

## $\alpha$ -C–H Bond Dissociation Energies of Some Tertiary Amines

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The  $\alpha$ -C–H bond dissociation energies of 14 tertiary, trialkyl- and arylalkylamines have been measured by photoacoustic calorimetry (PAC). In general, the data lead to an upward revision of the bond dissociation energies (BDE's). The effects of  $\alpha$ -phenyl and  $\alpha$ -vinyl substitution have been quantified for the first time.  $\alpha$ -Phenyl substitution was found to have a significantly smaller effect on lowering  $\alpha$ -C–H BDE's than  $\alpha$ -vinyl substitution. These data provide a thermochemical confirmation of the stereoelectronic hypothesis proposed by Lewis et al. in 1982.

### Introduction

The  $\alpha$ -C–H bond dissociation energies (BDE's) of tertiary amines, and radical stabilization energies (RSE's) derived from them, have been the subject of experimentation, calculations, and debate for more than 20 years.<sup>1</sup> In 1973, Sen Sharma and Franklin determined the gas phase heat of formation of  $\text{Et}_2\text{NCH}_2^*$ , which leads to a C–H BDE for  $\text{Et}_2\text{NCH}_2\text{–H}$  of 90 kcal/mol.<sup>2</sup> From this, a RSE for  $\text{Et}_2\text{NCH}_2^*$  of 15 kcal/mol can be calculated by using the C–H BDE of methane (105 kcal/mol)<sup>3</sup> as a reference. A somewhat larger RSE was later obtained by Richey and Shull for the  $-\text{NMe}_2$  group (19 kcal/mol) on the basis of the relative activation energies for rearrangement of *trans*-2-(*N,N*-dimethylamino)vinylicyclopropane vs vinylicyclopropane.<sup>4</sup> An even larger RSE for  $\text{Me}_2\text{NCH}_2^*$  of 21 kcal/mol was subsequently determined by Griller and Lossing on the basis of a BDE for  $\text{Me}_2\text{NCH}_2\text{–H}$  of 84 kcal/mol, which was derived from appearance potential measurements on *N,N,N,N*-tetramethylethylenediamine.<sup>5</sup> These investigators also reported a surprisingly large effect of *N*-alkyl substitution on the  $\alpha$ -C–H BDE's of amines. For example,  $\text{BDE}(\text{H}_2\text{NCH}_2\text{–H})$  was reported to be 10 kcal/mol higher than  $\text{BDE}(\text{Me}_2\text{NCH}_2\text{–H})$ . The effect of *N*-alkyl substitution was later questioned on the basis of quantum chemical calculations. Using the UHF/6-31G\* method, Goddard calculated a slightly lower BDE for  $\text{H}_2\text{NCH}_2\text{–H}$  (96.7 kcal/mol) than for  $\text{Me}_2\text{NCH}_2\text{–H}$  (97.4 kcal/mol).<sup>6</sup> The results of Griller and Lossing were also challenged by later experimental work. On the basis of the low-pressure thermolyses of substituted ethylenediamines and phen-

ethylamines, Grela and Colussi reported  $\text{BDE}(\text{H}_2\text{NCH}_2\text{–H}) = 88\text{--}89$  kcal/mol and  $\text{BDE}(\text{Me}_2\text{NCH}_2\text{–H}) = 85\text{--}87$  kcal/mol.<sup>7</sup> A significantly higher value BDE for  $\text{H}_2\text{NCH}_2\text{–H}$  (94.6 kcal/mol) was reported by Pasto et al. on the basis of ROHF/4-31G calculations.<sup>8</sup> Recent experimental determinations of the  $\alpha$ -C–H BDE of  $\text{Me}_3\text{N}$  by photoacoustic calorimetry place it at 87–89 kcal/mol.<sup>9,10</sup> These values are significantly higher than the recent MP2/6-31+G\* estimate by Armstrong et al. (83.6 kcal/mol)<sup>11</sup> but lower than a G2-derived BDE (92.5 kcal/mol) later reported by the same group.<sup>10</sup> Similar high-level ab initio methods, known to provide BDE's with an accuracy of  $\pm 1$  kcal/mol, have been reported separately by Wiberg et al.<sup>12</sup> and Armstrong et al.<sup>10</sup> to give  $\text{BDE}(\text{H}_2\text{NCH}_2\text{–H}) = 92\text{--}94$  kcal/mol.

