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Carbones ($-C^{2-}-$), carbenes ($-C:-$) and carbodications ($-C^{2+}-$) on the magnetic criterion†

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The spatial magnetic properties, particularly the through-space NMR shieldings (TSNMRSs, the anisotropy effect in ^{1}H NMR spectroscopy) of carbenes, carbones and carbodication (carbo2+) compounds (with and without stabilization by NMe_2 π-donation) and those of a number of carbo2+ analogues have been calculated using the GIAO perturbation method, employing the nucleus-independent chemical shift (NICS) concept, and visualized as iso-chemical-shielding surfaces (ICSS) of various sizes and directions. TSNMRSs prove the electronic structure of carbo2+ compounds to be completely different from those of carbenes and carbones, preferring both the π-electron distribution and the structure of allenes/cumulenes despite the central carbon atom being the most electrophilic centre.

Introduction

Carbenes are a class of bivalent carbon species with six valence electrons (one σ-type lone pair and one vacant p_z orbital). In N-heterocyclic carbenes (NHCs) and cyclic(alkyl)(amino)-carbenes (CAACs), the extreme stabilization by one or two nitrogen atom(s) adjacent to the carbene electron-deficient centre was already emphasized in the initial reports[1,2] [the electronegativity of the nitrogen atom(s) (−I substituent effect) and the electron donation of the N-lone pair(s) (+M substituent effect) stabilize the carbenes via ylide mesomeric contributor(s) (Scheme 1)]:

The π-donation of the nitrogen lone pair(s) into the formerly empty p_z orbital of the ylide carbon atom is proved by dynamic NMR studies of the restricted rotation about the partial C,N double bonds (Scheme 1) in non-cyclic bis(dialkylamino)carbenes (NCACs): dependent on the substituents at nitrogen, the C,N bonds have variable but substantial double bond character ($\Delta G^{\#}$ = 10.7 to 19.35 kcal mol^{-1}).[3,4]

Carbones bear comparable allene-like, carbene-like and carbone-like resonance contributors, among them the one with the central carbon atom carrying two negative charges (Scheme 2).[5–9]

Besides allene-like and carbene-like mesomeric contributors (the latter in phosphorus allenes), a multiplicity of carbone-like compounds (bent allenes, carbodiphosphoranes and chalcogen-stabilized carbones) can be identified.

Finally, another carbon species was very recently discovered by Bertrand and coworkers[10] with a mesomeric contributor of two positive charges on the central carbon atom (carbo2+, doubly oxidized carbene); however, it can stabilize itself in a number of allene-like, cumulene-like canonical structures, and even a higher degree of multiple bond character on the central carbon atom is suspected (Scheme 3).[10]

After unequivocally identifying the dominant mesomeric contributors in carbenes (ylide structures)[11] and carbones (bent allenes, carbodiphosphoranes and chalcogen-stabilized carbones) on the magnetic criterion,[12] we were strongly interested in how the extremely conjugated carbo2+ structure (Scheme 3) behaves under the same criteria. The main goal hereby was to identify the predominant mesomeric contributor and, from this, to assign the existing π-electron distribution and thus the electronic structure of the novel carbo2+ compound.[10] This is the main object of this paper.

We employed our through-space NMR shielding (TSNMRS) concept[13–15] to qualify the spatial magnetic properties (actually, the anisotropy effects in ^{1}H NMR spectroscopy) of the studied species. Along this concept, the NICS values were calculated for a grid of ghost atoms surrounding the molecules in order to locate diatropic and paratropic regions around the structures. The TSNMRSs were visualized as iso-chemical-shielding surfaces (ICSS) and employed to qualify and quantify the anisotropy effects of the studied compounds. While the normally employed specifications of NICS values to quantify *e.g.* (anti)aromaticity are theoretical items, the experimental $\Delta\delta$/ppm in proton NMR spectra are the molecular response properties of TSNMRS values.[16]

