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Bifurcate Hydrogen Bonds. Interaction of Intramolecularly H-Bonded Systems with Lewis Bases

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The structure and the hydrogen bonding in the systems formed by the intramolecularly H-bonded systems, namely, maltol (3-hydroxy-2-methyl-4-pyrone), **5**, 2,4,6-trinitrophenol, **6**, acetylacetone enol, **7**, with Lewis bases, phosgene, **8**, dioxane, **9**, and DMSO, **10**, have been studied by density functional theory (B3LYP) and MP2 using the 6-311G* basis set. The continuum solvent effect was simulated by IEF-PCM model. The hydrogen bond analysis using the atoms in molecules (AIM) method was applied by using the MP2(full)/6-311++G** electron density to establish the nature of the bifurcate hydrogen bond (BHB) in these systems as well as contributory factors for its stabilization. The nature of interaction in the intermolecular H-complexes formed by compounds **5**−**7** with the Lewis bases **8**−**10** was shown to depend on the strength of the intramolecular hydrogen bond $O\cdots H$ and the strength of the base. The critical values of the $C{=}O\cdots H$ and $N{=}O\cdots H$ angles for which the formation of BHB is possible, have been determined.

Introduction

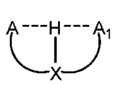
The suggestion of participation of the hydrogen atom in the formation of one covalent and two (rather than one, as usual) hydrogen bonds, was put forward by Albrecht and Corey[1] to rationalize the arrangement of the NH and CO groups in α-glycines. Such a contact of three electronegative atoms and the hydrogen atom was characterized as a bifurcate or three-centered hydrogen bond (BHB). Later on, it turned out that BHBs are not exotic. Judged from the X-ray and neutron diffraction results, BHBs can be found in a variety of structures, in particular, in macromolecular structures of biogenic origin.[2] According to the number of molecules participating in formation of BHB and to the relative arrangement of the proton donor XH and proton acceptor groups A and A_1 (A and A_1 may be identical) the three-centered H-bonds can be classified into several types.

(i) Groups XH, A, and A_1 belong to the same molecule (type **1**).

(ii) Two proton acceptor groups A and A_1 belong to one molecule and the proton donor XH to another (type **2**). The systems of similar structure (with H^+ instead of X−H) are known in the literature as proton sponges.[3]

(iii) The three-centered hydrogen bond is formed by three molecules (type **3**).

(iv) However, another sort of BHB (type **4**) is possible if to consider an interaction of an intramolecularly H-bonded compound with an external proton acceptor possessing the same (A) or different (A_1) basic center. In the former case the dimers of either cyclic (type **4′**) or chain (type **4″**) structure can be formed.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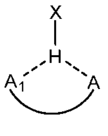
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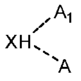
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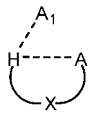
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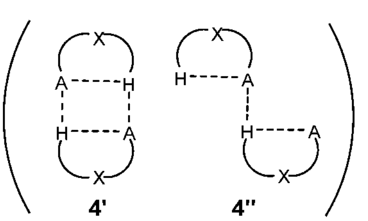
4′ **4″**

From the aforementioned four possibilities of the formation of the bifurcate hydrogen bond the first three are the most theoretically studied.[4] For identification of BHB of the type **4** only the truncated[5] (that is, without analysis of its angular characteristics) geometric criteria were invoked rather than the well approved quantum topological AIM approach.[6] At the same time, the formation of a three-centered hydrogen bond of the type **4** is feasible under the conditions of specific solvation of the intramolecularly H-bonded species with basic solvents. Because the spectroscopic (IR, NMR) experiment does not allow us to make a straightforward conclusion on the geometry in solution, the experimental evidences of existence of bifurcate hydrogen bond in solution were sometimes based on indirect and to some extent questionable indications.[5a,7]

Therefore, the goals of this work were (i) to determine the structure of complexes $A\cdot B$ formed by the intramolecularly H-bonded systems A (A = maltol, **5**; 2,4,6-trinitrophenol, **6**; acetylacetone enol, **7**) with weak, medium, and strong bases B (B = phosgene, **8**; dioxane, **9**; DMSO, **10**); (ii) to use quantum topological AIM analysis for identification and investigation of the nature of BHB in complexes $A\cdot B$; and (iii) to establish factors favoring stabilization of complexes $A\cdot B$ by a three-centered bifurcate hydrogen bond.

One of the reasons for choosing the objects of investigation was as follows: the stability of the maltol dimers **5**·**5** of the type **4′** (**4″**) in the gas phase (or in an inert solvent)[5b] as well as

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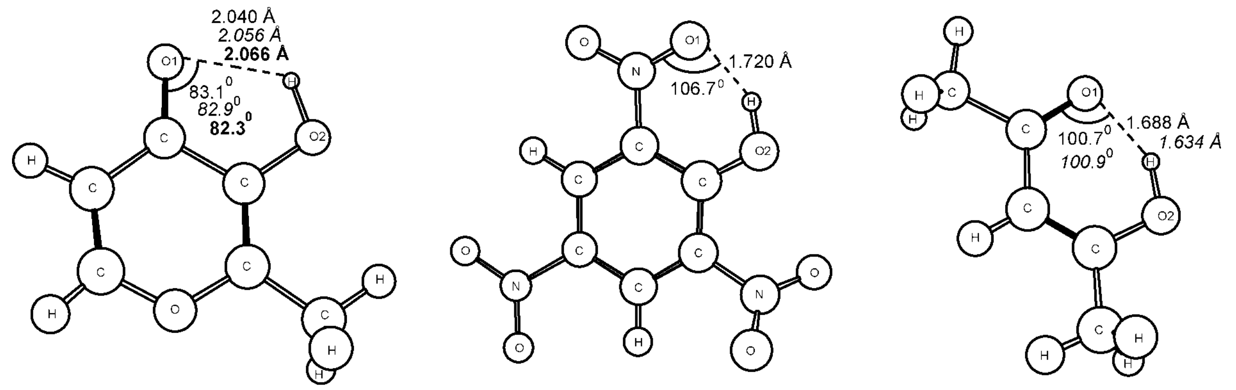


Figure 1. B3LYP/6-311G*, B3LYP/6-311++G** (italic) and MP2/6-311G* (bold) optimized geometries of compounds **5**−**7**.

