at 6.00–6.01 μ (XI–XIII). If the Pauling electronegativities[10] of carbon (2.5) and oxygen (3.5) are considered, then it appears reasonable that the stronger electronegative element, oxygen, will "tighten" the C=N link by its inductive effect to a greater extent than the carbon atom. It has been found that for some cases group frequency shifts parallel electronegativities of the atoms concerned.[11] This fact is borne out herein when the 1-pyrrolines, dihydro-1,3-thiazines, and dihydro-1,3-oxazines are compared.[12]

In order to exclude the possibility that the comparison of the dihydro-1,3-thiazines and dihydro-1,3-oxazines reported herein is not valid because of the presence of a 6-methyl group in the oxazine system, a dihydro-1,3-thiazine containing a 6-methyl group (V) was compared with one not containing this substituent (IV). The C=N absorption of both these compounds revealed no significant differences.

EXPERIMENTAL[13,14]

All the infrared spectra were performed in a Perkin-Elmer 21 Recording Spectrophotometer using sodium chloride optics. All the samples were studied in a 5–7% solution in chloroform.

2-Substituted 4,4,6-trimethyldihydro-1,3-oxazines. The method of preparation of these compounds was taken from the procedure described by Ritter and Tillmanns.[4]

2-Ethyl-4,4,6-trimethyldihydro-1,3-thiazine (V). This compound was prepared by treating the corresponding dihydro-1,3-oxazine with phosphorus pentasulfide and the details are described in a previous communication;[3] b.p. 66–67° (1.5 mm.), n_D^{30} 1.4842, picrate, m.p. 113–114°.

2-Substituted 4,4-dimethyldihydro-1,3-thiazines. The experimental details describing the preparation of these compounds have recently been reported.[3]

Acknowledgment. The author wishes to express his gratitude to the National Institutes of Health (RG-6248) for funds granted to support a study of which the present work is a part.

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(10) L. Pauling, *The Nature of the Chemical Bond*, Cornell Univ. Press, Ithaca, New York, 1948, p. 60.

(11) See ref. 7, p. 394.

(12) It is considered reasonable here to compare a five-membered ring (1-pyrrolines) containing the C=N link with the two six-membered ring systems (oxazines and thiazines) since it has been found that 2-thiazolines containing the same 2-substituents as the dihydro-1,3-thiazines exhibited C=N absorptions in exactly the same spectral region. Compare data of thiazines given in Table I with data of thiazolines reported in ref. 2.

(13) All melting points and boiling points are uncorrected.

(14) Microanalyses performed by Alfred Bernhardt, Mulheim (Ruhr), West Germany.

[CONTRIBUTION FROM THE ORGANIC CHEMISTRY DIVISION, U. S. NAVAL ORDNANCE LABORATORY]

Absorption Spectra and Positions of Protonation of 2-Arylindoles

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Structure-spectra correlations are drawn for the 2-arylindoles. It is shown that substitution at the 3-position causes a "type 1" steric effect, substitution on the nitrogen a "type 2" steric effect. At the 4(6)- and 5-positions substituents exert electromeric effects and shift maxima accordingly. In acid media the spectra are consistent with the indoleninium salt structure (XXIV).

In order to lay the groundwork for a proposed study of the more complex spectral behavior of indole alkaloids related to alstoniline and sempervirine, it was deemed desirable to determine the ultraviolet spectra in neutral and acidic media of a number of 2-arylindoles and related compounds. These spectra were of interest *per se*, as they illustrated electronic and steric effects in this series and offered evidence regarding the position of protonation. In Table I are listed the positions and extinction coefficients of maxima and minima determined in the course of the present investigation.[1]

EXPERIMENTAL

Materials. 3-Phenylindole (II), 1-methyl-2-phenylindole (III) and 2-(*p*-biphenylyl)indole (XII) were kindly supplied to us by Dr. B. Witkop, National Institutes of Health. They had been prepared by the Fisher indole synthesis using polyphosphoric acid.[2] Dr. K. Schofield, Washington Singer Laboratories, Exeter, was good enough to furnish us a sample of 6-nitro-2,3-diphenlyindole (XI), prepared by the cyclization of desoxybenzoin *m*-nitrophenylhydrazone.[3] The compound had decomposed slightly on arrival, but a single recrystallization from ethanol gave a pure sample as orange crystals, m.p. 227° (lit.,[3] m.p. 225–227°). 2-Phenylindole (I) was commercially available from K. and K. Laboratories, Long Island City, N. Y. The material melted at 187.5–188° (lit.,[2] m.p. 187–188°) after one recrystallization from ethanol.

