[CONTRIBUTION FROM SOCONY-VACUUM LABORATORIES, A DIVISION OF SOCONY-VACUUM OIL CO., INC., RESEARCH AND DEVELOPMENT DEPARTMENT]

Physical Properties of 2-Acetylthiophene

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Manufacture of 2-acetylthiophene began recently. At once the compound was widely investigated as an intermediate in the preparation of many compounds, especially pharmaceuticals. An examination of the literature indicated that only a few of the physical properties of 2-acetylthiophene had been determined. In the belief that further data would be of general value, this study on purified (99.9 + mole per cent.) 2-acetylthiophene has been made.

Purification of 2-Acetylthiophene.—Crude 2-acetylthiophene was withdrawn from the pilot unit and distilled in a column having about ten theoretical plates. From the materials distilling on a plateau at 101° (uncor.) at 18 mm., 25% by volume was taken as a distillation middle fraction. This material was pale yellow and was shown by the freezing point measurements which are described below to be 99.82 mole per cent pure. A portion of it (1400 g.) was recrystallized four times from the melt. Generous rejections were made so that only one-sixth of the 2-acetylthiophene survived the purification procedure. Supercooling was evident during the chilling. The fractions were seeded at about 10° each time and the crystals were grown while the container was cooled in an ice–water-bath. The material that had been recrystallized four times was faintly colored. It was used for the determination of the physical properties which are summarized in Table I.

TABLE I

PHYSICAL PROPERTIES OF 2-ACETYLTHIOPHENE

Freezing point, °C.	10.45
Boiling point at 760 mm., °C.	213.9
Change in b. p. with pressure °C./mm.	0.055
Refractive index, $n^{20}\mathrm{D}$	1.5667
$n^{20}\mathrm{E}$	1.5727
$n^{20}\mathrm{G}$	1.6017
$(\Delta n_\mathrm{D}/\Delta t)$	−0.00049
Density, g./ml. at 20°	1.1709
$(\Delta d_4/\Delta t)$	−0.00097
Viscosity at 30°, centipoises	2.32
Surface tension at 30°, dynes/cm.	44.5
Solubility	
g. 2-acetylthiophene/100 g. water at 30°	1.4
g. water/100 g. 2-acetylthiophene at 30°	2.4

The data in the literature give the following values of physical properties: b. p. at 760 mm., 213.5,[2] 213,[3] 212–213,[4] 214,[5] 213–214,[10] 213.5–214.5,[11] 200–215°[12]; b. p. at 13 mm., 91–92,[7] 94.5–96.5[8]; b. p. at 19 mm. 101[9]; b. p. at 9 mm. 89–91[13]; m. p. below −15°,[2] 9°[6]; refractive index, n_D at 20°, 1.5669 (calcd. from n_He at 21.8°),[9] 1.566[13]; density at 20°, g./ml. 1.171 (calcd. from value at 24°),[2] 1.1696 (calcd. from value at 21.8),[9] 1.168.[13]

Experimental

Freezing Point.—The sample was placed in a vacuum-jacketed tube immersed in a cooling bath of ice-water. A vertical dasher was used for stirring and the time–temperature cooling curve was measured. Temperature measurements were made with a copper–constantan thermocouple made from selected wire and calibrated at the freezing point of mercury and condensation temperature of steam relative to a junction held at the ice point. The sample was seeded as soon as the temperature dropped below 10.4°. The freezing point of the purified material was 10.425°. The method of Glasgow, Streiff and Rossini[1] was used to calculate that the 100% material would freeze at 10.45°. The distillation middle fraction froze at 10.37°.

Freezing points of two mixtures of 2-acetylthiophene and thiophene were obtained. The cooling curves were concave downward.

Moles thiophene (N_B)	0.0265	0.0636
Moles 2-acetylthiophene (N_A)	.9735	.9364
Freezing point lowering (ΔT)	1.18°	2.84°
$N_\mathrm{B}/\Delta T$	0.0224	0.0224
log $N_\mathrm{A}/\Delta T$	.988	1.005

From these data the purities were calculated from the relationship $N_\mathrm{B} = 0.0224\ \Delta T$ and the distillation middle fraction found to be 99.82 mole per cent. pure ($\Delta T = 0.08°$) and the purified material 99.94 mole per cent. pure ($\Delta T = 0.025°$).