It is clear from the above summary that the  $\alpha$ -C–H BDE's of even the simplest amines have an undesirable degree of uncertainty. In fact, one might plausibly argue that the "best" available values are those derived from recent high-level ab initio calculations. This situation is clearly unsatisfactory, not only because of the lack of benchmark experimental data but also because high-level calculations remain impractical for many systems of experimental interest. Indeed, we faced just this problem while studying the deprotonation of tertiary amine cation radicals, where  $\alpha$ -C–H BDE's for a series of *N,N*-dialkylanilines were needed in order to evaluate the  $pK_a$ 's of their corresponding cation radicals. At the outset of our work, only a crude estimate of the  $\alpha$ -C–H BDE for  $\text{PhNMe}_2$  (80 kcal/mol) was available from the literature.<sup>13</sup> It was made in 1989 on the basis of amine BDE's available at the time. The experimental determination of this BDE reported herein shows that the previous

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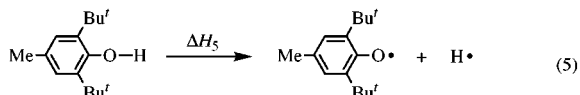
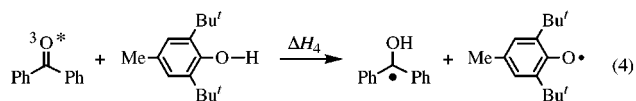
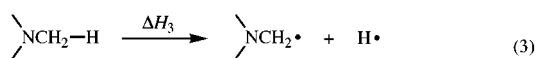
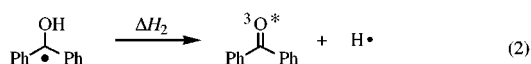
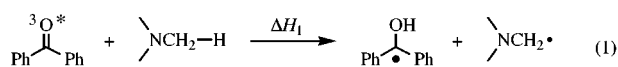
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value was underestimated by nearly 12 kcal/mol! In fact, our data generally lead to upward revisions of the  $\alpha$ -C-H BDE's accepted for tertiary amines, including several trialkylamines. Some surprising substituent effects are also reported.

### Results

The tertiary amine  $\alpha$ -C-H BDE's were determined by photoacoustic calorimetry (PAC).<sup>14</sup> Previously, PAC-derived C-H BDE's have been obtained by measuring the heats of reaction of substrates with the *tert*-butoxyl radical ( $\cdot$ OBu). We instead chose to use the triplet state of benzophenone as a hydrogen atom abstractor for several reasons. First, the photoacoustic response for a reaction is determined by both its exothermicity and its volume change. The  $\cdot$ OBu method requires a volume correction because it is based on the generation of  $\cdot$ OBu from the photolysis of di-*tert*-butyl peroxide, for which the volume change is substantial. With the benzophenone triplet as the hydrogen atom abstractor, however, the volume change for hydrogen atom transfer from a substrate is insignificant. Second, benzophenone has the attractive feature that it can be used in relatively low concentration because Ph<sub>2</sub>CO absorbs more strongly than (Bu<sup>o</sup>)<sub>2</sub> at convenient excitation wavelengths. Third, the benzophenone ketyl radical formed by hydrogen atom transfer has a convenient absorption at 545 nm which allows its formation to be quantitated by transient absorption spectroscopy. Finally, the reaction of triplet benzophenone with tertiary amines is a well-studied process; the reaction proceeds by an electron-transfer/proton-transfer mechanism involving net hydrogen atom transfer from the  $\alpha$ -C-H bonds.<sup>15</sup>

In principle, the  $\alpha$ -C-H BDE's of the amines can be determined from the energetic sum of reactions 1 and 2.  $\Delta H_1$  was measured by photoacoustic calorimetry as described below.  $\Delta H_2$  has been measured by Arnaut and Caldwell using photoacoustic calorimetry.<sup>16</sup> They report a value of  $110.8 \pm 1.5$  kcal/mol. Subsequently, a significantly lower value of  $103 \pm 3$  kcal/mol was obtained using photothermal lens spectroscopy.<sup>17</sup> The large differences between these values prompted us to pursue a slightly modified approach.



