CXXXI.—*The Anomalous Fifth Carbon Atom in n-Fatty Nitriles.*

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In some series of straight-chain carbon compounds the 5th, 10th, and 15th members exhibit maxima or minima in many physical and chemical properties (Lee, *Trans. Faraday Soc.*, 1927, **23**, 79; Lee and van Rysselberge, *J. Physical Chem.*, 1929, **33**, 1543), and similar anomalies have been noted in molecular rotatory power by Pickard and Kenyon. Moreover, in homologous series of such compounds the alternation of physical properties between the odd and the even members is well known. Müller (*Proc. Roy. Soc.*, 1929, *A*, **124**, 317) postulates a plane, or nearly plane, zigzag structure of the carbon chain in such cases, but Henderson (*Proc. Roy. Soc. Edin.*, 1928, **48**, 20), from *X*-ray investigations of the dibasic acids of the oxalic acid series, concluded that the carbon chain was in spiral form.

The systematic and comparative experiments recorded below, which were made by one of us (R. A. F.) on six consecutive members of the series of nitriles of the *n*-fatty acids, demonstrate that a well-defined anomaly exists in the chemical reactions of the C_5 nitrile. If a helicoidal configuration of the carbon atoms be assumed, every fifth carbon atom would correspond to one complete turn of the helix.

Experiments in Liquid Ammonia Solution.—Equimolecular quantities of the normal nitriles (from acetonitrile to hexonitrile) and of potassamide were electrolysed in liquid ammonia solution. The materials were carefully purified, and in all the experiments the conditions, *e.g.*, concentration, temperature (— 33°), and current density (0·5 amp./sq. cm.), were kept as nearly as possible the same. The electrolysis was carried out in an apparatus similar to that used by Kolbe and others. The gases evolved in the reactions were analysed by low-temperature fractionation according to the method of Burrell (*U. S. Bureau of Mines Bulletin*, No. 104), and the analyses were accurate to approximately 0·1%.

Attention is focused entirely on the anode reactions, and the electrolysis is essentially that of the potassium salt of the " ammono "-fatty acid (Franklin; see *e.g.*, Cornell, *J. Amer. Chem. Soc.*, 1928, **50**, 3311) formed thus: $CH_3{\cdot}CN + KNH_2 = CH_3{\cdot}C(:NH){\cdot}NHK$. Ammonocarbonic acid was always one of the products, and, except in the case of the ammonoacetate, hydrogen also was formed.

No. of C atoms in nitrile	2.	3.	4.	5.	6.
Methane, %	68·6	48·6	42·7	**2·0**	12·0
Ethane, %	None	None	None	**70·5**	50·0

The only variable in the different experiments was the length of the carbon chain. There is a definite " break " at the fifth carbon atom in the chemical reactions of these *n*-fatty nitriles. We assume that a stereochemical cause is responsible for this anomaly.

Fusion of n-*Fatty Nitriles with Potassamide.*—The nitriles were heated with potassamide in equimolecular quantity at 350°, the experiments being comparative. Again the only difference introduced was in the length of the chain.

No. of C atoms in nitrile.	2.	3.	4.	5.	6.
Gaseous products	CH_4	H_2, CH_4, C_2H_6	H_2, CH_4, C_2H_6, C_3H_8	CH_4, C_3H_8, C_4H_{10} (C_2H_6 trace)	C_2H_6, C_3H_8, C_5H_{12} (CH_4 trace)

At C_5 the yield of methane was a minimum with only a trace of ethane, whereas at C_6 the ethane yield was good, with only a trace of methane. There is again a distinct anomaly at C_5 in the reactions of these chemically similar nitriles. The mechanism of these reactions might be interpreted in different ways, and we lay less stress on these than on the electrolytic experiments. Nevertheless, there is some peculiarity which can be related to the number of carbon atoms in the chain.

Neither the ordinary plane formula of the organic chemist nor the plane zigzag of certain *X*-ray investigators accounts for this

chemical anomaly at the fifth carbon atom. The phenomenon is much more general than may have been supposed.

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