

Characteristics of ring critical point as descriptors of H-bond strength

Marcin Palusiak* and Slawomir J. Grabowski

Department of Crystallography and Crystal Chemistry, University of Łódź, ul. Pomorska 149/153 90-236 Łódź, Poland

The results of B3LYP/6-311+G* level of calculations show that the electron density and its Laplacian for the ring critical point (RCP) of the benzene ring as well as its position may be applied as useful parameters describing the H-bond strength for complexes of methoxybenzene with simple proton donors such as: HF, H₂O, C₂H₂, NH₂CH₃, CH₃F and C₂H₄.

Keywords: methoxybenzene, DFT calculations, H-bond strength, AIM theory, bond critical point, ring critical point

The geometrical parameters that are most often used as criteria for the existence of hydrogen bonding interaction, are also applied to assess the H-bond strength.¹ For example the proton...acceptor H...Y distance is often treated as a rough estimation of H-bond strength since for a homogeneous sample of systems the correlations between this parameter and H-bond energy have been found. The Bader theory² provides additional information on the nature of hydrogen bond, since topological parameters such as the electron density at the H...Y bond critical point ($\rho_{H...Y}$) and its Laplacian ($\nabla^2\rho_{H...Y}$) correlate with the binding energy.³ Recent studies show that the other topological parameters, not only those of H...Y bond critical point, may be useful as H-bond strength descriptors. For intramolecular H-bonds the ring of atoms connected through typical covalent bonds and H...Y contacts is created and for such a ring there is the ring critical point (RCP). It was pointed out that the electron density at the RCP ($\rho_{RCP-HB-intra}$) and its Laplacian ($\nabla^2\rho_{RCP-HB-intra}$) correlate well with the other parameters describing the H-bond energy such as the above mentioned characteristics of H...Y BCP.⁴

Geometrical, energetic and topological parameters were studied for the complexes of methoxybenzene with simple proton donors such as: HF, H₂O, C₂H₂, NH₂CH₃, CH₃F and C₂H₄, and correlations between these parameters were found.⁵ For such complexes the oxygen atom was the acceptor of protons, the interrelations between the C_{aromatic}-O, C_{methyl}-O bond lengths and their topological parameters were found as well as the agreement of these relations with those obtained from the bond valence model.⁶ In this work the estimation of the influence of the hydrogen bond on the aromatic system in the methoxybenzene specie is studied on the basis of topological analysis. For this purpose, the results from our earlier work⁵ on the complexes mentioned above are used. To obtain the results on these complexes the GAUSSIAN98 program⁷ was used and DFT calculations at the B3LYP/6-311+G* level of theory have been carried out, the geometry of single molecules and dimers were fully optimised. Analysis of electron density was performed using the AIM2000 program package.⁸ The binding energies have been calculated as

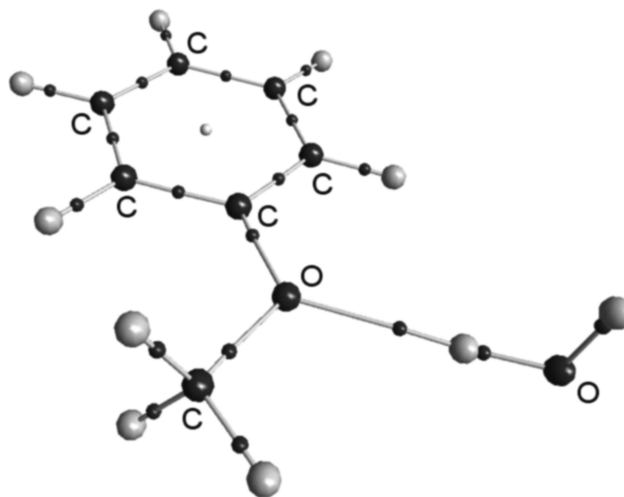


Fig. 1 Molecular graph of dimer methoxybenzene – water. Non-H atoms are designated. The bond and ring critical points are also viewed as small circles.

differences between energies of dimers and sums of energies of isolated monomers and corrected for BSSE using the counterpoise method of Boys and Bernardi.⁹ Figure 1 shows the molecular graph of one of complexes investigated earlier and investigated also in this study. The water molecule is a proton donor and the O-atom of the methoxy group plays the role of the accepting centre. Selected results from our previous work and the other results not yet considered and used in this study have been collected in Table 1. The main topic of this study is to analyse the characteristics of RCP of the benzene ring since they have not been yet analysed.

One can see (Table 1) that the electron density at the RCP of the benzene ring ($\rho_{RCP-benzene}$) of methoxybenzene correlates with the binding energy. The linear correlation coefficient for this relationship amounts to 0.920, the increase of electron density is connected with the increase of H-bond strength. The clearer interdependence is observed between the Laplacian

Table 1 Selected topological and geometrical parameters of considered model systems. Binding energies are also given.

Proton donator	Distance RCP – attractor (C _{ar}) Å	ρ_{RCP} [au]	$\nabla^2\rho_{RCP}$	$\rho_{H...O}$	$\nabla^2\rho_{H...O}$	(D)H...O /Å	D...O /Å	E_{bin} /kcal/mol
HF	1.379719484	0.021331686	0.158156177	0.0451	0.1508	1.890	2.636	-8.1
H ₂ O	1.383680760	0.021292042	0.157815045	0.0250	0.0973	1.951	2.909	-3.95
C ₂ H ₂	1.386008371	0.021276236	0.157634724	0.0140	0.0533	2.220	3.283	-1.83
NH ₂ CH ₃	1.385001960	0.021276822	0.157655241	0.0072	0.0240	2.591	3.654	-1.82
CH ₃ F	1.386317879	0.021279337	0.157561653	0.0124	0.0457	2.289	3.256	-0.94
C ₂ H ₄	1.387574880	0.021241618	0.157504053	0.0070	0.0233	2.586	3.623	-0.5
*	1.388112377	0.021232466	0.157429606	–	–	–	–	–

* The parameters of free methoxybenzene not involved in H-bond interactions.

