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Steric and Electronic Effects in the Dimerization of Wanzlick Carbenes: The Alkyl Effect[‡]

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The steric and electronic influence of *N*-alkyl substituents on the dimerization energies $\Delta G°$ of Wanzlick carbenes (imidazolidin-2-ylidenes) was investigated experimentally and through DFT methods for a series of non-symmetrically substituted Wanzlick carbenes. A series of 3-alkyl-1-*tert*-butylimidazolidin-2-ylidenes with decreasing steric demand of the alkyl substituent (isopropyl, ethyl and methyl) were obtained in four steps from the commercially available *N*-alkylaminoethanol compounds. The carbenes are hydrolytically sensitive, colorless oils that can be distilled without decomposition and show no sign of dimerization to the respective enetetramines, even after prolonged heating. Calculations at the B98/6-31G(d) level confirm that the dimerization of all three carbenes is thermodynamically unfavorable. To separate the steric and electronic stabilization of Wanzlick carbenes by *N*-alkyl substituents, the formation energies of R,H_3 mono-alkyl enetetramines were used to derive electronic increments for the *N*-alkyl substituents. The computational data show that all alkyl substituents electronically stabilize Wanzlick carbenes vs. their dimerization products with increments ranging from 2.97 kcal mol^{-1} (*N*-methyl) to as high as 6.28 kcal mol^{-1} (*N*-*tert*-butyl). For combinations of *N*-methyl, *N*-ethyl and *N*-isopropyl substituents, the increments are additive and the dimerization energies were found to be free of noticeably steric effects. Significant steric strain was found for all *t*Bu-substituted carbenes with strain energies of the dimerization products ranging from 6.92 kcal mol^{-1} [formation of (*E*)-Me_2tBu_2-enetetramine] to 24.23 kcal mol^{-1} (formation of tBu_4 enetetramine). The *tert*-butyl substituent thus assumes a unique position by strongly stabilizing the carbenes electronically as well as sterically.

1. Introduction

A limit to the steadily growing number of thermodynamically stable diamino carbenes[1] obtained since the isolation of a imidazol-2-ylidene (**A**, R = 1-adamantyl) in 1991 by Arduengo et al.[2] is their dimerization[3–5] to the respective enetetramines,[6] the very reaction preventing the isolation of 1,3-diphenylimidazolidin-2-ylidene investigated by Wanzlick's group more than 40 years ago.[3] While dimerization of the aromatically stabilized[7] carbenes of type **A** is thermodynamically unfavorable even for small substituents like R = Me, and has only been observed for the special case of the covalently tethered bis-carbene (formation of **B=B**)[8] all other diamino carbenes like **C** and **D** require sterically demanding substituents to be thermodynamically stable towards dimerization.[5–11] A notable exception may be the benzo-annellated carbene **E** that has recently been obtained by Metallinos et al.[12]

The crucial role of steric protection is particularly obvious from the behavior of Wanzlick carbenes **D** which dimerize for R = phenyl, the substituent originally chosen by Wanzlick's group, but are thermodynamically stable towards dimerization for R = *tert*-butyl[4] and mesityl.[13] For alkyl substituents, even a slight relaxation of the steric demand (R = isopropyl, ethyl, or methyl) the Wanzlick carbenes dimerize although the dimerization is slow enough to be observed by NMR methods.[4,5] The slow nature of the dimerization has since been strikingly highlighted by the successful isolation and structural characterization of a series of thermodynamically unstable amino carbenes like the tetramethyl analog of **C**,[10a] the tetraethyl analog of **C**[10b] and even the monoamino carbene **F** (Scheme 1).[10c] Irrespective of the kinetic aspect of the reaction, the presence of bulky substituents remains a prerequisite for the design of thermodynamically stable carbenes. For Wanzlick carbenes bearing identical *N*-substituents, the demarcation line separating stable from unstable carbenes is now established as tBu_2/iPr_2[4] and Mes_2/Ph_2.[13] Wanzlick carbenes bearing only *one* bulky *N*-alkyl substituent should dimerize to the (E)-enetetramines in which steric repulsion is minimized due to the large-small combination of alkyl substituents facing each other across the double bond (Scheme 2).

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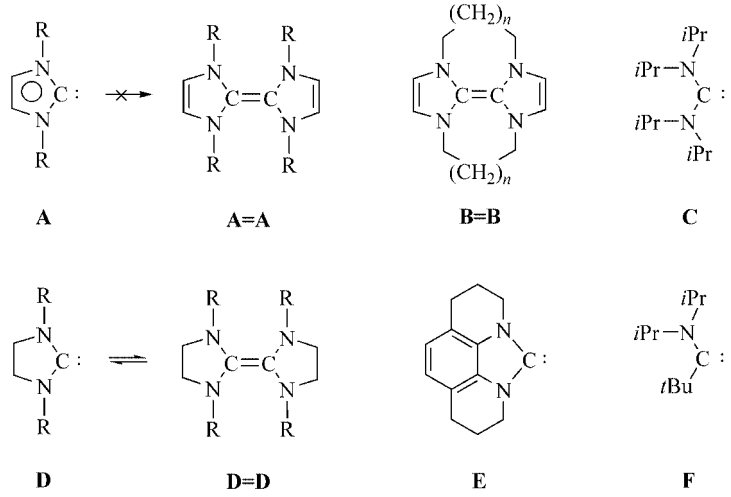
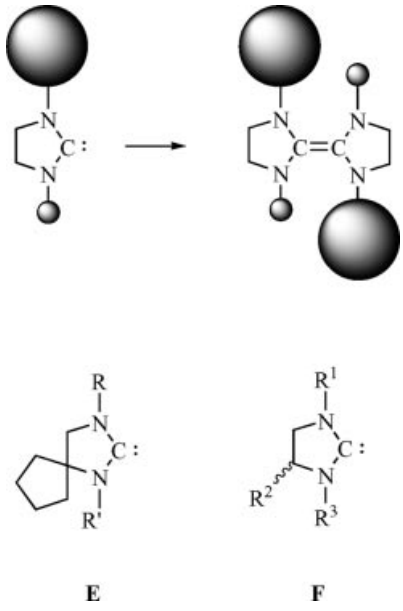