We were able to circumvent the uncertainty in  $\Delta H_2$  by measuring the difference in the heats of reaction of benzophenone triplet with amines vs a reference com-

pound, 2,6-di-*tert*-butyl-4-methylphenol (BHT). BHT has the virtues that it reacts rapidly with triplet benzophenone by hydrogen atom abstraction from the O-H bond (reaction 4) and its O-H BDE is accurately known from the careful EPR equilibration experiments of Pedulli and co-workers ( $81.02 \pm 0.15$  kcal/mol).<sup>18</sup> Thus,  $\Delta H_3$  can be determined from the sum  $\Delta H_1 - \Delta H_4 + \Delta H_5$ .

Photoacoustic experiments were performed with 365 nm excitation of benzophenone in argon-saturated 1,2-dichloroethane (DCE). This solvent was chosen to prevent separation of the triplet amine-cation-radical/benzophenone-anion-radical geminate pairs, which is known to occur in polar solvents such as acetonitrile.<sup>19</sup> In nonpolar solvents, in-cage proton transfer occurs from the amine cation radicals to benzophenone anion radical, thus generating  $\alpha$ -amino-radical/benzophenone-ketyl-radical pairs. These neutral, triplet radical pairs undergo diffusive separation. Although this reaction sequence has been well-established for a number of amines,<sup>15</sup> we felt it was important to measure the quantum yields for formation of benzophenone ketyl radical in order to confidently attribute partitioning of the heat deposited in the photoacoustic experiments. Nanosecond transient absorption spectroscopy was used to measure quantum yields for the reactions of benzophenone triplet with the amines. The quantum yields were found to be one within experimental error ( $\pm 0.04$ ).<sup>20</sup>

Deliberate care was taken to work at sufficiently low laser energies to avoid triplet-triplet excitation of the benzophenone. To probe for this, solutions containing only benzophenone were analyzed by PAC. From the heat evolved, a triplet energy for benzophenone of 68.8 kcal/mol was derived, in excellent agreement with the literature value (69 kcal/mol).<sup>21</sup> This rules out any significant triplet-triplet absorption, since otherwise the PAC-derived triplet would be lower than the true triplet energy due to the heat deposited by rapid nonradiative decay of the upper triplet state.

Reactions of the amines and BHT with triplet benzophenone were conducted at sufficiently high substrate concentrations (50–100 mM) that all of the heat was deposited rapidly with respect to the response time of the photoacoustic transducer. Consequently, the photoacoustic waves did not show any phase shift relative to that of the calibration compound (ferrocene), which deposits all of the absorbed photon energy as heat within

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(20) If a small amount of triplet to singlet intersystem crossing occurs in the geminate ion radical pair, which is followed by rapid return electron transfer, the measured heat deposition will be slightly larger than that due solely to hydrogen atom transfer from the amine to triplet benzophenone. This leads to an apparent  $\alpha$ -C-H amine BDE that is lower than the true value. A quantitative analysis shows that for quantum yields of benzhydrol radical formation  $\geq 0.96$ , the maximum BDE correction would be +2.2 kcal/mol.

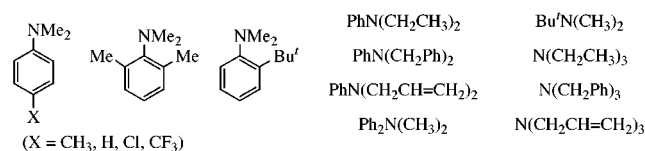
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**Table 1. Experimental α-C–H Bond Dissociation Energies (BDE's)**

