

amino-acids in these hydrolysates, showing that there was chemical combination of polymer with the wool.

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- ¹ Martin, jun., S. M., and Patrick, J. C., *Ind. Eng. Chem.*, **28**, 1145 (1936).
² Patrick, J. C., *Trans. Faraday Soc.*, **32**, 347 (1936).
³ Fettes, E. M., and Jorczak, J. S., *Ind. Eng. Chem.*, **42**, 11 (1950).
⁴ Thiokol Chemical Corp., *Bulletin No. LP-5* (May 1961).
⁵ Thiokol Chemical Corp., *Bulletin No. LP-4* (May 1961).
⁶ Thiokol Chemical Corp., *Bulletin No. LP-3* (July 1961).
⁷ Stannett, V., Araki, K., Gervasi, J. A., and McLeskey, S. W., *J. Polymer Sci.*, **A3**, 3763 (1965).
⁸ Simpson, I., thesis (1968).
⁹ Maclaren, J. A., *Austral. J. Chem.*, **15**, 824 (1962).
¹⁰ Springell, P. H., *Austral. J. Biol. Sci.*, **16**, 727 (1963).

Piezoelectric Resonances in Amino-acids

CRYSTALS of amino-acids may exhibit the property of piezoelectricity¹⁻⁴ and, like other crystals, may belong to one of the twenty-one so-called piezoelectric crystalline classes⁵. Our particular interest in investigating piezoelectric resonances in amino-acids was in connexion with our current study of nuclear quadrupole resonances (NQR). For this purpose, it is preferable to choose non-piezoelectric amino-acids so that there is no interference in the detection of the quadrupole spectra^{6,7}.

The results of our measurements on amino-acids⁸⁻¹¹ are given in Table 1. Experiments are performed on powders, using a superregenerative spectrograph¹² of NQR type¹³ specially adapted for this work¹⁴. We have

Table 1. COMPARISON OF EXPERIMENTAL AND THEORETICAL PIEZOELECTRICITY FOR AMINO-ACIDS

Amino-acid	Spatial group	Crystal-line class	Theoretical piezo-electricity ¹⁴⁻¹⁹	Experimental piezo-electricity
L-Alanine	P2 ₁ ,2 ₁	222	+	+
D-Alanine				+
DL-Alanine	Pna	mm2	+	+
β -Alanine	Pbca	mmm	-	-
L-Arginine·2H ₂ O	P2 ₁ ,2 ₁	222	+	+
D-Arginine·HCl				+
L-Asparagine·H ₂ O	P2 ₁ ,2 ₁	222	+	+
L-Aspartic acid	P2 ₁	2	+	+
DL-Aspartic acid	I2/a	2/m	-	-
L-Cysteine	P2 ₁	2	+	+
L-Cystine	P6 ₂ ,2	622	+	+
DL-Cystine				+
L-Glutamine	P2 ₁ ,2 ₁	222	+	+
L-Glutamic acid	P2 ₁ ,2 ₁	222	+	-
D-Glutamic acid				-
Glycine	See Table 2			+
L-Histidine				+
DL-Histidine				+
L-Hydroxyproline	P2 ₁ ,2 ₁	222	+	+
L-Isoleucine				+
D-Isoleucine				+
L-Leucine				+
D-Leucine	P2 ₁ ,2 ₁	222	+	+
DL-Leucine	P1	1	+	+
L-Lysine·HCl·2H ₂ O	P2 ₁	2	+	+
L-Methionine				-
DL-Methionine	See Table 2			-
L-Phenylalanine				-
D-Phenylalanine				-
L-Proline	P2 ₁ ,2 ₁	222	+	+
DL-Proline				+
L-Serine				+
DL-Serine	P2 ₁ /a	2/m	-	+
L-Threonine	P2 ₁ ,2 ₁	222	+	+
DL-Threonine		mm2	+	+
L-Tryptophan				-
DL-Tryptophan				-
L-Tyrosine				+
DL-Tyrosine				+
L-Valine	P2 ₁	2	+	+
D-Valine				+
DL-Valine	P1 or P $\bar{1}$	1 or $\bar{1}$	+ or -	-

studied principally the L isomers of amino-acids, the only ones occurring in proteins.