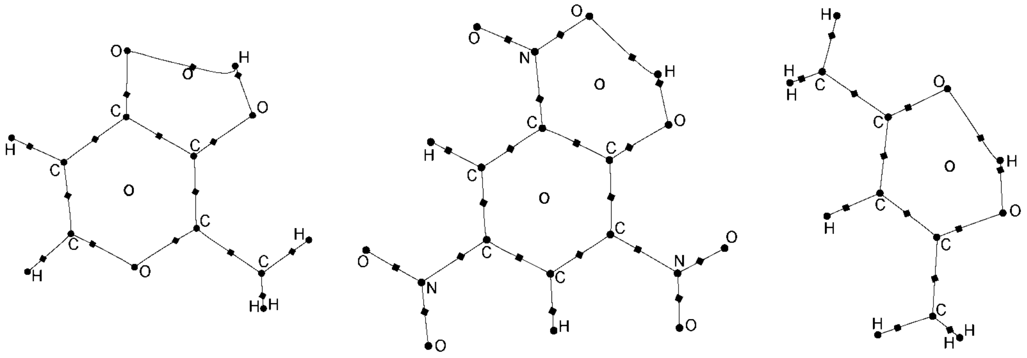
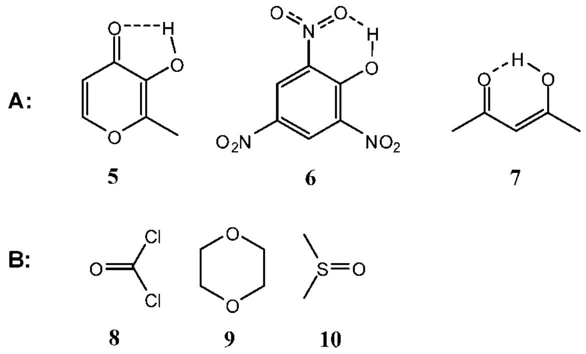


Figure 2. AIM molecular graphs for compounds **5**−**7**. Filled squares denote bond critical points (BCP) (3, −1) and empty circles denote ring critical points (RCP) (3, +1).

that of the solvate complexes of mono-, di- and trinitrophenols in dioxane and DMSO[5a,7a,d] is explained, on the basis of theoretical calculations[5b] or the IR and NMR spectroscopy data,[5a,7a,d] by the BHB formation in them.



Methods

The geometry optimization, energy calculations, and vibrational frequencies computations for the intramolecularly H-bonded systems **A** (**5**−**7**), the Lewis bases **B** (**8**−**10**), and their intermolecular complexes **A·B** (**5·8**, **5·9**, **6·8**, **6·9**, **6·10**, **7·8**, **7·9**, **7·10**) were performed at the B3LYP and MP2 levels of theory with the 6-311G* basis set. For structures **5**, **7**, **5·8** and **7·10** the B3LYP/6-311++G** basis set was also employed. All calculated structures correspond to minima on the potential energy surface as proved by positive eigenvalues of the corresponding Hessian matrix. The energy of formation of the intermolecular complexes **A·B** (E_{compl}) was estimated as the difference of the total energies of the system **A·B** and its components **A** and **B** with due regard to the zero point vibration energy: $E_{\mathrm{compl}} = E(\mathbf{A}\cdot\mathbf{B}) - E(\mathbf{A}) - E(\mathbf{B})$, where the values of $E(\mathbf{A})$ and $E(\mathbf{B})$ were determined on the geometry optimized for the isolated species. The effect of polarity of the medium on the geometry of intermolecular complexes **A·B** was approximated using the integral equation formalism for the polarizable continuum model (IEF-PCM).[8] All calculations were performed with the Gaussian03 suite of programs.[9] The AIM analysis as implemented in the MORPHY 1.0 program[10] was performed by using the electron densities from the MP2(full)/6-311++G** single point calculations.

Results and Discussion

1. Intramolecularly H-Bonded Molecules 5−7. The calculated distances O1···H in maltol (**5**), 2,4,6-trinitrophenol (**6**) and acetylacetone enol (**7**) (Figure 1) are substantially less than the sum of the van der Waals radii of the oxygen and hydrogen atoms (~2.7 Å).[11]

This may be indicative of the presence of a normal hydrogen bond O1···HO2 in molecules **5**−**7**. Indeed, the AIM analysis (Figure 2) of the electronic density $\rho(r)$ revealed in the internuclear region O1···H the bond critical point BCP (3, −1), whereas the chelate structure of molecules **5**−**7** is unequivocally proved by the ring critical points RCP (3, +1) found for the corresponding fragments O1CCO2H, O1NCCO2H and O1CCCO2H.

The values of electronic density $\rho(r_c)$ and the Laplacian $\nabla^2\rho(r_c)$ (see Table 1) at the BCP(O1···H) in molecules **5**−**7** fall in the intervals typical for hydrogen bonds: 0.002−0.04 and 0.024−0.13 au, respectively.[6a,d] Judged from the properties of BCP (O1···H) (Table 1), the five-membered chelate cycle

TABLE 1: Electronic Density at the Bond Critical Point (BCP), $\rho(r_c)$, the Laplacian, $\nabla^2\rho(r_c)$, and the Local Electronic Energy, $E(r_c)$, of Compounds 5−7 Optimized at the B3LYP/6-311G* Level (Bold Values for MP2/6-311G* and Italic Values for B3LYP/6-311++G Optimized Geometry)**

compound	$\rho(r_c)$, au	$\nabla^2\rho(r_c)$, au	$E(r_c)$, au	nature of O1···H contact
5	0.026	0.101	0.002	weak H-bond
	0.024	**0.099**	**0.002**	
	0.025	*0.099*	*0.002*	
6	0.046	0.143	−0.005	medium H-bond
7	0.050	0.138	−0.008	nedium H-bond
	0.057	*0.147*	*−0.011*	

O1CCO2H in maltol is closed, according to ref 6d, by a weak (1−4 kcal/mol) hydrogen bond of ionic nature. On the contrary, the negative sign of $E(r)$ for O1···H contacts in the six-membered chelate cycles O1NCCO2H of 2,4,6-trinitrophenol and O1CCCO2H of acetylacetone enol testifies that they are medium in energy[6d] (4−15 kcal/mol) and according to the Cremer-Kraka et al. criterion,[12] have a covalent component which, judged from the $|E(r)|$ values (Table 1), is notably larger in **7** than in **6**.

In the literature[13] such O1···H interactions as in **6** and **7** are considered as intermediate. By the value of $\rho(r_c)$ and $\nabla^2\rho(r_c)$ and the sign of $\nabla^2\rho(r_c)$ they are ionic, whereas by the sign and the value of $E(r_c)$ they are covalent.

Close mutual arrangement of critical points BCP (O1···H) and RCP (see Figure 2) in the O1CCO2H fragment of the maltol molecule **5** is an important indicator[14] of instability of its H-bonded structure as compared to such in molecules **6** and **7**. The reason for this can be sought in unfavorable angular characteristics for the O1···HO2 bonding in molecule **5**.[15] Indeed, although in molecule **7** the value of the C=O1···H angle differs from the optimal (107.1°)[16] by ∼7°, in molecule **5** this difference amounts to 15°.

