Evolution of nitrogen commenced at about 85°. Heating was continued until no more nitrogen was evolved; the solution was then neutralized with sodium hydroxide and evaporated to dryness when there remained as a residue about 1 g. of the sodium salt of (XI). This pulverized residue was gradually added to 3 g. of fused sodium hydroxide to which about 10% of water had been added, sufficient heat being used to just maintain fluidity in the reaction mixture. The melt was dissolved in about 500 cc. of water and carbon dioxide passed in when a crude form of (XII) precipitated as a dirty white amorphous material. This was collected, dissolved in warm sodium hydroxide solution, filtered, and rendered acid with hydrochloric acid. The milky liquid was now heated whereupon (XII) went into solution and the tarry matter coagulated. On filtering and cooling, the filtrate deposited (XII) as a white amorphous product which showed itself to have the qualitative properties of *p,p'*-diphenol.[5] Without further purification, the material showed a m. p. range of 267–271°, thus identifying it with the *p,p'*-diphenol, m. p. 272°.[5] As a further check, the diphenol so obtained was dissolved in 10 cc. of acetic anhydride and refluxed for two hours. The reaction product was then treated with water when crude (XIII) precipitated. This was recrystallized from dilute alcohol, and the short white needles thus obtained showed a m. p. of 160°. This corresponds with the m. p. (159–160°) as given in Beilstein.[6] In addition, another specimen of (X) prepared by another process[7] was treated similarly. It behaved in exactly the same manner as the (X) produced in the above synthesis, giving rise ultimately to (XII) and (XIII). Mixed m. p. on the two samples of (XII) and of (XIII) from the two specimens of (X) showed no depression.

Summary

1. The synthesis of the analog to sulfanilamide in the biphenyl series has been effected.
2. The reaction between *n*-acetoxenylamine and chlorosulfonic acid has been studied, the position of attack under the conditions employed has been determined, and conditions have been established for a 60% conversion to the *p*-(*p*-acetaminophenyl)-benzenesulfonyl chloride.
3. The following new compounds have been prepared and reported: (a) *p*-(*p*-acetaminophenyl)-benzenesulfonyl chloride, (b) *p*-(*p*-acetaminophenyl)-benzenesulfonamide, and (c) *p*-(*p*-aminophenyl)-benzenesulfonamide. The hydrochloride and sodium salt of (c) have also been prepared.

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[5] Beilstein, "Handbuch der organischen Chemie," fourth edition, Band VI, System No. 563, p. 991.

[6] *Ibid.*, p. 992.

[7] Shoppee, *J. Chem. Soc.*, 43 (1933).

PITTSBURGH, PENNA. RECEIVED JULY 31, 1940

[CONTRIBUTION FROM THE WILLIAM H. CHANDLER LABORATORY OF LEHIGH UNIVERSITY]

Optical Rotation of Aliphatic Acid Salts of Triethylenediamine-Cobaltic Hydroxide. Further Evidence for Ring Structure in Aliphatic Series

BY JAMES P. MCREYNOLDS AND JOHN R. WITMEYER

The use of a ring form in aliphatic compounds to explain certain well-known irregularities in properties, as developed by Smith[1] and amplified in terms of optical activity by Smith and McReynolds,[2] indicates that a qualitative prediction of the character of the curve showing molecular rotation as a function of chain length can be made for the aliphatic acid salts of an optically active strong base. The treatment would call for a different $\Delta[M]_D$ (change in molecular rotation upon the addition of one CH_2 group) between the propionate and the butyrate than between the acetate and the propionate since the butyrate would be the first ion in the series to contain the postulated ring. A further irregularity in $\Delta[M]_D$ should appear between butyrate and valerate since the valerate ring would be the first to contain an asymmetric carbon atom. After the valerate the $\Delta[M]_D$ values should again become regular since the only variable is in the length of the chain attached to the asymmetric atom of the ring.

Triethylenediamine-cobaltic hydroxide has been shown to be a strong base by Lamb and Yngve.[3] It should also be readily obtained in an optically active form.

Experimental

Preparation of Compounds.—Dextro-triethylenediamine-cobaltic bromide was prepared by the method of Werner.[4] From this compound dextro-triethylenediamine-cobaltic hydroxide was prepared by the method which Jörgensen[5] used to obtain the racemic form. The hydroxide was quite stable to racemization in solution at room temperature but racemized upon heating or long standing. The specific rotation $[\alpha]_D$ for a freshly prepared 1% solution was +173°, for a solution which had stood

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[1] Smith, THIS JOURNAL, **61**, 254, 1176 (1939); **62**, 1136 (1940).

[2] Smith and McReynolds, *ibid.*, **61**, 1963 (1939).

[3] Lamb and Yngve, *ibid.*, **43**, 2358 (1921).

