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# On the electron delocalization in cyclopropenylidenes – An experimental charge-density approach

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Dedicated to Anthony J. Downs

## Abstract

The extent and nature of cyclic electron delocalization in free and coordinated cyclopropenylidene carbenes has been analyzed by combined experimental and theoretical charge-density studies. The significant asymmetry of the C–C bond lengths in substituted cyclopropenylidene carbenes was identified as cooperative effect which depends on contributions of both  $\sigma$ - and  $\pi$ -bonding. We show that analyses of (i) the topology of the Laplacian of the electron density distribution and (ii) the out-of-plane atomic *quadrupole* moments – the charge-density analogues of  $p_\pi$  occupation – allow to distinguish between the influence of  $\sigma$ - and  $\pi$ -electrons on cyclic electron delocalization. These studies hint for pronounced electron localization in the carbene lone pair region which dominates the electronic structure of free cyclopropenylidene carbenes and hinders the establishment of true aromaticity. We further investigated the electron donating/withdrawing ability of cyclopropenylidene ligands relative to *N*-heterocyclic carbenes. The experimental benchmark systems  $\text{LCr}(\text{CO})_5$  ( $\text{L} = 2,3$ -diphenylcyclopropenylidene and 1,2-dimethylimidazol-2-ylidene) show that the cyclopropenylidene ligand clearly displays the higher  $\pi$ -acceptor capability relative to *N*-heterocyclic carbenes.

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**Keywords:** Cyclopropenylidene; Carbene complexes; Experimental charge density; Topological analysis; Cyclic electron delocalization; Quantum theory of atoms in molecules

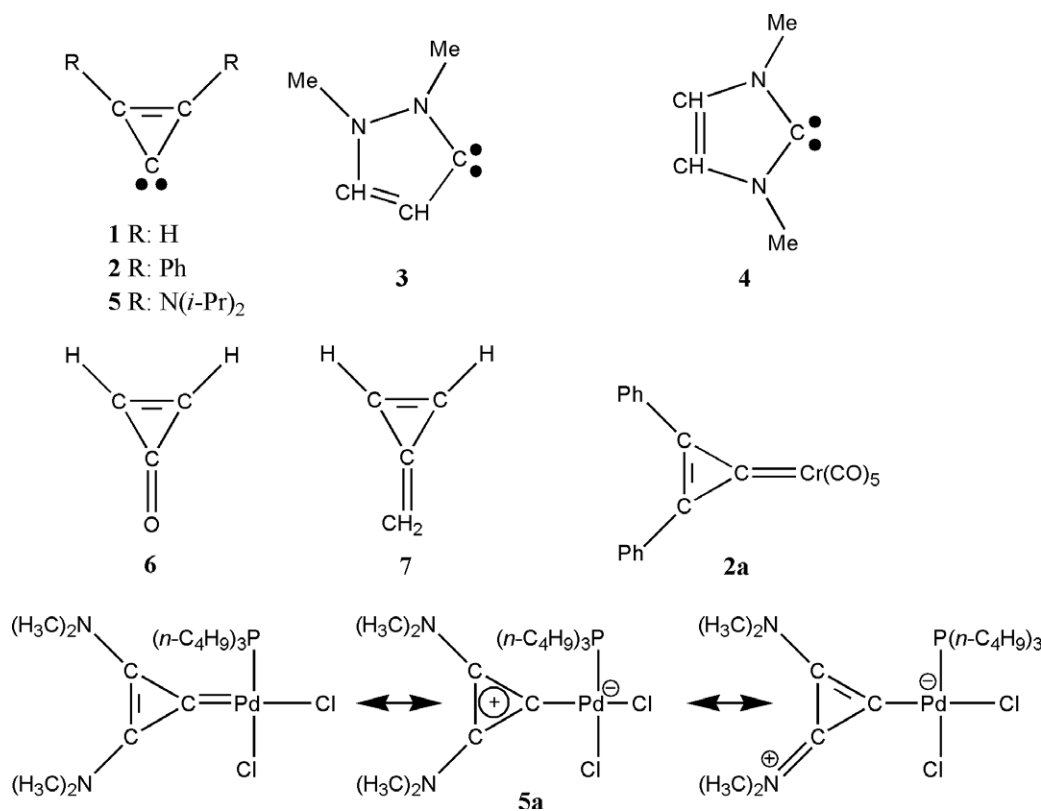
## 1. Introduction

Free cyclopropenylidene [1a] **1** and its diphenyl derivative [1b] **2** represent the prototypes of highly reactive singlet carbenes which could only be isolated so far in low-temperature matrices or detected indirectly in trapping reactions (Scheme 1). The instability of these carbenes is generally explained by the fact that the stability of singlet carbenes

critically depends on the presence of at least one  $\pi$ -donor substituent at the carbene centre [2]. However, for most free carbenes the presence of two  $\pi$ -donor substituents, of which at least one is an amino group is the prerequisite for a successful design of stable carbenes. For example, the *N*-heterocyclic 1,2-dimethylpyrazol-3-ylidene **3** has not been isolated yet while 1,3-dimethylimidazol-2-ylidene **4** displaying two  $\pi$ -donor substituents next to the carbene centre represents a text book example of a stable free carbene [3]. However, the pioneering isolation of bis(diisopropyl-amino)cyclopropenylidene **5** clearly contrasts the classical design concept for stable carbenes [4]. Lavallo et al. concluded that it is the  $\pi$ -donation from the amino group to the electron-deficient three-membered ring which renders **5** a thermally stable molecule with a melting point of

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Scheme 1.

