

end; therefore the product was isolated by evaporation of the solvent and hydrolyzed by means of 15% methyl alcoholic potassium hydroxide solution (10 cc.). The mixture of acids obtained was treated with ether. A first crop of the unsaturated acid (II) (1.2 g.) remained insoluble; from the mother liquor a second crop of the same substance was obtained (0.8 g.); then the saturated (1,2,3,4-tetrahydro-2-methyl-5,6-benzanthryl-1)-acetic acid separated and was recrystallized from ethyl alcohol: hexagonal leaflets, m. p. 192–194.5°, which gave a yellow color reaction with concentrated sulfuric acid. (Calcd. for $C_{21}H_{20}O_2$: C, 82.9; H, 6.6. Found: C, 83.0, 83.3; H, 6.8, 7.2.) The hydrogenation of the regenerated unsaturated acid (II) was accomplished by means of palladium black in ethyl acetate.¹²

Synthesis of (III).—1,2,3,4-Tetrahydro-2-methyl-5,6-benzanthryl-1)-acetic acid (0.46 g.) was dissolved in boiling benzene (10 cc.) and, after addition of phosphoric oxide (3 g.), boiled for three hours. The mass was poured onto ice, extracted with ether and washed with soda solution. The ether residue crystallized spontaneously; it was triturated with acetone and some petroleum ether (80–100°) and collected. It crystallized from ligroin containing some benzene, and then from propyl alcohol as needles, m. p. 168–170°; yield, 0.22 g. (Calcd. for $C_{21}H_{18}O$: C, 88.1; H, 6.3. Found: C, 87.7; H, 6.3.) Concentrated sulfuric acid gives an orange-yellow solution with green fluorescence.

Tetrahydromethylcholanthrene (IV).—The above ketone (0.2 g.) was reduced with amalgamated zinc wool (2 g.) and concd. hydrochloric acid. The product was isolated with ether and distilled at 0.15 mm. The yellowish oil which exhibited a violet fluorescence was triturated with acetone and methanol, collected and recrystallized from ethyl alcohol; fluorescent leaflets, m. p. 97–99°; yield, 0.12 g. (Calcd. for $C_{21}H_{20}$: C, 92.7; H, 7.3. Found: C, 92.2; H, 7.0.)

Methylcholanthrene (V).—The tetrahydro derivative (0.1 g.) was heated with selenium (2 g.) in a sealed tube at 330° for forty-eight hours. The product was extracted with ether and benzene and after evaporation of these solvents distilled at 0.05 mm. in presence of sodium metal. The orange-yellow distillate crystallized spontaneously and was triturated with a mixture of methyl and ethyl alcohols: from benzene, yellow rhombic crystals, m. p. 175–177°. The m. p. of Professor Cook's preparation was not depressed by admixture of our product; yield, 0.067 g. (Calcd. for $C_{21}H_{16}$: C, 94.0; H, 6.0. Found: C, 93.7; H, 6.2.)

(12) Reduction experiments with sodium amalgam failed owing to the insolubility of the alkali salts of (II).

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Structurally Equivalent Units and the Classification of Normal and Abnormal Liquids

BY RAYMOND H. EWELL

Certain liquids have long been designated as abnormal or "associated" liquids. This designation was made because they did not obey certain

physical rules, such as the rule of rectilinear diameters, Trouton's rule, the Ramsay-Shields equation, etc., which the so-called normal liquids did obey. Abnormal liquids also have much higher boiling points and viscosities than would be expected by analogy with normal liquids. The following classification is a somewhat more explicit one than is at present in the literature, as far as the writer is aware:

1. *Abnormal liquids.*—Compounds containing OH or NH groups, *i. e.*, compounds which form hydrogen bonds, giving rise to a positive intermolecular structure. Included are water, ammonia, alcohols, organic acids, phenols, primary and secondary amines, amides, etc., and also hydrogen fluoride.

2. *Intermediate group.*—Compounds containing C=O, C≡N or N=O groups, including ketones, esters, anhydrides, nitriles, nitro derivatives, etc.

3. *Normal liquids.*—All others (except molten metals and molten salts, which occupy separate categories altogether), including non-metallic elements, hydrocarbons and their halogen derivatives, ethers, tertiary amines, sulfides, mercaptans, fourth group tetrahalides, SO₂, S₂Cl₂, PCl₅, CS₂, HCl, HBr, HI, ICl, CO₂, etc.

The following table illustrates in part the basis of the classification.