The fact of the presence of a hydrogen bond in maltol **5** at the C=O1···H angles substantially lower than 90° is itself rare[2c,17] and deserves special consideration. In this connection we performed the AIM analysis of the MP2(full)/6-311++G** electron density on the MP2/6-311G* optimized geometry of the model complex formed by the molecules of formaldehyde H_2CO and methanol MeOH. For the three reasonable fixed values of $d_{O\cdots H}$, 1.8, 2.1 and 2.5 Å, the critical angle C=O···H ($\alpha_{crit.}$) at which the BCP (O···H) disappears was determined. The value of α_{crit} was found to notably depend on the intermolecular distance O···H being increased in parallel with $d_{O\cdots H}$ in the following order:

$$d_{O\cdots H}\ (\alpha_{crit}):\ 1.8\ \text{Å}\ (\sim 72^\circ) < 2.1\ \text{Å}\ (\sim 77^\circ) < 2.5\ \text{Å}\ (\sim 80^\circ) \tag{1}$$

Similarly, the following order was found for the model complex $MeNO_2\cdots HOMe$:

$$d_{O\cdots H}\ (\alpha_{crit}):\ 1.8\ \text{Å}\ (\sim 76^\circ) < 2.1\ \text{Å}\ (\sim 80^\circ) < 2.5\ \text{Å}\ (\sim 83^\circ) \tag{2}$$

The found minimal values of $\alpha_{crit.}$, allowing the formation of the C=O···H hydrogen bond, are in good accordance with the predicted values[2c,17] of ∼70° and ∼80° established from the results of statistical treatment of a large array of geometric parameters obtained by X-ray and neutron diffraction for the structures with the C=O···H fragment.

Comparison of sequences (1) and (2) allows one to conclude that more stringent requirements are imposed on the angular characteristics of the N=O···H than on those of the C=O···H bond for the two hydrogen bonds to be formed.

The energy of the intramolecular hydrogen bonding O1···H (E_{HB}) in molecules **5**−**7** can be estimated within the framework of the AIM analysis using the relationship

$$E_{HB} = -D_e = V/2 \tag{3}$$

where V is the local potential energy at the BCP (O1···H) and D_e is the HB dissociation energy.

This equation has been suggested for intermolecular H-complexes[18] and it gives a reasonable increasing order of E_{HB} for molecules **5**−**7**:

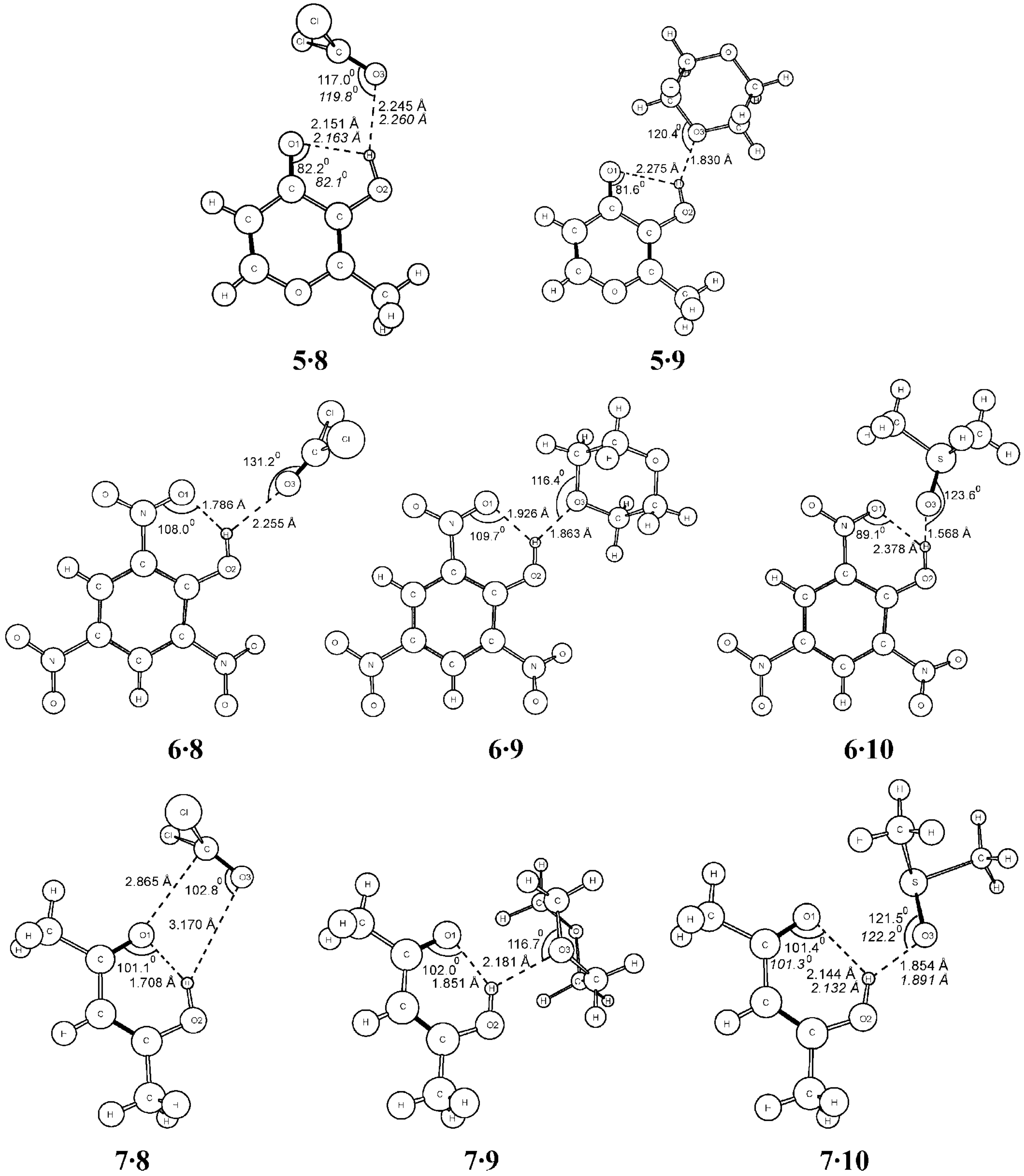
$$\mathbf{5}\ (6.8\ \text{kcal/mol}) < \mathbf{6}\ (14.4\ \text{kcal/mol}) < \mathbf{7}\ (15.7\ \text{kcal/mol}) \tag{4}$$