Scheme 1. Dimerization of aminocarbenes.



Scheme 2. Steric matching in non-symmetric Wanzlick carbenes.

To examine this prediction experimentally, we have obtained a series of 3-alkyl-1-*tert*-butylimidazolidin-2-ylidenes with alkyl substituents of decreasing size (R: *i*Pr, Et and Me). Much to our surprise, all three carbenes are perfectly stable and do not show any sign of dimerization even for the smallest substituent (Me). While surprising, the observed lack of dimerization is in good agreement with the behavior of 1,3,4-trisubstituted Wanzlick carbenes **E** and **F** (Scheme 2) which have been obtained via a new elegant synthetic protocol by Hahn's group while this work was in progress.[14]

The observed lack of dimerization is nevertheless hard to rationalize on purely steric grounds so that a more detailed computational examination of the steric and electronic influence of *N*-alkyl groups on the dimerization of Wanzlick carbenes seemed desirable.

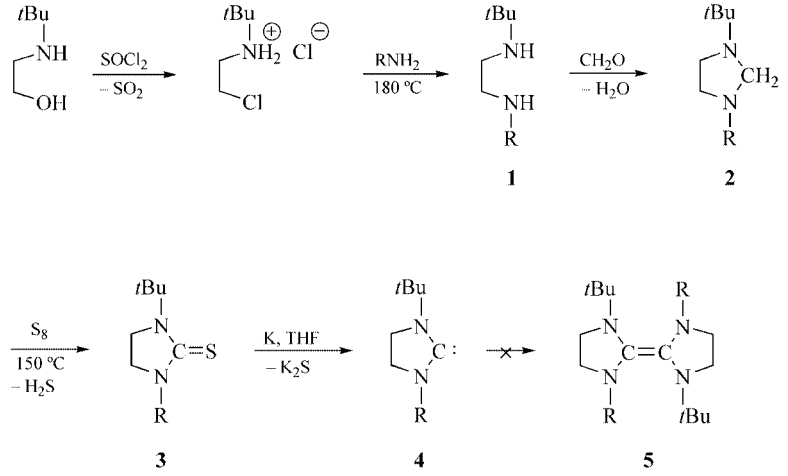
2. Results and Discussion

The synthesis of Wanzlick carbenes **4** bearing dissimilar substituents R, R′ on the nitrogen atoms is of obvious interest to understand the fine interplay of steric and electronic effects in the Wanzlick equilibrium but is also desirable to broaden the repertoire of N-heterocyclic carbenes used as steering ligands in catalysis. While the symmetrically substituted ethylenediamines RNH-CH_2CH_2-NHR′ (R = R′) are commercially available and are also readily accessible from 1,2-dibromoethane and primary amines,[15] ethylenediamines RNH-CH_2CH_2-NHR′ bearing dissimilar substituents are less well explored and accessible only through multistep reactions.[16] Except for R, R′ = Me,H the diamines are not commercially available.

Among the number of possible synthetic approaches tested in our group, only the reaction of primary amines with 2-chloroethylamines[17] proved to be the most useful (Scheme 3). Apart from being adaptable to a great variety of substituents R,R′ the reactions are readily scaled up and deliver acceptable yields and purities of the diamines.

The disadvantage of using the rather toxic 2-chloroethylamines is diminished by the fact that the stable and non-volatile hydrochloride salts can be used instead of the volatile free bases.

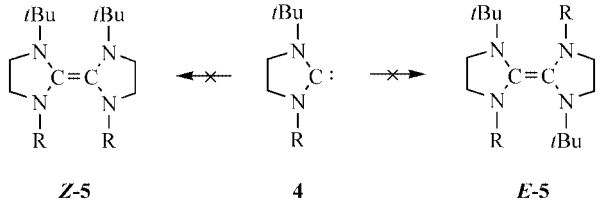
Reaction of 2-(*tert*-butylamino)ethanol with $SOCl_2$ followed by reaction with the respective primary amine thus gave the *N*-*tert*-butyl-*N*′-(alkyl)ethylenediamines (**1**). To obtain good yields of the respective ethylenediamines, the use of an excess of the primary amine (5 equiv. or more) as well as high reaction temperatures (180 °C) were found to be crucial. Lowering the amount of primary amine lead to the predominant formation of *N*,*N*′-di-*tert*-butylpiperazine through the competing self-condensation of the 2-chloroamine, while lower reaction temperatures were found to be inadequate to achieve complete conversion (detection of the free 2-chloroamine by GC-MS). The synthesis of the respective thioureas from the ethylenediamines turned out to be an additional obstacle. As we noted previously for



Scheme 3. Synthesis of 3-alkyl-1-*tert*-butylimidazolidin-2-ylidenes from 2-(*tert*-butylamino)ethanol.

