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A Bis(carbene)−Proton Complex: Structure of a C−H−C Hydrogen Bond

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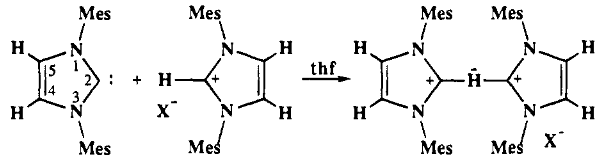
Hydrogen bonding plays a critical role in chemistry, frequently controlling structure and reactivity and often serving as a basis for molecular recognition.[1] The 3-center, 4-electron hydrogen bonds among the elements fluorine, oxygen, and nitrogen have been observed spectroscopically (UV, IR, NMR, etc.), and many examples have been structurally characterized by X-ray and/or neutron diffraction. Spectroscopic evidence for the existence of hydrogen bonds between carbon and other elements is available but scarce compared to examples with more electronegative elements.[2] In spite of the widespread use of carbon bases (carbanions) to deprotonate hydrocarbon acids, the list of examples with hydrogen bonds between two carbon centers is even shorter, with no structually characterized models of the C−H−C 3-center, 4-electron interaction.[3] We now report the structural characterization of a C−H−C hydrogen bond.

Carbene **1**[4] reacts with 1,3-dimesitylimidazolium salt **2a**[5] or **2b**[6] to form the bis(carbene)−proton complex **3a**[7] or **3b**.[8] The bis(carbene)−proton adducts **3a** and **3b** are colorless, high melting solids (mp 210 and 200 °C, respectively), consistent with their ionic structures. The imidazole units of the cations in **3a** and **3b** are linked by a C−H−C hydrogen bond.



(1)

1 Mes ≡ 1,3,5-mesityl

2a X = PF_6
2b X = CF_3SO_3

3a X = PF_6
3b X = CF_3SO_3

In thf-d_8 (thf ≡ tetrahydrofuran) solution at room temperature, the bridging protons in **3a** and **3b** resonate at δ 9.6, which is about 0.1−0.4 ppm downfield of the corresponding imidazolium salt (the hexafluorophosphate shows the larger $\Delta\delta$). The greatest shift differences upon C−H−C complex formation are actually observed for the imidazole ring protons at $C_{4(5)}$, which resonate at about δ 7.5, midway between their resonances in **1** (δ 7.0) and **2** (δ 8.0). In ^{13}C NMR spectra of **3a** and **3b**, the resonance for C_2 is ~175 ppm, which again is the average of the C_2 resonances in the carbene and carbenium (imidazolium) ion. This situation with averaged NMR resonances in solution for **3a** and **3b** is analogous to that which we recently reported for a structutally related bis(carbene)−I(1+) complex.[9] However, unlike the situation with I(1+), mixtures of **1** and **2** that are not exactly a 1:1 molar ratio exhibit averaged resonances. The observation of averaged resonances for the bis(carbene)−proton system even in nonstoichiometric ratios indicates that this system is more dynamic than the related iodine structure and undergoes exchange on the NMR time scale.

Crystals of **3a** and **3b** were grown from a thf solution by cooling. The two structures are very similar in spite of the difference in the anions, both of which play identical secondary hydrogen bonding roles (*vide infra*). The X-ray crystal structure of **3a** is depicted in Figure 1. The position of the bridging proton and its isotropic thermal parameter were refined in both structures. The central C−H−C unit is approximately linear (172.5°), with different C−H distances to the bridging proton (202.6(45) and 115.9(45) pm). The ring internal angles (N−C−N) at the former carbene centers reflect the proximity of the bridging proton. The carbon closest to the proton shows a ring internal N−C−N angle of 107.6(4)°, which is more relaxed (and imidazolium-like) than the other N−C−N angle of 102.8(4)° typical of the free carbenes. The two C−N bonds to the former carbene center that is most imidazolium-like have an average distance of 134 pm. The average C−N distance to the most carbene-like center is 136 pm. The variation in the C−N bond distances between the imidazolium- and carbene-like centers in **3a** has been previously recognized for the two independent species.[4,10]

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(5) A suspension of 1.0 g (2.9 mmol) of 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride in 50 mL of thf was treated with a solution of 742 mg (2.9 mmol) of $AgPF_6$ in 10 mL of thf. After being stirred for 3 h, the reaction mixture was filtered and the solvent evaporated. Recrystallization from thf/hexane gave **2a** as white needles: yield, 910 mg (69%); mp 237−238 °C; ^1H NMR (thf-d_8) δ 2.17 (s, 2,6-CH_3, 12 H), 2.35 (s, 4-CH_3, 6 H), 7.14 (s, Ar*H*, 4 H), 7.97 (d, $^4J_{HH}$ = 1.5 Hz, NC*H*, 2 H), 9.20 (t, $^4J_{HH}$ = 1.5 Hz, NC*H*N, 1 H). Anal. Calcd for $C_{21}H_{25}F_6N_2P$: C, 56.00; H, 5.59; N, 6.22. Found: C, 56.38; H, 5.83; N, 6.64.

