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Intermolecular =C–H···:C hydrogen bond in a crystalline unsaturated Arduengo-type carbene

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The presence of the =C–H···:C intermolecular hydrogen bond in 1,3-di-*tert*-butylimidazol-2-ylidene has been demonstrated by vibrational spectroscopy and confirmed by X-ray diffraction analysis and quantum-chemical calculations.

One of the most impressive achievements in organic chemistry in recent decades was the synthesis of thermally stable carbenes by Arduengo and co-workers.[1–6] The chemical and physical properties of these compounds have been studied with the aim of elucidating the reasons for the increased stability of unsaturated 'Arduengo-type' carbenes.[7–12] Our recent contribution to this problem[13] involved investigation of vibrational and electronic spectra of 1,3-di-*tert*-butylimidazol-2-ylidene **1** and quantum-chemical calculations for its isolated molecule. Here we present evidence of intermolecular hydrogen bonding of the type =C–H···:C in crystalline **1**. This appears to be the first example of a C–H···C hydrogen bond between neutral molecules.

While studying the Raman spectra of **1**,† we noted that the frequencies of the =C–H stretching vibrations, ν(=C–H), for the polycrystalline sample and its solution in toluene-d_8 differ significantly (Figure 1) whereas the frequencies of all other salient spectral features coincide within ±2 cm^{-1}.

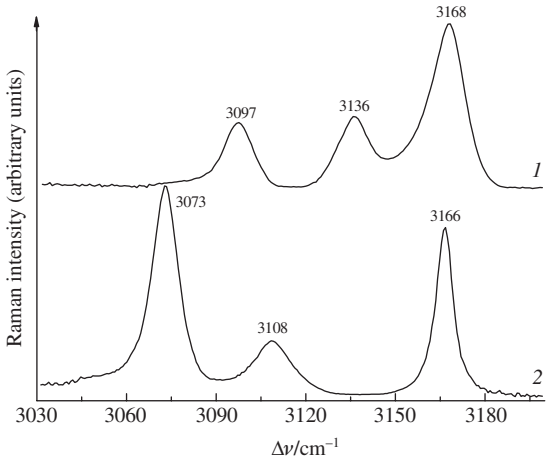

Figure 1 The ν(=C–H) region of the Raman spectrum of carbene **1**. (*1*) Solution in toluene-d_8, (*2*) solid sample.

† *1,3-Di*-tert-*butylimidazol-2-ylidene* **1** was synthesized according to a published procedure.[3] The Raman spectra were obtained using a Jobin-Yvon LabRAM laser Raman spectrometer with the 632.8 nm excitation line of a He–Ne laser (laser power less than 10 mW). The samples of solid **1** and its solution in toluene-d_8 were sealed in ampoules. All operations were carried out in an inert atmosphere. Toluene-d_8 (99%) was commercial of high quality and used as received.

The lowering of ν(=C–H) frequencies in the spectrum of polycrystalline **1** by about 25 cm^{-1} suggests a weak interaction of the =C–H bonds with an electron donor, the most likely candidate being the lone electron pair of the carbene center. Indeed, examination of the CCDC data on the X-ray crystalline structures of **1**[3,14] reveals that one of the =C–H bonds is directed just toward the carbene center of the neighboring molecule, the corresponding H···:C distance being 2.71 Å while the =C–H···:C angle is 166° (Figure 2).

The contact 2.71 Å was obtained after adjusting the C–H interatomic distance to its ideal value of 1.08 Å, as established by neutron diffraction.[15] This contact is shorter than the sum of van der Waals radii estimated as > 2.9 Å,[16] taking into account that the van der Waals radius of the divalent carbon atom should be somewhat larger than that of tetravalent carbon.

The fact that the frequencies of both ν^s(=C–H) and ν^{as}(=C–H) vibrations are lowered, although only one of the =C-H bonds participates in H-bonding, is explained by the calculated mode eigenvectors,[13] both bonds taking equal part in both vibrations. The line near 3167 cm^{-1} observed in the Raman spectra of both solid **1** and its solution (Figure 1) corresponds to an overtone 2ν(C=C).

The *ab initio* calculation‡ of a model dimer of **1** results in a reasonable value of the H-bond energy (1.2 kcal mol^{-1}), and in a geometry closed to the experimental one, with the H···:C distance of 2.8 Å and the C–H···:C angle of 167°. A calculation of the molecular graph of this model dimer according to the Bader's 'atoms in molecules' method[17] confirms the presence of the H-bond through the presence of the (3, –1) bond critical

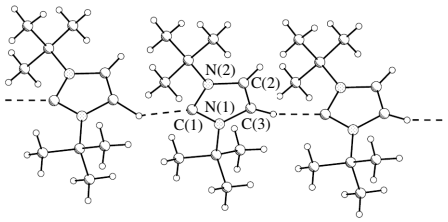

Figure 2 Extended X-ray crystal structure of carbene **1**.

‡ Quantum-chemical calculation of the geometry and energy of a model H-bonded dimer of **1** was carried out at MP2/G-31+G(d,p) level of theory using Gaussian03 software. AIM calculations according to Bader's method with the use of the experimental geometry were performed with AIM 2000 software.

point between the corresponding H and C atoms with electron density $\rho_b(r) = 0.008$ a.u., rather low but proper for a weak hydrogen bond.[18]

Thus, the vibrational frequency shift and the geometry data along with the results of quantum-chemical calculations indicate a weak intermolecular =CH···:C hydrogen bond in crystalline **1**. The formation of such an H-bond can be explained by the high basicity of the carbene center[9,11] and the acidic character of =C–H bonds, evidenced by their easy deuteration.[19]

The C–H–C hydrogen bonds are rare. Quantum-chemical evidence for their possibility was presented.[20] We have located only two experimentally well-authenticated examples,[21,22] both involving protonated species.[23] In addition, the results of an early IR and NMR study[24] were interpreted in terms of a C–H···C hydrogen bond in solution between phenylacetylene and benzyl isocyanide. Thus, this paper seems to report the first example of a C–H···C intermolecular hydrogen bond in a crystal involving neutral molecules.

The hydrogen bonds found for **1** form a chain throughout its crystal lattice (Figure 2), resembling those described previously,[22,25] in which the =C–H bonds of imidazole rings interacted with the corresponding anions or groups.

Note that examination of the X-ray crystal structures of the heavy analogues of carbene **1** – the silylene[26] and the germylene[27] – reveals no interactions of the =C–H···:Si or =C–H···:Ge type.

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