[4] Werner, *Ber.*, **45**, 125–128 (1912).

[5] Jörgensen, *J. prakt. Chem.*, [2] **39**, 12 (1889).

for forty-eight hours +170° and for a solution prepared from the solid obtained by slow evaporation at room temperature +94°.

The aliphatic acid salt solutions were prepared by the addition of the calculated quantity of a standard water solution of the hydroxide to a standard absolute alcohol solution of the acid. The reference standards were sodium hydroxide and hydrochloric acid solutions, respectively. All of the acids used except acetic, heptylic and pelargonic had been redistilled to high purity.[6] The acetic acid was ordinary glacial acetic, the heptylic and pelargonic acids were of 99% or better purity.

Optical Rotation.—All readings were taken upon a Schmidt–Haensch polarimeter equipped with a three-field end-point device. The scale was calibrated to 0.01° and the readings were reproducible to ±0.01°. The source of illumination was a commercial type General Electric sodium arc such as is commonly used in street lighting. All solutions were prepared to contain a constant amount of the active triethylenediamine-cobaltic ion so that observed rotations were directly comparable to molecular rotations.

A. To 5.5 ml. of 0.526 *N* solution of *d*-[Co en$_3$](OH)$_3$ (0.23 g.) was added the calculated amount of the standard acid solution which had been previously made up to 10 ml. with alcohol. The whole solution was then made up to 25 ml. with water. Data for this series are given in Table I and as curve A of Fig. 1.

TABLE I

SOLUTIONS MADE UP TO CONTAIN 10 ML. OF ALCOHOL AND 15 ML. OF WATER

RCOO⁻, R	*N*	Ml.	α°_D +		g. salt/ 100 ml.	$[\alpha]^\circ_D$ +	$[M]^\circ_D$ +
1	0.819	3.52	2.08	2.08	1.59	131	545
2	.740	3.90	2.11	2.13	1.76	120	553
3	.622	4.64	2.12	2.13	1.92	111	555
4	.515	5.62	2.13	2.12	2.09	102	555
5	.452	6.40	2.16	2.17	2.24	97	566
6	.442	6.64	2.20	2.23	2.41	92	576

Values listed for α_D represent the rounded average of five independent readings in each case.

B. Since pelargonic acid and its salt were thrown out of solution by the added water, it was found necessary to vary the procedure. To 5.5 ml. of the standard hydroxide the calculated amount of alcoholic acid solution was added. The whole solution was made up to 25 ml. with alcohol. For purposes of comparison this procedure was carried out for the valerate, caproate, heptoate and pelargonate. Data for this series are listed in Table II and as curve B of Fig. 1.

TABLE II

SOLUTIONS MADE UP TO CONTAIN 19.5 ML. OF ALCOHOL AND 5.5 ML. OF WATER

RCOO⁻, R	*N*	Ml.	α°_D +		g. salt/ 100 ml.	$[\alpha]^\circ_D$ +	$[M]^\circ_D$ +
4	0.515	5.62	2.37		2.09	113	613
5	.452	6.40	2.38		2.24	106	617
6	.442	6.64	2.39		2.41	99	620
8	.356	8.12	2.41	2.41	2.76	88	627

Values listed for α_D represent the rounded average of five independent readings in each case.

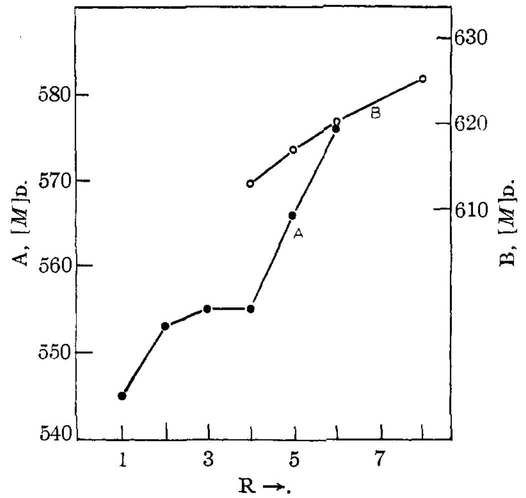

Fig. 1.—Molecular rotation as a function of chain length: ●, 10 ml. alcohol—15 ml. water (A); ○, 19.5 ml. alcohol—5.5 ml. water (B).

Conclusions

Curve A of Fig. 1 shows the characteristics already predicted for such a series of compounds. The effect of the ring closure superimposed upon the effect of an added CH$_2$ group results in a value of $\Delta[M]_D$ essentially equal to zero for the interval $R = 2$ to $R = 3$. The summation of the effects due to the appearance of an asymmetric atom and a further additional CH$_2$ group results in $\Delta[M]_D = 0$, for the interval $R = 3$ to $R = 4$. It will be noted that for all the intervals in which this treatment would indicate that the only variable is the effect of the added CH$_2$ group, the $\Delta[M]_D$ is positive and of fairly constant value.