	B. p., °C.	Viscosity at 25° (in millipoises)
$C_4H_9CH_3$	36	2.3
$C_4H_9NH_2$	78	6.8
C_4H_9OH	118	26.0
$C_2H_5 \begin{array}{l} \diagup \\ \diagdown \end{array} CH_2$	35	2.3
$C_2H_5 \begin{array}{l} \diagup \\ \diagdown \end{array} NH$	55.5	3.67
$C_2H_5 \begin{array}{l} \diagup \\ \diagdown \end{array} O$	34.5	2.35
$C_2H_5 \begin{array}{l} \diagup \\ \diagdown \end{array} CH$	93	3.6
$C_2H_5 \begin{array}{l} \diagup \\ \diagdown \end{array} N$	90	3.6
$C_2H_5 \begin{array}{l} \diagup \\ \diagdown \end{array} C=H_2$	66	...
$C_2H_5 \begin{array}{l} \diagup \\ \diagdown \end{array} C=O$	102	...
$C_4H_9C\equiv CH$	71.5	...
$C_4H_9C\equiv N$	141	...

Examination of the table leads to the following conclusions: (1) The CH_2 group is structurally equivalent to ether O, and the CH group is structurally equivalent to tertiary N. (2) The CH_3 group is not equivalent to NH_2 or OH, nor is CH_2 equivalent to NH, since hydrogen bond formation is possible when H is attached to N or O. (3) The CH_2 group is not equivalent to ketone O, nor is CH equivalent to nitrile N.

The abnormality of liquids containing $\text{C}=\text{O}$ or $\text{C}\equiv\text{N}$, as shown by this boiling point criterion and also by other criteria, is much less than that of liquids containing hydrogen bonds, and so these liquids are put into an intermediate classification. The abnormal character must arise from the interaction of the $\text{C}=\text{O}$ or $\text{C}\equiv\text{N}$ polar groups, which are quite strongly polar and occupy exposed positions on the molecules.

Conclusion (1) is to be expected since CH_2 and O, and CH and N, have nearly the same mass and electronic structures, and the bond angles around C, N and O are probably the same. This structural equivalence does not appear to hold in aromatic compounds since pyridine has a much higher viscosity and boiling point than benzene.

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Displacement Reactions in Fused Pyridinium Hydrochloride Solutions

BY ARTHUR F. SCOTT AND CLARENCE S. COE

Fused pyridinium hydrochloride has been shown¹ to act both as an "onium" acid and as an ionizing solvent for salts of metals. As an acid, pyridinium hydrochloride dissolves metals above hydrogen in the electromotive series; it also dissolves copper readily, but it does not attack antimony, bismuth or arsenic, even though these elements are above copper in the series. Since this apparently irregular position of copper is the same as it is in the electromotive series of metals² in solvents of fused aluminum bromide and zinc bromide, it appeared possible that the series for pyridinium hydrochloride is in general like the abnormal series found with the other fused salts. To test this possibility we have attempted to establish the series for pyridinium

hydrochloride by means of displacement reactions.

Weighed amounts of different metals were added to melts of various metallic chlorides in pure pyridinium hydrochloride. The molecular concentration³ of the chlorides in the melt was about 1 *M*, the extreme variations being 0.5 and 1.9 *M*. The amount of the metal added was approximately equivalent to two-tenths of the metal in the melt. The time allowed for the reaction varied between fifteen minutes and one hour, depending on how rapidly the reaction appeared to take place. Finally, after the melt was cooled, the metallic residue was recovered and its weight ascertained. As a rule, in order to facilitate the separation of the metallic residue from the solid pyridinium hydrochloride solution, the latter was treated with hot water or hydrochloric acid solution.

Complete, *i. e.*, more than 95% displacement took place as follows: gold, by mercury, bismuth and antimony; arsenic, by mercury and bismuth; mercury, by antimony; bismuth, by antimony and silver. Partial, *i. e.*, 95-50% displacement took place as follows: mercury, by bismuth and by silver, and antimony by silver. Gold was not displaced by platinum, nor mercury by arsenic, nor bismuth by mercury, nor antimony by mercury.

On the basis of these reactions and that of copper with pyridinium hydrochloride we may write the displacement series for metals in pyridinium hydrochloride as in (I) below. The series for these metals in fused zinc bromide and fused aluminum bromide as found by Isbekow² from measurements of the decomposition potentials as well as from displacement reactions is given in (II).

(I)	Cu	H	Ag	Sb	Bi	Hg	As	Au	Pt
(II)	Cu		Ag	Hg	Sb	Bi			

On comparing these two series it can be seen that the series for pyridinium hydrochloride differs from that for fused zinc bromide and aluminum bromide only in the position of Hg. Both of these series (I and II) differ from the usual series in that Cu and Ag are above Sb, Bi and As. From the fact that Cu in the pyridinium chloride is above H it would appear that the abnormal sequence is due to a displacement of Cu, Ag and possibly Hg and Au.

In conclusion, it may be noted that some of the displacement reactions in pyridinium chloride which go to completion may be of practical value. For instance, preliminary experiments indicate

(1) Audrieth, Long and Edwards, *THIS JOURNAL*, **58**, 428 (1936).
(2) Isbekow, *Z. physik. Chem.*, **116**, 304 (1925); *Z. anorg. Chem.*, **186**, 324 (1930).

(3) The concentration of the auric chloride was small but not determined. The solutions of arsenic were prepared by dissolving arsenous oxide.