nisms in which the CONH₂ group is supposed to remain in-plane, and therefore passive with respect to stereospecificity, seem insufficiently supported. However, our theory is at least partly sustained by Dutler's mechanism for the hydride transfer catalyzed by liver alcohol dehydrogenase.¹² He envisaged the (dihydro)-

(12) See ref 1, Dutler, H., 347.

pyridine ring to have enough freedom of motion to change its position during the hydrogen transfer, a movement possibly accompanied by rotation of the CONH₂ group out of the plane of the (dihydro)pyridine ring. However, no mention was made of an active role of the $CONH_2$ group in the reaction.

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Enthalpy of Steric Inhibition to Solvation due to *tert*-Butyl Groups on an Anion Radical

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Abstract: Electron-spin-resonance techniques have been utilized to measure the enthalpy of electron transfer from the anion radical of naphthalene (N^-, K^+) to 2-tert-butylnaphthalene (TBN) and from the anion radical of TBN (TBN⁻, K⁺) to 2,6-di-tert-butylnaphthalene (DTBN) in dimethoxyethane (DME). These endothermic enthalpies of electron transfer were combined with the heat of solvation of the gas-phase anion radical of naphthalene plus the gas-phase potassium cation in DME, the heats of solvation of the neutral hydrocarbons in DME, and the heats of vaporization of the hydrocarbons in a thermochemical cycle to yield the enthalpy of solvation of $(DTBN^{-})_g + (K^+)_g$ in DME. This enthalpy of solvation is about 17 kcal/mol less exothermic than that for $(N^{-})_g + (K^+)_g$ and is attributed to the steric inhibition to solvation by the *tert*-butyl groups on DTBN⁻. The enthalpy of solvation of $(N^{-})_g + (K^+)_g$ (-162 kcal/mol) was determined by combining the enthalpy of the reaction of the DME solvated anion radical with water with a series of well-known constants in a thermochemical cycle. Thus, by utilizing a combination of calorimetric and ESR techniques a complete picture of the thermodynamic parameters controlling the stabilities of the solvated and gas-phase anion radicals of N and DTBN has been generated.

Lawler and Tabit¹ have determined the relative solution electron affinities of benzene and a series of alkyl-substituted benzenes, including tert-butylbenzene, based upon the free energy change for the reaction shown in reaction 1. Mixtures of carefully

$$(\overrightarrow{\circ}) + (\overrightarrow{\circ})_{soln} = +1.6 \text{ kcal/mol} \\ (\Delta H^\circ)_g = -2.1 \text{ kcal/mol}$$
(1)

measured quantities of benzene and the alkyl-substituted benzene were reduced with sodium-potassium alloy in a mixture of dimethoxyethane (DME) and tetrahydrofuran (THF), and the relative intensities of the two simultaneously observed ESR spectra were used to calculate the equilibrium constant. In this manner ΔG° , which was assumed to be equal to the enthalpy of the reaction, was found to be +1.6 kcal/mol. The endothermic nature of the electron transfer (proving that the solution electron affinity of benzene is greater than that of *tert*-butylbenzene) is consistent with what was thought to be the intrinsic electron-releasing nature of the tert-butyl group. These authors made the statement that this endothermicity should also be observed in the gas phase, a valid assumption based upon the experimental evidence available at the time. However, 7 years later Jordan et al.² found that the free energy and enthalpy of the reaction depicted in eq 1 in the gas phase are opposite in sign from those in solution. In fact, the gas-phase electron affinities of tert-butylbenzene and benzene are -28.7 and -26.6 kcal/mol, respectively.²

From this work and the fact that the basicity of methoxide is greater than that of *tert*-butoxide³ in the gas phase (the reverse

of that found in solution) it is clear that the destabilizing effect that the tert-butyl group has upon the solvated anionic species is not due to its electron-releasing nature but is due to its ability to inhibit solvation (including ion association) of the anion. This steric inhibition of solvation and possibly ion association is evidently important enough in a thermodynamic sense to reverse the electron affinities of the gas phase and solvated benzene and tert-butylbenzene.

In solution, both the solvation enthalpy of the neutral and anionic species are of importance in controlling the electron transfer depicted in eq 1, but that of the anion radical is certainly of much more importance. This is, the capture of an electron from a gas-phase donor by a gas-phase acceptor (A) to yield the solvated anion radical ion pair (reaction 2) is much more exothermic than the same reaction to yield the gas-phase anion radical and cation (reaction 3). The extra exothermicity of reaction 2 is due to the

$$A_{g} + Na_{g} \rightarrow (A^{-}, Na)_{soin}$$
(2)

$$A_{g} + Na_{g} \rightarrow A^{-} \cdot_{g} + Na^{+}_{g}$$
(3)

specific anion-solvent and cation-solvent interactions as well as the ion association.

