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# Vibrational and electronic spectra and the electronic structure of an unsaturated Arduengo-type carbene

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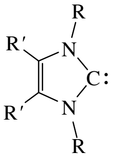
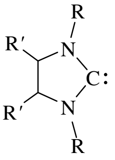
**The Raman, IR and UV spectra of 1,3-di-*tert*-butylimidazol-2-ylidene ($Bu^tNCH=CHNBu^t$)$C^{II}$ and quantum chemistry calculations of its normal mode frequencies and eigenvectors and the NICS index are reported.**

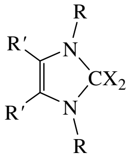
One of the most exciting recent results in chemistry is the synthesis of thermally stable heterocyclic diaminocarbenes **1**.[1–5] The first unsaturated molecule with R′ = H and R = Ad was reported by Arduengo *et al.*[1] as colourless crystals stable in the absence of air, which could be melted at 240 °C. Subsequently, a family of analogous carbenes with R′ = H and R = $Bu^t$ (**1a**),[4] Mes, *p*-tolyl, *p*-chlorophenyl,[2] 2,6-diisopropylphenyl,[5] Me (the latter is stable only in solution)[2] was published by the same group. Related carbenes with various R and R′ were also reported.[6–9]



**1a** R = $Bu^t$, R′ = H
**1b** R = R′ = H



**2**



**3a** R = $Bu^t$, R′ = X = H
**3b** R = R′ = X = H

Soon, the saturated congeners of **1**, compounds **2**, were synthesized, which also appeared stable, although less than **1**, and more reactive.[10,11]

Enhanced stability of **1** compared to **2** could be explained by aromaticity. Since the molecule of **1** contains six π-electrons in a planar cycle, it obeys the Hückel rule. The aromaticity of **1** was discussed[4,12–14] and confirmed using energetic, chemical, structural and magnetic criteria. However, different approaches lead to diverse conclusions regarding the degree of cyclic π-electron delocalization in **1**. For instance, Arduengo believed that this phenomenon does not play a dominant role in the stability of **1**; in particular,[15] the stability of carbenes **1** was regarded as kinetic and explained by electron density accumulation around the carbene center, which protects the molecules from an attack by nucleophiles.

Since the role of aromaticity in **1** is still debated, any new information may shed light on the subject. An informative indicator of π-conjugation is vibrational spectroscopy, especially Raman intensity data. As found by Shorygin,[16,17] π-conjugation leads to a decrease in frequency and a many-fold increase in the intensity of Raman lines corresponding to the symmetric stretching vibrations of the bonds participating in conjugation.

The vibrational and electronic spectra of carbenes **1** and their tetravalent analogues **3** were not studied previously. Only the IR spectra of **1a** and **3a** (as pressed pellets and Nujol mulls) in a limited region were reported as a set of figures.[18] Dixon and Arduengo[19] computed the vibrational frequencies of model compound **1b** and its tetravalent analogue **3b** at the MP2/cc-pVTZ level of theory.

Here, we report the Raman, IR and UV spectra of **1a** and the quantum-chemical calculations of the molecular geometry, normal mode frequencies and eigenvectors and the NICS index.[‡] As no analogues of **1a** with the tetravalent C atom (**3**) were available, we made the same calculations for the molecule of **3a**.

Previously,[25,26] we briefly reported the Raman and UV spectra of Si and Ge analogues of **1a** and related compounds of tetravalent El atoms. The results of this study will enable a comparison in the series El = C, Si, Ge.

The planar structures of the ring and the $C_3N$ moieties in **1a** were demonstrated by X-ray investigations.[4,18] Not taking into account the hydrogen atoms in $Bu^t$ groups, the test molecule belongs to the symmetry point group $C_{2v}$ and its 39 normal modes are distributed among the symmetry species as follows:

$$\Gamma(C_{2v}) = 13A_1 + 7A_2 + 12B_1 + 7B_2.$$

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[‡] Carbene **1a** was synthesized according to a published method.[4]

Raman spectra in the region 100–3600 $cm^{-1}$ were measured using a Jobin-Yvon LabRAM laser Raman spectrometer equipped with a CCD detector and a microscope. Excitation line was 632.8 nm of a He/Ne laser. The solid samples were sealed in capillaries under an inert atmosphere. IR spectra in the region 300–3600 $cm^{-1}$ were recorded with a Carl Zeiss M-82 spectrophotometer and a FT-IR Nicolet Fourier spectrometer, UV spectra with a Carl Zeiss M-80 spectrophotometer. Samples for UV and IR spectroscopy were obtained by sublimation on a cooled (77 K) target in a vacuum cryostat. The IR spectrum, being obtained by a more adequate technique for this unstable substance, significantly differs from that reported previously.[18]

