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Substituent effects in mono- and disubstituted 1,3,5,7-cyclooctatetraene derivatives in natural and planar conformations†‡

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Substituent effect in cyclooctatetraene (COT) has been investigated by means of quantum-chemical (DFT-B3LYP) calculations. Two substituents, nitroso (π-electron-withdrawing) and hydroxy (π-electron-donating), have been examined and compared with monosubstituted and unsubstituted systems. Additionally, both the natural (tub-shaped) and the planar geometries of the COT have been taken into account. The behavior of COT ring, being the antiaromatic $4n$ π-electron system, has been compared with that of the benzene ring, being the aromatic $4n + 2$ system. The 1,4-substitution differs significantly from the 1,3- and 1,5-substitution, which corresponds to an analogous situation found for benzene derivatives (*para vs. meta* substitution). Substituents influence COT more effectively in its planar geometry as compared with the tub-shaped geometry. This is due to the better overlapping of the p_z orbitals of the carbon atoms within the ring in its planar conformation. As far as the π-electron communication between the substituents is concerned, the behavior of both $4n$ and $4n + 2$ systems is in some way similar. Both systems tend to keep their π-electronic structures. Nevertheless, benzene ring, *i.e.* $4n + 2$ system seems to be a clearly worse medium for transmission of the substituents communication than its $4n$ counterpart.

Introduction

Substituent effects[1,2] are quantified by the use of the Hammett[3] or the Hammett-like substituent constants.[4–6] In most cases, both in the past[3,7–9] as well as more recently, these problems were considered more for aromatic systems[10–29] and seldom for non-aromatic systems[30,31] and quasi-aromatic systems.[32,33] A general conclusion for the substituent effect in monosubstituted benzene is that this interaction is rather weak.[34–36] Benzene is a π-electron system fulfilling the Huckel rule $4n + 2$ and its ring does not tend to have either more or less π-electrons. As distinct from $4n + 2$ π-electron systems, these kinds of effects are very strong for cyclic systems containing $4n + 1$ or $4n - 1$ π-electrons, as shown for exocyclically substituted derivatives of fulvene for electron releasing substituents[37,38] or heptafulvene for electron attracting substituents.[39] Undoubtedly these systems tend to have either more π-electrons (the five member rings as in fulvene derivatives) or less π-electrons (the seven member rings as in heptafulvene derivatives). This kind of behavior is also well known for other non-alternant hydrocarbons, *e.g.* cyclopentadiene, which has been known for more than a century as the C–H acid,[40] with $\mathrm{p}K_\mathrm{a} \approx 18$,[41] which after deprotonation becomes a relatively stable anion with ASE ≈ 13 kcal mol^{-1}.[42]

A question arises of how the systems with $4n$ π-electrons behave, since they are antiaromatic[43–45] by definition and have to accept or to release two electrons in order to become aromatic. This is the case for cyclooctatetraene (hereafter abbreviated as COT) which when reduced to its dianion becomes a relatively stable system.[46–48] In terms of Hammett's ideas the substituents can act as either electron donating ($\sigma < 0$) or electron accepting ($\sigma > 0$), but the charge transfer, characteristic of substituent effects being relatively large for non-alternant systems, in the case of benzene derivatives is much smaller than two electrons.

The purpose of this article is to study how the substituent effect works in mono- and disubstituted COT derivatives in their natural and planar conformations. Experimental geometry by electron diffraction[49] and by X-ray diffraction[50] shows a non-planar (tub-shaped) structure and a substantial CC bond length alternation. Planarization of COT may 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. This was done by a model procedure[51] following the ideas of Stanger[52] and Maksic *et al.*[53] addressed to benzene. Another consequence of this procedure is a decrease of bond length alternation. However, despite these typical changes, which could suggest aromatization of the ring, the energetic and magnetic (NICS[54] and magnetic susceptibility) criteria of aromaticity excluded such a possibility. The analysis of ring currents of COT derivatives planarized in various ways[55,56] showed decisively that planarization in these cases has nothing in common with aromatization. Moreover, bond

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† Dedicated to Dr Bohdan Kamienski on the occasion of his 70th birthday.