The heat of fusion was calculated to be 28.5 cal./g. by the relationship $\Delta H_\mathrm{f} = 2.3026\,RT_0^2J/M$ where J is the limit of $\log_{10}N_\mathrm{A}/\Delta T$ as N_A approaches one and $R = 1.986$; $T_0 = 283.61$; M 126.17; J 0.977.

Boiling Point.—A Cottrell type apparatus was used, the temperature being measured relative to the freezing point of a sample of tin certified by the National Bureau of Standards to freeze at 231.90°. A value of 213.62° at 755.2 mm. was observed and corrected by the pressure variation described below to give 213.9° at 760.0 mm.

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(2) Peter, *Ber.*, **17**, 2643 (1884); **18**, 537 (1885).

(3) Biedermann, *ibid.*, **19**, 636 (1886).

(4) Volhard and Thiele, *Ann.*, **267**, 172 (1892).

(5) Nahke, *Ber.*, **30**, 2040 (1897).

(6) Voerman, *Rec. trav. chim.*, **26**, 293 (1907).

(7) Steinkopf and Bauermeister, *Ann.*, **403**, 50 (1914).

(8) Steinkopf, *ibid.*, **413**, 343 (1917).

(9) Auwers and Kohlhaas, *J. prakt. Chem.*, **108**, 321 (1924).

(10) Stadnikoff and Rakowsky, *Ber.*, **61**, 268 (1928).

(11) Stadnikoff and Goldfarb, *ibid.*, **61**, 2341 (1928).

(12) Goldfarb, *J. Russ. Phys.-Chem. Soc.*, **62**, 1073 (1930).

(13) Johnson and May, "Organic Syntheses," John Wiley & Sons, Inc., New York, N. Y., 1943, Coll. Vol. II, p. 8.

(1) Glasgow, Streiff and Rossini, *J. Research Natl. Bur. Standards*, **35**, 355 (1945).

The rate of change of the boiling point with pressure was determined by comparison with the boiling point of water over the range 709–807 mm. The two ebulliometers were connected to a large ballast tank in a closed system. Pressure measurements were made relative to atmospheric pressure with a manometer filled with 2-acetylthiophene. With the hot junction in condensing 2-acetylthiophene and the cold junction in condensing steam the value of the e. m. f. was found to change at the rate of 0.00121 mv./mm. near 760 mm. pressure. Use was made of the relation

$$\mathrm{d}(e_B - e_A)/\mathrm{d}p = (\mathrm{d}e_B/\mathrm{d}t_B)\cdot(\mathrm{d}t_B/\mathrm{d}p) - (\mathrm{d}e_A/\mathrm{d}t_A)\cdot(\mathrm{d}t_A/\mathrm{d}p)$$

where A represents water and B 2-acetylthiophene. $\mathrm{d}t_A/\mathrm{d}p$ was 0.036858,[14] $\mathrm{d}e_A/\mathrm{d}t$ 0.0468 mv./°C. near 100.0°, $\mathrm{d}e_B/\mathrm{d}t$ 0.0538 mv./°C. near 213.9°.[15] From the equation $\mathrm{d}t_B/\mathrm{d}p$ was 0.0546°/mm.

The heat of evaporation of 2-acetylthiophene at the normal boiling point was calculated to be 90 cal./g. by $\Delta H_v = T\Delta V(\mathrm{d}p/\mathrm{d}t)/M$ in which ΔV is the difference between the liquid and vapor volumes at the boiling point. The liquid volume was extrapolated from low temperature density data and the vapor volume was calculated from the perfect gas law. The perfect gas law gives volumes which are too high, often about 5%, so that the result is uncertain to this extent.

Refractive Index.—The determinations were made with a Bausch and Lomb precision refractometer calibrated at each temperature and wave length with toluene certified as to its refractive index by the National Bureau of Standards. Measurements were made with the sodium D doublet (yellow) and for the mercury G (blue) and E (green) lines. The values for the hydrogen F and C lines and for ∞ were calculated to be 1.5851, 1.5601 and 1.5378, respectively, at 20° from the formula

$$(1/\phi)_\lambda = 3.06259 - 0.0061002 \times 10^{28}(\nu^2_\lambda - \nu^2_D) - 0.0000336 \times 10^{56}(\nu^2_\lambda - \nu^2_D)^2$$

where $(1/\phi)_\lambda = (n^2_\lambda + 2)/(n^2 - 1)$ and ν was the frequency of the light of wave length λ. This is a new interpolation formula closely similar to that discussed by Bauer.[16] The formula is designed for use with high dispersion materials and reproduces the toluene 20° values to 2 parts in 100,000 when the appropriate constants are used.

