[CONTRIBUTION FROM THE CENTRAL EXPERIMENT STATION, U. S. BUREAU OF MINES]

Molecular Complexes with 2,4,7-Trinitrofluorenone[1]

BY MILTON ORCHIN[2] AND E. OSCAR WOOLFOLK[2]

Most aromatic polynuclear compounds form complexes with picric acid; and these complex compounds, inaccurately called picrates, have proved extremely useful for purposes of characterization and purification. Following the intensive investigation of Sudborough,[3] the 1,3,5-trinitrobenzene complexes have come into prominent use in recent years. The use of picric acid and trinitrobenzene for the characterization of high-molecular-weight polynuclear compounds suffers from the disadvantage that the hydrocarbon is relatively so insoluble that it often precipitates before the complex or is precipitated in excess on the complex compound. This is probably the case with the chrysene-trinitrobenzene complex which has been variously reported to melt at 192–194,[4] 184,[5] 188.5–189.5[6] and 186°.[3] The use of 2,7-dinitroanthraquinone[7] to form complexes with relatively insoluble compounds helps to circumvent this difficulty, but this quinone is so hard to prepare in good yield as to discourage its extensive use.

We have found that 2,4,7-trinitrofluorenone forms beautiful, stable complex compounds with a wide variety of aromatic compounds. 2,4,7-Trinitrofluorenone (abbreviated T.N.F.) is readily available since it can be prepared in good yield by the one-step nitration of fluorenone.[8] It is less soluble in organic solvents than picric acid or trinitrobenzene but more soluble than 2,7-dinitroanthraquinone. The molecular complexes between twenty-nine polynuclear compounds[9] and T.N.F. are described in Table I. These complexes are all formed in the molar ratio of 1:1. The complexes are all highly colored and generally melt sharply without decomposition. The favorable solubility of T.N.F., its ready availability and the stability of its complexes make T.N.F. particularly useful for the characterization of polynuclear compounds.

The molecular complexes with T.N.F. can also be used for purposes of purification since the hydrocarbon portion of the T.N.F. complex can be readily recovered by passing a solution of the complex over a column of activated alumina. The chromatographic separation of the components of the complex is facilitated because of the strong affinity of alumina for T.N.F. The components of the complex can also be separated by the catalytic or chemical reduction of the nitro groups of the T.N.F. The resulting amine is shaken out with acid, leaving the pure hydrocarbon.

The ultraviolet absorption spectra[10] of fluoranthene–T. N. F. complex and anthracene–T. N. F. complex are shown in Fig. 1 and 2. The spectra of the pure components and the calculated curve obtained by adding the molar extinction coefficients of the hydrocarbon and T. N. F. are also shown for comparison. The spectra of the complexes nearly equal the sum of the components and indicate that the T. N. F. complexes are completely dissociated in very dilute solution. Similar observations have been reported about other complex compounds.[11]

Several polynuclear compounds that were investigated did not form a homogeneous complex with T. N. F. These will be studied by means of melting-point–composition diagrams.

Experimental[12]

2,4,7-Trinitrofluorenone.—To a cold mixture of 200 cc. of red fuming nitric acid (sp. gr. 1.59) and 100 cc. of 96% sulfuric acid there was added portionwise, with shaking after each addition, 10 g. of pure powdered fluorenone. The solution was refluxed for two hours and poured onto ice. The precipitate was filtered and dried and consisted of 16.1 g., melting point 165–170°. After two recrystallizations from acetic acid, 12.8 g. (73%) of pure T.N.F. was obtained as a yellow powder, m. p. 175–176°.

Complex Compound Formation.—Equimolecular proportions of the pure T. N. F. and the hydrocarbon component were dissolved separately in absolute ethanol or ethanol–

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(3) Sudborough, *J. Chem. Soc.*, **109**, 1339 (1916).

(4) Sturrock and Lowe, *Can. J. Research*, **17B**, 71 (1939).

(5) Chuang, Huang and Ma, *Ber.*, **72B**, 713 (1939).

(6) Jones and Neuworth, THIS JOURNAL, **66**, 1497 (1944).

(7) The origin of the use of 2,7-dinitroanthraquinone for complex compound formation has been ascribed to E. Schmidt, *J. prakt. Chem.*, **9**, 241 (1874) (see Fieser, "Chemistry of Natural Products Related to Phenanthrene," Reinhold Publishing Corp., N. Y., 2d edition, 1937, page 19). However, some years earlier (1868), J. Fritzsche, working at St. Petersburg, Russia, described the preparation and complex compound forming properties of 2,7-dinitroanthraquinone. The German account of this work appeared under Fritzsche's name in *J. prakt. Chem.*, [1] **105**, 129 (1868). A long abstract of this work was also published in the obscure journal, *Z. Chem.*, 114 (1869). This latter journal was discontinued in 1871. More recently Börnstein, Schliewiensky and Georg Victor Szczesny-Heyl, *Ber.*, **59B**, 2812 (1926), improved the preparation of 2,7-dinitroanthraquinone and referred to this compound as "Fritzsche's reagent."

