# Cyclooctatetraene in metal complexes—planar does not mean aromatic†

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*Received (in Montpellier, France) 25th January 2010, Accepted 29th March 2010*
**DOI: 10.1039/c0nj00060d**

The cyclooctatetraene (COT) ring may act as an effective π-type ligand in metal complexes and very often in such complexes it adopts the planar structure, which in fact is not the most favourable conformation when compared with the free COT molecule. Such planarization is usually considered as an effect of COT ring aromatization due to charge transfer from the metal centre into the COT ligand and reorganization of the π-electron structure from a $4n$ to $4n+2$ Hückel system. In this paper it has been shown that the conformational changes of the COT ring, leading to its planarization and partial bond equalization, in the first order are connected with the complexation efficiency and not with the aromatization of COT itself. Such a conclusion was drawn on the basis of statistical analysis of X-ray data collected in the Crystal Structure Database (47 COT rings were taken into consideration, all found in the selected highest quality X-ray measurements) and advanced quantum-chemical calculations, including analysis of the electron density distribution made in the framework of *Atoms-in-Molecules Quantum Theory*.

## Introduction

1,3,5,7-Cyclooctatetraene (COT) is a simple [8]annulene, $C_8H_8$. Being a $4n$ cyclic π-conjugated system, it is often considered as an example of a nonaromatic (or antiaromatic, when planar) species.[1] Both in the gas phase[2,3] and crystal state[4] COT adopts a tub-like conformation ($D_{2d}$ symmetry) with clearly localized single and double bonds of 1.47 Å and 1.33 Å length, respectively. This closed-shell nonplanar structure is accompanied by a chemical behaviour being characteristic of conjugated alkenes.[5] The process of planarization of tub-shaped COT was investigated and it was found that the planar structure can be forced, for instance, by annelation with rigid bridges leading to geometric constrains that result in bond delocalization in the COT ring.[6–8] Planarization of COT can also be reached by a partial rehybridization at the carbon atom due to a forced decrease of the HCC bond angles at carbon atoms forming the double bond.[9] However, it should be emphasized that the analysis of ring currents of COT derivatives planarized in various ways clearly showed that planarization in these cases has nothing in common with aromatization.[10,11] For a very recent review on theoretical and experimental studies regarding the planar COT structure see ref. 12. It was also reported that the COT ring exhibits a very unusual electron-density topology resulting from specific orbital overlapping in the tub-like conformation.[13] It was found that this through-space orbital interaction is mostly connected with exchange repulsion between filled p-type orbitals centred on oppositely placed carbon atoms. The substituent effect in COT was also investigated by means of computational methods.[14,15]

The efficient electron affinity of COT is well known and it has been frequently reported that COT forms a stable dianionic structure, for instance in the presence of electron-donating alkali[16–19] and some transition metals.[20–23] However, although it was repeatedly reported that COT forms stable complexes with transition metals and that in many such complexes it adopts a dianionic aromatic form (with $4n+2$ π-electrons), the isolated dianion $COT^{2-}$ itself has a very short lifetime,[24] which indicates a relatively low kinetic stability of that species. The $COT^{2-}$ lifetime is 6 fs, which is drastically short as compared with, for instance, 260 and 6500 fs for $C_4^{2-}$ and $CO_3^{2-}$, respectively.[24]

The COT ring formally possesses four bonds of π-type (double CC bonds in free COT), thus it is an effective π-type ligand. What is interesting, as a ligand it exhibits the whole conformational spectrum—from tub-like up to planar structure—and different coordination modes, *i.e.* $\eta^2$, $\eta^4$, $\eta^6$ and $\eta^8$.[16,25–31] Therefore, an essential conformational variety of the COT ring can be observed for metal complexes. These changes in conformational properties are often considered as the result of charging of the COT ring and in consequence full or partial aromatization of that ring ($4n$ π-electron structure in COT *vs.* $4n+2$ π-electron structure in its dianion).

Since such an essential conformational variety of COT can be observed for metal complexes, we decided to check if there is any direct relationship between COT conformation and its aromatic character. For the purposes of our studies we analyzed experimental data collected in the Crystal Structure Database.[32] Additionally, selected molecular systems found in the CSD were chosen for more detailed computational studies.

## Methodology

### Crystal structure database searching

The search through CSD[32] (release 2009) was done in order to collect selected data for further analysis. The presence of an unsubstituted COT ring in the crystal structure was the main criterion of the search. Additionally, the search was limited to data derived from high-quality X-ray measurements ($R \leq 0.075$). Crystal structures with errors, disordered structures, powder

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† Electronic supplementary information (ESI) available: CSD refcodes, results of population analysis, geometries and total energies of the systems studied. See DOI: 10.1039/c0nj00060d

data, ionic and polymeric structures were also excluded from the search. 47 COT rings were found. It should be pointed out that in some specific crystal structures more than one COT was present within the molecule (TM complex), thus the number of crystal structures fulfilling the above criteria is lower. See ESI file† for all CSD refcodes. The values of CC bond lengths and torsion angles in COT rings were collected for further statistical analysis.