Density.—A density balance method similar to that described by Forziati, Mair and Rossini[17] was used. The scale of the balance was extended by adding an additional counterpoise. The sample was held at a constant but not predetermined temperature near that of the room by an oil-bath contained in a vacuum jacket. Densities at round values of temperature were calculated from the temperature variation of density, the measurement of which is described below. The bob was suspended by a blacked platinum wire of 0.125 mm. diameter. Small corrections were made for errors in notch positions and chain weight and for the surface tension effects of the various liquids. Water was used as the calibration liquid. The calibration was checked with *n*-heptane. The observed density at 23.90° was 1.1671.

The change in density with temperature was found to be −0.000974 g./ml./°C. The measurements were made with a 2 ml. dilatometer at 0, 17 and 30°, the measurements at 0° being with supercooled liquid. *n*-Heptane was used for calibration, its temperature variation being given by Griswold and Chew[18] as $d^t_4 = d^{20}_4 - 0.000852 (t - 20) - 5.0 \times 10^{-7} (t - 20)^2$.

Viscosity.—The viscosity measurements at 30° were made as described by Fawcett and Rasmussen.[19] Nine values for the efflux time for water were averaged and seven values for 2-acetylthiophene. The viscosity of water was taken as 0.8007 centipoise at 30.00° as given by Dorsey.[20] The determined value for 2-acetylthiophene at 30.00° was 2.315 centipoises.

Surface Tension.—The determinations were made by measuring the rise of liquid in a graduated capillary, water being used for the calibration. The wide tube had a diameter of 50 mm. The value for the surface tension of water at 30.00° was taken as 71.221 dynes/cm. as given by Harkins.[21] Measurements of the radius of the capillary both at the meniscus and throughout the length of the portion filled with liquid were made to insure the required uniformity.

Solubility.—Approximately equal volumes of water and 2-acetylthiophene were shaken together at 50° and then placed in a bath at 30.00°. After swirling for an hour samples were taken from each layer, diluted with an equal volume of the appropriate solvent and analyzed by refractometric methods. The results are given in Table I.

2-Acetylthiophene proved to be miscible at 25° with triethylene glycol, methanol, ethanol, *t*-butyl alcohol, ethyl ether, dioxane, butyl cellosolve, ethyl acetate, acetone, acetonitrile, carbon disulfide, carbon tetrachloride, nitromethane, acetic acid, thiophene, tetralin, amylbenzene and benzene.

2-Acetylthiophene was immiscible at 25° with water, glycerol, ethylene glycol, decalin, cyclohexane, diisobutene, 1-hexadecene and *n*-heptane.

With an equal volume of *n*-heptane, 2-acetyl-

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[14] Keenan and Keyes, "Thermodynamic Properties of Steam," John Wiley & Sons, Inc., New, York, N. Y., 1936, p. 78.

[15] American Institute of Physics, "Temperature, Its Measurement and Control," Reinhold Publishing Co., New York, N. Y., 1941, p. 1306.

[16] Bauer, *Refractometry*, in "Physical Methods of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1945, p. 660.

[17] Forziati, Mair and Rossini, *J. Research Natl. Bur. Standards*, **35**, 513 (1945)

[18] Griswold and Chew, *Ind. Eng. Chem.*, **38**, 364 (1946).

[19] Fawcett and Rasmussen, THIS JOURNAL, **67**, 1705 (1945).

[20] Dorsey, "Properties of Ordinary Water Substance," Reinhold Publishing Co., New York, N. Y., 1940, pp. 183–184.

[21] Harkins, *Surface and Interfacial Tensions*, in "Physical Methods of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1945, Vol. I, p. 163.

thiophene was miscible above 60.8° and with ethylene glycol above 31.1°.

Enolization.—A drop of 2-acetylthiophene was diluted with 5 ml. of absolute alcohol and a dilute solution of ferric chloride was added dropwise. No color other than the light yellow of the ferric chloride was observed, whereas the enol form of carbonyl compounds (*e. g.*, ethyl acetoacetate) usually gives red or purple colors.[22,23] Hence, it was concluded that 2-acetylthiophene exists in the keto form.

Infrared Absorption Spectra.—The infrared absorption spectra of 2-acetylthiophene and other thiophene derivatives will be reported by other workers from this laboratory.

