[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WASHINGTON]

Alkyl Substituent and Solvent Effects in the "Principal" Ultraviolet Transition of Some Positive Ions

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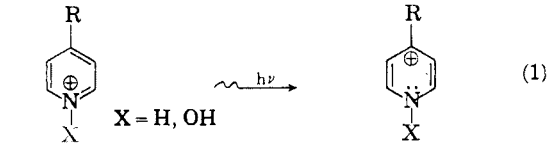
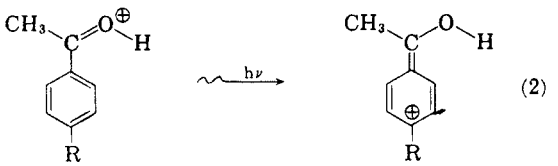
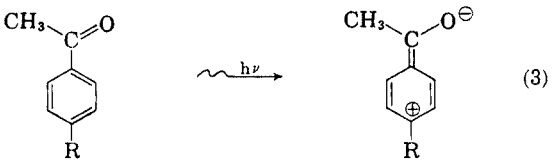
The energy of the "principal" electronic transition has been determined for the conjugate acids of *p*-alkylnitrobenzenes, the conjugate acids and acylonium ions of 4-alkyl-2,6-dimethylbenzoic acids, the conjugate acids of *p*-alkylacetophenones, 4-alkylpyridinium ions, and 4-alkyl-1-hydroxypyridinium ions. The excitation energies of the latter three series of compounds were measured in a number of solvents. For all the series and in all solvents, stabilization of the excited state relative to the ground state was in the inductive order, indicating that C—H hyperconjugation is *not* the most important mode of electron release by alkyl groups in these highly electron-demanding transitions. In keeping with the nature of the transitions, solvent effects in shifting the spectra or changing the excitation energy spreads between members of a series were small.

This paper deals with the effect of changing alkyl substituent and changing solvent upon the "principal" electronic transition of a number of positive ions, including 4-alkylpyridinium and 4-alkyl-1-hydroxypyridinium ions, conjugate acids of *p*-alkylacetophenones and *p*-alkylnitrobenzenes, and conjugate acids and acylonium ions of 4-alkyl-2,6-dimethylbenzoic acids. The "principal" transition involves a redistribution of charge, with the transition moment lying in the long axis of the molecule, and is represented approximately by Equations 1 and 2.[2]







In a previous study of the principal electronic transition of neutral *p*-alkylnitrobenzenes and *p*-alkylacetophenones (Equation 3) it was found that: (1) in the gas phase the order of excitation energies is H (greatest)>>Me>Et>iPr>tBu[3] and (2) basic solvents tended to invert the gas phase order, giving a resultant jumbled order of excitation energies. It was concluded that the *order* of inherent electron release by alkyl, in such electron demanding transitions at least, is the inductive one; *i.e.*, that C—H hyperconjugation is *not* a predominant mode of electron release. The Baker-Nathan Effect[4] on the excitation energies in basic solvents was ascribed to steric hindrance to solvation *near* the alkyl substituent. This factor would tend to invert the inductive order of excitation energies since solvent stabilization of the excited state relative to the ground state would be decreased with increasing bulk of the substituent.[3]

It appeared of interest to determine, if possible, whether the inductive order of inherent electron release also would prevail in principal electronic transitions of the types of Equations 1 and 2, since these are presumably even more demanding of electron release by the substituent. It also was considered necessary to study the effect of changing solvent on the excitation energies of a number of the positive ions, since previous experience has shown that the order of inherent substituent effects may be masked by solvent.[3]

EXPERIMENTAL

Materials. The preparation and purification of the *p*-alkylacetophenones,[3] *p*-alkylnitrobenzenes,[3] 4-alkyl-2,6-dimethylbenzoic acids,[6] and of pyridine, 4-methylpyridine, 4-ethylpyridine, and their perchloric acid salts[2] has been described. Fractional distillation through a 40-plate spinning band column was used to purify 4-isopropylpyridine,[7] b.p. 122° (127 mm.), $n_D^{25.5}$ 1.4941, and 4-*t*-butylpyridine,[7] b.p. 135° (131 mm.), $n_D^{25.5}$ 1.4934. The perchloric acid salts were prepared and purified by the method used previously.[2] The 4-isopropylpyridinium perchlorate melted at 60.1–60.8°.

