decomposed by the addition of sodium bisulfite. The resulting solution was concentrated *in vacuo* to a volume of 13 cc. The oxidation product appeared to be very soluble in the aqueous medium. However, extraction with three 30-cc. portions of chloroform yielded a white crystalline product melting at 137–141°. Recrystallization from benzene yielded the pure diester acid melting at 147–148°.

Anal. Calcd. for $C_{11}H_{17}O_7N$: C, 47.99; H, 6.23; N, 5.09; neut. equiv., 275. Found: C, 47.96; H, 6.21; N, 4.73; neut. equiv., 277.

DL-**Aspartic Acid.**—The acid diester was hydrolyzed by refluxing with concentrated hydrochloric acid for a period of four hours. After the removal of the excess hydrochloric acid *in vacuo* and neutralization until just acid to methyl red, the aspartic acid was isolated as blue copper salt. The DL-aspartic acid was recovered as described by Dunn and Fox[7] and melted with decomposition at 300°.

(7) M. S. Dunn and S. W. Fox, *J. Biol. Chem.*, **101**, 493 (1933).

CHEMICAL LABORATORIES
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Complexing of Pyridine with Phenol and Other Acids in Benzene Solution[1]

BY C. GARDNER SWAIN AND JOHN F. BROWN, JR.

The complexing of pyridine with phenol, *p*-nitrophenol, 2,4-dinitrophenol, benzoic acid and 2-hydroxypyridine has been studied in benzene solution at 25° by a dynamic vapor pressure method. This supplements cryoscopic and kinetic data previously reported.[2] In solutions of pyridine and phenol, the data indicate the presence of 1:1 and 1:2 pyridine–phenol complexes, in agreement with the results of a freezing-point study on the pyridine–phenol system.[3] The following equilibria appear to be present.

$$2C_6H_5OH \rightleftharpoons (C_6H_5OH)_2$$

(from the literature[4]) $K_x = 0.57\ M^{-1}$

$$C_5H_5N + C_6H_5OH \rightleftharpoons C_5H_5N\cdot C_6H_5OH$$

$K_y = 18.4\ M^{-1}$

$$C_5H_5N + 2C_6H_5OH \rightleftharpoons C_5H_5N\cdot 2C_6H_5OH$$

$K_z = 109\ M^{-2}$

The complexing of pyridine with several other acidic species was examined briefly, and the equilibrium constants for the formation of 1:1 pyridine–acid complexes are estimated in Table I.

TABLE I

THE COMPLEXING OF PYRIDINE WITH ACIDS IN BENZENE AT 25°

Acid	Total acid, *M*	Total pyridine, *M*	Free pyridine, *M*	K_y, M^{-1}
p-Nitrophenol	0.0482	0.0396	0.0120	110
2,4-Dinitrophenol	.102	.00989	.00915	0.8
Benzoic acid[a]	.100	.0495	.0197	210
2-Hydroxypyridine	.100	.0099	.0104	0.0

[a] K_y based upon monomeric benzoic acid. The dimerization constant of the benzoic acid was calculated from literature data[5] to be 617 M^{-1}.

(1) For more complete experimental data see J. F. Brown, Jr., Ph.D. Thesis, M.I.T., July, 1950, pp. 178–183.

(2) C. G. Swain and R. W. Eddy, THIS JOURNAL, **70**, 2993 (1948).

(3) A. Bramley, *J. Chem. Soc.*, **109**, 469 (1916).

(4) E. N. Lassettre and R. G. Dickinson, THIS JOURNAL, **61**, 54 (1939).

(5) F. T. Wall and F. W. Banes, *ibid.*, **67**, 898 (1945).

Experimental

The complexing between pyridine and various acidic species in benzene solution was studied by slowly passing a fixed volume (about 4 liters) of dry, benzene-saturated air through 25 ml. of a benzene solution of pyridine and the acid in question, and then through 10 ml. of 0.10 *M* hydrochloric acid. This resulted in the transfer of about 2% of the free pyridine in the benzene solution to the aqueous acid. The latter was then boiled to expel traces of benzene, cooled, diluted to 25 ml. with 0.10 *M* hydrochloric acid, and examined in a spectrophotometer in the region 250–275 mμ to determine the pyridine concentration.

In some of the determinations where phenol was the acid, appreciable amounts of it were also carried over, and the observed extinction had to be corrected for light absorption by phenol. To do this, the phenol concentrations were determined from the extinction at 275 mμ, where there was negligible absorption by pyridinium ion.