For the purposes of this analysis we define the following parameter as a measure of bond length alternation:

$$\Delta d_{\mathrm{CC}} = \frac{1}{n}\sum_{i=1}^{n} |\bar{d}_{\mathrm{CC}} - d_i|$$

where $\bar{d}_{\mathrm{CC}}$ is an average value of CC bond lengths in the considered COT ring and $d_i$ is the length of a given CC bond. In the case of the COT ring $n$ equals 8.

As a geometry-based indicator of local aromaticity, the HOMA index was applied. According to its definition[33,34] HOMA can be expressed by the following equation:

$$\mathrm{HOMA} = 1 - \frac{1}{n}\sum_{j=1}^{n} \alpha_i (R_{\mathrm{opt},i} - R_j)^2$$

where $n$ represents the total number of bonds in the molecule and $\alpha_i$ is a normalization constant (for CC bond: $R_{\mathrm{opt,CC}} = 1.388$ Å, $\alpha_{\mathrm{C-C}} = 257.7$) fixed to give HOMA = 0 for a model nonaromatic system, *e.g.*, the Kekulé structure of benzene and HOMA = 1 for the system with all bonds equal to the optimal value $R_{\mathrm{opt,i}}$, assumed to be realized for fully aromatic systems.[33] The higher the HOMA value, the more "aromatic" is the ring in question and hence the more delocalized are the π-electrons of the system. As distinct from $\Delta d_{\mathrm{CC}}$ parameter, which shows how far the bonds are equalized in the COT ring, HOMA reflects how far the CC bonds lengths are close to CC bonds lengths in the system considered as fully aromatic. This significant difference should be clearly pointed out for the purposes of further discussion.

In order to quantify the degree of planarity of the COT ring we introduce two parameters. The first one, $\bar{h}_{\mathrm{CPL}}$, is a simple average of distances between carbon atoms forming the COT ring and the least-squares plane calculated for that ring. The second parameter is defined as follows:

$$\Delta\mathrm{Tor} = \frac{\sum_i |\varphi_i|}{\sum |\varphi_{\mathrm{ref}}|}$$

where $|\varphi_i|$ are the absolute values of torsion angles measured for a given COT ring, and $\sum|\varphi_{\mathrm{ref}}|$ is the summation over absolute values of torsion angles in the reference COT ring. The torsion angles $\varphi$ are defined by positions of successive (bonded) carbon atoms in COT ring. There are eight such torsion angles taken for estimation of each $\sum_i|\varphi_i|$ value. Once estimated, the value of $\sum|\varphi_{\mathrm{ref}}|$ was treated as a constant. In the case of CSD data analysis as the reference data we use the value from X-ray structure of COT in the crystal state[4] ($\sum|\varphi_{\mathrm{ref}}| = 228.26°$, CSD refcode: ZZZSAE01).

### Computational details

In order to find model systems suitable for our analysis we performed a detailed search through the CSD collection. The CSD refcodes corresponding to selected X-ray structures are as follows: COCTTI10, ROGDOG, ROGDUM, ROGFAU. Geometries from crystal structures were taken as the starting parameters for further modification as a result of which the molecular models shown in Fig. 1 were obtained. Molecular geometry taken from crystal structure COCTTI10 was used as the starting geometry for optimization of system **I**. In order to get the analogue of I with only one metal centre we simply removed from the molecule of **I** the external COT ring together with the bonded Ti atom and in this way, after geometry optimization, we obtained system **II**. Systems **III**, **IV** and **V** were obtained after simple modifications of geometries from crystal structures ROGFAU, ROGDUM and ROGDOG, respectively. In the case of those systems all methyl substituents in *tert*-butyl or isopropyl groups (in crystal structures attached to COT counterligands) were exchanged with hydrogen atoms to reduce the computational effort. Geometries of systems **I–V** (Fig. 1) were optimized without any symmetry constrains using DFT methods implemented in the Gaussian09 set of codes.[35] The B3LYP functional[36–39] was applied in conjunction with the 6-311++G(d,p) basis set[40,41] for all atoms (note that for this basis set the f-type polarization functions are included for first-row transition metals). The frequency analysis at the same level of theory was used to verify that the optimized geometries correspond to stationary points. No imaginary frequencies were found. (The only exception is the free COT ring for which planar structure was forced.) It should be pointed out that in order to ensure the adequate convergence and the reliability of computed frequencies the cutoffs on forces and step size that are used to determine convergence were tightened in the case of geometry optimizations (Opt = Tight option in the optimization procedure). Additionally, the full SCF convergence was requested for all SP calculations (SCF = Tight option).