ethylenediamines bearing *two* bulky *N*-alkyl substituents, the respective thioureas can only be obtained in poor yields via the textbook CS_2 route or its many variations.[18] The reaction of the ethylenediamines **1a**–**1c** with CS_2 gave likewise only trace amounts (GC-MS) of the thioureas **3a**–**3c**. The presence of only *one* sterically demanding substituent (*tert*-butyl) is obviously sufficient to block the CS_2 route.[18] To circumvent these problems, the thioureas **3a**–**3c** were obtained by oxidation of the respective formaldehyde aminals (imidazolidines) **2a**–**2c** with elemental sulfur, S_8, a two-step one-pot approach recently developed in our group to overcome the problems of the CS_2 method.[18] Reductive desulfurization of the thioureas with potassium (Kuhn method)[19] gave the respective carbenes in high yields (85–95%).

The carbenes were obtained as spectroscopically pure (^{1}H NMR, ^{13}C NMR) oils that are readily distilled without decomposition. In line with the previously examined Wanzlick and Arduengo carbenes[20] the carbenes **4a**–**4c** were found to be unreactive towards dry oxygen but readily hydrolyze in air.[21] Most remarkably, the carbenes did not show any sign of dimerization either as such or in C_6D_6 at room temperature or at 100 °C even after 12 months. The dimerization of the carbenes **4a**–**4b** can in principle lead to the formation of either the respective (*E*)- or the (*Z*)-enetetramines (Scheme 4).



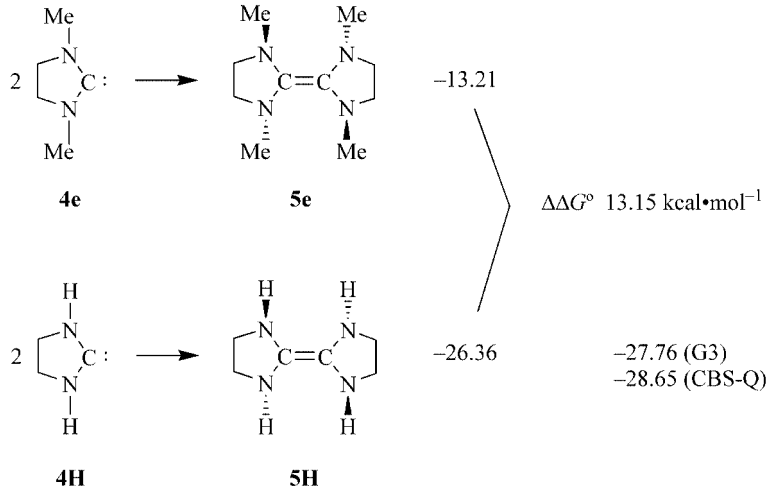
Scheme 4. Potential formation of enetetramines **5** from carbenes **4a**–**4c**.

While the (*Z*)-enetetramine is likely to suffer from significant steric front-strain due to the interaction of the *tert*-butyl groups and might be unstable for steric reasons, the argument cannot be applied to the (*E*)-isomer. The fact that neither of the two possible dimerization products could be observed is therefore hard to justify on purely steric grounds and points towards the importance of electronic effects in the stabilization of **4**. To clarify this issue, the steric and electronic influence of different *N*-alkyl substituents on the dimerization energies of Wanzlick carbenes was investigated through DFT calculations.

Computational Studies

DFT calculations of symmetrically substituted diamino carbenes have already generated significant insight into the nature of the dimerization reaction,[5] and have recently been reviewed by Alder et al.[1a] Of particular importance is the conclusion that calculated dimerization energies $\Delta G°$ are in good qualitative agreement with the experimentally observed dimerization behavior.[1a] The precise balance of steric and electronic effects on the stability of the carbenes towards dimerization on the other hand is less clear. DFT calculations at the B98/6-31G(d) level were carried out to establish if the dimerization of the carbenes **4a**–**4c** has a thermodynamic basis and to quantify steric and electronic effects of the respective *N*-alkyl substituents. The B98 functional was selected because it offers improved thermochemical accuracy over the B3LYP method without adding computational cost.[23] To obtain a benchmark for the accuracy of the DFT calculations, the dimerization energy of the hypothetical unsubstituted carbene **4H** was calculated with the high precision CBS-Q[26] and G3[27] methods. All calculations were carried out with the Gaussian03 suite of programs.[22] Local minima were confirmed through the absence of virtual frequencies. The geometry selected for the enetetramines **5** is that found experimentally for all solid-state structures of *N*-alkyl-substituted enetetramines.[28]

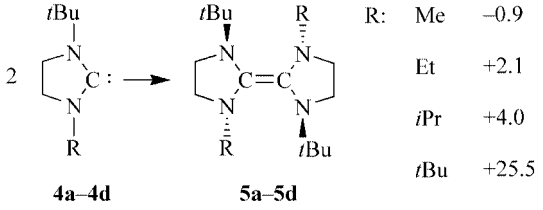
The surprisingly strong effect of *N*-alkyl substituents on the dimerization of Wanzlick carbenes is readily apparent from a comparison of the dimerization energies $\Delta G°$ of *N*,*N*′-dimethylimidazolidin-2-ylidene (**4e**) with that of the unsubstituted carbene **4H** (Scheme 5). The dimerization energies reveal a net stabilizing effect caused by the presence



Scheme 5. Influence of *N*-methyl substitution on the dimerization energy of imidazolidin-2-ylidene. Dimerization energies $\Delta G°$ (in kcal mol^{-1}) at the B98/6-31G(d), CBS-Q and G3 level.

of four methyl groups ca. 13 kcal mol^{-1}. The high accuracy of the B98/6-31G(d) approach can be inferred by the excellent agreement of the dimerization energy of **1H** (–26.4 kcal mol^{-1}) with the respective G3 (–27.8 kcal mol^{-1}) and CBS-Q data (–28.7 kcal mol^{-1}).