107–109 °C [4]. According to these authors **5** represents a 2- $\pi$  Hückel aromatic compound and is thus a neutral analogue of the classical cyclopropenium salts explored by Breslow in the fifties [5]. In 1968 Öfele [6] showed another route to stabilize cyclic singlet carbenes by isolating and characterizing the complex of 2,3-diphenylcyclopropenylidene with penta-carbonylchromium, **2a**. This complex is remarkably stable (up to 200 °C) and its stability is likely due to the cyclopropenium cation nature of the carbene ligand as illustrated for the related diaminocyclopropenylidene palladium complex **5a** [7] in Scheme 1. In this respect **5**, **5a** and **2a** should display related electronic structures.

Indeed, X-ray structural analysis of **2a** [8] and **5** [4] showed that the three C–C distances in the cyclopropenylidenes are not identical: the distance between the formally double-bonded carbon atoms (C2–C3) is approximately 0.05 (**2a**) and 0.06 Å (**5**) shorter than the other two in the three-membered ring. It is interesting to note, that a similar type and extent of C–C bond asymmetry inside a three-membered ring has been found before in cyclopropenone **6** [9] – another prominent candidate for a neutral 2- $\pi$  Hückel aromatic which was first isolated in 1967 by Breslow and Ryan [10]. The fact that the extent and nature of aromaticity in **6** and methylenecyclopropene **7** [11] is still a matter of debate has been foreseen by Breslow who concluded already in 1973 “This again raises the question of the correlation between the different criteria of aromatic character and issues a caution that statements about *aromaticity* should be made only with respect to well-defined criteria and models.” [9a].

Indeed, ‘classical’ definitions of aromaticity as determined by Katritzky et al. [12] like geometrical criteria might be misleading in three-membered ring systems. The asymmetry of the C–C bond lengths in substituted cyclopropenylidenes and cyclopropenones is a cooperative effect which depends on contributions of both  $\sigma$ - and  $\pi$ -bonding [13]. Hence, a concept is needed which distinguishes between the influence of  $\sigma$ - and  $\pi$ -electrons on cyclic electron delocalization. Recently [14], combined experimental and theoretical charge-density studies of *N*-heterocyclic carbenes showed that a direct analysis of the electron density, based on the “Atoms in Molecules” approach [15], provides a wealth of information on the electronic structure of carbenes and carbene complexes. Here we present a topological analysis of the charge density of the classical example of carbene complex (**2a**) to shed more light on nature and extent of electron delocalization in cyclopropenylidene species.

## 2. Results and discussion

### 2.1. Structural analyses

Experimental charge densities of **2a** were obtained by fitting a multipole model [16,17] to high-resolution X-ray data (see Section 4), which were compared with the theoretical charge-density distribution obtained by DFT calculations at the B3LYP/6-311G(d,p) level of approximation [18,19]. A comparison of the relevant bond distances of

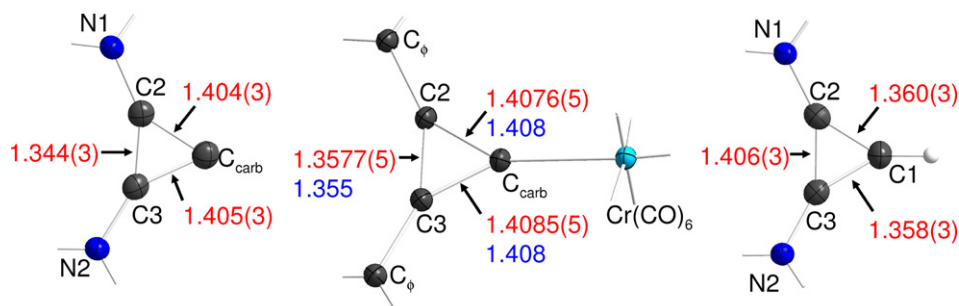


Fig. 1. Molecular structures of **5** [4], **2a** (this work), and the cyclopropenium cation [5-H]<sup>+</sup> [4]. The anisotropic displacement ellipsoids of **2a** at 100 K are shown at the 50% probability level; selected experimental (red, above) and theoretical (blue, below) structural parameters are specified in [Å/deg]. Only the parent atoms of the isopropyl and phenyl substituents were drawn for clarity reasons. (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

**2a** (Fig. 1 and Table 1) reveals a good agreement between theory and experiment.

Analysis of the salient geometrical parameters of **2a** obtained from multipolar refinements indicates already that cyclic electron delocalization inside the cyclopropenylidene unit appears to be hindered: the formal C=C double bond distance of 1.3577(5) Å within the three-membered ring in **2a** is 0.05 Å shorter than the corresponding C<sub>carb</sub>–C distances.<sup>2</sup> However, the bond length asymmetry is less pronounced relative to cyclopropenes, where such differences in C–C distances may exceed values of 0.2 Å [20]. We further note, that the bond length asymmetry is also pronounced in the free cyclopropenylidene **5**, which displays a shorter C=C double bond of 1.344(3) Å relative to **2a** or the more delocalized cyclopropenium cation ([5-H]<sup>+</sup>, 1.406(3)).

