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Structure of Ammonium/Phenoxide Ion-Pairs in Solution

F. M. Menger* and Philippe A. Barthelemy

Department of Chemistry, Emory University,
Atlanta, Georgia 30322

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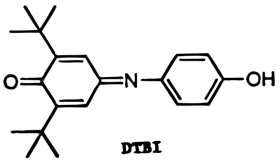
2,6-Di-*tert*-butylindophenol (DTBI)[1] dissolved in ethanol (4.2×10^{-5}M) gives a pale, peach-colored solution ($\lambda_{max} = 484$ nm). When amines are mixed with the dye, one of three types of effects, depending upon the amine, was observed: (a) The solution becomes a turquoise-blue with a λ_{max} at 590 nm; the absorbance at 484 nm is relegated to a tail on the main peak. (b) The original spectrum remains essentially unchanged. (c) An intermediate situation exists in which the band at 484 nm persists, but it now has a weak shoulder at 590 nm; these solutions are a nondescript blue-grey. One hardly needs a spectrophotometer to differentiate the three categories of amines; the naked eye suffices. The present communication describes our attempts to unveil structural information concealed in the dependence of dye-color upon the nature of the amine.



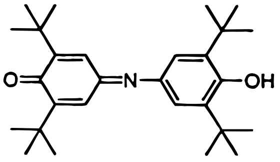
DTBI

Complexes of phenols and amines have been popular objects of study owing, no doubt, to the ease with which the donor−acceptor properties can be almost continuously varied. By far the greatest number of such studies have involved physical−chemical determinations of association constants, spectral perturbations, enthalpy changes, etc. in systems where hydrogen-bonding, not proton-transfer, predominates.[2−8] Proton-transfer to aliphatic amines has been shown to occur, however, with sufficiently acidic phenols dissolved in more polar solvents.[9,10] For example, 2-chlorophenol and pentachlorophenol in acetonitrile lose 6% and 100% of their protons, respectively, to *n*-propylamine.[11] Our work has a different slant from most of that in the past. A protic solvent, ethanol, was used because aliphatic amines induce only small spectral changes with DTBI in nonpolar solvents such as chloroform, cyclohexane, and tetrachloroethylene. Use of ethanol, a hydrogen-bonding solvent, allows solvent participation in the DTBI/amine complexation. Our emphasis on structural information in solution overshadows any attempt to characterize physical constants of the complexes. As will be shown, we can detect what are believed to be both intimate ion-pairs and "free" ions.

The key data are presented in Table 1 under the DTBI columns. It is seen that the various amines can be categorized into three classes according to how effectively they produce a band-shift from 484 to 590 nm. Thus, a few amines (labeled ++) create a strong peak at 590 nm. Other amines (labeled +) maintain the peak at 484 nm but, in addition, show a weak absorbance at 590 nm. And, finally, a group of amines (labeled −) perturb the DTBI spectrum very little from that with no amine at all.

The band at 590 nm, generating a blue color, represents total proton-transfer from dye to amine. Evidence for this contention comes from the observation that simple hydrogen-bonding between dye and amine in the absence of any proton-transfer (as occurs in nonpolar solvents) fails to produce a blue color. Moreover, proton loss by the dye in the presence of a strong base ($Na^+ \, ^-OEt$ in EtOH) is also accompanied by a long-wavelength band (592 nm).

Absorption at 590 nm undoubtedly reflects an aryl oxide that is closely associated either with ethanol or, *via* ion-pairing, to the ammonium counterion. Proof of this statement derives from studies of a second dye, TTBI, in which the phenolic OH is butressed by two *tert*-butyl groups. This dye has its major band at 681 or 677 nm in ethanolic solutions of ++ amines or $Na^+ \, ^-OEt$, respectively.



TTBI

The *ca.* 90 nm red-shift of TTBI relative to DTBI is too large to arise from an electronic substitutent effect by the additional alkyl groups. Instead, the *tert*-butyl groups must sterically impede hydrogen-bonding of the ArO^- to both the solvent and protonated amine, thereby enhancing delocalization of TTBI's negative charge into its ring system.

