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Properties of a Ring Critical Point as Measures of Intramolecular H-Bond Strength

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Summary. The topological parameters derived from the *Bader* theory such as the electron density and its *Laplac*ian at the ring critical point (RCP) are analysed here as possible measures of the H-bond stength for intramolecular H-bonds. The parameters of RCP correlate well with the other properties of intramolecular H-bonds which are known as good measures of the H-bond strength. The calculations were performed on two samples of compounds with intramolecular H-bonds: the derivatives of malonaldehyde and the derivatives of *o*-hydroxybenzaldehyde. MP2 and HF calculations were carried out using a 6-311++G** basis set.

Keywords. Ring critical point; *Bader* theory; *Ab initio* calculations; Intramolecular H-bond; Malonaldehyde; *o*-Hydroxybenzaldehyde.

Introduction

The estimation of H-bond energies is one of the most often investigated problems of theoretical chemistry. In the case of intermolecular systems the H-bond energy is calculated as the difference between the energy of the complex and the energies of the isolated molecules forming a dimer. These energies are usually calculated for fully optimised geometries of species – the complex and the isolated molecules.

The situation is less clear for intramolecular H-bonds, for which the procedure presented above can not be applied. For such systems H-bond energies may be only roughly estimated. For example, for malonaldehyde the following procedure was applied [1]. The difference between the energy of the bridged intramolecular system and the energy of the ''open conformation'' obtained after the rotation of the O–H bond 180° around the C–O bond (Scheme 1) was treated as a rough estimation of the H-bond energy.

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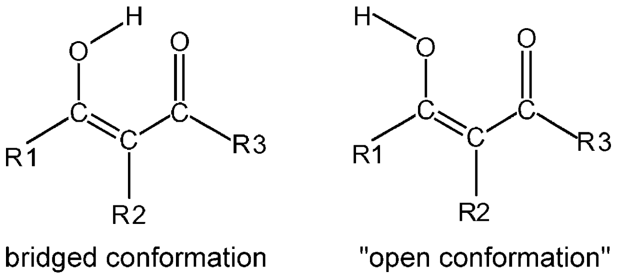
Dedicated to Professor *T. M. Krygowski* on the occasion of his 65th birthday



Scheme 1

Such an approach is not satisfactory because of the following reason. The rotation breaks the H-bond but other effects come into play, such as the unfavourable approach of the lone pairs of the two oxygen atoms [2].

In recent years the *Bader* theory (atoms in molecules theory – AIM) [3] has been often used in the analysis of chemical bonds and intermolecular interactions. The AIM theory allows to study interactions in terms of the topological properties of the electron density ρ. The electron density at the H ... Y bond critical point (Y is the proton accepting centre) is often treated as a measure of the H-bond strength of an X-H ... Y bridge since it correlates well with the H-bond energy, especially for homogeneous samples [4–6]. Such correlation was also detected for intramolecular H-bonds [1]. Recently it has been shown that different topological and geometrical parameters often correlate with the H-bond energy [7].

The ring critical point (RCP) is a point of the minimum electron density within the ring surface and a maximum on the ring line [8]. For example, in the case of benzene the RCP lies in the centre of the ring due to symmetry constraints. In the absence of symmetry an RCP can be found anywhere inside the ring. Figure 1 shows the molecular graph of the 6-fluoro derivative of *o*-hydroxybenzaldehyde, including the bond paths, bond critical points and two RCPs – one for the benzene ring and the second one for the ring created due to the intramolecular H-bond formation.

The electron density at RCP and its *Laplac*ian are analysed in the present study as possible properties describing the H-bond strength. Such properties have not been reported earlier as possible measures corresponding to the intramolecular H-bond energy.

