Three Crystalline Forms of Iminodiacetic Acid*

By Yuko TOMITA, Takeshi ANDO and Keihei UENO

(Received May 16, 1964)

There have been reports on the polymorphism of such amino acids as glycine[1,2] and ethylenediaminetetraacetic acid (EDTA),[3] however, no mention has been made of the polymorphism of iminodiacetic acid (IDA).

During the course of our investigation of the infrared spectra of aminopolycarboxylic acid metal chelates, we have found new forms of IDA which do not match the standard spectrum of IDA. Chemical analyses have proved the compounds to be IDA with different spectra and X-ray diffraction patterns.

Further work has then been undertaken to substantiate these three crytsal forms of IDA.

Experimental

When IDA is dissolved into hot water and the solution is allowed to cool to room temperature, the stable form of IDA (α) is obtained. When the hot solution is rapidly chilled to 0°C, a metastable form (γ) is obtained. Another metastable form (β) is obtained by adding ethanol to an aqueous solution of IDA at room temperature. The results

* Contribution No. 67 from the Department of Organic Synthesis, Faculty of Engineering, Kyushu University.

1) J. D. Bernal, *Z. Krist.*, **78**, 363 (1931).
2) Y. Iitaka, *Proc. Japan Acad.*, **30**, 109 (1954).
3) R. B. LeBlanc and H. L. Spell, *J. Phys. Chem.*, **64**, 949 (1960).

of elementary analyses show the chemical identity of three forms:

Anal. Calcd. for IDA		Found for α	Found for β	Found for γ
C	36.09%	36.04%	36.03%	36.03%
H	5.30%	5.32%	5.27%	5.32%

The melting point (232°C with decomposition) is also the same for the three forms.

The main differences between the three forms are observed in their infrared absorption spectra and X-ray diffraction patterns. The infrared absorption curves of the three forms in KBr disks are reproduced in Fig. 1, which indicates that the α-, β-, and γ-forms of IDA have different crystalline structures. However, when their spectra were taken in a D_2O solution using a cell with calcium fluoride windows, they gave an identical curve in 5000—1200 cm^{-1} region, the only transparent region for a D_2O solution.

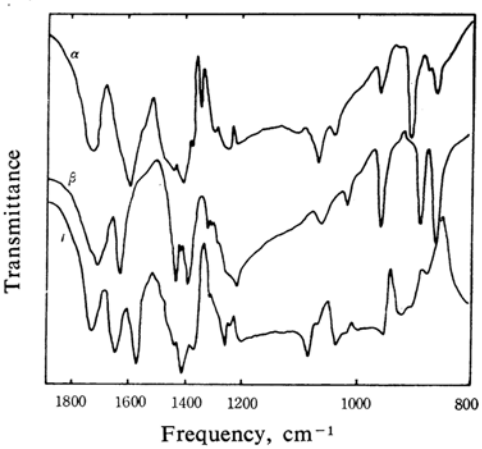

Fig. 1. Infrared spectra of three forms of iminodiacetic acid. (KBr disks)

TABLE I. X-RAY DIFFRACTION PATTERNS FOR THE THREE FORMS OF IMINODIACETIC ACID*

α Form d, Å	I/I_1	β d, Å	I/I_1	γ d, Å	I/I_1
7.47	(36)	7.50	(8)	6.11	(6)
6.42	(9)	6.55	(20)	4.77	(24)
5.14	(10)	6.33	(10)	4.48	(4)
4.69	(9)	4.48	(24)	4.30	(100)
4.31	(9)	4.11	(40)	4.05	(6)
4.23	(15)	3.71	(13)	3.95	(6)
4.12	(26)	3.68	(15)	3.68	(5)
3.74	(100)	3.55	(11)	3.52	(15)
3.50	(9)	3.42	(100)	3.42	(3)
3.30	(50)	3.27	(9)	3.14	(25)
3.23	(12)	3.03	(40)	2.97	(11)
3.04	(24)	2.86	(35)	2.79	(3)
2.79	(6)	2.81	(9)	2.71	(9)
2.63	(10)	2.75	(13)	2.65	(4)
2.49	(31)	2.62	(7)	2.59	(4)
2.34	(5)	2.58	(8)	2.46	(3)
2.25	(2)	2.47	(10)	2.42	(5)
		2.42	(10)	2.39	(4)
		2.23	(20)		

* The diffractions data were obtained with a Norelco X-ray diffractometer by using the copper $K\alpha$ radiation.

The data of X-ray diffraction which were taken on the powdered sample are shown in Table I; they also support the polymorphism of IDA.

Metastable β- and γ-forms can be converted to the stable α-form by simple heating; their transitions are observed around 184°C under a polarized microscope. The transitions can also be observed by a differential thermal analysis, in which a broad weak peak can be noticed at around 180°C. The conversions from β- and γ-forms to the α-form were confirmed by comparing the infrared spectra and X-ray diffraction patterns of the samples before and after heating. After heating, the samples gave spectral and X-ray diffraction patterns completely identical with those of the α-form.

Discussion

No difference in chemical properties was observed for the three forms of IDA, nor was any difference observed in the physical properties in a solution. In the case of glycine, three modifications are known to give different spectra; their differences can be attributed to the differences in the crystalline structures. By analogy, it seems reasonable to assume that the differences in the infrared spectra and X-ray diffraction patterns of IDA are caused by the differences in the crystalline structures. However, the change in the infrared spectra of the γ-form is so drastic compared with the other two forms that it seems also probable that the γ-form has a different molecular configuration rather than a different crystalline structure. As we have not been successful so far in obtaining single crystals which are large enough to give diffraction data for the crystalline structure analysis, no conclusive structure can be given for any of the forms.

Some of the expenses of the work reported on in this paper were supported by a research grant provided by the Ministry of Education, to whom the author's thanks are due.

Department of Organic Synthesis
Faculty of Engineering
Kyushu University Hakozaki, Fukuoka