The classification of **5** as a true 2- $\pi$  Hückel aromatic is therefore not supported on the basis of geometrical criteria. Indeed, from a chemical point of view carbene **5** is well-known to act as  $\sigma$ -donor ligand which is prone to enhance its cyclic delocalization by donating charge to transition metal carbonyls. As a consequence, the diaminocyclopropenylidene palladium complex **5a** [7] (Scheme 1) displays three equal C–C bond distances [1.380(4)–1.385(5) Å] in the three-membered ring. Also the three valence angles closely conform to the ideal angle of 60° in **5a**. Increased electron delocalization upon metal coordination has also found in *N*-heterocyclic carbene complexes and could here also be correlated with the  $\sigma$ -donor/ $\pi$ -acceptor capabilities of carbene ligands [14]. In the following we analyze the topology of the charge density of **2a** to get further insight in the interplay between  $\sigma$ -donor/ $\pi$ -acceptor interactions

Table 1

Topological parameters at the bond (BCP) and ring critical points (RCP) of experimental and theoretical charge densities for **2a**<sup>a</sup>

Bond		$r(A-B)$	$\rho(r_c)$	$L(r_c)$	$\epsilon^b$
Cr–C <sub>carb</sub>	Exp	2.0437(4)	0.571(8)	–7.26(1)	0.08
	Calc <sup>c</sup>	2.0478	0.597	–7.176	0.07
Cr–C(O) <sub>ax</sub>	Exp	1.8815(5)	0.76(1)	–11.10(2)	0.02
	Calc	1.8922	0.78	–11.81	0.16
Cr–C(O) <sub>eq</sub>	Exp <sup>d</sup>	1.9073	0.805	–10.69	0.01
	Calc <sup>d</sup>	1.9086	0.750	–11.40	0.04
C–O <sub>ax</sub>	Exp	1.1585(12)	3.19(4)	22.4(3)	0.10
	Calc	1.1485	3.13	–10.6	0.001
C–O <sub>eq</sub>	Exp <sup>d</sup>	1.1478	3.14	–2.34	0.04
	Calc <sup>d</sup>	1.1470	3.14	–10.87	0.002
C <sub>carb</sub> –C2	Exp	1.4076(5)	1.84(2)	6.02(5)	0.76
	Calc	1.4083	1.94	13.92	0.30
C <sub>carb</sub> –C3	Exp	1.4085(5)	1.91(2)	8.08(5)	0.56
	Calc	1.4083	1.94	13.92	0.30
C2–C3	Exp	1.3577(5)	2.00(2)	10.14(5)	0.32
	Calc	1.3548	2.09	16.68	0.13
RCP	Exp		1.67(2)	–5.95(4)	
	Calc		1.64	–7.57	

<sup>a</sup> Bond distances ( $r$ ) in Å,  $\rho(r_c)$  in e Å<sup>–3</sup>,  $L(r_c)$  in e Å<sup>–5</sup>.

<sup>b</sup> The ellipticity  $\epsilon = \lambda_1/\lambda_2 - 1$  of a bond is a measure of the asymmetry in the charge distribution [26].

<sup>c</sup> B3LYP/6-311G(d,p) level of approximation.

<sup>d</sup> Average value.

and electron delocalization phenomena inside the cyclopropenylidene ring.

## 2.2. Electron localization in the lone pair region of the carbene atoms

We note that one of the phenyl substituents of **2a** is significantly rotated out-of-plane with respect to the cyclopropenylidene ring [7.49(3)°] [21]. Furthermore, a twisting of the phenyl groups by 6.9° with respect to the cyclopropenylidene moiety is predicted by the calculations resulting in an overall C<sub>2</sub> symmetry of the molecule in the gas phase. This distortion away from the ideal C<sub>2v</sub> symmetry is therefore not a result of crystal packing effects and causes slightly different experimental charge-density properties at the bond critical points of the C<sub>carb</sub>–C2 and C<sub>carb</sub>–C3 bonds

<sup>2</sup> The observed bond lengths in the cyclopropenylidene fragment in the closely related (2,3-diethoxycyclopropenylidene)-pentacarbonylchromium complex **8** are similar to those in **2a** with the formal C=C double bond distance within the three-membered ring in **8** being 0.02 Å shorter than in **2a** [28a]. At the same time, the differences between the single and double CC bonds observed in **2a** and **8** are in the small range of 0.03–0.07 Å found in related cyclopropenylidene species [28d].