amine	α-C–H BDE (kcal/mol)	amine	α-C–H BDE (kcal/mol)
N(CH <sub>2</sub> CH <sub>3</sub> ) <sub>3</sub>	90.7 ± 0.4	<i>o,o</i> -Me <sub>2</sub> PhN(CH <sub>3</sub> ) <sub>2</sub>	90.2 ± 1.5
Bu <sup>t</sup> N(CH <sub>3</sub> ) <sub>2</sub>	90.0 ± 1.2	PhN(CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	91.6 ± 1.0
<i>p</i> -CH <sub>3</sub> PhN(CH <sub>3</sub> ) <sub>2</sub>	89.9 ± 2.5	Ph <sub>2</sub> NCH <sub>3</sub>	90.7 ± 0.4
PhN(CH <sub>3</sub> ) <sub>2</sub>	91.7 ± 1.3	PhN(CH <sub>2</sub> Ph) <sub>2</sub>	85.4 ± 2.1
<i>p</i> -ClPhN(CH <sub>3</sub> ) <sub>2</sub>	89.8 ± 1.4	N(CH <sub>2</sub> Ph) <sub>3</sub>	89.1 ± 0.6
<i>p</i> -CF <sub>3</sub> PhN(CH <sub>3</sub> ) <sub>2</sub>	92.2 ± 1.7	PhN(CH <sub>2</sub> CH=CH <sub>2</sub> ) <sub>2</sub>	81.1 ± 0.7
<i>o</i> -Bu <sup>t</sup> PhN(CH <sub>3</sub> ) <sub>2</sub>	94.7 ± 1.3	N(CH <sub>2</sub> CH=CH <sub>2</sub> ) <sub>3</sub>	82.6 ± 0.8

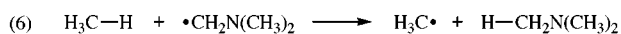
1 ns. The amine BDE values were obtained from an average of five to nine separate determinations. The reported errors (2σ) contain the propagated experimental errors for both the PAC measurements and the O–H BDE of BHT.<sup>18</sup> Since the heat of reaction of benzophenone with BHT (Δ*H*<sub>4</sub>) was always used as a reference, it was measured a relatively large number of times (>25). From an average of these measurements, Δ*H*<sub>2</sub> can be determined from Δ*H*<sub>4</sub> – Δ*H*<sub>5</sub>. We found Δ*H*<sub>2</sub> = 110.7 ± 1.2 kcal/mol, in excellent agreement with the value reported by Arnaut and Caldwell (110.8 ± 1.5 kcal/mol).<sup>16</sup>

Shown as follows are the amines studied in the present work. Their α-C–H bond dissociation energies derived from photoacoustic calorimetry are listed in Table 1.



### Discussion

We begin with the BDE for the simplest tertiary amine, NMe<sub>3</sub>. This amine was difficult to properly handle in the PAC experiment due to its low boiling point (3 °C) therefore, we calculated its α-C–H BDE from the isodesmic reaction shown in eq 6 using CBS-Q model chemis-



try,<sup>22</sup> which has been shown to reproduce experimental BDE's to ±1 kcal/mol.<sup>12</sup> From the calculated enthalpies at 298.15 K, Δ*H*<sub>6</sub> = +12.3 kcal/mol, which taken together with the experimental BDE for CH<sub>4</sub> (104.9 ± 0.1 kcal/mol)<sup>3</sup> gives α-C–H BDE(NMe<sub>3</sub>) = 92.6 kcal/mol. This is higher than previous experimental values (84–89 kcal/mol)<sup>5,9,10</sup> but in excellent agreement with recent G2 calculations (92.5 kcal/mol) of Armstrong et al.<sup>10</sup> The calculational results for NMe<sub>3</sub> seem more likely to be correct since they predict a slightly higher BDE for NMe<sub>3</sub> than our experimental BDE for NEt<sub>3</sub> (90.7 kcal/mol).

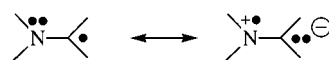
The CBS-Q-derived α-C–H BDE for NMe<sub>3</sub> (92.6 kcal/mol) is quite similar to that obtained for H<sub>2</sub>NMe using comparable high-level ab initio methods (92–93 kcal/mol).<sup>10,12</sup> Given the known accuracy of these methods and our BDE for NEt<sub>3</sub>, we agree with Armstrong et al.<sup>10</sup> that, contrary to earlier conclusions,<sup>5</sup> *N*-methylation does not

lead to an increase in the stabilization of α-amino radicals, at least as judged by their α-C–H BDE's.