Similar runs on solutions of pyridine alone in benzene showed that the amount of pyridine vaporized by the air stream and transferred to the aqueous acid was directly proportional to the pyridine concentration of the benzene solution; hence, knowing the amount of pyridine transferred to the aqueous acid made it possible to calculate the pyridine concentration of the benzene solution.

In calculating the values of K_y and K_z from the association measurements, a graphical method was used. Taking the results of any one association measurement, various values of the concentration of the 1:1 complex were assumed, and for each assumed value a pair of values of K_y and K_z was determined. Plotting these one against the other gave a curve on a plot of K_y *vs.* K_z. From the other association measurements other curves were calculated, and their intersection gave the desired solution for K_y and K_z, with a precision of ± 2%.

From K_x, K_y and K_z, the amounts of free phenol and free pyridine in each solution in Table II were calculated by a method of successive approximations.

TABLE II

THE COMPLEXING OF PYRIDINE AND PHENOL IN BENZENE AT 25°

Total phenol, *M*	Total pyridine, *M*	Free phenol (calcd.)	Free pyridine (calcd.)	Free pyridine (found)
0.200	0.0099	0.159	0.00148	0.00150
.100	.0099	.083	.00302	.00303
.050	.0099	.042	.00502	.00500
.209	.103	.096	.0274	.0276
.104	.103	.042	.0526	.0528

DEPARTMENT OF CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE 39, MASSACHUSETTS RECEIVED JULY 27, 1951

NEW COMPOUNDS

Preparation of 5-Nitro-2-chlorothiophene

5-Nitro-2-chlorothiophene was prepared from 2-chlorothiophene by a modification of the method of Babasinian.[1]

An ice-cold mixture of 50 g. of fuming nitric acid (sp. gr. 1.51) and 100 ml. of acetic anhydride was added dropwise over a period of 2.5 hours to a vigorously-stirred mixture of 50 g. of 2-chlorothiophene and 100 ml. of acetic anhydride in a one-liter flask cooled by an ice–salt mixture so that the temperature did not rise above 0°. An orange-colored precipitate formed. Stirring was continued an additional hour. The flask was then packed in an ice–salt mixture and allowed to stand in an ice-box for 24 hours. The mixture was then poured with stirring onto 400 g. of crushed ice. The yellowish-red oil was separated, dissolved in 500 ml. of petroleum ether, washed several times with sodium bicarbonate solution and with water, and decolorized with

(1) V. S. Babasinian, THIS JOURNAL, **57**, 1763 (1935).

charcoal. There remained after distillation of the solvent 39.5 g. (57%) of red oil which was purified by fractional distillation using a glass helices packed column. The pale yellow product distilled at 141–143° at 50 mm. pressure. A second preparation was purified by sublimation at 16–18 mm. pressure, using a Dry Ice condenser and an oil-bath temperature of 80–85°. Further purification by recrystallization from petroleum ether at −20° gave white needles which melted at 23–24° to form a pale yellow oil.

Anal. Calcd. for $C_4H_2ClNO_2S$: S, 19.60. Found: S, 19.43.

5-Nitro-2-chlorothiophene is very soluble in benzene, methanol, ethanol and ether, slightly soluble in petroleum ether, and is insoluble in water. It penetrates the skin rapidly, producing a painful burning sensation. It could not be converted to 5-nitro-2-cyanothiophene by the method which Dann[2] used with 5-nitro-2-iodothiophene.

The authors wish to express their appreciation to the Research Corporation for financial support of this work.

(2) O. Dann, *Ber.*, **76B**, 419 (1943).

DEPARTMENT OF CHEMISTRY
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RECEIVED JANUARY 31, 1952

Some Coumarin Derivatives

Some years ago a number of coumarin derivatives were made for testing against schistosomes.[1] Samples have also been furnished for a study of fluorescence.[2] Four of these compounds do not appear to have been described previously.

7-*n*-Propoxycoumarin-3-carboxylic acid.—Umbelliferone-3-ethylcarboxylate was alkylated with *n*-propyl iodide and potassium hydroxide (1 mol each) in methanol. Most of the solvent was evaporated and the residue was saponified with aqueous alkali. On acidification the product separated as a light-colored powder. It was crystallized from aqueous acetone and from glacial acetic acid, forming pale yellowish prisms; m.p. 199–200°.

Anal. Calcd. for $C_{13}H_{12}O_5$: C, 62.9; H, 4.9. Found: C, 62.8; H, 4.8.