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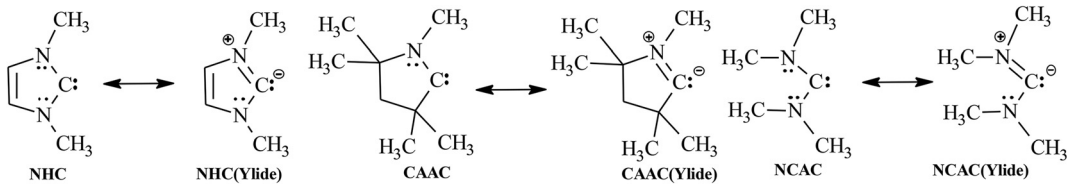
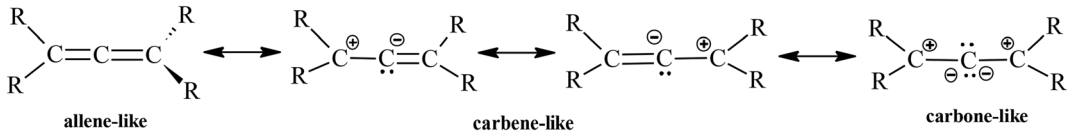
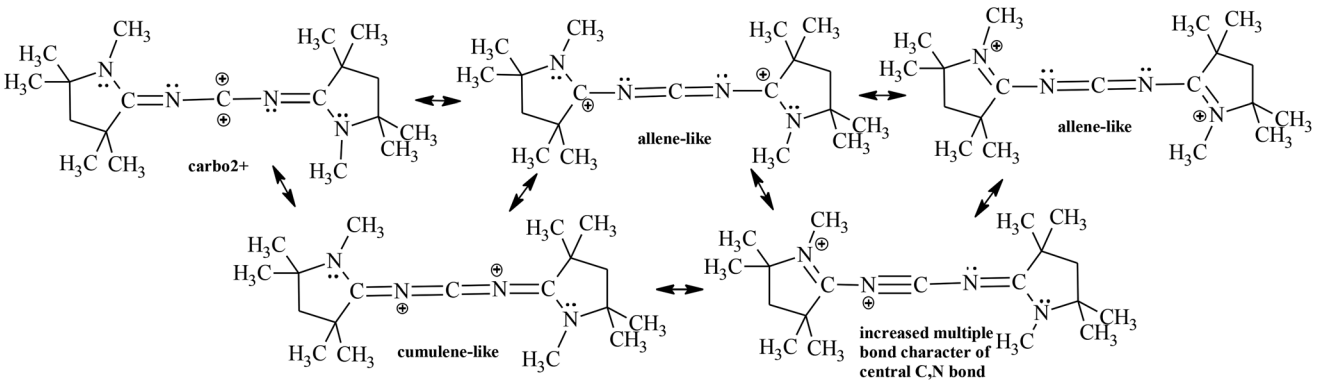


Scheme 1 Mesomeric contributors of NHCs, CAACs and NCACs.



Scheme 2 Mesomeric contributors of carbones.

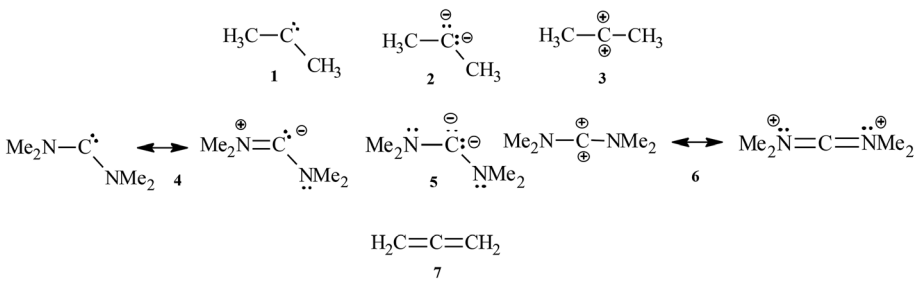


Scheme 3 Mesomeric contributors of carbo2+ compounds.

Results and discussion

Introducing the topic, the various ICSSs of the TSNMRS of singly non-conjugated carbenes **1** (Me_2C:), carbones **2** (Me_2C^{--}) and the carbo2+ relative **3** ($Me_2C^{+\ +}$) have been calculated (Scheme 4)[17] and are shown in Fig. 1. While anisotropy effects of the central carbon atom of carbenes and carbones are comparable in size and extension, the corresponding anisotropy effect in the comparable carbon2+ compound **3** proves to be completely different: the carbon2+ compound **3** is linear (see also Table 1); the distinct shielding anisotropy effect above/below plane in the angled carbenes and carbones disappeared and are replaced by a paratropic area located at the central carbon atom; the shielding ICSSs (familiar from carbenes and carbones, Fig. 1) are shifted to the methyl carbon atoms.

