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Steric Stabilization of Nucleophilic Carbenes**

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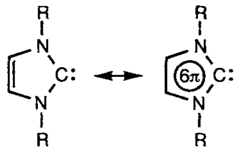
After early studies by Wanzlick,[1] the chemistry of stable carbenes [1-7] underwent a revival in 1991 with the structural characterization of **1** (R = 1-adamantyl).[2] Stable carbenes such as **1** are now easily accessible and show a rich reaction chemistry.[2-4] Computational studies have confirmed that carbenes of type **1** possess aromatic stabilization.[5] The numerous aromatic carbenes **1** currently have only two nonaromatic counterparts, compounds **2**[6] and **3** (R = mesityl).[7] The isolation of the stable bis(diisopropylamino)carbene (**2**) by Alder et al.[6a] demonstrates for the first time that neither aromatic stabilization nor the constraints resulting from ring geometry are necessary to obtain stable diaminocarbenes. The dimerization of carbenes to olefins[8-11] can prevent their isolation but is thermodynamically unfavorable for carbenes **1**, as was shown by Taton and Chen.[11]

R:
Me **a**
Et **b**
*i*Pr **c**
*t*Bu **d**



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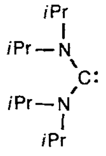

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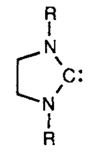

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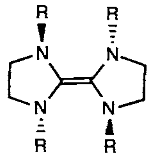

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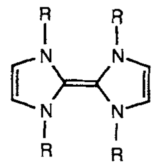

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Following studies on stable silylenes,[12] germylenes,[13] and phosphenium cations[14] isostructural to **1** and **3**, we demonstrate herein that the successful isolation of carbenes **3** has kinetic reasons (in contrast with **1**) and is critically dependent on the bulk of the substituent R. The new carbenes **3a**–**3d**[6b] were obtained by reductive desulfurization from the corresponding thioureas[15] with potassium in boiling THF, a method used in the aromatic series (carbenes **1**) by Kuhn et al.[16] The analogous ureas are inert even after prolonged treatment with molten potassium. Carbene **3d**, the sterically most shielded carbene in this series, is a low-melting, colorless solid that distills without decomposition and is stable indefinitely under exclusion of air and moisture. For R = Me (**3a**), Et (**3b**), and *i*Pr (**3c**), the carbenes persist in solution but slowly dimerize to give the olefins **4a**–**4c**. Attempted distillation of the carbenes **3a**–**3c** (60 °C/0.1 Torr) yields the olefins as easily sublimable, air- and moisture-sensitive colorless solids. Compound **4a** was previously obtained by other methods[17,18] but has not been structurally characterized. The slow dimerization of **3a**–**3c** in solution suggests a substantial activation barrier. The dimerizations obey (^{1}H NMR) a second-order rate law and, accordingly, are concentration dependent.[19] The pure carbenes **3a**–**3c** dimerize within minutes, but frozen solutions of **3a**–**3c** in benzene can be stored indefinitely at −20 °C. Olefins of type **4** can fragment to give transition metal carbene complexes.[17] The dissociation of **4** to free carbenes **3** is of interest as a possible pathway for these reactions; however, high-temperature ^{1}H NMR spectra did not show any signs of this dissociation.[20]

The additional electronic stabilization in diaminocarbenes **1** is evident, for example, in that while **3c** dimerizes, the aromatic 4,5-dimethyl-substituted analogue of **1c** is stable.[21] Indeed, not a single carbene of type **1** has been observed to dimerize and olefins of type **5** require additional covalent bridging of the substituents R to be stable, as was shown by Taton and Chen.[11] The lack of aromatic stabilization in carbenes **3** is also shown by the deshiedling of the carbene-carbon atom ($\Delta\delta(^{13}C) \approx 30$ relative to those in **1**).[2-5,21]

A single-crystal X-ray structure analysis of **3d**[22] shows the two nitrogen atoms to be in nearly planar environments (sum of bond angles: N(1) 356°, N(2) 357°; see Figure 1). The valence angle at the carbene-carbon atom is significantly larger (106.44(9)°) than the N-Si-N and N-Ge-N angles of the