For the optimized geometries a detailed analysis of the electron distribution function was performed according to the concept of the "Atoms in Molecules" theory proposed by R. W. F. Bader,[42] using AIM2000[43,44] program for graphical representations and AIMAll[45] program for numerical analysis. In order to increase the quality of AIM calculations PROMEGA 1st order algorithm[46] in connection with *very high* basin quadrature was used for all atoms in AIMAll calculations. For all calculations the Poincaré-Hopf relationship was satisfied.[47] Properties of the electron density function were analyzed in the framework of AIMQT. The following parameters are discussed: electron density measured at BCP, $\rho$(BCP), its Laplacian, $\nabla^2\rho$(BCP), and the values of proper delocalization indices, $\delta_{\mathrm{A,B}}$. According to its definition the delocalization index value between atoms A and B, $\delta_{\mathrm{A,B}}$, was obtained by double integration of the exchange–correlation density,[48] $\Gamma_{\mathrm{XC}}(\vec{r}_1, \vec{r}_2)$, over the basins of atoms A and B, which are defined from the zero-flux gradient condition applied to the one-electron density, $\rho(r)$:

$$\delta_{\mathrm{A,B}} = -\iint\limits_{\mathrm{A}\,\mathrm{B}} \Gamma_{\mathrm{XC}}(\vec{r}_1, \vec{r}_2)\,\mathrm{d}\vec{r}_1\mathrm{d}\vec{r}_2 - \iint\limits_{\mathrm{B}\,\mathrm{A}} \Gamma_{\mathrm{XC}}(\vec{r}_1, \vec{r}_2)\,\mathrm{d}\vec{r}_1\mathrm{d}\vec{r}_2$$

$$= -2\iint\limits_{\mathrm{A}\,\mathrm{B}} \Gamma_{\mathrm{XC}}(\vec{r}_1, \vec{r}_2)\,\mathrm{d}\vec{r}_1\mathrm{d}\vec{r}_2$$

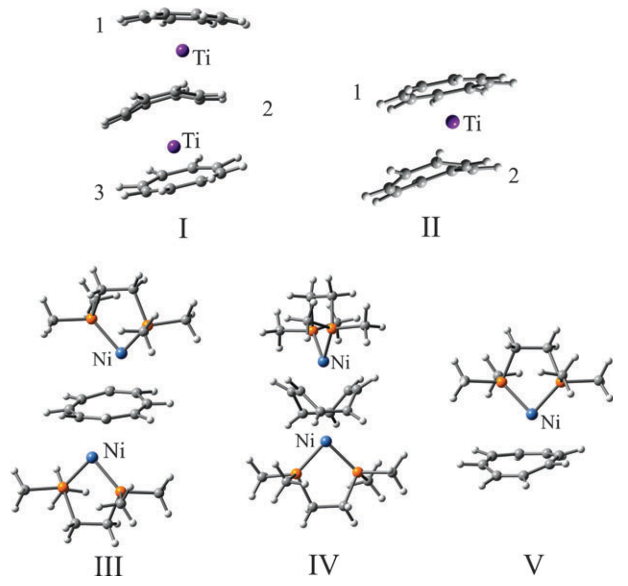

**Fig. 1** Graphical representation of all systems investigated theoretically. Atoms are coloured according to the following scheme: Ti—big purple circles, Ni—blue circles, C—gray circles, H—small white circles, P—orange circles.

$\delta_{A,B}$ provides a quantitative idea of the number of electrons delocalized or shared between atoms A and B. In the case of two atoms formally interacting in the chemical bond the value of $\delta_{A,B}$ may be considered as the AIM-based bond order. We discuss also the $\Sigma\delta_{C,TM}$ parameter which is the sum of $\delta_{A,B}$ estimated for all individual pairs of atoms sharing electrons due to metal–ligand bonding. The $\sum\delta_{C,TM}$ parameter gives the information on the efficiency of metal–ligand bonding in complexes under investigations.