Quantum-chemical calculations of the molecular geometry and normal coordinate analysis for **1a** and **3a** were carried out using GAUSSIAN 03.[20] They were performed at various levels of theory: PBE/6-31+G(d),[21] B3LYP/6-31+G(d)[22] and MP2/6-311+G(d,p).[23] Vibrational frequencies obtained with PBE/6-31+G(d) appeared closest to the experimental values. This is especially true of the $\nu_{C=C}$ vibration, the most important for this study (calculated, 1553; experimental, 1556 $cm^{-1}$). That is why we present for **1a** and **3a** the results computed at this level. NICS index for **1a** was computed[24] at the B3LYP/6-31+G(d,p) level.

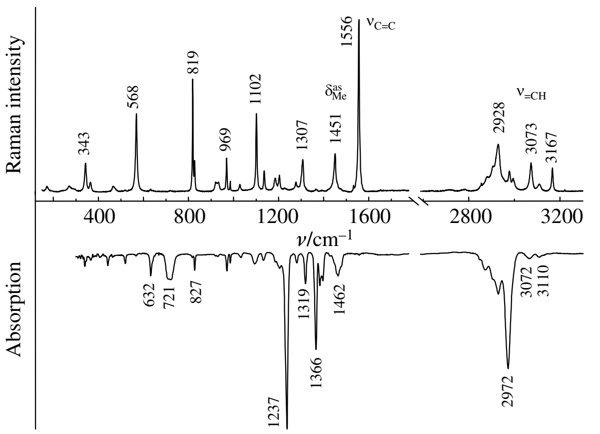

**Figure 1** Raman and IR spectra of polycrystalline **1a**.

The $A_1$, $B_1$ and $B_2$ modes are both Raman and IR active, while $A_2$ ones are only Raman active. As usual, the vibrations of Me groups obey their own local symmetry $C_{3v}$. The Raman and IR spectra of **1a** are presented in Figure 1 and Table 1. The assignment of the salient spectral features based on their IR and Raman intensity, on comparison with the spectra of related molecules and the results of normal coordinate analysis, is given in Table 1 (only coordinates that contribute mostly to the normal mode are indicated). As normal coordinate analysis was done in a harmonic approximation, it is natural that it overvalues the frequencies of the modes with H atom participation, especially the $\nu_{CH}$ stretching frequencies.

**Table 1** Vibrational spectrum of **1a**.[a]

| Calculated PBE/6-31+G(d) | | Experimental frequencies/cm$^{-1}$ | | Symmetry species | Assignment |
|---|---|---|---|---|---|
| Frequency/cm$^{-1}$ | IR intensity | IR | Raman | | |
| | | | 3167 (m) | | $2\nu_{C=C}$ |
| 3226 | 7 | 3110 (w) | 3110 (w) | $B_1$ | $\nu^{as}_{=CH}$ |
| 3201 | 1 | 3072 (w) | 3073 (m) | $A_1$ | $\nu^{s}_{=CH}$ |
| | | | 2994 (w) | | |
| 2980– | 45 | 2972 (vs) | 2978 (w) | | $\nu^{as}_{CH}$ in Me |
| 3080 | 51 | 2927 (m) | 2928 (s) | | $\nu^{s}_{CH}$ in Me |
| | | 2904 (sh) | 2904 (sh) | | $2\delta^{as}_{Me}$ |
| | | 2870 (w) | 2875 (w) | | |
| | | | 2775 (vw) | | |
| | | | 2705 (w) | | |
| 1553 | 2 | | 1556 (vs) | $A_1$ | $\nu_{C=C}$ |
| 1480 | 13 | 1462 (s) | 1451 (m) | | $\delta^{as}_{Me}$ |
| 1380 | 13 | 1396 (m) | | | $\delta^{s}_{Me}$ |
| 1373 | 36 | 1366 (vs) | 1365 (vw) | | $\delta^{as}_{=CH} + \nu^{as}_{=C-N}$ |
| 1305 | 13 | 1319 (s) | 1307 (m) | $A_1$ | $\nu^{s}_{=C-N} + \delta_{Me}$ |
| 1276 | 5 | 1280 (m) | 1277 (w) | $B_1$ | $\nu^{as}_{C^{II}-N} + \delta_{Me}$ |
| 1218 | 161 | 1237 (vs) | | | $\delta^{s}_{Me} + \delta_{CH} + \nu_{C-C}$ |
| 1209 | 2 | 1203 (w) | 1202 (w) | | $\nu^{as}_{C^{II}-N}$ |
| 1194 | 19 | 1186 (sh) | 1184 (w) | | $\nu^{s}_{C^{II}-N}$ |
| 1117 | 10 | 1132 (w) | 1135 (w) | $B_1$ | $\delta^{as}_{=CH} + \delta_{Me}$ |
| 1073 | 10 | 1094 (m) | 1102 (s) | $A_1$ | $\delta^{s}_{=CH} + \nu_{C-C}$ |
| 1024 | 1 | 1031 (w) | 1026 (w) | | $r_{Me}$ |
| 965 | 2 | 985 (w) | 984 (w) | $A_1$ | $\delta^{s}_{=CH} + \delta^{s}_{=C-N}$ |
| 960 | 14 | 969 (m) | 969 (m) | $B_1$ | $\delta^{as}_{=CH} + \delta^{as}_{=C-N}$ |
| 817 | 6 | 827 (m) | 827 (m) | | $r_{Me}$ |
| 806 | 1 | 816 (vw) | 819 (vs) | $A_1$ | $\delta_{=CH} + \delta_{N-C^{exo}}$ |
| 665 | 53 | 721 (s) | | | $\rho^{as}_{=CH}$ |
| 622 | 21 | 632 (s) | 631 (vw) | $B_2$ | $\rho^{s}_{=CH}$ |
| 555 | 2 | 568 (vw) | 568 (s) | $A_2$ | ring puckering |
| 509 | 5 | 518 (m) | | | ring puckering |
| 455 | 2 | 466 (vw) | 464 (vw) | | |
| 428 | 6 | 443 (m) | | | |
| 353 | 3 | | 364 (w) | | |
| 330 | 2 | | 343 (m) | | |
| 269 | 1 | | 267 (w) | | $\tau_{Me}$ |
| 160 | 0 | | 172 (w) | | |