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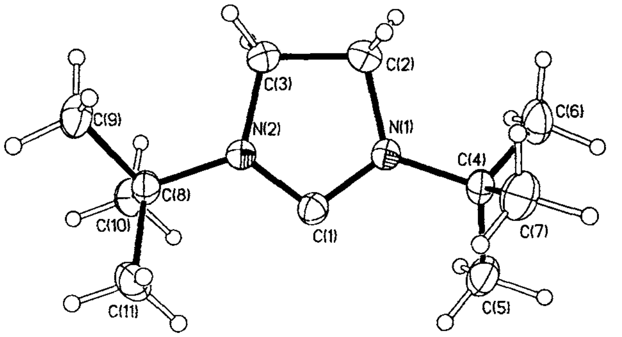

Figure 1. Molecular structure of **3d** in the solid state (ORTEP view, thermal ellipsoids are at the 50% probability level). Selected bond lengths [pm] and angles [°]: C(1)-N(1) 134.8(1), C(1)-N(2) 134.7(1), N(1)-C(2) 147.6(1), N(1)-C(4) 148.0(1), C(2)-C(3) 151.2(2), N(1)-C(1)-N(2) 106.44(9); C(1)-N(1)-C(2) 112.51(8), N(1)-C(2)-C(3) 101.34(9), C(4)-N(1)-C(2) 120.53(8), C(4)-N(1)-C(1) 123.10(8).

isostructural silylenes (95.4(1)[12] and germylenes 88.0(1).[13] The short $C^{II}-N$ bond length (135 pm) indicates a partial double bond.

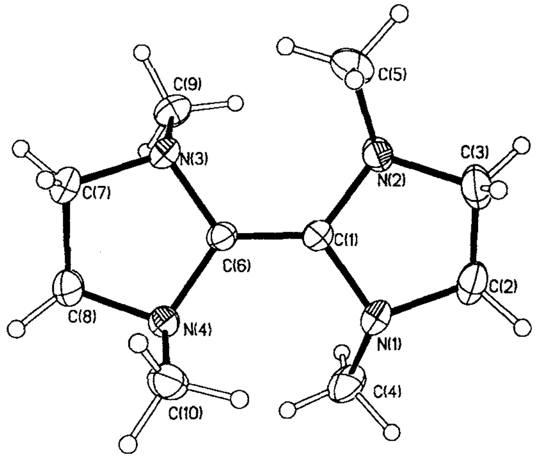

Figure 2. Molecular structure of **4a** (ORTEP view, thermal ellipsoids are at the 50% probability level). Selected bond lengths [pm], bond angles [°], and torsional angles [°]: C(1)-C(6) 134.94(11), N(1)-C(1) 142.05(11), N(2)-C(1) 141.77(11), N(3)-C(6) 143.63(11), N(4)-C(6) 144.30(10) N(2)-C(3) 146.34(12), C(3)-C(2) 150.7(2), N(4)-C(8) 147.20(11), C(8)-C(7) 152.54(14), C(7)-N(3) 147.02(12); N(1)-C(1)-N(2) 108.71(7), N(3)-C(6)-N(4) 111.29(7), N(3)-C(6)-C(1)-N(2) 5.94(13); N(3)-C(6)-C(1)-N(1) −173.57(7), N(4)-C(6)-C(1)-N(1) 8.01(13), N(4)-C(6)-C(1)-N(2) −172.47(7).

A comparison of the carbene **3d** with the olefin **4a** highlights characteristic changes in the five-membered C_2N_2C framework (Figure 1 and 2): the C−N bond lengths increase from the carbene (**3d**: 135 pm) to the dimer (**4a**: 142−147 pm), and the nitrogen atoms pyramidalize (sum of the nitrogen bond angles in **4a**: 331−340°). The N-C-N bond angles of **3d** and **4a** are nearly identical. The twisting of the $N_2C{=}CN_2$ framework in **4a** (N-C-C-N torsional angles of 6 and 8°) is reproduced by calculations (AM1, MP4/6-31G*) both for **4a** and the unsubstituted derivative (R = H) and has, presumably, electronic rather than steric origins.

The structures of the open-chain carbene **2**[6] and the cyclic carbene **3d** show significant differences. The N-C-N bond angle in **3d** (106.44(9)°) is compressed compared to that in **2** (121.0(5)°) and the $C^{II}-N$ bond length is shortened (134.8(3) pm in **3d**, 136.3(6) pm in **2**). The ^{13}C NMR shifts reflect the structural differences: the carbene–carbon atom in **3d** ($\delta = 238$) is strongly shielded compared to that in **2** ($\delta = 256$). We conclude that the ring geometry in carbenes **3** stabilizes the carbene (shortened C−N bond, shielded carbene signals) through an additional compression of the N-C-N valence angle. In support of our conclusion, diaminocarbenes and silylenes show decreased thermal stability if the ring size is increased from five (C_2N_2E:) to six (C_3N_2E:).[24]

