coset $K_{iS}p_S$ can be expressed as:

$$K_{iS}p_S = (R_{iS}k_SR_{fS}' \cup R_{iS}k_S'R_{fS}' \cup \ldots)p_S$$

An arbitrary element of $K_{iS}p_S$ can be written as:

$$r_{iS}k_Sr_{fS}'p_S = (r_{iS})(k_Sp_S)(p_S^{-1}r_{fS}'p_S)$$

$$= (r_{iS}r_{iL})(k_Sp_S)(r_{iL}^{-1})(p_S^{-1}r_{fS}'p_S)$$

$$= (r_{iS}r_{iL})(k_Sp_S)(r_{iL}^{-1})(p_S^{-1}p_Sr_{fS}p_S^{-1}p_S)$$

$$= (r_{iS}r_{iL})(k_Sp_S)(r_{iL}^{-1})(r_{fS})$$

where $r_{iS}r_{iL} \in R_{iLS}$, which is the form of an element of the double coset from formula 1. r_{iL}^{-1} will be in L_L since r_{iL} permutes constitutionally equivalent ligands. The final rotation group R_{fS} will be a subgroup of R_S.

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Thermodynamics of Ionization of Some Mono- and Disubstituted *tert*-Butylpyridinium Ions in Alcohol–Water Systems

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Abstract: Thermochemical measurements on the ionization process for the 2- and 4-*tert*-butylpyridinium ions and the 2,4- and 2,6-di-*tert*-butylpyridinium ions have been performed in 40.9% by weight ethanol–water and 90.0% by weight methanol–water. The thermodynamic pK_a values are 4.50, 4.42, 4.69, and 3.22, respectively, in 40.9% by weight ethanol–water and 4.13, 4.22, 4.45, and 2.22 in 90.0% by weight methanol–water, respectively. In the same solvent systems the corresponding standard enthalpies of ionization in kcal mol^{-1} are 6.00, 5.65, 6.31, and 3.82 and 4.38, 4.27, 5.02, and 3.54. From these data the corresponding entropies of ionization are calculated and analyzed in terms of current solution theory. A combination of the analysis of the entropy data and the comparison of the enthalpy data with the gas phase data indicates that steric hindrance to solvation of the cation does not completely account for the unusual acidity of the 2,6-di-*tert*-butylpyridinium ion.

The substituent effect of the *tert*-butyl group on the acidity of the pyridinium ion was first investigated by Brown and Kanner[1] who determined approximate pK_a values for several mono- and disubstituted *tert*-butyl pyridinium ions in 50% by volume ethanol–water. These workers reported that introduction of a *tert*-butyl group in the 2- or 4-position decreased the acidity, but substitution simultaneously at both the 2- and 6-positions causes a dramatic increase in acidity (1.8 pK_a units) relative to the pyridinium ion. Brown and Kanner postulated that this increase was due to the steric requirements of the *tert*-butyl group which could cause either (1) an intrinsic strain effect in the N–H bond of the 2,6-di-*tert*-butylpyridinium ion (2,6-DTBPH$^+$) which was greater than that for the lone pair of the neutral pyridine or (2) a steric inhibition of the solvation of 2,6-DTBPH$^+$ cation. Since the observed decrease in the pK_a found for the 2,6-DTBPH$^+$ ion was much larger than was expected from trends found for other alkyl-substituted pyridinium ions, inhibition of the overall electrostatic solvation was not thought to be the cause of the substituent-induced decrease in pK_a. Consequently, Brown and Kanner favored the first postulate and stated "the steric requirements of a lone pair on

the nitrogen atom are less than the steric requirements of a lone pair bonding a proton to the nitrogen atom". However, they did recognize that the hydrogen bonding of the N–H hydrogen to the solvent could be severely hindered in the 2,6-DTBPH$^+$ ion, which would account in part for the increased acidity of this cation. Unfortunately, it was not possible from their data to separate the intrinsic steric effects from the inhibition of the solvation of the 2,6-DTBPH$^+$ cation.