(Table 1). This subtle effect is however not indicated by our DFT calculations. The topology of the charge-density distribution at the C2–C3 bond critical point (BCP;  $\rho(\mathbf{r})_{\text{exp}} = 2.00(2)$  and  $\rho(\mathbf{r})_{\text{calc}} = 2.09 \text{ e } \text{\AA}^{-3}$ ) shows that the C=C double bond is only slightly weakened compared to that in **2** ( $r = 1.342$ ;  $\rho(\mathbf{r})_{\text{calc}} = 2.12 \text{ e } \text{\AA}^{-3}$ ;  $L(\mathbf{r})_{\text{calc}} = 16.9 \text{ e } \text{\AA}^{-5}$ ;  $\varepsilon = 0.21$ ), whereas the C<sub>carb</sub>–C2 and C<sub>carb</sub>–C3 bonds display significant partial double bond character with pro-

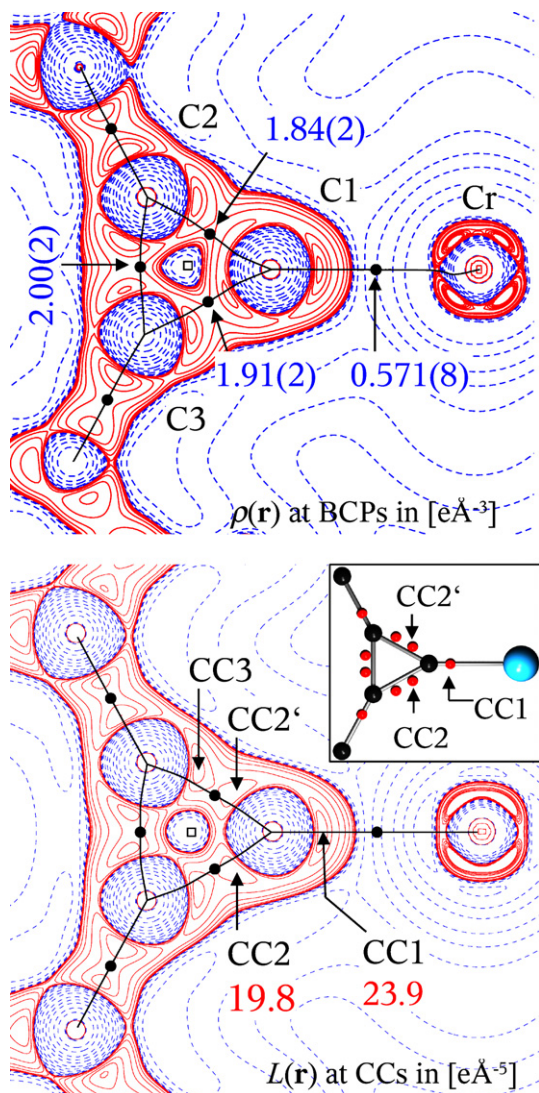


Fig. 2. Contour map of the negative Laplacian of the experimental (above) and calculated (below) electron density ( $L(\mathbf{r}) = -\nabla^2\rho(\mathbf{r})$ ) of **2a** in the Cr, C<sub>carb</sub>, C2 plane. Contour levels are drawn at 0,  $\pm 2.0 \times 10^{-4}$ ,  $\pm 4.0 \times 10^{-4}$ ,  $\pm 8.0 \times 10^{-4} \text{ e } \text{\AA}^{-5}$ , where  $n = 0, \pm 3, \pm 2, \pm 1$ ; extra levels at 15, 25, 84, 105, 240, 280, 320, 350  $\text{e } \text{\AA}^{-5}$ ; positive and negative values are marked by solid and dashed lines, respectively. Bond and ring critical points are marked by closed circles/open squares, respectively, while the bond paths are drawn by solid lines. The  $L(\mathbf{r})$  maps reveal regions where the charge-density distribution in the valence shell is locally concentrated ( $L(\mathbf{r}) > 0$ ). The corresponding local maxima at C(1) are denoted as charge concentrations CC1, CC2 and CC2'. The inset shows the relative location of all nine charge concentrations (red balls) in the valence shell of the carbon atoms of the C<sub>3</sub>-ring moiety. (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

nounced bond ellipticities. However, large C–C bond ellipticities in combination with exocyclic-curved C–C bond paths also occur in cyclopropane and originate from the severe ring strain present in three-membered rings [22]. Indeed, the presence of severe bond strain in the cyclopropenylidene fragment of **2a** is revealed by exocyclic-curved C–C bond paths in fine agreement between experiment and theory (Fig. 2). We will also see later that bond ellipticities are no suitable measure to study the extent of  $\pi$ -delocalization in three-membered ring systems.

A more useful microscopic tool which allows us to study the electronic origin of this bond strain scenario is, however, provided by the topology of the negative Laplacian of the charge density,  $L(\mathbf{r}) = -\nabla^2\rho(\mathbf{r})$ . In Fig. 2 regions where charge is locally concentrated are mapped by areas where  $L(\mathbf{r}) > 0$  [23,24]. We identify for each of the carbon atoms of the cyclopropenylidene ring of **2a** three individual valence shell charge concentrations (denoted CC in the following) in agreement with an approximate  $sp^2$ -hybridization. These charge concentrations are directed towards the CC bonds and span two valence angles larger ( $133.2^\circ$ ) and one angle smaller ( $93.4^\circ$ ) than the ideal value of  $120^\circ$  at the carbene centre (Fig. 2 and Table 2). Note, that we referred to the theoretical values which we will use also in the following when we compare the topology of **2a** with that of the models **2**, **[2-H]<sup>+</sup>** and **[1-H]<sup>+</sup>**.