(8) Schmidt and Bauer, *Ber.*, **38**, 3758 (1905); Ray and Francis, *J. Org. Chem.*, **8**, 57 (1943).

(9) We wish to thank Prof. M. S. Newman of the Ohio State University for small samples of fourteen of these compounds.

(10) The spectra measurements were kindly carried out by Dr. R. A. Friedel and Miss Lois Lutz. Part of their report states: "In these complex spectra the regions of highest absorption of T. N. F. tend to mask weak fine structure which may be present in the hydrocarbon spectrum. Thus the weak anthracene band at 295 mμ is not detectable in the complex because of its proximity to the strong wide T. N. F. absorption band around 280 mμ."

(11) Halban and Zimpelman, *Z. physik. Chem.*, **117**, 461 (1925); Fieser and Newman, THIS JOURNAL, **57**, 1602 (1935); Hunter, Qureisky and Samuel, *J. Chem. Soc.*, 1576 (1936); Jones and Neuworth, ref. 6.

(12) All melting points are corrected.

TABLE I

Polynuclear component	Solvent	Appearance complex	Molecular formula of complex	M. p. complex (cor.), °C.	N Analyses,[a] % Found	Calcd.
Anthracene	Ethanol	Deep red prisms	$C_{27}H_{15}N_3O_7$	193.8–194.0	8.50	8.52
Fluorene	Ethanol	Yellow-orange needles	$C_{26}H_{15}N_3O_7$	179.0–179.4	8.50	8.74
Chrysene	Ethanol	Dull yellow needles	$C_{31}H_{17}N_3O_7$	247.8–249.0	7.87	7.73
Pyrene	Ethanol	Deep red prisms	$C_{29}H_{15}N_3O_7$	242 –243	8.23	8.12
Phenanthrene	Ethanol	Brilliant yellow needles	$C_{27}H_{15}N_3O_7$	196.4–197.2	8.52	8.52
Fluoranthene	Ethanol	Canary yellow needles	$C_{29}H_{15}N_3O_7$	215.4–216.0	8.17	8.12
1,2,3,4-Tetrahydroanthracene	Ethanol	Orange prisms	$C_{27}H_{19}N_3O_7$	182.4–182.8	8.35	8.45
Acenaphthene	Ethanol	Bright red prisms	$C_{25}H_{15}N_3O_7$	175.0–175.8	9.23	8.95
Carbazole	Ethanol	Brownish red needles	$C_{25}H_{14}N_4O_7$	173.4–174.4	11.62	11.62
1,2-Benzanthracene	Ethanol	Red needles	$C_{31}H_{17}N_3O_7$	223.6–224.0	7.58	7.73
1-Ethylpyrene[b]	Ethanol	Red needles	$C_{31}H_{19}N_3O_7$	186.6–187.6	7.73	7.70
6-Chloro-10-methyl-1,2-benzanthracene[b]	Ethanol	Pinkish red crystals	$C_{32}H_{18}N_3O_7Cl$	253 –254	6.98	7.10
7-Chloro-10-methyl-1,2-benzanthracene[b]	Ethanol	Red crystals	$C_{32}H_{18}N_3O_7Cl$	218.6–219.0	7.00	7.10
5-Methylchrysene[b]	Ethanol	Orange needles	$C_{32}H_{19}N_3O_7$	234.2–234.6	7.41	7.54
6-Methylchrysene[b]	Ethanol	Bright orange needles	$C_{32}H_{19}N_3O_7$	251 –252	7.31	7.54
5,6-Dimethylchrysene[b]	Ethanol	Light red needles	$C_{33}H_{21}N_3O_7$	205.4–205.8	7.30	7.35
5-Ethylchrysene[b]	Ethanol	Bright orange needles	$C_{33}H_{21}N_3O_7$	210.4–211.0	7.38	7.35
6-Ethylchrysene[b]	Ethanol	Red crystals	$C_{33}H_{21}N_3O_7$	215.4–216.8	6.98	7.35
Stilbene	Ethanol	Bright red prisms	$C_{27}H_{17}N_3O_7$	148.4–148.8	8.38	8.48
Perylene	EtOH-Bz	Black needles	$C_{33}H_{17}N_3O_7$	270 –271	7.12	7.41
Cholanthrene[b]	EtOH-Bz	Olive green needles	$C_{33}H_{19}N_3O_7$	245 –246	6.92	7.38
2-Phenylphenanthrene[b]	EtOH-Bz	Orange needles	$C_{33}H_{19}N_3O_7$	168.8–169.4	7.08	7.38
2-Phenylnaphthalene	EtOH-Bz	Yellow-orange needles	$C_{29}H_{17}N_3O_7$	169.5–170.5	8.09	8.02
1-Methylpyrene[b]	EtOH-Bz	Dull red needles	$C_{30}H_{17}N_3O_7$	229.6–230.6	7.90	7.91
2,2′-Dinaphthyl	EtOH-Bz	Orange-red needles	$C_{33}H_{19}N_3O_7$	170.6–171.0	7.23	7.37
Anthanthrene[c]	EtOH-Bz	Dark green needles	$C_{35}H_{17}N_3O_7$	268 –269	7.13	7.10
Picene[b]	Bz	Bright orange needles	$C_{35}H_{19}N_3O_7$	257.0–257.8	7.06	7.08
5-Methylpicene[b]	Bz	Reddish orange needles	$C_{36}H_{21}N_3O_7$	264 –265	6.89	6.92
13-Methylpicene[b]	Bz	Reddish orange needles	$C_{36}H_{21}N_3O_7$	235.0–235.2	6.79	6.92

