employed to make the ring. The optical spectra show that ZnTBP resembles porphyrin much more than phthalocyanine, and the uv spectra are in quite good agreement with theory.[10] The sharpness of the Soret band in vapor is unusual and undoubtedly is related to the fact that the low-temperature Soret band shows quasilines and that the Soret band fluoresces.[14] This must reflect a very small vibronic coupling between B and Q, which may stem from the large energy gap ($8700\ \mathrm{cm}^{-1}$) between them (Table I). Further study of the yields of the three emissions of this compound [$S_2 \rightarrow S_0$, $S_1 \rightarrow S_0$, and $T_1 \rightarrow S_0$] as a function of temperature and of variation in the molecular skeleton and in the central metal would throw a new light on radiationless decay processes.[16] Finally, the existence of an impurity with a Soret band at 460 nm and a fluorescence at 647 nm is very surprising. These peaks suggest a closely related compound, and determination of what this compound is may give insight into the peculiar stability of the TBP ring system.

Acknowledgments. This research was supported in part by Public Health Research Grants GM 14292 and AM 16508 from the National Institutes of Health. The vapor studies were performed by L.E. at the Chemistry Department of Harvard University, where Dr. John M. Wright performed the mass spectra. Dr. Alan D. Adler, of Western Connecticut State College, gave helpful advice.

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An Unusual Reversible Valence Bond Isomerization Hemi-Dewar Naphthalene to Naphthalene

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Abstract: Evidence obtained by electron spin resonance indicates that 1,3,6,8-tetra-*tert*-butylnaphthalene and 1,3,8-tri-*tert*-butylnaphthalene isomerize through the dianion intermediate to form the corresponding hemi-Dewar naphthalenes. The isomerization reactions are facilitated through the nonplanarity of the parent naphthalene compounds. ESR spectra of the anion radical of the hemi-Dewar naphthalene anions are reported.

Introduction

The subject of valence bond isomerization has received a great deal of attention during the past several years.[1] In particular, the isomerization of benzene to Dewar benzene has been studied both theoretically and experimentally. Alkyl-substituted benzenes[2] as well as perfluoroalkyl-substituted[3] benzenes have been shown to yield Dewar benzene during continuous uv irradiation. It is still questioned whether the isomerization involves a singlet or triplet excited state.[4] Theoretical studies[5] suggest that the isomerization of benzenes occur through excitation of two electrons into the lowest un-

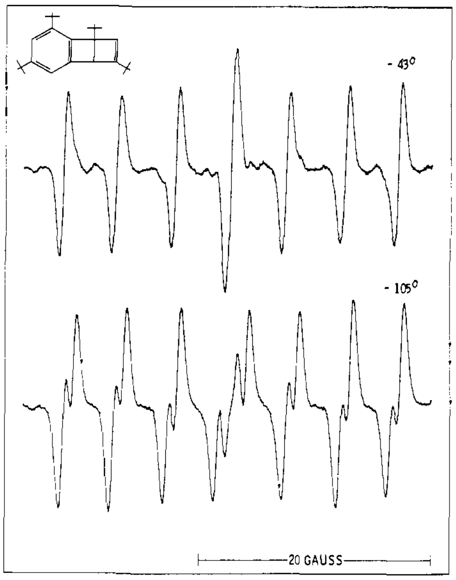
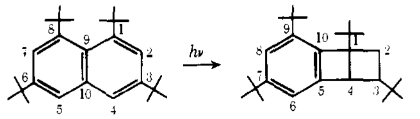


Figure 1. ESR spectra of 1,3,7,9-tetra-*tert*-butyl hemi-Dewar naphthalene anion in 40% dimethoxyethane-tetrahydrofuran reduced with Na-K alloy: upper, −43 °C; lower, −105 °C.

occupied symmetric molecular orbital from the highest occupied symmetric orbital. This electronic configuration favors bonding between the 1 and 4 positions and leads to the formation of Dewar benzene.