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(1) The method used to describe spectra conforms with the recommendations of the Editorial Board of Organic Electronic Spectral Data, Inc., J. D. Cawley and H. E. Ungnade, *Anal. Chem.*, 31, No. 2, 42A (1959).

(2) H. M. Kissman, D. W. Farnsworth, and B. Witkop, *J. Am. Chem. Soc.*, 74, 3948 (1952).

(3) D. W. Ockenden and K. Schofield, *J. Chem. Soc.*, 3175 (1957).

TABLE I

SPECTRA DETERMINED IN PRESENT INVESTIGATION

Compound	Solvent[a]	λ_{max}(log ε)[b]	λ_{min}(log ε)	Compound	Solvent[a]	λ_{max}(log ε)[b]	λ_{min}(log ε)
2-Phenylindole (I)	CH_3OH	240(4.23)	268(3.58)	4(6)-Chloro-2,3-diphenylindole (VII)	CH_3OH	249(4.46)	236(4.43)
		309(4.39)[c]				258s(4.41)	276(3.95)
	H_3PO_4	264(3.83)	278(3.64)			313(4.27)	
		343(4.34)[d]			H_3PO_4[f]	324(4.18)[h]	288(4.04)
3-Phenylindole (II)	CH_3OH[e]	201(4.47)	210(4.46)	5-Chloro-2,3-diphenylindole (VIII)	CH_3OH[e]	207(4.55)	226(4.37)
		224(4.56)	245(3.95)			244(4.43)	270(3.86)
		269(4.25)				309(4.28)	
		280s(4.21)			H_3PO_4[f]	339(4.20)[d]	295(4.01)
1-Methyl-2-phenylindole (III)	CH_3OH[e]	207(4.44)	214(4.45)	4(6)-Methoxy-2,3-diphenylindole (IX)	CH_3OH	242s(4.32)	251(4.29)
		224(4.46)	264(3.68)			259(4.30)	280(3.92)
		237s(4.33)				325(4.23)	
		298(4.26)			H_3PO_4	331(4.1)	
	H_3PO_4	250(3.48)	260(3.30)			380s(3.9)[i,j]	
		322(4.18)[d]			HCl	272(4.04)	289(3.81)
2,3-Diphenylindole (IV)	CH_3OH	248(4.34)	268(3.96)			328(4.14)	
		308(4.22)				390s(3.90)	
	H_3PO_4	255(3.93)	279(3.68)	5-Methoxy-2,3-diphenylindole (X)	CH_3OH	255s(4.20)	271(4.02)
		344(4.20)[d]				317(4.34)	
	H_2SO_4[f]	343(4.20)			H_3PO_4	266(4.02)	306(3.65)
	HCl	255(3.94)	279(3.68)			381(4.18)[d]	
		342(4.19)			HCl	268(4.06)	310(3.69)
4(6)-Methyl-2,3-diphenylindole (V)	CH_3OH	250(4.35)	238(4.33)			383(4.17)	
		314(4.24)	274(3.96)	6-Nitro-2,3-diphenylindole (XI)	CH_3OH	250(4.34)	229(4.21)
	H_3PO_4[f]	345(4.14)[d]				292(4.09)	285(4.09)
	HCl	260(3.95)	285(3.59)			342(4.02)	317(3.98)
		343(4.14)				396(4.13)	355(4.02)
5-Methyl-2,3-diphenylindole (VI)	CH_3OH	243(4.37)	241(4.36)	2-(*p*-Biphenylyl)indole (XII)	CH_3OH[e]	208(4.60)	240(4.09)
		249(4.39)	246(4.36)			257(4.25)	278(3.82)
		255(4.39)	252(4.37)			329(4.58)	
		313(4.29)	274(4.00)	2,3-Diphenylbenzofuran (XIII)	CH_3OH	235(4.36)	256(3.79)
	H_3PO_4	254(3.88)	256(3.87)			302(4.36)	
		261(3.94)	284(3.40)			315s(4.25)	
		365(4.14)[g]		5-Methyl-2,3-diphenylbenzofuran (XIV)			
	HCl	255(4.10)	239(3.87)		CH_3OH	238(4.31)	230(4.26)
		261(4.12)	258(4.09)			306(4.39)	256(3.73)
		363(4.16)	284(3.72)			320s(4.29)	
				trans-Stilbene (XV)	CH_3OH	295(4.47)	242(3.10)
						306(4.45)	
						319s(4.26)	