[a] Analyses performed by Dr. T. S. Ma, University of Chicago. These were microanalyses by the Dumas method. [b] Sample furnished by M. S. Newman. [c] Orchin and Friedel, THIS JOURNAL, **68**, 573 (1946).

benzene and the two hot, nearly saturated solutions mixed. Compound formation was usually evidenced by the instantaneous formation of a deep color, and generally the complex precipitated immediately. The complex was filtered, dried, and its melting point determined. All the complexes were recrystallized once from absolute alcohol, alcohol–benzene, or benzene and the melting points of the recrystallized material recorded in Table I.

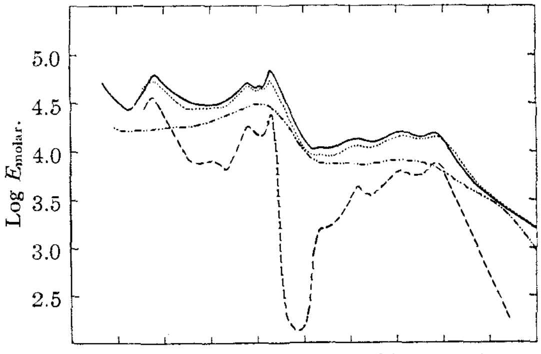

Fig. 1.—Ultraviolet absorption spectra: — — — — fluoranthene; —·—·—·— 2,4,7-trinitrofluorenone (T.N.F.); ....calculated spectrum for fluoranthene–T. N. F. complex; ————experimental spectrum for fluoranthene–T. N. F. complex.

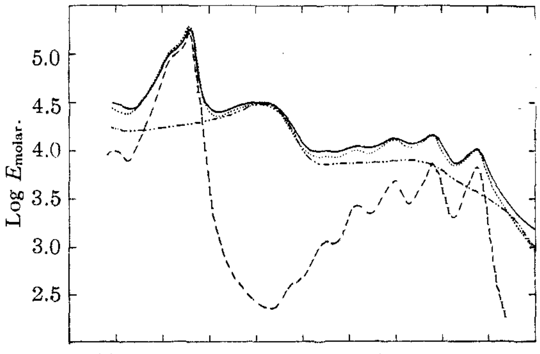

Fig. 2.—Ultraviolet absorption spectra: — — — — anthracene; —·—·—·— 2,4,7-trinitrofluorenone (T. N. F.); ....calculated spectrum for anthracene–T. N. F. complex; ————experimental spectrum for anthracene–T. N. F. complex.

Recovery of Anthracene from Anthracene–T. N. F. Complex

Chromatographic Separation.—A benzene solution of 0.6014 g. anthracene–T. N. F. complex was passed over a short column of activated alumina. The T. N. F. formed a dark ring at the top of the column which moved slowly down the column while the anthracene was readily eluted with benzene. The movement of the anthracene was followed by its fluorescence in ultraviolet light. When all the anthracene was eluted, the T. N. F. was still on the column. A quantitative recovery of anthracene was obtained by evaporation of the percolate.

Reduction with Tin and Hydrochloric Acid.—To a solution of 0.378 g. of anthracene–T. N. F. complex in 30 cc. of glacial acetic acid there was added 1 g. of tin and 5 cc. of concentrated hydrochloric acid. The mixture was refluxed twenty minutes, during which time all the tin went into solution and the mixture turned from a deep red to a very light red. The hot mixture was poured onto ice and the precipitate filtered and dried. The precipitate was dissolved in benzene, treated with norite, filtered and the filtrate concentrated. There was recovered 0.112 g. of anthracene, m. p. 213–215°.