Interestingly, our experimental BDE for Bu<sup>t</sup>NMe<sub>2</sub> (90.0 kcal/mol) is slightly lower than that calculated for NMe<sub>3</sub> (92.6 kcal/mol). Although the difference is small, it is consistent with what might be expected on the basis of relief of internal strain in the bond dissociation process. Calculations show that the nitrogen atoms in α-amino radicals are substantially less pyramidal than in the corresponding amines.<sup>10,11</sup> Consequently, the α-C–H bond dissociation should result in greater relief of internal strain for Bu<sup>t</sup>NMe<sub>2</sub> than for NMe<sub>3</sub>, thus leading to a lower BDE for Bu<sup>t</sup>NMe<sub>2</sub>.

Next we turn to the α-C–H BDE's for the *N,N*-dimethylanilines. As stated in the Introduction, the BDE for PhNMe<sub>2</sub> was previously estimated to be 80 kcal/mol.<sup>13</sup> This estimate was based on nearly the same PAC experiment described here. Previously, the reactions of triplet benzophenone with PhNMe<sub>2</sub> or NEt<sub>3</sub> (in acetone) were reported to deposit the same amount of heat within experimental error (±2 kcal/mol). Thus, it was concluded that these amines have the same α-C–H BDE's. Our current PAC data are completely consistent with the earlier results (note the similar BDE's for PhNMe<sub>2</sub> and NEt<sub>3</sub> in Table 1). The absolute BDE's do not agree, however. This is because the BDE for NEt<sub>3</sub> in the earlier experiments was estimated from the previously accepted α-C–H BDE for NMe<sub>3</sub> of 84 kcal/mol,<sup>5</sup> after correcting for the incremental stabilization of α-methyl substitution, which was estimated to be ≈4 kcal/mol. This led to BDE's of 80 kcal/mol for both NEt<sub>3</sub> and PhNMe<sub>2</sub>. The majority of the error in the earlier estimates can now be traced to the BDE value for NMe<sub>3</sub> of 84 kcal/mol, which was clearly too low. It is also clear that the magnitude of the incremental effect for α-methyl was previously overestimated by ca. 2 kcal/mol (vide supra).

Data for the substituted *N,N*-dimethylanilines in Table 1 show that substituents on the aromatic ring can influence the α-C–H BDE's. The relative BDE's for the para-substituted anilines are consistent with a modest polarity effect. Note that the aniline containing the strongly electron-withdrawing *p*-CF<sub>3</sub> group has the highest BDE. It is tempting to attribute the effect to destabilization of the corresponding α-amino radical. This can be rationalized by a simple resonance model wherein the zwitterionic resonance form of the α-amino radical is destabilized by the electron-withdrawing substituent (see below). We were unable to test this hypothesis further because *N,N*-dimethylanilines containing powerful electron-donating (e.g. *p*-OCH<sub>3</sub>) or electron-withdrawing (e.g. *p*-NO<sub>2</sub>) substituents absorbed strongly at the excitation wavelength.



Curiously, the α-C–H BDE's of *o,o*-Me<sub>2</sub>PhNMe<sub>2</sub> and *o*-Bu<sup>t</sup>PhNMe<sub>2</sub> show opposing effects of ortho-substitution relative to PhNMe<sub>2</sub>. The structures of the amines and their α-amino radicals were calculated by ab initio methods (UHF/6-31G\*) to identify possible explanations for this behavior. The calculations reveal that the nitrogen in *o*-Bu<sup>t</sup>PhNMe<sub>2</sub> is substantially more pyramidal than in *o,o*-Me<sub>2</sub>PhNMe<sub>2</sub>.<sup>23</sup> For the former amine, non-bonded interactions between the *o*-*tert*-butyl group and the *N*-methyl groups cause the nitrogen to be more