In an attempt to resolve this ambiguity McDaniel and Ozcan[2] measured pK_a values for the cations of pyridine, 2-*tert*-butylpyridine (2-TBP), and 2,6-*di-tert*-butylpyridine (2,6-DTBP) in several alcohol–water systems which according to these workers possessed varying steric requirements. The pK_a values decreased with increasing alcohol content for all three pyridinium ions. In addition the differences in the pK_a values between aqueous methanol and aqueous 2-propanol at fixed alcohol content were the greatest for 2,6-DTBPH$^+$ but were appreciably greater even for 2-TBPH$^+$ than those found for the pyridinium ion. These results appeared to these authors to support the contention of Condon[3] that a single *tert*-butyl group in a 2-position results in a steric hindrance to solvation

of the ion and that the increased acidity of the 2,6-DTBPH$^+$ cation is due to steric inhibition to solvation.

In a recent report[4] on the comparison of gas vs. solution phase acidities of substituted pyridinium ions, it was reported that the 2,6-DTBPH$^+$ ion deviated from the general linear relationship found between proton affinity (PA) and $\Delta G_i°$ (ionization) by ca. 3.5 kcal mol^{-1}. The PA (kcal mol^{-1}) of *tert*-butylpyridine (4-TBP) is 229.5 compared to 224.3 for pyridine, whereas the PA of 2,6-DTBP is 235, indicating that little, if any, steric strain occurs in the gas phase for the protonated or neutral species. These results suggest that the dramatic decrease in the pK_a observed for the 2,6-DTBPH$^+$ ion relative to the pyridinium ion is entirely due to solvation effects and that the first postulate of Brown and Kanner is incorrect.

le Noble and Asano[5] recently reported the pK_a values and the partial molal volumes of ionization ($\Delta V_i°$) for the cations of several 2,6-dialkyl-substituted pyridines in pure methanol. The pK_a values of the methyl, ethyl, and isopropyl 2,6-disubstituted pyridines are quite similar, but the pK_a observed for the 2,6-DTBPH$^+$ cation is over two pK_a units lower, again demonstrating the dramatic solution phase substituent effect of the *tert*-butyl group in the 2,6-DTBPH$^+$ ion. For this series the same trend is observed for the $\Delta V_i°$ values, i.e., a sudden break occurs at 2,6-DTBPH$^+$. However, the $\Delta V_i°$ for 2,6-DTBPH$^+$ is 11.2 ml mol^{-1} larger than that of 2,6-diisopropylpyridinium ion, which is a change in $\Delta V_i°$ that is opposite in sign to what is predicted by solution theory if the solvation of the 2,6-DTBPH$^+$ ion is less than that of the other cations in the series. le Noble and Asano conclude that "there is no evidence for a conspicuous lack or absence of electrostriction around the cation" in 2,6-DTBPH$^+$.

In view of the conflicting solution phase interpretations and the apparent unambiguous conclusion arrived at from the gas-phase data it seemed appropriate to perform additional thermochemical investigations on the ionization process for the available mono- and disubstituted *tert*-butylpyridinium ions in solvent systems where the solubilities of these compounds are adequate for precise thermochemical measurements. Consequently, the pK_a values and the enthalpies of protonation were determined in the 40.9% by weight ethanol-water and 90% by weight methanol-water solvent systems for 2,4-di-*tert*-butylpyridine (2,4-DTBP), 4-TBP, 2-TBP, and 2,6-DTBP. These data are combined to yield the entropy change ($\Delta S_i°$) for the ionization process for each substituted pyridinium ion. Analysis of the thermodynamic data in terms of solution theory should provide additional insight regarding the effect of the *tert*-butyl group on the ionization equilibria of pyridinium ions.

Experimental Section

Chemicals. Reagent grade pyridine (Fisher ACS certified) was dried by distillation from calcium hydride and stored over molecular sieves (Linde 5A). 4-TBP was obtained from Aldrich Chemical Co. with a stated purity of at least 99%. The 2-*tert*-butyl- and the 2,6-di-*tert*-butylpyridines were received from the Chemical Sample Co. with a stated purity of 99%. 2,4-DTBP was also obtained from the Chemical Sample Co. with a purity of 97%. This compound was distilled at 10 mm of pressure with the fraction collected at 100–101 °C used in the calorimetry and pK_a measurements.

Large quantities of the methanol-water, 90% by weight, and ethanol-water, 40.9% by weight, solutions used in this study were prepared to minimize the variation of the solvent composition between experimental determinations. The hydrochloric acid solutions and all buffers were prepared from Fisher reagent grade chemicals by mixing the reagents with the appropriate amounts of water and alcohol.

