Crystal and Electronic Structure of Stable Nitrenium Ions. A Comparison with Structurally Related Carbenes

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Received October 30, 1995. Revised Manuscript Received March 20, 1996[⊗]

Abstract: The isolation of bis-amino-substituted carbenes of the Arduengo (**3a**) and Wanzlick type **4a** has prompted us to look for stable nitrenium ions of the related structural type **3d**$^+$ and **4d**$^+$. Thus **5**$^+$**I**$^-$ (**6**$^+$**I**$^-$) and **18**$^+$**ClO$_4$**$^-$ were isolated and structurally characterized by X-ray crystallography. Theoretical studies give insight into the different (electronic) structures and stabilities of **3a,d**$^+$, **4a,d**$^+$, and of related compounds.

Introduction

Nitrenium ions **1**$^+$ (or more correctly: ions pairs of nitrenium ions **1**$^+$**X**$^-$, Chart 1), which are isoelectronic with carbenes R$_2$C|, are discussed as reactive intermediates in many reactions.[1−3]

Some nitrenium ions **1**$^+$ have been studied by mass spectroscopy.[4] Nitrenium ions **1**$^+$ with R^1 = aryl, R^2 = H, or C(O)-CH$_3$, or SO$_3$$^-$, are considered to be the ultimate carcinogens in the carcinogenesis initiated by aromatic amines.[5−7] This is suggested from the structures of the *in vivo* and *in vitro* formed adducts with the guanine residues of the DNA.[8−10] Recent studies by laser flash photolysis allowed for the first time to measure the UV spectra of such short-lived (80−200 ns) species.[11−14] A systematic study of the crystal as well as electronic structure of stable nitrenium ions, however, has not been performed to date. Since the related phosphenium ions are generally stable if substituted with two amino groups (**2**$^+$**X**$^-$, Chart 1),[15−22] and since the imidazol-2-ylidenes **3a**, Chart 1, as discovered by A. J. Arduengo III et al.,[23−27] allowed for the first time the isolation and structural characterization of stable crystalline carbenes—the stable silylenes **3b**[28] and germylenes[29] **3c** (Chart 1) have a similar structure—, nitrenium ions of that type, i.e., **3d**$^+$**X**$^-$, Chart 1, should also be stable. In the following we report on the X-ray crystal structures of **5**$^+$**I**$^-$ and **6**$^+$**I**$^-$, Chart 2, and **18**$^+$**ClO$_4$**$^-$, Chart 4. Furthermore, by means of theoretical calculations the importance of stabilization by delocalization in the model nitrenium ions **3d**$^+$ and **4d**$^+$, R^1, R^3−R^5 = H, Chart 1, is elaborated and compared with the situation in the carbenes **3a** and **4a**, R^1, R^3−R^5 = H, Chart 1. Carbenes of the structural type **4a** have been extensively studied by Wanzlick et al.[30] although these authors have been unable to isolate a crystalline species. Finally, the question about the nitrenium ion character of compounds of the type **3d**$^+$**X**$^-$ and **4d**$^+$**X**$^-$ is addressed.

Results and Discussion

The Structures of 5$^+$I$^-$ and 6$^+$I$^-$ in the Crystal. Benzotriazoles and 1,2,3-triazoles, but also 1,2,3-triazolines and triazines, all containing the structural element **7**, react with

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[⊗] Abstract published in *Advance ACS Abstracts,* May 1, 1996.

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S0002-7863(95)03627-4 CCC: $12.00

Chart 1

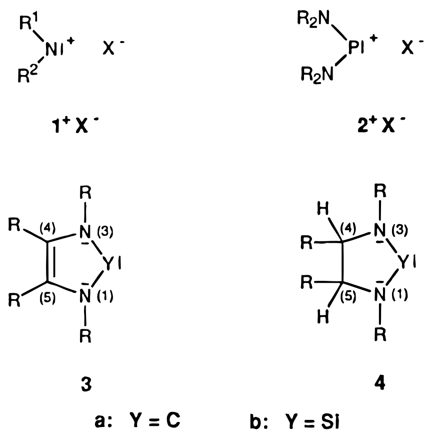
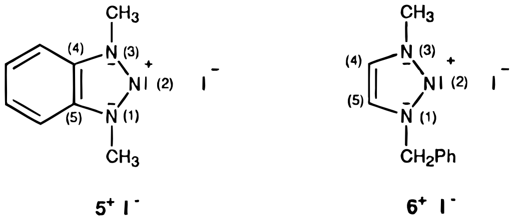
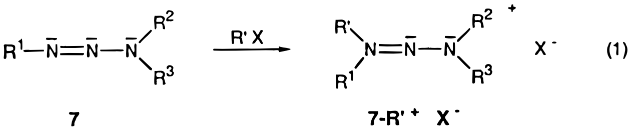


