DFT and AIM studies on two-ring resonance assisted hydrogen bonds

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Abstract

DFT calculations on molecules with intramolecular hydrogen bonds have been performed at B3LYP/6-311++G(d,p) level of theory. The investigated 2,4-dihydroxybut-2-ene-4-dial molecule and its derivatives contain two intramolecular H-bonded rings. Each ring is the resonance-assisted system. The results of calculations show that two rings within the same molecule do not cause an increase of the resonance effect. It is shown that the topological parameters such as features of bond critical points and ring critical points may be treated as measures of H-bond strength.
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Keywords: Resonance assisted hydrogen bonds; The Bader theory; DFT calculations; Bond critical points; Ring critical points; 2,4-Dihydroxybut-2-ene-4-dial

1. Introduction

Hydrogen bonding is one of the most important interactions playing a dominant role in chemical and biochemical reactions [1,2]. It is strong enough to influence the arrangement of molecules in crystals and even the geometry of molecules participating in these interactions [1–4]. It is well known that the X–H proton donating bond in X–H···Y system is usually elongated due to the H-bond formation [5,6]. This elongation is greater for stronger H-bonds and may be treated for homogeneous samples of complexes as a measure of

the H-bond strength [7]. It is worth mentioning that the proton acceptors are also changed owing to the H-bond interaction. For example, the C=O carbonyl bond is elongated within C=O···H–O systems in which H-bonds are strong enough [8]. The methoxy group was investigated recently as a possible H-bond proton acceptor and the elongation of C–O bonds of the methoxy group are observed. It is greater for stronger H-bonds [9]. These geometrical changes are observed for both intermolecular and intramolecular H-bonds.

Charge assisted and resonance assisted H-bonds (CAHBs and RAHBs) belong to the strongest interactions of that type and thus for such systems the changes of geometry are the greatest [10–13]. For the resonance assisted intramolecular H-bonds existing for malonaldehyde and its derivatives (Scheme 1) there are the following changes of
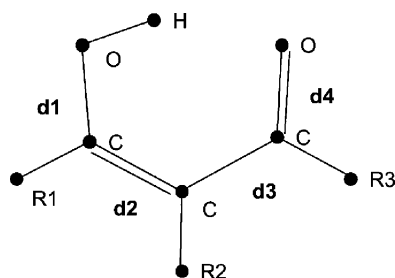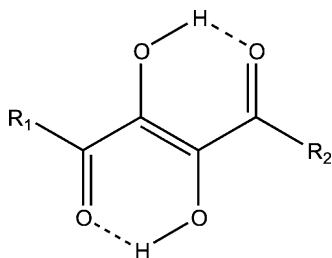

Scheme 1. The derivative of malonaldehyde with the intramolecular resonance assisted hydrogen bond.

the energetic and geometrical parameters of molecules being the consequences of the π-electron delocalisation within the intramolecular ring [12]:

- the strengthening of H-bonds;
- the shift of the proton towards the middle of O···O distance;
- the shortening of O···O distance up to 2.4 Å or even to shorter distances;
- the equalisation of C=C and C–C bonds (d_2 and d_3, Scheme 1)
- the equalisation of C–O and C=O bonds (d_1 and d_4, Scheme 1).

In other words the changes of the geometry of molecules involved in RAHBs are greater than the changes for usual H-bonds since RAHBs belong to the strongest H-bonded systems.

The aim of the present work is to investigate the features of systems containing conjugated single and double bonds (Scheme 2). We see that they contain two rings each of them may be considered as resonance assisted hydrogen-bonded system. One of the main characteristics investigated in this study is the coexistence of two rings within the same molecule. The question arises if such coexistence

influences the strengths of intramolecular hydrogen bonds. The investigation is based on DFT calculations and on the use of Bader's theory ('atoms in molecules' theory—AIM) [14].