Calorimetric Measurements. The solution calorimeter and the calorimetric procedures have been described previously.[6] A 200-ml capacity reaction vessel was used in all experiments with a Hewlett-Packard digital voltmeter (Model 3450A) and digital printer (Model

5055A) for recording the data. For all the substituted pyridines, except for 2,6-DTBP, 0.4–0.7 mmol were dissolved in 200 ml of a 40.9% by weight ethanol-water solution and the heat of protonation determined by introducing 5.0 ml of 40.9% by weight ethanol-water which was 0.411 M in HCl. The enthalpy associated with the dilution of 0.411 M HCl in 40.9% by weight ethanol-water to 0.010 M was determined separately. The average value for four determinations found for this dilution was −1.01 ± 0.03 cal. The solubility of 2,6-DTBP limited the amount of this pyridine in solution to 0.045 mmol or less.

The experimental procedures for the 90% by weight methanol-water solutions were identical except that 0.9–1.4 mmol of the pyridines were dissolved in 200 ml. The protonation was accomplished by adding 6.0 ml of 0.826 M HCl in 90% by weight methanol-water solution to the reaction vessel. In this experiment the enthalpy of dilution of the HCl to 0.024 M was found to be −6.67 ± 0.03 cal from four independent runs.

At least four calorimetric determinations were made for each of the pyridines in both mixed solvent systems. All calculations were carried out on a Univac 70/7 series time-sharing computer.

The pK_a values were determined by a spectrophotometric procedure[7] with a Beckman Model Acta V UV-visible spectrophotometer. All pH measurements were made on a Fisher Accumet Model 320 expanded scale research pH meter with an immersion type glass electrode and a potassium chloride saturated calomel reference electrode. The pH meter was calibrated with a standard aqueous potassium acid phthalate buffer solution before each series of measurements. In order to obtain the negative logarithm of the activity of the hydrogen ion in the mixed solvent medium, the correction due to the medium effects was applied:[8a-c] Pa$_H$ = pH − δ where δ is the correction that must be applied to the experimentally determined pH value to compensate for the medium effect. deLigny[8b] has reported a value of −0.51 for δ in the 90% by weight methanol-water system. Using deLigny's data for the ethanol-water system,[8c] a δ value of +0.19 was calculated for the 40.9% by weight ethanol-water system.

The pH of the buffered solutions was measured immediately following the absorbance measurements. All of the pH and absorbance readings were taken at a temperature of 25.0 ± 0.1 °C. The ionic strength of the buffer solution was varied by altering the concentration of the buffers.

Results

The apparent pK_a values for substituted pyridinium ions were determined in each solvent system at several ionic strength values below 0.02 M where linear plots were always obtained for pK_a vs. the square root of the ionic strength (I). In Table I the slopes and intercepts (pK_a) for the plots of pK_a vs. $I^{1/2}$ for each pyridinium ion are given for the two solvent systems. In all cases the correlation coefficients were 0.960 or greater. The theoretical Debye–Hückel slopes are approximately 1.55 and 0.97 for the 90% by weight methanol-water and 40.9% by weight ethanol-water solvent systems. The latter is close to the observed values, whereas the slopes in 90% by weight methanol-water are two to three times larger than the theoretical value.

Since the concentrations of all solutions species in this study were determined on a molarity basis, the pK_a values reported here are for the hypothetical 1/M infinite dilution standard state in the mixed solvent. The uncertainties given in the tables are derived from the least-squares analysis, but the absolute uncertainties are probably much larger (±0.1) due to the well-known difficulties associated with electrochemical measurements[8a] with glass electrodes in alcohol-water systems. However, the relative uncertainties of the pK_a values in the same solvent system are probably ±0.01 pK_a units.