Topological analyses of calculated density distributions show that the valence angle asymmetry is even more pronounced in the free carbene **2** where CC2 and CC2' span an acute angle of  $89.6^\circ$  with the carbene centre. This distortion of the electronic structure is a apparently a direct consequence of the dominance of the carbene lone pair density in the total  $\rho(\mathbf{r})$  distribution of **2**. Indeed, CC1 which characterizes the maximal concentration of charge in the lone pair region displays a  $L(\mathbf{r})_{\text{CC1}}$  value of  $26.8 \text{ e } \text{\AA}^{-5}$  in combination with a charge density  $\rho(\mathbf{r})_{\text{CC1}}$  of  $2.04 \text{ e } \text{\AA}^{-3}$  (Table 2). On contrary, the charge density at the bond-directed charge concentrations CC2 and CC2' is less concentrated ( $L(\mathbf{r})_{\text{CC2}} = 18.6 \text{ e } \text{\AA}^{-5}$ ;  $\rho(\mathbf{r})_{\text{CC2}} = 1.91 \text{ e } \text{\AA}^{-3}$ ). Hence, it is the dominance of the

Table 2

Topology of the Laplacian, atomic charges,  $Q_{\text{AIM}}$ , and eigenvalues of the atomic quadrupole moment tensors  $Q_{\text{ip/oop}}$  at the carbene carbon atom of **2**, **5**, **2a**, and the protonated carbene centre in **[2a-H]<sup>+</sup>** and **[1-H]<sup>+</sup>**

	$Q_{\text{AIM}}^a$	$Q_{\text{ip}}^{a,b}$	$Q_{\text{oop}}^{a,b}$	$L(\mathbf{r})_{\text{CC1}}^c$	$L(\mathbf{r})_{\text{CC2}}$	$\rho(\mathbf{r})_{\text{CC1}}$	$\rho(\mathbf{r})_{\text{CC2}}$
<b>2</b>	−0.01	0.26	−0.17	26.8	18.6	2.04	1.91
<b>5</b>	−0.07	0.20	−1.03	24.5	17.1	1.96	1.91
<b>2a</b>	−0.11	1.98	−1.41	23.9	19.8	1.94	1.97
<b>[2-H]<sup>+</sup></b>	−0.02	2.56	−1.89	30.3	22.6	2.11	2.14
<b>[1-H]<sup>+</sup></b>	+0.09	2.11	−1.21	33.0	23.8	2.19	2.17

<sup>a</sup>  $Q_{\text{AIM}}$  and  $Q_{\text{ip/oop}}$  values are specified in atomic units.

<sup>b</sup> The indices specify the orientation of the eigenvectors: *in-plane* (ip) defines the vector originating at the carbene centre to CC(1), while the index *out-of-plane* (oop) denotes the vector orientated perpendicular to the molecular planes of the three-membered ring systems.

<sup>c</sup>  $L(\mathbf{r})$  and  $\rho(\mathbf{r})$  values are given in [ $\text{e } \text{\AA}^{-5}$ ] and [ $\text{e } \text{\AA}^{-3}$ ], respectively, while CC1/2 denote valence shell charge concentrations as defined in Fig. 2.



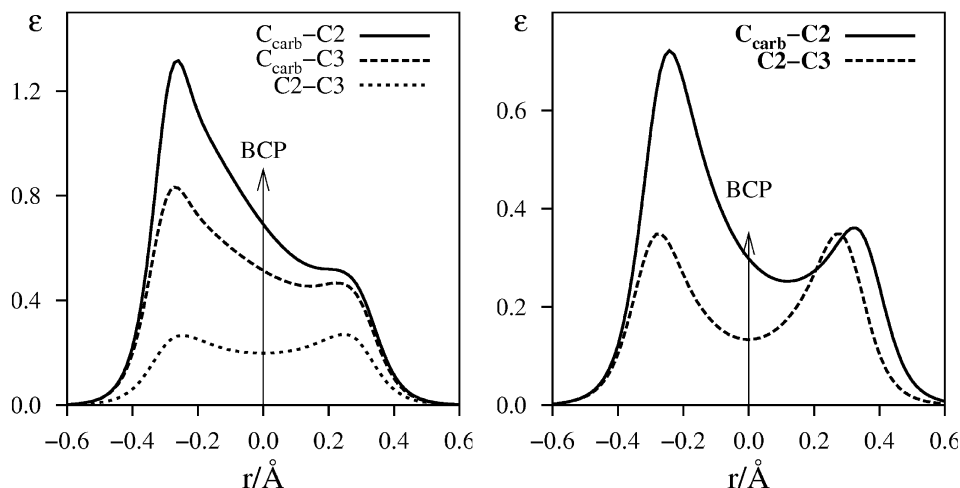


Fig. 3. Variation in the experimental (left) and calculated (right) bond ellipticities,  $\varepsilon$ , along the C–C bond paths in the cyclopropenylidene ring in **2a**. The left-hand nucleus from the BCP is the carbene carbon atom. Note, that the maxima in the bond path ellipticity profiles occur at a distance of about 0.3 Å from the carbon atoms. Apparently, these maxima are a consequence of the close proximity of the bond-directed charge concentrations CC2 and CC3 (Fig. 2).

carbene lone pair which causes an acute valence angle  $\angle\text{CC2}, \text{C}_{\text{carb}}, \text{CC2}'$  in accordance with the rules of the VSEPR model [24]. We therefore suggest to use this simple criterion *based on physical observable properties* as a measure of the dominance of the lone pair density in the total charge-density distribution of cyclopropenylidenes.