Recently,[6] the compounds 1,3,8-tri-*tert*-butylnaphthalene (TB3N) and 1,3,6,8-tetra-*tert*-butylnaphthalene (TB4N) have been shown to isomerize to their corresponding hemi-Dewar isomers:



Electron spin resonance (ESR) has been used to investigate several cases in which valence bond isomerization may occur. For example, bicyclo[3.1.0]hexenyl radicals were converted to the corresponding cyclohexadienyl radicals by uv irradiation.[7] The reverse process was observed for isoelectronic pyridinium cations which were shown to isomerize to several bicyclic derivatives by uv or γ irradiation.[8] Attempts to observe ring opening of the radical anion of naphtho[1′,8′]bicyclo[3.2.0]hepta-2,6-diene yielded only the diprotonated product, the radical anion of dihydropleiadine.[9] Similarly, the radical anion of dibenznorcaradiene yielded the radical anion of the dihydro-product dibenzo[*a*,*c*]cyclohexadiene.[10] Ring opening of a naphthobicyclobutane anion was observed, however, in tetrahydrofuran-dimethoxyethane to yield the anion of pleiadine.[11]

We report here ESR investigations on the reduction of TB3N, TB4N, and their corresponding hemi-Dewar naphthalenes in dimethoxyethane and dimethoxyethane-tetrahydrofuran solutions by sodium potassium alloy.

Experimental Section

The materials TB3N,[12] TB4N, 1,3,6-tri-*tert*-butylnaphthalene,[13] 1,3,7,9-tetra-*tert*-butyl hemi-Dewar naphthalene (TB4DN), and 1,3,9-tri-*tert*-butyl hemi-Dewar naphthalene (TB3DN)[14] were prepared as described in the literature. Anion radicals were prepared by reduction with Na or K in dry purified dimethoxyethane (DME) or 60% tetrahydrofuran (THF)-40% DME by volume.

Spectra were recorded on a modified Varian V-4502 ESR spectrometer with a Magnion 38-cm magnet. Due to the instability of some of these radicals, it was necessary to use computer averaging methods to collect the spectra so that the intensity of the lines was not significantly changed during each scan. This apparatus and the methods utilized are described elsewhere.[15,16] One modification to this method at sweep rates less than 20 G/min was to control relays which either started or stopped the field sweep or changed the direction of the field scan. This permitted sufficient reproducibility for averaging up to 64 spectra. The decay of the radical was monitored by stepping to a predetermined magnetic field and following the ESR signal as a function of time.

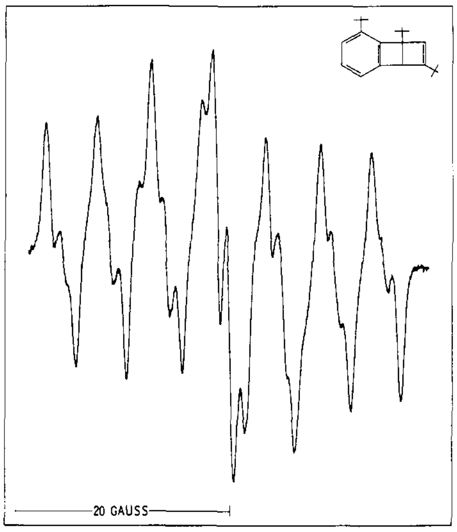


Figure 2. ESR spectrum of 1,3,9-tri-*tert*-butyl hemi-Dewar naphthalene anion in 40% dimethoxyethane-tetrahydrofuran reduced with Na-K alloy at −93 °C.

Results and Discussion

ESR Spectra. Spectra obtained from solutions of TB4DN and TB3DN reduced with Na-K alloy in 40% DME-THF solutions are shown in Figures 1 and 2. The spectrum of TB4DN$\cdot^-$ as well as a blue color associated with the spectrum fades at temperatures above −70 °C and disappears completely by −40 °C. Both the color and spectrum begin to reappear at temperatures below about −40 °C and reach similar intensities as the initial spectra recorded at −70 °C or less. The hyperfine splittings (hfs) are summarized in Table I. The spectra of TB4DN$\cdot^-$ between −115 and −75 °C are assigned to two components. As the temperature is increased, the intensity of the second component decreases relative to the first, and at temperatures above −75 °C, the second component is not sufficiently resolved to permit analysis. The hfs of the first component are slightly temperature dependent. TB3DN$\cdot^-$ is considerably less stable than TB4DN$\cdot^-$, and reasonable spectra could be recorded between only −115 and −75 °C. Here also, there appears to be two components with equal *g* factors, but only the analysis of one of these can be completed. The primary component appears to be due to the Dewar isomer in which two *tert*-butyl groups are on the Dewar portion of the compounds. This is consistent with the synthesis product.[6,12] Spectra of TB4N$\cdot^-$ and TB3N$\cdot^-$ are discussed in detail in ref 15. Anions of 1,3,6-tri-*tert*-butylnaphthalene and 1,3-di-*tert*-butylnaphthalene exhibit spectra in which the hfs are similar in magnitude to naphthalene anions. The assignment given in Table I is based on Hückel molecular orbital (HMO) calculations. Hfs obtained from the spectra of TB4DN$\cdot^-$ and TB3DN$\cdot^-$ were assigned on the basis of the following argument: Alkyl substitution does not significantly alter the spin distribution in a radical if there is nominal steric interactions so that the 1.6 G hfs in TB3DN$\cdot^-$ is assigned to the proton at the 7 position. The 16 G hfs in TB3DN$\cdot^-$ and TB4DN$\cdot^-$ are too large to result from α-proton interactions so that these are assigned to the β proton on C-4 coupled to spin at C-5. Splittings due to β protons, a_H, are related to the spin