For the dis-dimethylamino analogues in Fig. 2, stabilization by conjugation proves to be an alternative: the conjugated carbenes **4** stabilize themselves essentially,[11] if not exclusively,[5,6] *via* ylide structures and thereby significantly reduce the anisotropy effect of the central electron-deficient center; due to the angled structure of the ylide, the dimethylamino substituents are slightly twisted from the common resonance plane



Scheme 4 Dis-methyl- (**1–3**), dis-dimethylamino-carbene, -carbone and -carbo2+ (**4–6**) and allene (**7**).

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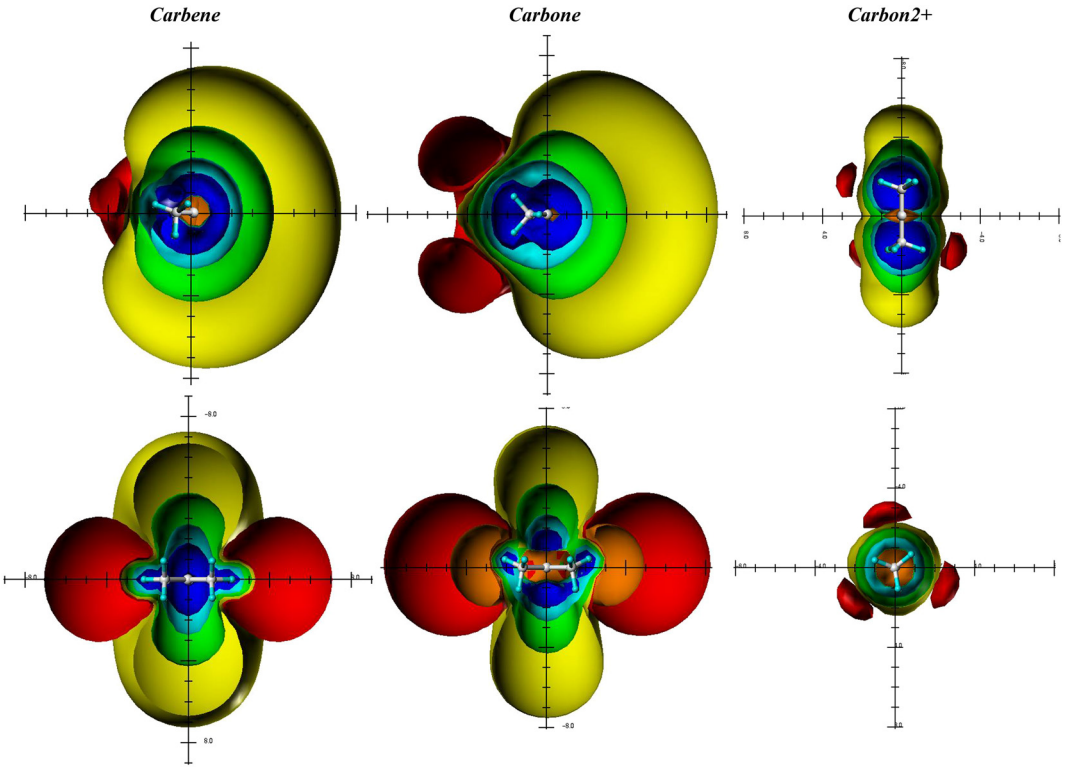

Fig. 1 Visualisation of the spatial magnetic properties (TSNMRSs) of dimethylcarbene **1**, dimethylcarbone **2** and dimethylcarbon2+ **3** by different ICSS of −0.1 ppm (red) deshielding and 5 ppm (blue), 2 ppm (cyan), 0.5 ppm (green) and 0.1 ppm (yellow) shielding.

