Estimates of the Energy of Intramolecular Hydrogen Bonds

Mirosław Jabłoński, Anna Kaczmarek,[†] and Andrzej J. Sadlej*

Department of Quantum Chemistry, Institute of Chemistry, Nicolaus Copernicus University, PL-87 100 Toruń, Poland

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A method for the estimation of the energy of intramolecular hydrogen bonds in conjugated systems existing in a variety of conformations is presented. The method is applied to determine the intramolecular hydrogen bond energy in 3-aminopropenal and 3-aminopropenthial. According to the proposed estimation scheme, the intramolecular H-bond energies are found to be of the order of 5−7 kcal/mol. These results are compared with those obtained by using other estimation schemes as well as with the recent results by other authors. Also, the H-bond energies in dimers and trimers of the two molecules are calculated and compared with the corresponding data for internally hydrogen-bonded monomers. This comparison shows that the bond equalization effect is primarily due to proton donor−proton acceptor proximity. In comparison with intermolecular hydrogen bonds, the rigidity of the chelate skeleton enhances this proximity effect. The same effect can be seen in systems with intermolecular hydrogen bonds, although its magnitude is diminished because of the absence of additional forces which pull the proton donor and proton acceptor groups toward each other. No specific resonance-assisted origin of the intramolecular hydrogen bond energy seems to be needed to elucidate the energetics of these bonds.

I. Introduction

The hydrogen bond represents one of the most intriguing forms of intermolecular interaction.[1,2] Despite numerous theoretical studies,[3−5] its understanding is far from complete. Though the simple electrostatic model of the H-bond may correctly describe its origin and energetics, the pattern of interactions in what is called the hydrogen bridge Y···H−X appears to be far more complicated.[6] There seems to be no single feature of the Y···H−X interaction which would simultaneously account for the variety of its physical aspects and would fully explain the nature of the hydrogen bond. The highly simplistic point of view which recognizes the H-bond formation as one of the local minima on the Born−Oppenheimer energy hypersurface does not meet the quest for explanations asked by a chemist.

Yet, even more intriguing is the case of *intramolecular* hydrogen bonds, in particular, those linking the two ends of a conjugated π system.[7] These intramolecular hydrogen bonds are known to stabilize quasi-cyclic structures whose geometry resembles that of the benzene ring. This structural form of the intramolecular hydrogen bonding is recognized as a particular case of the H-bonded interaction which is believed to be possibly accompanied by certain conjugation effects.[8] For these bonds, G. Gilli et al.[9] have coined a special term the resonance-assisted hydrogen bonding (RAHB), which is meant to account for the changes in the π system induced and accompanied by the presence of the intramolecular H-bond.

In the case of intramolecular hydrogen bonds, one of the primary goals is usually to find some value of what can be called the intramolecular hydrogen bond energy. This is rooted in the ideas of the bond separability and the additivity of bond energies. However, at variance with the intermolecular hydrogen bonding, there is no reference system which would simultaneously assume the geometric structure close to that of the intramolecularly H-bonded molecule and had no hydrogen bond. This has led to the development of additivity schemes which attempt to define and determine the intramolecular H-bond energy.

According to the model discussed by G. Gilli, P. Gilli, et al.,[9,10] the relevant part of the total energy E of a molecule featuring the RAHB is partitioned into the H-bond energy, E_{HB}, the so-called resonance contribution, E_{RES}, the E_{BP} term which represents the energy required for the creation of the opposite fractional charges on A and B in A···H−B, and the van der Waals (E_{vdw}) contribution due to nonbonded interactions

$$E = E_{\mathrm{HB}} + E_{\mathrm{RES}} + E_{\mathrm{BP}} + E_{\mathrm{vdw}} \tag{1}$$

Obviously, such a model introduces energy contributions whose unique definition within a single molecule is essentially impossible. Hence, the model carries a heavy semiempirical flavor and brings about the unavoidable double, or even multiple, counting of interactions. On the other hand, it gives some numerical results for what can be considered the energy of the intramolecular H-bond. Indeed, on the basis of the crystal structure data, G. Gilli et al.[9] seem to have given some evidence for the importance of the E_{RES} term. However, the particular significance of the π-conjugation contribution, which would be associated solely with the quasi-cyclic form of the intramolecular hydrogen-bonded structure, appears to have a little support from the electronic structure considerations.[11,12] In the case of X and Y being the first-row atoms, the required overlap between 2pπ orbitals in the Y···H−X bridge is usually too small to lead to any significant delocalization. If there is such an effect, it may eventually become of certain importance in H-bonded systems involving atoms of the second row of the periodic table. On the other hand, the proximity of the proton donor and proton

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* E-mail: teoajs@chem.uni.torun.pl (all coauthors).

