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.

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

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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).

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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 J. Woodward, *ibid.*, **4**, 391 (1951).
(6) S. C. Abrahams, *ibid.*, **3**, 194 (1950).