Chart 2

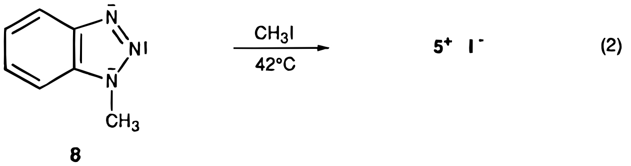


alkylating reagents R′X to give compounds of the general type $\mathbf{7\text{-}R'^+X^-}$ (eq 1).[31−34]

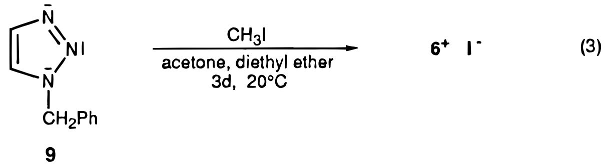


(1)

This gives a first hint on the stability of cations of this kind. When we reacted 1-methyl-benzotriazole **8** (eq 2) and 3-benzyl-1,2,3-triazole **9** (eq 3), respectively, with methyl iodide, $\mathbf{5^+I^-}$ and $\mathbf{6^+I^-}$, respectively, were isolated in 90 (70)% yield.



(2)



(3)

Figure 1 shows the structure of $\mathbf{5^+I^-}$ in the crystal, while the structure of $\mathbf{6^+I^-}$ is given in Figure 2.[35]

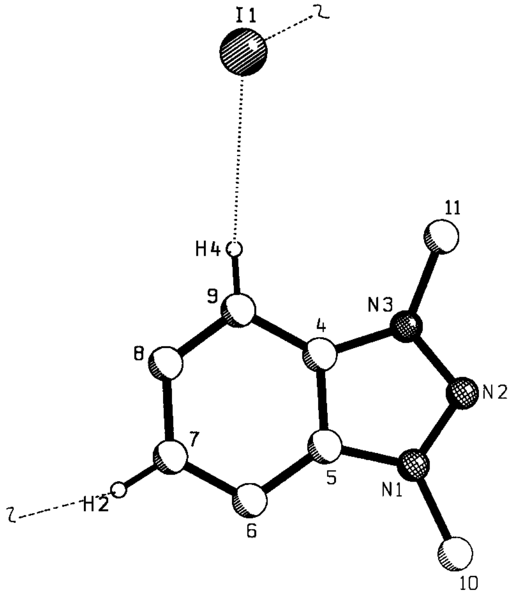


Figure 1. Structure of $\mathbf{5^+I^-}$ in the crystal. Selected bond distances (pm) and bond angles (deg): N(1)−N(2) 130.2(6), N(2)−N(3) 132.0(5), N(3)−C(4) 136.8(5), C(4)−C(5) 138.5(6), C(5)−N(1) 136.4(6); N(2)−N(1)−C(5) 112.1(4), N(1)−N(2)−N(3) 106.3(3), N(2)−N(3)−C(4) 11.4(3), N(3)−C(4)−C(5) 105.0(4), C(4)−C(5)−N(1) 105.2(4).

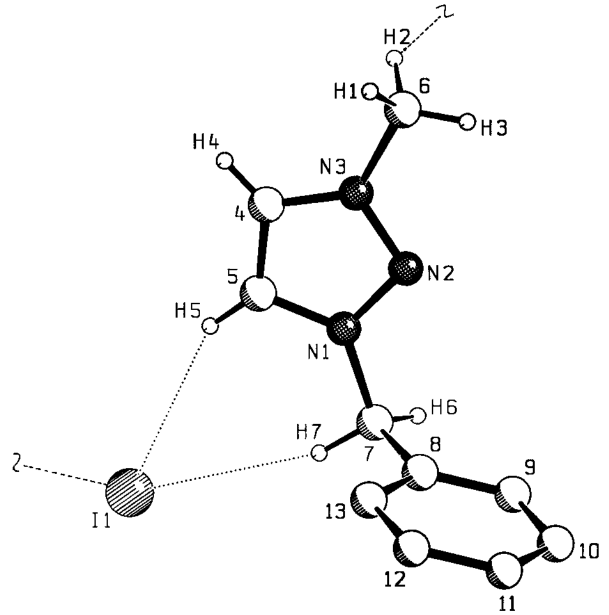


Figure 2. Structure of $\mathbf{6^+I^-}$ in the crystal. Selected bond distances (pm) and bond angles (deg): N(1)−N(2) 131.6(3), N(2)−N(3) 131.9(3), N(3)−C(4) 134.3(4), C(4)−C(5) 135.5(4), C(5)−N(1) 134.2(3); N(2)−N(1)−C(5) 112.7(2), N(1)−N(2)−N(3) 103.8(2), N2−N3−C(4) 112.4(2), N(3)−C(4)−C(5) 105.7(2), N(1)−C(5)−C(4) 105.4(2).

