TABLE I
RAMAN SPECTRA OF FRESH AND AGED POTASSIUM CYANATE SOLUTION

Fresh Solution			Aged Solution		
$\Delta\nu$	I	ρ	$\Delta\nu$	I	ρ
..	..	...	1003	8	0.4
..	..	...	1033	8	.3
..	..	...	1064	10	.3
1225	4	0.6	..	..	...
1315	6	.6	..	..	...
2171	10	.3	..	..	...

In the spectrogram made on the third day, the lines observed for the fresh solution had disappeared and three new lines slightly above 1000 cm.$^{-1}$ had appeared. In addition, the solution which originally had been odorless had acquired the odor of ammonia. Observance of NH_4^+ lines was impossible because of the strong continuous background in that region.

Discussion

Goubeau[4] found a weak line at 857, a very weak, questionable line at 970 and a line of medium intensity at 2192 cm.$^{-1}$ in the Raman spectrum of solid potassium cyanate. In aqueous solution, he found 852, very weak, and 2185, weak. Pal and Sen Gupta[5] also reported frequencies at 838 and 2183, and in addition listed frequencies at 1229 and 1314, not found by Goubeau. These two frequencies were found also in the present investigation.

As Williams points out, these lines cannot be attributed to vibrations of the linear $O—C\equiv N^-$ group. The fact that Goubeau found lines at 1204 (weak) and 1307 (strong) for cyanic acid suggests the possibility that there may be some of this acid in the potassium cyanate solution. Another possibility is that mercury cyanate or silver cyanate may have been present as an impurity. Goubeau found lines at 1232 (weak) and 1302 (medium) for the former and at 1233 (weak) and 1297 (medium) for the latter. He attributed these frequencies to the doublet ν_1, 2 ν_2 (analogous to the resonance doublet in carbon dioxide) of the linear $O=C=N^-$ group.

Aqueous solutions of potassium carbonate and potassium bicarbonate have Raman frequencies at 1069 and 1035 cm.$^{-1}$, respectively.[6] Measurements of the Raman spectra of aqueous solutions of ammonium carbonate and ammonium bicarbonate, for which no data were found in the literature, gave 1020(6)0.1 and 1007(4)0.3, respectively. These data suggest the origins of the lines observed at 1003, 1033 and 1064 in the spectrum of the aged potassium cyanate solution.

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RECEIVED AUGUST 27, 1940

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[4] J. Goubeau, *Ber.*, **68**, 912 (1935).

[5] N. N. Pal and P. N. Sen Gupta, *Ind. J. Phys.*, **5**, 11 (1930).

[6] M. Magat, "Tables Annuelles de Constantes et Données Numériques, Effet Raman," Volume XII, Hermann & Cie., Paris, 1937.

Some Tertiary Amides of Adipic, Azelaic and Sebacic Acids

BY REYNOLD C. FUSON, JOHN W. ROBINSON, JR., AND LYELL C. BEHR

Tertiary amides have been studied but little and those of the higher acids scarcely at all. From the standpoint of solubility and basicity, this type of amide is of especial interest in connection with the theory of hydrogen bonding. Primary and secondary amides, being able to serve at once as donors and as acceptors, are associated in solution.[1] They have, accordingly, lower solubility in water than that to be expected for the monomeric form. Tertiary amides cannot associate through hydrogen bonding and hence do not share this abnormality.[2] Striking examples of these differences have been encountered with certain tertiary amides of adipic, azelaic and sebacic acids, prepared in connection with the synthesis of diketones by the Beis[3] method. The amides of this group are particularly interesting because solubility predictions based on structure place them near the borderline between so-called water-soluble and water-insoluble compounds.[4] That the primary and secondary amides fall in the latter group is evidence that they are associated.

The new amides were made by the interaction of acid chlorides with suitable secondary amines according to the general procedure of Maxim[5] and Montagne.[6] They proved to be water-soluble and were sufficiently basic to form hydrochlorides, chloroplatinates and chloroaurates.

Experimental

N,N,N',N'-Tetraethyladipamide was made from diethylamine and adipyl chloride. After three recrystallizations from low-boiling petroleum ether, it melted at 52.5–53.5°.

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[1] Meldrum and Turner, *J. Chem. Soc.*, **93**, 876 (1908); **97**, 1605, 1805 (1910); von Auwers, *Ber.*, **70**, 964 (1937).

[2] Chaplin and Hunter, *J. Chem. Soc.*, 1114 (1937); 1034 (1938).

[3] Beis, *Compt. rend.*, **137**, 575 (1903).

[4] Shriner and Fuson, "Systematic Identification of Organic Compounds," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., (1940, p. 10.

[5] Maxim, *Ann. chim.*, [10] **9**, 58 (1928).

[6] Montagne, *ibid.*, [10] **13**, 40 (1930).

Anal.[7] Calcd. for $C_{14}H_{28}O_2N_2$: N, 10.92. Found: N, 10.64.

This amide is soluble in water.

N,N,N′,N′-Tetramethylsebacamide crystallized from a mixture of low- and high-boiling petroleum ether. It formed glistening white plates which melted at 87–88° and were soluble in water and organic solvents.

