

Communications to the Editor

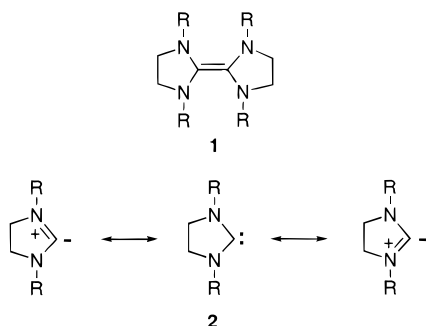
Thermodynamics of a Diaminocarbene–Tetraaminoethylene Equilibrium

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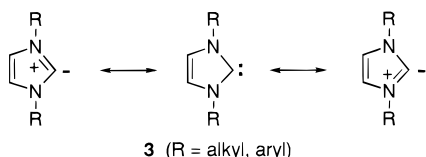
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The first tetraaminoethylene was prepared by Pruett in 1950,¹ but the systematic study of molecules of this type began a decade later when Wanzlick reported the synthesis of **1** (R = Ph).^{2,3}



Primarily on the basis of its chemical reactions, he postulated in a series of papers that the “Wanzlick dimer” dissociates readily into diaminocarbene “halves” (**2**, R = Ph).⁴ Crossover experiments performed in the mid-1960s demonstrated that tetraaminoethylenes of the type **1** (R = aryl or alkyl) do not dissociate into diaminocarbenes even at quite high temperatures.^{5–7} Beginning in 1991, however, Arduengo synthesized a remarkable series of diaminocarbenes of the type **3** (and ring-substituted derivatives



thereof), carbenes so stable that they show no tendency to dimerize.^{3,8,9} Carbenes of the type **2** and acyclic analogues thereof

(1) Pruett, R. L.; Barr, J. T.; Rapp, K. E.; Bahner, C. T.; Gibson, J. D.; Lafferty, R. H., Jr. *J. Am. Chem. Soc.* **1950**, *72*, 3646.

(2) Wanzlick, H.-W.; Schikora, E. *Angew. Chem.* **1960**, *72*, 494.

(3) Arduengo, A. J., III; Krafczyk, R. *Chem. Ztg.* **1998**, *32*, 6.

(4) For reviews of this early work, see: Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 754. Wiberg, N. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 766. Lemal, D. M. In *The Chemistry of the Amino Group*; Patai, S., Ed.; Interscience: New York, 1968; p 701.

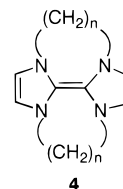
(5) Lemal, D. M.; Lovald, R. A.; Kawano, K. I. *J. Am. Chem. Soc.* **1964**, *86*, 2518.

(6) Winberg, H. E.; Carnahan, J. E.; Coffman, D. D. *J. Am. Chem. Soc.* **1965**, *87*, 2055.

(7) In a very recent paper Denk has challenged the early findings, demonstrating that crossover can indeed occur between the same pairs of tetraaminoethylenes studied independently by the groups of Lemal and Winberg (Denk, M. K.; Hatano, K.; Ma, M. *Tetrahedron Lett.* **1999**, *40*, 2057). His conclusion that the new work “supports the existence of the Wanzlick equilibrium” is flawed, however. Finding the absence of crossover is compelling evidence against unimolecular dissociation of a tetraaminoethylene, as small amounts of impurities could not inhibit such a process. On the other hand, the observation of crossover is subject to a variety of interpretations including catalyzed dissociation, e.g. via the mechanism presented in ref 5. Regarding catalysis in the present work, see ref 23.

have been prepared recently and shown to dimerize irreversibly,^{10,11} as would be expected from the 1960’s crossover experiments.¹² The relative energy of tetraaminoethylenes and their diaminocarbene “halves” is a matter of much current interest, all the more so because of the striking variability of this relationship.¹³

Clearly, quantitative information about the strength of the carbon–carbon double bonds in tetraaminoethylenes is badly needed. Taton and Chen approached this problem cleverly by synthesizing the doubly bridged molecules **4** ($n = 3, 4$).¹⁴ They found that while **4** ($n = 3$) fails to dissociate even at 100 °C, **4**



($n = 4$) exists predominantly as written at –33 °C but as a pair of carbenes at room temperature. From these results Chen arrived at a “reasonable estimate” of the bond dissociation energy for unbridged tetraaminoethylenes of the type **3**, viz. $\Delta H = 4 \pm 3$ kcal/mol. The failure to detect them is thus a consequence of the strongly positive entropy of dissociation.

