The quantitative methods of analysis used were checked and were generally found to be reliable within ± 10 %.

Acknowledgements. This work is part of an investigation of the mechanism of oxidation with nitric acid supported by the *Swedish Council for Applied Research.* We are also indebted to Dr. Erik Bengtsson for his kind interest in the work.

Mass spectrometric analyses were performed by Dr. Ragnar Ryhage at Karolinska Institutet, Stockholm. The experimental work was done with the skilful assistance of Mr. Hasse Hansson and of Mr. Tore Elström, who did most of the analytical work. Gas analyses were done by Mr. Olle Kronblad. The English was checked by Dr. K. H. Baggaley.

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Received August 17, 1967.

Interpretation of Proton Magnetic Resonance Spectra of α-Amino Acids in Terms of Rotational Isomers

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α-Amino acids, except glycine, are mixtures of 3 different rotational isomers (I, II, III) generated by rotation about the $C_\alpha - C\beta$ single bond. The life-time of such "rotamers" may be so short that PMR spectra of α-amino acids are effectively averaged at room temperature. In fact, earlier investigators [1-6] have all agreed that one PMR spectrum is observable per α-amino acid, meaning a rapid interconversion between I, II, and III. In a recent paper Aruldhas [7] has analyzed freshly recorded PMR spectra (100 MHz instrumental frequency) of DL-threonine (CH_3-$CHOHCHNH_2COOH$) and DL-valine ($(CH_3)_2CHCHNH_2COOH$) dissolved in D_2O (28°C). Aruldhas believes to have observed 2 superimposed spectra in each of these cases. His interpretation is that two of the rotamers, II and III, are separated by a very large barrier while the remaining barriers of the internal rotation potential function are low, causing the interconversions I → II and I → III to be rapid, while II → III is slow. We are unable to see why this is a satisfactory explanation of the alleged occurrence of 2 spectra since the interconversion II → III could still take place rapidly enough *via* the rotamer I to produce one and only one averaged spectrum per amino acid.

On the experimental side Aruldhas paper is in disagreement with, for example, the results obtained by Taddei and Pratt,[1] not cited by Aruldhas. These authors investigated PMR spectra (at 60 MHz) of DL-threonine and the diastereomeric *allo*-threonine under experimental conditions (pH, solvent, and temperature) similar to Aruldhas'. In separate experiments (as far as can be seen) Taddei and Pratt observed one methyl group spin-doublet for DL-threonine, and one for *allo*-threonine, the chemical shift difference being 0.12 ppm. At 100 MHz (Aruldhas' experiment) this corresponds to a chemical shift difference of 12 cps. Fig. 2(b) of Aruldhas' paper shows that there is a chemical shift difference between his two recorded methyl doublets of 11.5 cps. There can be little doubt, therefore, that Aruldhas' sample of alleged DL-threonine has been contaminated (to 30–40 %) by the *allo* isomer. To exclude any doubt (since the spectra of DL-threonine and *allo*-threonine are only details in the paper by Taddei and Pratt) we have again recorded the PMR spectrum of DL-threonine in D_2O at 60 MHz. The spectrum of the methyl group is a clear-cut doublet (Fig. 1, lines a and b of this paper) in contrast to the triplet to be expected according to Aruldhas.

In the case of DL-valine there is no "*allo*" isomer to complicate matters. Yet, two methyl group spin-doublets were again observed by Aruldhas and the spectrum was tentatively interpreted in anology with DL-threonine. This feature and the re-

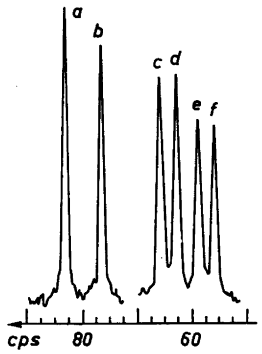

Fig. 1. Proton magnetic resonances (at 60 MHz) of the methyl groups of 2 % solutions of DL-threonine (a,b) and DL-valine (c,d,e,f) in D_2O. Increasing field from left to right. Chemical shifts in cycles sec^{-1} (cps) relative to internal sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS).

maining spectrum, also recorded by Taddei and Pratt, was interpreted correctly by them by assigning different chemical shifts to the two methyl groups of valine which, in general, are magnetically non-equivalent because of unequal life-times of the rotamers I, II, and III. For the spin-coupling constant, $J(H(\beta),CH_3(\gamma))$, Taddei and Pratt found the same value, 7.0 cps, for each of the two methyl groups, in harmony with values derived from other amino acid spectra, while Aruldhas' analysis involves the unusual values of 5.0 and 5.1 cps. Fig. 1, lines c, d, e, and f of this paper, records the methyl group resonances of DL-valine (60 MHz) in D_2O at 28° as re-observed by us. Without prejudice, this spectrum can be interpreted in 3 ways, namely, as consisting of (1) two spin-doublets separated by 3 cps; (2) two spin-doublets separated by 6.8 cps; (3) one spin-doublet separated by 3.8 cps and a second separated by 9.8 cps. Correspondingly, Aruldhas' spectrum (Fig. 4b of his paper) shows spin-doublet separations of either 5 cps (2 pairs); 7 cps (2 pairs); or 2 cps for one pair, 12 cps for the remaining. Since spin-couplings are independent on field intensity the acceptable solution is the one (2) common to both formal interpretations, that is, $J(H(\beta),CH_3(\gamma)) = 6.8$ cps. In conclusion no evidence has been presented to disprove that PMR spectra of α-amino acid rotamers at room temperature are effectively averaged to one spectrum. In this respect, the behavior of aqueous solutions of these acids is quite similar to what is found for solutions in CF_3COOH, even at 220 MHz.[5] Of course, the molecular species in CF_3COOH are ions ($CH_3CHOHCHNH_3^+COOH$) and not "zwitterions" ($CH_3CHOHCHNH_3^+COO^-$) as in water, but this difference would seem less important in stereochemical respect.

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Received August 22, 1967.

Organic Selenium Compounds

IV. Esters of Triselenocarbonic Acid

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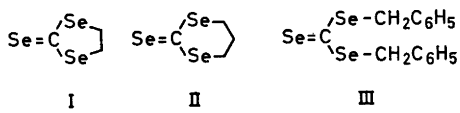
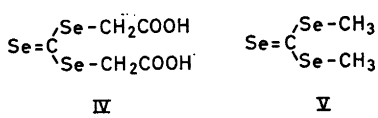
As a part of a current investigation at this laboratory of the chemistry of carbon diselenide,[1,4] we have prepared a series of esters of triselenocarbonic acid (I—V).



I II III



IV V