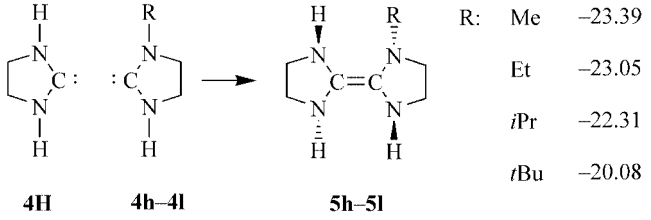
The lack of dimerization observed for the carbenes **4a**–**4c** can in principle have thermodynamic reasons ($\Delta G° > 0$) or kinetic reasons (high $\Delta G^{‡}$). The kinetic stabilization of Wanzlick carbenes bearing only *one* sterically demanding substituent may in fact be expected from the orbital symmetry required non-least-motion pathway.[24] The calculations do however reveal that the dimerization of the carbenes **4a**–**4d** is in fact thermodynamically unfavorable: dimerization is predicted to be thermodynamically unfavorable for **4b** and **4c** and close to thermoneutral for **4a** (Scheme 6). The stable carbene **4d** which was obtained earlier in our group[4] has been included for comparison as the sterically most crowded member of the series.



Scheme 6. Dimerization energies $\Delta G°$ (in kcal mol^{-1}) of imidazolidin-2-ylidenes **4a**–**4d** at the B98/6-31G(d) level of theory.

A comparison of the individual reaction energies is instructive. While the dimerization energies $\Delta G°$ show only small incremental changes from **4a**–**4c** a steep rise of ca. 20 kcal mol^{-1} occurs from **4c** to **4d**. While it is tempting to assign this discontinuous change in the dimerization energy to the onset of steric crowding, a rational, quantitative separation of steric and electronic factors is desirable.

To reveal the electronic effects of *N*-alkyl substituents on the dimerization reaction, the formation of the mono-alkyl enetetramines **5h**–**5l** from the respective carbenes were examined (Scheme 7). The presence of only *one* alkyl substituent in the enetetramines **5h**–**5l** eliminates the possibility of steric effects resulting from alkyl–alkyl repulsion. The variation in the dimerization energies will thus reflect the electronic effect of the *N*-alkyl substituent.



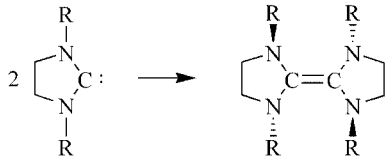
Scheme 7. Formation of mono-substituted enetetramines **5h**–**5l** from the respective carbenes **4H**, **4f**–**4i**. Energies $\Delta G°$ at the B98/6-31G(d) level.

Comparison of the dimerization energies in Scheme 7 with those obtained for the unsubstituted enetetramine **5H** (Scheme 5, $\Delta G° = –26.4$ kcal mol^{-1}) leads to electronic increments of the *N*-alkyl substituents as +2.97 kcal mol^{-1} (Me), +3.31 kcal mol^{-1} (Et), +4.04 kcal mol^{-1} (*i*Pr) and +6.28 kcal mol^{-1} (*t*Bu). While all four *N*-alkyl substituents electronically stabilize the carbene vs. the dimer, the effect increases along the series Me < Et < *i*Pr < *t*Bu. Although the electronic influence of the individual alkyl substituents may appear small, it must be born in mind that the overall effect is anything but negligible for the fully substituted enetetramines. The electronic effect of replacing four methyl substituents with four *tert*-butyl substituents amounts to 13 kcal mol^{-1}, a large caloric change considering that the dimerization reactions are close to equilibrium.

The electronic increments obtained above can now be used to separate electronic and steric effects of the *N*-alkyl substituents.

Addition of four electronic increments to the base value corresponding to the formation of unsubstituted enetetramine **5H** from the unsubstituted carbene **4H** (–26.36 kcal) will give the strain-free, electronic component ΔG_{el} of the dimer-

ization energies. Comparison of ΔG_{el} with the fully optimized values ΔG_{FC} leads to the quantitative estimate of strain energies ΔG_{st} according to $\Delta G_{FC} = \Delta G_{el} + \Delta G_{st}$. Scheme 8 shows the results for the symmetrically substituted carbenes.



4d–4h **5d–5g**

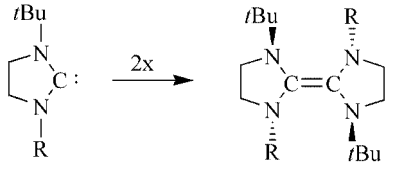
R	ΔG_{fc}	ΔG_{el}	ΔG_{st}
Me	–13.21	–14.48	+ 1.27
Et	–12.73	–13.12	+ 0.39
*i*Pr	–9.65	–10.20	+ 0.55
*t*Bu	+ 25.47	+1.24	+ 24.23

Scheme 8. Dimerization energies $\Delta G°$ (in kcal mol^{-1}) of symmetrically substituted Wanzlick carbenes at the B98/6-31G(d) level. Comparison of fully optimized energies (ΔG_{FC}) with those derived from the addition of electronic alkyl increments (ΔG_{el}). Steric contributions ΔG_{st} derived according to $\Delta G_{FC} = \Delta G_{el} + \Delta G_{st}$.