2. Computational details

The calculations have been performed with the program GAUSSIAN 98 [15] using the standard 6-311++G** basis set [16] at the hybrid Hartree–Fock density functional method (B3LYP) [17]. All systems considered in this study were fully optimised. The simple modelled systems, the molecule of 2,4-dihydroxybut-2-ene-4-dial and its derivatives were investigated in this study (Scheme 2). H, F and Li atoms were chosen as R_1 and R_2 substituents: neutral, strongly electronegative and strongly electropositive. Additionally Bader's theory [14] is applied here to get more detailed insight into the nature of the investigated systems. AIM2000 program [18–20] was used to localise bond critical points and ring critical points (BCPs and RCPs). The electron densities at BCPs and at RCPs were calculated (ρ_{BCP}'s and ρ_{RCP}'s). Laplacians of these densities were also calculated ($\nabla^2\rho_{BCP}$'s and $\nabla^2\rho_{RCP}$'s).
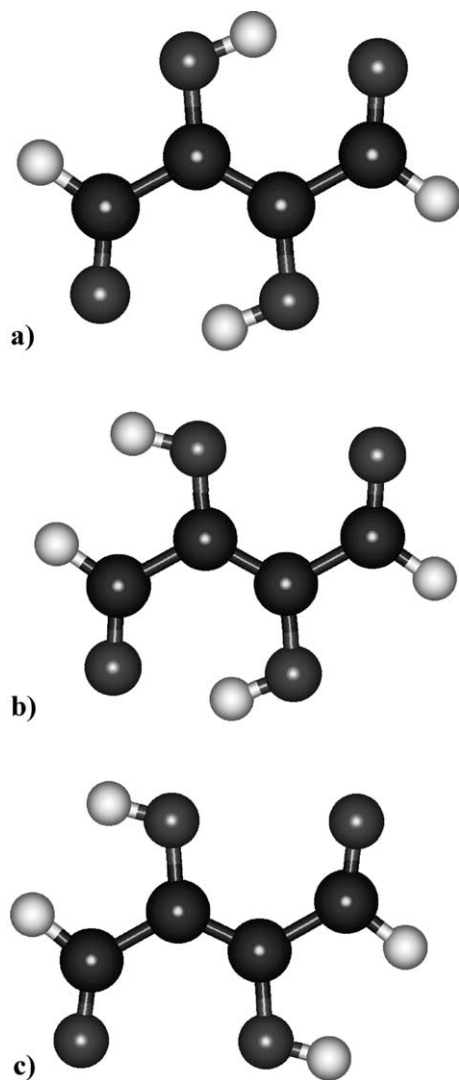
3. Results and discussion

3.1. π-Electron delocalisation for resonance assisted H-bonds

One of the most important features of RAHBs is the equalisation of the appropriate bonds within the system. For the description of this feature

Scheme 2. The diketone derivatives considered in this study.
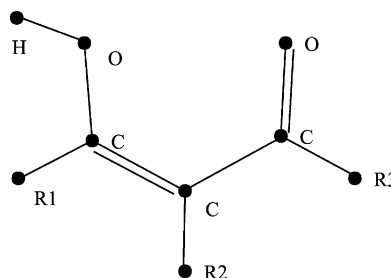
Scheme 3. The open configuration of RAHB system.

Scheme 4. Possible configurations for the systems of diketone derivatives considered in this study; a: closed, b: closed-open, c: open configurations.

the Q-parameter was introduced [12].

$$Q = (d_1 - d_4) + (d_3 - d_2) \tag{1}$$

where d_1, d_2, d_3 and d_4 are bond lengths (Scheme 1).

Q decreases for the RAHB systems, the smaller its value the greater the effect of the equalisation of bonds and consequently the stronger hydrogen bond [12,21].

The resonance effect can be studied by comparing the so-called open configuration (Scheme 3) and

the closed one (Scheme 1). For the closed configuration, for which hydrogen bonding exists, the effect is greater than for the open one [21]. For the systems investigated in this study we shall consider three configurations: closed configuration, the closed-open configuration and the open one (Scheme 4).

For the species related to malonaldehyde (Scheme 1) it was pointed out that an increase of the delocalisation of the π-conjugated HO–C=C–C=O system, and hence the decrease of Q-value, may be caused by appropriate substituents: R1 being an electron withdrawing and R3 as an electron donating substituent [12]. The same effect may be induced due to additional H-bonds or C–H contacts to the C=O carbonyl group. This finding was nicely confirmed by the ab initio calculations on simple RAHB systems [21].