Table 1 Geometry and NMR parameters of carbodications and comparable compounds, fully optimized at the MP2/6-311G(d,p) level of theory without constraints

	Geometry		NMR parameters	
No.	Bond length (Å) dC–C/C–N	Bond angle C–C–C/N–C–N	$\delta(^{13}C)$/ppm	ICSS (+5, +2 and 0.5)/(Å)
$Me_2C\#$				
1	1.481	111.6°	820.0	2.0, 2.7 and 4.25
2	1.454	103.55°	152.0	1.8, 2.7 and 4.2
3	1.346	Linear	325.7	paratropic hole
$(NMe_2)_2C\#$				
4	1.354	116.1°	283.4	1.6, 2.1 and 3.0
5	1.339	145.0°	145.1	1.3, 1.7 and 2.3
6	1.245	Linear	189.8	1.0, 1.4 and 2.1
$CH_2{=}C{=}CH_2$				
7	1.430	Linear	203.5	1.2, 1.5 and 2.1, but above centers of C=C bonds: 1.5, 1.8 and 2.3

(Table 1). Conjugated carbone structures **5** also significantly reduce the anisotropy effect but retain the characteristic ball-like anisotropy effect of the central carbon atom ($-C^{2-}-$).[12] The carbone molecule is also angled (Table 1), as the $Me_2N^+{=}C^-{-}NMe_2$ carbene analogue **4** is perfectly symmetric with the $=NMe_2$ moieties exactly orthogonal to each other, but the NMe_2 groups are structurally pyramidal; because of the already existing doubly negatively charged central atom in carbones, the π-donor effect of the amino groups can only develop to an extent reduced accordingly.

The carbon2+ structure **6**, finally, exhibits a completely different behavior on the magnetic criterion: the distinctive but not very strong deshielding zone around the central carbon atom in **3** disappeared, but the linearity in **6** remained. An allene-conform structure can be seen (see also Table 1), which has C=N double bonds in-plane of the $C{=}(NMe_2)_2$ fragments, with the $C{=}C(NMe_2)_2$ moieties exactly orthogonal to each other. In-plane of the completely planar $C(sp){=}C(NMe_2)_2$ fragments, the anisotropic effect of the C=N double bonds emerges clearly as in real allene structures (*vide infra*).

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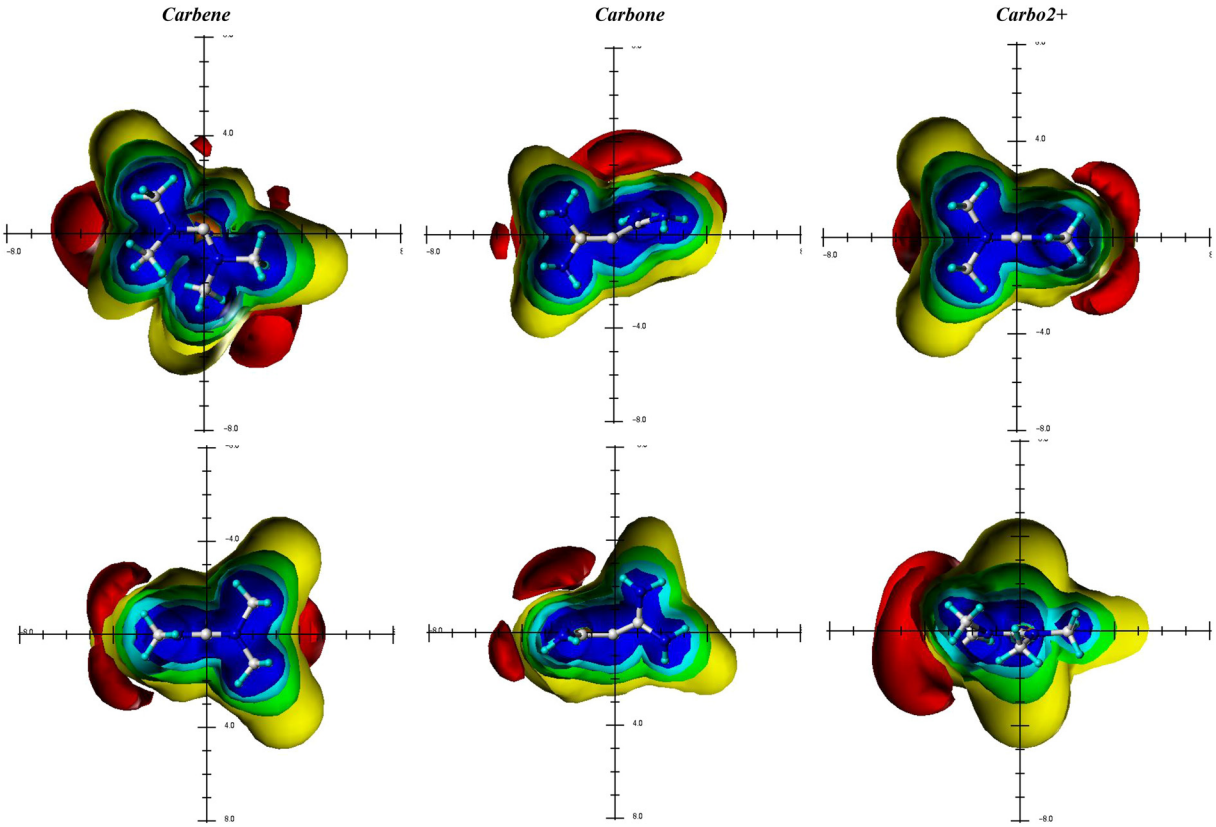