Table I. Proton Hyperfine Splittings of Hemi-Dewar Naphthalene and *tert*-Butylnaphthalene Anions

	Hyperfine splittings[a]		
Position	Component 1	Component 2	Temperature (°C) and solvent
	1,3,7,9-Tetra-*tert*-butyl hemi-Dewar naphthalene$\cdot^-$		
5 (β)	16.45	16.57	−105
6	4.82	4.79	40% DME-
8	10.97	8.94	THF
5 (β)	16.23	not present	−43
6	5.10		40% DME-
8	10.79		THF
	1,3,7-Tri-*tert*-butyl hemi-Dewar naphthalene$\cdot^-$		
5 (β)	15.69	unresolved	−95
6	5.14		40% DME-
7	1.56		THF
8	10.40		
	1,3,6-Tri-*tert*-butyl naphthalene$\cdot^-$		
2	1.731		−55
4	4.390	none	DME
5,8	4.984		
7	2.162		
	1,3-Di-*tert*-butyl naphthalene$\cdot^-$		
2	1.628		−60
6,7	1.956		DME
4	5.06	none	
5	4.456		
8	5.18		

[a] The assignment of hyperfine splittings for the Dewar naphthalene anions is based on the argument in the text. Those of the *tert*-butylnaphthalenes are based on Hückel molecular orbital calculations assuming an inductive model for the *tert*-butyl group.

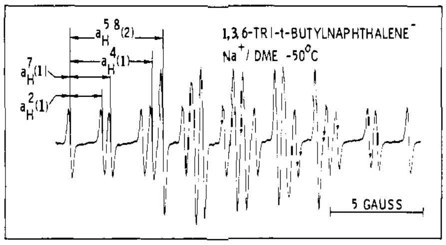


Figure 3. ESR spectrum of 1,3,6-tri-*tert*-butylnaphthalene anion in dimethoxyethane at −50 °C.

density on the trigonal carbon atom ($\rho_C{}^\pi$) by:

$$a_H = Q_{CCH}{}^H\rho_C{}^\pi = (B_0 + B_2\cos^2\phi)\rho_C{}^\pi \qquad (1)$$

where $Q_{CCH}{}^H$ is the proportionality constant between the spin density and the hfs given by $B_0 + B_2\cos^2\phi$. B_0 is the contribution due to spin polarization and has a value between +3 and −3 G, and B_2 is the contribution due to hyperconjugation and is about +50 G. The angle ϕ is the azimuthal angle between the axis of the C–C σ bond of the CCH fragment. For cyclobutene fragments, however, the value of $|Q_{CCH}{}^H|$ varies between 27 and 52 G and depends on σ–π interactions across the four-membered ring.[18,19] Selecting an intermediate value of about 40 G for $Q_{CCH}{}^H$ suggests that the spin density at the 5 position is approximately 0.4, which is near the spin density assigned to the symmetric orbital of benzene in *o*-xylene and *m*-xylene anion radicals.[20] If this is correct, then the carbon atom in the 8 position should also contain a high spin density, and thus the 9–10 G hfs are assigned to this position. This leaves the 4 G hfs to be assigned to the 6 position. It must be remembered here that in these molecules, the effect of asymmetric ion pairing as well as nonuniform bond lengths and angles and steric interactions can perturb the hfs from that which would be observed for a true symmetric orbital.