As an electron-density-based index of aromaticity we use the aromatic fluctuation index (FLU)[49] which describes the fluctuation of electronic charge between adjacent atoms in a given ring. It is defined as:

$$\mathrm{FLU} = \frac{1}{n}\sum_{\mathrm{A-B}}^{\mathrm{RING}}\left[\left(\frac{V(\mathrm{B})}{V(\mathrm{A})}\right)^{\alpha}\left(\frac{\delta(\mathrm{A,B})-\delta_{\mathrm{ref}}(\mathrm{A,B})}{\delta_{\mathrm{ref}}(\mathrm{A,B})}\right)\right]^2$$

with the sum running over all adjacent pairs of atoms around the ring, $n$ being equal to the number of members in the ring, $\delta_{\mathrm{ref}}(\mathrm{C,C})$ = 1.389e (the $\delta(\mathrm{C,C})$ value in benzene) and $V(\mathrm{A})$ is the global delocalization of atom $A$ given by:

$$V(\mathrm{A}) = \sum_{\mathrm{B}\neq\mathrm{A}}\delta(\mathrm{A,B})$$

Finally, $\alpha$ is a simple function to make sure that the first term in FLU eqn is always greater or equal to 1, so it takes the values:

$$\alpha = \begin{cases} 1 & V(\mathrm{B}) > V(\mathrm{A}) \\ -1 & V(\mathrm{B}) \leq V(\mathrm{A}) \end{cases}$$

FLU is close to 0 in aromatic species, and differs from it in non-aromatic ones.

Additionally, the geometry-based parameters defined in previous section, namely $\Delta d_{\mathrm{CC}}$, HOMA and ΔTor, were calculated for the COT rings present in the theoretically investigated systems. In this case, however, the ΔTor parameter was modified so that the reference system was the tub-shaped COT ring in its fully optimized geometry.

## Results and discussion

### Results of CSD search

The planarization of the COT ring in TM complexes is commonly explained as the result of partial or full aromatization of that ring. Usually such aromatization is considered as the result of charge transfer from the TM or alkali metal centre into the COT ring. COT in its ground state is a $4n$ π-electron system, usually considered as an nonaromatic species. However, in its dianionic form it is a $4n+2$ system, that is, a system fulfilling one of the basic criteria of aromaticity—the Hückel rule.[50]

In the case of aromatic rings the equalization of bonds is usually observed.[51] Thus, one would expect a linear relation between $\Delta d_{\mathrm{CC}}$ and HOMA values estimated for the set of COT rings from the CSD, since the more aromatic the given ring is, the more equalized should be the bonds forming that ring. In Fig. 2(a) the relation between $\Delta d_{\mathrm{CC}}$ and HOMA is shown. At first sight an approximately linear interrelation between those two parameters can be noticed. The correlation coefficient (cc) for the linear regression equals 0.945. Therefore, in agreement with expectations, the bond equalization in the analyzed COT rings would be related to the effect of aromatization. However, an interesting observation can be made if one takes into consideration only the part of the data which corresponds to positive HOMA values, that is, the set of rings which have characteristics in between aromatic and non-aromatic. (Note that the negative HOMA corresponds to antiaromatic systems.) In such a case the linear relation disappears (see Fig. 2(b)) and the cc parameter adopts a value of 0.772. This may be surprising, since for COT rings with the characteristics closer to those of aromatic systems the linear relation between the bond alternation parameter and aromaticity index should be expected. For the part of data corresponding to rings with negative HOMA values, *i.e.* for antiaromatic rings, such a relation is even worse and the cc parameter is 0.717. The seemingly linear relation between $\Delta d_{\mathrm{CC}}$ and HOMA is just an effect of specific point distribution on the scatter plot—two clusters of points are simulating the linear regression. Therefore, it can be said that the bond equalization in COT does not necessarily have to be connected to the effect of ring aromatization. However, as will be shown in the next section, some general relation between HOMA and bond alternation parameter can be found for the reduced set of model systems.

Another common characteristic of the aromatic systems is the planar or close to planar structure of the given ring considered as aromatic. As mentioned, the COT ring itself is not planar because of the ring strains present in that species. The tub-like conformation is forced by intramolecular effects. It is worth mentioning here that the chair-like conformation cannot be considered as a stable geometry of the COT ring, since in such a conformation the 90° twisting along the formally double bonds should essentially destabilize the whole system. The planar conformation of COT is the transition