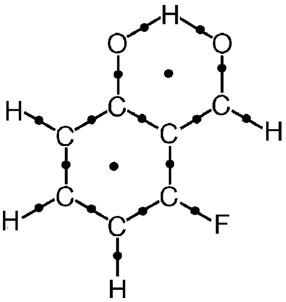
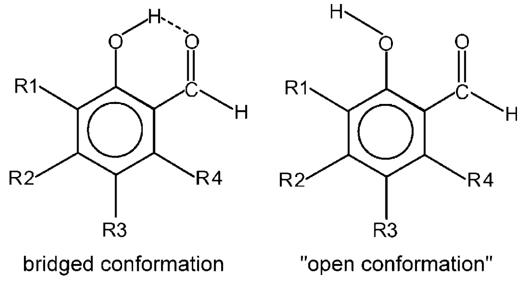


Fig. 1. Molecular graph of a fluoro derivative of *o*-hydrohybenzaldehyde; the continuous lines correspond to the bond paths, circles to the bond critical points and to the ring critical points



Scheme 2

Computational Details

The calculations were carried out at the *ab initio* level, using the *Gauss*ian 98 program [9]. The 6-311++G** basis set was used for all calculations. The effects of the electron correlation were examined by second order *Møller-Plesset* perturbation theory (MP2) [10] for both conformations of malonaldehyde (MA) and their fluoro and chloro derivatives (Scheme 1). The SCF level of theory was used for calculations on *o*-hydroxybenzaldehyde (*o-HBA*) and its fluoro derivatives. For both samples of molecules the geometry optimisations were performed on both conformations: bridging system and the corresponding one called as "open conformation" (Scheme 2). The sample of derivatives of *o-HBA* contains all possible fluoro derivatives where hydrogen atoms of benzene ring may be substituted.

For all molecules AIM calculations [11] based on the *Bader* theory [3] were performed. The bond critical points (BCPs) were localised and their properties were analysed (electron densities and their *Laplac*ians).

Results and Discussion

Malonaldehyde is often the subject of theoretical investigations. For example, the analysis of the H-bond strength for malonaldehyde and its simple derivatives has been performed [1]. The *ab initio* calculations on the rotamers and rotations of malonaldehyde has been also carried out [12]. The following parameters of the bridging configuration (Scheme 1) were taken into account in this study as those which may be used for description of the H-bond strength: $r_{H\ldots O}$, $\rho_{H\ldots O}$, $\nabla^2\rho_{H\ldots O}$, E_{HB}, Q; where: $r_{H\ldots O}$ is the H...O intermolecular distance, $\rho_{H\ldots O}$ and $\nabla^2\rho_{H\ldots O}$ are the topological parameters of H...O contact – the electron density at BCP and its *Laplac*ian, respectively. E_{HB} is the rough estimation of H-bond energy being the difference in energy between bridging configuration and the "open" one. Q is the parameter introduced by *Gilli* and co-workers [13, 14] for the description of the resonance assisted intramolecular H-bonds (RAHBs). For malonaldehyde this parameter may be defined in the following way:

$$Q = r_{C-O} + r_{C-C} - r_{C=C} - r_{C=O}$$

where r-values correspond to the appropriate bond lengths within the bridging system. The closer the values of the corresponding bonds C=O and C–O or C=C and C–C are, the stronger is the intramolecular H-bond. It was shown that these parameters correlate with the approximate estimation of H-bond energy – E_{HB} [1].

Table 1 presents the parameters of H-bond for malonaldehyde and its derivatives obtained within the MP2/6-311++G** level of theory. There are also $E_{HB}{}^*$

Table 1. Some of geometrical (in Å) and topological parameters (in au) of malonaldehyde and its derivatives, E_{HB} energies (in kcal/mol) and Q-values are also given; $E_{HB}{}^{*}$'s correspond to energies calculated at the HF/6-311++G** level of theory

R1, R2, R3	$r_{H\ldots O}$	$\rho_{H\ldots O}$	$\nabla^2\rho_{H\ldots O}$	ρ_{RCP}	$\nabla^2\rho_{RCP}$	E_{HB}	$E_{HB}{}^{*}$	Q
H, H, H	1.687	0.0497	0.1387	0.0205	0.1277	– 12.15	– 10.41	0.160
H, F, H	1.776	0.0402	0.1232	0.0185	0.1126	– 9.73	– 8.38	0.184
H, Cl, H	1.717	0.0461	0.1349	0.0197	0.1215	– 10.83	– 9.68	0.178
H, H, F	1.825	0.0352	0.1161	0.0186	0.1096	– 9.14	– 9.14	0.210
H, H, Cl	1.793	0.0380	0.1222	0.0189	0.1136	– 9.24	– 8.63	0.191
F, H, H	1.449	0.0910	0.1386	0.0257	0.1647	– 13.47	– 8.67	0.083
Cl, H, H	1.54	0.0719	0.1499	0.0237	0.1509	– 12.49	– 8.82	0.121