Chromatography.—2-Acetylthiophene lies between ethyl ether and benzene on the scale of adsorption on silica gel methanol > acetone > ethyl ether > benzene > chloroform > carbon tetrachloride > *n*-heptane. 2-Acetylthiophene is more strongly adsorbed than thiophene and less strongly adsorbed than acetic acid. 2-Acetylthiophene is more strongly adsorbed than acetophenone in the same way that thiophene is more strongly adsorbed than benzene. The experiments were all made by percolating an equal volume mixture of the pair being examined through a column of silica gel and analyzing the effluent refractometrically. The pale yellow color which existed in the distillation middle fraction was not completely removed by percolation through silica gel at room temperature.

Molar Refractivity.—The equation used was $R^{20}{}_{\mathrm{D}} = (n^2 - 1)/(n^2 + 2)\cdot(M/d)$ and the value found was 35.178. A calculated value was obtained by the method of Fajans[24] using $R^{20}{}_{\mathrm{D}}$ for thiophene 24.365,[19] CH_2 4.618, C 2.418, carbonyl oxygen 2.211 to give 33.612. Hence, 2-acetylthiophene shows marked exaltation when compared with thiophene. Furthermore, 2-acetylthiophene also shows exaltation but thiophene shows depression when compared with the usual values which are based on aliphatic compounds containing sulfide linkages, isolated double bonds and an isolated carbonyl group.

Specific Refractive Dispersion.—The calculations $10^4(n_{\mathrm{F}} - n_{\mathrm{C}})\cdot(1/d) = 213.4$ and $10^4 (n_{\mathrm{g}} - n_{\mathrm{D}})(1/d) = 340.9$ show high values and indicate marked dispersion for 2-acetylthiophene, further indicating light absorption in the near ultraviolet.

Parachor.—From the equation $P = M\gamma^{1/4}/(D - d)$ a value of 281.9 at 30° was found. Sufficient data on thiophene derivatives are not available for a precise calculated value. The values of Mumford-Phillips[25] show 277.6.

Summary

1. Determinations of the physical properties of purified 2-acetylthiophene have been made, including m.p., b. p., change of b. p. with pressure, $n^{20}{}_{\mathrm{D}}$, $\Delta n_{\mathrm{D}}/\Delta T$, refractive dispersion, $d^{20}{}_4$, $\Delta d_4/\Delta t$, η^{30}, γ^{30} and water solubility. Derived values have been calculated for heat of fusion, heat of evaporation and molar refractivity.
2. An equation for the index of refraction at 20° as a function of wave length is presented.

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[22] Watson, "Modern Theories of Organic Chemistry," Oxford University Press, London, 1941, pp. 159–180.

[23] Huntress and Mulliken, "Identification of Pure Organic Compounds," John Wiley & Sons, Inc., New York, N. Y., 1941, p. 20.

[24] Fajans, *Additivity of Molar Refraction and Its Limitations*, in "Physical Methods of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1945, pp. 673, 680.

[25] Mumford-Phillips, *J. Chem. Soc.*, 2112 (1929).

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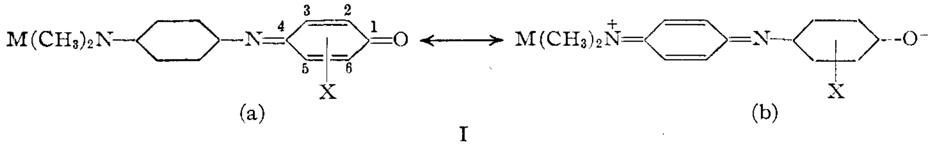
Indoaniline Dyes. II.[1] The Effect of Multiple Substitution on the Absorption of Phenol Blue

BY PAUL W. VITTUM AND GORDON H. BROWN

Substituted phenol blue dyes (Ia ⟷ Ib) have been shown[1] to have markedly different absorptions, depending on the nature of the substituent groups (X) in the oxygen-containing ring. The change in absorption can be explained adequately in terms of the manner in which the substituents affect the contribution of the dipolar resonance structure, Ib. If X exerts an inductive or resonance effect which facilitates the separation of the charge in Ib, the substituted dye absorbs more strongly and has a higher $\lambda_{\mathrm{max.}}$ value. Conversely, if X renders the oxygen-containing ring less capable of accommodating the negative charge in Ib, both $\lambda_{\mathrm{max.}}$ and $\epsilon_{\mathrm{max.}}$ of the dye are lowered.



(a) (b)

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The examination of indoaniline dyes has now been extended to some members having more than

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[1] Part I, THIS JOURNAL, **68**, 2235 (1946).