Experimental Section

All operations were performed under argon (99.995%) with usual Schlenk techniques. The respective thiourea [15] (10 mmol), potassium (30 mmol), and THF (50 mL) were boiled under reflux for 30 min. After filtration and removal of the solvent under vacuum (−20 °C), the carbenes **3a**−**3c** were obtained as yellow, viscous oils. Distillation of **3d** (0.1 Torr, 120 °C oil bath) yielded the pure **3d** as a colorless, low-melting solid (m.p. 22−23 °C). Yields: quantitative for **3a**−**3c**, 85−95% for **3d**. Attempted distillation of **3a**−**3c** (0.1 Torr, 60 °C oilbath) led to sublimation of the olefins **4a**−**4c** as colorless, crystalline solids in quantitative yields. NMR data: C_6D_6, 20 °C, TMS.

3a: ^1H NMR: $\delta = 2.43$ (s, 2H; CH_2), 2.81 (s, 3H; CH_3); ^{13}C NMR: $\delta = 34.78$ (t, ^1J(C,H) = 145.7 Hz; CH_2), 47.48 (q, ^1J(C,H) = 137.6 Hz; CH_3), 239.8 (s; C:).

3b: ^1H NMR: $\delta = 1.06$ (t, ^3J(H,H) = 7.3 Hz; CH_3), 2.93 (s; NCH_2), 3.41 (q, ^3J(H,H) = 7.3 Hz; CH_2CH_3); ^{13}C NMR: $\delta = 12.05$ (q, ^1J(C,H) = 126.1 Hz; CH_3), 42.17 (tq, ^1J(C,H) = 138.1 Hz, ^2J(C,H) = 4.4 Hz; CH_2CH_3), 45.00 (tt, ^1J(C,H) = 144.6 Hz, ^2J(C,H) = 4.3 Hz; NCH_2), 237.7 (s; C:).

3c: ^1H NMR: $\delta = 1.18$ (d, ^3J(H,H) = 6.6 Hz; CH_3), 2.91 (s; CH_2), 3.92 (sept, ^3J(H,H) = 6.6 Hz; CH); ^{13}C NMR: $\delta = 22.08$ (q, ^1J(C,H) = 124.9 Hz; CH_3), 44.61 (t, ^1J(C,H) = 142.0 Hz; CH_2), 50.53 (d, ^1J(C,H) = 136.7 Hz; CH), 236.8 (s; C:).

3d: ^1H NMR: $\delta = 1.36$ (s; CH_3), 3.04 (s; CH_2); ^{13}C NMR: $\delta = 29.83$ (CH_3), 44.36 (CH_2), 55.68 ($C(CH_3)_3$), 238.25 (s; C:).

4a: ^1H NMR: $\delta = 2.62$ (s; CH_3), 2.76 (s; CH_2); ^{13}C NMR: $\delta = 40.21$ (q, ^1J(C,H) = 134.5 Hz; CH_3), 52.70 (t, ^1J(C,H) = 139.7 Hz; CH_2), 129.61 (C=).

4b: ^1H NMR: $\delta = 1.06$ (t, 7.5 Hz; CH_3), 2.80 (s; NCH_2), 3.05 (q, 7.5 Hz; CH_2CH_3); ^{13}C NMR: $\delta = 12.98$ (q, ^1J(C,H) = 124.8 Hz; CH_3), 45.62 (t, ^1J(C,H) = 135.0 Hz; CH_2), 49.08 (t, ^1J(C,H) = 139.2 Hz; CH_2), 125.67 (s; C=).

4c: ^1H NMR: $\delta = 1.03$ (d, ^3J(H,H) = 6.6 Hz; CH_3), 2.75 (s; CH_2), 4.12 (sept, ^3J(H,H) = 6.6 Hz; CH); ^{13}C NMR: $\delta = 19.7$ (br.; CH_3), 46.4 (d, ^1J(C,H) = 139.9 Hz; CH), 43.1 (t, ^1J(C,H) = 136.8 Hz; CH_2), 124.3 (C=).