[†] Present address: Research Group for Modeling and Synthesis of Novel Materials, Institute of Chemistry, Nicolaus Copernicus University, PL-87 100 Toruń, Poland.

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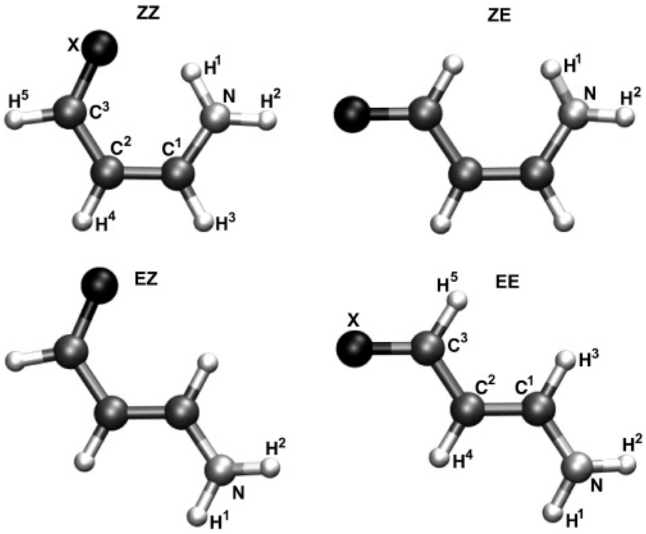


Figure 1. Four conformations of 3-aminopropenal and 3-aminopropenthial. Conformer symbols and the numbering of atoms.

acceptor groups in the chelate form will certainly lead to some rearrangement of the π-electron distribution and change the conjugation pattern. The proximity of the two groups is additionally enhanced by the relatively rigid planar structure of the quasi-cyclic arrangement.

The present paper offers a simple way of estimating the energy of the intramolecular hydrogen bond from the energy data for a series of molecules known as enaminoaldehydes and enaminothioaldehydes. The two model compounds studied in this paper, 3-aminopropenal and 3-aminopropenthial (Figure 1), have four conformations which differ by the configuration at the C=C double bond (cis (Z) and trans (E) forms) and conformation at formally single C−C bond (s-cis (Z) and s-trans (E) forms). This leads to four different structures, ZZ, ZE, EZ, and EE, which are shown in Figure 1. The quasi-cyclic ZZ form is stabilized by the intramolecular hydrogen bond. The other three forms differ formally from the ZZ structure by rotations about single and double CC bonds. Once the relative energies of all four conformers are known, one may attempt to find some approximately additive scheme which accounts for the energy change due to conformation/configuration differences[13] and returns an estimate of the intramolecular hydrogen bond energy. The estimated energy of the intramolecular hydrogen bond can be compared with intermolecular H-bond energies in similar systems. These comparisons may reveal if there are any unique[9,10] features of the intramolecular hydrogen bond which lead to quasi-cyclic structures in unsaturated systems.

The method proposed in this paper is based on the approximate isolation of the energy contribution which occurs upon the transition from the ZZ to other forms of the investigated molecules and arises solely from changes in bond distances and (planar) bond angles. The use of this approach is obviously restricted to molecules with a large enough number of conformers of certain specific form. Despite this limitation, the present method clearly defines a set of approximations which can be used to separate the energy contribution due to intramolecular hydrogen bonding. Our results for intramolecular hydrogen bonds in ZZ forms of 3-aminopropenal and 3-aminopropenthial will be compared with those obtained by using other methods.[8,14−16] To discuss the possible uniqueness of intramolecular hydrogen bonds in unsaturated quasi-cyclic (chelate) structures, we shall also compare the present estimates of the intramolecular hydrogen bond energy with energies of intermolecular hydrogen bonds in dimers and trimers of the investigated molecules. These results will give additional support to the ideas of Alkorta et al.[12,14] concerning the origin of what is referred to as the "aromatic" character of the chelate structures.[8]

The energies of intramolecular hydrogen bonds in a series of systems similar to those investigated in the present paper have been recently studied by Buemi and Zuccarello.[15] These authors have attempted to determine the intramolecular hydrogen bond energy from the calculated barriers for internal rotations of the end groups. They concluded that this method gives the hydrogen bond energies consistent with the simplest scheme, based on the comparison of energies of the open and H-bonded conformations. Among several other molecules, Buemi and Zuccarello[15] have also used their method for 3-aminopropenal and obtained the intramolecular hydrogen bond energy of 10.2 kcal/mol (MP2 calculations with 6-31G** basis set). This value, however, appears to be quite high in comparison with the usual intermolecular hydrogen bond energies.