The spectra obtained here are difficult to assign to species other than TB4DN$\cdot^-$ or TB3DN$\cdot^-$. Spectra of TB3N$\cdot^-$ and TB4N$\cdot^-$ [16] exhibit hfs which are much smaller than that of the naphthalene anion, while hfs of other *tert*-butyl-substituted naphthalene anions[21] are similar in magnitude to the naphthalene anion itself. This precludes the assignment of the spectra of Figures 1 and 2 to a naphthalene derivative. Spectra which result from dimerization processes would be expected to be considerably more complex due to additional hyperfine interactions. The *g* factor of TB4DN$\cdot^-$ was measured and found to be 2.00276 ± 0.00002[22] at −95 °C. This is in agreement with values for *p*-xylene$\cdot^-$ and toluene$\cdot^-$ [23] ions in which the orbital degeneracy of the benzene is lifted. Greater delocalization of the unpaired electron should reduce the *g* factor. A structure in which TB4N$\cdot^-$ and TB3N$\cdot^-$ are protonated in the 1 and 4 positions would also exhibit a similar *g* factor, but hfs from two additional β protons should be observed. The spectrum of the tetrahydronaphthalene anion has been reported[24] to exhibit β-proton hfs of 2 G and α-proton hfs of 7.5 and 2 G, so that the 16 G hfs could not be explained by this assumption.

Assuming that these spectra are therefore due to TB4DN$\cdot^-$ then two possible explanations can account for the presence of several species. Since ethers are a poor solvating medium, ion pairing is likely to occur. Because these hemi-Dewar naphthalenes have no symmetry axes, an ion pair formed when the counter ion is on the same side of the benzenoid nucleus as the 2 and 3 positions (endo conformation) should exhibit a different spectrum than one in which the counterion is on the opposite side of the plane of the benzenoid nucleus (exo conformation). The lower energy configuration should be that of the exo conformation. At lower temperatures, however, the solvation of alkali metal ions by ethers increases so that the distance of closest approach of the ions increases, and thus the energy of both configurations are more nearly equal. Thus, at higher temperatures only the exo configuration would be observed. Since the relative intensities change, and the hfs are not averaged, on the time scale of the spectrum individual configurations are detected. An alternative explanation could be that two different solvation states of ion pairs are observed. These are usually rapidly averaged. Since there are no significant line width variations, and two distinct sets of hfs are observed, this seems a less likely alternative.

Identical spectra with those shown in Figures 1 and 2 are observed when solutions of TB4N and TB3N are reduced in DME–THF until the radical anion disappears and the solution is then cooled below −50 °C. This suggests that the naphthalene dianion can isomerize to the Dewar naphthalene dianion. Solutions of TB4N in DME[16] reduced with Na or K are also unstable at temperatures above −50 °C. Initially, a brownish-red colored solution is obtained which has been assigned to the radical anion. At 0 °C, the radical anion is stable only for several minutes. The solution slowly becomes clear. Subsequent reduction yields a green solution which exhibits an ESR spectrum identical with that obtained from 1,3,6-tri-*tert*-butylnaphthalene$\cdot^-$ [21] (Figure 3). TB3N$\cdot^-$ behaves in a similar manner, except that the secondary spectrum results from two species. The spectrum of the major component is identical with that of the 1,3-di-*tert*-butylnaphthalene$\cdot^-$.[21] The second component may be due to 1,6-di-*tert*-butylnaphthalene; however, this portion of the spectrum overlaps that of the major component such that unequivocal assignment is not possible. In neither case is the ESR spectrum of the Dewar compound observed.

Kinetics. The formation and decay of the ESR signal of TB4DN$\cdot^-$ due to isomerization could be monitored from the

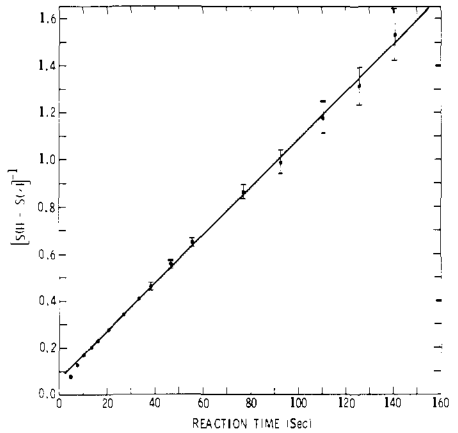
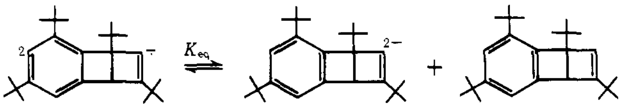


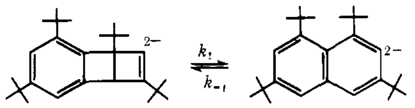
Figure 4. Plot of the reciprocal of the ESR signal with time for the decay of the 1,3,7,9-tetra-*tert*-butylnaphthalene spectrum at 5 °C.

