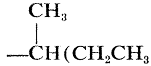
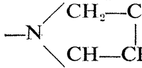
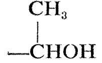
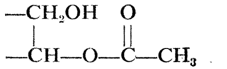
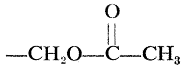
Table 3. Conformational classification of α-amino acids and six numbers of peptide units containing these (*4*).

α-Helix-forming amino acids	R	*Six numbers* of peptide bond (See II)	
		Total	Heteroatoms in position six
Alanine	$-CH_3$	3	0
Aspartic Acid Esters	$-CH_2COO$ Alkyl	6	2
Glutamic Acid	$-CH_2CH_2COOH$	6	0
Glutamic Acid Esters	$-CH_2CH_2COO$ Alkyl	6	0
Leucine	$-CH_2CH-(CH_3)_2$	6	0
Lysine	$-(CH_2)_4-NH_2$	6	0
Methionine	$-CH_2CH_2SCH_3$	6	1
Phenylalanine	$-CH_2-$	5	0
Tyrosine	$-CH_2-\quad -OH$	5	0
Norleucine	$-CH_2-CH_2-CH_2CH_3$	6	0
Norvaline	$-CH_2-CH_2CH_3$	6	0
o-acetylhomoserine	 $-CH_2-CH_2-O-\underset{O}{\underset{\Vert}{C}}-CH_3$	6	0
Valine	$-CH(CH_3)_2$	9	0
Isoleucine	 $-\overset{CH_3}{\overset{\vert}{C}}H(CH_2CH_3)$	9	0
Proline		12	0
Threonine	 $-\overset{CH_3}{\overset{\vert}{C}}HOH$	7	1
o-acetyl threonine	 $-\overset{-CH_2OH}{\overset{\vert}{C}}H-O-\overset{O}{\overset{\Vert}{C}}-CH_3$	7	1
Serine	$-CH_2OH$	4	1
o-acetyl serine	 $-CH_2O-\overset{O}{\overset{\Vert}{C}}-CH_3$	4	1
s-methyl cysteine	$-CH_2-S-CH_3$	4	1

of the effect of steric factors on the main chain conformations of polypeptides and proteins, the tendency of these macromolecules to crystallize, and the tendency for hydrophobic bonds to form. Six numbers have not been suggested previously, however, for use in such problems, but they have possible applications.

For example, it has been proposed that the amino acid sequence of polypeptides and proteins has an influence on main-chain conformations and hence, at least indirectly, exerts some influence on secondary and tertiary structure of proteins. Blout (*4*) has reviewed the status of work of this type. The α-amino acids are divided into two groups: those that tend to favor and permit α-helix formation and those that favor the β- and random coil conformations and appear not to form an α-helix. This classification is based on results obtained with synthetic polypeptides. Whether it will also apply to proteins remains to be shown. Amino acids are listed in Table 3, along with the six number for peptide bonds in homopoly-α-amino acids of each. It will be noted that for α-amino acids with no heteroatoms in position 6 of the side chain (with the exception of methionine and aspartic esters), those with a six number greater than 6 do not favor α-helix formation. Also, the presence of a heteroatom in position six works against α-helix formation. Blout has made the generalization that amino acids not forming the α-helix include those with either a heteroatom or with disubstitution on the β-carbon atom. As will be noted from the previous discussion, disubstitution on the β-carbon atom results in high six numbers; a heteroatom on the β-carbon atom will be in position 6 in the *B* location of an *-A-B-* peptide, in the 5 position in the *A* location. Six numbers should prove particularly useful in predicting the preferred conformations of various copolypeptides and of proteins of known sequence. For example, an alternating copolymer of valine and glycine would have peptide bonds with six numbers of 6 and 3 and would exist in the α-helix conformation, whereas an alternating copolymer of valine and alanine would have six numbers of 9 and 3 and would not prefer the α-helix conformation (there is a large steric hindrance to intramolecular H-bond formation in such cases). By assigning each amino acid in a copolypeptide a value proportionate to its molar ratio in the molecule and its own six number, the average six number for a peptide bond of the copolymer can be estimated, and the probable chain conformation "guessed at." The utility of six numbers for this purpose remains to be demonstrated.

Likewise, six numbers should prove useful in making a qualitative estimate of the tendency towards hydrophobic bond formation at specific locations along a polypeptide chain. This tendency should be greater at positions with higher six numbers, since the higher the six number the greater the local intramolecular concentration of hydrophobic groups.

In applying six numbers to polypeptide and protein chemistry, other factors will contribute simultaneously—electrostatic and dispersion forces, H-bonding, *cis-trans* isomerism about peptide bonds, and absolute configuration of the asymmetric carbon. This qualitative method is not a substitute for the more difficult and more quantitative treatments in which the actual magnitude of steric energies is estimated to the best approximation.

ROBERT E. WHITFIELD
*Western Regional Research Laboratory,
United States Department of
Agriculture, Albany, California*

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3 June 1963

Suspended Clay in a Water Sample from the Deep Ocean

During a recent cruise of the research vessel *Conrad* from New York to Martinique an attempt was made to recover particulate matter in suspension in ocean water. Fifteen samples of 3000 liters each from a depth of 3 meters were processed by pumping water aboard and separating suspended particles by means of a continuous-flow centrifuge. All these samples contained dinoflagellates, pollen grains, arthropods, and copepods, but none contained mineral matter. One sample of 200 liters was obtained from a depth of 4030 meters, 160 meters above the sea bottom, at 32°15′N, 74°45′W. This relatively small amount of sea water contained, apart from some organisms, about 0.50 g. of suspended clay, a surprisingly large quantity.