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[a] Absolute methanol; spectrum covers range 220–400 mμ; syrupy (85%) phosphoric acid containing 2% absolute methanol, 250–400 mμ; concentrated hydrochloric acid containing 12% methanol, 220–400 mμ. [b] Wave length followed by s denotes shoulder, plateau or inflection. [c] Blades and Wilds (ref. 15) report 241(4.34), 309(4.47). The present values were determined in duplicate and agree closely with data reported by Wiegand and Merkel (ref. 13). [d] Position of maximum substantially unchanged after three days standing. [e] Spectra determined on Cary, Model 14. Range 200–400 mμ. [f] Only long wavelength maximum recorded. [g] After three days standing position of maximum shifted to 345 mμ. [h] After three days, maximum 336 mμ. [i] After three days no maximum above 300 mμ. [j] Extinction coefficients could not be accurately determined because of poor solubility.

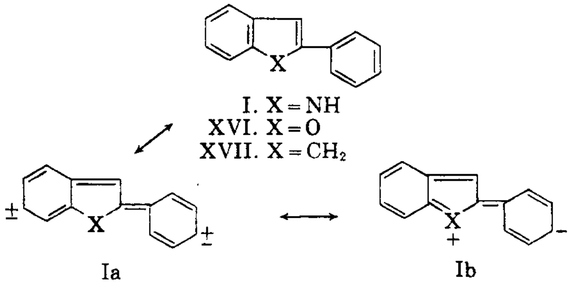
The 2,3-diarylindoles IV–X were prepared in the laboratories of Dr. E. F. Pratt, University of Maryland, by the cyclization of α-anilino-α-phenylacetophenones (desyl anilines) in refluxing *p*-cymene.[4] Melting points of the 5-methyl (VI), 5-chloro (VIII), and 5-methoxy (X) derivatives agreed closely with values reported by Ockenden and Schofield,[3] who prepared these compounds by Fisher indole syntheses from the desoxybenzoin *p*-X-phenylhydrazones. As the question of whether the α-(*m*-X-anilino)-α-phenylacetophenones cyclize *ortho* or *para* to X is as yet unresolved[5,6] the structures of V, VII and IX cannot be assigned with certainty. The weight of evidence[6] favors the 4-methoxy-2,3-diphenylindole structure for IX. Because electronic effects of 4- and 6-substituents on spectra would be expected to be about the same, further consideration of this problem will be deferred to a forthcoming publication by Pratt and Kamlet. Details of syntheses and physical properties will also be discussed together with the kinetics and mechanism of the cyclization reaction.

Fusion of equimolar *p*-cresol and benzoin with catalytic amounts of zinc chloride at 180° for 1.5 hr. gave mainly unchanged benzoin together with small amounts of 5-methyl-2,3-diphenylbenzofuran (XIV), which was separated by virtue of its greater solubility in ether. After several recrystallizations from ethanol the product melted at 114.5° (lit.,[7] m.p. 114°). A similar procedure using phenol gave 2,3-diphenylbenzofuran (XIII), m.p. 123–124° (lit.,[7] m.p. 123°), also in poor yields. Attempts to prepare these and other substituted 2,3-diphenylbenzofurans by refluxing cymene solutions of benzoin, the appropriately substituted phenol, and *p*-toluenesulfonic acid, yielded only tetraphenylfuran, m.p. 169–170°, which has been described as arising from benzoin by a series of oxidation-reduction and autocondensation reactions.[8]

Absorption spectra. The spectra were measured in 1-cm. silica cells using either a Cary Model 14 or a Beckman DU Spectrophotometer. To check for instrumental errors several spectra were determined on both machines and agreed within 1% in extinction coefficients and within one half millimicron in positions of the maxima. Solutions were 4.0 ± 0.1 × $10^{-5}M$ and previously described precautions[9] were taken to guard against photochemical transformations which are quite common at these low concentrations.