The situation for the species considered here (Scheme 2) is not so clear. Table 1 shows the Q-parameters for the systems for which R1 and R2 substituents are identical. The Q-values were obtained from the geometrical parameters present in Table 2. The R_1 and R_2 substituents of diketones studied here (Scheme 2) correspond to R_3 substituents of malonaldehyde derivatives (Scheme 1). According to Bertolasi et al. [12] the delocalisation of π-electrons for malonaldehyde derivatives should be greater for electron donating R_3-substituents, like for example Li substituent. Hence for diketones analysed here the effect of delocalisation should be greater for Li-substituents at R_1 and R_2 positions. The opposite effect should be observed for F-substituents. We see (Table 1) that the lowest Q-values are observed for H-substituents for open and closed systems. For

Table 1

Q-values for different configurations of diketones considered in this study; the changes of Q-values are also given

R_1, R_2	Open	Closed-open [a]	Closed
H, H	0.275	0.188 (0.270)	0.210
Li, Li	0.357	0.165 (0.212)	0.287
F, F	0.289	0.224 (0.283)	0.236
Change of Q-values			
H, H	0	0.087 (0.005)	0.065
Li, Li	0	0.192 (0.145)	0.080
F, F	0	0.065 (0.006)	0.053

[a] Q-values for the open ring are given in parentheses.

Table 2
The geometrical parameters (in Å) of the closed systems studied here; the bold designations of substituents show that the presented parameters correspond to the ring with the bolded substituent; for $R_1 = R_2$ the geometry of both rings is the same

R_1, R_2	O–H	O···H	C–O	C=O	C–C	C=C	O···O
H, H	0.982	1.798	1.348	1.226	1.463	1.375	2.647
Li, Li	1.012	1.658	1.391	1.254	1.496	1.346	2.572
F, F	0.978	1.831	1.342	1.201	1.470	1.375	2.662
H, Li	0.991	1.729	1.386	1.233	1.455	1.362	2.594
H, **Li**	0.992	1.773	1.353	1.244	1.510	1.362	2.654
H, F	0.983	1.776	1.342	1.224	1.466	1.374	2.633
H, **F**	0.976	1.858	1.349	1.202	1.467	1.374	2.680
Li, F	0.995	1.740	1.346	1.243	1.515	1.360	2.631
Li, **F**	0.981	1.821	1.387	1.207	1.461	1.360	2.647

closed-open systems the lowest *Q*-values are observed for Li-substituents. For closed-open systems two *Q*-values are given: one for the closed ring and the second one for the open ring without H-bond. The situation is clearer if we consider the change of *Q*-value after transition from the open configuration to another one (Table 1). The greatest decrease of *Q*-value is observed for Li-substituents and the lowest for F-substituents. We see that the rapid decrease of *Q* is observed for the transition from open to closed-open configuration and there is no further change for the transition to the closed configuration. Surprisingly for closed configurations there is the increase of *Q*-value in comparison with the closed-open configurations. There are also changes within open rings of the closed-open configurations; negligible for molecules with H- and F-substituents and greater for molecules with Li-substituents.

The results presented in Table 1 show that the greatest changes of π-electron delocalisation are observed for the transition from open to closed-open configurations. The further transition to closed configurations causes a weaker delocalisation. In other words the existence of two-ring system does not increase the delocalisation of π-electrons and does not increase the strength of hydrogen bonds.