More recently, the virtues of 3-aminopropenal as a model system for the determination of the intramolecular hydrogen bond energy have been also recognized by Nowroozi et al.,[16] who have carried out DFT calculations for 28 different structural isomers and conformers of this molecule, including enolimine and ketoimine forms. By combining the energy data for four conformers of 3-aminopropenal with those for related systems with a "perpendicular" $-NH_2$ group, they estimated the energy of the intramolecular hydrogen bond in ZZ 3-aminopropenal as 8.35 kcal/mol.

In the present context, one should also mention the method used by Lipkowski et al.[17] which is based on a "thermodynamic cycle" of transitions between different structures. They have applied this method to estimate the intramolecular hydrogen bond energy in the *ortho*-(*N*-dialkylaminomethyl)phenyl molecule and its derivatives. The method used by Lipkowski et al.[17] is very similar to that devised earlier by the present authors[18,19] and assumes that intramolecular rotations of different groups do not lead to major changes in the π-conjugated skeleton. This approximation seems to be well-satisfied for molecules studied by Lipkowski et al.[17] and gives the estimate of the intramolecular $O-H\cdots N$ bond energy of the order of 8 kcal/mol. In molecules studied in this paper, the π-conjugated skeleton may undergo significant structural changes upon the rotation about single and double CC bonds, and thus, the "thermodynamic cycle" approach would be a rather crude approximation.[18,19]

It should also be noted that the present model systems are not completely artificial.[20,21] Although obtaining all four structures for either of the two molecules may not be possible experimentally, all of the conformers are known for the so-called enaminoketones, and their equilibria have been extensively investigated, including the determination of barriers to intramolecular rotation of functional groups.[22−27] Similar studies have also been carried out for enaminothials.[28]

II. Calculations

All energy values used for estimating the intramolecular H-bond energy have been obtained by using standard methods of the electronic structure theory and the Gaussian suite of programs.[29,30] For each of the two molecules, the four minimum-energy structures (Figure 1) were determined at the level of the self-consistent field (SCF) HF and MP2 approximations with 6-31G*, 6-31G**, and 6-311++G** basis sets of the *Gaussian98*/*Gaussian03* basis set library. In what follows, these basis sets will be referred to as basis a, b, and c, respectively. Most

TABLE 1: Energies (in kcal/mol) of Different Fully Optimized Structures of 3-Aminopropenal and 3-Aminopropenthial Relative to the ZZ Conformer as Calculated in the SCF HF and MP2 Approximations with 6-31G* (a), 6-31G (b), and 6-311++G** (c) Basis Sets**

	SCF HF			MP2		
basis set	EZ	EE	ZE	EZ	EE	ZE
			3-Aminopropenal			
a	3.07	3.18	6.33	5.00	4.75	7.88
b	3.20	3.37	6.56	5.11	4.81	7.91
c	3.30	2.56	5.95	4.77	3.77	6.50
			3-Aminopropenthial			
a	2.93	2.33	5.12	5.56	4.14	6.42
b	3.04	2.45	5.26	5.78	4.30	6.52
c	3.17	2.09	4.88	6.07	4.09	6.02

of the calculated data will be those for basis sets b and c. The moderately sized 6-311++G** (c) set is usually considered to give fairly reliable results for hydrogen-bonded systems.[11,12] All electrons have been correlated in MP2 calculations with basis sets a and b, whereas the MP2/6-311++G** calculations have been performed in the frozen core approximation. One should also mention that the graphical material included in this paper has been produced by using *Visual Molecular Dynamics* software by Humphrey et al.[31]

The main energy data obtained in present calculations are summarized in Table 1. These results are the electronic energies relative to the energy of the ZZ conformer and do not include corrections for the zero-point vibrational energy (ZPE). As shown by the data of Table 1, all three basis sets give fairly similar results for relative energies of different conformers. The electron correlation effects increase the relative energies of the SCF HF approximation by about 1−3 kcal/mol. This increase, however, depends on both the conformer and the basis set used in calculations and may even lead to the change of the ordering of the conformer energies. This happens in the case of MP2/6-31G** calculations for the (EZ, EE) pair of 3-aminopropenal; the ordering of relative MP2 energies is different from that obtained in SCF HF calculations. Moreover, on passing from basis b to basis c, the MP2 ordering of the (EZ, ZE) pair is also inversed in the MP2 approximation. One should note, however, that the ordering of (EZ, EE) pairs calculated at the level of the MP2 approximation does not depend on the basis set.