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length alternation depends very weakly on the planarization. The difference between tub-shaped and planar conformations of COT is that in the latter case a more efficient overlap is possible between the $2p_z$ orbitals. Thus, in these two conformations one can expect a different substituent effect. This is a subject of study in this article. In the case of benzene there are two kinds of interactions for disubstituted systems, the *meta* and *para*, which differ mostly in a different blend of the resonance and inductive effects (for review see ref. 8,21,22). These two kinds of interactions between the substituents of opposite electron properties (donating *vs.* attracting) were also observed and documented for disubstituted naphthalene derivatives.[57]

In this article we present the results for monosubstituted COT derivatives and a series of disubstituted ones in positions 1,3, 1,4 and 1,5 considered in both the planar and natural conformations. Additionally, some observations made for the COT system have been related to its benzene counterpart.

Methodology

All molecular systems were optimized using DFT-B3LYP[58–61] hybrid functional in conjunction with 6-311+G(d)[62,63] basis set. For tub-shaped COT derivatives and for all benzene derivatives the full optimization without any symmetry restraints was done. In the case of planar COT derivatives the planar symmetry was forced. The frequency analysis was used to verify whether the optimized geometries correspond to the ground state stationary points or transition states. No imaginary frequencies were found for tub-shaped COT and benzene derivatives. Since planar geometry of COT corresponds to the transition state of this system, the corresponding imaginary frequency was found. Additionally, imaginary frequencies corresponding to the out-of-plane vibration of the nitroso group were also found for planar COTs (it resulted from the symmetry restraints forcing planar geometry). All calculations were performed with the use of Gaussian03 set of codes.[64] CHelpG scheme[65] was used for atomic charges analysis.

As a geometry-based indicator of local aromaticity, the HOMA index was applied. According to its definition[66,67] 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 α_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 non-aromatic 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.[68] The higher the HOMA value is, the more "aromatic" the ring in question is and, hence, the more delocalized the π-electrons of the system are. Additionally, HOMA$^{\#}$ values were estimated according to the same procedure as in the case of HOMA, but for the sequence of bonds linking the substituted carbon atoms. It should be mentioned that HOMA can be used for any π-electron systems or parts of the systems, and also for non-planar systems.[69–74]

Results and discussion

We analyzed 1,3,5,7-cyclooctatetraene, COT, and its simple mono- and disubstituted derivatives. Two substituents were taken into account: the nitroso group, as a typical π-electron-withdrawing substituent, and the hydroxy group, which reflects π-electron-donating properties. In both cases they are tentatively taken as interacting through a mesomeric effect. Resonance contributions for NO and OH are $R^- = 1.14$ and $R^+ = -1.25$, respectively. For comparison, field effects are substantially smaller and amount to $F = 0.49$ and $F = 0.33$, respectively.[4] Both mono- and disubstituted systems were analyzed. In the case of disubstituted systems all possible combinations of the relative placement of substituents were considered. The unsubstituted COT ring served as a reference system.

First of all, let us discuss some energetic properties of the COT and its simple derivatives. Table 1 contains selected energetic parameters characterizing the system under consideration. The following energetic parameters were used to quantify the role of substitution in COT:

$$E^{\ddagger} = E_{\mathrm{planar}} - E_{\mathrm{tub\text{-}shaped}} \qquad (1)$$

$$E^{\dagger} = E_{\mathrm{OH\text{-}substituted}} + E_{\mathrm{NO\text{-}substituted}} - E_{\mathrm{disubstituted}} - E_{\mathrm{unsubstituted}} \qquad (2)$$

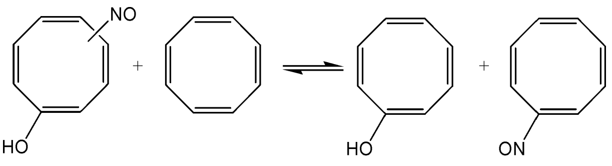
$$\Delta E^{\dagger} = E^{\dagger}{}_{\mathrm{planar}} - E^{\dagger}{}_{\mathrm{tub\text{-}shaped}} \qquad (3)$$

Eqn (1) defines a simple difference in total energies of the planar and tub-shaped COT. Since the planar symmetry of the given COT is in fact a transition state corresponding to the transition between two tub-shaped ground states, this parameter may be treated as the energetic barrier of the inversion of tub-shaped COT or its derivative. Eqn (2) is the energy balance of the homodesmotic reaction shown in Scheme 1. This parameter reflects the extra stabilization or destabilization due to the interaction between two substituents, –NO and –OH, through the COT ring. Finally, eqn (3) defines the difference between $E^{\dagger}$ estimated for planar and tub-shaped COT.