The crystal structures of $\mathbf{5^+I^-}$ and $\mathbf{6^+I^-}$ show that the anion $\mathbf{I^-}$ is not directly connected to the positively charged part of the respective cation. Rather, in both cases $\mathbf{I^-}$ holds together two cations by means of C−H···I$^-$ hydrogen bonds[36,37] with the following structural details. $\mathbf{5^+I^-}$: *C(7)−H(2)···I(1)*: C(7)···I(1): 390.1(5), C(7)−H(2) 93.0(7), H(2)···I(1) 298.5(5) pm, C(7)−H(2)−I(1) 168.5(5)°; *C(9)−H(4)···I(1)*: C(9)···I-

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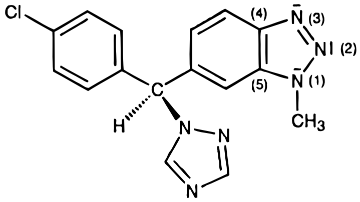
(35) The details of the crystal structure determinations for the compounds $\mathbf{5^+I^-}$ and $\mathbf{6^+I^-}$ may be found in the supporting information. The data were collected on an Enraf Nonius CAD4 diffractometer equipped with graphite-monochromated MoKα radiation and were corrected for absorption. The structures were solved by automated patterson methods and refined by full matrix least squares using F^2 values with anisotropic thermal parameters for all non-hydrogen atoms. For $\mathbf{5^+I^-}$, hydrogen atoms were refined "riding" on their C-atoms with fixed isotropic thermal parameters. For $\mathbf{6^+I^-}$, hydrogen atoms were located and refined isotropically. $R_F = 0.0270$, $R_{wF^2} = 0.0815$, and $S = 1.05$ for $\mathbf{5^+I^-}$ and $R_F = 0.0193$, $R_{wF^2} = 0.0522$, and $S = 1.06$ for $\mathbf{6^+I^-}$.

(1) 389.1(5), C(9)−H(4) 93.0(7), H(4)···I(1) 296.6(5) pm, C(9)−H(4)−I(1) 173.6(5)°; $\mathbf{6}^+\mathbf{I}^-$: *C(5)−H(5)···I(1)*: C(5)···I(1) 385.2(3), C(5)−H(5) 89.5(1.0), H(5)···I(1) 303.9(1) pm, C(5)−H(5)−I(1) 152.(1)°; *C(6)−H(2)···I(1)*: C(6)···I(1) 384.2(3), C(6)−H(2) 97.8(1.0), H(2)···I(1) 298.9(1.0) pm, C(6)−H(2)−I(1) 146.5(1.0)°; *C(7)−H(7)···I(1)*: C(7)···I(1) 394.8(3), C(7)−H(7) 95.4(1.0), H(7)···I(1) 302.6(1.0) pm, C(7)−H(7)−I(1) 163(1)°. In the following, the bond lengths and angles in the 1,2,3-triazolium five-membered rings of $\mathbf{5}^+\mathbf{I}^-$ and $\mathbf{6}^+\mathbf{I}^-$ are compared with the values in the 1,2,3-triazole part of (*S*)-6-[(4-chlorophenyl)(1*H*-1,2,4-triazol-1-yl)methyl]-1-methyl-1*H*-benzotriazole **10**.[38]



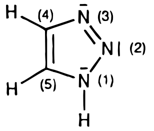
10

The bond angles N(1)−N(2)−N(3) in $\mathbf{5}^+\mathbf{I}^-$ ($\mathbf{6}^+\mathbf{I}^-$) are smaller (106.3(2) (103.8(2)°)) than those in **10** (108.3(5)°). A similar, however stronger narrowing as at N(2) is observed at the carbene C(2) atoms of the Arduengo carbenes **3a**,[23−27] an *N*-lithiated thiazol-2-ylidene[39] and an *N*-lithiated imidazol-2-ylidene.[40] Concomitantly, the angles at N(1) and N(3) of $\mathbf{5}^+\mathbf{I}^-$ (112.1(4) and 111.4(3)°) and $\mathbf{6}^+\mathbf{I}^-$ (112.7(2) and 112.4(2)°) are widened as compared to the ones in **10** (109.4(4) and 108.7(5)°), again in agreement with the carbene **3a**.[23−27] The bonds N(1)−N(2) and N(2)−N(3) in $\mathbf{5}^+\mathbf{I}^-$ (130.2(6) and 132.0(5) pm) as well as in $\mathbf{6}^+\mathbf{I}^-$ (131.6(3) and 131.9(3)) are distinctly shorter than the N(1)−N(2) bond (137.5(7) pm) and only slightly longer than or equal to the N(2)−N(3) bond (130.2(8) pm) in **10**. In Arduengo's **3a** the corresponding C(2)−N(1,3) bonds elongate as the carbene is formed from the corresponding imidazolium salt.[23−27] The overall shortening of the N(2)−N(1,3) bonds in $\mathbf{5}^+\mathbf{I}^-$ and $\mathbf{6}^+\mathbf{I}^-$ is indicative of a strong delocalization at least within the N(1)−N(2)−N(3) framework of these species. In $\mathbf{5}^+\mathbf{I}^-$ and **10** one can furthermore compare the N−C and C−C bond lengths of the five-membered rings. In $\mathbf{5}^+\mathbf{I}^-$ N(3)−C(4) (136.8(5) pm) and N(1)−C(5) (136.4(6) pm) almost correspond to the mean value 136.9 pm of the N(3)−C(4) (138.0(7) pm) and N(1)−C(5) (135.8(6) pm) bond lengths of **10**. The C(4)−C(5) bond in $\mathbf{5}^+\mathbf{I}^-$ (138.5(6) pm) is slightly elongated if compared to the analogous bond (C(4)−C(5) 137.9(6) pm) in **10**. Rather insignificant changes of these bonds are also observed in the carbenes **3a**.[23−27]