We wished to find an unbridged tetraaminoethylene–diaminocarbene system in which both components are present in measurable amounts at equilibrium.¹⁵ The contrast in stability toward dimerization between **2** and **3**, with its 6π electrons in the five-membered ring, has been attributed to aromaticity in the

(8) (a) Arduengo, A. J., III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361. (b) Arduengo, A. J., III; Dias, H. V. R.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1992**, *114*, 5530. (c) Arduengo, A. J., III.; Davidson, F.; Dias, H. V. R.; Goerlich, J. R.; Khasnis, D.; Marshall, W. J.; Prakasha, T. K. *J. Am. Chem. Soc.* **1997**, *119*, 12742. (d) Arduengo, A. J., III; Goerlich, J. R.; Krafczyk, R.; Marshall, W. J. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1963.

(9) See also: Herrmann, W. A.; Köcher, C.; Goossen, L. J.; Artus, G. R. *J. Chem. Eur. J.* **1996**, *2*, 1627. Kuhn, N.; Kratz, T. *Synthesis* **1993**, 561.

(10) Alder, R. W.; Blake, M. E. *J. Chem. Soc., Chem. Commun.* **1997**, 1513. Alder, R. W.; Allen, P. R.; Murray, M.; Orpen, A. G. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1121.

(11) Denk, M.; Thadani, A.; Hatano, K.; Lough, A. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2607.

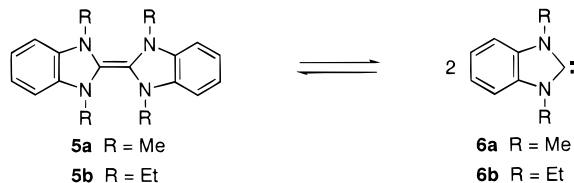
(12) Because of its very bulky substituents, **2** (R = mesityl) does not dimerize. Arduengo, A. J., III; Goerlich, J. R.; Marshall, W. J. *J. Am. Chem. Soc.* **1995**, *117*, 11027.

(13) For recent reviews on tetraaminoethylenes and diaminocarbenes, see: Warkentin, J. In *Advances in Carbene Chemistry*; Brinker, U. H., Ed.; Jai Press: London, 1998; Vol. 2, p 245. Herrmann, W. A.; Köcher, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2162. Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 725.

(14) Taton, T. A.; Chen, P. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1011. Chen, P. In *Advances in Carbene Chemistry*; Brinker, U. H., Ed.; Jai Press: London, 1998; Vol. 2, p 45. Compound **4** ($n = 3$) was independently synthesized in Thummel’s laboratory. Shi, Z.; Goulle, V.; Thummel, R. P. *Tetrahedron Lett.* **1996**, *37*, 2357.

(15) Recently, both a thiazol-2-ylidene and its dimer have been isolated and characterized. Arduengo, A. J., III; Goerlich, J. R.; Marshall, W. J. *Liebig’s Ann./Recl.* **1997**, 365.

latter.¹⁶ We surmised that bis(benzimidazol-2-ylidene) (**5a**)¹⁷ would dissociate much more readily than **1** (R = Me) because the fused benzene ring would confer a measure of aromaticity on the resulting carbene **6a**, albeit significantly less than that enjoyed by **3** (R = Me).^{18,19}