The involvement of solvent in the aryloxide of DTBI, and not that of TTBI, is futher revealed by Table 2 in which the λ_{max} values are recorded in five different alcohol solvents. It is seen that a change from methanol to 2-propanol causes a 42 nm red-shift for DBTI aryloxide but only a 3 nm red-shift for TTBI aryloxide. The simplest explanation is that, as deduced above, solvent is directly associated with the DTBI anion (or its RNH_3^+ ion-pair) but not with the "free" TTBI anion.

Having established that (a) DTBI engages in complete proton-transfer with ++ amines and that (b) ethanol is somehow involved in the resulting ionic species, we must now examine why the amines in Table 1 behave so differently. Note, first of all, that there is no apparent relationship between the category of amine (++, +, or

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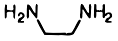
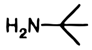
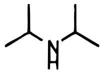
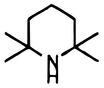
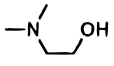
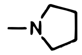
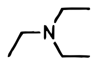
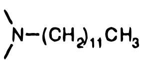
Table 1. Spectral Properties of 2,6-Di-*tert*-butylindophenol (DTBI) and 2,3′,5′,6-Tetra-*tert*-butylindophenol (TTBI) in the Presence of Amines[a,b]

Amine	2,6-di-*tert*-butylindophenol (DTBI)			2,3',5',6-tetra-*tert*-butylindophenol (TTBI)		
	Effect	Abs $_{484nm}$	Abs $_{590nm}$	Effect	Abs $_{492nm}$	Abs $_{680nm}$
None		0.41	0.02		0.25	0.01
	++	0.20	1.27	++	0.02	2.05
	++	0.19	1.21	++	0.01	2.3
	++	0.21	1.25	++	0.01	2.07
	++	0.30	0.77	++	0.01	1.90
	+	0.39	0.17	+	0.2	0.4
	+	0.39	0.14	+	0.24	0.32
	+	0.33	0.25	+	0.20	0.62
$N(C_4H_9)_3$	-	0.41	0.03	-	0.25	0
	-	0.40	0.03	-	0.24	0.07

[a] In absolute ethanol, [TTBI] = 3.3 × 10^{-5} M, [DTBI] = 4.2 × 10^{-5} M, 25 °C ± 0.1. [b] [Amine] = 0.04–0.15 M. Concentration differences in this range are not critical; a + effect does not convert into a ++ effect (or a − into a +) even at 1.0 M amine.

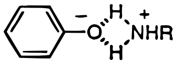
Table 2. Effect of the Solvent on the Position of the Absorption Maxima of DTBI and TTBI in the Presence of an Excess of Amine[a]

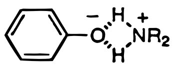
solvent	2,6-di-*tert*-butylindophenol (DTBI)		2,3′,5′,6-tetra-*tert*-butylindophenol (TTBI)	
	[DTBI] × 10^3 (mol/L)	λ_{max},[b] nm	[TTBI] × 10^3 (mol/L)	λ_{max},[b] nm
methanol	4.2	576	1.9	676
ethanol	4.2	590	3.3	681
1-butanol	4.3	600	2.4	680
2-butanol	3.2	605	2.6	680
2-propanol	3.8	618	2.4	679

[a] 3 ×10^{-1} > [amine] 1 × 10^{-2} M; 25 °C ± 0.1. [b] The position of the absorption maxima (λ_{max}) of DTBI and TTBI observed in the presence of a ++ or a + effect (Table 1) is independent of the amine.

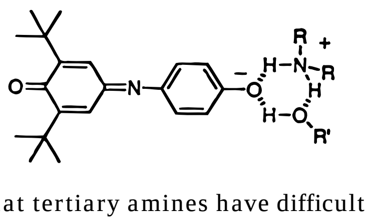
−) and the pK_a of the amine.[12] For example, *tert*-butylamine (pK_a = 10.5) is a proton-removing ++ amine, whereas the more basic tri-*n*-butylamine (pK_a = 10.9) is a − amine (signifying an inability to remove the dye's proton). Likewise, steric effects provide no viable explanation for the data. For example, 2,2,6,6-tetramethylpiperidine, a hindered amine, falls within the ++ category. In contrast, the less hindered triethylamine and dodecyldimethylamine are only + and − amines, respectively.