Model Calculations of the (Electronic) Structures of $\mathbf{3d}^+$ and $\mathbf{4d}^+$, $\mathbf{R^1, R^3{-}R^5 = H}$. First the structures of $\mathbf{3d}^+$ and $\mathbf{4d}^+$, R^1, R^3−R^5 = H, were calculated together with the structure of 1,2,3-triazole **11**, see Table 1.

Table 1. MP2/6-31G(d) Bond Lengths (pm) and Angles (deg) of the Nitrenium Ions $\mathbf{3d}^+$ and $\mathbf{4d}^+$, R^1, R^3−R^5 = H, and of 1,2,3-Triazole **11**

	$\mathbf{3d}^+$	**11**	$\mathbf{4d}^+$
N(1)−N(2)	133.0	135.2	128.6
N(2)−N(3)	133.0	133.1	128.6
N(3)−C(4)	135.3	136.2	147.7
C(4)−C(5)	138.3	138.3	154.5
C(5)−N(1)	135.3	135.6	147.7
N(1)−N(2)−N(3)	102.0	106.3	108.7
N(2)−N(3)−C(4)	114.4	108.8	115.0
N(3)−C(4)−C(5)	104.7	109.4	100.6
C(4)−C(5)−N(1)	104.7	103.3	100.6
C(5)−N(1)−N(2)	114.4	112.3	115.0



11

Because of the calculated large energy differences between the (more stable) singlets and the triplets in the cases of NF_2^+ (57.3 kcal mol^{-1})[41] and $PhNH^+$ (21.2 kcal mol^{-1})[42] as well as **3a**, R^1, R^3−R^5 = H, (79.4 kcal/ mol),[25] we concluded that the singlet is likewise considerably more stable than the triplet in the case of $\mathbf{3d}^+$ and $\mathbf{4d}^+$, R^1, R^3−R^5 = H. The structures of these species, as outlined in Table 1, thus correspond to those of the most stable singlets. From the structural calculations of the triazolium ion $\mathbf{3d}^+$ and the triazole **11** a similar picture emerges as from the comparison of the experimentally determined bond lengths and angles in $\mathbf{5}^+\mathbf{I}^-$ ($\mathbf{6}^+\mathbf{I}^-$) and **10**: the N(1,3)−N(2) bonds are shorter in $\mathbf{3d}^+$ than in **11**, while the N(3)−C(4) and N(1)−C(5) bonds are of comparable length. The calculated bond angle in $\mathbf{3d}^+$ N(1)−N(2)−N(3) (102.0°) is clearly smaller than the one in **11** (106.3°), while the angles at N1 and N3 are wider in the cation $\mathbf{3d}^+$. The angles at C(4) and C(5) of $\mathbf{3d}^+$ are somewhat more narrow than those in **11**. We will comment below on the structure of the saturated $\mathbf{4d}^+$.

One of the most intriguing questions with respect to carbenes of the type **3a** and **4a** concerns their electronic structure. Besides several conflicting reports on (theoretical) investigations and their interpretation, dealing with the amount of (cyclic) delocalization in these species,[25−27,43−47] two recent publications[48,49] come to the conclusion that the saturated Wanzlick carbenes of the type **4a** are well stabilized through π-donation by the two amino substituents and that carbenes **3a** of the Arduengo type profit additionally from cyclic delocalization (partial aromaticity). We were interested in a comparison of the electronic structures of the cations $\mathbf{3d}^+$ and $\mathbf{4d}^+$ with those

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(36) (a) Berkovitch-Yellin, Z.; Leiserowitz, L. *Acta Crystallogr.* **1984**, *B40*, 159−165. The criteria for C−H···I$^-$ hydrogen bridges are the following: 1. $d(\mathrm{C}\cdots\mathrm{I}^-) < r(\mathrm{C}) + r(\mathrm{I}^-) + 50$ pm, 2. $d(\mathrm{H}\cdots\mathrm{I}^-) < r(\mathrm{H}) + r(\mathrm{I}^-) - 12$ pm, 3. angle C−H−I$^-$ > 100.0°. Since the H···I$^-$ distances as determined by X-ray crystallography are systematically too long, condition 2. is even better fulfilled than indicated by the experimental data. (b) Jeffrey, G. A.; Maluszynska, H.; Mitra, J. *Int. J. Biol. Macromol.* **1985**, *7*, 336−348.

