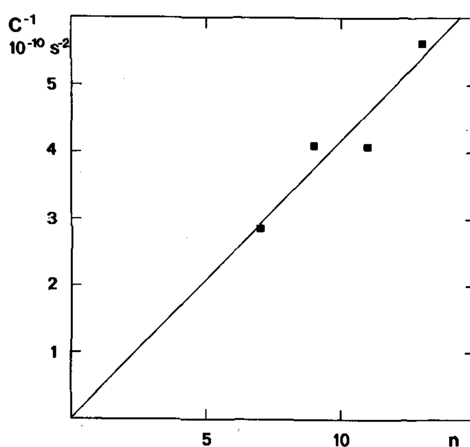


Figure 6. The variation of the inverse relaxation constant C^{-1} with the number of protons in amino acid molecules for relaxation by methyl group reorientation.

is $0{\cdot}8 \times 10^{10}$ s^{-2}. Using equation (4) this corresponds to an inter-proton distance of 1·782 Å, and assuming tetrahedral angles yields a C–H bondlength of 1·091 Å, with an uncertainty of order 0·02 Å. Koetzle and Lehmann [18] have summarized 19 observations of the C–H bond length in α amino acids determined by neutron diffraction and find a range 1·091 to 1·109 Å with mean value 1·101 Å. Here too the agreement is excellent and the origin and strength of this relaxation mechanism in solid amino acids seems reasonably understood, apart from the anomaly of leucine where there are two relaxing methyl groups attached to the same carbon atom.

The values of activation energy for methyl group reorientation fall in the range 6·7 to 22·5 kJ/mole. These values are much lower than for the $-NH_3$ groups and reflect the much greater freedom of the methyl groups which do not participate in hydrogen bonding. Actually five of the seven values in table 3 fall in the restricted range 11·3 to 13·2 kJ/mole. In methionine (6·7 kJ/mole) the methyl group is bonded to sulphur and has larger distances to neighbours. Alanine (22·4 kJ/mole) is a compact molecule and the methyl group is close to

charged amino and carboxyl groups, all attached to the same α carbon atom. The relative constancy of the barriers suggests either that they are largely intramolecular in origin, or that the influence of the surroundings is very similar in the different compounds, or both.

For 200 K the value of $\hbar/kT$ is 4×10^{-14} s. The values of τ_0 derived from the measurements are of this order, though somewhat longer.

Grateful acknowledgement is made to the British Council for a scholarship to R. O. I. Sjöblom, and to the Science Research Council for a research studentship to M. G. Hutchins.

Note added in proof.—The experimental data on DL-methionine and L-isoleucine reported in paper II have been extended to lower temperatures by Mr. T. J. Green and reveal T_1 minima due to methyl group reorientation at 93 K and 128 K respectively. An error has been noted in the caption of figure 3 of paper I. The two amino acids which have almost identical activation parameters are L-cystine and L-histidine.

Downloaded By: [Sjoblom, Rolf] At: 21:53 19 November 2010

References

[1] Andrew, E. R., Hinshaw, W. S., Hutchins, M. G., and Sjöblom, R. O. I., 1976, *Molec. Phys.*, **31**, 1479.

[2] Andrew, E. R., Hinshaw, W. S., Hutchins, M. G., Sjöblom, R. O. I., and Canepa, P. C., 1976, *Molec. Phys.*, **32**, 795.

[3] Hilt, R. L., and Hubbard, P. S., 1964, *Phys. Rev.* A, **134**, 392.

[4] Wind, R. A., Emid, S., Pourquié, J. F. J. M., and Smidt, J., 1976, *J. Phys.* C, **9**. 139.

[5] Kubo, R., and Tomita, K., 1954, *J. phys. Soc. Japan*, **9**, 888.

[6] Zaripov, M. R., 1974, *Radiospektroskopiya*, p. 193 (English translation, British Library Lending Division RTS 9205, 39 pp.).

[7] Verbist, J. J., Lehmann, M. S., Koetzle, T. F., and Hamilton, W. C., 1972, *Acta crystallogr.*, B, **28**, 3006.

[8] Koetzle, T. F., Frey, M. N., Lehmann, M. S., and Hamilton, W. C., 1973, *Acta crystallogr.* B, **29**, 2571.

[9] Bloembergen, N., 1949, *Physica*, **15**, 386.

[10] Frey, M. N., Koetzle, T. F., Lehmann, M. S., and Hamilton, W. C., 1973, *J. chem. Phys.*, **58**, 2547.

[11] Harding, M. M., and Long, H. A., 1968, *Acta crystallogr.* B, **24**, 1096.

[12] Kerr, K. A., and Ashmore, J. P., 1973, *Acta crystallogr.* B, **29**, 2124.

[13] Kerr, K. A., Ashmore, J. P., and Koetzle, T. F., 1975, *Acta Crystallogr.* B, **31**, 2022.

[14] Frey, M. N., Koetzle, T. F., Lehmann, M. S., and Hamilton, W. C., 1973, *Acta crystallogr.* B, **29**, 876.

[15] Lehmann, M. S., Verbist, J. J., Hamilton, W. C., and Koetzle, T. F., 1973, *J. chem. Soc. Perkin Trans. II*, 133.

[16] Koetzle, T. F., Lehmann, M. S., and Hamilton, W. C., 1973, *Acta crystallogr.* B, **29**, 231.

[17] Abragam, A., 1961, *The Principles of Nuclear Magnetism* (Clarendon Press).

[18] Koetzle, T. F., and Lehmann, M. S., 1976, *The Hydrogen Bond*, edited by P. Schuster (North-Holland Publishing Co.).

[19] Glasstone, S., Laidler, K. J., and Eyring, H., 1941, *Theory of Rate Processes* (McGraw-Hill Book Co.).

[20] Brot, C., 1969, *Chem. Phys. Lett.*, **3**, 319.