The values of E_{HB} for molecules **5** and **7** go beyond (especially for **5**) the limits of energetic intervals typical, according to,[6d] for weak (1−4 kcal/mol) and medium (4−15 kcal/mol) H-bonds. In this connection, it is pertinent to note that reliable quantitative assessment of the energy of intramolecular donor-acceptor bonds is principally problematic due to difficulties in choosing adequate model compounds.[19] That is why the values of E_{HB} determined either from eq 3 or by any other approaches[20,21] are to a considerable degree speculative. Nevertheless, the values of E_{HB} for compounds **6** (13.6 kcal/mol at the B3LYP/6-311G* level) and **7** (12.0 kcal/mol at the MP2/6-31+G**//MP2/6-31+G* level)[22] are in good agreement with those found by us [see (4)] using the AIM analysis. In our opinion, the universal AIM relationship (3) allows one to make hereinafter a unified and quite correct comparison of the relative strength of the intra- and intermolecular H-bonds in complexes **5·8**, **5·9**, **6·8**, **6·9**, **6·10**, **7·8**, **7·9** and **7·10**.

It should be mentioned that, on the example of maltol **5**, we ensured (see Figure 1 and Table 1) satisfactory agreement between the ab initio and DFT calculated values of structural parameters for molecules **5**−**7**. In fact, the difference between the MP2 and B3LYP values for all bond distances and bond angles in **5** does not exceed 0.02 Å and 2°, respectively. Also, comparison of Figures 1 and 3 clearly demonstrates that the geometry of both monomers and complexes is only slightly affected by extension of the basis set from 6-311G* to 6−311++G**. Therefore, for geometry optimization of the molecules and complexes under consideration the less time-consuming method B3LYP/6-311G* was chosen.

2. Complexes of Maltol, 2,4,6-Trinitrophenol and Acetylacetone Enol with the Lewis Bases. Table 2 represents the results for intermolecular complexes **A·B**. Two reasonable trends are noteworthy here. First, as expected, for all H-donors the energy of complexation increases with increasing basicity of the protophilic counterpartner. Second, the sensitivity to variation of the basicity of the Lewis base is the least for the H-donor with the most strong intramolecular H-bond (acetylacetone enol), as less susceptible to the influence of an external base.

The most principal question is whether the intramolecular contact O1···HO2 existing in monomeric molecules **5**−**7** will be retained upon their interaction with protophilic molecules **8**−**10**. The formal application of the standard geometrical criterion and taking into account exceeding the sum of the van der Waals radii of the oxygen and hydrogen atoms (∼2.7 Å) over the internuclear distances O1···H in all complexes under consideration (Figure 3) would give a positive answer. However,



5·8 **5·9**

6·8 **6·9** **6·10**

7·8 **7·9** **7·10**

Figure 3. B3LYP/6-311G* and B3LYP/6-311++G** (italic) optimized structures for complexes of molecules **5**−**7** with the Lewis bases **8**−**10**.

from the results of the AIM analysis (Figures 4–6), it drastically depends on the strength of the original hydrogen bond O1···HO2 in **5**−**7** as well as on the basicity of proton acceptor **8**−**10**.

Indeed, in molecule **5** involved in complexes **5·8** and **5·9** no bond critical points BCP(3, −1) were found in the internuclear region O1···H but only in the intermolecular fragments O3···H (Figure 4).

That means that complexes **5·8** and **5·9** are stabilized by conventional intermolecular hydrogen bonds O3···HO2 of ionic nature (see Table 2) rather than by BHB as stated in ref 5b. With this, judged from the value of $\rho(r_c)$ at the BCP(O3···H) and the value of E_{HB} (Table 2), such an intermolecular hydrogen bond in complex **5·9** formed by maltol and the Lewis base of medium strength is stronger than in its complex **5·8** with a weaker base.

The previous (section 1) instability of the chelate five-membered cycle O1CCO2H in **5** can be considered as a possible reason for its easy opening upon the interaction of maltol with

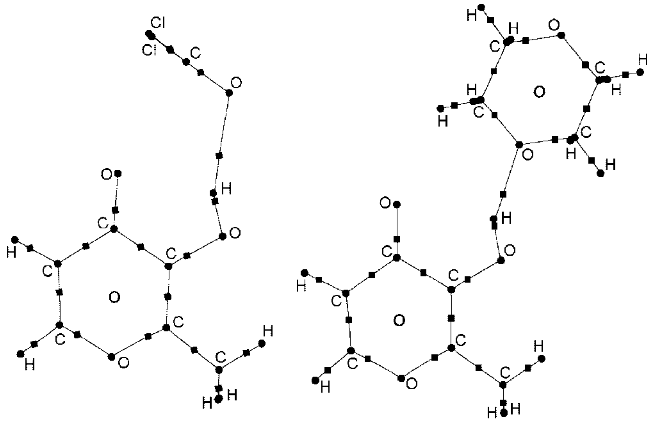
TABLE 2: Electronic Density at the Bond Critical Point (BCP), $\rho(r_c)$, the Laplacian, $\nabla^2\rho(r_c)$, the Local Electronic Energy, $E(r_c)$, the Energy of Hydrogen Bond, E_{HB}, in Complexes of Compounds 5−7 with the Lewis Bases 6−10, and the Energy of Complexation (E_{compl}) Calculated at the B3LYP/6-311G* Level (Italic Values for the B3LYP/6-311++G Optimized Geometry)**

complex	contact	$\rho(r_c)$, au	$\nabla^2\rho(r_c)$, au	$E(r_c)$, au	E_{HB}, kcal/mol	$E_{compl.}$, kcal/mol	nature of contact (according to ref 6d)
5·8	H···O1						no H-bond
						3.1	
	H···O3	0.010	0.040	0.002	2.0	*2.5*	weak H-bond
		0.009	*0.039*	*0.002*	*1.9*		
5·9	H···O1					6.5	no H-bond
	H···O3	0.031	0.114	0	8.8		weak H-bond
6·8	H···O1	0.040	0.132	−0.003	12.1	2.0	medium H-bond
	H···O3	0.010	0.046	0.002	2.3		weak H-bond
6·9	H···O1	0.029	0.106	0	8.0	6.7	weak H-bond
	H···O3	0.029	0.111	0.001	8.2		weak H-bond
6·10	H···O1					11.3	no H-bond
	H···O3	0.060	0.159	−0.013	20.5		medium H-bond
7·8	H···O1	0.048	0.136	−0.007	14.8		medium H-bond
	H···O3					2.1	no H-bond
	C(**8**)···O1	0.010	0.039	0.001			VdW interaction
7·9	H···O1	0.034	0.110	−0.002	9.5	3.3	medium H-bond
	H···O3	0.016	0.059	0.001	3.7		weak H-bond
7·10	H···O1	0.019	0.064	0.001	4.5		weak H-bond
		0.019	*0.065*	*0.001*	*4.6*	4.6	
	H···O3	0.029	0.110	0.001	8.1	*2.6*	weak H-bond
		0.027	*0.102*	*0.001*	*7.2*		

phosgene and dioxane. This interaction results in a decrease of the angle C═O1···H, which approaches the critical value of α_{crit} of ~77−80°. That is why there is no need to consider specific solvation of maltol (**5**) with such a strong base as DMSO (**10**).