Table 1 gives for each crystalline compound the spatial group and the corresponding crystalline class in the Hermann-Mauguin notation as stated by Gurskaya¹⁶, Derissen *et al.*¹⁷, Harding and Long¹⁸ and Albrecht *et al.*¹⁹. In the fourth column, a plus sign indicates a piezoelectric class; a minus, a non-piezoelectric one. The last column records our experimental results, a plus sign being assigned for the samples in which piezoelectricity has been identified. Glycine is a special case: it has three crystalline forms (Table 2). Piezoelectricity is detected in the powder^{3,8,15}, but not in single crystals, in agreement with Guibé's experiments (personal communication). Because the γ -form is the most stable at room temperature¹⁸, it is reasonable to think that glycine powder is in the γ -form and single crystals are in the non-piezoelectric α -form.

Table 2. COMPARISON OF EXPERIMENTAL AND THEORETICAL PIEZOELECTRICITY FOR GLYCINE AND DL-METHIONINE

Amino-acid	Spatial group	Crystal-line class	Theoretical piezo-electricity ¹⁸	Experimental piezo-electricity
α -Glycine	P2 ₁ /n	2/m	-	-
β -Glycine	P2 ₁	2	+	+ (β or γ)
γ -Glycine	P3 ₁ or P3 ₂	3	+	+
α -DL-Methionine	P2 ₁ /a	2/m	-	+ (α or β)
β -DL-Methionine	I2/a	2/m	-	-

Our experimental results agree well with crystalline studies. In spite of the weakness of the piezoelectric resonances, it was generally possible to confirm this effect in those crystalline classes for which it would be expected. Recent crystallographic results^{17,18} confirm our experiments. For DL-methionine, which crystallizes in two forms (Table 2), and DL-serine, experimental piezoelectricity is exhibited in contradiction with the findings on crystal structure. This discrepancy needs to be resolved. In about twenty cases—for lack of crystal data—it is impossible to make a comparison, but we believe our results will be of importance in the assignment of crystal structure. It is interesting to note that of the twenty L-amino-acids we have studied (glycine included), nineteen exhibit theoretical and/or experimental piezoelectricity.

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- ¹ Duchesne, J., and Monfils, A., *CR Acad. Sci.*, **241**, 749 (1955).
² Duchesne, J., Depireux, J., Bertinchamps, A., Cornet, N., and Van der Kaa, J., *Nature*, **188**, 405 (1960).
³ Toulsky, S., and Read, M., *CR Acad. Sci.*, **260**, 7030 (1965).
⁴ Toulsky, S., Kukushkin, A., Blyumenfeld, L., and Lomonosov, M., *Molekul. Biophys., Akad. Nauk., SSSR, Inst. Biol. Fiz., Sb. Statei*, **41** (1965).
⁵ Cady, W., *Piezoelectricity* (Dover, New York, 1962).
⁶ Livingston, R., *Ann. NY Acad. Sci.*, **55**, 800 (1952).
⁷ Guibé, L., *CR du 9ème Colloque Ampère, Pisa*, 657 (1960).
⁸ Mesnard, G., and Vasilescu, D., *CR Acad. Sci.*, **260**, 4843 (1965).
⁹ Vasilescu, D., Mesnard, G., Moussiegt, J., and Cornillon, R., *Abstr. Second Intern. Cong. Biophys.*, Vienna (1966).
¹⁰ Vasilescu, D., Cornillon, R., and Mallet, G., *CR Acad. Sci.*, **265**, 631 (1967).
¹¹ Cornillon, R., thesis (University of Nice, 1968).
¹² Whitehead, J., *Superregenerative Receivers* (Cambridge University Press, 1950).
¹³ Dean, C., *Rev. Sci. Instrum.*, **31**, 934 (1960).
¹⁴ Vasilescu, D., Moussiegt, J., Cornillon, R., Farges, J.-P., and Mallet, G., *CR 92ème Congrès des Sociétés Savantes, Strasbourg* (1967).
¹⁵ Mason, W., *Piezoelectric Crystals and their Application to Ultrasonics* (Van Nostrand, New York, 1950).
¹⁶ Gurskaya, G. V., *The Molecular Structure of Amino Acids; Determination by X-Ray Diffraction Analysis* (Consultants Bureau, New York, 1968).
¹⁷ Derissen, J. L., Endeman, H. J., and Peerdeman, A. F., *Acta Cryst.*, **B24**, 1349 (1968).
¹⁸ Harding, M. M., and Long, H. A., *Acta Cryst.*, **B24**, 1096 (1968).
¹⁹ Albrecht, G., Schnakenberg, G., Dunn, M., and McCullough, J., *J. Phys. Chem.*, **47**, 24 (1943).