The ordering of MP2/6-31G** energies has been confirmed by single-point CCSD(T)[32] calculations at MP2/6-31G**-optimized molecular geometries. For the 3-aminopropenal molecule, the relative CCSD(T) energies of the EE, EZ, and ZE structures are 4.36, 4.51, and 7.11 kcal/mol, respectively. In the case of 3-aminopropenthial, the MP2 ordering of energies, $E^{ZZ} < E^{EE} < E^{EZ} < E^{ZE}$, also remains the same at the level of the CCSD(T) approximation with the energy values (relative to E^{ZZ}) equal to 4.04, 5.10, and 6.06 kcal/mol, respectively. The higher-order electron correlation effects lead to certain reduction of all relative energies.

For either of the two molecules, both SCF HF and MP2 calculations predict that in all four conformers the $Y{=}C{-}C{=}C{-}N$ ($Y = O, S$) skeleton is essentially planar. For some conformers, depending on the basis set used in calculations, some out-of-plane deformation (pyramidalization) of the $-NH_2$ group may occur. However, from the point of view of the method proposed in this paper for the estimation of the intramolecular hydrogen bond energy, this local nonplanarity is quite irrelevant.

TABLE 2: Selected Geometry Parameters of the Four Conformers of 3-Aminopropenal[a]

		configuration/conformation			
parameter[b]	basis set	ZZ	EZ	EE	ZE
C^1N	b	1.344	1.362	1.367	1.372
	c	1.352	1.368	1.371	1.376
C^1C^2	b	1.368	1.353	1.353	1.357
	c	1.372	1.357	1.357	1.362
C^2C^3	b	1.435	1.455	1.449	1.449
	c	1.444	1.464	1.455	1.455
C^3O	b	1.246	1.233	1.229	1.231
	c	1.239	1.226	1.223	1.225
NH^1 [c]	b	1.012	1.005	1.006	1.005
	c	1.016	1.009	1.009	1.008
NH^2	b	1.001	1.003	1.004	1.004
	c	1.006	1.007	1.008	1.007
$\angle(H^1NC^1)$	b	116.9	118.7	117.5	118.7
	c	116.7	118.0	117.4	118.5
$\angle(NC^1C^2)$	b	124.4	126.8	126.6	128.3
	c	124.6	126.3	126.3	128.1
$\angle(C^1C^2C^3)$	b	121.4	119.1	119.3	124.7
	c	121.7	119.9	119.3	124.5
$\angle(C^2C^3O)$	b	125.0	125.1	125.2	124.4
	c	124.7	125.4	125.1	124.4
$\angle(C^2C^3H^5)$	b	116.1	115.0	114.4	116.3
	c	116.0	114.8	114.5	116.5

[a] Results of MP2/6-31G** (b) and MP2/6-311++G** (c) calculations. Bond distances in Å, bond angles in deg. [b] The numbering of atoms as in Figure 1. [c] H^1 is the H-bonded proton in the ZZ structure.

TABLE 3: Selected Geometry Parameters of the Four Conformers of 3-Aminopropenthial[a]

		configuration/conformation			
parameter[b]	basis set	ZZ	EZ	EE	ZE
C^1N	b	1.338	1.355	1.363	1.367
	c	1.334	1.365	1.370	1.373
C^1C^2	b	1.378	1.359	1.359	1.364
	c	1.381	1.361	1.363	1.366
C^2C^3	b	1.415	1.435	1.428	1.428
	c	1.423	1.446	1.435	1.435
C^3S	b	1.657	1.640	1.635	1.636
	c	1.655	1.636	1.634	1.635
NH^1 [c]	b	1.017	1.005	1.006	1.005
	c	1.023	1.009	1.010	1.009
NH^2	b	1.003	1.002	1.004	1.004
	c	1.008	1.007	1.008	1.008
$\angle(H^1NC^1)$	b	117.8	119.8	118.2	119.0
	c	116.9	118.6	117.6	118.4
$\angle(NC^1C^2)$	b	125.4	126.0	125.9	127.8
	c	125.0	125.7	125.6	127.5
$\angle(C^1C^2C^3)$	b	126.0	122.4	120.6	124.8
	c	125.7	122.5	120.8	124.7
$\angle(C^2C^3S)$	b	129.3	128.7	126.2	125.7
	c	128.9	128.3	125.6	125.2
$\angle(C^2C^3H^5)$	b	114.2	113.8	114.8	116.5
	c	114.3	113.8	115.0	116.8

[a] Results of MP2/6-31G** (b) and MP2/6-311++G** (c) calculations. Bond distances in Å, bond angles in deg. [b] The numbering of atoms as in Figure 1. [c] H^1 is the H-bonded in the ZZ structure.