Fig. 2 Visualisation of the spatial magnetic properties (TSNMRSs) of dis-dimethylamino-carbene **4**, dis-dimethylamino-carbone **5** and dis-dimethylamino-carbon2+ **6** by different ICSS of −0.1 ppm (red) deshielding and 5 ppm (blue), 2 ppm (cyan), 0.5 ppm (green) and 0.1 ppm (yellow) shielding.

These initial results of the model carbenes, carbones and carbo2+ structures brings us significantly forward in answering the initial question: as Guy Bertrand and coworkers suggested,[10] due to the higher electronegativity of nitrogen compared to carbon and the distinctive lone pair donation (+M effect) of the amino groups, the positive charges are not mainly located on the central carbon of the carbon2+ compound **6** but on the neighboring nitrogen atoms in exact allene structures; the direct comparison of the spatial magnetic properties with the allene $CH_2{=}C{=}CH_2$ **7** in Fig. 3 proves to be

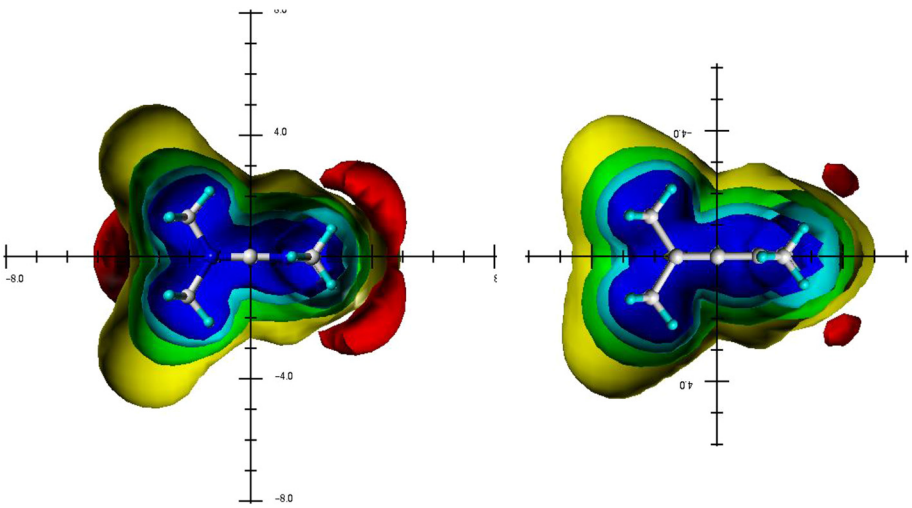

Fig. 3 Visualisation of the spatial magnetic properties (TSNMRSs) of dis-dimethylamino-carbon^{2+} (**4**) and allene $CH_2{=}C{=}CH_2$ (**7**) by different ICSS of −0.1 ppm (red) deshielding and 5 ppm (blue), 2 ppm (cyan), 0.5 ppm (green) and 0.1 ppm (yellow) shielding.