It is pertinent to note that in complex **5·8** the intramolecular contact O1···H is by 0.09 Å shorter than the intermolecular contact O3···H (Figure 3). Nevertheless, the BCP (3, −1) was found in the O3···H rather than in the O1···H region. This is a good example of poor reliability of the standard geometrical criterion for identification of hydrogen bonds.

The structure of complexes of 2,4,6-trinitrophenol (**6**) having more strong intramolecular contact O1···HO2 than in maltol (**5**), with the same bases **8** and **9**, is principally different. According to the AIM analysis (see Figure 5 and Table 2) they are stabilized, unlike complexes **5·8** and **5·9**, by bifurcate hydrogen bonds. Indeed, the hydrogen atom of the hydroxy group O2H in **6·8** and **6·9** lies on both the O1···H and O3···H hydrogen bonding pathways.



5·8 **5·9**

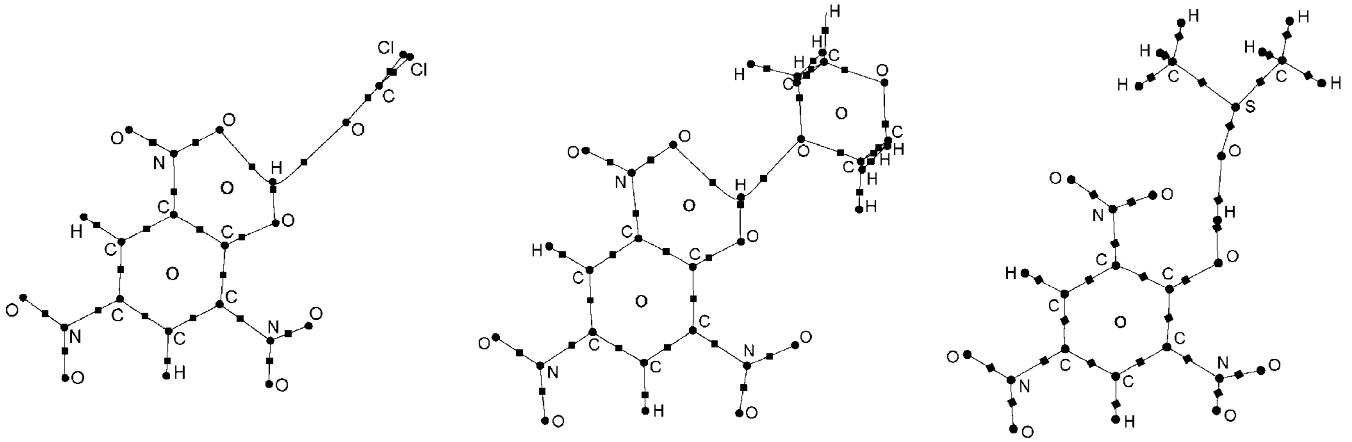
Figure 4. AIM molecular graphs for complexes **5·8** and **5·9**. Filled squares denote bond critical points (BCP) (3, −1) and empty circles denote ring critical points (RCP) (3, +1).

Judging from the properties of BCP (O1···H), BCP(O3···H) and the values of E_{HB}, the ionic−covalent intramolecular component O1···HO2 of the bifurcate hydrogen bond in complex **6·8** is substantially stronger than its ionic intermolecular component O3···HO2. On going from complex **6·8** to complex **6·9** of 2,4,6-trinitrophenol with dioxane which is more protophilic than phosgene a notable weakening of the intramolecular contribution (O1···H) and strenhthening of the intermolecular one (O3···H) into the bifurcate contact O1···H···O3. In complex **6·9** they are virtually equal and have ionic nature.

Opening of the H-bonded chelate structure of 2,4,6-trinitrophenol occurs upon its interaction with such a strong base as DMSO. In this case (see Figure 6 and Table 2) the solvate complex **6·10** is stabilized by an intermolecular ionic-covalent hydrogen bond O3···HO2 of medium strength. The results of the AIM analysis are in compliance with the literature data for complex **6·9** but disagree with those for complex **6·10**. According to the IR and NMR spectroscopy data, both complexes have bifurcate structure.[7a,d]

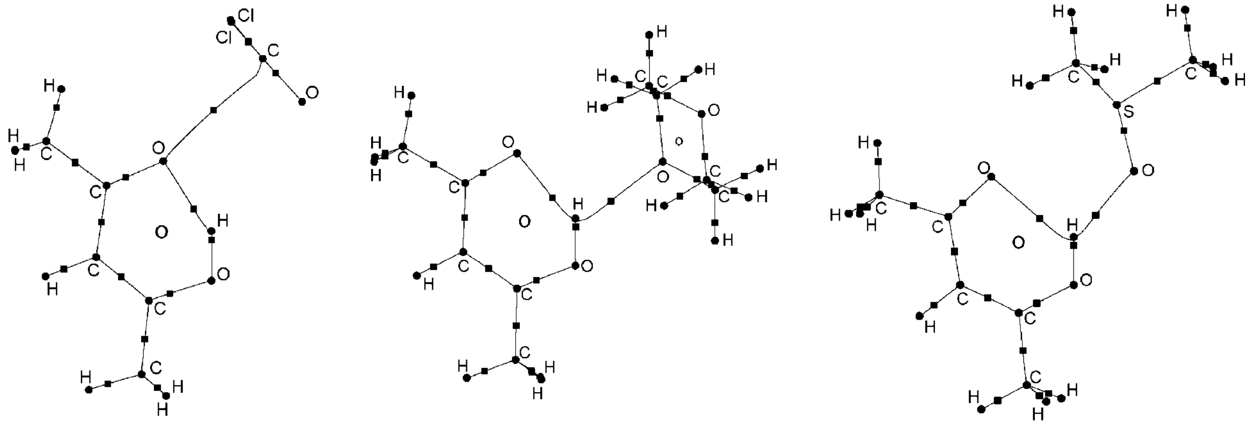
It should be emphasized that in complex **6·10** (see Figures 1 and 3 and eq 2) the N═O1···H angle is ~17° smaller than in the isolated molecule **6** and is close to its critical value α_{crit} ~ 83°. On the contrary, in complex **7·10** the intramolecular hydrogen bond O1···HO2 is retained (see Figure 6 and Table 2) and the stability of the complex is provided by the three-centered contact O1···H···O3. Note that its ionic intermolecular component O3···HO2 is substantially stronger than the intramolecular component O1···HO2 of the same nature.