[a] The C–N bonds which involve the divalent C atom in the ring are denoted as $C^{II}$–N, those in the ring, of the =C–N type, as =C–N. N–$C^{exo}$ corresponds to the *exo*-C–N bonds between the N atoms and Bu$^t$ groups.

The assignment of Me group vibrations is straightforward. These include stretching $\nu^{s}_{CH}$ and $\nu^{as}_{CH}$ modes at 2927 and ~2975 cm$^{-1}$, deformations $\delta^{as}_{Me}$ at ~1460 cm$^{-1}$ and $\delta^{s}_{Me}$ at ~1390 cm$^{-1}$, Me rocking modes at ~1030 and 827 cm$^{-1}$, and a Me twisting mode at 267 cm$^{-1}$. The presence of the HC=CH fragment is characterized by a so-called double bond stretching vibration $\nu_{C=C}$ at 1556 cm$^{-1}$, by symmetric and antisymmetric =CH bond stretches, $\nu_{=CH}$ at 3072 and 3110 cm$^{-1}$, and by in-plane $\delta_{=CH}$ (~1100 and ~817 cm$^{-1}$) and out-of-plane $\rho_{=CH}$ (~720 and ~630 cm$^{-1}$) vibrations. The frequencies of these features fall within the same regions as those of cyclopentene and 3-alkylcyclopentenes.[27] All other vibrations of **1a** are of heavily mixed origin, possessing complex eigenvectors (see Table 1).

The most informative is the $\nu_{C=C}$ mode. Before considering the implications of its frequency and intensity, it is necessary to ascertain that this normal mode is well localized. Indeed, normal coordinate analysis shows that its eigenvector involves predominantly the $\nu_{C=C}$ stretching coordinate (61% in PED). Various angle deformations participate in this mode as well, in particular, $\delta^{s}_{=CH}$, but each to a very small extent. It is important that the dicoordinate $C^{II}$ atom does not take any part in this vibration. This means that it is a real $\nu_{C=C}$ vibration and its frequency and intensity reflect electronic properties of the C=C bond. In the Raman spectrum of **1a**, the $\nu_{C=C}$ line exhibits a frequency of 1556 cm$^{-1}$, lowered compared to that of cyclopentene and 3-alkylcyclopentenes (~1615 cm$^{-1}$).[27] This comparison is not absolutely correct; it takes into account the influence of the five-membered ring geometry but does not make allowance for the interaction of the double bond with nitrogen atoms. A legitimate model to compare with **1** would be a related molecule like **3** with a tetravalent central carbon atom. As the IR spectrum of **3a** was published,[18] this molecule was chosen to carry out corresponding calculations.

