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A CRYSTALLINE MOLECULAR COMPLEX OF A CARBONIUM ION SALT

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In the course of a spectroscopic investigation of complexes of stable carbonium ions with aromatic compounds (1), we have isolated a 1:1 complex of phenothiazine and dibenzotropylium tetrafluoroborate. We believe this is the first example of a crystalline molecular complex (π-complex) of a carbonium ion salt.

Dibenzotropylium fluoroborate was prepared from 5H-dibenzo[a,d]-cyclohepten-5-ol (Aldrich Chemical Co.) and 45% aqueous fluoroboric acid in acetic anhydride. The deep red salt, m. p. 111°, dec., dissolves in acetonitrile, acetic anhydride or methylene chloride to give red solutions, but it is destroyed by atmospheric moisture, acetone, dimethylformamide, dimethyl sulfoxide and more basic solvents. The visible spectrum of the salt in acetonitrile (λ_{max} 502 mμ, logε 3.95; 530 mμ, logε 3.93) resembles that of the corresponding alcohol in concentrated H_2SO_4 (2). When aromatic compounds are added to solutions of the salt in methylene chloride, a color change is noted immediately; for example, solutions of pyrene and dibenzotropylium fluoroborate are dark green. We believe that these colors denote the formation of donor-acceptor complexes in solution, and the results of our spectroscopic investigation of these complexes, as well as those of other stable carbonium ions will be presented soon.

When a methylene chloride solution of an equimolar mixture of phenothiazine and dibenzotropylium fluoroborate is concentrated and petroleum ether is added, a deep purple, microcrystalline compound is precipitated, which may be recrystallized from methylene chloride. The purple compound, m.p. 215°, dec., is a 1:1 complex of the salt and phenothiazine. Anal. Calcd.for $C_{27}H_{20}BF_4NS$: C, 67.94; H, 4.19; N, 2.94. Found: C, 68.58; H, 4.71; N, 3.03.

The visible spectrum of the complex in acetonitrile shows the characteristic bands of the cation displaced to a maximum at 542 mμ (logε 3.75) (3), and new bands at 665 mμ (logε 2.91), 750 mμ (logε 2.92) and 830 mμ (logε 2.83). When the frequencies of new absorption bands of dibenzotropylium fluoroborate with aromatic donors are plotted against the frequencies of charge-transfer bands of complexes of the same donors with tropylium ion or chloranil, straight lines are obtained with approximately unit slope. Based on these graphs, the 830 mμ band of the complex appears in the expected region for a charge-transfer band of phenothiazine and the cation (4). Although NMR spectra of the dibenzotropylium cation and phenothiazine are clearly distinguishable, no conclusive information was obtained from the spectrum of the complex because of its relative insolubility in solvents in which it is stable.

The properties of the complex remain unchanged after several weeks in a closed vial at room temperature. Solutions of the complex in methylene chloride are deep purple, but the addition of water, alcohols or amines discharges the color immediately because of reaction with the carbonium ion. It is remarkable that the complex is not destroyed by adding it directly to water, in which it is insoluble. Unchanged phenothiazine was recovered by vacuum sublimation after the complex was destroyed by pyridine.

There is a significant contrast between the chemical properties of the complex described here and σ-complexes of carbonium ions and aromatic compounds (arenonium ions) (5), which are stable only at low temperatures and which decompose to alkylated aromatic compounds. We have found no evidence of alkylation products from the dibenzotropylium fluoroborate-phenothiazine complex, and consequently can provide no information about the role of π-complexes in alkylation reactions.

Further work on the structure and physical properties of the solid complex is in progress.

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