Fig. 1 shows the energies of different configurations of 2,4-dihydroxybut-2-ene-4-dial. The most stable is the closed configuration; the next is the closed-open one and the open configuration has the greatest energy. The energy difference between closed-open and closed configurations amounts to
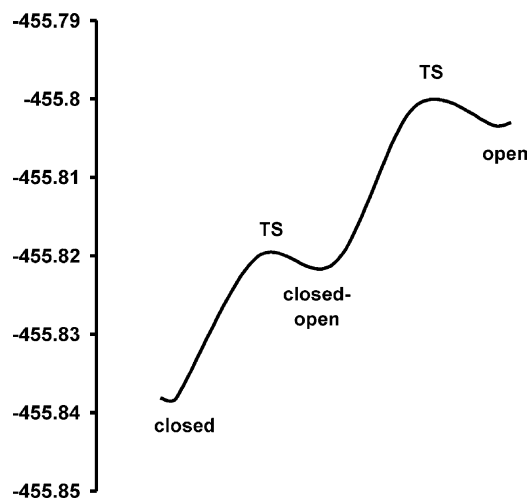

Fig. 1. The energies (in hartrees) for different configurations of 2,4-dihydroxybut-2-ene-4-dial molecule, the transition states between configurations are also present.

10.9 kcal/mol, this difference between open and closed-open configurations is the same. Therefore the closure of a ring involves a constant energy of 10.9 kcal/mol. The potential barrier height for the reaction path open–closed-open configuration is of 1.6 kcal/mol while this barrier for the reaction path closed-open–close configuration amounts to 0.3 kcal/mol.

3.2. H-bond energies

One of the most important features of intramolecular H-bond is its strength. It is not possible to calculate it in the same way as for intermolecular H-bonds for which the H-bond energy is usually calculated as a difference between the energy of the complex and the energies of isolated molecules. One of ways of the estimation of intramolecular H-bond energy is the calculation of the difference in energy between closed and open configurations (Schemes 1 and 3). However, in such a case the other effects may exist which disturb the real H-bond energy [13,21,22]. Another approach is based on the consideration of the isodesmic reactions [23,24]. Again this way does not guarantee to obtain the proper H-bond energies. In recent years the powerful method of Bader [14] is often applied for the estimation of H-bond energy [25–30]. It was checked that the electron density at
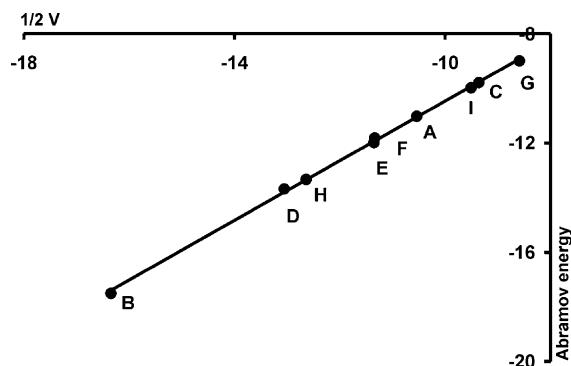
Fig. 2. The correlation between H-bond energy obtained from the Abramov relations (E^*) and H-bond energy derived from the potential energy density at the H···O bond critical point (E). Letter designations of species correspond to those of Table 3.

the H···Y BCP (Y is a proton acceptor for the X–H···Y H-bonds) correlates well with the H-bond energy, particularly for homogeneous samples of complexes [13,31].

Theoretical studies are able to obtain a full description of both topological and energetic properties at critical points. It is possible to calculate such energetic parameters as the local kinetic energy density, $G(r)$, and the local electron potential energy density, $V(r)$. Experimental studies of electron density do not provide the description of energetic properties of critical points. However, Abramov has proposed the evaluation of $G(r)$ in terms of electron density $\rho(r)$, its gradient $\nabla\rho(r)$ and its Laplacian $\nabla^2\rho(r)$ functions [32]. At the critical point, where $\nabla\rho(r_{CP}) = 0$ the Abramov relation takes the form:

$$G(r_{CP}) = (3/10)(3\pi^2)^{2/3}\rho^{5/3}(r_{CP}) + (1/6)\nabla^2\rho(r_{CP}) \quad (2)$$

All values in this relation are expressed in atomic units. The local potential energy density $V(r_{CP})$ can be obtained from the virial equation [32]:

$$2G(r_{CP}) + V(r_{CP}) = (1/4)\nabla^2\rho(r_{CP}) \quad (3)$$

It was found [33] that $V(r_{BCP})$ correlates with the H-bond energy—E_{HB} ($E_{HB} \approx 1/2V(r_{BCP})$. $V(r_{BCP})$ designates the local electron potential energy density at the H···Y BCP; Y designates the proton acceptor in X–H···Y hydrogen bond. Hence the topological theory of Bader [14] is also useful for the estimation of H-bond energy from the electron density obtained experimen-

tally like, for example, X-ray diffraction measurement applied to the crystal structure determination [31].