energies in the table which were calculated at the HF/6-311++G** level of theory. $E_{HB}{}^{*}$ was calculated in the same way as E_{HB} – as a differences between the energy of bridging system and the energy of the "open configuration" (Scheme 1). Hence the difference between E_{HB} and $E_{HB}{}^{*}$ reflects the electron correlation effect within the intramolecular H-bridge. We see (Table 1) that this effect is greater for smaller values of Q, this means, for greater resonance effects. The linear correlation coefficient for the dependence between Q and the ($E_{HB} - E_{HB}{}^{*}$) difference for malonaldehyde derivatives amounts to 0.993. Additionally ρ_{RCP} and $\nabla^2\rho_{RCP}$ are given in Table 1 – the electron density at the ring critical point (RCP) and its *Laplac*ian for the ring (H–O–C=C–C=O) created by the H-bond formation. Table 2 presents the linear correlation coefficients of correlations between ρ_{RCP} and $\nabla^2\rho_{RCP}$ with the other parameters investigated earlier. Figure 2 shows one of the regressions summarised in Table 2 – ρ_{RCP} *vs* $\rho_{H\ldots O}$ for which the correlation coefficient amounts to 0.994. These findings (Fig. 2, Table 2) suggest that the properties of RCP of the ring of intramolecular H-bond (bridging system) may be treated as measures of H-bond strength. ρ_{RCP} and $\nabla^2\rho_{RCP}$ correlate well with the other parameters.

The properties of RCP were also analysed for intramolecular H-bonds of *o*-hydroxybenzaldehyde (*o-HBA*) derivatives. Table 3 summarises some of the geometrical, topological and energetic parameters of these systems. Structures of various rotamers of *o-HBA*, including the process of the proton transfer from enol to keto form were investigated earlier [15]. In this study emphasis is put on the

Table 2. Correlation coefficients for linear regressions between the parameters of RCP (electron density and its *Laplac*ian) and other parameters usually applied as measures of the H-bond strength for derivatives of malonaldehyde

	ρ_{RCP}	$\nabla^2\rho_{RCP}$
$r_{H\ldots O}$	0.997	0.997
$\rho_{H\ldots O}$	0.994	0.994
E_{HB}	0.915	0.933
Q	0.981	0.989

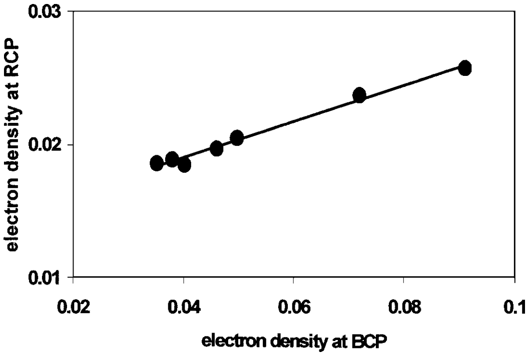


Fig. 2. Relationship between the electron density at the H...O bond critical point – $\rho_{H...O}$ and the electronic density at the ring critical point – ρ_{RCP} – for malonaldehyde derivatives; ρ-values in au

Table 3. Some of geometrical (in Å) and topological parameters (in au) of *o*-hydroxybenzaldehyde and its derivatives, E_{HB} energies (in kcal/mol) and Q-values are also given