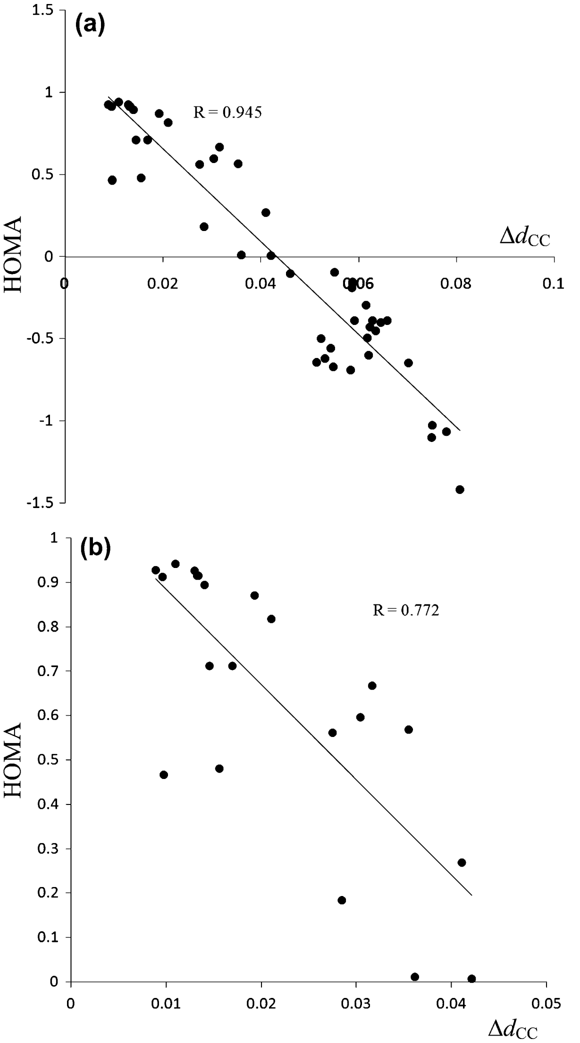

**Fig. 2** HOMA values plotted against the values of $\Delta d_{CC}$. Data for all COT rings found in the CSD search can be seen in graph (a), while in graph (b) only data corresponding to COT rings with positive HOMA values was taken into account.

state geometry corresponding to tub-shaped COT inversion.[15] However, in many alkali and transition metal complexes the planar geometry of COT may be observed. This planarization of COT is usually explained as the result of COT aromatization. Graphical representations of the interrelation between HOMA and parameters reflecting the degree of COT ring planarity, namely $\bar{h}_{CPL}$ and ΔTor, are shown in Fig. 3(a) and (b). In both cases the relations can hardly be considered as close to linear. Even more chaotic distribution of points can be observed if one considers data for the reduced set of COT rings with only positive or only negative HOMA values. Therefore, the COT ring planarization in metal complexes cannot be directly connected with aromatization, at least for the set of crystal structures taken into consideration in these studies.

Since the above conclusions drawn on the basis of observations made from CSD collection are in some way against the general considerations for COT species, we decided to perform additional studies for the specific systems selected from the set of metal-COT complexes collected in CSD. For the purposes of these studies we used advanced quantum-chemical calculations based on Density Functional Theory as specified in the Methodology section. The results of this analysis will be discussed in the next section.

### DFT calculations for selected model systems

The values of selected parameters defined in the Methodology section were obtained for all COT rings present in metal complexes shown in Fig. 1. Numerical results are collected in Table 1. For comparison, the corresponding values were also estimated for the free fully optimized COT ring and for the COT ring in which a planar structure was forced (the transition state structure with imaginary frequency corresponding to out-of-plane vibration). It is worth mentioning that we performed the population analysis using Mulliken,[52] NPA,[53] APT,[54] AIM[42] and ChelpG[55] schemes. However, for each population scheme we obtained results essentially different both quantitatively and qualitatively. For this reason we do

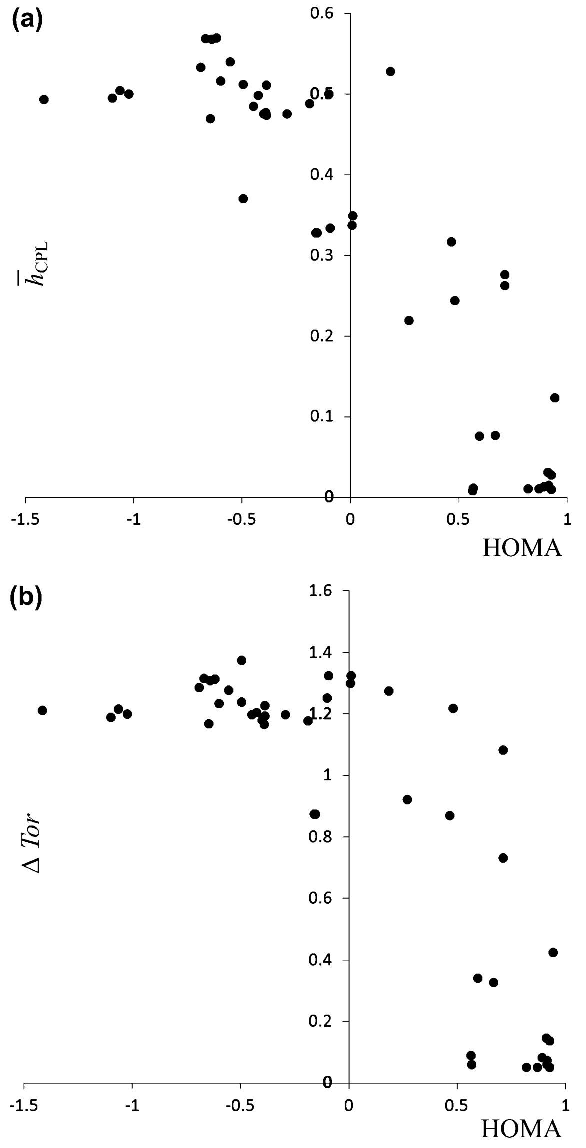

**Fig. 3** Values of parameters describing planarity of COT ring, $\bar{h}_{CPL}$, (a), and ΔTor, (b), plotted against the values of HOMA.