The actual heats of solvation of a series of polyacene anion radicals with the sodium cation in THF have been measured and found not to vary far from -180 kcal/mol⁴ (reaction 4). The

$$A^{-} \cdot_{g} + Na^{+}_{g} \rightarrow (A^{-} \cdot, Na^{+})_{THF}$$
(4)

$$\Delta H^{\circ} \simeq 180 \text{ kcal/mol}$$

heat of formation of a solvated anion radical-cation ion pair from the gas-phase metal and neutral molecule (ΔH° for the reaction shown in reaction 2) can be obtained from this data by simply adding the electron affinity (EA) of the polyacene and subtracting

(3) Brauman, J. I.; Blair, L. K. J. Am. Chem. Soc. 1970, 92, 5986.
 (4) Stevenson, G. R.; Williams, E. J. Am. Chem. Soc. 1979, 101, 5910.

⁽¹⁾ Lawler, R. G.; Tabit, C. T. J. Am. Chem. Soc. 1969, 91, 5671. (2) Jordan, K. D.; Michejda, J. A.; Burrow, P. D. J. Am. Chem. Soc. 1976, 98, 1295.

the ionization potential (IP) of the sodium metal as shown below.

$$A^{-}_{g} + Na^{+}_{g} \rightarrow (A^{-}, Na^{+})_{THF} \qquad \Delta H^{\circ} = -180 \text{ kcal/mol}$$

$$A_{g} + e^{-}_{g} \rightarrow A^{-}_{g} \qquad \Delta H^{\circ} = -EA$$

$$Na_{g} \rightarrow Na^{+}_{g} + e^{-}_{g} \qquad \Delta H^{\circ} = IP$$

$$A_{g} + Na_{g} \rightarrow (A^{-}, Na^{+})_{THF} \qquad \Delta H^{\circ} = -180 - EA + IP$$

For the anthracene anion radical the enthalpy of solvation is -178.7 kcal/mol.⁴ Thus, when A represents anthracene the enthalpies for the reactions depicted in reactions 2 and 3 are -47.4 and +105.7 kcal/mol respectively.

Due to the obvious importance of the steric inhibition to solvation that the tert-butyl group exhibits upon the thermodynamic stability of solvated anions, we were prompted to carry out ESR studies similar to those of Lawler and Tabit1 but, this time, on systems where the actual enthalpy of formation for one of the anion radical systems could be measured. By "anchoring" (measuring the heat of solvation of the separated anion radical and cation) one of the anion radical systems and measuring the enthalpies of vaporization and solution for the neutral species, we hoped to measure the actual enthalpy of this steric inhibition of solvation.

The benzene and tert-butylbenzene anion radicals are not sufficiently stable to allow the necessary calorimetric measurements to be made. For this reason, the anion radicals of naphthalene and 2,6-di-tert-butylnaphthalene (DTBN) were the systems of choice.5

Experimental Section

The naphthalene anion radical solutions for the calorimetry experiments were generated via potassium reduction in exactly the same manner described previously.^{4,6} Samples of these naphthalene anion radical (N^{-}, K^{+}) solutions were sealed into small evacuated glass bulbs, which were subsequently broken under 100 mL of deoxygenated water in a modified Parr solution calorimeter. The procedure and the calo-rimeter have been described previously.^{4,7}

The ESR experiments were carried out on a Varian E-4 ESR spectrometer that is coupled to a MINC II data acquisition system. The relative concentrations of the different anion radicals were determined from the relative intensities of the ESR lines. The intensities were determined by finding free lines and multiplying the line heights by the square of the line widths. The relative concentrations found in this manner were then checked by generating a computer simulation of the combined spectrum. The simulations were generated by using Lorentzian line shapes and line widths varying from 100-400 mG.

Vapor pressure measurements were done with a modified isoteniscope in a manner identical with that described by Solsky and Grushka.8 The isoteniscope was placed in an oil bath, which was heated on a hot plate. The oil bath was stirred with a overhead stirrer. Readings in the difference in the Hg level in the isoteniscope were carried out with a cathetometer.