Catalytic Reduction.—In a preliminary experiment 78.8 mg. of pure T. N. F. was reduced in ethanol solution with Adams platinum oxide catalyst at room conditions. At the end of forty-eight minutes, 9 moles of hydrogen per mole of T. N. F. was absorbed, and the compound continued to take up hydrogen slowly. An ethanol–benzene solution of 0.6128 g. of anthracene–T. N. F. complex was hydrogenated under similar conditions. At the end of 132 minutes, 8.2 moles of hydrogen per mole of compound was absorbed, at which point the reduction was interrupted. The reaction mixture was extracted with dilute hydrochloric acid and the organic layer separated, washed with water and dried. After treatment with norite, the solution gave, on concentration, 0.1590 g. of anthracene, m. p. 212–215°.

Summary

The molecular complexes between 2,4,7-trinitrofluorenone and twenty-nine aromatic polynuclear compounds are described. The hydrocarbon portion of these complexes can be readily recovered. The advantages of using the molecular complexes of 2,4,7-trinitrofluorenone for the characterization and purification of polynuclear aromatic compounds are indicated.

Pittsburgh, Penna. Received April 17, 1946

[Contribution from the Departments of Chemistry of the University of Washington and of Emmanuel Missionary College]

X-Ray Crystallographic Studies of Organic Sulfonates. II. The Hemihydrates of Certain Sodium 1-Alkane-sulfonates[1]

By L. H. Jensen[1a] and E. C. Lingafelter

In the first paper of this series[1b] we reported the unit cells and space groups of the quarterhydrates of sodium 1-octane-, 1-decane-, 1-tetradecane-, 1-hexadecane- and 1-octadecanesulfonate. We have now prepared satisfactory single crystals of the hemihydrates of sodium 1-dodecane-, 1-tetradecane-, 1-hexadecane- and 1-octadecanesulfonate. Sodium 1-octanesulfonate and 1-decanesulfonate have not formed hemihydrates under the conditions so far investigated.

Experimental

The compounds used were of the same batch as in the previous work.[1b] The crystals were grown by slow evaporation from mixtures of carbon tetrachloride and water at temperatures between *ca.* 30 and 50°. Sodium 1-dodecanesulfonate and 1-tetradecanesulfonate hemihydrates were also obtained from water alone. The crystals of all four substances are thin tabular parallel to {001} and elongated parallel to the *a* axis. The tablet is outlined by {010} and {12*l*} in most cases, rarely by {010}, {11*l*} and {12*l*} or by {010} and {11*l*}. (*l* index could not be obtained because of the extreme thinness of the crystals.)

The degree of hydration was measured by the weight loss in a vacuum drying experiment as described in the previous paper.[1b] The weight loss corresponded to the hemihydrate.

Data were obtained from oscillation and equi-inclination Weissenberg photographs using unfiltered copper radiation from a hot-cathode X-ray tube.

The constants of the monoclinic unit cells are given in Table I. In Table II the ratio a_0/b_0 is compared with the value obtained by measurement of the angle between the zone axes $\{\bar{2}10\}$ and $\{\overline{21}0\}$, using a microscope with a rotating stage.

Table I

Constants of the Unit Cell

Substance	a_0, kX.	b_0, kX.	c_0, kX.	β
$C_{12}H_{25}SO_3Na\cdot{}^1/_2H_2O$	6.86	15.40	29.40	96°30′
$C_{14}H_{29}SO_3Na\cdot{}^1/_2H_2O$	6.85	15.36	32.74	90°36′
$C_{16}H_{33}SO_3Na\cdot{}^1/_2H_2O$	6.86	15.35	36.36	94°23′
$C_{18}H_{37}SO_3Na\cdot{}^1/_2H_2O$	6.86	15.36	39.73	91°36′

Table II

Comparison of X-Ray and Goniometric Values

Substance	a_0/b_0, X-ray	a/b, goniometric
$C_{12}H_{25}SO_3Na\cdot{}^1/_2H_2O$	0.4455	0.4464
$C_{14}H_{29}SO_3Na\cdot{}^1/_2H_2O$	.4460	.4471
$C_{16}H_{33}SO_3Na\cdot{}^1/_2H_2O$	.4469	.4477
$C_{18}H_{37}SO_3Na\cdot{}^1/_2H_2O$	.4466	.4475

The densities were determined by the flotation method,[1b] using mixtures of 1,4-dioxane and car-

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[1] Presented at the Northwest Regional Meeting, Seattle, Washington, October 20, 1945.

[1a] At Emmanuel Missionary College, Berrien Springs, Michigan.

[1b] Jensen and Lingafelter, This Journal, **66**, 1946 (1944).