DISCUSSION

2-Phenylindole (I) shows two regions of intense absorption above 220 mμ in the ultraviolet. A secondary B-band[10] with a maximum at 240 (4.23),[11] probably arising from a styryl "partial," is superimposed on high intensity shorter wave length absorption so that the manner in which it shifts with substitution in the indole nucleus is often obscured. The primary B-band maximum at 309(4.39), however, is sufficiently remote that the variation in its position and intensity is less influenced by complications due to band overlap. The latter band may derive from the *trans*-stilbene chromophore (Ia) shifted bathochromically due to resonance contributions by structures like Ib. *trans*-Stilbene (XV) exhibits twin maxima at 295(4.47) and 306(4.45).

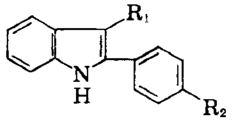


I. X = NH
XVI. X = O
XVII. X = CH_2

Ia Ib

2-Phenylbenzofuran (XVI) and 2-phenylindene (XVII), which incorporate the same chromophore with resonance stabilization by structures like Ib, have spectra resembling I. For XVI splitting of the primary B-band persists with maxima at 302(4.39) and 315(4.28)[12] while XVII, like I, shows fusion of the maxima with a single peak at 305-(4.40, dioxane).[13] The displacement of the B-bands with changing X is as anticipated,[14] NH> O>CH_2. For comparison, 3-phenylindole has a spectrum reminiscent of the alkylindoles with maxima at 224(4.56) and 269(4.25) and a weak inflection at 280 (4.2).

The 3-substituent of 2-arylindoles influences only slightly the position of the primary B-band maximum, but affects strongly its intensity; the greater the bulk of the grouping, the lower is ϵ_{max}. Thus the band corresponding to 309(4.39) for I has its maximum at 307.5(4.32)[15] for 3-methyl-2-phenylindole (XVIII), at 306(4.21)[16] for 2-phenyltryptophane (XIX), and at 308(4.22) for 2,3-diphenyl-



I. R_1 = H, R_2 = H
IV. R_1 = C_6H_5, R_2 = H
XVIII. R_1 = CH_3, R_2 = H
XIX. R_1 = $CH_2CH(NH_2)COOH$, R_2 = H
XX. R_1 = CH_3, R_2 = Cl
XXI. R_1 = H, R_2 = Cl

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[4] M. J. Kamlet, Ph.D. thesis, University of Maryland, 1954.

[5] A. H. Orr and M. Tomlinson, *J. Chem. Soc.*, 5097 (1951).

[6] H. J. Tauber and K. Schnee, *Ber.*, 91, 2089 (1958).

[7] B. T. Arventi, *Bull. Soc. Chim. France*, [5] **3**, 598 (1936).

[8] O. Dischendorfer, *Monatsh.*, **74**, 287 (1943).

[9] M. J. Kamlet and L. A. Kaplan, *J. Org. Chem.*, **22**, 576 (1957).

[10] The band nomenclature system is that of W. F. Forbes, *Can. J. Chem.*, **36**, 1350 (1958). The B-band corresponds to the "primary band" of Doub and Vandenbelt, the "C-band" of Klevins and Platt, and the "K-band" of the European school.

[11] The same system of denoting positions and extinction coefficients of maxima is used in the text as in Table I; wave lengths are given in millimicrons followed by $\log \epsilon$ in parentheses. Unless otherwise stated spectra from the literature were determined in ethanol.

[12] P. Yates, *J. Am. Chem. Soc.*, **74**, 5376 (1952).

[13] C. Wiegand and E. Merkel, *Med. u. Chem.*, **4**, 585 (1942).

[14] E. A. Braude in E. A. Braude and F. C. Nachod, *Determination of Organic Structures by Physical Methods*, Academic Press, New York, 1955, pp. 153–154.