Anal. Calcd. for $C_{14}H_{28}O_2N_2$: C, 65.57; H, 11.00; N, 10.89. Found: C, 65.21; H, 10.48; N, 10.91.

The amide formed a hygroscopic crystalline salt on treatment with dry hydrogen chloride; m. p. 122–126°. Chloroplatinic acid gave an orange-colored solid melting at 156.5–158°—presumably the chloroplatinate—which, like the hydrochloride, was difficult to purify. The **chloroaurate** crystallized from dilute alcohol in yellow plates melting at 158–158.5°.

Anal. Calcd. for $C_{14}H_{29}O_2N_2AuCl_4$: C, 28.18; H, 4.90; Au, 33.07. Found: C, 28.17; H, 4.91; Au, 32.94.

N,N,N′,N′-Tetraethylsebacamide did not solidify and was not very soluble in water. However, it dissolved readily in 10% hydrochloric acid and was reprecipitated from this solution by the addition of excess sodium hydroxide. The hydrochloride melted at about 0° and the chloroplatinate at 148.5–150°. The amide was identified by conversion to the **chloroaurate**. The latter was purified by repeated recrystallization from aqueous alcohol. It formed flaky yellow crystals melting at 130–131°.

Anal. Calcd. for $C_{18}H_{37}O_2N_2Cl_4Au$: C, 33.01; H, 5.71; Au, 30.22. Found: C, 32.76; H, 5.58; Au, 30.18.

N,N,N′,N′-Tetraethylazelamide resembled tetraethylsebacamide with respect to solubility in water, acids and bases. Likewise it failed to crystallize. The hydrochloride was an oil and the chloroplatinate a solid melting at 140–142°. A more satisfactory derivative was the **chloroaurate**. It separated from dilute alcohol as yellow crystals melting at 136.5–137°.

Anal. Calcd. for $C_{17}H_{35}O_2N_2Cl_4Au$: C, 31.93; H, 5.53; Au, 30.84. Found: C, 32.01; H, 5.48; Au, 30.75.

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(7) The analyses in this paper are microanalyses and were carried out by Mr. C. W. Beazley, Mr. L. G. Fauble and Miss Mary S. Kreger.

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RECEIVED NOVEMBER 7, 1940

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p-(*p*-Aminophenyl)-benzenesulfonamide and Derivatives

BY I. F. HALVERSTADT AND W. D. KUMLER

In view of the recent publication[1] by Van Meter, Bianculli and Lowy on the above subject it seems desirable to give an account of work we have completed on these compounds.

Before the above article appeared we had prepared *p*-(*p*-acetaminophenyl)-benzene sulfonyl chloride I, *p*-(*p*-acetaminophenyl)-benzenesulfonamide II and *p*-(*p*-aminophenyl)-benzenesulfonamide III and had sent the last two compounds together with *p*-(*p*-nitrophenyl)-benzenesulfonamide to Dr. L. A. Sweet of Parke, Davis and Company for pharmacological evaluation.

The compounds were prepared by the same series of reactions as described by the above authors and the yields were about the same except in case of the *p*-(*p*-aminophenyl)-benzenesulfonamide which was obtained in 85% yield compared with the reported yield of about 60%. Different methods of purification were used and the observed melting or decomposition points are higher than those reported. All melting points are corrected.

The crude damp I was dissolved in acetone, neutralized with sodium bicarbonate, filtered and the filtrate concentrated to precipitate yellow crystals of the compound.

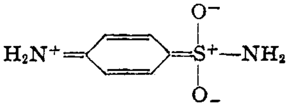
These crystals were extracted with ether using a Soxhlet apparatus and the product thus obtained from the ether did not melt on heating, but sintered at 180° and slowly decomposed at higher temperatures.

Gelatinous II was boiled with water, filtered, triturated with acetone, filtered, and recrystallized from 50% dioxane–water as white crystals, m. p. 295.0-296.5° with some decomposition.

To make III, pure II was refluxed with 12% hydrochloric acid, cooled with neutralizing to *p*H 6, filtered and washed. The precipitate was dissolved in acetone, decolorized with Norit and the solution concentrated at room temperature to give white, fine crystals of m. p. 259–260° and 266–267° with slight decomposition. The double m. p. is observed only if the rate of heating is slow in order to promote crystal formation in the molten compound at the first m. p.

To prove the position of the sulfonamide group *p*-(*p*-nitrophenyl)-benzenesulfonamide m. p. 225.5–227.0° was prepared by the method of Gabriel and Dambergris.[2] The nitro compound was then reduced to the amino compound with tin and a 10% solution of hydrochloric acid in 70% ethanol. The compound gave the same melting point as III and the same mixed melting point with III.

These compounds are part of a series we are making to investigate the effect of substituting different nuclei with the same resonance type as benzene, between the amino and sulfonamide groups.

A current theory in regard to the action of sulfanilamide is that the active agent is an oxidized form of the compound. The ease of oxidation would be correlated with the contribution made by resonating forms such as  and this should be related to the stability and consequently the reduction potentials of the corresponding *p*-quinones. An examination of such potentials suggested to us the preparation of the

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(1) Van Meter, Bianculli and Lowy, THIS JOURNAL, **62**, 3146 (1940)

(2) Gabriel and Dambergris, *Ber.*, **13**, 1408 (1880).