In the theoretical case, where the wave function corresponding to the applied level of theory, is accessible both $G(r_{BCP})$ and $V(r_{BCP})$ values may be obtained directly. Additionally $V(r_{BCP})$ may be estimated from the Abramov relations (Eqs. (2) and (3)) and it may be treated as an approximation of the true $V(r_{BCP})$ value. We see that the theoretical electron density may be useful to check the Abramov approach. The correlation between $V(r_{BCP})$-values obtained from both approaches is excellent for homogeneous samples of H-bonded systems [34]. There is also good correlation for the sample considered here (Fig. 2); the linear correlation coefficient for $1/2V(r_{BCP})$—values obtained from the Abramov relation applied to the electron density and directly from the theoretical wave function amounts to 1.000. It is not a trivial result since the correlation presented earlier [34] was applied for the samples of the strongly related intermolecular systems. Fig. 2 shows that the Abramov relation may be successfully used for the intramolecular H-bonds.

In this study it is assumed for further relationships that $1/2V(r_{BCP})$ energy obtained from the B3LYP/6-311++G** wave function approximately corresponds to the H-bond energy. This energy correlates well with the other parameters usually known as descriptors of H-bond strength. Fig. 3 presents
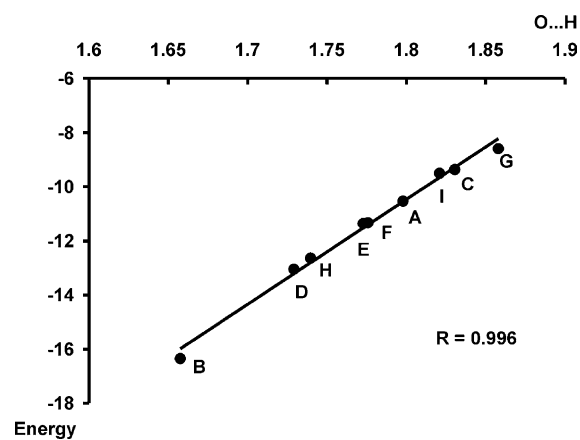

Fig. 3. The relationship between H···O distance of O–H···O H-bond and the H-bond energy obtained from the potential energy density (E). Letter designations of species correspond to those of Table 3.

Table 3
The topological (in a.u.) and energetic parameters (in kcal/mol) of the closed systems studied here; the bold designations of substituents show that the presented parameters correspond to the ring with the bolded substituent; for $R_1 = R_2$ the topology of both rings is the same. $\rho_{H\cdots O}$ and ρ_{RCP} are the electron densities of the H$\cdots$O bond critical point and of the RCP, respectively; $\nabla^2\rho_{H\cdots O}$ and $\nabla^2\rho_{RCP}$ are Laplacians of these densities; E^* and E are H-bond energies obtained from the Abramov attitude and from V-value

Designation	R_1, R_2	$\rho_{H\cdots O}$	$\nabla^2\rho_{H\cdots O}$	ρ_{RCP}	$\nabla^2\rho_{RCP}$	E^*	E
A	H, H	0.0383	0.1219	0.0175	0.1057	−11.0	−10.5
B	Li, Li	0.0546	0.1289	0.0195	0.1173	−17.5	−16.3
C	F, F	0.0348	0.1184	0.0176	0.1015	−9.8	−9.4
D	**H**, Li	0.0450	0.1308	0.0183	0.1118	−13.7	−13.1
E	H, **Li**	0.0412	0.1191	0.0179	0.1077	−12.0	−11.4
F	**H**, F	0.0402	0.1264	0.0180	0.1089	−11.8	−11.3
G	H, **F**	0.0328	0.1125	0.0171	0.0979	−9.0	−8.6
H	**Li**, F	0.0445	0.1250	0.0185	0.1123	−13.3	−12.6
I	Li, **F**	0.0355	0.1177	0.0174	0.1003	−10.0	−9.5

the linear correlation between H$\cdots$O distance of the intramolecular H-bond and $1/2V(r_{BCP})$ energy. The correlation coefficient is equal to 0.996. There are the similar good correlations for the sample of derivatives of 2,4-dihydroxybut-2-ene-4-dial studied here between the energy described above and the other parameters such as O–H bond length, the electron density at OH or H$\cdots$O BCP, Laplacians of these densities (Table 3).