(1) National Science Foundation Predoctoral Fellow, 1956–58.

(2) W. M. Schubert and J. Robins, *J. Am. Chem. Soc.*, **80**, 559 (1958).

(3) W. M. Schubert, J. Robins, and J. L. Haun, *J. Am. Chem. Soc.*, **79**, 910 (1957).

(4) The term "Baker-Nathan Effect" is defined as an order of *experimental quantities* that either corresponds with or tends to correspond with the number of α-hydrogens on the alkyl substituent.[5]

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TABLE I

VALUES OF ν_{max} (Cm.$^{-1}$) FOR THE PRINCIPAL BAND OF 4-ALKYLPYRIDINIUM PERCHLORATES IN VARIOUS SOLVENTS[a,b,c]

Group	98% H_2SO_4	70% $HClO_4$	50% $HClO_4$	36% $HClO_4$	1% $HClO_4$[c]	MeOH[e]	EtOH[e]
H	+3820	+3760	+3720	+3650	+3620	+3100	+2320
Me	45660	45620	45790	45980	46080[d]	45980	46020
Et	−430	−380	−340	−430	−400	−320	−340
i-Pr	−650	−520	−540	−650	−630	−480	−480
t-Bu	−900	−720	−720	−790	−770	−630	−610

[a] The absolute value of ν_{max} is given for the 4-methyl compound; the ν_{max} values of the other compounds are relative to the methyl compound. [b] Average of 2 runs, duplicable to ±20 cm.$^{-1}$ [c] Negligible amount of free pyridine in any of the solvents (H. C. Brown and X. R. Mihm, *J. Am. Chem. Soc.*, 77, 1725 (1955). [d] Has λ_{max} = 217.0 mμ, ϵ_{max} = 5400. [e] Contain 1% by volume of H_2SO_4.

TABLE II

VALUES OF ν_{max} (Cm.$^{-1}$) FOR THE PRINCIPAL BAND OF 4-ALKYL-1-HYDROXYPYRIDINIUM IONS IN ACIDIC MEDIA[a,b,c]

Group	98% H_2SO_4	62% H_2SO_4	70% $HClO_4$	9% $HClO_4$	MeOH[e]	EtOH[e]
H	+2010	+1830	+2130	+1680	+1420	+1290
Me	44400	44250	44400	44000[d]	43670	43560
Et	−410		−340	−250	−230	−230
i-Pr	−620		−480	−350	−320	−330
t-Bu	−750		−630	−480	−380	−370

[a] Protonation to the 1-hydroxypyridinium ion greater than 90% complete in 9% $HClO_4$ (H. H. Jaffé and G. O. Doak, *J. Am. Chem. Soc.*, 77, 4441 (1955). [b] The absolute value of ν_{max} is given for the 4-methyl compound; the ν_{max} values of the other compounds are relative to the methyl compound. [c] Average of 2 runs, duplicable to ±20 cm.$^{-1}$ [d] Has λ_{max} = 227.3 mμ, ϵ_{max} = 8500. [e] Contain 10% by weight of H_2SO_4.

Anal. Calcd. for $C_8H_{12}NO_4Cl$: C, 43.67; H, 5.46. Found: C, 43.41; H, 5.35.

The 4-*t*-butylpyridinium perchlorate melted at 100.8–101.2°.

Anal. Calcd. for $C_9H_{14}NO_4Cl$: C, 46.20; H, 5.99. Found: C, 46.44; H, 5.97.

Preparation and purification of pyridine-1-oxide and 4-methylpyridine-1-oxide were described previously.[2] The same procedure was used to prepare the other pyridine oxides. The 4-ethylpyridine oxide melted at 111.0–111.5°.