A study of the amount and type of suspended mineral matter contained in sea water at various depths should provide information concerning (i) the transportation of sediments in the ocean basins and (ii) post depositional diagenetic changes (*1*).

JOHAN J. GROOT
MAURICE EWING
Lamont Geological Observatory,
Columbia University,
Palisades, New York

Note

1. Contribution No. 653 from the Lamont Geological Observatory.

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Barium Xenate

Abstract. *Barium xenate was prepared by the addition of barium hydroxide to xenic acid. The resulting white amorphous precipitate was shown by elementary analysis to be* Ba_3XeO_6.

At the recent Argonne Conference on Noble Gas Compounds one of us (A.D.K.) reported (*1*) on the preparation of barium xenate. At the same meeting, sodium and heavier metal perxenates were described by J. G. Malm *et al.* (*2*). In this paper we give more detailed information on the xenate.

First of all, the properties of the noble gas compounds generally follow the expected properties of their neighbors in moving from the left to right in the same period of the periodic system. Thus, the xenon compounds are similar to the iodine compounds; the compounds of tellurium, the element just preceding iodine, show even greater similarity in view of the same even valences. Therefore, the xenon and tellurium compounds have identical formulas and probably identical geometry for the corresponding compounds. Recognition should be given, of course, to the fact that Te is more electropositive than Xe. As an example, the close similarity of XeF_6 and XeF_4 to TeF_6 and TeF_4 both in their physical and chemical properties may be described (*3*, *3a*).

Table 1. Distillation of aqueous xenic acid solution at 0°C.

Stage of test	Volume (cm³)	Concentration (mmole/cm³)	Total (mmole)	
Start	3.00	0.018_9	0.057*	
Distillate	1.50	.0097	.015	0.058
Residue	1.50	$.028_5$	.043	

* Corrected for decomposition of xenic acid at 0°C during distillation.

Xenic acid, $Xe(OH)_6$, first described by Dudley *et al.* (*4*) and Williamson and Koch (*5*), is like $Te(OH)_6$ (*3*), a very weak acid. It is a strong oxidizer and can be titrated (*4*) quantitatively by titrating I_2 with standard thiosulfate in line with the equation :

$$Xe(OH)_6 + 6\ KI + 6\ HCl \rightarrow Xe + 6\ H_2O + 3\ I_2 + 6\ KCl.$$

We have prepared xenic acid by slowly hydrolyzing XeF_4 (*6*) or xenon oxyfluorides at 0°C with water. Our yields varied between 30 to 40 mole percent, based on the XeF_4 content. A simple way of obtaining pure xenic acid solution free of HF was to agitate the solution with a slight excess (approximately 5 percent above the amount of HF determined by titration) of powdered $Ca(OH)_2$ or $CaCO_3$ at 0°C. Calcium fluoride is rapidly formed and is then filtered or centrifuged off, after the reaction is complete.

The $Xe(OH)_6$ was titrated in line with the above equation, while the free HF was titrated with standard alkali. For storage the xenic acid solution was kept in a freezer at −20° to −30°C without decomposition for weeks.

We expected that salts of xenic acid would be stable and that barium xenate would be a slightly soluble salt similar to barium tellurate. This proved to be the case. Barium xenate was prepared by adding, at 0°C, 3 moles of barium hydroxide solution to 1 mole of pure xenic acid. The reaction was complete and yields up to 100 percent were obtained provided the addition was rapid enough to avoid decomposition of the xenic acid. The composition of the very slightly soluble, white amorphous precipitate was very close to Ba_3XeO_6, regardless of whether the base was added in one or several portions. The ratio of Ba to $Xe(OH)_6$ in the precipitate was 2.97:1 when the base was added all at once; and it was 2.80, 3.17, and 2.95:1 when the base was added in three steps. The solubility of the barium xenate in water is 0.25 g per liter at 20°C.

Sodium and potassium salts of xenic acids have also been prepared in our laboratories, but they have not, as yet, been fully characterized. Aqueous solutions (7 to 8m*M*) of Na or K salts did not noticeably lose their oxidizing power at 0°C after 70 hours at *p*H 7 and *p*H 11.5. These xenates, as well as our barium xenate, are thermally stable at room temperature for at least a month. Barium xenate begins to decompose slowly at 125°C and the decomposition is complete at 250°C. To be sure of this, it was heated to 485°C and there was no further evolution of gas; the BaO residue was tested with acidic potassium iodide solution and was free from undecomposed xenate and also BaO_2, a possible product of decomposition if perxenate was present. The decomposition follows the equation:

$$Ba_3XeO_6 \rightarrow 3\ BaO + Xe\uparrow + 1.5\ O_2\uparrow$$

The salt and the BaO residue were analyzed as follows: BaO by acid titration and as $BaSO_4$; xenic acid by the I_2 liberated from KI; and Xe and O_2 by gas analysis. The results in percent by weight of two samples were as follows: BaO, 72.9, 71.75 (calculated for Ba_3XeO_6, 71.96); Xe, 19.8, 20.60 (calculated, 20.53), and O, 7.0, 7.55 (calculated, 7.51). The molar ratio of O_2/Xe in the thermal decomposition is 1.43, 1.52 ± 0.04 (calculated, 1.50). The second sample was also tested for $BaCO_3$ and found to contain none. Thus, our salt is a xenate and not a perxenate, which would require a 2.00 to 1 ratio.

The thermal stability of barium xenate and the greater stability of alkali xenates offer the interesting possibility that xenon may exist in nature, not only in the atmosphere as the free element but in hydrothermal minerals or in the waters of the ocean like the iodates (*7*).

A. D. KIRSCHENBAUM
A. V. GROSSE
Research Institute of Temple University,
Philadelphia, Pennsylvania, 19144

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