(22) Calculations performed using the Gaussian 94 suite of programs: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, Revision C.3; Gaussian, Inc., Pittsburgh, PA, 1995.

pyramidal. Conversion to the corresponding  $\alpha$ -amino radical results in greater internal strain between these groups due to the flattening that occurs at nitrogen. This leads to a less stable  $\alpha$ -amino radical and thus a greater  $\alpha$ -C–H BDE. On the other hand, in *o,o*-Me<sub>2</sub>PhNMe<sub>2</sub>, the nitrogen is less pyramidal due to opposing nonbonded interactions between the two *ortho*-methyl groups and the *N*-methyl groups. Conversion to the  $\alpha$ -amino radical partially relieves this strain due to flattening at nitrogen, which results in a lower BDE.

Next we compare the BDE's for Ph<sub>2</sub>NMe and PhNET<sub>2</sub> to PhNMe<sub>2</sub>. The BDE for Ph<sub>2</sub>NMe is only 1 kcal/mol lower than PhNMe<sub>2</sub>, showing a negligible effect of substitution. Similarly, the measured BDE's for PhNET<sub>2</sub> and PhNMe<sub>2</sub> are indistinguishable (91.6 vs 91.7 kcal/mol). The virtually identical BDE's for the latter two amines provide a modest contrast to the decrease in BDE caused by  $\alpha$ -methyl substitution for the trialkylamines NMe<sub>3</sub> (92.6 kcal/mol) and NEt<sub>3</sub> (90.7 kcal/mol). The data provide preliminary evidence that the transference of  $\Delta$ BDE increments for tertiary amines of different structure should be done with caution.

The  $\alpha$ -C–H BDE effects for  $\alpha$ -phenyl and  $\alpha$ -vinyl substitution provided some intriguing results. We start with the effects of  $\alpha$ -phenyl substitution. Comparison of the  $\alpha$ -C–H BDE's for N(CH<sub>2</sub>Ph)<sub>3</sub> and PhN(CH<sub>2</sub>Ph)<sub>2</sub> to those for N(CH<sub>3</sub>)<sub>3</sub> and PhN(CH<sub>3</sub>)<sub>2</sub> revealed surprisingly small effects of  $\alpha$ -phenyl substitution: 3.5 and 6.3 kcal/mol, respectively. These  $\Delta$ BDE values are substantially smaller than those observed for simple alkyl-substituted radicals.<sup>24</sup> We attribute the smaller increments for the tertiary  $\alpha$ -amino radicals to a stereoelectronic effect. As shown in **a**, benzylic stabilization of tertiary  $\alpha$ -amino



radicals is expected to result in an unfavorable steric interaction between one of the *ortho*-phenyl hydrogens and the *syn*-substituent at nitrogen. Relief of this interaction by rotation around either the C–C<sub>Ph</sub> or C–N bonds presumably results in diminished radical stabilization. This hypothesis is supported by *ab initio* calculations (UHF/6-31G+\*). As shown in **a**, for R = CH<sub>3</sub>, the phenyl group in the fully optimized  $\alpha$ -amino radical is fully conjugated with the radical center, while the nitrogen lone pair is nearly orthogonal to it.

This stereoelectronic proposal is completely analogous to that first suggested by Lewis to rationalize the kinetic regioselectivity observed in the reaction of the stilbene singlet excited state with PhCH<sub>2</sub>NMe<sub>2</sub>, which occurs with preferential, net hydrogen atom transfer from the methyl

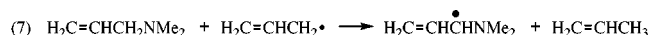
carbon rather than from the benzyl carbon.<sup>26a</sup> Our BDE data provide thermodynamic information relevant to Lewis' proposal. If the BDE's for (PhCH<sub>2</sub>)<sub>3</sub>N (89.1 kcal/mol) and N(CH<sub>3</sub>)<sub>3</sub> (92.6 kcal/mol) are used to approximate the corresponding  $\alpha$ -C–H BDE's in PhCH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>, then the differential stabilization between the two  $\alpha$ -amino radicals is calculated to be  $\approx$ 3.5 kcal/mol, with the benzylic  $\alpha$ -amino radical being more stable. This shows that the regioselectivity observed in the reaction of the stilbene excited state with PhCH<sub>2</sub>NMe<sub>2</sub> indeed has a kinetic origin; i.e., the relative transition state energies leading to the  $\alpha$ -amino radicals are not reflected by the relative radical stabilities.