Anal. Calcd. for C_7H_9NO: C, 68.26; H, 7.36. Found: C, 68.21; H, 7.20.

The 4-isopropylpyridine oxide melted at 78–79°.

Anal. Calcd. for $C_8H_{11}NO$: C, 70.04; H, 8.08. Found: C, 69.40; H, 7.83.

The 4-*t*-butylpyridine oxide melted at 103.9–104.3°.

Anal. Calcd. for $C_9H_{13}NO$: C, 71.48; H, 8.66. Found: C, 70.86; H, 8.26.

Spectral determinations. Spectral measurements were made at room temperature as previously described. The instrument used was a Beckman DU spectrophotometer, equipped with a photomultiplier and a special fused quartz prism that extended the wave-length range to 185 mμ. Values of ν_{max} were determined in the graphical manner previously described.[3]

RESULTS

Plotted in Fig. 1 are the spectra of 4-methylpyridinium perchlorate in 1% perchloric acid, 4-methyl-1-hydroxypyridinium ion in 9% perchloric acid, and *p*-methylacetophenone conjugate-acid in 92.1% sulfuric acid. These spectra are representative of each class of compound and display well defined symmetrical bands. On variation of the 4-substituent of each class of compound the position of the band was shifted but did not change in shape. Values of ν_{max} in various solvents are given for 4-alkylpyridinium ions in Table I, for 4-alkyl-1-hydroxypyridinium ions in Table II, and for *p*-alkylacetophenone conjugate acids in Table III. Table IV lists ν_{max} and ϵ_{max} values for *p*-alkylnitrobenzene conjugate acids in 101.5% sulfuric acid. Table V lists ν_{max} and ϵ_{max} values for the conjugate acids (in 88% H_2SO_4) and acylonium ions (101% H_2SO_4) of 4-alkyl-2,6-dimethylbenzoic acids.

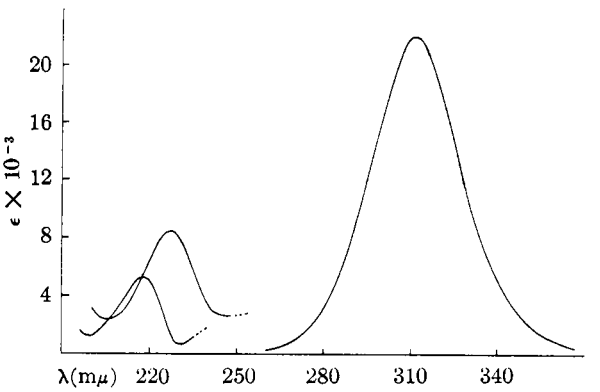

Fig. 1. Spectra of 4 methylpyridinium perchlorate in 1% $HClO_4$, 4-methyl-1-hydroxypyridinium perchlorate in 9% $HClO_4$ and *p*-methylacetophenone conjugate acid in 92.1% H_2SO_4 (reading from left to right).

DISCUSSION

Solvent effects. A main feature of the results of Tables I, II, and III is the fact that changing solvent has very little effect on the principal band

TABLE III

VALUES OF ν_{max} (Cm.$^{-1}$) FOR THE PRINCIPAL BAND OF *p*-ALKYLACETOPHENONES IN CONCENTRATED H_2SO_4[a,b,c]

Group	99.0% H_2SO_4	92.1% H_2SO_4	85.2% H_2SO_4
H	+1840	+1900	+1940
Me	32030	32110[d]	32270
t-Bu	−380	−330	−310

[a] Protonation to conjugate acid practically complete in all solvents (M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957). [b] The absolute value of ν_{max} is given for the *p*-methyl compound; the ν_{max} of the other compounds are relative to the methyl compound. [c] Average of 2 runs, duplicable to ±20 cm.$^{-1}$ [d] Has λ_{max} = 311.4 mμ, ϵ_{max} = 22100.

