side (II): α-anomer (98%), m.p. 90–91°, $[\alpha]^{23}_{\mathrm{D}}$ +135° ($CHCl_3$); β-anomer (94%), m.p. 98–99°, $[\alpha]^{24}_{\mathrm{D}}$ +35° ($CHCl_3$). Found: (α), C, 49.5; H, 6.80; N, 5.07; (β), C, 49.7; H, 6.56; N, 4.69. Hydrolysis of II with 1% hydrochloric acid gave authentic 3-amino-3-deoxy-D-ribose hydrochloride.[7]

O-Deacetylation of either anomer of II, O-benzoylation and removal of the O-methyl group with hydrogen bromide in acetic acid[8] gave 48% of 2,5-di-O-benzoyl-3-acetamino-3-deoxy-α-D-ribofuranose, m.p. 153–154°, $[\alpha]^{25}_{\mathrm{D}}$ +108° (Pyr.). Found: C, 63.2; H, 5.89; N, 3.41. Acetylation with acetic anhydride–pyridine at 100° gave 98% of an anomeric mixture (III) of 1-O-acetyl-2,5-di-O-benzoyl-acetamino-3-deoxy-D-ribofuranosides, from which one anomer was obtained crystalline, m.p. 152–154°, $[\alpha]^{25}_{\mathrm{D}}$ +63° (pyr.). Found: C, 62.2; H, 5.31; N, 3.46.

Addition of titanium tetrachloride to a mixture of III, the chloromercury derivative[9] of 2-methylmercapto-6-dimethylaminopurine[10] and ethylene dichloride followed by a 20-hour reflux afforded a crude nucleoside. Raney nickel desulfurization and O-debenzoylation with methanolic sodium methoxide gave 6-dimethylamino-9-(3′-acetamino-3′-deoxy-β-D-ribofuranosyl)-purine (23% from III), m.p. 187–188°, which was identical in all respects with the N-acetyl derivative of I. Found: C, 49.8; H, 5.93; N, 25.2. Removal of the N-acetyl group with barium hydroxide gave 80% of I.

[8] H. G. Fletcher, Jr., THIS JOURNAL, **75**, 2624 (1953).

[9] B. R. Baker, J. P. Joseph and J. H. Williams, Paper IV of this series, *J. Org. Chem.*, in press.

[10] B. R. Baker, J. P. Joseph and R. E. Schaub, THIS JOURNAL, **75**, 2624 (1953).

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RECEIVED JUNE 30, 1954

THE STRUCTURE OF COLLAGEN

Sir:

A structure[1] has been deduced for that part of the collagen molecule which is responsible for the observed X-ray diffractions.[2–4] This structure is in agreement with all experimental facts known to the writer.

The sequence of residues is given by the formula $(RR'R'')_n$, where R″ represents a residue which is usually proline or hydroxyproline and R and R′ denote other types. The 3-residue group, RR′R″, has the bond structure indicated within the rectangle in the figure (in which R′ and R″ have been taken as glycine and hydroxyproline residues, respectively). The chain is coiled in a left-handed helix. The coördinates in the table have been computed, assuming: (1) 30 residues per 3 turns[4] and per 28.6 Å.; (2) Pauling–Corey bond angles and lengths in the polypeptide chain; (3) rectilinear N–H · · · O hydrogen bonds, of equal length; (4) planar C–CO–NH–C groups; (5) dimensions in the hydroxyproline ring like those in hydroxyproline itself.[5]

TABLE I

COÖRDINATES*

	x	y	
C_1	4.04	0.00	0.00
C_2	3.13	1.23	0.00
C_3	3.88	1.34	2.39
C_4	2.87	0.74	3.38
C_5	2.34	3.09	3.85
C_6	1.19	3.64	3.00
C_7	5.38	0.33	0.66
C_8	1.93	1.36	5.47
C_9	2.42	2.57	6.25
C_{10}	2.34	3.69	5.26
N_1	3.41	−1.12	0.72
N_2	3.16	1.87	1.21
N_3	2.17	1.64	4.04
O_1	2.46	1.57	−0.92
O_2	2.64	−0.48	3.37
O_3	1.39	4.00	1.83
O_4	3.82	2.36	6.64
$O_{1(3)}$	2.91	−0.18	7.66
H_1	3.13	−0.89	1.68
H_2	3.89	−0.29	−1.05
H_3	2.52	2.64	1.44
H_4	4.59	0.59	2.07
H_5	4.41	2.21	2.88
H_6	3.30	3.28	3.35
H_7	2.50	0.47	5.77
H_8	0.85	1.23	5.64
H_9	1.74	2.77	7.09
H_{10}	3.22	4.35	5.37
H_{11}	1.42	4.26	5.42
H_{12}	3.52	1.53	6.97

*Referred to a left-handed rectangular coördinate system, in Å.