As noted above, comparison of the  $\alpha$ -C–H BDE's for PhN(CH<sub>2</sub>Ph)<sub>2</sub> and N(CH<sub>2</sub>Ph)<sub>3</sub> to those for PhN(CH<sub>3</sub>)<sub>2</sub> and N(CH<sub>3</sub>)<sub>3</sub> lead to different  $\alpha$ -phenyl radical stabilization increments: 6.3 vs 3.5 kcal/mol. The results once again demonstrate the difficulty encountered in transferring  $\Delta$ BDE increments from one tertiary amine system to another.

Lewis' stereoelectronic hypothesis leads to the prediction that the conjugative stabilization of an  $\alpha$ -amino radical by a vinyl group will not suffer from the severe steric interference experienced by phenyl (cf. **b** vs **a**). This



prediction is supported by the UHF/6-31G+\* optimized  $\alpha$ -amino radical structure shown above. Note that both the vinyl group and the nitrogen lone pair are properly aligned for good  $\pi$  overlap. Consequently, for tertiary  $\alpha$ -amino radicals, an  $\alpha$ -vinyl group is expected to lead to more effective radical stabilization and thus substantially lower BDE's than an  $\alpha$ -phenyl group. This prediction is confirmed by the low  $\alpha$ -C–H BDE's measured for N(CH<sub>2</sub>CH=CH<sub>2</sub>)<sub>3</sub> (82.6 kcal/mol) and PhN(CH<sub>2</sub>CH=CH<sub>2</sub>)<sub>2</sub> (81.1 kcal/mol). These low BDE's are also consistent with the isodesmic calculation shown in eq 7. CBS-Q



model chemistry gives  $\Delta H_7 = -11.2$  kcal/mol. From  $\Delta H_7$  and the experimental BDE for propene (88.6 kcal/mol),<sup>25</sup> the allylic C–H BDE for CH<sub>2</sub>=CHCH<sub>2</sub>NMe<sub>2</sub> is calculated to be 77.4 kcal/mol, in reasonable agreement with our experimental BDE's. Finally, we note that, in contrast to the  $\alpha$ -phenyl systems, calculation of the  $\alpha$ -vinyl radical stabilization energies for N(CH<sub>2</sub>CH=CH<sub>2</sub>)<sub>3</sub> and PhN(CH<sub>2</sub>CH=CH<sub>2</sub>)<sub>2</sub> (relative to NMe<sub>3</sub> and PhNMe<sub>2</sub>) lead to very similar values: 10.0 and 10.6 kcal/mol, respectively.

## Conclusions

The  $\alpha$ -C–H bond dissociation energies for a number of tertiary amines have been determined by photoacoustic calorimetry. The data lead to a general upward revision of the BDE's. The effects of  $\alpha$ -phenyl and  $\alpha$ -vinyl substitution were also quantified for the first time. The PAC

(23) The degree of nonplanarity at nitrogen of the amines and their  $\alpha$ -amino radicals (numbers in parentheses) can be judged by the sum of the C–N–C internal bond angles which are 339° (344°) and 350° (354°) for *o*-Bu/PhNMe<sub>2</sub> and *o,o*-Me<sub>2</sub>PhNMe<sub>2</sub>, respectively. For comparison, in calculations on a hypothetical PhNMe<sub>2</sub> structure where the nitrogen lone pair is orthogonal to the plane of the aromatic ring, the sum of C–N–C bond angles is 341°.

(24) For example, BDE(H<sub>3</sub>C–H) = 104.9<sup>3</sup> vs BDE(PhCH<sub>2</sub>–H) = 89.9 kcal/mol.<sup>25</sup>

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data reveal that  $\alpha$ -phenyl substitution has a significantly smaller effect on lowering  $\alpha$ -C-H BDE's than  $\alpha$ -vinyl substitution, consistent with Lewis' stereoelectronic hypothesis. Finally, our data suggest that incremental effects of substitution on  $\alpha$ -C-H BDE's of tertiary amines may not be generally transferable from one amine structural type to another.