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Table 2. (a) p(π) Populations and (b) Atomic Contributions (%) to the Atom 1−Atom 2 and Atom 2−Atom 3 σ Bonds of the Carbenes **3a**, **4a**, **12**, and **13** and the Nitrenium Ions **3d**$^+$, **4d**$^+$, **14**$^+$, and **15**$^+$; MP2-NBO/6-31G(d)//MP2/6-31G(d)

(a) p(π) Populations

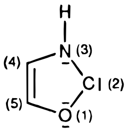
	atom				
	1 (N, O, or S)	2 (C or N$^+$)	3 N	4 C	5 C
3a, R^1,R^3−R^5 = H[a]	1.54	0.67	1.54	1.08	1.08
4a, R^1,R^3−R^5 = H[a]	1.68	0.54	1.68		
12	1.65	0.62	1.54	1.08	1.04
13	1.56	0.71	1.50	1.05	1.10
3d$^+$, R^1,R^3−R^5 = H	1.41	1.17	1.41	0.96	0.96
4d$^+$, R^1,R^3−R^5 = H	1.48	0.99	1.48		
14$^+$	1.54	1.15	1.37	0.95	0.91
15$^+$	1.34	1.24	1.38	0.93	1.02

(b) Atomic Contributions (%) to the σ Bonds

	bond 1 - 2		bond 2 - 3	
	atom 1	atom 2	atom 2	atom 3
3a, R^1,R^3−R^5 = H[a]	67.4	32.6	32.6	67.4
4a, R^1,R^3−R^5 = H[a]	66.2	33.8	33.8	66.2
12	74.2	25.8	31.8	68.2
13	53.1	46.9	33.2	66.8
3d$^+$, R^1,R^3−R^5 = H	54.4	45.6	45.6	54.4
4d$^+$, R^1,R^3−R^5 = H	52.0	48.0	48.0	52.0
14$^+$	63.0	37.0	44.4	55.6
15$^+$	38.8	61.2	45.8	54.2

[a] See also refs 45 and 49.

Chart 3



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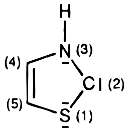

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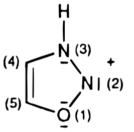
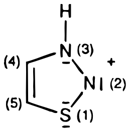


14 $^+$



15 $^+$

of the carbenes **3a** and **4a**, and included in these investigations the 1,3-oxazol-2-ylidene **12**, 1,3-thiazol-2-ylidene **13**, 1-oxo-2,3-diazolium ion **14**$^+$ and 1-thio-2,3-diazolium ion **15**$^+$, Chart 3.

Tables 2(a) and (b) summarize the results of an NBO analysis.[50] In Table 2(a) the p(π) populations at the various atoms in the five-membered rings of these carbenes and nitreniums ions are given, while Table 2(b) contains the atomic contributions to the σ bonds between atoms 1, 2, and 3.

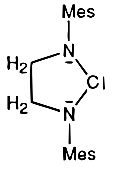
As one can see from Table 2(a), the p(π) populations at C(2) of the carbenes **3a**, **4a**, **12**, and **13**, although already being rather large (between 0.54 and 0.71), are exceeded by those at N(2) of the nitrenium ions **3d**$^+$, **4d**$^+$ **14**$^+$, and **15**$^+$ (between 0.99 and 1.24). Concomitantly, the p(π) populations decrease from 1.54−1.68 at N,O,S(1) and 1.50−1.68 at N(3) in the carbenes to 1.34−1.54 at N,O,S(1) and 1.37−1.48 at N(3) in the nitrenium ions. In the nitrenium ions the p(π) populations at C(4) and C(5) are also smaller than in the carbenes. The exchange of a divalent carbon atom in the carbenes for a divalent nitrogen atom bearing a positive charge in the nitrenium ions thus leads to a further increase of the delocalization. Therefore, the nitrenium ions **3d**$^+$, **4d**$^+$, **14**$^+$, and **15**$^+$ should be even more stabilized thermodynamically than their carbene analogues **3a**, **4a**, **12**, and **13**. A strong stabilization was also noticed for phosphenium ions of the type **2**$^+$.[15−22]

Table 3. X-ray Crystal Structure Data of the Triazolinium Ions **17**$^+$**Cl**$^-$ [52] and **18**$^+$**ClO**$_4^-$ [54]

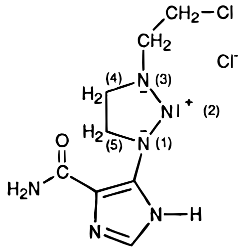
	17$^+$Cl$^-$	**18**$^+$ClO$_4^-$
N(1)−N(2)	128.9(7)	127.1(3)
N(2)−N(3)	127.2(6)	129.5(3)
N(3)−C(4)	147.3(7)	146.7(4)
C(4)−C(5)	150.3(7)	150.8(5)
C(5)−N(1)	144.8(8)	146.6(4)
N(1)−N(2)−N(3)	108.2(4)	109.7(2)
N(2)−N(3)−C(4)	115.3(4)	113.0(2)
N(3)−C(4)−C(5)	100.0(4)	101.8(3)
C(4)−C(5)−N(1)	102.7(4)	101.4(2)
C(5)−N(1)−N(2)	114.0(4)	114.1(2)

[a] Bond lengths (pm) and angles (deg).