[15] C. E. Blades and A. L. Wilds, *J. Org. Chem.*, **21**, 1013 (1956).

[16] H. M. Kissman and B. Witkop, *J. Am. Chem. Soc.*, **75**, 1967 (1953).

indole (IV). Similarly 2-(*p*-chlorophenyl)-3-methylindole (XX), 310.5(4.36)[15] shows a slight hypsochromic shift and diminished intensity relative to 2-(*p*-chlorophenyl)indole (XXI), 313.5(4.43).[15]

This corresponds to the steric effect referred to by Braude and co-workers as "type 1" behavior,[17] *i.e.*, a reduction in intensity without a significant shift in position of λ_{max} due to substitution in a vicinal atom by a nonconjugating group. Spectral bands exhibiting "type 1" behavior are believed to derive from transitions between ground states where the energetically preferred conformation is nonplanar and excited states where the preferred conformation is planar or near planar. In this series the 3-substituents, by increasing the angle of deviation from planarity of the 2-phenyl grouping with reference to the indole nucleus in the preferred ground state conformation, decrease the transition probability with a corresponding decrease in ϵ_{max}. Preferred interplanar angles, θ, calculated from Braude's equation, $\cos^2\theta = \epsilon/\epsilon_0$ where ϵ is the molar extinction coefficient of the 3-substituted derivative and ϵ_0 that of the parent compound,[18] are listed in Table II.

TABLE II

STERIC EFFECTS IN 3-SUBSTITUTED 2-ARYLINDOLES

Indole	ϵ/ϵ_0	θ
2-Phenyl (I)	1.000	0°
3-Methyl-2-phenyl (XVIII)	.846	23
2-Phenyltryptophane (XIX)	.650	36
2,3-Diphenyl (IV)	.680	34
2-(*p*-Chlorophenyl) (XXI)	1.000	0°
2-(*p*-Chlorophenyl)-3-methyl (XX)	.842	23

A similar, albeit weaker, effect is noted with the benzofurans. The 2,3-diphenyl derivative (XIII) shows a maximum at 302(4.36) and an inflection at 315(4.25) compared with twin maxima at 302-(4.39) and 315(4.28)[12] for the parent compound XVI. From this the interplanar angle is calculated to be 15°.

While substitution at the 1-position has about the same effect on intensity as it does at the 3-position, the displacement of λ_{max} is far more pronounced, *N*-methylation resulting in a hypsochromic shift of 10 to 15 mμ. Thus 1-methyl-2-phenylindole (III) has its primary maximum at 298(4.26), $\Delta\lambda = -11$ mμ, $\epsilon/\epsilon_0 = 0.73$ and 2-(p-chlorophenyl)-1-methylindole shows λ_{max} at 298.5(4.32), $\Delta\lambda = -15$ mμ, $\epsilon/\epsilon_0 = 0.77$. The magnitude of these effects is about the same as has been observed with the 2-arylbenzimidazles,[19] whose geometry and conjugated system closely resemble the present series. The *N*-methyl-2-phenyl, *N*-methyl-2-(*p*-hydroxyphenyl), *N*-methyl-2-(*p*-anisyl), and *N*-methyl-2-(*p*-aminophenyl) derivatives all showed hypsochromic shifts of 13–16 mμ relative to the parent *N*-hydrogen compounds with ϵ/ϵ_0 values of 0.70–0.76.

It seems likely that these shifts derive from steric rather than electronic causes[20] and conform with the effect described by Braude[17] as "type 2" behavior, *i.e.*, reduction in intensity coupled with a pronounced hypsochromic displacement. Such behavior is a consequence of the vicinal substituent completely inhibiting adoption of the uniplanar conformation required for maximal electronic interaction between the rings. The energy of the noncoplanar electronic excited state is raised relative to that of the noncoplanar ground state with a consequent increase in transition energy and lowering of λ_{max}. We cannot with certainty explain why a methyl group should cause a "type 1" effect on a vicinal carbon atom but a "type 2" effect on a vicinal nitrogen. The problem may relate to the geometry at the 1- and 3-positions. The angle between the carbon atoms of the 3-methyl and the 2- and 3-positions is probably greater than 120° and within the plane of the indole nucleus. On the other hand, the angle formed by the carbon of the 1-methyl group, the nitrogen, and the carbon at the 2-position may be less than 120° and out of the plane.