The pK_a values found in this study are not in good agreement with the previously determined pK_a values reported by Brown and Kanner[1] or those of McDaniel and Ozcan in 40.9% by weight ethanol-water.[2] Apparently these workers did not correct their pH readings for the solvent medium effect after standardizing the pH meter with an aqueous buffer. For ex-

Table I. Parameters from the pK_a(apparent) vs. $I^{1/2}$ Plots for the Pyridinium and Mono- and Di-*tert*-butylpyridinium Ions in 90% Methanol–Water and 40.9% Ethanol–Water at 298K

| | 90% by wt methanol–water | | | 40% by wt ethanol–water | |
	pK_a(intercept)	Slope		pK_a(intercept)	Slope
PY	3.776 ± 0.001	4.56 ± 0.02			
4-TBP	4.218 ± 0.004	3.75 ± 0.05	4-TBP	4.423 ± 0.001	1.58 ± 0.02
2-TBP	4.126 ± 0.001	3.72 ± 0.01	2-TBP	4.496 ± 0.001	0.36 ± 0.01
2,4-DTBP	4.448 ± 0.003	2.77 ± 0.03	2,4-DTBP	4.685 ± 0.001	1.43 ± 0.01
2,6-DTBP	2.222 ± 0.001	5.69 ± 0.01	2,6-DTBP	3.220 ± 0.001	0.70 ± 0.03

[a] The uncertainties listed were obtained from the least-squares analysis of the data and are considerably less than the estimated uncertainties. (See text.)

Table II. Thermodynamics of Ionization of Pyridinium and Substituted *tert*-Butylpyridinium Ions in 40.9% Ethanol–Water and 90% Methanol–Water at 298K[a]

| | 40.9% by wt ethanol–water | | | | 90% by wt ethanol–water | | |
	ΔG_i° [d]	ΔH_i° [c]	ΔS_i°		ΔG_i° [d]	ΔH_i° [c]	ΔS_i°
Pyridine	5.73 [b]	4.95 ± 0.03	-2.6	Pyridine	5.15	3.24 ± 0.03	-6.4
4-TBP	6.03	5.65 ± 0.02	-1.3	4-TBP	5.75	4.27 ± 0.05	-5.0
2-TBP	6.13	6.00 ± 0.05	-0.4	2-TBP	5.63	4.38 ± 0.04	-4.2
2,4-DTBP	6.39	6.31 ± 0.03	-0.3	2,4-DTBP	6.07	5.02 ± 0.08	-3.5
2,6-DTBP	4.39	3.82 ± 0.17	-1.9	2,6-DTBP	3.03	3.54 ± 0.07	$+1.7$

[a] ΔG_i° and ΔH_i° values in kcal mol^{-1}, ΔS_i° values in cal deg^{-1} mol^{-1} (1 cal = 4.184 J). [b] Calculated from the corrected pK_a value of 4.20 taken from ref 1. [c] The uncertainties listed are the standard deviations calculated from the four reproducible calorimetric determinations. [d] Assuming an absolute uncertainty in the individual pK_a values of ± 0.1, the estimated uncertainties in ΔG_i° are less than ± 0.025 kcal mol^{-1} in all cases.

ample, when the appropriate solvent medium effect correction, δ, is applied to the value reported for 2-TBPH$^+$ by McDaniel and Ozcan a pK_a value of 4.57 is obtained. Since McDaniel and Ozcan did not apply an ionic strength correction to their data, which would further lower the pK_a value, their corrected value (4.57) is in reasonable agreement with the value reported here.

The calorimetrically determined enthalpies of ionization for the substituted pyridinium ions in the two solvent systems are listed in Table II as the average of four reproducible determinations. An uncertainty of 0.08 kcal mol^{-1} or less was obtained in all cases except the 2,6-DTBPH$^+$ ion in the 40.9% by weight ethanol–water solvent where the low solubility of 2,6-DTBP limited the observable heat effect. Since the calorimetric measurements were made at an ionic strength of 0.01 (molar) in 40.9% by weight ethanol–water and 0.024 in 90% by weight methanol–water, the standard state enthalpies of ionization must be obtained by correcting for dilution effects. In pure water this correction is estimated by a procedure previously described[9] to be less than 0.025 kcal mol^{-1} for both ionic strengths. The dilution enthalpy is actually the difference between the enthalpy of dilution of HCl and the pyridinium chloride. While the actual enthalpies of dilutions for these salts are not expected to be the same in these solvent systems as in water, it is assumed here that the difference will not vary appreciably and that the correction due to dilution effects is less than the experimental uncertainties. The average values shown in Table II are, therefore, taken to be the infinite dilution 1 M standard state enthalpies of ionization. It should also be noted that conductance studies on salts in the two solvent systems[10,11] employed here indicate that ion pairs will not be formed at the concentration of this study so that the dilution correction need not contain a term for ion pairing.

