methyl groups showed the mixture to be composed of alcohol If (≅10%) and IIf (≅90%). The spectral properties of this mixture (pK_a 7.2) were as follows: uv max (H_2O, pH 1) 263.5 mμ (ε 12,700), (pH 7) 266.0, (pH 10) 270.5 (13,200) and 280.0.

C. At 25°.—The above sequence was repeated on alcohol If (1.0 g). The nmr hydrogen integral analysis of the pendent methyl groups of the crude product (0.9 g) showed it to contain alcohol If (≅10%), IIf (≅55–60%), and a third unidentified material XI (≅30–35%). The mixture had the following element analysis: C, 38.56; H, 4.52; Cl, 25.7; Cl^-, 18.6. These results suggest that the third component (XI) contains covalently bonded chlorine.

D. At −70°.—The above sequence was repeated on alcohol If (1.0 g). The nmr analysis of the isolated crude product (0.95 g) indicated it to be composed of If (60%) and IIf (40%).

Registry No.—Id, 16958-58-0; Ie, 16958-59-1; If, 16958-60-4; Ig, 16958-61-5; Ih, 16969-36-1; IId, 16958-64-8; IIe, 16958-65-9; IIf, 16958-62-6; IIg, 16958-63-7; IIh, 16958-66-0.

Acknowledgment.—The author is grateful to Mr. B. Page and Mr. R. Singer who helped with experimental work and to Mr. L. W. Ferrara and his staff for most of the analytical results. We wish to thank Dr. W. Simon of Simon Research Laboratory, Elgin, Ill., for his help in interpreting the nmr spectra, Dr. M. Hamer and Dr. R. P. Mariella for their stimulating discussions, and Dr. C. W. Huffman for his encouragement.

Self-Condensation of Anthranilic Acid

A. Chatterjee and M. Ganguly

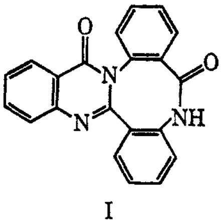
Department of Chemistry, University College of Science, Calcutta 9 India

Received March 12, 1968

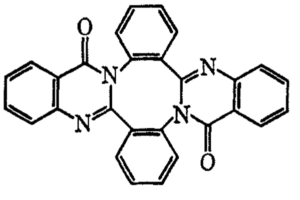
Anthranilic acid undergoes condensation with a wide variety of compounds[1,2] but its self-condensation reaction has not been reported as yet. The present communication concerns studies on the self-condensation products of anthranilic acid.

Heating anthranilic acid with phosphorous pentoxide in refluxing xylene furnished[3] a compound with mp 285° as the major product together with a minor compound (yield, 2%) with mp >360°.

On the basis of its molecular formula, $C_{21}H_{13}N_3O_2$ (M^+339), spectral data [uv λ_{max}^{EtOH} 280 and 306 mμ (log ε 4.53 and 4.30) and ir λ_{max}^{Nujol} 5.9, 6.05, and 6.3 μ], and, most importantly, its mode of formation, the major compound was assigned the structure I, a trimer of anthranilic acid. This is further supported by the nmr spectrum[4] of the compound which shows all of the 13 protons in its molecule appearing as a broad multiplet between δ 7.2 and 8.0.



I



II

The minor component, mp >360°, shows spectral properties (uv, ir, and nmr) very much similar to those of I. These observations conjointly with its molecular formula, $C_{28}H_{16}N_4O_2$ (M^+440), led us to propose structure II for the compound, a tetramer of anthranilic acid. The fact that II could also be obtained by heating I with additional anthranilic acid provided final confirmation for the assigned structure of the minor component.

Experimental Section[5]

Anthranilic acid (0.5 g) in dry xylene (8 ml) was refluxed for 3 hr over phosphorous pentoxide (1.5 g). The reaction mixture after cooling was poured over crushed ice and diluted with benzene. The benzene layer was then separated and extracted with three 40-ml portions of 6 *N* hydrochloric acid. The total acidic extract was subsequently basified with ammonia and treated with three 60-ml portions of chloroform. The chloroform extract was then washed and dried. The residue upon concentration of the chloroform extract was chromatographed over alumina. Benzene–chloroform (9:1) eluate gave II (yield, 0.01 g) which crystallized from methanol as granules: mp >360°; λ_{max}^{EtOH} 280 and 306 mμ (log ε 4.26 and 4.05); λ_{max}^{Nujol} 5.95, 6.25, 6.30, and 6.40 μ; nmr 16 H (broad multiplet) between δ 7.4 and 8.05.

Anal. Calcd for $C_{28}H_{16}N_4O_2$: C, 76.36; H, 3.64; N, 12.72; O, 7.27. Found: C, 76.20; H, 3.83; N, 12.66; O, 7.50.

The chloroform eluate on removal of solvent gave I (yield, 0.30 g) crystallized from a chloroform–acetone mixture, mp 285°.

Anal. Calcd for $C_{21}H_{13}N_3O_2$: C, 74.33; H, 3.83; N, 14.15; O, 9.43. Found: C, 74.20; H, 3.51; N, 14.20; O, 9.70.

Compound I (0.65 g) mixed with anthranilic acid (0.30 g) was refluxed in dry xylene (10 ml) for 3 hr. The reaction mixture was treated as above. The basic portion in chloroform extract after concentration was chromatographed and gave II (0.09 g) together with I (0.50 g).

Registry No.—I, 17-223-74-4; II, 17-223-75-5; anthranilic acid, 118-92-3.

Acknowledgments.—The authors wish to express their sincere thanks to Dr. B. C. Das, Institut de Chimie des Substances Naturelles, Gif-sur-Yvette, France, for determining the mass numbers, and to the Council of Scientific & Industrial Research, New Delhi, for financial assistance to one of them (M. G.).

---

[1] Wl. Baczynski and St. V. Niementowski, *Ber.*, **52**, 461 (1919).

[2] Br. Pawlewski, *ibid.*, **38**, 136 (1905).

[3] These compounds were also obtained for the first time during the synthesis of deoxyvasicinone from anthranilic acid and γ-aminobutyric acid. The major compound, designated as DVQ, was also assigned a tentative structure mainly on the basis of spectral evidence which in the present communication is being revised: A. Chatterjee and M. Ganguly, *Phytochemistry*, **7**, 307 (1968).

[4] The nmr spectra were taken in DMSO in a 60-Mc instrument with tetramethylsilane as the internal standard.

[5] Melting points were determined on a Kofler block and are uncorrected.