Recently it has been pointed out that the topological properties of the RCP may be useful to describe the intermolecular and intramolecular H-bond strength [35,36]. The RCP is a point of the minimum electron density within the ring surface and a maximum on the ring line [37]. For example, in benzene, the RCP lies in the centre of the ring due to symmetry constraints. In the case of the absence of symmetry the RCP lies anywhere inside the ring. The topological meaning of the ring is not identical as in the classical chemistry. It is the set of atoms connected through bond paths like for benzene, thiazolidine etc. However, it may be also the system of atoms creating the intramolecular hydrogen bond since from the topological point of view there is the bond path between the hydrogen atom and the proton acceptor. Such rings may also exist for intermolecular H-bonds, like for example for bifurcated H-bonds. Such a case of bifurcated H-bonds has been investigated recently; the study on complexes between derivatives of squaric acid and ammonium cation [35] shows the correlation between the binding energy and the electron

density at the RCP. There is also a linear correlation for this sample of species between the binding energy and Laplacian of the electron density at RCP. The properties of RCP characterise H-bond since the complexation of the ammonium cation with squaramide leads to the creation of two BCPs and one RCP [35].

It was found that for rings of intramolecular H-bonds there are also RCPs which properties are good descriptors of H-bond strength [36]. The similar situation is observed here since there is the linear relationship between $1/2V(r_{BCP})$ energy and the electron density at the RCP. Fig. 4 shows such relationship, the correlation coefficient amounts to 0.980.
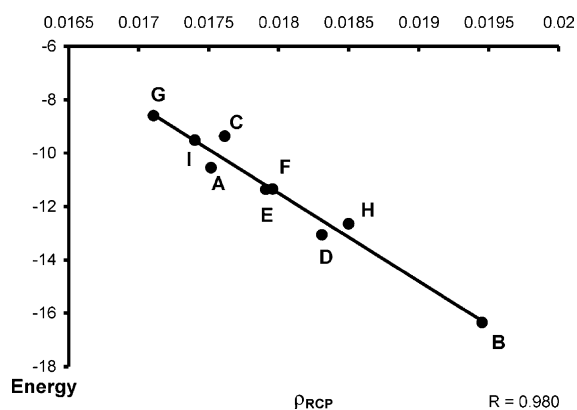

Fig. 4. The correlation between the electron density at the ring critical point and the H-bond energy obtained from the potential energy density (E). Letter designations of species correspond to those of Table 3.

4. Conclusions

The results of B3LYP/6-311++G** calculations on the derivatives of 2,4-dihydroxybut-2-ene-4-dial show that the π-electron delocalisation for the rings created by the H-bond formation exists. Such delocalisation is greater for the closed-open configurations than for the configurations with two closed rings. We may also observe the effects similar to those detected for simple RAHB systems with one intramolecular H-bond; the electron withdrawing and electron donating substituents may influence on the π-electron delocalisation.

The results of this study also show that the topological parameters derived from the theory of Bader [14] may be applied to estimate the H-bond strength. The properties of the RCPs are useful descriptors for the strength of intramolecular H-bonds.

References

[1] G.A. Jeffrey, W. Saenger, Hydrogen Bonding in Biological Structures, Springer, Berlin, 1991.

[2] G.R. Desiraju, T. Steiner, The Weak Hydrogen Bond in Structural Chemistry and Biology, Oxford University Press, New York, 1999.

[3] J.D. Dunitz, X-ray Analysis and the Structure of Organic Molecules, Cornell University Press, Ithaca, London, 1979.

