

nearly crystalline when drawn than a polymer which was a random mixture of both structures and because of this greater degree of orientation would have an anisotropy closer to the maximum possible value.

It is clear that in unstretched polystyrene there is, as expected, a negligible preferred orientation of the aromatic groups, and that this preferred orientation remains small in stretched polystyrene. But the introduction of additional groups into the aromatic ring may cause a large preferred orientation. This conclusion is in agreement with the X-ray results reported by Baker.¹¹ The magnetic method described has obvious applications to other substituted polystyrenes and to related polymers.

Some confirmation of the calculations is to be found in the reported average susceptibility of -102 per repeating unit of poly-2,5-dichlorostyrene. This agrees reasonably well with the value of -101.0 calculated from Pascal's constants, and also with the value of $(2K_{\perp} + K_{\parallel})/3 = -103$ obtained from the maximum possible calculated principal susceptibilities.

(11) W. O. Baker, in "High Polymers," edited by S. B. Twiss, Reinhold Publ. Corp., New York, N. Y., 1945, p. 141.

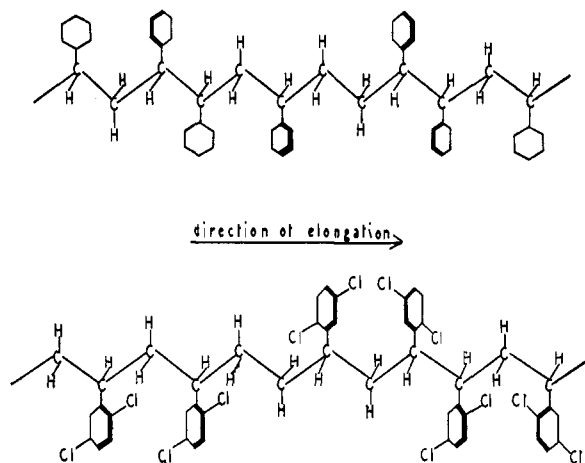


Fig. 1.—In oriented polystyrene the aromatic groups deviate only slightly from random orientation. In oriented poly-2,5-dichlorostyrene the aromatic groups assume a definite preferred direction such that the normals to the planes of the rings tend to be parallel to the direction of elongation.

EVANSTON, ILL.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORQUIMA S. A.]

Structural Studies on Polynuclear Pyridine Compounds

BY P. KRUMHOLZ

The ultraviolet absorption spectra and the basic dissociation constants of isomeric phenylpyridines, dipyrindyls and phenanthrolines have been determined. Some correlations between the absorption spectra and the structure of the compounds have been discussed.

The study of the ultraviolet spectra of substituted biphenyls has provided valuable information on the structure of those compounds. It has been shown that the spectral properties are intimately connected with the electronic interaction between both benzene rings and that inhibition of this interaction by steric hindrance destroys the specific spectral behavior of the biphenyls.¹

As benzene and pyridine show a similar spectroscopic behavior² it seemed to us to be of some interest to study the spectra of the isomeric phenylpyridines and dipyrindyls and their salts, inasmuch as in this case relations between physical properties and molecular structure may be studied on sets of isomeric compounds.

We report below the ultraviolet absorption spectra of the three isomeric phenylpyridines, of the six isomeric dipyrindyls, and of three isomeric phenanthrolines (ortho, meta and para), in the form of free bases, as well as of the corresponding mono- and bivalent pyridinium ions, and of the quaternary N-methylpyridinium ions. We present furthermore the data on the dissociation constants of the bases.

(1) L. W. Pickett, G. F. Walter and H. France, *THIS JOURNAL*, **58**, 2296 (1936); M. T. O'Shaughnessy and W. H. Rodebush, *ibid.*, **62**, 2906 (1940); B. Williamson and W. H. Rodebush, *ibid.*, **63**, 3018 (1941).

(2) See for instance H. Sporer, *J. Chem. Phys.*, **14**, 101 (1946).

Experimental Part

Preparation and Purification of the Material.—The three isomeric phenylpyridines were prepared from benzene diazonium chloride and pyridine³ separating the isomers by fractional crystallization of the picrates. The free bases were isolated by treating the picrates with an excess of 10% potassium hydroxide, filtering the potassium picrate and extracting the filtrate and the solid residue with ether. After drying with solid potassium hydroxide and evaporating the ether, the residue was distilled at 10^{-2} mm.