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[22] Crystal data for **3d**: $M_r = 182.31$, monoclinic, space group $P2_1/n$, $a = 6.2116(5)$, $b = 18.510(2)$, $c = 10.1210(9)$ Å, $\beta = 92.732(7)°$, $V = 1162.3(2)$ Å^3, $\rho_{calcd} = 1.042$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 0.62$ cm^{-1}, $T = 173$ K, 3651 reflections collected ($3.0 < \theta < 30.0°$) and no absorption correction. Structure refined on F^2 and hydrogen atoms were refined with isotropic thermal parameters. Final $R1$ $[I > 2\sigma(I)] = 0.0447$ for 2698 observed reflections and $wR2$ (all data) $= 0.1166$ for 3383 independent reflections. Maximum and minimum peaks in final ΔF map were 0.31 and -0.26 e Å^{-3}. **4a**: $M_r = 196.30$, monoclinic, space group $P1$, $a = 7.731(3)$, $b = 8.100(2)$, $c = 9.912(2)$ Å, $\alpha = 96.74(2)$, $\beta = 99.37(2)$, $\gamma = 113.21(2)°$, $V = 551.5(2)$ Å^3, $\rho_{calcd} = 1.182$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 0.75$ cm^{-1}, $T = 173$ K, 3395 reflections collected ($3.0 < \theta < 30.0°$) and no absorption correction. Structure refined on F^2 and hydrogen atoms in calculated positions. Final R_1 $[I > 2\sigma(I)] = 0.0411$ for 2342 observed reflections and wR_2 (all data) $= 0.1209$ for 3178 independent reflections. Maximum and minimum peaks in final ΔF map were 0.48 and -0.18 e Å^{-3}. Both structures were solved and refined by using SHELXTL/PC [23]. Crystallographic data (excluding structure factors) for **3d** and **4a** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100576. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: Int. Code +(1223) 336-033; e-mail: deposit@chemcrys.cam.ac.uk).

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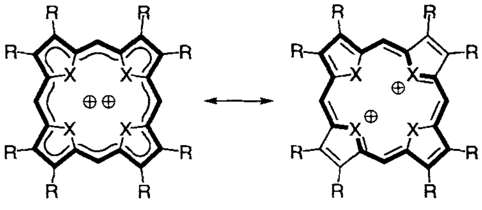
Octaethyltetraselenaporphyrin Dication**

Emanuel Vogel,* Christoph Fröde, Andreas Breihan, Hans Schmickler, and Johann Lex

Dedicated to Professor Marianne Baudler
on the occasion of her 75th birthday

The oxygen analogue of porphyrin, the D_{4h} symmetrical dication **1** (as its perchlorate),[1,2] constitutes a key compound in the chemistry of nonnatural porphyrins. There exists a close relationship between **1** and porphyrin, both in terms of their synthesis and their aromaticity, as evident from spectra and molecular structure. However, the two macrocycles differ markedly in their chemical properties. Unlike porphyrin and the neutral monooxa- and dioxaporphyrins,[3] **1** is no longer able to form complexes with metal ions because of its positive charge. Central to the chemistry of **1** are nucleophilic additions (and subsequent transformations) and the tetraoxaporphyrin redox system, which is derived from the dication and is interesting from many viewpoints.[4]



1–6

R=H **1:** X=O, **2:** X=S, **3:** X=Se (in solution only)
R=C_2H_5 **4:** X=O, **5:** X=S, **6:** X=Se

The recently synthesized tetrathiaporphyrin dication **2** (as its perchlorate)[5,6] and the tetraselenaporphyrin dication **3**,[5] which has until now only been obtained in solution, both resemble **1** in terms of their reactivity and spectral characteristics, even though the ring system deviates significantly from planarity because of the steric interactions of the heteroatoms. Since the study of **1–3** is adversely affected by problems associated with solubility and/or crystallization, it is sensible to follow the lead of porphyrin chemistry and turn to the octaethyl compounds **4–6**. After the syntheses of **4**[7] and **5**,[8] that of **6**, presented here, has also been achieved, and with it the set of chalcogenaporphyrins—with the exception of the tellura compound[9]—is now complete.

The 2-(hydroxymethyl)-3,4-diethylselenophene (**7**)[10] was chosen as the starting material in the synthesis of the octaethyltetraselenaporphyrin dication **6** (as its perchlorate). This would allow use of the route already proven in the synthesis of **1**, **4**, and **5**—the tetracyclocondensation to "porphyrinogen" and its oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) with addition of $HClO_4$.

Treatment of **7** with one equivalent of *p*-toluene sulfonic acid in nitromethane at 80 °C (10 min) gave the expected octaethyltetraselenaporphyrinogen **8**, albeit only in small amounts. Analogous to the cyclocondensation of 2-(hydroxymethyl)-

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