In the row **2**, **2a**,  $[\mathbf{2-H}]^+$  the  $\angle\text{CC2}, \text{C}_{\text{carb}}, \text{CC2}'$  valence angles of 89.6°, 93.4°, and 100.1°, respectively, can be correlated with reduced electron localization in the carbene lone pair region. Accordingly, the differences between the magnitudes of  $\rho(\mathbf{r})$  at CC1 and the bond-directed charge concentrations CC2/CC2' is only pronounced in the case of the free carbene **2** but rather balanced in complex **2a** and the cyclopropenium cation  $[\mathbf{2-H}]^+$  (Table 2):  $\rho(\mathbf{r})_{\text{CC1/CC2}} = 2.04/1.91 \text{ e } \text{\AA}^{-3}$  (**2**); 1.94/1.97  $\text{e } \text{\AA}^{-3}$  (**2a**); 2.11/2.14  $\text{e } \text{\AA}^{-3}$  ( $[\mathbf{2-H}]^+$ ). We note, that in the cyclopropenium cation  $[\mathbf{2-H}]^+$  the magnitudes of CC1 and CC2 have nearly reached the optimal values calculated for  $[\mathbf{1-H}]^+$  (Table 2).<sup>3</sup>

These findings indicate that the location and magnitude of the valence charge concentrations can be employed to directly reveal *electronic localization phenomena* on the basis of *experimental observables*. They further show that pronounced electron localization in the carbene lone pair region dominates the electronic structure of free cyclopropenylidenes like **2**. In the following we will outline that either *charge transfer* from the lone pair region to an electron-deficient transition metal fragment in complex **2a** or *protonation* ( $[\mathbf{2-H}]^+$ ) or  $\pi$ -donation by amino substituents (**5**) is necessary to initiate true cyclic  $\pi$ -delocalization.

### 2.3. $\pi$ -Electron delocalization

So far we have been focussing basically on the  $\sigma$ -bonding inside the cyclopropenylidene moiety which is responsible for the geometrical prerequisites (reduced C–C bond length asymmetry) of efficient cyclic  $\pi$ -delocalization [25]. We will now analyze  $\pi$ -bonding effects in the charge-density distribution of **2a**. One option to reveal even subtle changes in  $\pi$ -bonding is usually to trace bond ellipticities,  $\varepsilon$  [26], along the complete bond paths of the C3 ring system. This concept has been successfully used to explore subtle changes in  $\pi$ -bonding due to negative hyperconjugation in transition metal alkyls [27] or cyclic electron delocalization in *N*-heterocyclic carbenes [14a]. We observe slightly different bond ellipticity profiles along the individual  $\text{C}_{\text{carb}}\text{--C2}$  and  $\text{C}_{\text{carb}}\text{--C3}$  bonds (Fig. 3, left) in the experimental  $\rho(\mathbf{r})$ . This result is in agreement with the fact that both C–C bonds display different distances in **2a** (Table 1). Otherwise, the agreement with the corresponding theoretical ellipticity profiles is remarkably good (Fig. 3, right). Closer inspection of the ellipticity profiles reveals in experiment and theory that the *major axis* of curvature of  $\rho(\mathbf{r})$  along the three C–C bond paths lies *in* the ring plane. On contrary, in the case of the C–C bonds of the phenyl substituents of **2a** this axis is *perpendicular* to the corresponding ring plane due to *pronounced* cyclic  $\pi$ -electron delocalization. However, also our benchmark  $[\mathbf{1-H}]^+$  model representing a truly delocalized cyclic  $\pi$ -system displays an in-plane orientation of the C–C bond ellipticities due to the peculiarities of three-membered ring systems. Indeed, as a geometrical consequence all C–C distances in three-membered cyclopropenylide or cyclopropenium rings are short ( $d_{\text{C-C}} = 1.3626 \text{ \AA}$  in  $[\mathbf{1-H}]^+$ ) causing an accumulation of charge at the central ring critical point. Accordingly, the major axis of curvature points to the ring centre of  $[\mathbf{1-H}]^+$  – the direction where the negative curvature of  $\rho(\mathbf{r})$

<sup>3</sup> Note, that the magnitude of the bond-directed CCs is highly correlated with the charge density at the corresponding bond critical points and thus with the strength of C1–C2 bonding in **2**, **2a**,  $[\mathbf{2-H}]^+$ ,  $[\mathbf{1-H}]^+$ :  $\rho(\mathbf{r}_{\text{c}}) = 1.91 \text{ e } \text{\AA}^{-3}$  (**2**); 1.94  $\text{e } \text{\AA}^{-3}$  (**2a**); 2.08  $\text{e } \text{\AA}^{-3}$  ( $[\mathbf{2-H}]^+$ ); 2.12  $\text{e } \text{\AA}^{-3}$  ( $[\mathbf{1-H}]^+$ ).

is minimal. The same is true for models **2**, **2a**,  $[2\text{-H}^+]$  and **5**. Thus, the ellipticity profiles are versatile tools to reveal subtle, aspherical differences in the charge-density distribution along the bond paths but are not necessarily useful to analyze the  $\pi$ -bonding situation in three-membered ring systems.