From the data collected in Table 1 it can be seen that there is some similarity in parameters obtained for 1,5- and

Table 1 Selected energetic parameters characterizing the COT system and its derivatives in planar and tub-shaped geometry (B3LYP/6-311+G* level of theory). All values in kcal mol^{-1}. $E^{\ddagger}$ for unsubstituted COT is 10.796 kcal mol^{-1}

	$E^{\ddagger}$	$E^{\dagger}{}_{\mathrm{(tub\text{-}shaped)}}$	$E^{\dagger}{}_{\mathrm{(planar)}}$	$\Delta E^{\dagger}$
1,5-Disub.	9.350	−0.404	−1.561	−1.157
1,4-Disub.	8.048	1.912	2.057	0.145
1,3-Disub.	9.547	−1.247	−2.601	−1.354



Scheme 1

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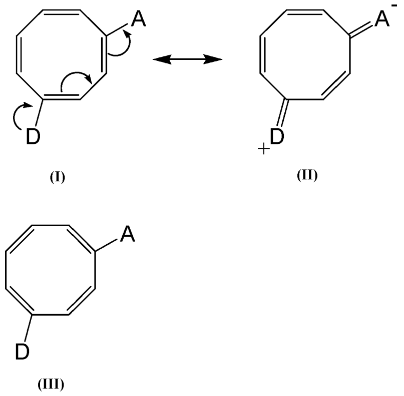

Scheme 2

1,3-substituted COTs. It can be found that the presence of substituents slightly lowers the energetic barrier of the tub-shaped COT inversion. The data obtained for 1,4-substituted derivative clearly differ from the two previous cases. The difference results from the fact that in the case of 1,4-substitution the conjugation between formal double bonds allows π-electronic interaction between two substituents (push–pull effect), which can be schematically illustrated with two frontier canonical structures as shown in Scheme 2. Such an interaction, *i.e.* a better π-communication, cannot take place in the case of 1,5- and 1,3-substitution, unless the double charge separation is considered.

The situation is analogous to *para* and *ortho versus meta* substitution in benzene and naphthalene. (See ref. 57 for a detailed discussion and graphical representation of single and double charge separation canonical structures of benzene and naphthalene.) It has to be mentioned that an alternative valence isomer of the tub-shaped 1,4-substituted COT can also be considered (see structure **III** in Scheme 2). In this case, similar to the case of 1,3- and 1,5-substitution, the conjugation between CC bonds cannot occur, unless the double charge separation is considered. The total energy difference for structures **I** and **III** from Scheme 2 is 1.438 kcal mol^{-1} (B3LYP/6-311+G*). This difference is obviously connected with the better π-electron communication between substituents in COT structure **I**. As it could be expected, structure **III** is not a stable conformation of the planar 1,4-substituted COT and structure **I** of tub-shaped COT will be preferred in natural conditions. Interestingly, for the 1,4-disubstituted COT the value of $E^\dagger$ is positive, both for planar as well as for tub-shaped COT. Thus, only in this case the presence of both substituents thermodynamically stabilizes the COT ring system. A slightly more effective stabilization is present in planar COT. This results from the fact that the planar structure of the COT ring allows a more favorable overlap of p_z orbitals and hence favors the π-conjunction along the sequence of bonds linking the two substituents. (However, it should be pointed out that the difference is relatively small, about 0.15 kcal mol^{-1}.) The opposite effect can be observed for 1,5- and 1,3-substituted COTs. In these cases the presence of two substituents seems to destabilize the system thermodynamically, which is reflected by the negative values of $E^\dagger$. Moreover, in the case of the planar geometry the system is *destabilized* more effectively than in the case of the tub-shaped one. As a consequence, the difference of $\Delta E^\dagger$ values obtained for differently substituted COTs corresponds perfectly with the differences in the values of $E^\ddagger$. Thus, a question may arise, why in the case of 1,5 and 1,3-substitution does the presence of substituents destabilize the system? Some explanation may be given by the analysis of the atomic charge summarized for C and H atoms in COT ring (see Table 2).