To determine effects of substitution in the indole nucleus the spectra of a number of 4(6)- and 5-substituted 2,3-diphenylindoles were determined. For these compounds in methanolic solution the order of increasing λ_{max} was H (IV), 308(4.22)<5-Cl (VIII), 309(4.28)<4(6)-Cl (VII) 313(4.27) $\cong$ 5-CH_3 (VI), 313(4.29)<4(6)-CH_3 (V), 314(4.24)<5-OCH_3 (X), 317(4.34)<4(6)-OCH_3 (IX), 325(4.23).[21] The order and the magnitudes of the shifts were as might have been predicted. Substituents in the 4(6)-position, conjugated with the stilbene chromophore, caused greater bathochromic displacements than like substituents in the 5-position which is out of conjugation. For the 4(6)-substituted compounds the order of increasing λ_{max} corresponds with increasing electromeric polarizability of the substituent group; for the 5-substituted derivatives the order corresponds to the increase in the combined effects

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(17a) E. A. Braude, E. R. H. Jones, H. P. Koch, R. W. Richardson, F. Sondheimer, and J. B. Toogood, *J. Chem. Soc.*, 1890 (1949). (b) E. A. Braude and F. Sondheimer, *J. Chem. Soc.*, 3754 (1955).

(18) Ref. 14, p. 174.

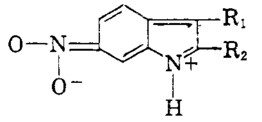
(19) A. Mangini and F. Montanari, *Boll. sci. fac. chim. ind. univ. Bologna*, **14**, 36 (1956).

(20) On the latter basis it would be anticipated that the methyl group would by induction increase the availability of the free pair of electrons on nitrogen with a consequent bathochromic effect due to increased resonance stabilization by structures like Ib. Such an electronic effect is observed in comparing aniline, methylaniline, and dimethylaniline with maxima at 230, 244, and 250 mμ, respectively, F. G. Bordwell and P. J. Bouton, *J. Am. Chem. Soc.*, **78**, 87 (1956).

(21) 5-Amino-2-phenylindole absorbs maximally at 316.5 (4.36), R. Adams and W. P. Samuels, Jr., *J. Am. Chem. Soc.*, **77**, 5375 (1955). For comparison with the above series the 2,3-diphenyl derivative may be considered to absorb at about the same position.

of secondary resonance structures and induction.[22] The 17 mμ displacement of IX relative to IV compares with shifts of 13 mμ each for the maxima of *p*-methoxystilbene at 308(4.44) and 319(4.46) relative to the twin maxima of stilbene.[23] The increased extinction coefficients of V–X relative to IV reflect the greater tendency of the 2-phenyl group to retain the coplanar conformation as a result of resonance stabilization.[24]

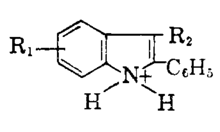
6-Nitro-2,3-diphenylindole (XI) was an interesting member of the above series which did not display the expected spectrum. By comparison with *p*-nitrostilbene, λ_{max} 350(4.42),[23] it was anticipated that the longest wave length band of XI would have its maximum 35–40 mμ lower than the observed position of 396(4.12). The problem was resolved on comparing the overall spectrum with that of 3-ethyl-2-methyl-6-nitroindole (XXII), λ_{max} = 251(3.96), 272(3.79) 340–350s(3.85), 397-(3.97).[25] From the overall similarity between the two it is apparent that the transition to the first electronic excited state in XI does not encompass the stilbene chromophore but more probably the 6-nitroindole chromophore represented by XIa.