R1, R2, R3, R4	$r_{H...O}$	$\rho_{H...O}$	$\nabla^2\rho_{H...O}$	ρ_{RCP}	$\nabla^2\rho_{RCP}$	E_{HB}	Q
F, F, H, F	1.868	0.0302	0.1212	0.0160	0.1039	– 7.37	0.185
F, H, H, F	1.875	0.0297	0.1200	0.0158	0.1028	– 6.94	0.195
F, F, F, F	1.878	0.0296	0.1193	0.0158	0.1026	– 7.24	0.198
F, H, F, F	1.886	0.0290	0.1179	0.0157	0.1014	– 6.82	0.207
F, F, H, H	1.902	0.0279	0.1131	0.0155	0.0996	– 6.86	0.193
F, H, H, H	1.910	0.0274	0.1118	0.0153	0.0985	– 6.45	0.202
F, F, F, H	1.912	0.0273	0.1113	0.0153	0.0983	– 6.79	0.205
F, H, F, H	1.920	0.0268	0.1098	0.0152	0.0971	– 6.38	0.216
H, F, H, F	1.860	0.0308	0.1231	0.0160	0.1051	– 10.47	0.181
H, H, H, F	1.869	0.0301	0.1215	0.0159	0.1038	– 10.16	0.190
H, F, F, F	1.870	0.0300	0.1208	0.0158	0.1038	– 10.29	0.191
H, H, F, F	1.879	0.0294	0.1192	0.0157	0.1021	– 9.96	0.201
H, F, H, H	1.894	0.0284	0.1150	0.0155	0.1008	– 9.93	0.187
H, H, H, H	1.903	0.0278	0.1133	0.0154	0.0993	– 9.62	0.197
H, F, F, H	1.904	0.0278	0.1130	0.0154	0.0993	– 9.82	0.199
H, H, F, H	1.912	0.0273	0.1115	0.0152	0.0981	– 9.50	0.209

intramolecular H-bond for *o-HBA* and its fluoro derivatives. All E_{HB} energies were obtained (Table 3) in the same way as those calculated for malonaldehyde derivatives. The equalisation of C=O and C–O or C–C (the bond between the benzene ring and aldehyde group) and C$\overset{\cdots}{-}$C bond (the bond within the benzene ring) is not as visible as it was for malonaldehyde derivatives. Hence the Q-parameter describing resonance effect within the ring of intramolecular H-bond does not correlate with $r_{H...O}$, $\rho_{H...O}$, E_{HB}, and the other parameters describing the H-bond strength (Table 4). We observe a similar situation for E_{HB}, which does not correlate with the other parameters. We see that in the case of *o-HBA* derivatives E_{HB} is not a good descriptor of the H-bond energy. It may be caused by additional effects like substitution of the benzene ring by fluorine atoms.

Table 4. Correlation coefficients for linear regressions between some of the parameters describing the H-bond strength for *o*-hydroxybenzaldehyde derivatives; RCP (electron density and its *Laplac*ian) measures are also given

	$\rho_{H\ldots O}$	E_{HB}	Q	ρ_{RCP}	$\nabla^2\rho_{RCP}$
$r_{H\ldots O}$	0.999	0.374	0.739	0.984	0.998
$\rho_{H\ldots O}$		0.362	0.731	0.985	0.997
E_{HB}			0.461	0.251	0.385
Q				0.734	0.769

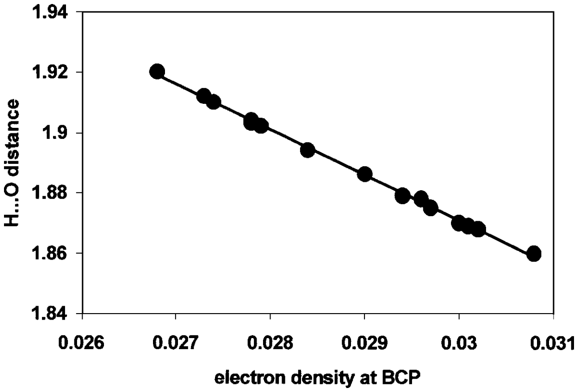


Fig. 3. Correlation between the electron density at H...O BCP (in au) and H...O distance (in Å) for *o*-hydroxybenzaldehyde derivatives