### Experimental Section

**Materials.** All compounds were purchased from Aldrich unless otherwise noted. Ferrocene, BHT, tribenzylamine, and benzophenone were recrystallized from ethanol. *p*-Chloro-*N,N*-dimethylaniline was sublimed. *N,N*-Dibenzylaniline (99+%) was purchased from TCI and used as received. The following compounds were distilled prior to use and stored at  $-20$  °C: triethylamine, *N,N*-dimethylaniline, *N,N*-dimethyltoluidine, diphenylmethylamine (Kodak), *N,N*-diethylaniline, and triallylamine. The following *N,N*-dimethylamine derivatives were prepared by reductive formylation<sup>27</sup> and distilled prior to use: *tert*-butyldimethylamine, *o-tert*-butyl-*N,N*-dimethylaniline, 2,6-*N,N*-tetramethylaniline, and *p*-(trifluoromethyl)-*N,N*-dimethylaniline (recrystallized, pentane,  $-70$  °C). *N,N*-Diallylaniline was prepared according to a literature method<sup>28</sup> and distilled. 1,2-Dichloroethane (DCE) was distilled from calcium hydride under nitrogen.

**Photoacoustic Calorimetry.** Photoexcitation was conducted at 365 nm using the  $N_2$  laser-pumped dye emission of BPBD (butylphenylbiphenyloxadiazone) (PRA nitrogen laser, Model LN 1000); a monochromator was used to isolate the 365 nm line. The light was attenuated using an iris diaphragm to  $<0.01$  mJ/pulse (approximately 1 Hz repetition rate). The acoustic waves were detected using a 0.5 MHz lead-zirconate lead-titanate piezoelectric transducer attached to a quartz cuvette at a right angle to the incident laser beam. Each photoacoustic waveform (400 data points, average of 50 pulses) was normalized to the laser energy which was measured by a

Laser Precision RJP-735 pyrolytic probe. Sample absorbances were determined with a second pyrolytic probe positioned behind the sample. The photoacoustic signals were amplified (Panametrics preamp, Model 5676), digitized (Tektronix TDS 620), and transferred to a laboratory computer for normalization and deconvolution of the acoustic waveforms.

Experiments were done on argon-degassed samples at room temperature (22 °C). The optical densities (OD's) of the sample and reference solutions were 0.45–0.55 at 365 nm and were matched to within 1–2% in order to avoid different concentration gradients of heat-producing transients. The reference waveform was obtained from photoexcitation of ferrocene. No phase shift relative to the reference solution was observed for amine concentrations  $> 10$  mM, except for  $Bu^tNMe_2$  and  $Et_3N$ , whose waveforms were therefore subjected to deconvolution. Typical concentrations used were 50–80 mM for all of the amines. At these concentrations *N,N*-dibenzylaniline had a slight absorbance at 365 nm, and its reported BDE was corrected for this absorption.

**Actinometry.** The quantum yields were determined using transient absorption, nanosecond laser spectroscopy.<sup>29</sup> A XeCl excimer-laser pumped dye laser was used to photoexcite an argon-purged, DCE solution of benzophenone at 343 nm (OD  $\approx 1$ ). Substrates were added at a sufficiently high concentration ( $\approx 10$  mM) so that benzhydrol radical formation occurred within the time frame of the laser pulse. The optical density of the benzhydrol radical was monitored at 545 nm on sufficiently short time scales that no signal decay was observable. Quantum yield measurements were not possible in the cases of *p*-(trifluoromethyl)-*N,N*-dimethylaniline, *N,N*-dibenzylaniline, and *N,N,N*-tribenzylamine because their  $\alpha$ -amino radicals were found to absorb at 545 nm. This was determined by independent generation of the radicals by 308 nm photolysis of DCE solutions containing the amines and di-*tert*-butyl peroxide.<sup>30</sup>

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