COMMUNICATIONS TO THE EDITOR

SYNTHETIC ELECTRICAL ANALOG OF PROTEINS¹ Sir:

Despite many specific chemical differences, most proteins possess a pattern of similarity in their electrical behavior; best known, perhaps, are the existence of the isoelectric point, with reversal of electrophoretic mobility at lower and higher values of pH, and the electro-viscous effect. It was suggested² that a synthetic polyampholyte might duplicate these properties. This result has been obtained experimentally.

An equimolar mixture of 2-vinylpyridine and methacrylic acid was copolymerized (four hours at 70° with 0.04% azo-bis-isobutyronitrile). The copolymer (25% conversion), precipitated twice from methanol with 1:2 methyl ethyl ketone and benzene, analyzed to 62 mole % vinylpyridine. We thus have a linear polymer which contains on the average three (weakly basic) pyridine groups to two (weakly acidic) carboxyl groups on every ten carbon atoms of the chain. The intrinsic viscosity in dimethylformamide is 0.10, corresponding to a molecular weight of the order of 10,000.

The copolymer is insoluble in water in the range $3.8 < \rho H < 6.8$, but becomes soluble outside this range. On the addition of acid, the viscosity initially rises as pyridine nitrogens are converted to pyridinium ions; on the addition of alkali, the viscosity also rises as neutral carboxyl groups are converted to negatively charged carboxyl ions. The viscosity increase is caused by intramolecular coulomb repulsion³ between the ions on the polymer chain. With excess acid or alkali, the viscosity again decreases, as has been observed for other polyelectrolytes.

Finally, electrophoretic mobilities at 0° were measured, using a Perkin-Elmer Tiselius apparatus. One per cent. solutions of the copolymer were made up in glycine-hydrochloric acid and diethylbarbituric acid-sodium hydroxide buffers, and dialyzed against the buffers; the ionic strength of the buffers was 0.10. The *p*H and specific conductance of the dialyzates are given in the table. Cell currents were 6.1–8.6 milamp. at 6.2–4.4 volts/cm. Both ascending and descending boundaries were photographed.

øН	10 ³ «	10 ⁵ u (asc.)	10 ^{\$} u (desc.)
2.23	6.357		10.9
2.97	5,427	13.3	10.9
8.22	3.225	-10.7	-8.5
8.80	3.234	-10.7	-8.5

(1) Office of Naval Research, Projects NR 054-022 and NR 054-002.

R. M. Fuoss and G. I. Cathers, J. Polymer Sci., 2, 12 (1947).
 R. M. Fuoss and U. P. Strauss, Ann. N. Y. Acad. Sci., 51, 836 (1949).

As seen in the table the mobility u (sq. cm./volt sec.) is of the same order as that of proteins and the expected reversal of sign appears in the range of pH where the copolymer is insoluble. We thus have a synthetic material which electrically is closely analogous to proteins.

POLYTECHNIC INSTITUTE OF BROOKLYN TURNER ALFREY, JR. BROOKLYN, NEW YORK HERBERT MORAWETZ STERLING CHEMISTRY LABORATORY YALE UNIVERSITY EMERSON B. FITZGERALD NEW HAVEN, CONNECTICUT RAYMOND M. FUOSS RECEIVED FEBRUARY 20, 1950

REANALYSIS OF THE ELECTRON DIFFRACTION DATA ON $Be(BH_4)_2$ and $Al(BH_4)_3$

Sir:

In a recent Note to THIS JOURNAL (72, 622 (1950)) on the reanalysis of electron diffraction data for $Be(BH_4)_2$ and $Al(BH_4)_3$, I regrettably failed to list the workers in this field who had suggested that unsymmetrical hydrogen bridge structures (γ) be considered as possible alternatives to the structures originally proposed (α). As was indicated in the above note, the results of X-ray diffraction work on crystals of LiBH₄, NaBH₄ and U(BH₄)₄ naturally led to the γ type configura-This form of bridge was also suggested tions. to me by Dr. W. C. Price, as a consequence of his infrared absorption studies, and independently by D. F. Stedman who based his deductions on a very interesting although unconventional theory of atom models. On the basis of this theory Dr. Stedman was led, in particular, to the γL model for $Al(BH_4)_3$.

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S. H. BAUER

RECEIVED MARCH 27, 1950

THE INSECTICIDAL ACTIVITY OF 1,1-DIANISYL-NEOPENTANE

Sir:

A consideration of the stereochemistry of the insecticide DDT, 1,1,1-trichloro-2,2-bis-(p-chlorophenyl)-ethane (I), suggested that it would be of interest to synthesize and test a 1,1-diarylneopentane. In such compounds, models indicate that definite steric hindrance exists. In consequence, the phenyl groups should tend to approach coplanarity.