not discuss atomic charge distribution in systems under investigation. Nevertheless, obtained numerical results can be found in the ESI, Table S1.†

Firstly, let us discuss two titanium complexes, that is, system **I** and **II** in Fig. 1. The selected systems are very useful for our analysis, since more than one COT ring is present in each of the complexes. This allows us to compare directly the parameters of COT rings which coordinate Ti atoms in various modes. Structurally, **I** and **II** are closely related. The main difference is that in **II** ring no. 2 coordinates only one Ti atom, whereas in **I** the same ring interacts with both metal centres. As can be seen from Table 1, in both structures the COT rings exhibit a different degree of aromatic character. This is reflected by HOMA values in the range of 0.905–0.755 and FLU values in the range of 0.003–0.006. Such values of aromaticity indices suggest partially or fully aromatic COT rings in **I** and **II**. The more aromatic are the rings numbered as 1 (both in **I** and **II**) and 3 (in **I**). Ring 2 is relatively less aromatic in both complexes. The aromatic character of the given ring is also related to the bond equalization, since it can be noticed that for a more aromatic ring the values of $\Delta d_{CC}$ are lower. (General interrelations between all parameters will be discussed at the end of this section.) What is interesting, however, is the fact that ring 2 is less aromatic in **I** than in **II**, but in **II** all CC bonds are more equalized. This clearly corroborates our previous conclusion made on the basis of CSD data: bond equalization does not necessarily have to be directly connected with aromatization of the COT ring.

Although the molecular structure of **I** and **II** may suggest that in the case of rings 1 (both in **I** and **II**) and 3 (in **I**) there is coordination of $\eta^8$ type, the detailed AIM analysis shows that bond paths connect Ti centre with only four C atoms. See Fig. 4 for example graphical representation. (Unfortunately, no graphic representations can be produced for larger systems due to technical limitations.) The values of $\rho(\mathrm{BCP})_{\mathrm{Ti–C}}$ are in the range of (4.60–4.75) × $10^{-2}$ a.u., (4.60–4.75) × $10^{-2}$ a.u. and (4.95–5.32) × $10^{-2}$ a.u. for ring 1-**I**, 3-**I** and 1-**II**, respectively. In all cases Laplacian of $\rho(\mathrm{BCP})_{\mathrm{Ti–C}}$, $\nabla^2\rho(\mathrm{BCP})_{\mathrm{Ti–C}}$, adopts positive values indicating a rather closed-shell interaction. Additionally, the values of $\rho(\mathrm{RCP})$ measured at ring critical points located in the region between both bond paths are also very close to those measured at proper BCPs. The values are: (4.17–4.72) × $10^{-2}$ a.u., (4.17–4.72) × $10^{-2}$ a.u. and (4.55–5.30) × $10^{-2}$ a.u. for ring 1-**I**, 3-**I** and 1-**II**, respectively. Thus, in the case of COT rings 1 and 3 the COT-Ti interaction should be considered as π-type coordination where two oppositely placed π-bonds interact with Ti coordination sphere. Interaction between Ti centre and two remaining formally double bonds seems to be relatively less effective. Such a conclusion may be supported by the fact that the distances between Ti and C atoms connected with bond paths are slightly but systematically shorter than the corresponding distances between Ti and C atoms for which no bond paths were present. Nevertheless, the difference is very small, by about 0.04 Å, which results from almost planar geometry of those COT rings (see ΔTor values in Table 1). In the case of ring 2 in both **I** and **II** the coordination mode is rather of $\eta^2$ type, although it should be pointed out that in **I** only single Ti-COT bond paths were found even for high grid search (note that the Poincaré-Hopf relationship was still satisfied). However, the detailed analysis suggests that although in **I** two bond paths between Ti and COT ring no. 2 are lacking, the interaction mode should be considered as very similar to those in **II** and the electron density measured in the region between interacting C and Ti atoms is very similar for both C–Ti with bond path and C–Ti without bond path. The values are 5.75 × $10^{-2}$ a.u. and 5.30 × $10^{-2}$ a.u. for the case with bond path and without it, respectively. Most probably the lack of the proper BCP and the corresponding bond path is connected with the flat curvature of electron density in the region between the ligand and central atom. A similar situation was already observed for Ti complexes.[56] As seen in Fig. 4a, only two bond paths are present in the case of **II**. In **I** the situation is similar, but in this case ring 2 coordinates two individual Ti centres. As a result, the number of electrons shared between COT ring 2 and Ti centres estimated as the summary of proper $\delta_{\mathrm{C,TM}}$ (parameter $\sum\delta_{\mathrm{C,TM}}$ in Table 1) is greater in **I** than in **II**. However, if we consider the interaction between COT and individual Ti atoms in **I**, then a value of 1.05 electrons will be obtained, which is exactly a half of the total value in Table 1. Interestingly, in **I** the value of $\sum\delta_{\mathrm{C,TM}}$ is very close for both inner and lateral rings, although the inner ring is significantly less aromatic and planar than the lateral ones.