In the case of the monosubstituted COT ring with –OH or –NO substituents attached the total charge of the COT ring is positive. This positive charge is compensated with the negative charge located on the substituents. This means that the substituents are withdrawing electrons from the ring. Moreover, when two substituents are attached, the positive charge concentration within the ring is almost additive, no matter which position the substituents are in. Both substituents are known to be relatively strong π-electron-donating/accepting groups; this, however, does not bear any clear effect on the charge of the ring. Interestingly, similar charging of the ring can be observed for the benzene derivatives (see Table 2). Moreover, the trace of similarity can be found between the amount of charge located within the given ring *vs.* the substitution of this ring. For instance, in 1,4-substitution practically the same charge is located on the rings. Therefore, from this point of view, one may expect that the substituents influence both COT and benzene ring in a similar way, apart

Table 2 The COT-ring atomic charges (obtained according to CHelpG scheme, given in electrons) are the summations of the charges located on C and H atoms in COT ring, HOMA values estimated for COT ring and HOMA$^\#$ values for the proper sequence of bonds (see text for details). Bond lengths are given in angstroms

	COT-ring atomic charges	HOMA	HOMA$^\#$	d(C–N)^a	d(C–O)^a
1,5-COT	0.54/0.56	−0.09	−0.102/−0.123	1.456/1.481	1.372/1.376
1,4-COT	0.61/0.63	0.01	0.621/0.844	1.437/1.438	1.364/1.356
1,3-COT	0.51/0.52	−0.10	−0.007/−0.073	1.458/1.481	1.372/1.376
ON-COT	0.37/0.37	−0.11	—	1.452/1.466	—
HO-COT	0.20/0.22	−0.16	—	—	1.374/1.374
COT	—	−0.21	—	—	—
1,4-Benzene	0.60	0.96	0.95	1.427	1.357
1,3-Benzene	0.58	0.98	0.99	1.443	1.365
ON-benzene	0.40	0.98	—	1.440	—
HO-benzene	0.22	0.99	—	—	1.370
Benzene	—	1.00	—	—	—

[a] The values estimated for COT system correspond to non-planar/planar geometry of the ring, respectively.

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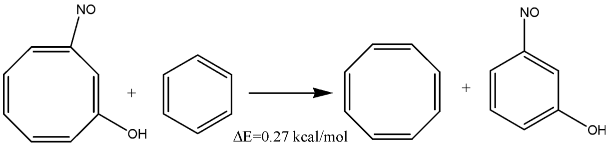
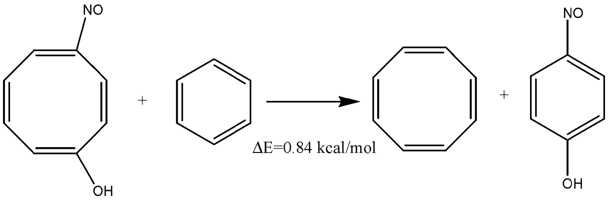
from the fact that both rings differ from each other by means of π-electron delocalization. This effect is most probably strictly connected with the σ-withdrawing properties of the –NO and –OH groups. The Huheey group electronegativities[75,76] in the Pauling scale are 4.65 and 3.51 for the –NO and –OH group, respectively, whereas for hydrogen it is only 2.2.[77] In the case of COT as well as benzene, the given ring bears a larger positive charge when substituted with the NO group (0.37 and 0.40, respectively) rather than with the OH group (0.20 and 0.22, respectively). Thus the observed positive charging of the COT and benzene ring seems to be a result of changes in σ-electron charges due to high electronegativity of NO and OH. This conclusion is in line with a recent study on σ- and π-electron population on carbon atoms of benzene and its monosubstituted derivatives.[78,79]

It can be seen from the data of Table 1 that only substitution in position 1,4 gives a stabilization effect for the homodesmotic reaction in Scheme 1, whereas for both other substitutions, 1,3 and 1,5, the substituent effect stabilization energy (SESE)[21] is negative. Parallel to these examinations higher values of HOMA were observed for 1,4-substitution whereas lower values were observed for two alternative substitutions. As it was mentioned, the planar structure allows a better overlap of the p-type orbitals, so for those systems the substituents are more effectively interacting with and through the COT ring. This is in agreement with the values of HOMA$^{\#}$ estimated for the sequence of bonds linking the substituted carbon atoms. In the case of 1,4-substitution the value of HOMA$^{\#}$ is positive and relatively close to 1, which corresponds to a delocalized system of bonds. In the case of two alternative substitutions the values of HOMA$^{\#}$ are negative, as for a strongly localized system.