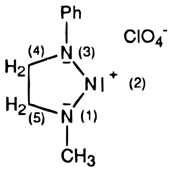
Chart 4



16



17$^+$ **Cl**$^-$



18$^+$ **ClO**$_4^-$

Table 2(a) reveals also that in the *saturated* imidazolin-2-ylidene **4a** the p(π) population at C(2) is smaller (0.54) than in the *unsaturated* **3a** (0.67) which indicates less stability of **4a**.[45,48,49] This, i.e., is related to the fact that—in contrast to the very stable, not dimerizing carbenes of the Arduengo type **3a**—a carbene of the Wanzlick type **4a**, namely the sterically crowded **16**, Chart 4, has only very recently been isolated and structurally characterized by A. J. Arduengo III et al.[51] Normally, carbenes **4a** have a high tendency toward dimerization.[30,45,48,49] A similar difference of p(π) at N(2) is observed between the *saturated* nitrenium ion **4d**$^+$ (0.99) and the *unsaturated* **3d**$^+$ (1.17). However, since the absolute value of the p(π) population at N(2) even for the *saturated* **4d**$^+$ is comparatively high, it is not surprising that a nitrenium ion of this structural type, **17**$^+$**Cl**$^-$, Chart 4, has been isolated and structurally characterized even earlier (although its properties were not discussed in connection with stabilized nitrenium ions and carbenes).[52] We determined the X-ray crystal structure of the 1-methyl-3-phenyltriazolinium perchlorate **18**$^+$**ClO**$_4^-$.[54] The bond lengths [pm] and angles [deg] in the triazolinium ion rings of **17**$^+$**Cl**$^-$ and **18**$^+$**ClO**$_4^-$ show good agreement with the calculated ones of **4d**$^+$ (see Tables 1 and 3).

As far as the atomic contributions to the σ bonds in the carbenes **3a** and **4a** and the cations **3d**$^+$ and **4d**$^+$ are concerned, Cioslowski concluded[44] that the unusual stability of **3a** is directly related to the substantional σ backdonation from C(2) (32.6%) to N(1, 3) (67.4%), Table 2(b). However, in a recent paper, Frenking et al.[49] refuted this argument for the following reasons: 1. the difference in σ polarity of the C−N bonds in **3a** and **4a** is insignificantly small (Table 2(b)), while the p(π) populations are distinctly different (Table 2(a)), in agreement with the different stabilities; 2. 1,3-dioxocyclopent-4-ene-2-ylidene, the dioxygen analogue of **3a**, has rather polar C−O σ bonds (C(2) 25.7%, O (1, 3) 74.3%) and only a small p(π)

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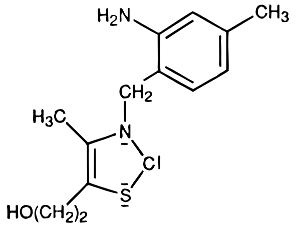
Chart 5



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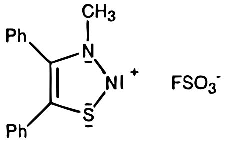

$\mathbf{20^+\ FSO_3^-}$

population at C2 (0.46), however, it is not more, but less stable than **3a**.[49] As shown in Table 2(b), in the model cations $\mathbf{3d^+}$ and $\mathbf{4d^+}$ the polarities of the N(2)−N(1,3) σ bonds are rather small ($\mathbf{3d^+}$ (N(2) 45.6%, N(1,3) 54.4%); $\mathbf{4d^+}$ (N(2) 48.0%, N (1,3) 52.0%)) and the p(π) populations rather large, see Table 2(a). Thus the polarities of the σ bonds are also not relevant for the stabilities of the cations $\mathbf{3d^+}$ and $\mathbf{4d^+}$.

1,3-Oxazol-2-ylidenes **12** should also be rather stable (Table 2(a)), however, it seems that decomposition (a-elimination at C(2)) occurs during their attempted preparation.[55] There are no reports in the literature on 1-oxo-2,3-diazolium ions of the type $\mathbf{14^+}$. The thiamine derived 1,3-thiazol-2-ylidene **19**, Chart 5, is an important example of its kind. The ultimate reagent in vitamine B1 catalyzed oxidative decarboxylations contains its structural element.[55−58] Related carbenes are used for *in vitro* catalyzed reactions.[55,58−60] According to Table 2(a), the model **13** is similarly stable (p(π) at C(2) 0.71) as imidazol-2-ylidenes **3a**, although a 1,3-thiazol-2-ylidene **13** (**19**) has not been isolated and structurally characterized as yet. The structure of an N-Li derivative, which should have a structure similar to that of other 1,3-thiazol-2-ylidenes, however, was recently published.[39] It is interesting to note, that the polarity of the C(2)−S(1) σ bond in **13** is much smaller (C(2) 46.9%, S(1) 53.9%) than that of a C(2)−N(1,3) bond in **3a** (Table 2(b)) which again supports the significance of the π donation to C(2) for the stability of such carbenes, and not of the σ-backdonation. Table 2(a) also shows that the corresponding nitrenium ion 1-thio-2,3-diazolium ion $\mathbf{15^+}$ (p(π) at N(2) 1.24) should be even more stabilized than **13**. The isolation and structural characterization of $\mathbf{20^+FSO_3^-}$,[61] Chart 5, is fully in accord with this conclusion.