The naphthalene and 2,6-di-tert-butylnaphthalene (Pfaltz and Bauer, Inc.) were sublimed prior to use. The DME was distilled from a mixture of potassium and benzophenone ketyl under nitrogen. It was then stored under vacuum with NaK₂ in a glass bulb equipped with a stopcock. It was then distilled from this bulb directly into the apparatus for anion radical generation.

Results and Discussion

The reduction of mixtures of DTBN and naphthalene (N) via potassium metal in DME always results in the formation of the naphthalene anion radical as the only ESR detectable species. Even when the mole ratio of DTBN to N is as high as 20, only the 25 line pattern for the naphthalene anion radical can be observed. This must mean that the equilibrium between the naphthalene anion radical and the DTBN (reaction 5) rests far to the left. In order for us to determine the thermodynamic

$$N^{-}, K^{+} + DTBN \longrightarrow N + DTBN^{-}, K^{+}$$
 (5)





reduction of a mixture of naphthalene and 2-tert-butylnaphthalene in DME at 25 °C. This and all other EPR spectra were recorded with low power (0.5 mW) and a small modulation amplitude (0.05 G).

Table I. Thermodynamic Parameters Controlling the Electron-Transfer Reactions at 25 °C

reaction	$\Delta H^{\circ a}$	K _{eq}	ΔS° , eu
$N^-, K^+ + TBN \rightarrow$	1.5 ± 0.2	$(8.6 \pm 0.9) \times 10^{-2}$	0.3 ± 0.3
$TBN^{-}, K^{+} + N$ $TBN^{-}, K^{+} + DTBN \rightarrow$	2.5 ± 0.3	$(4.5 \pm 1.9) \times 10^{-2}$	2 ± 1
$DTBN^{-}, K^{+} + TBN$ $N^{-}, K^{+} + DTBN \rightarrow$ $DTBN^{-}, K^{+} + DTBN \rightarrow$	4.0 ± 0.4	$(3.8 \pm 2.1) \times 10^{-3}$	2 ± 1
DIBN $\cdot, \mathbf{K}' + \mathbf{N}$			

^a In kcal/mol.

parameters controlling this reaction, it was necessary for us to determine these parameters for the electron transfer between naphthalene anion radical and 2-tert-butylnaphthalene (TBN) than that between TBN- and DTBN. Once these two reactions have been studied, Hess's law can be utilized to yield the parameters controlling the reaction depicted in reaction 5.

The reduction of a 1:1 mole mixture of N and TBN with a very small amount of potassium metal, again, results only in the observation of the anion radical of N. However, when a 10:1 mole ratio of TBN to N was reduced, both anion radicals could be observed simultaneously in the resulting ESR spectrum (Figure 1). The concentrations of the two anion radicals and thus the relative intensities of the two ESR spectra are controlled by the equilibrium constant for the reaction shown below (reaction 6).



The first line for N- and the first line for TBN- are free of overlap and represent 1/256 and 1/128 of the entire spectrum, respectively. The end region of the combined spectrum including the first two lines were enlarged in order to accurately measure the peak heights and widths. The relative concentrations of the two radical species were then obtained from the ESR line intensities and the use of eq 7, where h_N and h_{TBN} represent the

$$K_{eq} = [TBN^{-}, K^{+}][N] / [N^{-}, K^{+}][TBN] =$$

$$128(\Delta w_{TBN})^{2}h_{TBN}[N] / 256(\Delta w_{N})^{2}h_{N}[TBN]$$
(7)

heights of the first ESR lines for N-, and TBN-, respectively, and Δw represents the peak-to-peak line width in gauss. From six separate determinations the equilibrium constant for the reaction depicted in (6) was found to be $(8.6 \pm 0.9)10^{-2}$. Each of

⁽⁵⁾ Goldberg, I. B.; Peake, B. M. J. Phys. Chem. 1977, 81, 571.
(6) Stevenson, G. R.; Chang, Y. J. Phys. Chem. 1980, 84, 2267.
(7) Stevenson, G. R.; Williams, E.; Caldwell, G. J. Am. Chem. Soc. 1979, 101, 520.

⁽⁸⁾ Solsky, J. F.; Grushka, E. J. Phys. Chem. 1974, 78, 275.



Figure 2. Plots of $\ln K_{eq}$ vs. $10^3/RT$ for the electron transfer from N⁻. to TBN and for the electron transfer from TBN- to DTBN. Each line represents data taken from a different sample. Each separately prepared sample gave a different line, but those representing the same reaction had about the same slope. Several such lines were generated (only two for each system are shown here), and the error reported in ΔH represents the standard deviation in these slopes.