The dimerization energies obtained from full calculations (ΔG_{FC}) and those obtained through the increment approach (ΔG_{el}) are practically identical for R = Me, Et, and *i*Pr which rules out the presence of significant steric strain for these alkyl substituents. For R = *t*Bu, the pronounced difference between ΔG_{FC} (+25.47 kcal mol^{-1}) and ΔG_{el} (+1.24 kcal mol^{-1}) confirms a strong steric destabilization (+24.23 kcal mol^{-1}) of the enetetramine. The same approach can now be used to check if the enetetramines **5a**–**5c** are indeed free from steric strain as the large-small size match of the alkyl substituents (Scheme 2) seems to suggest.

The quantitative analysis (Scheme 9) contradicts this simplistic pictorial prediction by revealing strain energies ΔG_{st} ranging from +6.92 kcal mol^{-1} (*t*Bu,Me) to +10.25 kcal mol^{-1} (*t*Bu,*i*Pr). Steric strain is in fact a crucial factor for the thermodynamic stability of the carbenes **4a**–**4c** because dimerization would occur otherwise ($\Delta G_{el} < 0$).

The thermodynamic stability of Wanzlick carbenes **4** towards dimerization can in principle be ascribed to an inherent stabilization of the carbenes **4**, a destabilization of the enetetramines **5** or a combination of both. While dimerization energies, experimental or computational, cannot differentiate between these two possibilities, a comparison of other relevant data with the dimerization energies may nevertheless provide some insight. Table 1 compares the influence of the *N*-alkyl substituent on the ^{13}C NMR shifts and dimerization energies of Wanzlick carbenes **4**, with the calculated length of the carbon–carbon double bond and the associated valence vibrations in the dimers **5** arranged in order of decreasing carbene dimerization energies $\Delta G°$.



4 **5a–5c**

R	ΔG_{fc}	ΔG_{el}	ΔG_{st}
Me	–0.94	–7.86	+6.92
Et	+2.13	–7.18	+9.31
*i*Pr	+4.54	–5.72	+10.25

Scheme 9. Dimerization energies $\Delta G°$ (in kcal mol^{-1}) of non-symmetrically substituted Wanzlick carbenes at the B98/6-31G(d) level. Comparison of fully optimized energies (ΔG_{FC}) with those derived from the addition of electronic alkyl increments. Steric contributions ΔG_{st} derived according to $\Delta G_{FC} = \Delta G_{el} + \Delta G_{st}$.

Table 1. Dimerization of Wanzlick carbenes: comparison of ^{13}C NMR shifts and calculated dimerization energies $\Delta G°$ of carbenes **4** with calculated double bond lengths and valence vibrations of the corresponding (*E*)-enetetramines **5**.

R		δ N_2C [ppm]		ν(C=C) [cm^{-1}]	*d*(C=C) [pm]	$\Delta G°$ [kcal mol^{-1}]
Me,Me	**4e**	239.8	**5e**	1771	135.23	–13.21
Et,Et	**4f**	237.7	**5f**	1765	135.28	–12.73
*i*Pr,*i*Pr	**4g**	236.8	**5g**	1746	135.80	–9.65
*t*Bu,Me	**4a**	239.7	**5a**	1715	136.45	–0.94
*t*Bu,Et	**4b**	238.8	**5b**	1710	136.43	+2.13
*t*Bu,*i*Pr	**4c**	237.6	**5c**	1704	136.70	+4.54
*t*Bu,*t*Bu	**4d**	238.3	**5d**	1671	137.47	+25.47

The increase in double bond lengths and decrease in the C=C stretching frequencies of the enetetramines **5** correlates well with the dimerization energies of **4**. The ^{13}C NMR shifts (N_2C) of the carbenes **4** on the other hand show only a negligible variation regardless of whether the respective carbene dimerizes (**4e**, **4f**, **4g**) or not (**4a**–**4d**). It therefore seems likely, that the variation in dimerization energies is predominantly caused by a progressive destabilization of the enetetramines **5** rather than a stabilization of the carbenes **4**. The thermodynamic stability of Wanzlick carbenes **4** towards dimerization may thus reflect the stability of the dimers **5** rather than those of the carbenes **4**.[25]

A comparable analysis of how the respective activation energies of the dimerization are influenced by steric and electronic factors would be very desirable and will be the subject of future studies.

3. Conclusions

The stability of Wanzlick carbenes towards dimerization is the result of a complex interplay between electronic and steric effects of the nitrogen substituents. There is a smooth increase of stability along the series R = Me, Et, *i*Pr, *t*Bu,

the *tert*-butyl substituent occupies a special position by strongly stabilizing the carbenes electronically as well as sterically. A comparison of spectroscopic and computational data suggests that the dimerization energies of Wanzlick carbenes may in fact reflect variations in the stabilities of the enetetramines rather than that of the carbenes themselves.