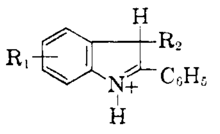
XIa. $R_1 = R_2 = C_6H_5$
XXIIa. $R_1 = C_2H_5$, $R_2 = CH_3$

The protonated indoles. It was considered that if the primary B-bands in this series did indeed derive from the stilbene chromophore with transition energies lowered by contributions from additional resonance structures like Ib, shifts to shorter wave lengths would result if the free electrons on nitrogen were tied up by protonation to the indolium salts (XXIII). By analogy with the anilinium ion which has its B-band maximum at exactly the same position as does benzene (203 mμ), we anticipated that the positions of the bands of I and IV in acidic media would approximate that for stilbene itself. When the spectra were measured in 85% phosphoric acid, there were observed instead bathochromic displacements to 343(4.34) and 344(4.20) mμ, respectively. To confirm that these spectra were not of mixtures of protonated and unprotonated material, the spectrum of IV was also determined in concentrated hydrochloric acid and in concentrated sulfuric acid. In both solvents the positions and intensities of λ_{max} were about the same, 342–344(4.19–4.20).

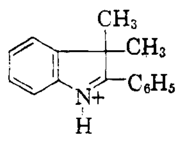
Although difficult to explain on the basis of structures XXIIIa and b, these shifts can readily be rationalized by assuming that the salts had the indoleninium structures XXIVa and b as a result of protonation at the 3-position. Witkop, Patrick, and Kissman[26] have shown that the primary B-band maximum of 3,3-dimethyl-2-phenylindolenine at 306(4.18) is shifted to 332(4.13) by protonation to the indoleninium salt XXV in alcoholic hydrochloric or *p*-toluenesulfonic acid. Both XXIV and XXV incorporate the protonated benzylideneaniline chromophore and the 10–12 mμ hypsochromic displacement and lowered absorption intensity of XXV relative to XXIVa or b are of such magnitudes as would be expected to result from a "type 2" steric effect caused by two neighboring methyl groups.



XXIIIa. $R_1 = R_2 = H$
b. $R_1 = H$, $R_2 = C_6H_5$



XXIVa. $R_1 = R_2 = H$
b. $R_1 = H$, $R_2 = C_6H_5$



XXV

With 1-methyl-2-phenylindole (III) the same sort of bathochromic displacement was observed. In 85% phosphoric acid, III showed λ_{max} at 322-(4.18), a red shift of 24 mμ relative to the unprotonated compound.

Further evidence regarding the position of protonation may be derived from the spectra of the 2,3-diphenylindoles V–X. In 85% phosphoric acid λ_{max} for this series increased in the order 4(6)-Cl (VII), 324(4.18)<4(6)-OCH_3 (IX), 328-(4.18)<5-Cl (VIII), 339(4.20)<H (IV), 344-(4.20)<4(6)-CH_3 (V), 345(4.14)<5-CH_3 (VI), 365-(4.14)<5-OCH_3 (X), 381(4.18). The spectra of V, VI, IX, and X were also determined in concentrated hydrochloric acid and showed about the same locations and intensities of maximal longer wave-length absorption.

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[22] The nature and magnitudes of these effects are discussed by M. J. Kamlet and D. J. Glover, *J. Am. Chem. Soc.*, 77, 5696 (1955).

[23] M. Calvin and H. W. Alter, *J. Chem. Phys.*, 19, 765 (1951).

[24] The relative extinction coefficients of the 5- and the 4(6)-substituted compounds may provide evidence regarding the positions of the substituents in the latter series. For each pair the 5-substituted derivative showed greater longer wavelength absorption intensity than the 4(6)-compound. In an extended search we were able to find no example of a class of compounds where substituents *meta* to a chromophoric system caused hyperchromic effects relative to the same substituents *para* to that chromophore (as would be the case here if the substituents were in the 6-position). If in the present series the substituents were in the 4-position, the diminution of intensity could be ascribed to a "type 1" steric effect resulting from buttressing of the 4-substituent against the 3-phenyl grouping.

[25] E. Shaw and D. W. Wooley, *J. Am. Chem. Soc.*, 75, 1877 (1953).

[26] B. Witkop, J. B. Patrick, and M. Kissman, *Ber.*, 85, 953 (1952).