At the same time, in the bifurcate complex **7·9** formed by acetylacetone enol with a less basic (as compared to DMSO) proton acceptor, the ratio of the two contributions into the O1···H···O3 interaction is reversed: the ionic−covalent intramolecular component O1···HO2 dominates over the ionic intermolecular component O3···HO2 (Table 2). Starting from the basic properties of proton acceptors **8−10**, the retention of the H-bonded chelate structure of subunit **7** in complex **7·8** is quite expected. Nonetheless, the BCP (3, −1) found in its internuclear region lies on the bonding pathway C(**8**)···O1 rather than on O3···H (Figure 6). Therefore, with due regard



6·8 **6·9** **6·10**

Figure 5. AIM molecular graphs for complexes **6·8**, **6·9** and **6·10**. Filled squares denote bond critical points (BCP) (3, −1) and empty circles denote ring critical points (RCP) (3, +1).



7·8 **7·9** **7·10**

Figure 6. AIM molecular graphs for complexes **7·8**, **7·9** and **7·10**. Filled squares denote bond critical points (BCP) (3, −1) and empty circles denote ring critical points (RCP) (3, +1).

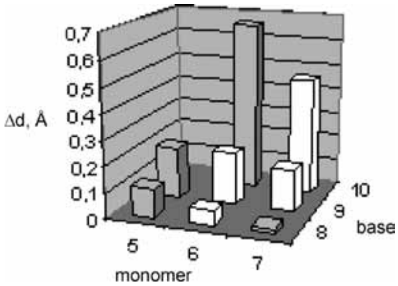


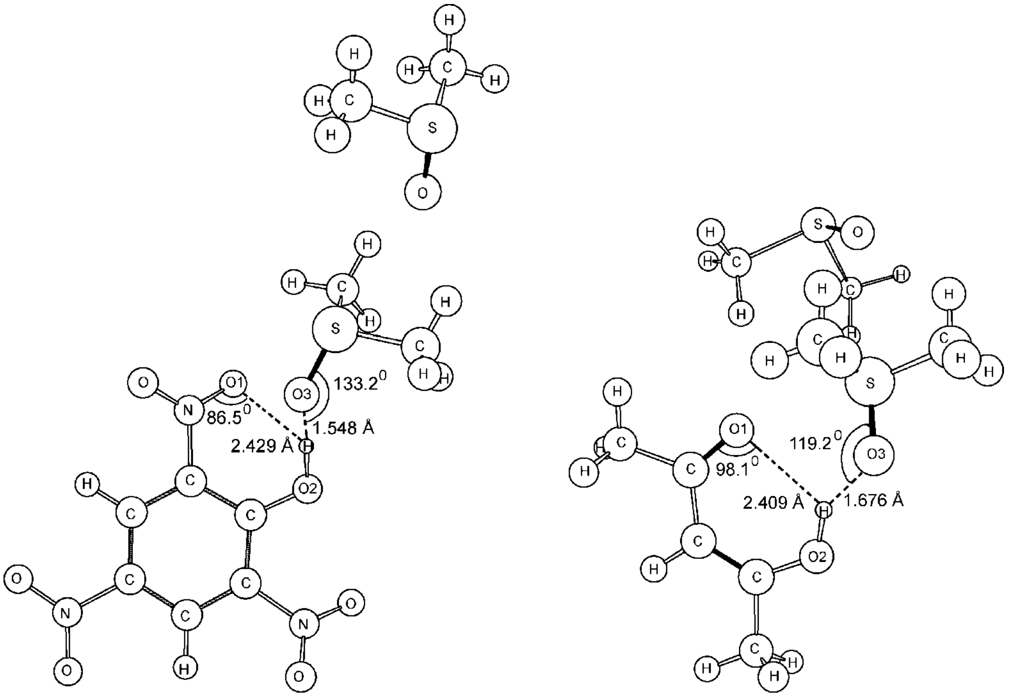
Figure 7. Relative internuclear distances O1···H (Δ*d*, Å) in complexes **5·8**, **5·9**, **6·8**, **6·9**, **6·10**, **7·8**, **7·9** and **7·10** [referred to the values of d_{O1H} in the corresponding subunits; $\Delta d = d(\text{complex}) - d(\text{monomer})$]. White columns refer to complexes stabilized by bifurcate hydrogen bond.

to the values of $\rho(r_c)$ and $\nabla^2\rho(r_c)$ (Table 2), it seems more reasonable to assign complex **7·8** to the van der Waals type complexes.

The data presented in Tables 1 and 2 definitely show that the size of the basis set (6-311G* or 6-311++G**) has no effect on the topology of the electron distribution and the properties of the critical points for the systems under consideration.

When molecules **5**−**7** are incorporated in the composition of complexes **5·8**, **5·9**, **6·8**, **6·9**, **6·10**, **7·8**, **7·9** and **7·10**, elongation of the corresponding contact O1···H with regard to that in the isolated species is always observed. The degree of this deformation of the intramolecular hydrogen bond O1···H, Δd_{O1H}, depends on its original strength in molecules **5**−**7** as well as on the proton acceptor properties of molecules **8**−**10** (Figure 7). In general, there is no correlation between Δd_{O1H} and the structure of the analyzed complexes. For example, with comparable values of Δ*d* in complexes **5·9** and **6·9** the former is stabilized by a two-centered hydrogen bond whereas the latter by a three-centered one. As judged from the results obtained, for the systems containing BHB the values of Δd_{O1H} fall in the interval ~0.05−0.5 Å. The most probable seems the formation of BHB upon the interaction of medium in strength H-bonded chelate structures with proton acceptors of medium basicity, as in complexes **6·9** and **7·9** (Figure 7). Such associates are characterized also by intermediate values of Δd_{O1H} ~0.2 Å. In other cases, when BHBs were (**6·8**, **7·10**) or were not (**6·10**, **7·8**) observed, the crucial point is the a priori poorly predicted fine difference between the energies of the O1···H hydrogen bonds in **6** and**7** as H-donors with respect to an external Lewis base.