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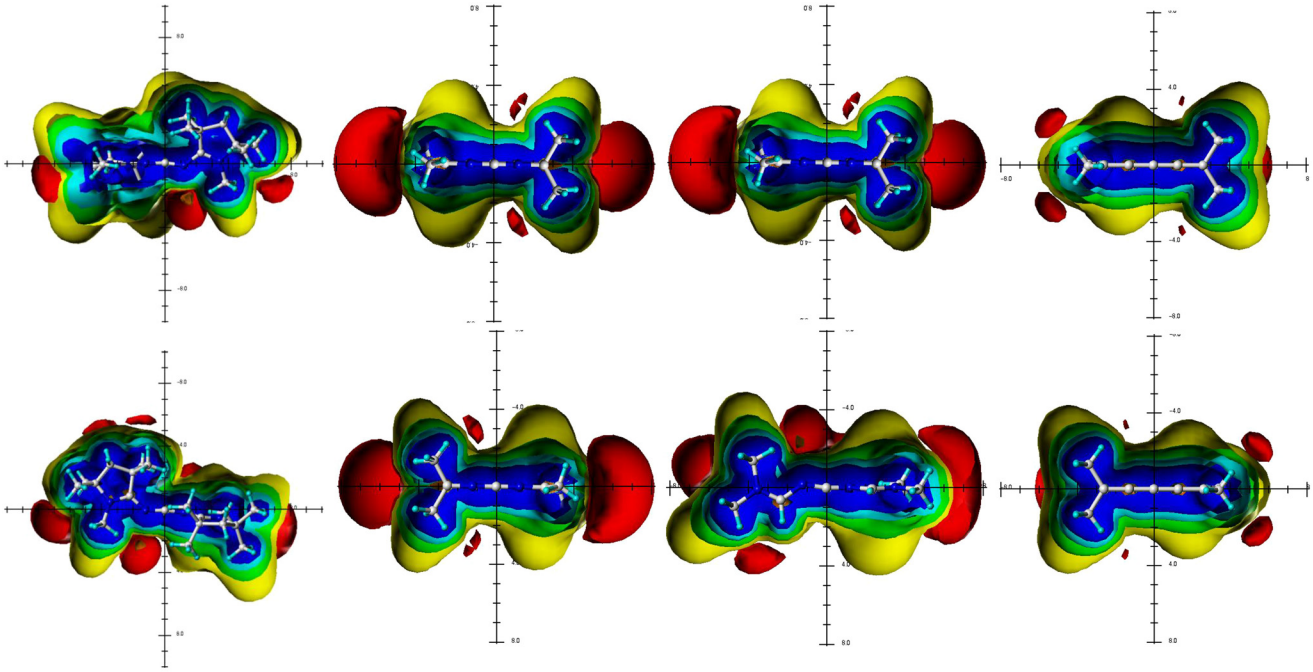

Fig. 4 Visualisation of the spatial magnetic properties (TSNMRSs) of carbodication $\mathbf{1}^{2+}$ (**8**), two analogues (**9** and **11**) and tetramethyl-[4]cumulene (**10**) (from left) by different ICSS of −0.1 ppm (red) deshielding and 5 ppm (blue), 2 ppm (cyan), 0.5 ppm (green) and 0.1 ppm (yellow) shielding.

unequivocal. Especially crucial proves to be, at this point, the characteristic anisotropy effect of the C═N and C═C double bonds, respectively, of the two C═X(NMe$_2$)$_2$ (X = C, N) fragments.

Now to the recently synthesized carbo2+ structure **8**,[10] two analogues (**9**, **10**) and [4]cumulene **11** that are intended to support the generality of the former conclusions from the model compounds **1–7** on the magnetic criterion: the TSNMRS values as ICSSs of different size and direction are given in Fig. 4., and structural and magnetic data for **8–11** are given in Table 2. The occurrence of allene-like structures of the carbon2+ compounds **8–10** compared with the [4]cumulene structure **11** is confirmed. This is particularly demonstrated by the orthogonality of the terminal moieties. However, only **9** (as **6**) is still linear; **8** and **11** deviate from linearity, with N–C–N at 168.5° and 163.2°, respectively, and C–N–C at 168.0° for both. On the other hand, the spatial magnetic properties (TSNMRSs) are even more convincing. As in [4]cumulene **11**, the various ICSSs of **8–10** are spread more or less evenly over the allene (cumulene)-like double bonds and rise slightly towards the end of the molecules [see ICSS (+0.1 ppm) yellow]; perpendicular to this (the other side of the molecule due to sp hybridization of the central carbon atom), they fall off quickly. All in all, the present allene(cumulene)-like structure is convincingly depicted. The TSNMRSs of the CAAC molecule **8** are somewhat confusing due to the highly substituted 5-membered rings, but despite the extensive substitution, the present allene(cumulene)-like structure and corresponding π-electron distribution proves to be predominant (Scheme 5).