The dipyrindyls were prepared from the product of the thermal decomposition of pyridine by fractional crystallization of the picrates as previously described.⁴ The free bases were isolated in the same way as the phenylpyridines and purified by distillation and, whenever possible, by crystallization. γ,γ' -Dipyrindyl was furthermore prepared by the action of metallic sodium on pyridine,⁵ the α,β and β,β' -isomer by oxidation of meta and para phenanthroline with permanganate and subsequent decarboxylation of the dicarboxylic acids.⁶

Absorption spectra and dissociation constants of the compounds prepared by different methods were identical within experimental error. The three phenanthrolines were prepared by the commonly used Skraup synthesis from the corresponding phenylenediamines.

Melting points of the free bases and their picrates were identical with the data in the literature and are thus not

(3) J. W. Haworth, I. H. Heilbron and D. H. Hey, *J. Chem. Soc.*, 349 (1940).

(4) P. Krumholz, *Selecta Chimica*, **8**, 1 (1949).

(5) Anderson, *Ann.*, **154**, 274 (1870); C. R. Smith, *THIS JOURNAL*, **46**, 414 (1924).

(6) C. R. Smith, *ibid.*, **52**, 397 (1930).

repeated. Only β, β' -dipyridyl could not be obtained in solid form.⁷

We have included in this study the probable sixth isomeric (β, γ -) dipyridyl whose structure has been made probable by spectroscopic and electrochemical data⁸ but not yet confirmed by ordinary chemical means.

The quaternary salts were prepared by heating the bases for two hours at 100° with an excess of methyl iodide and some methanol in a sealed tube and purified by means of several crystallizations from ethanol or ethanol-water mixtures.

To avoid complications by the ultraviolet absorption of the iodide ion, the iodides were converted into the corresponding chlorides, by agitating the solution for an hour with an excess of freshly prepared silver chloride. The concentration of the chloride in the filtered solution was determined by potentiometric titration with silver nitrate. In all cases 98 to 100% of the amount corresponding to the quantity of the quaternary iodide used, have been recovered, thus confirming the purity and correct formula of the prepared compounds.

It may be interesting to note that the bismethiodide of γ, γ' -dipyridyl crystallizes from ethanol in two distinctly different forms, one dark and the other bright red, easily separable mechanically. Both forms have identical composition as shown by the potentiometric determination of the iodine content. The solutions of the corresponding chlorides prepared from the two forms show identical absorption spectra. The intense color of the quaternary iodide is surprising, as the aqueous solution shows no marked color.

Determination of the Dissociation Constants.—The dissociation constants of the pyridine derivatives were determined by potentiometric titration of the bases dissolved in water or diluted ethanol, with hydrochloric acid, using a glass electrode for the determination of the pH. The temperature during the titration was held at $20 \pm 0.5^\circ$, the ionic strength being adjusted with potassium chloride to μ 0.2 for the aqueous solutions and to $\mu = 0.1$ for the solutions in 20 vol. % ethanol.⁹

The basic strength of the pyridine derivatives is expressed in the form of the acid dissociation constants of the corresponding pyridinium ions. The constants of the monoacid bases were computed from the pH values in the same way as previously reported for α, α' -dipyridyl.⁹

In the case of the diacid bases the dissociation constants as functions of the concentrations¹⁰ have to be expressed by equations

$$K_1 = \frac{(H^+)(B)}{(HB^+)} = (H^+) \frac{(B)_0 + (H^+) + (H_2B^{++})}{(HB^+)_0 - (H^+) - 2(H_2B^{++})} \quad (1)$$

$$K_2 = \frac{(H^+)(HB^+)}{(H_2B^{++})} = (H^+) \frac{(HB^+)_0 + (H^+) - 2(B)}{(H_2B^{++})_0 - (H^+) + (B)} \quad (2)$$

In those equations (B), (HB⁺) and (H₂B⁺⁺) represent the actual concentrations of the free base and its mono- and bivalent ions, ()₀ the analytical concentrations. The quantities (H₂B⁺⁺) in equation (1) and (B) in equation (2) may be calculated from

$$(H_2B^{++}) = \frac{(H^+)(HB^+)}{K_2} = \frac{(H^+)\{(HB^+)_0 - (H^+)\}}{K_2\{1 + 2(H^+)/K_1\}} \quad (3)$$

$$(B) = \frac{K_1(HB^+)}{(H^+)} = \frac{K_1\{(HB^+)_0 + (H^+)\}}{(H^+)\{1 + 2K_1/(H^+)\}} \quad (4)$$

As the calculation of K_1 needs the unknown numerical value of K_2 (and *vice versa*) we first computed an approximate value of K_1 neglecting the unknown

quantity (H₂B⁺⁺) in (1). With this value a first set of K_2 values was calculated from (2) and (4) for different points of the titration curve. Using the mean K_2 value a set of K_1 values was computed and so on until further approximations did not change substantially the values of the constants. The results of the computation of the dissociation constants of γ, γ' -dipyridyl are shown in Table I for illustration.