Note that in highly basic DMSO solution the formation of complexes of 2,4,6-trinitrophenol **6** and acetylacetone enol **7** with two molecules of DMSO **6·**(**10·10**) and **7·**(**10·10**) is feasible. At the B3LYP/6-311G* level these complexes (Figure 8) are ~9 kcal/mol more favorable than the above considered 1:1 complexes **6·10** and **7·10**. In the 1:2 complexes, the conditions for existence of the intramolecular hydrogen bond



6·(10·10) **7·(10·10)**

Figure 8. B3LYP/6-311G* optimized structures for 1:2 complexes of 2,4,6-trinitrophenol and of acetylacetone enol with DMSO.

O1···H are much worse than in the 1:1 complexes. This is witnessed by the values of d_{O1H}, ∠NOH, and ∠COH for complexes **6**·(**10**·**10**) and **7**·(**10**·**10**) as compared to those for complexes **6**·**10** and **7**·**10** (in brackets): $d_{\mathrm{O1H}} = 2.429$ Å (2.378), ∠NOH = 86.5° (89.1); $d_{\mathrm{O1H}} = 2.409$ Å (2.143), ∠COH = 98.8° (101.6). Therefore, the 1:2 complexes of 2,4,6-trinitrophenol with DMSO, as well as its 1:1 complexes, are stabilized by conventional intermolecular hydrogen bonds O3···H. On the contrary, for complex **7**·(**10**·**10**) the AIM analysis reveals the existence of a weak intramolecular hydrogen bond O1···H and, hence, the bifurcate hydrogen bond. Possibly, the formation of the latter is favored by more appropriate angular characteristics for the bonding contact O1···H in **7**·(**10**·**10**) as compared to that in **6**·(**10**·**10**).

Finally, it is worthwhile to mention that there are no reasons to doubt the validity of the made conclusions even if to take into account the effect of polar medium on the geometry of the above complexes. In fact, within the framework of the continuum model PCM, the shortening of the internuclear distance O1···H with simultaneous elongation of O3···H does not exceed 0.04 Å in complex **5**·**8** (for $\varepsilon = 4.3$) and **6**·**9** (for $\varepsilon = 2.2$) as compared to the corresponding values in the isolated species. The effect of nonspecific solvation of the complex of 2,4,6-trinitrophenol with two molecules of DMSO (for $\varepsilon = 46.7$) is structurally more pronounced ($\Delta d^{s}_{\mathrm{O1H}}$ ~0.15Å). Nevertheless, such deformations of the O1···H hydrogen bonds do not affect appreciably the topology of $\rho(r_c)$ in complexes **5**·**8**, **6**·**9** and **6**·(**10**·**10**) nor change their structure.

Conclusions

The above DFT and MP2 analysis using the quantum topological AIM approach of the structure of the intramolecularly H-bonded systems **5**−**7** (maltol (**5**), 2,4,6-trinitrophenol (**6**) and acetylacetone enol (**7**)) and their associates with the Lewis bases **8**−**10** (phosgene (**8**), dioxane (**9**) and DMSO (**10**)) leads to the following conclusions.

The intramolecular hydrogen bond in maltol is weak (1−4 kcal/mol) and has ionic nature. In 2,4,6-trinitrophenol and acetylacetone enol these bonds are medium in energy (4−15 kcal/mol) and have ionic−covalent nature.

The critical values of the C=O···H (72−80°) and N=O···H (76−83°) angles for which the formation of the O1···H hydrogen bond is still possible depend on the O1···H internuclear distance. The solvate complexes of maltol with the Lewis bases **8** and **9** are stabilized by conventional intermolecular hydrogen bonds O3···H rather than the three-centered O1···H···O3 bond, as suggested previously. In complexes of 2,4,6-trinitrophenol **6** with phosgene **8** and dioxane **9** the formation of BHB O1···H···O3 is observed (for **6**·**9** this is in compliance with the literature data). On the contrary, in its complex with DMSO, **6**·**10**, the chelate structure of 2,4,6-trinitrophenol is destroyed. The associates of acetylacetone enol **7** with dioxane **7**·**9** and DMSO **7**·**10** have bifurcate structure, whereas its complex with the least basic Lewis base, phosgene, **7**·**8**, apparently, belongs to the van der Waals complexes.

Therefore, the present investigation confirmed the reality of formation of BHB under the conditions of specific solvation of the intramolecularly H-bonded molecules with basic solvents. The most probable is the formation of such BHBs upon the interaction of medium in strength H-bonded chelates with the Lewis bases of medium basicity, like **6**·**9** and **7**·**9**. In other cases, the formation of BHB depends on small differences in the energies of the O1···H hydrogen bonds in the intramolecularly H-bonded chelates acting as H-donors with respect to the external Lewis base.

The conclusions made about the bifurcational/nonbifurcational structure of the solvate complexes remain valid also when this model of specific solvation used is refined by taking into account the effects of polar environment at the IEF-PCM level and/or formation of DMSO dimers.

Supporting Information Available: Cartesian coordinates of all investigated structures. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Albrecht, G.; Corey, R. B. *J. Am. Chem. Soc.* **1939**, *61*, 1087.

(2) (a) Donohue, J. *Structural Chemistry and Molecular Biology*; Freeman: San Francisco, 1968. (b) Jonsson, P. G.; Kvick, A. *Acta. Crystallogr.* **1972**, *B28*, 1827. (c) Taylor, R.; Kennard, O.; Versichel, W. *J. Am. Chem. Soc.* **1983**, *105*, 5761. (d) Jeffrey, G. A.; Saenger, W. *Hydrogen Bonding in Biological Structures*; Springer-Verlag: Berlin, Heidelberg, 1991. (e) Parthasarathy, R. *Acta Crystallogr.* **1969**, *B25*, 509. (f) Jeffrey, G. A.; Takagi, S. *Acc. Chem. Res.* **1978**, *11*, 264. (g) Martinez-Martines, F. G.; Padilla-Martinez, I. I.; Brito, M. A.; Geniz, E. D.; Rojas, R. C.; Saavedra, J. B. R.; Höpfl, H.; Tlahuextl, M.; Contreras, R. *J. Chem. Soc., Perkin Trans.* **1998**, *2*, 401. (h) Lin, H.; Wu, J.; Xu, Y. X.; Jiang, X. H.; Li, Z. T. *Tetrahedron Lett.* **2007**, *48*, 7247. (i) Desiraju, G. R.; Steiner, T. *The weak hydrogen bond in structural chemistry and biology*; Oxford University Press, Inc.: New York, 1999.

(3) Lamas-Saiz, A.; Foces-Foces, C.; Elguero, J. *Mol. Struct.* **1994**, *328*, 297.