p-Anisylmagnesium bromide was treated with ethyl pivalate to give 1,1-bis-(p-methoxyphenyl)-2,2-dimethylpropanol-1 (m. p. 81-83°. Anal. Calcd. for $C_{19}H_{24}O_3$: C, 75.97; H, 8.05. Found: C, 75.51; H, 7.84), which was then reduced over copper chromite to 1,1-bis-(p-methoxyphenyl)-2,2-dimethylpropane (II) m. p. 59-61°. Anal. Calcd. for $C_{19}H_{24}O_2$: C, 80.24; H, 8.51. Found: C, 80.42; H, 8.55). This compound, more conveniently called 1,1-dianisylneopentane, is related to "methoxychlor" (III), the $p_{,p}$ '-dimethoxy analog of DDT, in the sense that the trichloromethyl group of "methoxychlor" has been replaced by a tbutyl group. The neopentane has insecticidal activity of the same order, although lower, as "methoxychlor." Some approximate LD 50 dosage ratios (1,1-dianisylneopentane: "methoxychlor") are as follows: German cockroaches (contact), 1:2; milkweed bugs (contact), 4:1; webbing clothes moth and carpet beetle larvae (wool impregnation), each 2:1; mosquito larvae (A. aegypti), 4:1; houseflies (spray), 4:1.¹ The tremors and paralysis characteristic of DDT and "methoxychlor" are produced by the neopentane. It has also been observed that the Ellenville strain of DDT-resistant houseflies is markedly more resistant to this compound than are ordinary strains of flies.^{2,3}

The hypothesis of Martin and Wain,⁴ that DDT toxicity is caused by hydrogen chloride release, obviously fails to explain the effectiveness of the chlorine-free product. Lauger's lipoid-solubility hypothesis⁵ and a possible relationship between steroids and DDT-type compounds⁶ will be discussed in a later publication.

(1) Tests by the Wisconsin Alumni Research Foundation.

(2) Barber and Schmitt, N. J. Agr. Exp. Sta. Bull., 742 (1948); Barber, Starnes and Starnes, Soap and San. Chem., 24 [11] 120 (1948).

(3) We are greatly obliged to the staff of our Entomological Laboratory for certain of the biological tests reported above and to Mr. Ordway Starnes and the late Dr. George W. Barber of the Department of Entomology, Rutgers University, and N. J. Agr. Exp. Station for tests with resistant strains of flies.

(4) Martin and Wain, Nature, 154, 512 (1944).

(5) Lauger, Martin and Mueller, *Helv. Chim. Acta*, 27, 892 (1944).
(6) Lauger, Pulver, Montigel, Weismann and Wild, "Mechanism of Intoxication of DDT Insecticides in Insects and Warm-Blooded Animals." Lecture, Washington, D. C., July 31, 1945, Geigy Company Inc., New York, N. Y., 1946.

RESEARCH LABORATORIES

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RECEIVED FEBRUARY 20,	1950

CITRIC ACID FORMATION BY ASPERGILLUS NIGER THROUGH CONDENSATION OF 3C₂ MOIETIES

Sir:

Biogenesis of citric acid via condensation of oxalacetate and acetate (C_4 dicarboxylic acid + C_2) is a reasonably well-accepted hypothesis. The C_4 dicarboxylic acid is generally presumed to originate via the Wood-Werkman reaction (pyruvate and carbon dioxide), though now the C_2 condensation must also be considered.¹ The following experiments were intended to demonstrate the relative participation of the two modes of genesis of the C_4 moiety.

Radioactive citrate was produced from sucrose by washed Aspergillus niger submerged mycelium (200 mg. dry wt.) in the presence of 2 mg. of high specific activity methyl-C¹⁴-labeled acetate and carbon dioxide containing 19.2 atom % C¹³O₂. To the 38 mg. of citric acid produced in forty hours (at which time considerable unconsumed sucrose remained) carrier citric acid (350 mg.) was added; calcium citrate was isolated and purified by precipitation and twofold reprecipitation from hot solution.

The radioactive citric acid was converted to pentabromoacetone, which represents the noncarboxyl carbons of the citric acid. The noncarboxyl carbons were also obtained in the form of acetone, by dilute acid-dichromate oxidation of another portion of citric acid. The acetone was further degraded to iodoform and acetic acid; the acetic acid was then degraded² to methylamine and carbon dioxide. Specific activity measurements were made on barium carbonate obtained by wet combustion.

C¹³ AND C¹⁴ VALUES

	Fraction	Specific activity ^a	Ato	m % C13
1	Total citric acid	0.16	1.107	± 0.005°
2	Non-carboxyl carbons			
	Pentabromoacetone	.15	1.084	$\pm 0.002^{\circ}$
	Acetone	.15		
	Iodoform	.17		
	Acetic acid	.16		
	Methylamine	.15		
	Carbon dioxide	.17		
3	Carboxyl carbons			
	Primary carboxyls	.12	1.132	≠ 0.009°
	Secondary carboxyl	.16	1.090	$\pm 0.010^{\circ}$
4	CO2 in atmosphere			
	Initial	.00	19.2	± 0.1
	Final	.43	10.5	± 0.1

^a Counts/sec./mg. BaC¹⁴O₃ (measured on citrate diluted with carrier). ^b Measured as 4.3 counts/sec./mg. BaC¹⁴O₃, but calculated as if diluted same amount as the citrated. ^c Measurements made on citrate diluted with carrier, and its degradation products.

The mean C^{13} content of the atmospheric carbon dioxide (19.2 + 10.5/2 = 14.9 atom %)enables one to calculate that CO_2 -carbon from the atmosphere entered citrate to the extent of 1.3%of the total citrate carbon; if the Wood–Werkman reaction were entirely responsible for net citrate synthesis, the figure should be 16.7%. Unlabeled intracellular carbon dioxide from sucrose theoretically could also account for some net synthesis; we have been unable to conceive a definitive experiment on this point. On the other hand,

Foster, et al., Proc. Natl. Acad. Sci., U. S., 35, 663-672 (1949).
 Phares, to be published.