We therefore noted previously [14a] that analysis of atomic *quadrupole* polarizations may provide a more robust measure of the extent of cyclic  $\pi$ -electron delocalization in molecules rather than studying bond ellipticities. Our theoretical findings indicate a promulgation of the charge density *out* of the cyclopropenylidene ring plane in all our model systems. Accordingly, **2**, **2a**, and  $[2\text{-H}^+]$  exhibit a large *negative* eigenvalue of the out-of-plane component of the traceless quadrupole moment tensor (Table 2):  $Q_{\text{oop}} = -0.17$  (**2**),  $-1.41$  (**2a**),  $-1.89$  ( $[2\text{-H}^+]$ ). Hence, cyclic  $\pi$ -electron delocalization is at a maximum in the cyclopropenium cation  $[2\text{-H}^+]$  for this series of benchmarks models. Delocalization is also pronounced in complex **2a** and the free amino-substituted carbene **5**. On contrary, carbene **2** carrying two phenyl substituents does not reveal any significant cyclic  $\pi$ -electron delocalization in agreement with the presence of pronounced electron localization in the carbene lone pair region. Hence, our charge-density analyses confirm that cyclic  $\pi$ -electron delocalization (in three-membered ring systems) is a cooperative effect which depends on contributions of both  $\sigma$ - and  $\pi$ -bonding.

#### 2.4. $\sigma$ -Donor and $\pi$ -acceptor capabilities of cyclopropenylidenes

In the next step we have analyzed the  $\sigma$ -donor and  $\pi$ -acceptor capabilities of cyclopropenylidenes. The  $\text{LCr}(\text{CO})_5$  complexes **2a** (L = cyclopropenylidene **2**) and **3a** (L = *N*-heterocyclic carbene **3**) display clearly different Cr–C bonding characteristics:  $r(\text{Cr}–\text{C}) = 2.0437(4)$  and  $2.1327(4)$  Å in **2a** and **3a**, respectively [14a].<sup>4</sup> Furthermore, topological analysis of experimental  $\rho(\mathbf{r})$  maps points out an accumulation of charge of  $0.571(8) \text{ e } \text{\AA}^{-3}$  at the Cr–C<sub>carb</sub> BCP in **2a** which is larger than that found in **3a** ( $0.543(6) \text{ e } \text{\AA}^{-3}$ ) [14a].

<sup>4</sup> The Cr–C<sub>carb</sub> bond distance of  $2.010(7) \text{ \AA}$  found in (2,3-diethoxycyclopropenylidene)-pentacarbonylchromium [28a] **8** [ $\text{X1} = \text{X2} = \text{OEt}$ ; were X1 and X2 are substituents of the cyclopropenylidene moiety], is slightly shorter compared to that observed in our work for **2a** [ $2.0437(4) \text{ \AA}$ ], whereas the Cr–C<sub>carb</sub> bond distances in several other cyclopropenylidene complexes determined by X-ray diffraction method so far ( $2.071(8) \text{ \AA}$  in **9** [ $\text{X1} = \text{OEt}$ ,  $\text{X2} = \text{O}–\text{Re}(\text{CO})_5$ ] [28b] and  $2.066(3) \text{ \AA}$  in **10** [ $\text{X1} = \text{OEt}$ ,  $\text{X2} = \text{Fe}(\text{CO})_2(\text{Cp})$ ] [28c]) are somewhat larger than that in **2a**. We also note that a substitution of the phenyl ring by the *N*-alkyl groups such as in complex **11** [ $\text{X1} = \text{NMe}_2$ ,  $\text{X2} = \text{NEt}_2$ ] [28d] results in a *lengthening* of the Cr–C<sub>carb</sub> bond distance ( $0.04 \text{ \AA}$ ) whereas the averaged C<sub>carb</sub>–C2 bond distance becomes by  $\sim 0.01 \text{ \AA}$  *shorter* and the C2–C3 bond distance by  $\sim 0.01 \text{ \AA}$  *longer*, respectively. This trend was confirmed by our calculations on the model compound **12** [ $\text{X1} = \text{X2} = \text{NMe}_2$ ]. Thus, our results confirmed previous findings [29] based on the spectral data ( $^{13}\text{C}$  NMR and IR) that the  $\sigma$ -donating and  $\pi$ -acceptor capabilities of cyclopropenylidene ligands depend significantly on the presence or absence of amino substituents.