(4) (a) Fritsch, V.; Westhoff, E. *J. Am. Chem. Soc.* **1991**, *113*, 8271. (b) Sponer, J.; Hobza, P. *J. Am. Chem. Soc.* **1994**, *116*, 709. (c) Rozas, I.; Alcorta, I.; Elguero, J. *J. Phys. Chem. A* **1998**, *102*, 9925. (d) Gu, J.; Leszczynsky, J.; Bansal, M. *Chem. Phys. Lett.* **1999**, *311*, 209. (e) Mallinson, P.R.; Smith, G. T.; Wilson, C.C.; Grech, E.; Wozniak, K. *J. Am. Chem. Soc.* **2003**, *125*, 4259. (f) Parra, R. D.; Ohlssen, J. *J. Phys. Chem. A* **2008**, *112*, 3492.

(5) (a) Vokin, A. I.; Gavrilova, G. A.; Shulunova, A. M.; Krivoruchka, I. G.; Aksamentova, T. N.; Turchaninov, V. K. *Russ. J. Gen. Chem.* **2004**, *74*, 239. (b) Chipanina, N. N.; Shainyan, B. A.; Sherstyannikova, L. V.; Turchaninov, V. K. *Russ. J. Org. Chem.* **2004**, *40*, 301. (c) Mukha, S. A.; Chipanina, N. N.; Sterhova, I. V.; Aksamentova, T. N.; Medvedeva, S. A.; Turchaninov, V. K. *Chem. Heterocycl. Comput.* **2006**, 1635.

(6) (a) Koch, U.; Popelier, P. L. A. *J. Phys. Chem.* **1995**, *99*, 9747. (b) Popelier, P. L. A. *J. Phys. Chem.* **1998**, *102*, 1873. (c) Hocquet, A. *Phys. Chem. Chem. Phys.* **2001**, *3*, 3192. (d) Grabowski, S. J. *J. Phys. Org. Chem.* **2004**, *17*, 18.

(7) (a) Bureiko, S. F.; Golubev, N. S.; Pihlaja, K.; Mattiney, J. *Zh. Struct. Khim.* **1991**, *32*, 87. (b) Lutskii, A. E.; Prezhdo, V. V.; Degtereva, L. I.; Gordienko, V. G. *Russ. Chem. Rev.* **1982**, *51*, 802. (c) Schreiber, V.; Koll, A.; Kulbida, A.; Majerz, I. *J. Mol. Struct.* **1995**, *348*, 365. (d) Bureiko, S. F.; Golubev, N. S.; Pihlaja, K. *J. Mol. Struct.* **1999**, *480−481*, 297. (e) Grech, E.; Nowicka-Scheibe, J.; Olejnik, Z.; Lis, T.; Pawelka, Z.; Malarski, Z.; Sobczyk, L. *J. Chem. Soc., Perkin Trans.* **1996**, *2*, >343. (f) Goutev, N.; Matsuura, H. *J. Phys. Chem. A* **2001**, *105*, 4741. (g) Krivoruchka, I. G.; Vokin, A. I.; Aksamentova, T. N.; Shulunova, A. M.; Sorokin, M. S.; Dubinskaya, E. I.; Turchaninov, V. K. *Russ. J. Gen. Chem.* **2004**, *74*, 120. (h) Fedorov, S. V.; Krivoruchka, I. G.; Shulunova, A. M.; Sherstyannikova, L.V.; Trofimova, O. M.; Vokin, A. I.; Turchaninov, V. K. *Russ. J. Gen. Chem.* **2005**, *75*, 100.

(8) (a) Cances, M. T.; Mennucci, B.; Tomasi, J. *J. Chem. Phys.* **1997**, *107*, 3032. (b) Mennucci, B.; Tomasi, J. *J. Chem. Phys.* **1997**, *106*, 5151.

(9) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G. ; Rega, N.; Petersson, G. A.; Nakatsuji, H. ; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M. ; Nakajima, T.; Honda, Y. ; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R. ; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q. ; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian03, revision B.03; Gaussian, Inc.: Pittsburgh, PA, 2003.

(10) (a) Popelier, P. L. A. *Comput. Phys. Commun.* **1996**, *93*, 212. (b) Popelier, P. L. A. *Chem. Phys. Lett.* **1994**, *228*, 160.

(11) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(12) (a) Cremer, D.; Kraka, E. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 627. (b) Olsson, L.; Ottosson, C.-H.; Cremer, D. *J. Am. Chem. Soc.* **1995**, *117*, 7460. (c) Ottosson, C.-H.; Cremer, D. *Organometallics* **1996**, *15*, 5309.

(13) (a) Korlyukov, A. A.; Lyssenko, K. A.; Antipin, M. Yu. *Russ. Chem. Bull., Int. Ed.* **2002**, *51*, 1423. (b) Gervasio, G.; Bianchi, R.; Marabello, D. *Chem. Phys. Lett.* **2004**, *387*, 481. (c) Sidorkin, V. F.; Belogolova, E. F.; Pestunovich, V. A. *Chem. Eur. J.* **2006**, *12*, 2021.

(14) Bader, R. F. *Atoms in Molecules: A Quantum Theory*; Clarendon Press, Oxford, U.K., 1990; p *458*.

(15) The proton acceptor (CO, NO) and proton donor (OH) fragments in molecules **5**−**7** lie in the same plane; hence, the position of atom H with respect to C═O and N═O bonds is unambiguously defined by the d(OH) distance and C(N)═OH angle.

(16) (a) Optimal angles for the H-bonds C═O···H (107.1°) and N═O···H (99.3°) are defined as angles characterizing the orientation of the lone pair of the carbonyl and the nitrosyl oxygen atom (CO^{lp} and NO^{lp}) relative to the CO and NO fragments in acyclic model molecules H_2CO and $MeNO_2$, respectively. In the AIM analysis the values of CO^{lp} and NO^{lp} were estimated by standard procedure[14,16b] by identification of nonbonding maxima of the negative Laplacian $-\nabla^2\rho$ at the MP2/6-311++G** level of theory. (b) Bader, R. F.; MacDougall, P. J.; Lau, C. D. H. *J. Am. Chem. Soc.* **1984**, *106*, 1594.

(17) Taylor, R.; Kennard, O. *Acc. Chem. Res.* **1984**, *17*, 320.

(18) Espinosa, E.; Molins, E.; Lecomte, C. *Chem. Phys. Lett.* **1998**, *285*, 170.

(19) This causes serious difficulties when considering not only energetic but also other characteristics of intramolecular hydrogen bonds.[6a]

(20) Buemi, G.; Zuccarello, F. *J. Mol. Struct.* **2002**, *581*, 71.

(21) Buemi, G.; Zuccarello, F.; Venuvanalingam, P.; Ramalingam, M.; Ammal, S. S. C. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 3313.

(22) Wong, F. M.; Keeffe, J. R.; Wu, W. *Tetrahedron Lett.* **2002**, *43*, 3561.

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