Figure 3. ESR spectrum of the anion radicals formed by the potassium reduction of a mixture of 2-tert-butylnaphthalene and 2,6-di-tert-butylnaphthalene in DME at 25 °C.

the separately prepared samples were studied as a function of temperature, and van't Hoff plots were constructed (Figure 2). The enthalpy reported in Table I represents an average taken from six such plots, and the error reported in the enthalpy is the standard deviation in the different slopes.

The equilibrium constant for the electron transfer from TBN-. to DTBN (reaction 8) was measureable in the same manner.



When mole ratios of DTBN/TBN of about 10:1 were used, simultaneous spectra for the two anion radicals could be observed



Figure 4. Plots of ln of the vapor pressure of DTBN and N vs. $10^3/T$. The data were taken for naphthalene simply to verify that our experimental apparatus could be used to reproduce the literature value for its enthalpy of vaporization.

(Figure 3). The equilibrium constant for this reaction is given by eq 9. In this manner K_{eq} was found to be $(4.5 \pm 1.9)10^{-2}$.

$$K_{eq} = [DTBN^{-}, K^{+}][TBN] / [TBN^{-}, K^{+}][DTBN] = 64(\Delta w_{DTBN})^{2} h_{DTBN}[TBN] / 128(\Delta w_{TBN})^{2} h_{TBN}[DTBN] (9)$$

Again, the error in K_{eq} is relatively large, but each sample did yield a linear plot of $\ln K_{eq}$ vs. 1/RT all with about the same slope but with different intercepts. The error in ΔH° is the standard deviation in the slopes and is relatively small (Figure 2, Table I).

The thermodynamic parameters for the electron transfer from N^- to DTBN were obtained by simply adding those for the transfer from N- to TBN and from TBN- to DTBN. It is clear from the data in Table I that the entropy changes are all very small as predicted by Lawler and Tabit.¹ The endothermic nature of the electron transfer from the anion radical of naphthalene to the di-tert-butylnaphthalene must be due, in part, to the steric inhibition of solvation of the substituted anion. However, this enthalpy is small enough to be effected by the heats of solvation of the neutral molecules, N and DTBN. Thus, it is necessary to know these heats of solvation to gain any understanding as to the effect of the *tert*-butyl groups upon the thermodynamic stability of the solvated anion radicals.

In order to determine the heats of solvation of DTBN and N, it is necessary to measure the heats of solution and the heats of sublimation. The heats of sublimation were determined from plots of the natural logarithm of the vapor pressure vs. 1/RT. To make sure that the isoteniscope was working correctly, experiments were carried out on naphthalene and the enthalpy of sublimation ΔH°_{vap} compared to the literature values. The ΔH^{o}_{vap} of DTBN has not been reported. The Clausius-Clapeyron plots are shown in Figure 4. Our enthalpy of vaporization (17.8) for naphthalene is within experimental error of the accepted literature value of 17.4 kcal/mol,⁹ and that for DTBN was found to be 8.7 ± 0.2 kcal/mol (Figure 4). To obtain the solvation enthalpies in DME for N and DTBN, these heats of vaporization must be combined with the heats of solution in DME.

(9) Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: New York, 1970. (10) Gunn, S. R. J. Phys. Chem. 1967, 71, 1386.

- Hicks, W. T. J. Chem. Phys. 1963, 38, 1873.
 Lotz, W. J. Opt. Soc. Am. 1967, 57, 873.
 Shaw, R.; Golden, D. M.; Bensen, S. W. J. Phys. Chem. 1977, 81,
- 1716 (14) Becker, R. S.; Chen, E. J. Chem. Phys. 1966, 45, 2403.

The heats of solution of N and DTBN in DME were obtained by breaking glass bulbs containing DTBN or N under DME in the calorimeter. The change in the temperature of the calorimeter, upon dissolution of the neutral substrate in the DME, could then be multiplied by the heat capacity of the calorimeter filled with 100 mL of DME (63.6 cal/deg) to yield the heat of solution of the substrate in DME. Using sample sizes between 0.5 and 0.8 g gives temperature changes in the calorimeter of 0.0520 and 0.0518 deg/mmol for DTBN and N, respectively. Thus, both compounds have identical heats of solution of $\pm 3.31 \pm 0.05$ kcal/mol. This means that the solvation enthalpies of N and DTBN in DME are -14.1 and -5.4 kcal/mol, respectively.