TABLE IV

VALUES OF ν_{max} (Cm.$^{-1}$) AND ϵ_{max} FOR THE PRINCIPAL BAND *p*-ALKYLNITROBENZENES IN 101.5% H_2SO_4[a]

p-Group	ν_{max}[b,c]	$\epsilon_{max} \times 10^{-3}$[d,e]
Me	26610[d]	15.3
Et	−210	16.8
i-Pr	−240	16.0
t-Bu	−370	17.7

[a] The nitrobenzenes are 97–99% in the form of their conjugate acids (J. C. D. Brand, *J. Chem. Soc.*, 997 (1950)). [b] Absolute value given for methyl compound; the others are relative to methyl. [c] Average of two or more determinations, duplicable to ±30 cm.$^{-1}$ [d] λ_{max} = 375.8 mμ. [e] Estimated accuracy, ±5%. Spectra determined quickly due to slow sulfonation.

TABLE V

VALUES OF ν_{max} (Cm.$^{-1}$) AND ϵ_{max} FOR THE PRINCIPAL BAND OF 4-ALKYL-2,6-DIMETHYLBENZOIC ACIDS IN STRONG H_2SO_4

	88% H_2SO_4[a]		101% H_2SO_4[b]	
p-Group	ν_{max}[c]	$\epsilon_{max} \times 10^{-3}$[d]	ν_{max}[c]	$\epsilon_{max} \times 10^{-3}$[d]
Me	35460[e]	7.2	35520	20.0
Et	35340	8.2	35270	21.7
i-Pr	35270	7.9	35150	22.2

[a] Substrate primarily in the form of the conjugate acid, $ArCO_2^+H_2$.[6] [b] Substrate practically completely in the form of the acylonium ion, $ArCO^+$.[6] [c] Determined to ±60 cm.$^{-1}$ [d] Estimated accuracy, ±3%. [e] λ_{max} = 282 mμ.

position of each compound; *i.e.*, the *difference* between solvent stabilization of ground and excited states is not very sensitive to a change in medium.[8] This is not surprising since the transitions involve a redistribution of positive charge (Equations 1 and 2). The Franck-Condon Principle applies, of course, which means that there is practically no movement of the solvent atomic nuclei in the short time of the electronic excitation. Solvent stabilization at the functional group (*e.g.*, H-bonding to the acidic proton) is less in the excited state than in the ground state, since the positive charge at the functional group is decreased in the excitation. This factor acts to raise the excitation energy (relative to the gas phase). However, solvent stabilization of the ring is greater in the excited than in the ground state, since the positive charge in the ring is increased in the excitation, and this would act to lower the excitation energy. These two solvation forces appear to be approximately balanced.

There are only slight differences in the solvent shifts for the three series of compounds. For example, compare the effect of decreasing strength of aqueous mineral acid. As aqueous solvent basicity is increased, the excitation energies of the 1-hydroxypyridinium ions decrease slightly (Table II), those of the pyridinum ions increase slightly (Table I) and those of the acetophenone conjugate acids increase somewhat more rapidly (Table III). In other words, the quantity, solvent stabilization of the excited state *minus* solvent stabilization of the ground state, increases slightly for the hydroxypyridinium ions, decreases slightly for the pyridinium ions and decreases to greater degree for the acetophenone conjugate acids. Since the Franck-Condon Principle applies, which means that the orientation of solvent molecules in the excited state is that fixed by the ground state, interpretation of these small differences in behavior between the three series of compounds is difficult. However, the results imply that as one proceeds from the hydroxypyridinium ions to the pyridinium ions to the acetophenone conjugate acids, there is a reduction in the importance of solvation of the ground state at sites that increase in positivity in the excitation *relative to* solvation at sites that decrease in positivity. This may mean that the positive charge in the ground state of the ions is dispersed to the greatest extent in the hydroxypyridinium ions and to the least extent in the acetophenone conjugate acids. Such a conclusion is perhaps an oversimplification, however.

Substituent effects. For each series of positive ions (some of them incomplete) the principal band excitation energies follow the inductive order (Tables I–V). Furthermore, in those instances in which the solvent was varied (Tables I–III), this order is maintained and solvent shifts on the spectrum of a particular compound are small. Therefore, it is safe to conclude that the *order* of inherent electron release in these highly electron demanding transitions is the inductive one. Thus, as in the principal electronic transitions of neutral *p*-alkyl-nitrobenzenes and acetophenones,[3] C—H hyperconjugation is not the most important factor in the total electron release effects of the alkyl groups.