When tetraaminoethylene **5a** was heated in diglyme-*d*₁₄ under argon, a new set of ¹H NMR signals slowly grew out of the baseline but disappeared after the sample was cooled to room temperature. At 110 °C the resonances for **5a** appeared at δ 6.64 and 6.49 (AA'BB', 8H, aryl) and 2.91 ppm (s, 12H, CH₃); the new signals, mirroring those of the dimer but shifted downfield, were found at δ 7.27, 7.12, and 3.82 ppm. To confirm that the new signals represented diaminocarbene **6a**, it was important to detect the highly characteristic, very low field ¹³C resonance of the carbene carbon.⁸ A sample of the dimer was equilibrated briefly at 140 °C, then immediately quenched in liquid nitrogen to freeze the monomer–dimer equilibrium. Its proton-decoupled ¹³C NMR spectrum measured at –50 °C and 125 MHz revealed a signal at δ 225.3 ppm that left no doubt about the identity of the new species. The location of this carbene carbon resonance between those of typical imidazol-2-ylidenes and those of imidazol-2-ylidenes²⁰ is to be expected for a benzimidazol-2-ylidene.

Tetraaminoethylene **5b** was prepared analogously to the methyl compound,¹⁷ viz. by deprotonation of *N,N'*-diethylbenzimidazolium iodide²¹ with sodium hydride in THF, and purified by multiple recrystallizations from hexanes/toluene under argon. The ¹H NMR spectrum of **5b** in diglyme-*d*₁₄ at 110 °C comprised signals at δ 6.63, 6.53 (AA'BB', 8H, aryl); 3.44 (q, *J* = 7 Hz, 8H, CH₂); and 0.99 ppm (t, *J* = 7 Hz, 12H, CH₃). At room temperature these were the only significant resonances, but as the temperature was raised a new set became prominent. At 110 °C they appeared at δ 7.29, 7.10 (AA'BB', 4H, aryl); 4.25 (q, *J* = 7 Hz, 4H, CH₂); and 1.46 ppm (t, *J* = 7 Hz, 6H, CH₃). A sample in diglyme-*d*₁₄ was equilibrated for 20 min at 115 °C, then

(16) The degree of aromaticity and of ylidic character in carbenes of type **3** remains a matter of controversy. Boehme, C.; Frenking, G. *J. Am. Chem. Soc.* **1996**, *118*, 2039. Heinemann, C.; Müller, T.; Apeloig, Y.; Schwarz, H. *J. Am. Chem. Soc.* **1996**, *118*, 2023. Sauer, R. R. *Tetrahedron Lett.* **1996**, *37*, 149. Olsson, M. H. M.; Boroski, P. *Theor. Chim. Acta* **1996**, *93*, 17. Arduengo, A. J., III; Dias, H. V. R.; Dixon, D. A.; Harlow, R.; Klooster, W. T.; Koetzle, T. F. *J. Am. Chem. Soc.* **1994**, *116*, 6812.

(17) Cetinkaya, E.; Hitchcock, P. B.; Küçükbay, H.; Lappert, M. F.; Al-Juaid, S. *J. Organomet. Chem.* **1994**, *481*, 89.

(18) Other bis(benzimidazol-2-ylidenes) have been synthesized as well, but none has been observed to dissociate. (a) Shi, Z.; Thummel, R. P. *Tetrahedron Lett.* **1994**, *35*, 33. Shi, Z.; Thummel, R. P. *Tetrahedron Lett.* **1995**, *36*, 2741. Shi, Z.; Thummel, R. P. *J. Org. Chem.* **1995**, *60*, 5935. (b) Hünig, S.; Scheutzow, D.; Schlaf, H.; Quast, H. *Justus Liebig's Ann. Chem.* **1972**, *765*, 110. Hünig, S.; Scheutzow, D.; Schlaf, H. *Justus Liebig's Ann. Chem.* **1972**, *765*, 126. (c) Bourson, J. *Bull. Soc. Chim. Fr.* **1971**, 3541.

(19) A recent report describes the first isolation of a benzimidazol-2-ylidene, the sterically hindered *N,N'*-bis(2,2-dimethylpropyl) derivative. Hahn, F. E.; Wittenbecher, L.; Boese, R.; Bläser, D. *Chem. Eur. J.* **1999**, *5*, 1931.