Table 2 Geometry and NMR parameter of carbodications and comparable compounds, fully optimized at the MP2/6-311G(d,p) level of theory without constraints

	Geometry		NMR parameters		
	Bond lengths (Å)				
No.	dC^1–N (Å)	dC^2–N(Å)	Bond angles N–C—N/C^2–N–C^1	δ(^{13}C)/ppm	Others
C═C═C═C═C					
10	1.284	1.326	Linear	126.5	C^2 (189.0); C^3 (114.5)
C═N═C═N═C					
8	1.225; 1.197	1.368; 1.349	168.5°;163.2° 1.361°;147.8°	138.6; 119.8	C^3 (183.0); CAAC units almost orthogonal (79.6°)
9	1.210	1.311	Linear	245.4	═CMe$_2$ units (85.2°)
11	1.223	1.336; 136.8°	168.0°	135.2	C^3 (157.9); –CH═NMe$_2$ units (83.4°)
4	1.245	—	Linear	189.8	–NMe$_2$ units orthogonal

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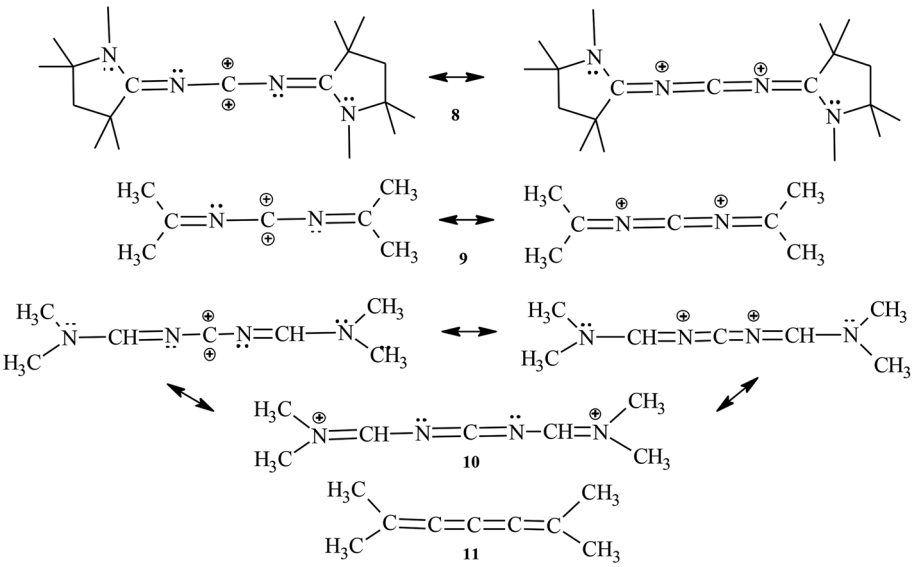
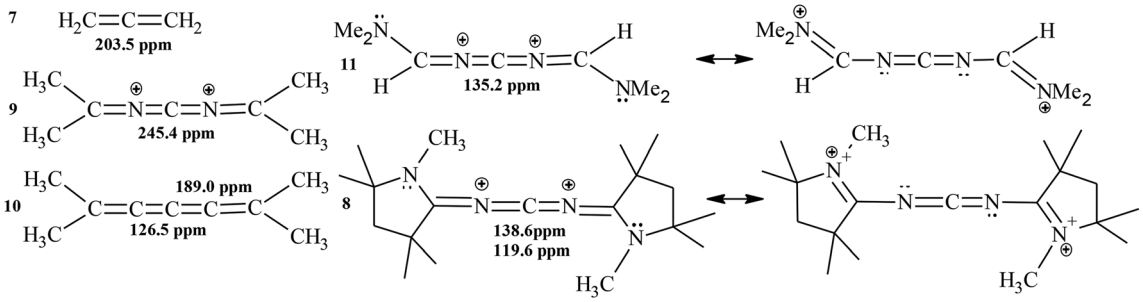


Scheme 5 Structures of the carbo2+ family **8–10** and [4]cumulene **11**.