TABLE I
 $t = 20^\circ, \mu = 0.2$

| (D) ₀ × 10 ³ | (HD ⁺) ₀ × 10 ³ | (H ₂ D ⁺⁺) ₀ × 10 ³ | (H ⁺) | K |
|---------------------------------------|--|---|-----------------------|---------------------------------|
| 12.7 | 3.56 | | 4.25×10^{-6} | 1.54×10^{-6} (K_1) |
| 8.95 | 7.02 | | 1.12×10^{-6} | 1.50×10^{-6} |
| 5.34 | 10.32 | | 2.52×10^{-6} | 1.50×10^{-6} |
| 3.24 | 12.30 | | 4.10×10^{-6} | 1.48×10^{-6} |
| 1.86 | 13.55 | | 5.90×10^{-6} | 1.50×10^{-6} |
| | 13.65 | 1.50 | 1.48×10^{-4} | 6.8×10^{-4} (K_2) |
| | 10.15 | 4.75 | 3.56×10^{-4} | 7.2×10^{-4} |
| | 6.77 | 7.90 | 6.95×10^{-4} | 6.8×10^{-4} |
| | 3.50 | 10.95 | 1.35×10^{-3} | 6.65×10^{-4} |

The titration of the other bases, carried out in 0.01 to 0.03 molar solutions, leads to similarly concordant results, excepting the phenanthrolines. In the latter case K_1 shows an increase of about 30% passing from the beginning to the end of the neutralization.¹¹

The low solubility of meta and para phenanthroline (0.004 to 0.008 *m*) in water permits only a rough determination of K_2 . The approximate K values of the phenanthrolines obtained are, however, sufficient for the interpretation of the absorption spectra of the salts (see below). A comparison of the absorption spectra at different acidities confirms furthermore the right order of magnitude of the potentiometric K_2 values. Due to the still lower solubility of the phenyl pyridines, those compounds were titrated in a 20% ethanol-water mixture. The dissociation constants of pyridine and α, α' -dipyridyl were determined in the same solvent for comparison.

For the calculation of (H⁺) from the hydrogen activities measured in this solvent, the value of 0.78 for the activity coefficient of the hydrogen ion has been used, calculated approximately from the activities of hydrochloric acid in ethanol-water mixtures.¹²

The constants presented are not true thermodynamic values and depend on the ionic strength of the solutions. It has been shown previously⁹ that the dissociation constant of α, α' -dipyridyl depends only slightly on the ionic strength, the value of the thermodynamic constant being about 15% higher than the value at $\mu = 0.2$. A similar dependence on μ has been found in orienting measurements of K_1 of other dipyridyls. The constants K_2 could not be calculated with sufficient accuracy from measurements at low concentrations.

(11) A similar trend of the K values is visible in the titration curve of ortho phenanthroline, presented by T. S. Lee, I. M. Kolthoff and D. L. Leussing, THIS JOURNAL, 70, 2349 (1948), and probably responsible for the rather large discrepancy between the potentiometric and the conductometric values of K .

(12) H. S. Harned and B. Owen, "The Physical Chemistry of Electrolytic Solutions," Second Ed., Reinhold Publ. Corp., New York, N. Y., 1950, p. 550.

(7) See G. T. Morgan and T. H. Burstall, J. Chem. Soc., 20 (1932), for difficulties to obtain this dipyridyl in crystallized form.

(8) P. Krumholz, THIS JOURNAL, to be published.

(9) For the experimental arrangement and the accuracy of the measurements see P. Krumholz, THIS JOURNAL, 71, 3654 (1949).

(10) See for instance S. Glasstone, "Introduction to Electrochemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1942, p. 322.

Approximate values of K_2 at different ionic strengths may be computed, using known values of activities of mono-bivalent electrolytes. Such calculations show that the thermodynamic constant K_2 should be two to three times larger than its value at $\mu = 0.2$.

Ultraviolet Absorption Spectra.—The ultraviolet absorption spectra were determined by using a Beckman D. U. spectrophotometer with quartz cells of 10 mm. optical depth. The solvent was twice distilled water, containing 1% ethanol in the case of phenylpyridines. The concentrations were $5 \times 10^{-5} m$ for the phenylpyridines and dipyrindyls, $3 \times 10^{-5} m$ for the phenanthrolines, and $2 \times 10^{-4} m$ for pyridine. The temperature was $20 \pm 2^\circ$. The solutions of the free bases contained ammonia in a concentration of 0.02 m , to prevent the formation of pyridinium ions. The spectra of the pyridinium ions of the monoacid bases were measured in solutions containing hydrochloric acid in a concentration of 0.05 m . Such solutions contain less than 1% of the free base. To determine the spectra of the uni- and bivalent ions of the diacid bases, solutions of suitable acidity were prepared, containing preferentially one ionic species. The relative proportions of the different molecular and ionic species present in solution may easily be calculated from the dissociation equilibria of the uni- and bivalent ions, using values of the dissociation constants corrected for the influence of varying ionic strength. Including the experimental error, the values of K_1 should be correct within 10%. The error to the μ correction of K_2 may be several times greater. It may be shown by simple calculations that at suitable acidities the error in the extinction coefficients due to the uncertainty of the K values should be at most a few per cent.