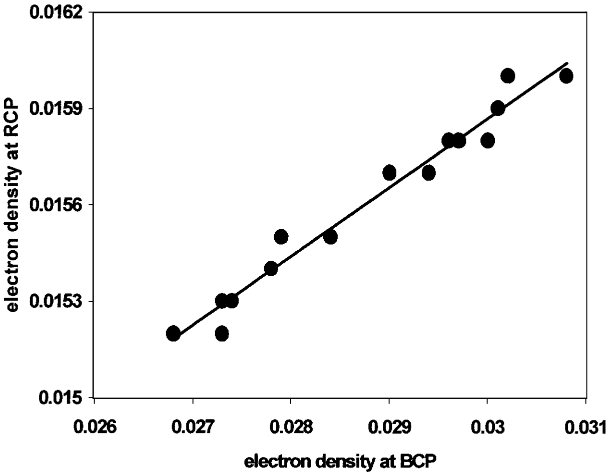


Fig. 4. Relationship between the electron density at the H...O bond critical point – $\rho_{H\ldots O}$ and the electronic density at the ring critical point – ρ_{RCP} – for *o*-hydroxybenzaldehyde derivatives; ρ-values in au

The $\rho_{H...O}$ parameter describes well the H-bond strength, comparable with other samples which were investigated previously [4–6]. Figure 3 shows that $\rho_{H...O}$ correlates with the H...O distance ($r_{H...O}$). It is well known that shorter H...O distances within O–H...O bridges correspond to stronger H-bonds [16, 17].

ρ_{RCP} – the parameter investigated in this study – correlates well with $\rho_{H...O}$ (Fig. 4) and the linear correlation coefficient amounts to 0.985. For *o-HBA* derivatives Table 4 shows some of the correlations between the properties of RCP (ρ_{RCP} and $\nabla^2\rho_{RCP}$) and the other parameters. We see that the *Laplac*ian of the electron density at RCP – $\nabla^2\rho_{RCP}$ also correlates with such measures as H-bond strength as H...O distance or $\rho_{H...O}$. In other words the properties of RCP – ρ_{RCP} and $\nabla^2\rho_{RCP}$ may be probably treated as measures of the H-bond strength since they correlate with the other well known measures for both samples of the present investigation.

Conclusions

The studies on derivatives of malonaldehyde and *o*-hydroxybenzaldehyde show that the properties of the ring critical point of intramolecular H-bond may be useful for the estimation of the H-bond strength. The electron density at the RCP – ρ_{RCP} and its *Laplac*ian – $\nabla^2\rho_{RCP}$ correlate well with the other parameters which are usually used for the description of the H-bond energy.

In the case of malonaldehyde and its derivatives the properties of RCP (ρ_{RCP} and $\nabla^2\rho_{RCP}$) correlate with all descriptors investigated here. For *o*-hydroxybenzaldehyde (*o-HBA*) and its fluoro derivatives there are no correlations with the Q-parameter and E_{HB} energy. It seems to be justified because of the reasons given below. Q is a good descriptor for resonance assisted hydrogen bonds, however, in *o-HBA* the ring formed due to H-bond formation contains also a CC bond of the benzene ring and such system may not be treated as usual RAHB. E_{HB} is not a proper measure of H-bond strength for intramolecular H-bonds. In other words, as it is known from previous investigations, the properties of H...O BCP describe well the H-bond strength for homogeneous samples [6], H...O is also often the proper descriptor of the H-bond strength. For these measures: $r_{H...O}$, $\rho_{H...O}$ and $\nabla^2\rho_{H...O}$ give good correlations with the properties of RCP for both samples.

E_{HB} – as a difference in energy between two configurations – does not well describe H-bond strength [2]; the same is the case for the intramolecular hydrogen bond interaction energies calculated by means of the corresponding isodesmic equations [18]. Hence ρ_{RCP} and $\nabla^2\rho_{RCP}$ correlating with the H...Y distance and $\rho_{H...Y}$ (Y – the proton acceptor) are new powerful measures of H-bond strength. They are typical for intramolecular H-bonds since the ring critical point exists for "closed systems of atoms."

Since the RCP properties have not been investigated extensively as descriptors of H-bond strength, a detailed study on larger molecules and on the other parameters, for example atomic interaction energies obtained from AIM theory, is in progress.

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