**Table 1** Selected data estimated for the systems under discussion. $\sum\delta_{\mathrm{C,TM}}$ (in electrons) is the summation over all $\delta_{\mathrm{C,TM}}$ where C are carbon atoms in the given COT ring, while TM is the given metal centre coordinated by that ring. See the Methodology section for a detailed definition of all parameters collected in the table. Ring numbering corresponds to that in Fig. 1

| System | COT ring | $\Delta d_{CC}$ | ΔTor | HOMA | FLU | $\sum\delta_{\mathrm{C,TM}}$ |
|---|---|---|---|---|---|---|
| $\mathrm{COT}_{\text{tub-shaped}}$ | | 6.630 | 1.000 | −0.214 | 0.0563 | — |
| $\mathrm{COT}_{\text{planar}}$ | | 6.562 | 0.000 | −0.220 | 0.0517 | — |
| **I** | 1,3[a] | 0.095 | 0.094 | 0.905 | 0.0031 | 2.130 |
| | 2 | 1.297 | 0.688 | 0.755 | 0.0062 | 2.100[b] |
| **II** | 1 | 0.206 | 0.107 | 0.883 | 0.0033 | 2.160 |
| | 2 | 1.310 | 0.544 | 0.823 | 0.0059 | 1.740 |
| **III** | | 3.776 | 0.125 | 0.128 | 0.0290 | 2.840[b] |
| **IV** | | 5.731 | 1.297 | −0.592 | 0.0355 | 3.960[b] |
| **V** | | 4.156 | 0.351 | 0.300 | 0.0272 | 1.560 |

[a] Values were the same for both outside rings in **I**. [b] This is the summary value corresponding to interaction between COT ring and both metal centers coordinated by that ring.

All observations made for systems **I** and **II** show that it is difficult to find any direct relation between the aromatic character of the given COT ring and other properties of that ring. It seems that much depends on the coordination mode characteristic of the COT ring under consideration. Comparison of $\sum\delta_{\mathrm{C,TM}}$ indicates that Ti-COT electron sharing and possible formation of $4n+2$ π-electron structure does not explain planar conformation, or even more, the aromatic character of the ring.

Let us now consider another interesting situation in which an individual COT ring coordinates Ni centres as shown in Fig. 1, **III**, **IV** and **V**. The only formal difference between systems **III** and **IV** is the way in which Ni–($H_2PC_2H_4PH_2$) moieties are spatially located with respect to each other and

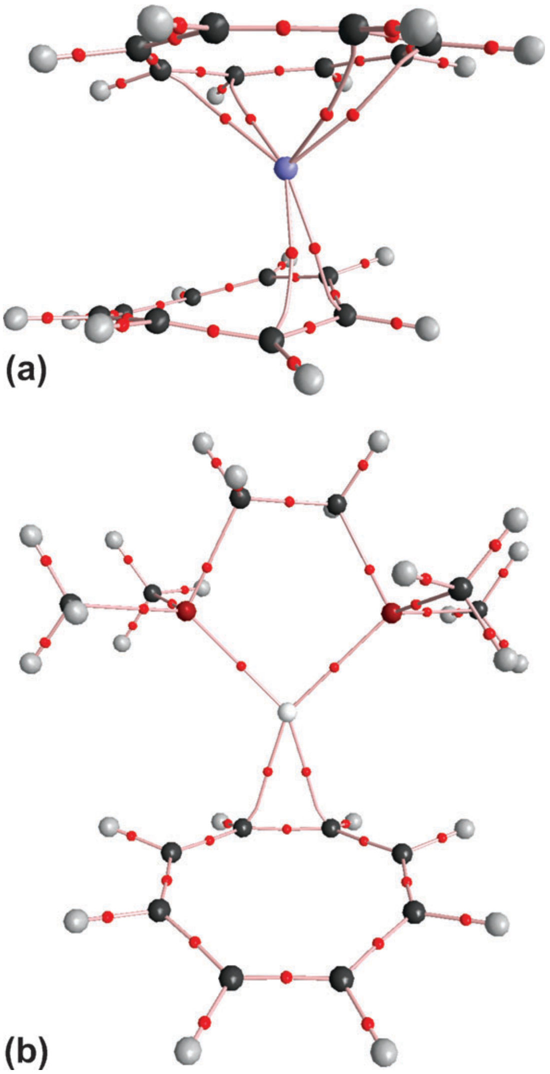

**Fig. 4** Molecular graphs showing attractors and BCPs distribution in **II**, (a), and V, (b). RCP are omitted for clarity. Big circles correspond to attractors (black—C atoms, gray—H atoms, blue—Ti atom, white—Ni atom), small ones to BCPs.