(6) A suspension of 1.0 g (2.9 mmol) of 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride in 60 mL of thf was treated with a solution of 754 mg (2.9 mmol) of silver triflate in 10 mL of thf. After being stirred for 45 min, the reaction mixture was filtered through Celite and the solvent evaporated. Recrystallization from thf/pentane gave **2b** as white crystalline solid: yield, 940 mg (71%); mp 190 °C; ^1H NMR (thf-d_8) δ 2.18 (s, 2,6-CH_3, 12 H), 2.35 (s, 4-CH_3, 6 H), 7.12 (s, Ar*H*, 4 H), 8.01 (d, $^4J_{HH}$ = 1.5 Hz, NC*H*, 2 H), 9.53 (t, $^4J_{HH}$ = 1.5 Hz, NC*H*N, 1 H).

(7) A solution of 450 mg (1 mmol) of **2a** in 20 mL of thf was treated with a solution of **1** (304 mg, 1 mmol) in 20 mL of thf. After being stirred for 30 min, the solvent was removed in vacuo. Recrystallization from hot thf gave **3a** as white crystals: yield, 450 mg (60%); mp at 210 °C (darkens), 227−229 °C dec (melts); ^1H NMR (thf-d_8) δ 2.05 (s, 2,6-CH_3, 24 H), 2.34 (s, 4-CH_3, 12 H), 7.04 (s, Ar*H*, 8 H), 7.49 (s, NC*H*, 4 H), 9.57 (s br, NC*H*N, 1 H); ^{13}C NMR (thf-d_8) δ 17.55 (s, 2,6-*C*H_3), 21.08 (s, 4-*C*H_3), 123.95 (s, N*C*C), 129.94 (s, Mes *C*-3,5), 135.54 (s, Mes *C*-1), 135.58 (s, Mes *C*-2,6), 140.08 (s, Mes *C*-4), 174.95 (s br, N*C*N). Anal. Calcd for $C_{42}H_{49}F_6N_4P$: C, 66.83; H, 6.54; N, 7.42. Found: C, 67.04; H, 6.91; N, 7.87.

(8) A 50-mL round-bottom flask was charged with 91 mg of **2b** (0.20 mmol), a stir bar, and 20 mL of thf. A solution of 61 mg of **1** (0.20 mmol) in 5 mL of thf was added as a single portion. After being stirred for 30 min, the solvent was removed under vacuum to give 0.152 g (100%) of **3b** as a white solid: mp 200 °C dec; ^1H NMR (thf-d_8) δ 2.07 (s, 2,6-CH_3, 24 H), 2.33 (s, 4-CH_3, 12 H), 7.03 (s, Ar*H*, 8 H), 7.53 (s, NC*H*, 4 H), 9.6 (s br, NC*H*N, 1 H); ^{13}C NMR δ 17.67 (s, 2,6-*C*H_3), 21.08 (s, 4-*C*H_3), 122.28 (q, $^1J_{CF}$ = 323 Hz, *C*F_3), 123.93 (s, N*C*C), 129.88 (s, Mes *C*-3,5), 135.60 (s, Mes *C*-2,6), 135.71 (s, Mes *C*-1),139.88 (s, Mes *C*-4), 176.11 (s br, N*C*N). Anal. Calcd for $C_{43}H_{49}F_3N_4SO_3$: C, 68.05; H, 6.51; N, 7.38. Found: C, 68.08; H, 6.09; N, 7.16.

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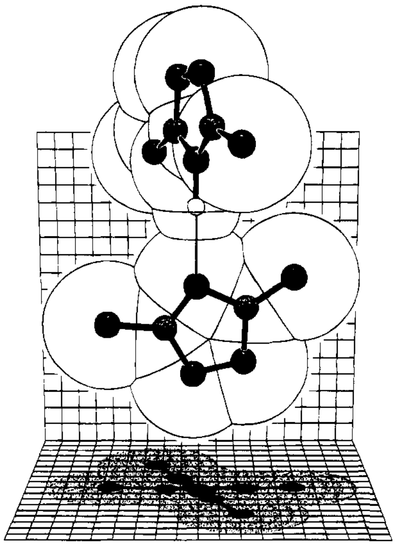

Figure 1. Space filling KANVAS[11] drawing of the X-ray structure of bis(carbene)−proton complex in **3a**. Hydrogens (except H_2) and mesityl groups (except ipso-carbons) have been omitted for clarity.