Curve B of Fig. 1 need be discussed only in respect to the indicated fact that the pelargonic salt lies upon a normal extension of that part of the curve in which the only variable is the length of the chain attached to the asymmetric carbon atom of the ring.

The kinetic studies used by Smith[1] in developing the ring treatment to account for irregularities in properties in series of aliphatic compounds has indicated that the same treatment must be given to the anions of aliphatic acids as is given to the un-ionized compounds. The previous treatment of optical activity[2] was of necessity limited to un-ionized compounds but the present work lends further support to the premise that the ions must be treated by the same method as the un-ionized compounds.

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[6] The authors wish to thank Prof. Hilton A. Smith for supplying the redistilled acids.

It is necessary to offer some explanation for the fact that the rotation due to the constant concentration of the dextro-triethylenediamine cobaltic ion should not be the same in all the solutions examined. Since the cation comes from a highly ionized hydroxide it seems hardly plausible to attribute the differences to incomplete ionization of the salts. Any variable of this type should cause the curve to show a shape similar to that of the curve for the dissociation constants of the acids, that is, a decrease from propionate to butyrate and an increase from butyrate to valerate corresponding to the higher dissociation constant of butyric acid.

The most probable explanation for the effect of the optically inactive anions upon the active cation seems to be the formation of secondary sphere coördination complexes. Brintzinger and Osswald[7] report compounds of this type with triethylenediamine cobaltic ion and oxalate, phosphate and arsenate ion. Such a phenomenon would explain the effect of increasing chain length and simple ring closure. The additional effect due to the appearance of the asymmetric carbon from the valerate up the series is undoubtedly due to asymmetric induction of the type observed by Pfeiffer and Quehl[8] with zinc and cadmium complex salts of camphorsulfonic acid and α-bromcamphor-π-sulfonic acid.

Summary

1. Optically active triethylenediamine cobaltic hydroxide was prepared for the first time and its optical rotation and stability to racemization determined.

2. The optical rotations of the aliphatic acid salts: acetate, propionate, butyrate, valerate, caproate, heptoate and pelargonate, of triethylenediamine cobaltic hydroxide were determined.

3. The effect of chain length upon molecular rotation in this series was shown to be consistent with the postulate that a ring form is present in butyrate and larger ions.

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(7) Brintzinger and Osswald, *Z. anorg. allgem. Chem.*, **224**, 283–288; **226**, 33–37, 365–368 (1935).

(8) Pfeiffer and Quehl, *Ber.*, **64B**, 2667–2671 (1931); **65B**, 560–565 (1932).

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[CONTRIBUTION FROM INSTITUT DE CHIMIE, MONTPELLIER, FRANCE]

Molecular Refraction of Ions of *l*-Aspartic Acid

BY V. A. PERTZOFF

Molecular refraction has been extensively used for determining the atomic arrangement in organic compounds. In such investigations the atomic refractivities of Roth and Eisenlohr have been widely used. These refractivities, derived from the study of non-ionic compounds, are of little use in calculating the molecular refractions of organic ions, in particular of amino-acids, since ionization has a considerable effect on refraction. It will be shown presently that the molecular refraction of amino-acid salts may be calculated by using both the atomic refractivities of Roth and Eisenlohr and the refractivities of certain organic and inorganic ions.

Determinations of the refractive indices were carried out in a Pulfrich refractometer. Mercury and sodium lamps were used as a source of light. Refractivities of two ions of *l*-aspartic acid, representing two types of ionization, were studied: the monosodium salt in water and the di-sodium salt in 0.5 molar sodium hydroxide. Molecular refractions of the salts were calculated with the help of the Lorentz–Lorenz equation for mixtures. Data and results of calculations, ex-

TABLE I

MOLECULAR REFRACTION OF IONS OF *l*-ASPARTIC ACID

Ion	Concn., molar	Wave length, Å.	Refractive index ±0.00003	Molecular refraction	
				Lorentz eq.	Calcd., see text
		25.0°			
$^+A^- + Na^+$	3.0044	5893	1.40528	28.67	
		5461	1.40791	28.92	
		4358	1.41540	29.41	
	1.9914	5893	1.38304	28.88	28.83
		5461	1.38488	29.02	
		4358	1.39185	29.52	
	0.9977	5893	1.35855	28.87	28.83
$A^= + 2Na^+$	1.9943	5893	1.39115	30.24	
		5461	1.39300	30.36	
		4358	1.40031	30.93	
	0.9955	5893	1.36589	30.35	30.35
		5461	1.36756	30.45	
		4358	1.37416	31.01	
	0.4983	5893	1.35219	30.39	30.35