with respect to the COT ring placed in the middle. This formal difference drastically diversifies the properties of **III** and **IV**. (See ref. 30 for experimental studies (including the synthesis and X-ray analysis) and ref. 31 for some theoretical studies devoted to analogues of those systems.) It can be seen from Table 1 that COT in **III** is almost planar, whereas in **IV** it adopts a tub-like conformation with ΔTor value even greater than in free COT in its natural conformation. Interestingly, although COT in **III** is practically planar, the HOMA value indicates a rather nonaromatic character of that ring. (A similar observation was made for the mentioned analogs of **III** using magnetic index of aromaticity, NICS.[29]) This shows that planarity of the COT ring may be forced by the coordination environment in the given complex, but it does not mean that the COT ring itself becomes aromatic in each case when it has the planar conformation. The large value of $\Delta d_{CC}$ in **III** additionally supports such a conclusion. An interesting situation occurs in **IV**, where COT coordinates two Ni atoms in a completely different way if compared with the remaining systems under investigation. In this case COT adopts the tub-like conformation. This conformation seems to be additionally stabilized by interaction with metal centres. This leads to additional double bond localization and an essentially antiaromatic character of COT (compare the values in Table 1 with those obtained for free $\text{COT}_{\text{tub-shaped}}$). What is interesting, coordination of the Ni centres in **IV** is relatively more effective than in the case of III, as $\sum\delta_{C,TM}$ adopts a larger value in this case

The AIM analysis indicates $\eta^2$ coordination mode in **III** and **V** (see Fig. 4(b)), and $\eta^4$ coordination mode in **IV**. The values of $\rho(\text{BCP})_{\text{Ni–C}}$ are as follows: $9.24 \times 10^{-2}$ a.u., $7.10 \times 10^{-2}$ a.u. and $9.39 \times 10^{-2}$ a.u. for **III**, **IV** and **V**, respectively, with positive values of $\nabla^2\rho(\text{BCP})_{\text{Ni–C}}$.

As far as the general dependences between parameters collected in Table 1 are concerned, both aromaticity indices are very well correlated (the correlation coefficient cc equals 0.987) with the only exception for system IV, for which the relation seems to be broken, probably because of the efficient orbital overlapping between metal centres and strongly distorted ring which influences values of FLU.[13] Practically there is no direct relation between HOMA or FLU and the rest of parameters. Perhaps the only exception is the relation between aromaticity indices and $\Delta d_{CC}$ for which the cc for a linear regression is of 0.953 and 0.977 value for HOMA and FLU, respectively. In general, such a linear correlation between aromaticity indices and $\Delta d_{CC}$ parameter should be expected, although even in that case the comparison of the values estimated for ring 2 in systems **I** and **II** shows that CC bond equalization in COT acting as the ligand should not be strictly associated with aromatization. This conclusion is strongly supported by the results obtained in the previous section with CSD statistical analysis. It can be said on the basis of theoretically investigated systems that the planarization of the COT ring (and in some way also bond length equalization) is mainly connected with the efficiency of COT-metal centre interaction of the specific COT conformer. A particularly good example in respect may be delivered by the comparison of data estimated for systems **III** and **IV**. The aromatization of the COT ring in metal complexes seems to be rather an effect of secondary importance.

## Conclusions

The search through Crystal Structure Database was performed and the selected geometrical parameters of COT rings acting as ligands in organometallic complexes were collected. Detailed statistical analysis shows that the planar geometry of the COT ring in metal complexes is not necessarily connected with aromatization of that ring. Also, the bond alternation parameter does not correlate directly with the aromaticity indicators. Theoretical studies performed for selected model systems shows that the main factor affecting COT structure is the efficiency of the metal centre-COT interaction of the COT ring in a given conformation. The aromatization, in such cases usually considered as the effect of leading importance, in fact seems to be rather a background effect.

## Acknowledgements

Calculations using the Gaussian09 set of codes were carried out in Wrocław Centre for Networking and Supercomputing (http://www.wcss.wroc.pl). Access to HPC machines and licensed software is gratefully acknowledged.

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