same samples by consecutively cooling and warming each sample and recording the ESR signal as a function of time. To record the decay of TB4DN·⁻, the temperature was set to about −90 °C and the signal was allowed to stabilize. The temperature was then reset to a value between −30 and +10 °C, and the ESR signal was recorded as a function of time (Figure 4). The first 90 s were rejected to allow for temperature equilibrium. Subsequent experiments indicated that somewhat more time was needed before a temperature within ±2 °C of the indicated value was attained. The activation energy for this process was found to be 4.0 ± 1.3 kcal/mol. To record the formation of TB4DN·⁻, a similar procedure was followed, except that the initial temperature was cooled to about −30 °C. At this temperature there was still no detectable signal due to the radical anion at equilibrium. The formation was monitored between −110 and −60 °C and was neither first nor second order; however, a plot of the reciprocal of the ESR signal showed considerably less curvature than did a plot of the logarithm of the signal. This may result from a condition where the radical anion was in equilibrium with its precursor. The activation energy of this step was in the order of 1.0 ± 0.5 kcal/mol assuming a second-order process. Typical reaction times were in the order of 1000 to 2000 s for a 1-mM solution.

It is possible that the formation and decay of TB4DN·⁻ could be due to the reduction and reoxidation of TB4DN by NaK. However, if this were the case, we would not expect that the rates observed for a given solution would be reproducible, nor would a second-order behavior be observed. We can tentatively conclude, based on the spectra and kinetic experiments, that the decay of the hemi-Dewar naphthalene anion proceeds through the dianion by the following equations:



(2)



(3)

Since we are unable to detect either TB4N^{2-} or TB4DN or TB4DN^{2-}, this mechanism must be treated as tentative. Based on eq. 2 and 3, in the absence of the hemi-Dewar naphthalene at equilibrium at higher temperatures, the disappearance of TB4DN·⁻ would be given by:

$$\frac{d[\text{TB4DN}\cdot^-]}{dt} = -k_1K_{eq}\frac{[\text{TB4DN}^-]^2}{[\text{TB4DN}]} \tag{4}$$

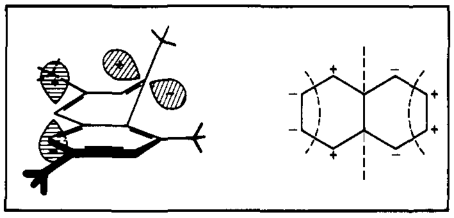
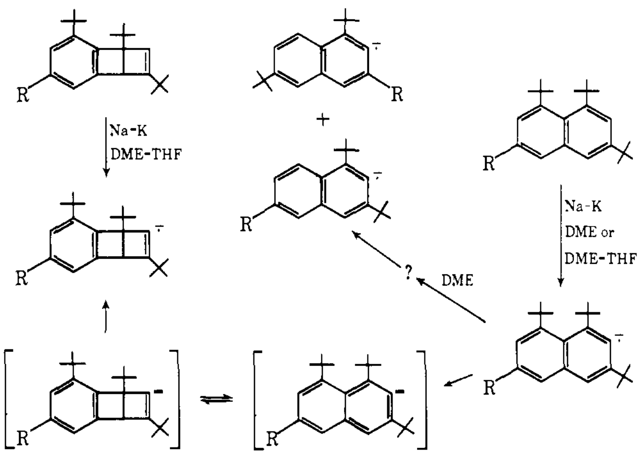


Figure 5. Structure of the intermediate of the isomerization of naphthalene to hemi-Dewar naphthalene and the symmetry of the lowest antibonding orbital of naphthalene.

which would approach a second-order behavior if the reduction potential of the NaK alloy were sufficient to reduce the hemi-Dewar naphthalene to completion and the disproportionation constant, K_{eq}, were sufficiently small. Since neither the naphthalene dianion nor the neutral hemi-Dewar naphthalene could be monitored, we do not know the concentrations that were present.

Mechanism. These results suggest the mechanism given in Scheme I may describe the reaction system.