Scheme 6 ^{13}C Chemical shifts of the central carbon atom in **7–11**.

The choice between cumulative (suggested by Bertrand *et al.*)[10] and allene resonance contributors (Scheme 3) cannot be decided only from the spatial magnetic properties: Wiberǵs bond orders in **8** [C^1–N^1 (1.92), N^1 –C^2 (1.29) and C^2–N^2 (1.63)][10] and in the CAAC (ylide) [(1.53)[11b] (Scheme 1)] point more urgently to a predominant allene resonance contributor. The dominating, if not complete, C═N double bond of the ylide structure of carbenes has been proven.[3,4] Furthermore, the ^{13}C chemical shifts of the central carbon atom in **8**, **9** and **11** also demonstrate the clear dependence on the presence of the CAAC nitrogen in **8** (and of the terminal nitrogen atom in **11**) and supports the presence of the allene-like resonance contributor. Without the terminal nitrogen atoms, the ^{13}C chemical shift of the central carbon atom is much further down field (Scheme 6).

Despite the by-far predominant allene (cumulene)-like mesomeric contributor, the canonical structure of the carbo2+ compound **8** with the corresponding vacant orbitals must be detectably present, because the central C atom is chemically confirmed (double bond formation, successful mono- and di-nucleophilic attack)[10] as the dominant electrophilic site of the molecule.

Conclusion

The spatial magnetic properties, through space NMR shieldings (TSNMRSs, the anisotropy effects in ^{1}H NMR spectroscopy) of carbenes, carbones and the recently synthesized new class of carbo2+ compounds have been calculated and, together with geometry and electronic structure, compared on the magnetic criterion. While carbenes prefer the ylide (N^+═C^-–), carbones, the carbone (C–C^{2-}–C) and not the allene (C═C═C) resonance contributor, carbo2+ compounds unequivocally occur as allene (N^+═C═N^+) canonical structure, confirmed by geometry and ^{13}C chemical shift data.

Author contributions

The authors declare equal participation.

Conflicts of interest

The authors declare no conflicts of interest.

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17 The quantum chemical calculations were performed using the Gaussian 09 program package[18] and carried out on LINUX clusters. The studied structures were fully optimized at the MP2/6-311G(d,p) level of theory without constraints.[19] The obtained structures have been confirmed as local minima by performing harmonic frequency calculations at the optimized geometries.[20] NICS values[21,22] were computed on the basis of the MP2/6-311G(d,p) geometries using the gauge-including atomic orbital (GIAO) method[23,24] at the B3LYP/6-311G(d,p)[25–27] theory level.[28] Variation of the basis set was found to be of non-significant influence on the NICS values. To calculate the spatial NICS, ghost atoms were placed on a lattice of −10 Å to +10 Å with a step size of 0.5 Å in the three directions of the Cartesian coordinate system. The zero points of the coordinate system were positioned at the centers of the studied structures. The resulting 68 921 NICS values, thus obtained, were analyzed and visualized by the SYBYL 7.3 molecular modeling software;[29] different iso-chemical-shielding surfaces (ICSS) of −0.5 ppm (orange) and −0.1 ppm (red) deshielding, and 5 ppm (blue), 2 ppm (cyan), 0.5 ppm (green) and 0.1 ppm (yellow) shielding were used to visualize the TSNMRSs of the studied structures in the various figures. ICSSs are a quantitative indication of the anisotropy effect in ^{1}H NMR spectroscopy;[3–5] the computed shielding (deshielding) ICSSs quantify the corresponding anisotropy effect in ^{1}H NMR spectroscopy subject to the distance from the center of the molecules (in Å).[13–15]

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28 The lattice points ("ghost atoms") should be sensor points only without energy contribution in the present calculations. Only if DFT or HF calculations are applied this is true; in case of electron correlation calculations, the "ghost atoms" get their own electron density and show some influence on the energy of the studied molecule. In these cases the TSNMRS surfaces are heavily distorted.
29 SYBYL 7.3 Tripos Inc., 1699 South Hanley Road, St. Louis, Missouri 63144, USA, 2007.

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