The spectra of the ions of the diacid bases were obtained in the following way: The approximate value of the extinction coefficient of the univalent ion was computed from the experimental value of ϵ at low acidities (10^{-4} to $10^{-3} m$), the correct value of ϵ of the free base and the value at high acidities (10^{-1} to $5 \times 10^{-1} m$) (instead of the correct value of the bivalent ion), using the proportions of the three absorbing species calculated from the dissociation equilibria. With this value a corrected ϵ value of the bivalent ion was obtained, used hereupon to calculate a better value of ϵ of the univalent ion.

The absorption of the different solutions was always measured against a blank of equal HCl or NH_3 content. The values of the extinction coefficients at a given wave length, measured at any time and with solutions prepared from different samples, were identical within $\pm 2\%$.

Results and Discussion

Dissociation Constants.—Table II lists the K_1 and K_2 values of the polynuclear pyridine compounds as compared with the parent base pyridine.

TABLE II

$t = 20^\circ$, $\mu = 0.1$ in dil. ethanol; 0.2 in water

| | K_1 | K_2 | Solvent |
|-------------------------------|---------------------------|-------------------------|-------------|
| Pyridine | 8.3×10^{-6} | | 20% ethanol |
| α -Phenylpyridine | 4×10^{-5} | | 20% ethanol |
| β -Phenylpyridine | 2.6×10^{-5} | | 20% ethanol |
| γ -Phenylpyridine | 7×10^{-6} | | 20% ethanol |
| α, α' -Dipyrindyl | 7.6×10^{-5} | | 20% ethanol |
| Pyridine | 4.8×10^{-6} | | Water |
| α, α' -Dipyrindyl | 3.6×10^{-5} | | Water |
| β, β' -Dipyrindyl | 2.5×10^{-5} | 1×10^{-3} | Water |
| γ, γ' -Dipyrindyl | 1.5×10^{-5} | 6.8×10^{-4} | Water |
| α, β -Dipyrindyl | 3.8×10^{-5} | 3×10^{-2} | Water |
| α, γ -Dipyrindyl | 1.7×10^{-5} | 6.5×10^{-2} | Water |
| β, γ -Dipyrindyl | (?) 1.4×10^{-5} | 1×10^{-3} | Water |
| <i>o</i> -Phenanthroline | $\sim 1.2 \times 10^{-5}$ | | Water |
| <i>m</i> -Phenanthroline | $\sim 1 \times 10^{-4}$ | $\sim 10^{-1}$ | Water |
| <i>p</i> -Phenanthroline | $\sim 1 \times 10^{-4}$ | $\sim 4 \times 10^{-3}$ | Water |

The values of K_1 of pyridine,¹³ α, α' -dipyrindyl

(13) See E. B. Hughes, H. H. G. Jellinek and B. A. Ambrose, *J. Phys. Coll. Chem.*, **63**, 410 (1949), for recent determinations.

and the phenanthrolines¹⁴ the latter in alcoholic solution, have already been reported. A comparison of the K values of the phenylpyridines and the symmetric dipyrindyls shows that the γ -substituted derivatives are the strongest bases, the α -substituted the weakest.

The K_2 values of the α, α' -dipyrindyls are high as compared with the other isomers, α, α' -dipyrindyl showing no indication whatsoever of the formation of a biacid salt. The high K_2 value of the α, γ -isomer induced us to check the structure of this compound, so far described erroneously as the β, γ -isomer.⁸

Ultraviolet Absorption Spectra.—The absorption spectra of the polynuclear pyridine compounds and their salts, together with the spectrum of the parent substance pyridine, are reproduced in Figs. 1 to 13.¹⁵ In those figures the spectra of the free bases are represented by plain lines, those of the univalent ions by dashed lines, those of the bivalent ions by dashed and dotted lines, those of

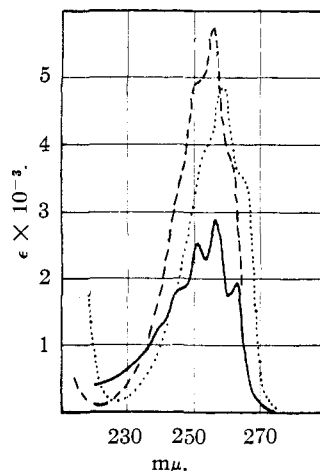


Fig. 1.—Pyridine.