For the two solvent systems the standard state thermodynamic values for the ionization of the substituted pyridinium ions studied here are summarized in Table II. The uncertainties in the entropies of ionization are ± 0.35 cal deg^{-1} mol^{-1} or less

except for the 2,6-DTBPH$^+$ ion in the 40.9% by weight ethanol–water system where it is ± 0.70 cal deg^{-1} mol^{-1}.

Conclusions

An inspection of the values in Tables I and II reveals several important points. The introduction of a *tert*-butyl group in the 2- or 4-position decreases the acidity (ΔG_i°) by approximately the same amount in both solvent systems; with the *tert*-butyl group at both 2- and 4-positions, the acidity is decreased still further. A similar result is obtained for the enthalpies of ionization. These results are consistent with the recently determined gas phase proton affinities which have shown that the alkyl substituents are very effective in increasing the basicity of the pyridine nitrogen. However, the almost regular increase in ΔG_i° and ΔH_i° suddenly is reversed at 2,6-DTBPH$^+$. The ΔS_i° values in the two solvent systems for 2,6-DTBPH$^+$ also are quite different from that which would be predicted from the trends established by the other pyridinium ions. It is now apparent that the gas and solution phase data are not consistent with the concept of a direct steric interaction in the 2,6-DTBPH$^+$ ion which was originally proposed by Brown and Kanner[1] as a possible explanation for the higher than expected acidity of the 2,6-DTBPH$^+$ cation. *A specific solvation phenomenon in the neutral pyridine or pyridinium ion must be responsible for the much larger solution phase acidity of 2,6-DTBPH$^+$ than that predicted from the gas phase data or the solution thermodynamic data of the other alkyl substituted pyridines.*

It has been suggested by several workers[2-4] that the 2,6-DTBPH$^+$ ion is not as well solvated in solution as the pyridinium ion. In this argument it is assumed that the majority of the solvation of the cation occurs in the first solvation layer and that the *tert*-butyl groups sterically inhibit this solvation in the 2,6-DTBPH$^+$ ion. A careful analysis of the entropy of ionization results provides a means of deciding whether this argument is consistent with the solution thermodynamic data.

Table III. The Estimated Difference in Entropy between Neutral and Protonated Species for the Pyridines Studies[a]

| | $\Delta = \bar{S}_{py} - \bar{S}_{pyH+}$ | |
	40.9% ethanol solvent system	90% methanol solvent system
Pyridine	5.4	7.0
4-TBP	6.7	8.4
2-TBP	7.6	9.2
2,4-DTBP	7.7	9.9
2,6-DTBP	6.1	15.1

[a] Values in cal deg^{-1} mol^{-1}.

Since the experimentally derived ΔS_i° values can be expressed as

$$\Delta S_i^\circ = \bar{S}_{H+} + \bar{S}_{py} - \bar{S}_{pyH+}$$

where $\bar{S}_{H+}$, $\bar{S}_{py}$, and $\bar{S}_{pyH+}$ are the partial molal entropies at infinite dilution for the hydrogen ion, the pyridine, and the pyridinium ion, respectively, it is convenient for discussion purposes to subtract the entropy of the hydrogen ion from ΔS_i°. The value of $\bar{S}_{h+}$ in each solvent can be estimated from available data[12,13] as -13.4 and -8.0 cal deg^{-1} mol^{-1} in the 90% by weight methanol–water and 40.9% by weight ethanol–water solvents. The actual values for $\bar{S}_{H+}$ are not crucial to the following analysis and the values for $\bar{S}_{py} - \bar{S}_{pyH+}$ (Δ) calculated from ΔS_i° and the estimated $\bar{S}_{H+}$ values are shown in Table III.

The partial molal entropy of a solute in solution can be considered from an application of scaled particle theory[14] to be:

$$\bar{S} = \bar{S}_c + \bar{S}_i + \bar{S}_g - R \ln (RT/\bar{V}) + \alpha_p RT$$

where $\bar{S}_c$ is the entropy due to forming a cavity for the solute to occupy in the solution, $\bar{S}_g$ is the gas phase entropy (vibrational, rotational, and translational), $\bar{S}_i$ is the entropy due to solute–solvent interactions, $\bar{V}$ is the partial molal volume, and α_p is the coefficient of thermal expansion. It is reasonable to assume[15] that $\bar{S}_c$ and $\bar{S}_g$ are approximately the same for the neutral pyridine and pyridinium ion for the pyridines studied in these solvents. Therefore, Δ, to a first approximation, is the difference in the solvation entropies of the charged and neutral species.