The computed (not assumed) NHO hydrogen bond length is 2.83 Å. The hydroxyl oxygen of the hydroxyproline residue is 2.9 Å. from a car-

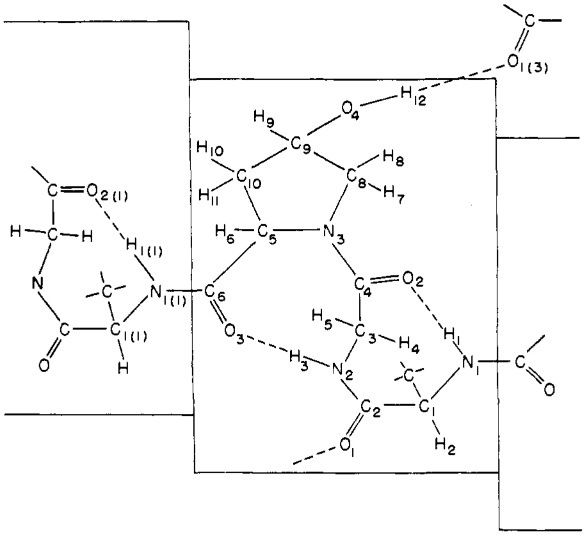

Fig. 1.—The bond structure in the proposed model for Collagen.

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[1] This structure was described briefly at the Pasadena Conference on the Structure of Proteins, Sept. 22, 1953.

[2] R. S. Bear, "Advances in Protein Chemistry," **7**, 69 (1952).

[3] C. Cohen and R. S. Bear, THIS JOURNAL, **75**, 2783 (1953).

[4] J. T. Edsall, *Science*, **119**, 302 (1954).

[5] J. Donohue and K. N. Trueblood, *Acta Cryst.*, **5**, 419 (1952).

bonyl oxygen in the next turn of the helix, indicating OHO hydrogen bonding. There are no unreasonably short distances between non-bonded atoms, provided R or R′ of each RR′R″ group is glycine. There are no large holes within the helix, although there appear to be suitable locations for some hydrogen-bonded water molecules, perhaps one per group of three residues.

Assuming[2] an average residue weight of 93 and close-packed helices 12.0 Å. apart, the computed density is 1.30 g./cc., or 1.38 if one molecule of bound water per three residues is assumed. The experimental *over-all* density of collagen has been reported as 1.35[2] and 1.41.[6]

The distribution of residues in the proposed structure will be discussed later.

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(6) C. D. Pomeroy and R. G. Mitton, *J. Soc. Leather Trades Chemists*, **35**, 360 (1951).

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RECEIVED JUNE 22, 1954

THE BICHLORIDE ION[1]

Sir:

The epimerization of *l*-menthyl *l*-*p*-toluenesulfinate in nitrobenzene is third order with a first-order dependence on the ester, hydrogen chloride, and chloride ion added as tetraethylammonium chloride. Hydrogen chloride alone, which in nitrobenzene is un-ionized,[2,3] has no effect on the ester at concentrations below 0.01 *M*. As the concentration of one catalyst is held constant and that of the other is increased, a point is reached at which no further increase in the rate of epimerization is achieved since proportional amounts of catalyst are removed as bichloride ion. From the results, the equilibrium constant in nitrobenzene at 24.96 ± 0.03° for the formation of the bichloride ion

$$Cl^- + H—Cl \rightleftarrows HCl_2^-$$

has been calculated to be 5×10^2 $(m./l.)^{-1}$. Essentially the same value for this equilibrium constant has been obtained by the use of the benzene- and *p*-anisolesulfinates. Actually, continued addition of hydrogen chloride at constant chloride ion concentration does lead to a very slight increase in the rate. From this it has been possible to calculate an activity for the bichloride ion as chloride donor of one twentieth that of the free chloride ion.