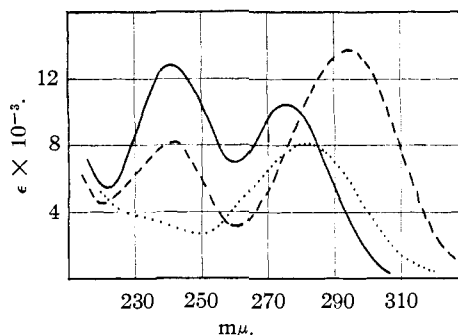
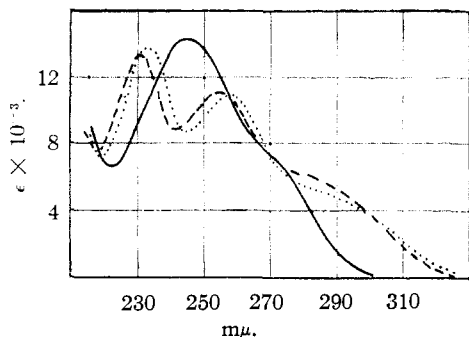
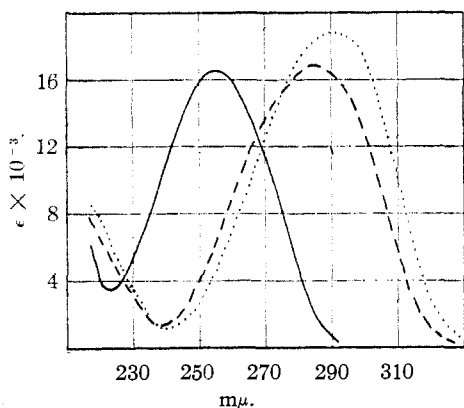
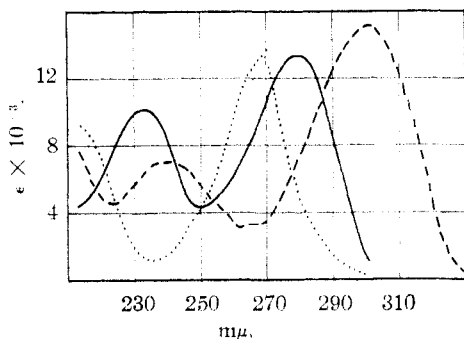
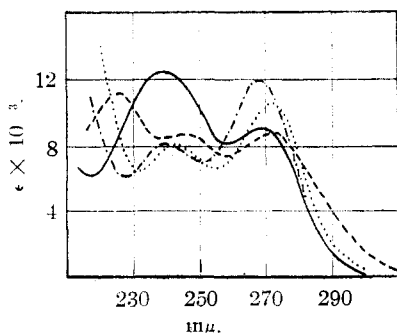
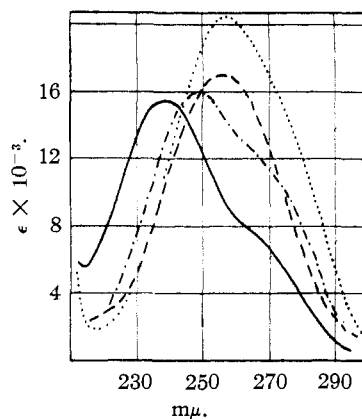
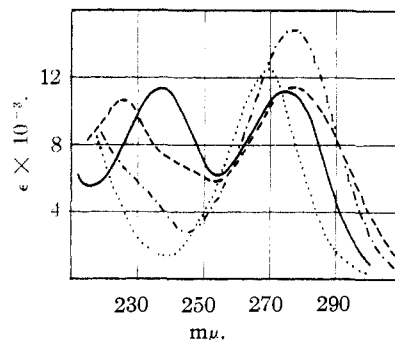
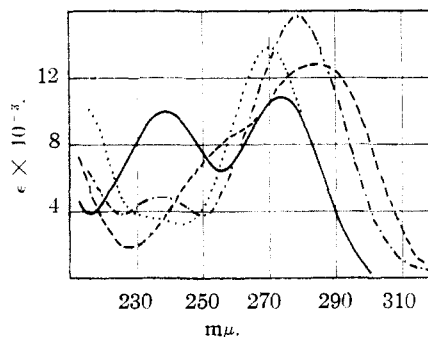
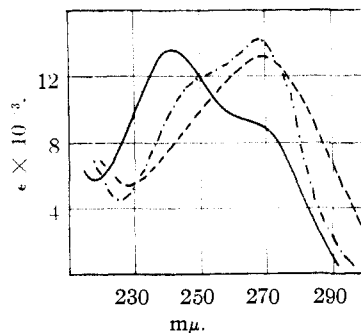


Fig. 2.— α -Phenylpyridine.