By adding 8.7 (14.1 – 5.4) to 4.0 kcal/mol (the enthalpy of electron transfer from N^- to DTBN in DME), the enthalpy for the reaction shown below is obtained. The enthalpy of this

$$(N^{-},K^{+})_{DME} + DTBN_{g} \rightarrow N_{g} + (DTBN^{-},K^{+})_{DME}$$
 (10)

$$\Delta H^{\circ} = 12.7 \text{ kcal/mol}$$

reaction (reaction 10) is not influenced by the solvation of the neutral species and is only a function of the electron affinities and the heats of solvation of the anion radicals. It is clear that the solvation enthalpies of the neutral species does indeed strongly influence the enthalpy of electron transfer in DME. However, the enthalpy of the reaction shown in reaction 10 is a function of the relative electron affinities and anion radical solvation enthalpies only.

If the actual enthalpy of formation of the DME solvated naphthalene anion radical from the gas-phase neutral naphthalene and potassium (reaction 11) can be obtained, that for 2,6-di-

$$N_g + K_g \to (N^-, K^+)_{DME}$$
(11)

tert-butylnaphthylene can also be obtained by simply adding 12.7 kcal/mol. By measuring the enthalpy for the reaction depicted in reaction 11, we can calculate the actual solvation enthalpy for the naphthalene anion radical. This will allow us a very good estimation of that for the DTBN anion radical. This enthalpy was determined by measuring the enthalpy of reaction of the naphthalene anion radical with water.

Small evacuated glass bulbs containing solutions of N^{-},K^{+} in DME were broken under 100 mL of water in a calorimeter. The change in the temperature of the calorimeter is due to the aquation of DME in water and the reaction of the anion radical with water to produce the dihydronaphthalene (reaction 12).

$$\bigcirc \bigcirc \bigcirc \bigcirc \land K^{+} + H_{2} \bigcirc \longrightarrow KOH_{aq} + (\overset{1}{V}_{2}) \bigcirc \bigcirc + (\overset{1}{V}_{2}) \bigcirc \bigcirc (12)$$

Since the heat evolved in the calorimeter is not only due to the reaction of the anion radical with water but also due to the aquation of DME, it is necessary to know the amount of heat evolved from this latter process. We have previously found that a plot of the amount of pure DME placed in the evacuated bulbs plotted against the change in the temperature of the calorimeter when the bulbs are broken under water yields a straight line with a slope of 0.530 deg/g.⁶ If the amount of DME in each bulb containing the anion radical solution is known, the heat evolved from the aquation of the DME can be obtained (the change in the temperature of the calorimeter due to the aquation of the DME = 0.530 deg/g multiplied by the number of grams of DME in the bulbs). Subtracting this from the total observed temperature change in the calorimeter yields that due to the reaction depicted in reaction 12. The slope of the line generated from a plot of the change in the temperature of the calorimeter minus that due to the DME (ΔT due to the anion radical reaction) vs. the mmoles of anion radical in the glass bulbs is linear (Figure 5).

From Figure 5 the enthalpy of the reaction shown in reaction 12 was determined by multiplying the slope of the line (0.184 deg/mmol) by 119.3 cal/deg (the heat capacity of the calorimeter charged with 100 mL of water) and was found to be -22.0 ± 0.9



Figure 5. Plot of the change in the temperature of the calorimeter vs. the mmoles of naphthalene anion radical in the glass bulbs.

Table II. Enthalpies of Reaction

reaction	ΔH° , kcal/mol	ref
$\overline{(\mathrm{NH}_2)_{\mathrm{s}} + \mathrm{N}_{\mathrm{s}} + 2(\mathrm{KOH})_{\mathrm{aq}}} \rightarrow 2(\mathrm{NH}_2)$	+44.0	this work
$2(N^{-},K^{-})_{DME} + 2(H_2O)_1$ $2K_s + 2(H_2O)_1 \rightarrow 2(KOH)_{aq} + (H_2)_q$	-94.0	10
$2K_g \rightarrow 2K_s$	-42.8	11
$2K_{g}^{+} + 2e_{g}^{-} \rightarrow 2K_{g}$	-200.2	12
$N_s + (H_2)_\sigma \rightarrow (NH_2)_s$	-3.2	13
$2N_{\sigma} \rightarrow 2N_{s}$	-34.8	9
$2(\tilde{N} \cdot)_g \rightarrow 2N_g + 2(e^-)_g$	+7.0	14
$\overline{N^{-} \cdot_{g} + K^{+}_{g} \rightarrow (N^{-} \cdot, K^{+})_{DME}}$	-162.0 ^a	