Scheme I



A recent report showed that, in TB4N·⁻ and TB3N·⁻, the 1 and 8 positions are, respectively, above and below the mean plane such that the plane of the 1, 2, and 9 carbons intersects the mean plane at about 20°.[16] This causes a relatively small redistribution of spin, but due to positive contributions to the carbon-13 and proton hfs, there is a large perturbation in the ESR spectrum from that which would be anticipated for the hypothetical planar conformation of the same radical anions. Nevertheless, this bending has the effect of breaking down the orthogonality of the σ and π orbitals which is reflected in the *g* factor[16,26] and also increases the overlap between the p orbitals at the 1 and 4 positions, Figure 5. When two electrons are added to the antibonding orbital of the naphthalene shown in Figure 5, the bond orders of the 2–3 bond is increased, while the bond orders of the 1–2 and 3–4 bonds are decreased. In addition, the bond order of the 1–4 bond becomes considerably less negative. We expect that the planarity decreases as more electrons are added to the lowest energy antibonding orbital. The displacement of the 1 or 8 carbon atoms therefore becomes more facile, and the formation of the hemi-Dewar isomer is thus favored. This mechanism is similar to that described for the formation of Dewar benzene.[5] It is noteworthy that the dianion of naphthalene[27] is puckered such that each ring is in a shallow boat configuration, and the bond lengths are altered from neutral naphthalene as predicted by HMO calculations. The puckering may be the result of interaction between the Li$^+$ ion and the dianion. This suggests that the formation of the Dewar naphthalene could be aided by ion association. It is also interesting that the major component of the spectrum of the isomerized TB3N solutions is identical with that of the spectrum of $TB3DN\cdot^{-}$. This indicates that the major isomerization product is that in which both *tert*-butyl groups are in the Dewar portion of the compound as was found in the photochemical synthesis.

The reaction of $TB4N\cdot^{-}$ and $TB3N\cdot^{-}$ in DME was not studied in detail. Apparently the solvent is sufficiently acidic to cause protonation of the strained 1 or 8 position of the naphthalene nucleus. The mechanism by which the *tert*-butyl group is removed is not clear.

Conclusions

Reduction of 1,3,6,8-tetra-*tert*-butylnaphthalene and 1,3,8-tri-*tert*-butylnaphthalene by NaK in dimethoxyethane or dimethoxyethane–tetrahydrofuran was studied. These solutions exhibited secondary spectra following reduction to the primary radical anion. In dimethoxyethane, the secondary spectra were assigned to *tert*-butylnaphthalene anions in which a *tert*-butyl group in either the 1 or 8 position was replaced by a proton. In 40% dimethoxyethane–tetrahydrofuran spectra were assigned to the formation of a hemi-Dewar naphthalene valence bond isomer. This conclusion was derived from the analysis of the hyperfine splittings and the *g* factors of the radical ions.

Acknowledgments. This work was supported by the Office of Naval Research. We thank Dr. D. Pilipovich for helpful discussions.

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Ionization of Methyl Derivatives of Imidazole, Histidine, Thyreotropin Releasing Factor, and Related Compounds

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Received December 22, 1975

Abstract: The pK_a values for imidazole and for its 1- and 2-methyl derivatives were determined electrometrically at seven temperatures in the range of 10–40 °C. The results are discussed in terms of inductive and resonance effects, and hydrogen bonding of water molecules to the protonated imidazolium nitrogen atoms. From the contribution of *N*-methyl groups to imidazole basicity a correction factor was derived to improve the estimation of imidazole tautomer ratios from the pK_a of the parent compound and that of the N^{τ}- or the N^{π}-methyl derivative. This analysis was applied to 4-nitroimidazole, histamine, histidine, *tert*-butoxycarbonylhistidine, and thyreotropin releasing factor.

The introduction of an alkyl substituent in one of the nitrogens of imidazole, and of some of its derivatives, does not produce significant changes in the basicity at the other nitrogen atom. Thus, the pK_a of 1-methylimidazole is only about 0.1 unit higher than that of imidazole.[1,2] However, correction for the statistical factor due to the presence of two equivalent protons in the imidazolium ion yields a pK_a 0.2 unit higher for imidazole than for its 1-methylderivative, leading to the conclusion that the methyl group must effectively reduce the basicity of the other nitrogen atom.[3] This is contrary to the expected inductive effect and to the reported good correlation between the pK_a values of 1-substituted imidazoles with either σ_I or σ_m values for the substituents.[4] However, this correlation does not hold for the case of imidazole when the statistical correction is made. This was observed on simple Hammett correlations using σ_I or σ_m, as well as with a dual substituent parameter treatment,[5a] which takes into account both inductive and resonance effects. Figure 1 shows that a very good fit of the data was obtained, except for imidazole, whose pK_a is 0.62 unit higher than predicted by the correlation. In order to