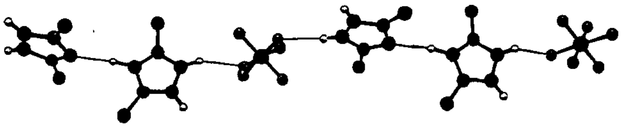

Figure 2. KANVAS[11] drawing of the extended structure of bis(carbene)−proton complex in **3a**. Mesityl groups (except ipso-carbons) have been omitted for clarity.

As mentioned previously, the anions in **3a** and **3b** both have a role in the secondary hydrogen bonding of the extended solid state structure. The anions form bridges between the hydrogens at the 4 and 5 positions of imidazole rings, producing a one-dimensional chain throughout the solid. This motif is illustrated in Figure 2 for **3a**. It should also be noted that a similar extended structure exists for the bis(carbene) complexes of silver(I) triflate and copper(I) triflate.[12]

Taking into account the much smaller size of a proton relative to iodine, the structures of **3a** and **3b** are reminiscent of a related bis(carbene)−iodine(1+) complex. However, in the iodine-bridged complex, the geometries of the two imidazole groups were almost identical, consistent with the more symmetric C−I−C structure. The 1,3-dimesitylimidazol-2-ylidenes seem to have a high tendency to form homoleptic bis(carbene) complexes with a range of elements (H, Ag, Cu, Ni, Pt, and I). We do not observe such facile bis(carbene) complex formation from many of the other imidazol-2-ylidenes we have prepared. This may be the result of the unique cavity that exists in the mesityl-substituted imidazol-2-ylidenes.

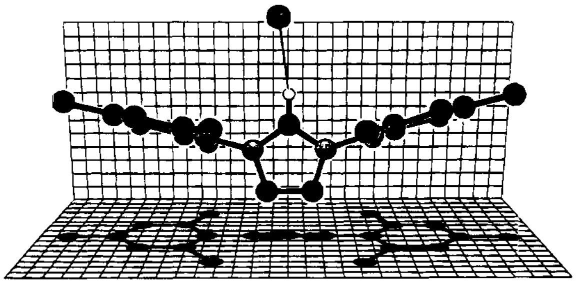

Figure 3. KANVAS[11] drawing of 1,3-dimesitylimidazolium chloride. Hydrogens (except H_2) have been omitted for clarity. A methanol of solvation is also present in the crystal and is hydrogen-bonded to the chloride.

The tendency of the proton in the 2-position of imidazolium cations to serve as a site for hydrogen bonding has been previously observed in the X-ray structures of several salts. In general, it is found that anions that can function as hydrogen bond acceptors are positioned in the crystal such that a near linear C−H−X arrangement is formed. This situation is illustrated in Figure 3 for 1,3-dimesitylimidazolium chloride. The C_2−Cl distances in such imidazolium chlorides are typically between 300 and 340 pm. A related structure on 1,3,4,5-tetramethylimidazolium chloride is included with the supplementary material.

IR and Raman spectroscopy were used to examine crystalline samples of **3a** and **3b**. We were not able to unambiguously assign an absorption to the bridging hydrogens. It seems likely that this absorption is quite broad and difficult to distinguish from the baseline. Preliminary calculations on model systems for **3**, which correctly reproduce the experimental geometry, predict the stretching frequency for the bridging proton to a shift of ~700 cm^{-1} from ν_{CH} for C_2−H in **2**.[13] Analogy with N−H−N hydrogen bonds in pyridine systems is consistent with the predicted magnitude of this shift of ν_{CH} in the C−H−C hydrogen-bonded complex.[14] Work is currently in progress to characterize ν_{CH} in other C−H−C hydrogen-bonded complexes related to **3**.

Acknowledgment. The excellent technical assistance of W. Marshall made the crystal structures possible.

Supplementary Material Available: A complete description of the X-ray crystallographic determination on **3a, 3b,** 1,3-dimesitylimidazolium chloride methanol solvate, and 1,3,4,5-tetramethylimidazolium chloride, including tables of fractional coordinates, isotropic and anisotropic thermal parameters, bond distances, and bond angles and ORTEP drawings (36 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(11) This drawing was made with the *KANVAS* computer graphics program. This program is based on the program *SCHAKAL* of E. Keller (Kristallographisches Institute der Universitat Freiburg, Germany), modified by A. J. Arduengo, III (E. I. du Pont de Nemours & Co., Wilmington, DE) to produce the back and shadowed planes. The planes bear a 50-pm grid, and the lighting source is at infinity so that shadow size is meaningful.

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(13) Both Hartree−Fock and nonlocal density functional theory calculations correctly predict the geometry for models of these hydrogen-bonded structures, including the asymmetric position of the hydrogen. Nonlocal DFT calculations predict ν_{CH} in the C−H−C hydrogen-bonded complex of 2530 cm^{-1}, compared to ν_{CH} of 3250 cm^{-1} in the free imidazolium cation. Arduengo, A. J., III; Dixon, D. A. submitted for publication in *J. Phys. Chem.*

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