That the bichloride ion exists in these solutions is also apparent from the fact that 0.659 m./l. of tetraethylammonium chloride dissolves in nitrobenzene which is 0.633 *M* in hydrogen chloride, although the normal chloride is only very slightly soluble in pure nitrobenzene. The vapor pressure of hydrogen chloride over the nitrobenzene is greatly diminished on addition of the salt.

The hydrogen chloride stretching frequency[4] at 2703 cm.$^{-1}$ completely disappears from its saturated solution in nitrobenzene on addition of tetraethylammonium chloride and is replaced by continuous absorption ranging from approximately 1667 to 730 cm.$^{-1}$ of sufficient intensity to mask most of the nitrobenzene absorption.

Isolation of tetraethyl- and tetramethylammonium bichloride from nitrobenzene has been accomplished by cooling or, preferably, by precipitation with ether or petroleum ether. The product, which recrystallized poorly, analyzed as 85–90% bichloride and 2–12% normal chloride. Passage of dry hydrogen chloride over the impure tetramethylammonium bichloride resulted in a product containing 98.46% tetramethylammonium bichloride (*Anal.* Calcd. for $C_4H_{13}NCl_2$: Cl, 48.55; HCl, 24.96. Found: Cl, 47.47; HCl, 24.58) with a chloride to proton ratio of 1.99/1.00.

The interaction of hydrogen chloride with chloride ion is also illustrated in the reported synthesis[5] of a liquid tetraethylammonium chloride trihydrochloride and of tetramethylammonium bichloride by the passage of hydrogen chloride over the quaternary salts at 0°. Further, the solvolytic behavior of hydrogen chloride on reactive organic chlorides[6] has led to the postulation[7] of the existence of the bichloride ion as a kinetic entity in solution. From our observations on the stability of the bichloride ion, we conclude, for reasons to be presented in detail in a later paper, that in certain of these solvolytic reactions the bichloride ion cannot be free but must exist in a tight ion pair with the organic cation.

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(1) Sponsored by the Office of Naval Research.

(2) M. Hlasko and E. Michalski, *Roczniki Chem.*, **6**, 534 (1926); *Chem. Zentr.*, **98**, I, 2803 (1927).

(3) D. M. Murray-Rust, H. J. Hadow and H. Hartley, *J. Chem. Soc.*, 215 (1931).

(4) W. Gordy and P. C. Martin, *J. Chem. Phys.*, **7**, 99 (1939).

(5) F. Kaufler and E. Kunz, *Ber.*, **42**, 385, 2482 (1909).

(6) H. Meerwein and K. van Emster, *Ber.*, **55**, 2500 (1922); P. D. Bartlett and I. Pöckel, THIS JOURNAL, **60**, 1585 (1938); see also H. Hart and F. A. Cassis, *ibid.*, **76**, 1634 (1954); R. Leimu and P. Salomaa, *Acta Chem. Scand.*, **1**, 353 (1947); K. H. Meyer, *Ber.*, **41**, 2568 (1908).

(7) P. D. Bartlett, "Organic Chemistry, An Advanced Treatise," Vol. III, Henry Gilman, Editor, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 66.

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RECEIVED JUNE 14, 1954

TRANSPORT NUMBERS IN PURE FUSED SALTS[1]

Sir:

We believe we have devised the first practical method for measuring the transport numbers of the ions in pure fused salts. By means of a cell which is simple to construct and operate we have determined the transport numbers for molten lead chloride.

A Hittorf-type cell cannot be used for pure salts, since electrolysis causes a change in quantity, rather than concentration, of electrolyte in each compartment. This accumulation of salt is not observed, since it is free to flow back to the depleted compartment unless a restraining membrane is inserted.[2] This membrane must allow the ready passage of the ions carrying the current and, at the same time, resist the flow of the bulk of the liquid. We have found that by offering the liquid a much more accessible path by which to equalize the hy-

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(1) Work was performed in the Ames Laboratory of the Atomic Energy Commission.

(2) S. Karpachev and S. Palguev, *Zhur. Fiz. Khim.*, **23**, 942 (1949).