Besides the p(π) population, the anisotropy of the magnetic susceptibility, $\Delta\chi$, and the energy ΔE_{isod} of the isodesmic reactions, shown in eq 4, shed some further light on the different properties of the *unsaturated* carbenes **3a** and their nitrenium ion analogues $\mathbf{3d^+}$. The results of the isodesmic reactions are shown in Table 4 together with those of the carbenes **12** and **13** and the nitrenium ions $\mathbf{14^+}$ and $\mathbf{15^+}$.

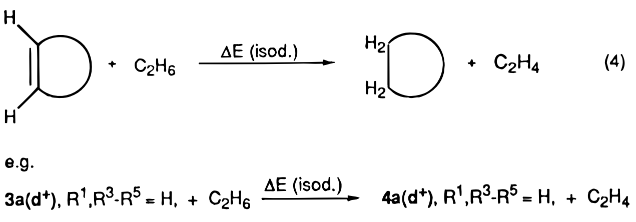

Table 4. ΔE (isod.) [kcal/mol^{-1}] (MP2/6-31G(d)//MP2/6-31G(d))

	$\mathbf{3a}^a$	**12**	**13**	$\mathbf{3d^+}$	$\mathbf{14^+}$	$\mathbf{15^+}$
DE (isod.) [kcal/mol^{-1}]	27.8	20.0	23.3	38.2	29.0	35.3

[a] See also refs 48 and 49.

Table 5. Anisotropies of the Magnetic Susceptibilities $\Delta\chi$ [ppm cgs] with $\Delta\chi = \chi_{xx} - 0.5\ (\chi_{yy} + \chi_{zz})$, $\Delta\chi_{xx}$ Vertical to the Ring Plane, and $\Delta\chi_{yy}$ and $\Delta\chi_{zz}$ in the Ring Plane (IGLO/II//MP2/6-31G(d))

	$\mathbf{3a}^a$	$\mathbf{4a}^a$	**12**	**13**	$\mathbf{3d^+}$	$\mathbf{4d^+}$	$\mathbf{14^+}$	$\mathbf{15^+}$
$\Delta\chi$ [ppm cgs]	27.7	8.14	25.0	32.3	35.1	11.6	34.3	39.5

[a] See also ref[48,49]

The results of Table 4 indicate that the hydrogenations of the nitrenium ions $\mathbf{3d^+}$, $\mathbf{14^+}$, and $\mathbf{15^+}$ require significantly more energy than those of the carbenes **3a**, **12**, and **13**. This is in agreement with the interpretation of the calculations of the p(π) populations (Table 2(a)).

The data of the isodesmic reactions are corroborated by the calculations of the anisotropies of the magnetic susceptibilities $\Delta\chi$ of the carbenes **3a**, **4a**, **12**, and **13**, and of the nitrenium ions $\mathbf{3d^+}$, $\mathbf{4d^+}$, $\mathbf{14^+}$, and $\mathbf{15^+}$, see Table 5.

Magnetic properties like the anisotropies of the magnetic susceptibilities $\Delta\chi$ calculated on the IGLO/II and other levels, have recently proven useful to indicate cyclic delocalization and thus "aromaticity".[62−68] The $\Delta\chi$ values of the *unsaturated* nitrenium ions $\mathbf{3d^+}$, $\mathbf{14^+}$, and $\mathbf{15^+}$ exceed clearly those of the *unsaturated* carbenes **3a**, **12**, and **13**. Since 1,2,3-triazole **11** and benzene have $\Delta\chi$-values of 37.0 and 50.5 [ppm cgs], respectively, one can attribute *unsaturated* nitrenium ions and carbenes partial aromatic character. The values for the *saturated* **4a** (8.14) and $\mathbf{4d^+}$ (11.6) are distinctly smaller, $\mathbf{4d^+}$ once more having the higher value.