(20) For example, the carbene carbon in 1,3-dimethylimidazol-2-ylidene resonates at δ 215.2 in THF-*d*₈ (ref 8b); that in 1,3-di-*tert*-butylimidazol-2-ylidene appears at δ 238.3 in C₆D₆ (ref 11).

(21) Nakazawa, Y.; Sawahara, M.; Hinata, M. French patent 1,534,386 (1968); *Chem. Abstr.* **1969**, *71*, 126008t.

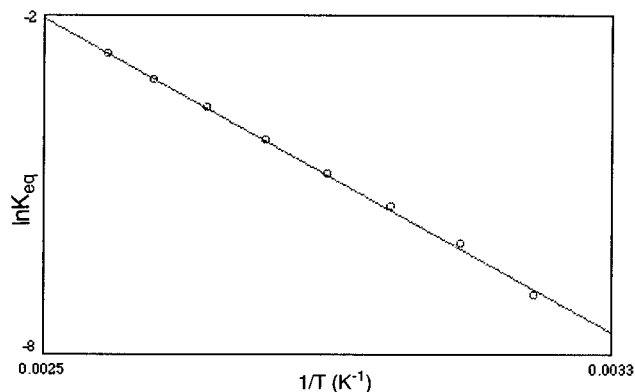


Figure 1. van't Hoff plot for the dissociation equilibrium of bis(benzimidazol-2-ylidene) (**5**, R = Et).

quenched in liquid nitrogen. Its proton-decoupled ¹³C NMR spectrum, measured at –50 °C, showed signals at δ 142.3, 121.2, 117.2, 110.0 (sp² C); 40.1 (CH₂); and 10.6 ppm (CH₃) for the dimer, and at δ 224.9 (C); 135.4, 122.0, 110.9 (aryl C); 43.4 (CH₂); and 16.6 ppm (CH₃) for the diaminocarbene **6b**.

Since dissociation of **5b** is significantly greater than that of its methyl analogue at a given temperature, the ethyl compound was chosen for a determination of the dissociation equilibrium constant as a function of temperature. Samples of this dimer in NMR tubes containing diglyme-*d*₁₄ (~0.1 M) with a known concentration of cyclodecane as an integration standard were prepared in a glovebox and sealed with a flame under dry nitrogen. Each was equilibrated at various temperatures and the ¹H NMR spectra were measured. Integration of the cyclodecane singlet and the methyl triplets of **5b** and **6b** determined the concentration of dimer and carbene at each temperature.²² After several runs were made to establish optimal measurement conditions, equilibrium constants were determined at ~10 °C intervals from 40 to 110 °C. The temperature range was limited at the low end by the small degree of dissociation and at the upper end by sample decomposition.²³ van't Hoff plots (see Figure 1 for one) constructed from the set of equilibrium constants obtained in each of two closely agreeing runs yielded these average values for the thermodynamic parameters for dissociation: Δ*H*^o = 13.7 ± 0.6 kcal/mol and Δ*S*^o = 30.4 ± 1.7 cal mol⁻¹ K⁻¹.

At 25 °C the free energy difference between **5b** and its “halves” is only about 5 kcal/mol. The enthalpy of dissociation of this tetraaminoethylene, i.e., the bond dissociation energy of an *N*-tetraalkylated bis(benzimidazol-2-ylidene), is ca. 10 kcal/mol above that estimated by Chen for the bond dissociation energy of the unobserved dimers of type **3** carbenes (R = alkyl). This energy difference is understandable as a consequence of benzenellation.

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(22) Concentrations were corrected for the volume expansion of the solvent with temperature.

(23) These measurements were feasible because of adventitious catalysis of the equilibrium, presumably by a trace electrophile. When potassium hydride was added to test for catalysis, establishment of equilibrium became impractically slow. This reagent has been used to prevent acid-catalyzed dissociation of a bis(thiazol-2-ylidene); see ref 15.