Interestingly, the experimental Cr–C<sub>carb</sub> bond ellipticities in these two carbene complexes are similar ( $\varepsilon = 0.08$ ). The average net atomic charges, obtained by integration over the atomic basins of the theoretical charge-density distribution of **2a**, are  $+1.12$ ,  $-0.11$  and  $-0.10 \text{ e}$  for the Cr, C<sub>carb</sub>, and the C2 atom, respectively. For the free carbene **2** we compute a reduced negative atomic charge of  $-0.01$  at the carbene carbon atom which might be taken as one indicator of significant  $\pi$ -back donation in cyclopropenylidene complexes (Table 2). Also structural details support the presence of  $\pi$ -back donation in **2a**. If we analyze the bond distances between the chromium atom and the carbonyl group in *trans* (CO<sub>ax</sub>) and *cis* (CO<sub>eq</sub>) position to the metal–carbene bond we find clear differences in **2a** (Cr–C(O)<sub>ax</sub> =  $1.8815(5)$  and Cr–C(O)<sub>eq,av</sub> =  $1.9073 \text{ \AA}$ ) since the cyclopropenylidene acts as weaker  $\pi$ -acceptor ligand than the carbonyl groups. However, the cyclopropenylidene ligand **2** is clearly the *better*  $\pi$ -acceptor ligand in comparison with the *N*-heterocyclic carbene in complex **3a** which displays in competition with the five carbonyl ligands an even shorter Cr–C(O)<sub>ax</sub> bond of  $1.8557(4)$  while the equatorial Cr–C(O)<sub>eq,av</sub> bond distance ( $1.8971 \text{ \AA}$ ) is comparable to that in **2a**. We note that our DFT calculations show the same trend but appear to be less sensitive to reveal these subtle but significant bond length differences in the  $\text{M}(\text{CO})_5$  fragments.

### 3. Conclusion

In conclusion, the results of the topological analysis of the experimental and theoretical charge densities show that the substituted cyclopropenylidene ligands **2** and **5** display pronounced charge concentrations in the lone pair region at the carbene centre which classifies these systems as  $\sigma$ -donor ligands. The additional  $\pi$ -donation due to the presence of amino substituents in **5** leads, however, to a noticeable increase of cyclic electron delocalization relative to **2**. This is clearly revealed in **5** by a large negative *out-of-plane* atomic quadrupole moment at the carbene carbon atom – which serves as a charge-density analogue of  $p_\pi$  occupation in the molecular orbital picture. Topological analyses of the transition metal complex **2a** also identified the pronounced  $\pi$ -acceptor capabilities of the cyclopropenylidene carbene **2** in clear contrast to *N*-heterocyclic carbenes like **3** and **4** which rather are characterized as  $\sigma$ -donor ligands. Accordingly, coordination of cyclopropenylidene carbenes to transition metal carbonyl fragments enhances both *in-plane* and *out-of-plane* electron delocalization [30] and contribute to the remarkable stability of our benchmark complex **2a**.

### 4. Experimental

Crystal data for **2a**:  $\text{C}_{20}\text{H}_{10}\text{CrO}_5$ ,  $M_r = 382.28$ , red prism; triclinic, space group  $P\bar{1}$ ,  $a = 9.2412(2)$ ,  $b = 9.7379(2)$ ,  $c = 10.1107(2) \text{ \AA}$ ,  $\alpha = 71.050(1)^\circ$ ,  $\beta = 86.823(1)^\circ$ ,  $\gamma = 89.872(1)^\circ$ ,  $V = 859.11(3) \text{ \AA}^3$ ,  $T = 100(1) \text{ K}$ ;  $Z = 2$ ,  $F(000) = 388$ ,  $D_{\text{calc}} = 1.478 \text{ g/cm}^3$ ,  $\mu = 0.69 \text{ mm}^{-1}$ . Bragg

reflections (80760) were collected on a Nonius kappa-CCD system with a rotating anode generator (Nonius FR591; Mo K $\alpha$ ,  $\lambda = 0.71073$  Å); 12878 independent reflections;  $R_{\text{int}} = 0.028$ . The data set was corrected for beam inhomogeneity and absorption effects [ $T_{\text{min}}/T_{\text{max}} = 0.814(2)/0.873(2)$ ]: 95% completeness in the data range  $\sin \theta_{\text{max}}/\lambda = 0.98$  Å $^{-1}$ . The deformation density was described by a multipole model in terms of spherical harmonics multiplied by Slater-type radial functions with energy-optimized exponents [16,17]. The refinement of 509 parameters against 10649 observed reflections [ $F > 3\sigma(F)$ ] converged to  $R_1 = 0.0163$ ,  $wR_2 = 0.0422$ , GOF = 0.78, and a featureless residual  $\rho(\mathbf{r})$ . Molecular geometries were fully optimized at the B3LYP/6-311G(d,p) level of theory using GAUSSIAN 03 [18,31] and imposing  $C_2$  (**2a**),  $C_{2v}$  (**2**, [**2-H**] $^+$ ),  $D_{3h}$  ([**1-H**] $^+$ ), and  $C_s$  (**5**) symmetry restraints. The topology of  $\rho(\mathbf{r})_{\text{calc}}$  was analyzed using the AIMPAC software package [19].

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## Appendix A. Supplementary material

CCDC 645784 contains the supplementary crystallographic data for **2a**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.ica.2007.05.050](https://doi.org/10.1016/j.ica.2007.05.050).

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