7-*n*-Propoxycoumarin.—The above acid was decarboxylated by heating at 240° with copper powder. Crystallized from ether–hexane mixtures it formed light yellow needles melting at 62.5–63°.

Anal. Calcd. for $C_{12}H_{12}O_3$: C, 70.6; H, 5.9. Found: C, 70.8; H, 5.9.

6,7-Dimethoxycoumarin-3-ethylcarboxylate.—Five grams of ethyl malonate and 5.5 g. of 2-hydroxy-4,5-dimethoxybenzaldehyde[3] were dissolved in 30 cc. of absolute ethanol. A few drops of glacial acetic acid and 0.5 cc. of piperidine were added and the solution was refluxed two hours: solid began to separate after ten minutes. The product, crystallized from ethanol, formed pale yellow needles and weighed 8 g. It melted at 197–197.5°.

Anal. Calcd. for $C_{14}H_{14}O_6$: C, 60.4; H, 5.1. Found: C, 60.3; H, 4.9.

The condensation can also be accomplished without the use of solvent but the product is less easily handled.

6,7-Dimethoxycoumarin-3-carboxylic Acid.—The ethyl ester (14.5 g.) was saponified with alcoholic potassium hydroxide in an inert atmosphere. On dilution with water and acidification the acid precipitated. After recrystallization from 500 cc. of glacial acid there was obtained 10 g. of pale yellow needles melting at 252–252.5° (dec.). (If heated too slowly the compound melts lower.)

Anal. Calcd. for $C_{12}H_{10}O_6$: C, 57.6; H, 4.0. Found: C, 57.6; H, 4.3.

Melting points below 220° are corrected. The analyses were performed by Mr. Samuel W. Blackman.

(1) Testing was by Dr. Maxwell Schubert of the New York University College of Medicine.

(2) R. H. Goodwin and F. Kavanagh, *Arch. Bioch.*, **27**, 152 (1950).

(3) F. S. H. Head and A. Robertson, *J. Chem. Soc.*, 2434 (1930).

THE WELLCOME RESEARCH LABORATORIES
TUCKAHOE 7, NEW YORK RICHARD BALTZLY

RECEIVED JANUARY 21, 1952

COMMUNICATIONS TO THE EDITOR

MECHANISM OF MOLECULAR COMPLEX FORMATION BETWEEN AROMATIC AMINES AND NITROHYDROCARBONS

Sir:

In a recent paper by Landauer and McConnell,[1] the formation and color of aniline–polynitrobenzene complexes is ascribed to an acid-base interaction, in the Lewis sense. Mulliken[2] has given a general quantum-mechanical treatment for the interaction between the π-electrons of a benzene ring and the acceptor orbitals of another molecule. Nakamoto[3] has suggested that aromatic molecular complexes are formed by the interaction of the π electrons of neighboring benzene rings.

A direct observation has been made[4] of a relatively strong bond between an oxygen atom of a nitro group and a carbon atom of an adjacent benzene ring in crystalline *p*-nitroaniline, which forms a self complex. This bond, of length 2.66 Å., is normal to the plane of the benzene ring to within 1°, and hence may well be due to a π-electron interaction of the Mulliken type. By measurement of the anomalous thermal expansion in *p*-nitroaniline, McKeown, Ubbelohde and Woodward[5] have shown by extrapolation that at absolute zero this bond might contract to 2.40 Å., corresponding to ionic contact between the carbon and the oxygen atom. The absence of self-complex formation in crystalline *p*-dinitrobenzene[6] shows that the π electrons require the activating influence of a suitable substituent in the aromatic ring before acting as donor.

These data lend support to the following mechanism for complex formation between *o*- and *p*-directing substituted aromatic hydrocarbons and nitrohydrocarbons. The attraction is of a Lewis acid–base nature, between the donated π electrons of the activated benzene ring and the accepting orbitals of a nitro group, thus forming a carbon–

(1) J. Landauer and H. McConnell, THIS JOURNAL, **74**, 1221 (1952).
(2) R. S. Mulliken, *ibid.*, **74**, 811 (1952).
(3) K. Nakamoto, *ibid.*, **74**, 1739 (1952).
(4) S. C. Abrahams and J. M. Robertson, *Acta Cryst.*, **1**, 252 (1948).
(5) P. J. A. McKeown, A. R. Ubbelohde and I. Woodward, *ibid.*, **4**, 391 (1951).
(6) S. C. Abrahams, *ibid.*, **3**, 194 (1950).