It has been pointed out that in neutral media compounds substituted at the 4(6)-position absorbed at longer wave lengths than the correspondingly substituted 5-derivatives because the former position was conjugated with the stilbene chromophore, the latter unconjugated. With protonation at the 3-position the chromophoric system changes and the 5- becomes the conjugated and the 4(6)- the unconjugated site with respect to the new benzylideneaniline chromophore. The spectra in acid media reflect this change. For each pair the 5-substituted compound now absorbed at longer wave lengths than the 4(6)- derivative, an inversion of their former relative positions.

This seems strong evidence that there was at least some protonation at the 3-position but does not necessarily imply that all seven compounds were converted exclusively to the indoleninium salts (XXIV, $R_2 = C_6H_5$), for on the latter basis it would be difficult to explain the hypsochromic positions of the maxima of VII and IX relative to IV.[27] It seems more likely that with I, III, IV, V, VI, VIII, and X the products were predominantly the indoleninium salts but that VII and IX were converted to mixtures of the latter with the indolium salts (XXIII), $R_2 = C_6H_5$).[28] The fact that the spectra of VII and IX were more diffuse than those of the others and a broad shoulder for IX at 360–390, which might be the manifestation of a bathochromic band, supports this suggestion.

To determine whether a rate versus equilibrium phenomenon was involved, the spectra of all compounds were redetermined after three days' standing in 85% phosphoric acid. The results were inconclusive. The maxima of I, III, IV, V, VIII, and IX remained at about the same place while that of VII shifted toward the red, that of VI shifted toward the blue and that of IX disappeared completely, probably because of decomposition. Details are given in the footnotes to Table I.

Indoles undergo Mannich[16] and Michael[29] reactions at the 3-position and it is the preferred site for alkylations, acylations, and other substitution reactions,[30] indicating a high electron density at this position. Protonation at the 3-position thus is consistent with the general tendency for electrophilic reactions. Indeed, the conversion of IV to XXIVb is exactly analogous with the reaction of 2,3-disubstituted indoles with methyl iodide. The products are the 2,3,3-trisubstituted indolenines and the indoleninium salts corresponding to XXIV (H = R) are intermediates.

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(27) The positions of the maxima of both VII and VIII were strongly influenced by overlap with very high intensity bands showing maxima below 260 mμ so that the hypsochromic position for VIII relative to IV causes no concern. With VII the shift was too great to be ascribed to band overlap alone.

(28) Partial protonation at the imino position by VII and IX might be ascribed to stabilization of the stilbene chromophore by the substituent causing a tendency to keep that substituent in the conjugated position.

(29) W. E. Noland and P. J. Hartman, *J. Am. Chem. Soc.*, **76**, 3227 (1954).

(30) *Cf.* Review by P. L. Julian, E. W. Meyer, and H. C. Printy in R. C. Elderfield, *Heterocyclic Chemistry*, Volume III, John Wiley and Sons, New York, 1952.

[CONTRIBUTION NO. 28 FROM THE EXPLORATORY RESEARCH LABORATORY, DOW CHEMICAL OF CANADA, LIMITED]

Organic Fluorine Compounds. XXVI.[1a] Acetoacetyl Fluoride[1b]

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Acetoacetyl fluoride was prepared from diketene and anhydrous hydrogen fluoride. Its properties and chemical reactivity as an acetoacetylating agent were investigated.

Acyl fluorides have been reported to be stable in cases where the corresponding chlorides or bromides are nonexistent or unstable. Formyl fluoride[2] and perchloryl fluoride[3] are representative of the high stability of acyl fluorides.

Acetoacetyl chloride has been prepared by Hurd and Kelso[4] but was found to be unstable above −20°. It could not be distilled or stored without

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(1a) Part XXV, *J. Org. Chem.*, **21**, 1319 (1956).

(1b) Presented at the Symposium on Recent Advances in Fluorine Chemistry, at the 138th Meeting of the American Chemical Society, September 12, 1960. New York, N. Y.

(2) A. N. Nesmeyanov and E. J. Kahn, *Ber.*, **67**, 370 (1934). G. A. Olah and S. J. Kuhn, *J. Am. Chem. Soc.*, **82**, 2380 (1960).

(3) A. Engelbrecht and H. Atzwanger, *Monatsheft.*, **83**, 1087 (1952).

(4) C. D. Hurd and C. D. Kelso, *J. Am. Chem. Soc.*, **62**, 1548 (1940).