As concerns the influence of substitution on the substituted ring, there is a clear difference in behavior of the COT ring as compared with the benzene ring. In COT the π-electron interaction between the substituents leads to a partial delocalization within the ring. This is reflected in the values of HOMA and HOMA$^{\#}$ being larger for 1,4-substituted COT than for the 1,3- or 1,5-substituted systems or the unsubstituted one. In the case of benzene ring the situation is exactly opposite. For the system with the most effective communication between the substituents (*i.e.* 1,4-substitution) the presence of substituents leads to a partial localization of π-electrons (*via* the so-called quinoid-like structure[80]) with respect to the unsubstituted benzene ring. Thus, it is worth taking a closer look at the differences between COT and benzene derivatives measured by means of energetic parameters of the set of homodesmotic reactions shown in Schemes 3–6. (Of course, tub-shaped COT was taken for consideration in this case, since the planar form is a transition state being less stable by about 9 kcal mol^{-1}, as shown in Table 1.) The homodesmotic reactions in Schemes 3 and 4 allow us to find which ring system with the presence of two interacting substituents is more favorable. The energy of reactions 3 and 4 indicates that the interaction between two substituents in the 4*n* π-electron system is slightly more favorable than in 4*n* + 2 ones. Moreover, they indicate a stronger interaction in the case of 1,4- than 1,3-substitutions. This is in line with the changes in π-electron delocalization estimated by HOMA values (Table 2) and shows the difference in transmitting ability of the spacer between 1,3 and 1,4 cases of substitution.



Scheme 3

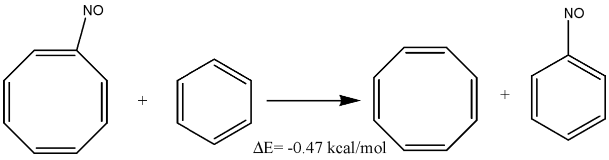


Scheme 4

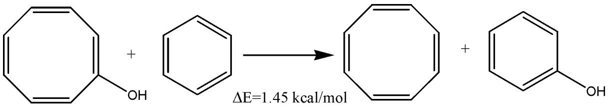
Previous observations allow us to assume that σ-withdrawing effect of both substituents is practically the same in the case of both rings. Therefore, it can be said that the 4*n* system is a better medium in communication between two substituents than the 4*n* + 2 system. Probably this is because the latter is an aromatic cyclic system which tends to keep its delocalized character (as it was mentioned, the presence of substituents reduces the aromatic character of the benzene ring).[36]

The analysis of homodesmotic reactions for monosubstituted systems (Schemes 5 and 6) allows us to point out a difference in interaction between the given substituent and the ring (by comparison of the 4*n* + 2 and 4*n* π-electron systems). In the case of a π-accepting NO substituent the substitution of benzene is slightly more favorable than that of COT. In the case of an π-electron-donating OH group we have an opposite effect for which HO–benzene is less thermodynamically stable than HO–COT. This may suggest that the COT ring amortizes the effect of electron donation more effectively, while the benzene ring is less sensitive to electron attraction.

One would expect that the changes in the length of the C–N and C–O bonds may reflect the contribution of given charge separated canonical structures (see *e.g.* Scheme 2). Clearly, the shorter the C–N and C–O bond is, the greater the contribution of the π-bonding in this bond is, so the larger the contribution of the corresponding canonical structure with separated



Scheme 5



Scheme 6

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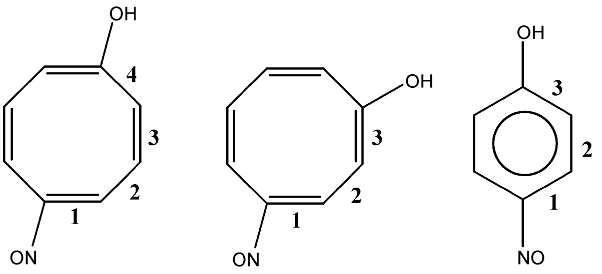
charge is. If we consider the COT substituted system, the shortest distance can be observed in 1,4-substituted COT. This is in agreement with the previous conclusion, since two substituents present in 1 and 4 positions with respect to each other will interact with the COT π-electron system more effectively. This interaction is stronger in planar conformation, thanks to better overlapping of p_z orbitals. The same conclusion can be drawn for the corresponding benzene derivative. Interestingly, if we compare the tub-shaped and planar conformations of COT, it can be found that in general the bonds in tub-shaped COT are relatively shorter. This is caused by the geometry of the ring in its two conformations. The planarization of the COT ring leads to the enlargement of the valence angle between CC bonds. This angle adopts a value of 127.6° in tub-shaped whereas 135.0° in planar COT (obviously in the benzene this angle equals 120.0°). As a result, the values of the corresponding C–C–N and C–C–O angles are reduced leading to a steric repulsion between the COT ring and the given substituent. This observation is in agreement with earlier studies on conjugated polyenes.[81,82] This also explains the relatively short C–N and C–O distances in benzene derivatives.