4. Experimental Section

Melting points were recorded in sealed capillaries and are uncorrected. EI-MS spectra were obtained with a Varian CP-3800 GC/Saturn 2000 MS combination at an ionizing voltage of 70 eV and a 30 × 0.25 mm Varian CP 5860 low-bleed phenyl(dimethyl)siloxane column (5% phenyl). Temperature program: 4 min 50 °C; 10 min constant heating rate of 20 °C/min; 6 min 250 °C. NMR spectra were recorded with Bruker 400 MHz (^{1}H) and 500 MHz (^{13}C) NMR spectrometers at room temperature. All NMR spectra are referenced vs. tetramethylsilane (internal). 2-(*tert*-Butylamino)ethanol, isopropylamine, ethylamine, methylamine, sulfur, paraformaldehyde and potassium were obtained from Aldrich Inc., thionyl chloride from Johnson Mathey. All operations were carried out under inert gas (99.999% Argon) unless indicated otherwise. [2-(*tert*-butylamino)ethyl chloride] hydrochloride was obtained from 2-(*tert*-butylamino)ethanol and thionyl choride according to ref.[17]

Synthesis of *N*,*N*′-Disubstituted Ethylenediamines 1a–c: 2-(*tert*-Butylamino)ethyl chloride hydrochloride (50 g, 0.29 mol), the primary amine (1.45 mol) and water (250 mL) were sealed in a 1-L stainless-steel autoclave and heated to 180 °C for 48 h. After cooling the autoclave to room temperature, water (100 mL) and NaOH pellets (75 g) were added to the autoclave. The resulting biphasic crude solutions were extracted with Et_2O (3 × 100 mL). The combined organic phases were dried by addition of NaOH pellets and decanting from the freshly forming aqueous phase until the NaOH pellets remained undissolved. After removal of the solvent in vacuo, the pure *N*,*N*′-dialkylethylenediamines were obtained by fractional distillation over a 20 cm Vigreux column under normal pressure.

Synthesis of 3-Alkyl-1-*tert*-butylimidazolidines 2a–c: A mixture of the respective *N*,*N*′-disubstituted ethylenediamine (**1a**, **1b** or **1c**, 30 mmol), ether (15 mL), and paraformaldehyde (1.2 g, 40 mmol) was stirred at room temperature for 24 h. The resulting turbid solutions were stirred with $MgSO_4$ (ca. 1 g, 24 h) and the imidazolidines isolated by filtration and subsequent evaporation of the solvent in vacuo. Yield quantitative.

Synthesis of 3-Alkyl-1-*tert*-butylimidazolidine-2-thiones 3a–b: Elemental sulfur S_8 (2.21 g, 8.64 mmol), the respective imidazolidine (34.5 mmol) and ether (15 mL) were sealed in a stainless steel autoclave and heated to 160 °C for 12 h. The cold reaction mixtures were extracted with methanol (3 × 10 mL), filtered, and the thioureas precipitated by dropwise addition of water (ca. 30 mL) to the methanol solution. Crystallization was typically completed after standing at room temperature for 24 h. A second crop of the thioureas could be obtained by cooling the mother liquor to –20 °C. After vacuum drying for 24 h, both fractions were adequate for the subsequent reduction to the carbenes.

Synthesis of 3-Alkyl-1-*tert*-butylimidazolidin-2-ylidenes 4a–c: A solution of the respective 3-alkyl-1-*tert*-butylimidazolidine-2-thione (75 mmol) in THF (200 mL) was boiled with potassium (8.80 g, 226 mmol) for 2 h. The slightly yellowish solutions were filtered through a medium-porosity glass frit and the carbenes isolated by removal of the solvent in vacuo.

***N*-*tert*-Butyl-*N*′-methyl-1,2-diaminoethane (1a):** Colorless oil, b.p. 151 °C, 12.9 g (34%). ^{1}H NMR ($CDCl_3$): δ = 1.09 [s, 9 H, C(CH_3)$_3$], 2.43 [s, 3 H, CH_3], 2.68 [s, 2 H + 2 H, identical shift, NHCH_2] ppm. ^{13}C NMR ($CDCl_3$): δ = 29.1 [C(*C*H$_3$)$_3$], 36.4 [N*C*H$_3$], 41.8 [*t*BuN*C*H$_2$], 50.1 [*C*(CH$_3$)$_3$], 52.6 [MeN*C*H$_2$] ppm. GC-MS: t_r = 5.2 min. *m*/*z* (rel. int.%) = 131 (100), 115 (23), 100 (8), 86 (55), 72 (23), 58 (74), 44 (76).

***N*-*tert*-Butyl-*N*′-ethyl-1,2-diaminoethane (1b):** Colorless oil, b.p. 165 °C, 27 g (64%), ^{1}H NMR ($CDCl_3$): δ = 1.10 [s, 9 H, C(CH_3)$_3$], 1.11 [t, ^3J(H,H) = 7 Hz, 3 H, CH$_2$CH_3], 2.65 [q, 2 H, CH_2CH$_3$], 2.71 [m, 4 H, NHCH_2 CH_2] ppm. ^{13}C NMR ($CDCl_3$): δ = 15.3 [CH$_2$**C**H$_3$], 29.0 [C(*C*H$_3$)$_3$], 42.1 [*t*BuN*C*H$_2$], 44.1 [EtN*C*H$_2$], 50.2 [*C*(CH$_3$)$_3$], 50.3 [*C*H$_2$CH$_3$] ppm. GC-MS: t_r = 6.1 min, *m*/*z* (rel. int.%) = 145 (100), 129 (18), 101 (10), 86 (50), 72 (85), 58 (92).