Conclusions

As shown by the X-ray crystal structures of $\mathbf{5^+I^-}$ (mp 185 °C without dec) and $\mathbf{6^+I^-}$ (mp 136 °C without dec) *unsaturated* bis-amino-substituted nitrenium ions of the type $\mathbf{3d^+}$ as well as $\mathbf{17^+Cl^-}$ [52] and $\mathbf{18^+ClO_4^-}$ [54] of the *saturated* type $\mathbf{4d^+}$ are very stable compounds. The experimental data agree well with theoretical calculations of their structures and stabilities. The results also fit into the picture of the structurally related carbenes **3a** and **4a**, which emerges from experimental[23−27,30,51] and theoretical[45,48,49] data. Are compounds of the type $\mathbf{3d^+}$ and $\mathbf{4d^+}$ *nitrenium ions*? Since the amazingly stable carbenes of the type **3a** already profit essentially from the electronic stabilization of the formally empty p(π) orbital at C(2) by the two amino-substituents,[48,49] this is even more so with the positively charged nitrogen N(2) in the case of $\mathbf{3d^+}$ and $\mathbf{4d^+}$. Thus, stable nitrenium ions (as their carbene analogues) are electronically distinctly different from normal ones.[69,70]

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Experimental Section

General Methods. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 300 spectrometer, ^{15}N NMR spectra on a Bruker AMX 500 spectrometer by means of the inverse gradient selected HMQC method.[71] Mass spectral data were recorded on a Varian Match 711 (FD) spectrometer. Elemental analysis were carried out with a Heraeus CHN rapid analysator.

Preparation of 1-Methylbenzotriazole 8. The preparation was performed according to ref 31. Yield: 75%; mp: 63−64 °C (63−64 °C^{31}).

Preparation of 1,3-Dimethylbenzotriazolium Iodide 5^{+}I^{-}. In analogy to ref 31, 1-methylbenzotriazole **8** (5.00 g; 37.0 mmol) was dissolved in 10 mL of methyl iodide (MeI) which was warmed to reflux (42 °C) for 12 h. Removal of MeI and recrystallization of the crude yellow crystals from ethanol led to yellow crystalline needles of **5**$^{+}$**I**$^{-}$ which were good enough for an X-ray crystal structure determination. Yield: 9.30 g (90%); mp: 185 °C (185 °C^{31}). ^{1}H NMR (DMSO-d_6) δ 8.43 (m, 2H), 8.10 (m, 2H), 4.71 (s, 6H). ^{13}C NMR (DMSO-d_6) δ 134.96, 130.75 113.84, 37.72. Anal. Calcd for $C_8H_{10}N_3I$: C, 34.93; H, 3.66; N, 15.28. Found: C, 35.20; H, 3.82; N, 15.42.

Preparation of 3-Benzyl-1,2,3-triazole 9. The preparation was performed according to ref 32b. Yield 93%; mp: 61−62 °C (61 °C^{32b}).

Preparation of 1-Benzyl-3-methyltriazolium Iodide 6^{+}I^{-}. In analogy to ref 32a, to 3-benzyl-1,2,3-triazole **9** (1.59 g, 10.0 mmol), dissolved in 10 mL of acetone and 5 mL of diethyl ether, was added 1 mL (2.27 g; 16.0 mmol) of MeI. After 3 days at 20 °C colorless crystals of **6**$^{+}$**I**$^{-}$ (2.4 g, 80% yield) were formed which on recrystallization from ethanol led to single crystalline material suitable for an X-ray crystal structure analysis (2.1 g, 70% yield). Mp: 136−137 °C (135−136 °C^{32a}). ^{1}H NMR (DMSO-d_6) δ 9.00 (s, 1H), 8.83 (s, 1H), 7.36−7.48 (m, 5H), 5.91 (s, 2H), 4.32 (s, 3H). ^{13}C NMR (DMSO-d_6) δ 132.39, 132.03, 130.79, 129.16, 128.99, 128.76, 56.01, 52.57. ^{15}N NMR (DMSO-d_6) δ −42.0 (N(2)); −132.0 and −141.0 (N(1,3)).[72] Anal. Calcd for $C_{10}H_{12}N_3I$: C, 39.89; H, 4.02; N, 13.95. Found: C, 39.90; H, 4.12; N, 13.93.

Computational Methods. All calculations on geometries, energies, and electronic properties were carried out at the MP2/6-31G(d) level of theory using the program packages TURBOMOLE[73] and GAUSSIAN92,[74] while the magnetic properties were calculated at the HF/II level of theory using the IGLO method[75] (implemented in the diglo program, which is used in combination with TURBOMOLE).

Acknowledgment. We are grateful to the Fonds der Chemischen Industrie, the Deutsche Forschungsgemeinschaft (SFB 260 and Graduiertenkolleg Metallorganische Chemie) for support of this work, to the Alexander von Humboldt-Stiftung for a stipend to Dr. P. Andrews, and to Deutschen Akademischen Austauschdienst for a stipend to Dr. K. S. Rangappa.

Supporting Information Available: Tables of crystallographic data, structure determination, atomic positional and thermal parameters, and bond lengths and bond angles for **5**$^{+}$**I**$^{-}$ and **6**$^{+}$**I**$^{-}$ (12 pages). Ordering information is given on any current masthead page.

JA9536274

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