(14) A. Albert, R. Goldacre and J. Phillips, *J. Chem. Soc.*, 2240 (1948); see also J. H. Baxendale and Ph. George, *Nature*, **162**, 777 (1948), as well as ref. (8).

(15) The spectra of several of those substances have already been reported: more recently: pyridine and pyridinium ion, see ref. (13); M. L. Swain, A. Eisner, C. F. Wood and B. A. Brice, *THIS JOURNAL*, **71**, 1341 (1949); phenylpyridines, A. E. Gillam, D. H. Hey and A. Lambert, *J. Chem. Soc.*, 364 (1941). α, α' -Dipyrindyl and its ion, J. H. Baxendale and Ph. George, *Trans. Faraday Soc.*, **46**, 55 (1950); α, α' -, β, β' -, γ, γ' -dipyrindyl, C. W. F. Spiers and J. P. Wibaut, *Rec. trav. chim.*, **56**, 573 (1937). These spectra, referring to different solvents, could not be used for our comparative purposes, but agree quite well with our determinations as to the shape of the absorption curves and the position of the maxima.

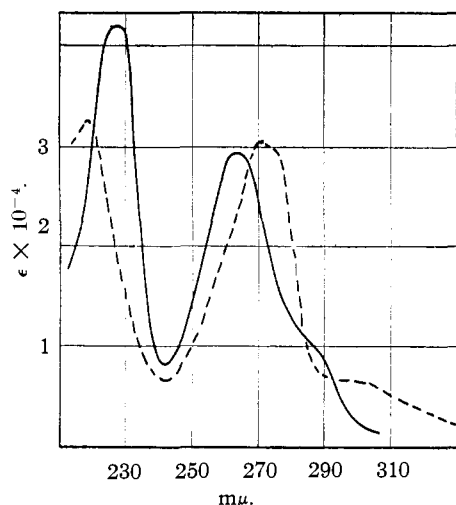
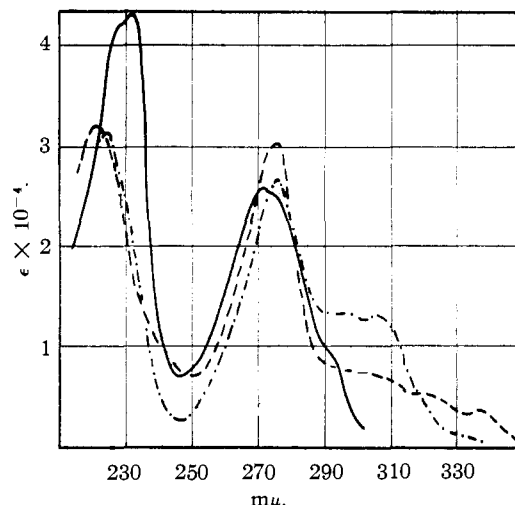
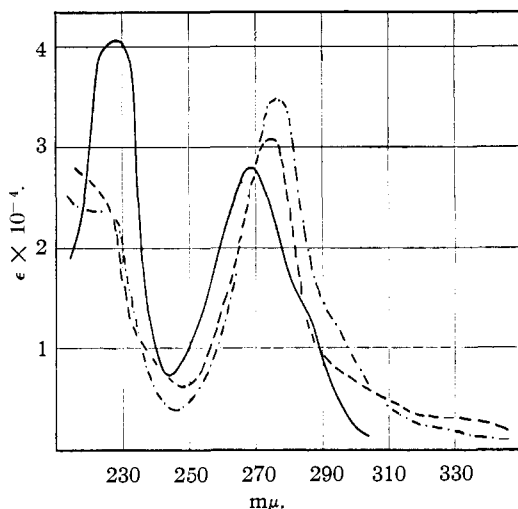
Fig. 3.— β -Phenylpyridine.Fig. 4.— γ -Phenylpyridine.Fig. 5.— α, α' -Dipyridyl.Fig. 6.— β, β' -Dipyridyl.Fig. 7.— γ, γ' -Dipyridyl.Fig. 8.— α, β -Dipyridyl.Fig. 9.— α, γ -Dipyridyl.Fig. 10.— β, γ -Dipyridyl (?).

the bivalent ions by dashed and dotted lines and those of the quaternary ions by dotted lines. The latter are the monoquaternary salts of the phenylpyridines and the biquaternary salts of dipyridyls.