In the 90% by weight methanol–water solvent Δ becomes more positive as the number of tert-butyl groups increases. It should also be noted that Δ is larger for 2-TBPH$^+$ than for 4-TBPH$^+$. If steric inhibition to solvation is occurring in the 2,6-DTBPH$^+$ ion, the value of Δ would be expected to be smaller than that of the pyridinium ion, 2-TBPH$^+$, 4-TBPH$^+$, or 2,4-DTBPH$^+$. However, the opposite trend is observed, which from this simple analysis does not appear to be consistent with the concept of steric inhibition of the general electrostatic solvation of the 2,6-DTBPH$^+$ cation in this solvent system. The conclusion arrived at in this analysis is identical with that obtained by le Noble and Asano[5] from their partial molal volume results for CH$_3$OH solutions. These workers observed that ΔV_i° for the tert-butyl pyridines studied here was the largest for 2,6-DTBP$^+$ which is inconsistent with the concept of steric inhibition of solvation for the 2,6-DTBPH$^+$ ion.

It is possible, however, that one or more internal vibrational degrees of freedom are substantially altered upon protonation of 2,6-DTBP. The hindered rotation of the methyl group of tert-butyl or the tert-butyl group itself could conceivably be different in the neutral and cation species. In fact the constriction of the solvent cage in the immediate vicinity of the N–H bond in the cation would be expected to increase the barrier to rotation in 2,6-DTBPH$^+$ more than the other pyri-

dinium ion studied. Such an increase in the barrier to rotation would cause a substantial decrease in the entropy of the cation, which is consistent with the observed variation in Δ found for the pyridinium ions studied here. It is possible that the unusual behavior of 2,6-DTBPH$^+$ in solution is related in part to a decrease in the rotational motion of the tert-butyl groups in the cation rather than a general steric inhibition to solvation.[16]

For the ionization equilibria of 2,6-di-tert-butylphenol in methanol Rochester[17] has shown that the ΔS_i° is more negative than that of phenol. These workers attribute this observation to a decrease in the rotational motions[17] of the tert-butyl group in the anion as has been suggested here for the 2,6-DTBPH$^+$ cation.

It should be noted that in the ethanol–water system the results do not lead to as definitive a conclusion as do those in the methanol–water system. In fact it is possible that both a steric inhibition to solvation and a reduced rotational motion is occurring for the 2,6-DTBPH$^+$ cation in solution since the contributions to Δ for these two effects have opposite signs.

The enthalpies of ionization for the 2-TBPH$^+$, 4-TBPH$^+$, and 2,4-DTBPH$^+$ cations are more positive than that of the unsubstituted pyridinium ion in both solvents. However, this trend is reversed for the 2,6-DTBPH$^+$ cation. The decrease found for the 2,6-DTBPH$^+$ cation in ΔH_i° relative to the other pyridinium ions studied is consistent with the concept of a steric inhibition to solvation for 2,6-DTBPH$^+$, since a decrease in the solvation of the cation would cause ΔH_i° to be less positive. Since the enthalpies of the gas phase ionization of 2,4-DTBPH$^+$ and 2,6-DTBPH$^+$ are nearly equal[18] and if the enthalpies of solution (gas to solution) for 2,4-DTBP and 2,6-DTBP are assumed to be equal, the difference in the enthalpies of solution (gas to solution) for the 2,6-DTBPH$^+$ and the 2,4-DTBPH$^+$ can be obtained from a thermodynamic cycle. This difference is 1.48 and 2.49 kcal mol^{-1} in 90% by weight methanol–water and 40.9% by weight ethanol–water, respectively. The larger difference found in the ethanol–water system is consistent with the entropy analysis. Since the enthalpy data suggest that a steric inhibition to solvation is occurring in the 2,6-DTBPH$^+$, it appears that both a steric inhibition to solvation and an increase in the rotational barrier in 2,6-DTBPH$^+$ may actually occur in solution.

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