^a By propagating the standard deviations, the error in the final enthalpy is about 2.5 kcal/mol.

kcal/mol. Combining this enthalpy with some well-known constants as described in Table II yields the enthalpy of solvation of the gas-phase anion radical plus the gas-phase potassium cation in DME (reaction 13). If the electron affinity of naphthalene

$$(13)$$

$$\Delta H^{\circ} = -162.0 \pm 2.5 \text{ kcal/mol}$$

(+3.5 kcal/mol) and the ionization potential of potassium (+100.1 kcal/mol) are left out of the calculation shown in Table II, then the enthalpy of formation of N^- , K^+_{DME} from the gas-phase neutral species (ΔH° for the reaction shown in reaction 11) is obtained. It is -65.4 ± 2.5 kcal/mol.

It was impossible to carry out similar calorimetry experiments on the substituted naphthalene anion radical due to its relative instability. However, the enthalpy of reaction of gas-phase DTBN with gas-phase potassium metal to yield the solvated anion radical must be -65.4 + 12.7 = -52.7 kcal/mol (reaction 14).

$$DTBN_{g} + K_{g} \rightarrow (DTBN^{-}, K^{+})_{DME}$$
(14)
$$\Delta H^{\circ} = -52.7 \text{ kcal/mol}$$

Conclusion

An energy diagram summarizing the thermodynamic measurements is shown in Figure 6. The difference in the enthalpy



Figure 6. Energy diagram for the K-N-DTBN system. The energy differences are in kcal/mol.

of reaction between the two gas-phase hydrocarbons and potassium metal to yield the solvated anion radicals (12.7 kcal/mol) represents $162.0 - \Delta EA - \Delta H_{solv}$ of (DTBN⁻₈ + K⁺₈, where EA is the difference in the electron affinities of DTBN and N. Since the electron affinity (EA) of DTBN is unknown, we can only make an estimation of this value.

The electron affinity of *tert*-butylbenzene is 2.1 kcal/mol greater than that for benzene. Since DTBN simply consists of two condensed benzene ring systems with two *tert*-butyl groups, it seems reasonable that the EA of DTBN should be about 2×2.1 kcal/mol greater than that of N. This estimate may be low due to the fact that the ring systems are condensed in the naphthalene system (5 sp² carbons/*tert*-butyl group as opposed to six in the two benzene systems). Thus, the heat of solvation of the gas-phase DTBN anion radical and potassium cation must be about -162.0 + 4.2 + 12.7 or about -145 kcal/mol (eq 15). This value is 17

$$(DTBN^{-})_{g} + K^{+}_{g} \rightleftharpoons DTBN^{-}, K^{+}_{DME}$$
 (15)

$$\Delta H^{\circ} = -145 \text{ kcal/mol}$$

kcal/mol less exothermic than that for the naphthalene system due to the steric inhibition to solvation (including ion association) of the anion by the *tert*-butyl groups.

The steric effect of the tert-butyl groups decreases the solvation enthalpy of the negative ions by about 17 kcal/mol, but this may in part be due to the steric inhibition of ion association. This, however, might not be the case as evidenced by the fact that DTBN-, Na⁺ ion pair in methyltetrahydrofuran yields an actual sodium hyperfine coupling of 0.4 G larger than that for N⁻, Na^{+,15} The large alkyl groups do force the cation away from the regions near the alkyl groups, which causes the cation to be more confined to the regions above each of the benzene rings and hence in the region of higher unpaired electron density.¹⁵ In DME with K⁺ serving as the cation, alkali metal splittings are not present; but ion association does exist. The increase in the sodium metal splitting does not necessarily mean that the cation is closer to the anion in DTBN- than in N- only that it is in a region of higher spin density. The steric interactions probably actually increase the interatomic distance allowing greater solvation of the alkali metal cation.

Despite the possible increase in cation solvation in DTBN⁻, K⁺ as compared to N⁻, K⁺ in DME, the enthalpy of solvation of DTBN⁻. + K⁺ is more endothermic than that of N⁻. + K⁺ by 17 kcal/mol. If the solvation of the cation is indeed increased for the di-*tert*-butyl system, the steric inhibition of the approach of the solvent molecules to the negatively charged ring may account for more than 17 kcal/mol.

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(15) (a) Goldberg, I. B.; Bolton, J. R. J. Phys. Chem. 1970, 74, 1965. (b) Goldberg, I. B.; Crowe, H. H. Ibid. 1976, 80, 2603.