A superficial comparison of the spectra shows that there is little similarity between the spectrum

of pyridine and the spectra of the polynuclear derivatives. The spectrum of γ -phenylpyridine is similar to the spectrum of biphenyl.¹⁶ The spectra of the other bases consist essentially of two

(16) See A. E. Gillam and D. H. Hey, *J. Chem. Soc.*, 1170 (1930), and ref. (15).

Fig. 11.—*o*-Phenanthroline.Fig. 13.—*p*-Phenanthroline.Fig. 12.—*m*-Phenanthroline.

bands, the longer wave length band denominated A band, the shorter wave length B band. The relative intensities of those bands vary largely in the different isomers. However, the total oscillator strength

$$f = 4.31 \times 10^{-9} \int \epsilon d\nu^{17}$$

taken (somewhat arbitrarily) between the short

TABLE III

The values of the total oscillator strength f are in arbitrary units. λ are the wave lengths of the absorption maxima, the values in parentheses representing inflection points, ϵ being the corresponding values of the molecular extinction coefficients.

| Compound | f | λ_A | ϵ_A | λ_B | ϵ_B |
|------------------------------|--------|-------------|--------------|-------------|--------------|
| α -Phenylpyridine | 90 | 2760 | 10.300 | 2410 | 12.800 |
| β -Phenylpyridine | 87 | (2700) | | 2460 | 14.300 |
| γ -Phenylpyridine | 91 | | | 2550 | 16.600 |
| α, α' -Dipyridyl | 92 | 2800 | 13.300 | 2330 | 10.200 |
| β, β' -Dipyridyl | 90 | 2690 | 9.100 | 2390 | 12.600 |
| γ, γ' -Dipyridyl | 100 | (2700) | | 2390 | 15.400 |
| α, β -Dipyridyl | 90 | 2750 | 11.100 | 2370 | 11.400 |
| α, γ -Dipyridyl | 82 | 2730 | 10.800 | 2380 | 10.000 |
| β, γ -Dipyridyl | (?) 92 | (2680) | | 2410 | 13.600 |

(17) N. G. Chako, *J. Chem. Phys.*, **2**, 644 (1934).

wave minimum and the long wave limit, is similar in all isomers, as shown by its values in Table III.

This indicates a rather strong mutual dependence of the transition probabilities of the electronic transitions, responsible for the two absorption maxima.

According to current ideas, the excited states of molecules are essentially contributed by polar forms.¹⁸

It may be assumed by analogy to biphenyl¹⁹ that in the polar forms of the phenylpyridines and dipyrindyls the rings are joined by a double bond.

That some kind of electronic interaction, involving a double (or π) bond between both rings, is related with the characteristic spectral behavior of the polynuclear compounds is indicated by the spectra of the quaternary N-methyl compounds. In all α -substituted quaternary compounds the absorption spectrum consists of one unique band of reduced total oscillator strength, as compared with the spectra of the free bases and their NH ions. The absorption maximum of the biquaternary ions of the α, α -dipyridyls is located at shorter wave length than that of the A band of the free bases and their NH ions. The shape of the absorption curve of those quaternary ions is very similar and not essentially different from the spectrum of two molecules of N-methylpyridinium chloride, as shown in Fig. 14.

In contrast, in β - and γ -phenylpyridine and the corresponding symmetric dipyrindyls, the absorption spectra of the quaternary and normal ions are very similar, the former being slightly shifted to longer wave lengths.

This behavior of the spectra indicates strongly that steric hindrance by the alpha N-methyl group prevents coplanarity of the rings and therefore structures involving a double bond between both rings.

The spectra of the NH ions of the phenylpyridines and the symmetric dipyrindyls differ in a characteristic and specific manner from the spectra of the free bases.

(18) R. S. Mulliken and C. A. Rieke, *Reports on Progress in Physics*, **8**, 231 (1941).

(19) See for instance G. W. Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944.

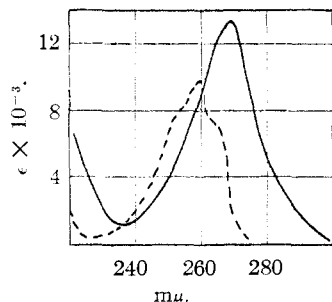


Fig. 14.— —, bis-N-methyl- α, α' -dipyridylium chloride; ---, N-methylpyridinium chloride.

In the α -substituted compounds the A band of the univalent ions as compared with the free bases is increased in intensity and shifted to longer wave lengths, whereas the B band is strongly suppressed. In the β -derivates the predominant B band of the bases is split in the ions into two distinct absorption maxima. The position of the A band of β, β' -dipyridyl is only slightly changed by salt formation.