One important generalization is indeed revealed by Table 1: Primary and secondary amines are far more effective in removing DTBI's proton than are tertiary amines (basicity and steric factors notwithstanding). Now if the anionic and cationic species created by proton-transfer were separated by solvent, then there would be no obvious reason why only primary and secondary amines should promote the transfer. We conclude that primary and second amines must form ion-pairs in which *two* ammonium protons are involved. Shown below are structures that incorporate this feature. A protonated tertiary amine lacks, of course, the necessary pair of donor protons.





In actual fact, the above structures seem unlikely. First, they do not include solvent which, as stated, is postulated as being an integral part of the complex. Second, the bifurcated hydrogen-bonds create four-membered rings. As is generally appreciated, five and six-membered rings are usually preferred when there is a choice. Bifurcated hydrogen-bonds are known, especially in the solid state,[13] but theoretical work, such as that on the water dimer,[14] mitigates against their relative stability. Thus, a model has been devised, shown below, to accommodate these considerations. The picture has intuitive appeal and explains all our conclusions: anionic dye, involvement of solvent, lack of bifurcation, and the requirement for two ammonium protons. Coplanarity of the hydrogen-bonded ring with the phenoxide ring, as would be expected from the sp^2 character of the phenoxide oxygen, also explains the steric effects of the two ortho *tert*-butyl groups in TTBI. It should be noted that the model is "minimal" in the sense that the spectrophotometric data cannot exclude the presence of additional solvent molecules loosely associated with the structure.



The fact that tertiary amines have difficulty removing a proton from the dye does not preclude the presence of

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[12] The pK_a values refer to aqueous solvents. It would be preferable, of course, to use pK_a values in ethanol were they available.

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a hydrogen-bonding association. Indeed, spectrophotometrically-determined association constants show that *tert*-butylamine and triethylamine bind similarly to DDBI ($K_{\text{assoc}} = 96$ and 41 M^{-1}, respectively). The main difference is that *tert*-butylamine can form a blue, ionic complex while the triethylamine, lacking the necessary protons, is relegated to a nonionic and almost colorless interaction.[15]

Experimental Section

Materials. 2,6-Di-*tert*-butylindophenol (DTBI) was prepared by condensation of 2,6-di-*tert*-butylbenzoquinone with 4-aminophenol in THF catalyzed by boron trifluoride diethyl etherate.[1] Synthesis of 2,3′,5′,6-tetra-*tert*-butylindophenol (TTBI) also followed a known procedure.[16] All amines were obtained from Aldrich and used as received; solvents were of spectrophotometric grade.

Measurements. All ultraviolet-visible spectra were recorded on Varian DMS-200 or DMS-300 double-beam spectrophotometers. In a typical experiment, 1.3 mg of DTBI was dissolved in 50 mL of absolute ethanol. A 1.00 cm quartz cuvette was then filled with 1.00 mL of this stock solution plus 1.00 mL of ethanol to give a final DTBI concentration of 4.2×10^{-5} M. After the cuvette was thermostated at 25.0 °C in the cell chamber of the spectrophotometer, spectra were recorded (310−750 nm) before and after the addition of 0.02 mL of amine. A similar method was used for TTBI and for the other alcoholic solvents. Equilibrium constants for phenol/amine association were obtained with the aid of the Benesi−Hildebrand method[17] (using 590 and 680 nm for DTBI and TTBI, respectively, as 5−50 uL of amine was added to 2.0 mL of 5.8×10^{-5} M dye in ethanol.

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[15] For another study of a phenolic dye plus amines in ethanol (and many relevant footnotes) see Kaneda, T.; Umeda, S.; Ishizaki, Y.; Kuo, H.-S.; Misumi, S. *J. Am. Chem. Soc.* **1989**, *111*, 1881.

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[17] Rose, N. J.; Drago, R. S. *J. Am. Chem. Soc.* **1959**, *81*, 6138.