***N*-*tert*-Butyl-*N*′-isopropyl-1,2-diaminoethane (1c):** Colorless oil, b.p. 181 °C, 32 g (70%). ^{1}H NMR ($CDCl_3$): δ = 1.06 [d, ^3J(H,H) = 6 Hz, 6 H, CH(CH_3)$_2$], 1.10 [s, 9 H, C(CH_3)$_3$], 2.68 [m, 4 H, NCH_2], 2.78 [sept, ^3J(H,H) = 6, Hz, 1 H, C*H*(CH$_3$)$_2$] ppm. ^{13}C NMR ($CDCl_3$): δ = 23.1 [CH(*C*H$_3$)$_2$], 29.2 [C(*C*H$_3$)$_3$], 42.6 [*t*BuN*C*H$_2$], 48.2 [*i*PrN*C*H$_2$], 48.8 [*C*H(CH$_3$)$_2$], 50.2 [*C*(CH$_3$)$_3$] ppm. GC-MS: t_r = 7.4 min, *m*/*z* (rel. int.%) = 159 (28), 143 (5), 100 (18), 86 (75), 72 (100), 57 (32).

1-*tert*-Butyl-3-methylimidazolidine (2a): Colorless oil, no CAS. ^{1}H NMR ($CDCl_3$): δ = 1.10 [s, 9 H, C(CH_3)$_3$], 2.37 [s, 3 H, NCH_3], 2.76 [m, 2 H, MeNCH_2], 2.92 [m, 2 H, *t*BuNCH_2], 3.50 [NCH_2N] ppm. ^{13}C NMR ($CDCl_3$): δ = 26.0 [C(*C*H$_3$)$_3$], 39.9 [*t*BuN*C*H$_2$], 45.8 [MeN*C*H$_2$], 52.8 [*C*(CH$_3$)$_3$], 55.2 [*C*H$_3$], 71.6 [N*C*H$_2$N] ppm. GC-MS: t_r = 6.19 min, *m*/*z* (rel. int.%) = 141 (100), 127 (48), 112 (47), 85 (73), 57 (18), 42 (37).

1-*tert*-Butyl-3-ethylimidazolidine (2b): Colorless oil, no CAS. ^{1}H NMR ($CDCl_3$): δ = 1.09 [s, 9 H, C(CH_3)$_3$], 1.10 [t, ^3J = 7 Hz, 3 H, CH$_2$-CH_3], 2.52 [q, ^3J = 7 Hz, 2 H, CH_2CH$_3$], 2.76 [m, 2 H, CH_2CH$_3$], 2.88 [m, 2 H, CH_2CH_2], 3.50 [s, 2 H, NCH_2N] ppm. ^{13}C NMR ($CDCl_3$): δ = 13.9 [CH$_2$*C*H$_3$], 26.0 [C(*C*H$_3$)$_3$], 45.0 [*t*BuN*C*H$_2$], 49.0 [EtN*C*H$_2$], 52.4 [*C*(CH$_3$)$_3$], 52.8 [*C*H$_2$-CH$_3$], 69.6 [N*C*H$_2$N] ppm. GC-MS: t_r = 7.0 min, *m*/*z* (rel. int.%) = 155 (100), 141 (25), 126 (13), 100 (5), 99 (52), 84 (43), 42 (25).

1-*tert*-Butyl-3-isopropylimidazolidine (2c): Colorless oil, no CAS. ^{1}H NMR ($CDCl_3$): δ = 1.08 [d, ^3J(H,H) = 7.0 Hz, 6 H, CH-(CH_3)$_2$], 1.09 [s, 9 H, C(CH_3)$_3$], 2.41 [sept, ^3J(H,H) = 7.0 Hz, 1 H, C*H*(CH$_3$)$_2$], 2.84 [m, 4 H, NCH_2CH_2], 3.54 [NCH_2N] ppm. ^{13}C NMR ($CDCl_3$): δ = 21.9 [CH(*C*H$_3$)$_2$], 26.0 [C(*C*H$_3$)$_3$], 45.2 [*t*BuN*C*H$_2$], 51.1 [*i*PrN*C*H$_2$], 52.2 [*C*H(CH$_3$)$_2$], 54.1 [*C*(CH$_3$)$_3$], 68.6 [N$_2$*C*H$_2$] ppm. GC-MS: t_r = 8.4 min, *m*/*z* (rel. int.%) = 169 (100), 155 (22), 140 (6), 113 (81), 98 (8), 84 (25), 71 (26), 55 (13).

1-*tert*-Butyl-3-methylimidazolidine-2-thione (3a): Colorless crystals, m.p. 96.5–97 °C (hexane). Yield 2.37 g, (40%). No CAS. ^{1}H NMR ($CDCl_3$): δ = 1.60 [s, 9 H, C(CH_3)$_3$], 3.09 [s, 3 H, N*C*H$_3$], 3.43 [m, 4 H, NCH_2], 3.60 [m, 4 H, NCH_2CH_2] ppm. ^{13}C NMR ($CDCl_3$): δ = 27.9 [C(*C*H$_3$)$_3$], 35.0 [N-*C*H$_3$], 44.7 [*t*BuN*C*H$_2$], 48.2 [MeN*C*H$_2$], 56.4 [*C*(CH$_3$)$_3$], 183.1 [*C*S] ppm. GC-MS: t_r = 10.7 min, *m*/*z* (rel. int.%) = 172 (100), 157 (20), 116 (55), 83 (12), 44 (30).