Near coincidence of the calculated (1553 cm$^{-1}$) and experimental (1556 cm$^{-1}$) $\nu_{C=C}$ frequencies for **1a** allows us to ascertain that the calculated $\nu_{C=C}$ frequency value for **3a** (1610 cm$^{-1}$) is correct, especially because a value of 1616 cm$^{-1}$ could be found among the IR features reported.[18] This value is also close to those observed for cyclopentene and 3-alkylcyclopentenes. Therefore, the interaction of the C=C bond with nitrogen atoms in **1a** does not significantly affect the $\nu_{C=C}$ frequency.

Thus, it is apparent that the $\nu_{C=C}$ frequency in the spectrum of **1a** is about 60 cm$^{-1}$ lower than that of the tetravalent C analogue **3a**, which could be a consequence of cyclic π-conjugation in **1a**. Note that almost the same difference between the calculated $\nu_{C=C}$ frequencies of **1b** and **3b** was obtained.[19]

As a measure of Raman intensity enhancement of the $\nu_{C=C}$ line, we used the ratio of this line intensity to that of the line at about 1450 cm$^{-1}$. The latter corresponds to the methyl group deformation $\delta^{as}_{Me}$ and is not sensitive to π-conjugation. For **1a**, the intensity ratio $I(\nu_{C=C})/I(\delta^{as}_{Me})$ is about 5. As mentioned above, we had no Raman spectra of tetravalent carbon atom compounds **3** to compare with this value. However, an indirect comparison could be made using the Raman intensity data[27] for various alkylcyclopentenes, which were measured using a so-called cyclohexane scale (the intensity of the cyclohexane line at 802 cm$^{-1}$ is taken as 250 units). Analysis of the data presented shows that all cyclopentene derivatives with non-conjugated C=C bond and alkyl substituents in the 3- and/or 4-positions exhibit a $\nu_{C=C}$ line with a nearly constant frequency (~1615 cm$^{-1}$) and intensity (average 135 units). According to the same source, the $\delta^{as}_{Me}$ line at ~1450 cm$^{-1}$ in the Raman spectra of various alkylcyclopentenes has also a nearly constant intensity per Me group (average 33 units). Thus, we could assume that, if an

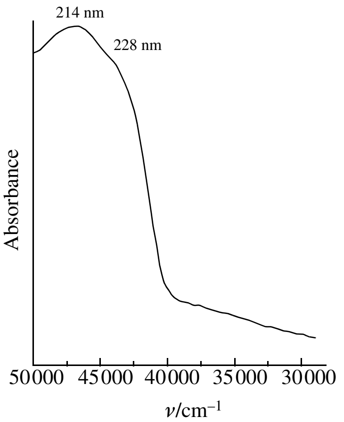

**Figure 2** UV spectrum of a solid film of **1a** (sublimed on a cooled 77 K target in a vacuum cryostat).

alkylcyclopentene possesses six Me groups attached to carbon atoms (as in **1a**), its intensity ratio $I(\nu_{C=C})/I(\delta^{as}_{Me})$ would be 135/198 ≈ 0.7. This value is much lower than ~5, which was observed for **1a**. This speculation is, of course, approximate and qualitative, but it highlights the significant enhancement of the $\nu_{C=C}$ line in the Raman spectrum of **1a**.

Another indicator of π-conjugation in the Raman spectrum of **1a** is the line of the overtone ($2\nu_{C=C}$) at 3167 cm$^{-1}$, too strong for an ordinary overtone. Raman intensity enhancement of the overtones of stretching vibrations, corresponding to conjugated bonds, was observed and explained by Shorygin.[16] Surprisingly, the frequency of this overtone is greater than 2×1556 cm$^{-1}$. This may be due to a very strong Fermi resonance of this overtone with the $\nu_{=CH}$ fundamental.

Thus, the Raman data support the aromatic nature of **1a** through the two independent criteria: $\nu_{C=C}$ line frequency lowering (reflecting a decrease in the C=C bond order) and intensity enhancement (due to cyclic π-electron delocalization).

The same conclusion can be made on the basis of the electronic absorption spectra. In the UV spectrum of solid **1a** sublimed on a cooled target (Figure 2), a broad absorption band is observed with two maxima at 214 and 228 nm. Cyclopentene[28] and its alkyl derivatives, for comparison, do not exhibit any absorption bands higher than 200 nm.

We have also calculated the NICS aromaticity index[24] for **1a** at a distance of 1 Å above the planar centroid (to avoid anisotropic effects). It was found equal to –9.7 compared to –10.2 for benzene. The negative sign points to the aromaticity of **1a**, whereas the lesser value indicates that the π-delocalization in **1a** is weaker than in benzene. The latter agrees well with the conclusions made previously.[13,14] Thus, the above data confirm the idea of aromaticity of **1a**, basing on optical spectroscopy and NICS criteria.

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