* Correspondence. E-mail: marcinp@uni.lodz.pl

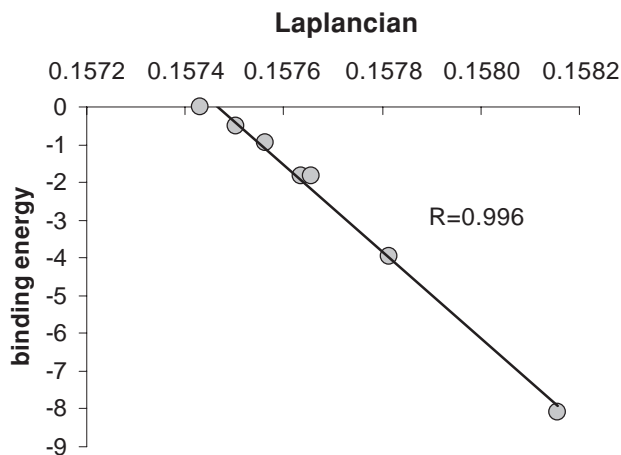


Fig. 2 Binding energy [kcal/mol] vs $\nabla^2\rho_{\text{RCP}}$.

of the RCP ($\nabla^2\rho_{\text{RCP-benzene}}$) and the binding energy. In this case the increase of binding energy is also connected with the increase of Laplacian value. This relationship is shown in Fig. 2 and the linear correlation coefficient (R) amounts to 0.996. Both correlations are probably the consequence of H-bridge formation and further the charge transfer occurring from inside of the aromatic ring to the part of molecule which is directly involved in H-bonding. This statement is also supported by the other dependencies described later.

Table 1 shows only slight changes for $\rho_{\text{RCP-benzene}}$ and $\nabla^2\rho_{\text{RCP-benzene}}$ in comparison with the changes of the electron density and its Laplacian for the bond critical point (BCP) of the X-H proton donating bond ($\rho_{\text{X-H}}$ and $\nabla^2\rho_{\text{X-H}}$ respectively) and for the BCP of the H...O contact ($\rho_{\text{H...O}}$ and $\nabla^2\rho_{\text{H...O}}$ respectively). The changes of $\rho_{\text{RCP-benzene}}$ and $\nabla^2\rho_{\text{RCP-benzene}}$ are within 0.0001 au and 0.0008 au, while those of $\rho_{\text{H...O}}$ and $\nabla^2\rho_{\text{H...O}}$ amount to 0.0381 and 0.1275, respectively. This is probably in line with the well known fact that the benzene ring is rather insensitive to environmental effects as are intermolecular H-bonds in our study. However, it should be pointed out that these very slight changes within the ring, occurring due to hydrogen bond interactions, are observed and that their quantity depends on the H-bond strength which is supported by the correlations described above. Of course the changes of the electron density, as topological parameters indicate, are greater within the X-H...Y bridge but they are transmitted over a few bonds and are even detectable within the benzene ring.

It should be mentioned that the characteristics of RCPs are not often used to analyse hydrogen bonded systems, a few papers deal with such analyses on RCPs created due to intramolecular H-bonds,^{4,10} or bifurcated H-bonds¹¹ but a study of RCPs of benzene rings has not been performed previously. We extend our investigations to the analysis of the position of the RCP within the benzene ring and the dependence of the strength of the H-bond on this position. The distance between the RCP and the attractor (local maximum which is attributed to position of nucleus) corresponding to the carbon atom substituted by the methoxy group is analysed (see Table 1). The increase of a binding energy leads to a shortening of analysing distance, Fig. 3 shows the corresponding relationship. The linear correlation coefficient R amounts to 0.986. One can see that the change of the position of the RCP follows the other changes in molecular geometry proceeding as a consequence of H-bonding formation (Table 1). The deeper analysis of the interrelations between geometrical, energetic and topological

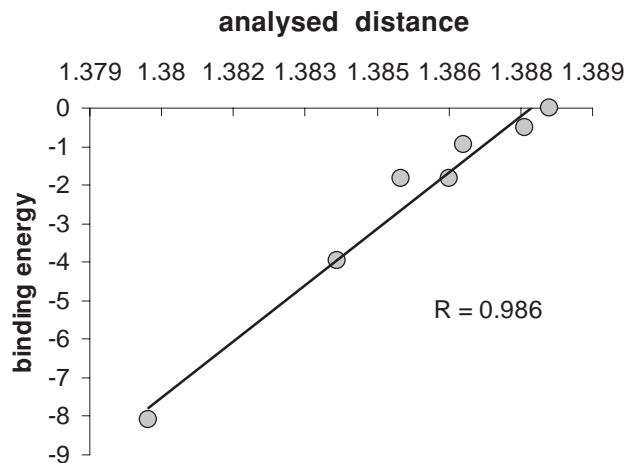


Fig. 3 Dependence of the distance (in Å) between RCP and attractor of C-atom substituted by the methoxy group and the binding energy (kcal/mol).

parameters was reported in our previous work,⁵ however, the characteristics of the RCPs were not taken into account.

The results presented here show that the topological parameters of RCP may be useful ones to characterise hydrogen bond interaction, especially its strength and that the effect of H-bond formation is transmitted far beyond the X-H...O bridge. Additionally it should be pointed out that such an application of analysis of electron distribution might be a powerful utility for exploration many of effects which proceed in aromatic systems and which would be unnecessarily associated with hydrogen bonding phenomena.

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