As the solvent is changed there are no dramatic changes in the spreads between excitation energies of the compounds of Tables I, II, and III such as were found for the neutral nitrobenzenes and aceto-

(8) By contrast, the principal band of *p*-nitrotoluene, *e.g.*, changes by 2080 cm.$^{-1}$, or 5.9 Kcal., from water to 70% perchloric acid as the solvent.[3]

phenones.[3] Since the total *difference* between solvent stabilization of the excited and ground states is changed very little with solvent, one would not expect the factor of steric hindrance to solvation near the alkyl group to greatly influence the excitation energy spreads from solvent to solvent. Certain minor trends possibly attributable to this factor may be discernible, although speculation seems unwarranted.

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Synthesis of Deuterated Biphenyls[1]

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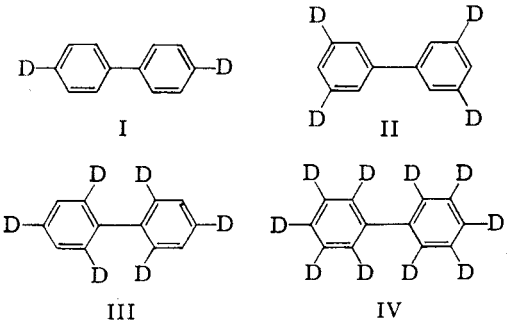
The preparation of four deuterated analogs of biphenyl, biphenyl-4,4′-d_2, biphenyl-3,3′,5,5′-d_4, biphenyl-2,2′,4,4′,6,6′-d_6, and biphenyl-d_{10} is described. The first compound was synthesized from 4,4-dibromobiphenyl, and the other three were formed by coupling the Grignard reagent of the appropriate deuterated bromobenzene.

Deuterium labeling has proved of great value for studies of substitution reactions in organic compounds.[2] Examination of the fragmentation of organic compounds by ionizing radiation[3,4] and the determination of molecular configuration by infrared spectrometry[5] have also been facilitated by deuterium labeling. Furthermore, the use of properly deuterated molecules greatly simplifies the interpretation of mass spectra of organic molecules[4,6] by enabling identification of the ionized fragments produced and analysis of the processes taking place.

In this laboratory we are studying aromatic hydrocarbons of the polyphenyl type by several of the above methods—irradiation, vibrational analysis, and mass spectrometry. Biphenyl, which is the simplest member of the polyphenyl series, is the simplest aromatic compound containing only benzene rings which has nonequivalent carbon-hydrogen bonds. This nonequivalence has been demonstrated in the substitution reactions of biphenyl, since the rates of reaction differ at the positions *ortho*, *meta*, and *para* to the bond joining the two rings.[7] Replacing hydrogen atoms by deuterium atoms at various sites in the biphenyl molecule allows the techniques mentioned above to furnish more information about the molecule. Consequently we have prepared four deuterium-substituted biphenyls: biphenyl-4,4′-d_2 (I), which has deuterium atoms in the two *para* positions; biphenyl-3,3′,5,5′-d_4 (II), which has deuterium atoms in the four *meta* positions; biphenyl-2,2′,4,4′,6,6′-d_6 (III), which has deuterium atoms in the four *ortho* and two *para* positions; and biphenyl-d_{10} (IV), which is completely deuterated. It can be seen that no molecular symmetry is lost in these deuterated biphenyls (in contrast to the case of the partially deuterated benzenes[5]), and therefore there is no increase in complexity of the vibrational spectra of the deuterated biphenyls over that of biphenyl itself.



I II III IV

Synthetic procedures. Deuterated benzenes and toluenes have been prepared by treatment of Grignard reagents[8] and organolithium compounds[9]

(1) This work was performed under AEC Contract AT(11-1)-GEN-8.

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