Finally, it is worth taking a look at the electron density distribution in systems discussed in this article. A topological analysis of electron density performed according to atoms in molecules quantum theory[83,84] has been applied and the following properties of the CC bonds in COT and benzene rings are discussed: electron density measured at BCP, ρ_{BCP}, its laplacian, $\nabla^2\rho_{\mathrm{BCP}}$, and ellipticity of the bond. It has been shown that the electron density parameters measured at bond critical points (BCPs) may reflect the properties of the bond under consideration.[57,85–89] In general, the stronger the given bond is, the greater the value of electron density measured at the BCP corresponding to this bond is. Also the laplacian of electron density indicates properties of the bond, adopting negative values for the strongest, covalent in nature bonds, and positive values for weak, closed shell interactions. Ellipticity is defined as $\varepsilon = (\lambda_1/\lambda_2) - 1$, where λ_1 and λ_2 correspond to two eigenvectors perpendicular to the direction of the bond (at BCP by definition: $\lambda_1 \leq \lambda_2 < 0$). This parameter illustrates how the electron density shape is flattened crosswise the bond path in BCP. The ε equals zero for ideally cylindrical bonds, *e.g.* single or triple CC bond, and differs from zero when the bond cross-section is elliptic, *e.g.* in the case of double CC bond.

AIM based characteristics of the CC bonds in selected COT and benzene systems have been collected in Table 3. The bond numbering has been shown in Scheme 7. As it can be seen, there are clear differences in parameters of formally single and double bonds in unsubstituted COT ring. In the case of 1,5-substituted COT ring these differences are similar to those in unsubstituted COT. Thus, as it was already mentioned, π-electron communication between substituents in 1,5-substitution is relatively weak. However, the differences between formally double and single CC bonds are already smaller in 1,4-substituted COT, particularly in its planar conformation. Also in *para*-substituted benzene there are differences in CC bond characteristics. Therefore, these observations confirm the previous conclusion that communication between substituents leads to partial delocalization in the antiaromatic COT system and partial localization in the aromatic benzene ring. On the basis of data collected in Table 3, the molecular systems can be ordered in the following way, according to increasing π delocalization (or decreasing π localization): unsubstituted COT (as fully antiaromatic system) < 1,5-substituted COT < 1,4-substituted COT in its tub-shaped and planar conformation < *para*-substituted benzene < benzene (as fully aromatic system).

Table 3 Properties of the electron density measured at CC bond critical points in selected COT and benzene derivatives. Electron density and its laplacian are given in au

	ρ	$\nabla^2\rho$	ε
Unsubstituted COT			
Formally double bond	0.336	−0.974	0.339
Formally single bond	0.267	−0.673	0.058
1,5-Substituted COT (tub-shaped conformation)			
1	0.332	−0.955	0.291
2	0.273	−0.701	0.057
3	0.337	−0.982	0.331
4	0.270	−0.701	0.074
1,4-Substituted COT (tub-shaped conformation)			
1	0.323	−0.910	0.269
2	0.282	−0.735	0.103
3	0.332	−0.964	0.358
1,4-Substituted COT (planar conformation)			
1	0.319	−0.896	0.215
2	0.288	−0.757	0.123
3	0.322	−0.922	0.306
1,4-Substituted benzene			
1	0.308	−0.863	0.193
2	0.312	−0.872	0.211
3	0.309	−0.872	0.223
Benzene			
Delocalized bond	0.308	−0.853	0.196



Scheme 7

Conclusions

The 1,4-substitution in COT allows more effective communication between the substituents than 1,3- and 1,5-substitution. This corresponds to an analogous situation found for benzene derivatives (*para vs. meta* substitution). The interaction between the substituents is stronger in the case of planar COT conformation due to a better overlapping of p_z orbitals.

In COT the presence of the substituents leads to a partial delocalization in the antiaromatic 4*n* π-electron system. The stronger the π-electron communication between the substituents is, the more delocalized the bonds linking the substituted carbon atoms are. In the case of benzene the exact opposite effect can be observed. Contributions from quinoid-like canonical structures of the benzene lead to partial localization

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of the aromatic π-bonds. These conclusions are confirmed by the AIM based topological analysis of electron density.

Finally, the COT ring, being a 4*n* π-electron system, is a better medium for communication between two substituents than benzene, being a 4*n* + 2 π-electron system. This is because the latter is an aromatic cyclic system which tends to keep its delocalized character.

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