[4] G.R. Desiraju, Crystal Engineering —the Design of Organic Solids, Elsevier, Amsterdam, 1989.

[5] M. Ichikawa, Acta Crystallogr. B34 (1978) 2074.

[6] S.J. Grabowski, T.M. Krygowski, Tetrahedron 54 (1998) 5683 and references cited therein.

[7] S.J. Grabowski, Chem. Phys. Lett. 338 (2001) 361.

[8] S.J. Grabowski, Tetrahedron 54 (1998) 10153.

[9] M. Palusiak, S.J. Grabowski, J. Mol. Struct. (2002) in press.

[10] J.W. Larson, T.B. McMahon, J. Am. Chem. Soc. 103 (1983) 2944.

[11] J.W. Larson, T.B. McMahon, J. Am. Chem. Soc. 106 (1984) 517.

[12] V. Bertolasi, P. Gilli, V. Ferretti, G. Gilli, J. Am. Chem. Soc. 113 (1991) 4917.

[13] S.J. Grabowski, J. Phys. Chem. A 105 (2001) 10739.

[14] R.F.W. Bader, Atoms in Molecules. A Quantum Theory, Oxford University Press, New York, 1990.

[15] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, L.R. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, G. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, GAUSSIAN 98, Revision A.6, Gaussian Inc., Pittsburgh, PA, 1998.

[16] R. Krishnam, J.S. Binkley, R. Seeger, J.A. Pople, J. Chem. Phys. 80 (1984) 3265.

[17] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.

[18] AIM2000 designed by Friedrich Biegler-König, University of Applied Sciences, Bielefeld, Germany.

[19] F.W. Biegler-König, R.F.W. Bader, Y.H. Tang, J. Comput. Chem. 3 (1982) 317.

[20] R.F.W. Bader, Y.H. Tang, Y. Tal, F.W. Biegler-König, J. Am. Chem. Soc. 104 (1984) 946.

[21] S.J. Grabowski, J. Mol. Struct. 562 (2001) 137.

[22] M. Cuma, S. Scheiner, T. Kar, J. Mol. Struct. (Theochem) 467 (1999) 37.

[23] W.J. Hehre, L. Radom, P.v.R. Schleyer, J.A. Pople, Ab Initio Molecular Orbital Theory, John Wiley & Sons, New York, 1986.

[24] I. Rozas, I. Alkorta, J. Elguero, J. Phys. Chem. A 105 (2001) 10462.

[25] M.T. Carrol, C. Chang, R.F.W. Bader, Mol. Phys. 63 (1988) 387.

[26] M.T. Carrol, R.F.W. Bader, Mol. Phys. 65 (1988) 695.

[27] U. Koch, P. Popelier, J. Phys. Chem. 99 (1995) 9747.

[28] O. Mó, M. Yáñez, J. Elguero, J. Chem. Phys. 97 (1992) 6628.

[29] O. Mó, M. Yáñez, J. Elguero, J. Mol. Struct. (Theochem) 314 (1994) 73.

[30] O. Mó, M. Yáñez, I. Rozas, J. Elguero, J. Chem. Phys. 100 (1994) 2871.

[31] E. Espinosa, M. Souhassou, H. Lachekar, C. Lecomte, Acta Crystallogr. B55 (1999) 563.

[32] Y.A. Abramov, Acta Crystallogr. A53 (1997) 264.

[33] E. Espinosa, E. Molins, C. Lecomte, Chem. Phys. Lett. 285 (1998) 170.

[34] E. Espinosa, I. Alkorta, I. Rozas, J. Elguero, E. Molins, Chem. Phys. Lett. 336 (2001) 457.

[35] D. Quiñonero, A. Frontera, P. Ballester, C. Garau, A. Costa, P.M. Deyà, Chem. Phys. Lett. 339 (2001) 369.

[36] S.J. Grabowski, Monatsch. für Chem. 133 (2002) 1373.

[37] P. Popelier, Atoms in Molecules. An Introduction, Prentice-Hall, Pearson Education Limited, Englewood Cliffs, NJ, 2000.