The unique band of γ -phenylpyridine is in its ion strongly shifted to longer wave lengths. A similar shift of somewhat smaller extent occurs in the spectrum of γ, γ' -dipyridyl.

The spectra of the unsymmetric dipyridyls and their salts show additive properties with regard to the spectra of the symmetric compounds; this is particularly true of the α, β -isomer, whose absorption spectrum, as shown in Fig. 15, is almost identical with the spectrum obtained by the superposition of two moieties of the symmetric compounds α, α' - and β, β' -dipyridyl. This additivity

may have no physical significance but may be of value in the determination of unknown structures as shown in the case of the probable β, γ -dipyridyl.⁸

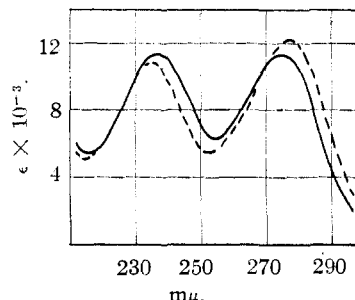


Fig. 15.— —, α, β -dipyridyl; ---, $\alpha, \alpha' + \beta, \beta'$ -dipyridyl.

The absorption spectra of the three phenanthrolines finally show a qualitative similarity with the spectra of the dipyridyls. The spectra of the three isomers, however, are not very different at least in regard to their two principal absorption bands.

The long wave band system, especially pronounced in the salts of para phenanthroline, bears some resemblance to the long wave absorption of phenanthrene.²⁰

Acknowledgment.—The author is especially indebted to Prof. H. Stammreich for the permission to carry out the spectral measurements in the Laboratory of the Physical Institute of the Universidade de São Paulo, and for his valuable suggestions and criticisms.

(20) E. Clar, *Ber.*, **65**, 1411 (1932).

SÃO PAULO, BRAZIL

RECEIVED NOVEMBER 13, 1950

[CONTRIBUTION FROM THE UNIVERSITY OF MISSOURI SCHOOL OF MINES AND METALLURGY, DEPARTMENT OF METALLURGY]

The System Sodium Tungsten Bronze–Lithium Tungsten Bronze–Tungsten(VI) Oxide¹

BY M. E. STRAUMANIS AND G. F. DOCTOR

The ternary system sodium tungsten bronze (containing 6.6% by weight tungsten(VI) oxide)–lithium tungsten bronze (with 42.6% tungsten(VI) oxide)–tungsten(VI) oxide has been investigated by measuring the lattice parameters of the phases and by observing the appearance of new lines on the X-ray films. All bronze samples were heated at 850° *in vacuo* and quenched in air. It was found: the sodium bronze dissolves the lithium bronze up to 65% under lattice contraction; there is a large region of the homogeneous cubic ternary solid solution in the sodium bronze corner, one two-phase region in the lithium bronze corner (both phases being cubic), one multiphase region adjacent to the first two regions, containing also tetragonal bronzes, and one small homogeneous region in the tungsten(VI) oxide corner. The cubic ternary sodium lithium bronze–tungsten(VI) oxide solid solution has the structure and the properties of the cubic sodium or lithium bronzes. The crystals of the solution represent simultaneously a cationic (Na^+ , Li^+ , vacant sites) and anionic (WO_3^- , WO_3) substitutional solid solution. The distribution is at random. The samples of the ternary solid solution have a good electrical conductivity (sp. resistance between 0.1 and 0.6 ohm). The resistance increased considerably when the limits of the homogeneous phase were exceeded. If the composition of the heated samples is known, the crystalline phases present and the lattice parameters of the phases can be read from the diagrams.

Introduction

Sodium tungsten bronze^{2a,b} and lithium tungsten bronze³ can absorb appreciable amounts of tungsten(VI) oxide at elevated temperatures and, as it will be shown in the present paper, the sodium bronze can dissolve also some amounts of the lithium bronze. The intention of the present

paper is, therefore, to determine the phases formed, their regions of stability and their limits in the ternary system sodium tungsten bronze–lithium tungsten bronze–tungsten(VI) oxide.

Although the bronzes and solid solutions have metallic properties,^{2b,3} they are not bronzes, alloys or intermetallic compounds. Nevertheless, the term bronze will be used throughout the paper because of its brevity.

There are a few remarks in the literature concerning the reactivity of lithium bronze with

(1) Based on a thesis submitted by G. F. Doctor to the Graduate School of the University of Missouri, School of Mines and Metallurgy in partial fulfillment of the requirements for the Master Degree.

(2) (a) G. Hägg, *Z. physik. Chem.*, **B29**, 192 (1925); (b) M. E. Straumanis, *This Journal*, **71**, 679 (1949).

(3) M. E. Straumanis and S. S. Hsu, *ibid.*, **72**, 4027 (1950).