1-*tert*-Butyl-3-ethylimidazolidine-2-thione (3b): Colorless crystals, m.p. 57.5–58 °C (hexane). Yield 0.96 g (15%) No CAS. ^{1}H NMR ($CDCl_3$): δ = 1.15 [t, ^3J(H,H) = 7 Hz, 3 H, CH$_2$CH_3], 1.61 [s, 9 H, C(CH_3)$_3$], 3.38–3.43 [m, 2 H, NCH_2], 3.43 [m, 2 H, NCH_2], 3.57 [m, 2 H, NCH_2], 3.66 [q, ^3J(H,H) = 7 Hz, CH_2CH$_3$] ppm. ^{13}C NMR ($CDCl_3$): δ = 11.8 [CH$_2$*C*H$_3$], 28.0 [C(*C*H$_3$)$_3$], 42.0 [*t*BuN*C*H$_2$], 44.8 [N*C*H$_2$], 45.0 [N*C*H$_2$], 56.4 [*C*(CH$_3$)$_3$], 182.3 [*C*S]

ppm. GC-MS: t_r = 11.0 min, *m*/*z* (rel. int.%) = 186 (100), 171 (13), 157 (5), 129 (45), 115 (43), 56 (13), 42 (16).

1-*tert*-Butyl-3-isopropylimidazolidine-2-thione (3c): Colorless crystals, m.p. 102.5–103.5 °C (hexane). Yield 2.84 g (41%) No CAS. ^{1}H NMR ($CDCl_3$): δ = 1.14 [d, ^3J(H,H) = 7 Hz, 6 H, CH(CH_3)$_2$], 1.61 [s, 9 H, C(CH_3)$_3$], 3.33 [m 2 H, NCH_2], 3.56 [m, 2 H, NCH_2], 4.98 [sept, ^3J(H,H) = 6.8 Hz, 1 H, CH(CH$_3$)$_2$] ppm. ^{13}C NMR ($CDCl_3$): δ = 20.0 [CH(*C*H$_3$)$_2$], 28.1 [C(*C*H$_3$)$_3$], 40.0 [*t*BuN*C*H$_2$], 44.9 [*i*PrN*C*H$_2$], 46.3 [*C*H(CH$_3$)$_2$], 56.4 [*C*(CH$_3$)$_3$], 181.8 [*C*S] ppm. GC-MS: t_r = 11.8 min, *m*/*z* (rel. int.%) = 200 (71), 185 (78), 157 (5), 143 (43), 129 (100), 111 (8), 102 (7), 84 (10), 70 (12).

1-*tert*-Butyl-3-methylimidazolidin-2-ylidene (4a): 8.7 g (83%). Colorless oil, b.p. 65 °C/0.1 Torr ^{1}H NMR (C_6D_6): δ = 1.35 [s, 9 H, C(CH_3)$_3$], 2.80 [m, 2 H, NCH_2], 2.98 [m, 2 H, NCH_2], 3.01 [s, 3 H, CH_3]. ^{13}C (C_6D_6): δ = 30.0, [C(*C*H$_3$)$_3$], 37.9 [N*C*H$_3$], 45.3 [*t*BuN*C*H$_2$], 50.8 [CH$_3$N*C*H$_2$], 53.7 [*C*(CH$_3$)$_3$], 239.7 [N$_2$*C*:] ppm.

1-*tert*-Butyl-3-ethylimidazolidin-2-ylidene (4b): 10.5 g (91%) Colorless oil, b.p. 67 °C/0.1 Torr. ^{1}H NMR (C_6D_6): δ = 1.07 [t, ^3J = 7 Hz, 3 H, CH$_2$-CH_3], 1.35 [s, 9 H, C(CH_3)$_3$], 2.90 [m, 2 H, NCH_2], 3.03 [m, 2 H, NCH_2], 3.46 [q, ^3J = 7 Hz, 2 H, CH_2CH$_3$]. ^{13}C (C_6D_6): δ = 14.8 [CH$_2$*C*H$_3$], 30.1 [C(*C*H$_3$)$_3$], 44.9 [*t*BuN*C*H$_2$], 45.7 [EtN*C*H$_2$], 48.1 [*C*H$_2$CH$_3$], 53.9 [*C*(CH$_3$)$_3$], 238.8 [N$_2$*C*:] ppm.

1-*tert*-Butyl-3-isopropylimidazolidin-2-ylidene (4c): 11.7 g (93%). Colorless oil, b.p. 70 °C/0.1 Torr. ^{1}H NMR (C_6D_6): δ = 1.16, [d, 6.7 Hz, 6 H, CH(CH_3)$_2$], 1.36 [s, 9 H, C(CH_3)$_3$], 2.93 [m, 2 H, NCH_2], 2.99 [m, 2 H, NCH_2], 4.00 [sept, 6.7 Hz, 1 H, CH(CH$_3$)$_2$]. ^{13}C (C_6D_6): δ = 22.1 [CH(*C*H$_3$)$_2$], 29.9 [C(*C*H$_3$)$_3$], 44.2 [*t*BuN*C*H$_2$], 44.9 [*i*PrN*C*H$_2$], 50.8 [*C*H(CH$_3$)$_2$], 53.8 [*C*(CH$_3$)$_3$], 237.6 [N$_2$*C*:] ppm.

Supporting Information (see also the footnote on the first page of this article): A table listing the energies, point groups and lowest frequencies of the calculated diamino carbenes **4** and enetetramines **5**.

Acknowledgments

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