Among other interesting features of the MP2 data presented in Table 1, let us mention that for both 3-aminopropenal and 3-aminopropenthial the EE conformation corresponds to the energy lower than that of the EZ form. In the case of 3-aminopropenal, the pertinent energy difference amounts to about 1 kcal/mol and increases to about 2 kcal/mol for 3-aminopropenthial (basis c results). These differences between EE and EZ forms can be most likely interpreted in terms of what is called the nonbonded interactions between O(S) and the H^3 atom; as compared to oxygen, the bulky sulfur atom leads to the increase of the valence repulsion in the EZ form.

For the purpose of the discussion of the possible conjugation effect upon the intramolecular H-bond energy, we also list some of the optimized geometry data for all conformers of the two molecules. The corresponding results obtained in MP2/6-31G** and MP2/6-311++G** calculations are presented in Table 2 (3-aminopropenal) and 3 (3-aminopropenthial). The data for the ∠(CCX) angle support the present interpretation of the relative stabilities of the EZ and EE conformers on passing from 3-aminopropenal to 3-aminopropenthial; in the latter case, the nonbonded repulsion between H^3 and S atoms makes the $\angle(C^2C^3S)$ angle larger than the corresponding angle in 3-aminopropenal. One should note, however, that in general the structural differences between EZ and EE conformers are quite small (see Tables 2 and 3). The largest difference is seen for the C^2C^3 bond and amounts to about 0.01 Å.

In addition to the selected geometry data of Tables 2 and 3, it is also worthwhile to consider some other intramolecular distances. According to MP2/6-31G** calculations, the $O\cdots H^1$ and $S\cdots H^1$ distances in ZZ conformers are equal to 1.925 and 2.230 Å, respectively. The corresponding numbers obtained in MP2/6-311++G** calculations are equal to 1.962 and 2.202 Å, respectively. In the case of the ZE conformer, the MP2/6-31G** value of the distance between H^5 and H^1 (see Figure 1) in 3-aminopropenal is equal to 2.141 Å and remains the same for the MP2/6-311++G** level of approximation. In 3-aminopropenthial, the distance between H^5 and H^1 is a little shorter and equal to either 2.130 Å (basis b) or 2.127 Å (basis c). In both molecules, the ZZ → ZE transformation causes a small increase of the $\angle H^1NC^1$ angle.

To compare the estimated values of the intramolecular H-bond energies with the respective values for intermolecular bonds, we have also carried out calculations for dimers and trimers of the two investigated molecules. These results have been obtained only at the level of the MP2/6-31G** approximation. In both cases, the monomer structure has been assumed to correspond to the EE conformation with the transoid arrangement of the two monomers. At variance with calculations for different structures of the isolated monomers, the interaction energies in dimers and trimers may be significantly affected by the basis set superposition error.[33]

In the case of the isolated monomers, there seems to be no obvious way to account for the difference arising from differently positioned atomic basis sets used for separate conformers. Since all four structures occupy rather similar areas of space, the error introduced by using the same basis set for all of them should be small. However, in the case of multimers, there is a significant increase of the basis set size when passing from the isolated monomers to their bound dimers or trimers. Simultaneously, the optimized monomer structures in the dimer are different from those of the separate monomers. These two effects have been taken into account by defining the interaction energy as[34]

$$\Delta E_b = -E_{HB} = \Delta E + \Delta_{def} \tag{2}$$

where ΔE is the usual BSSE-corrected interaction energy

$$\Delta E = E_A{}_B(\{AB\}, G_{AB}) - E_A(\{A\}, G_A) - E_B(\{B\}, G_B) + \Delta_{BSSE} \tag{3}$$

$$\Delta_{BSSE} = E_A(\{A\}, G_A) - E_A(\{AB\}, G_{AB}) + E_B(\{B\}, G_B) - E_B(\{AB\}, G_{AB}) \tag{4}$$

and

$$\Delta_{def} = E_A(\{A\}, G_{AB}) - E_A(\{A\}, G_A) + E_B(\{B\}, G_{AB}) - E_B(\{B\}, G_B) \tag{5}$$

The symbol $E_P(\{Q\}, G_R)$ denotes the energy of P calculated with the basis set $\{Q\}$ at the geometry G_R of P in the system R. The same method of correcting supermolecular interaction energies has been used for dimers and trimers. In the present paper, the geometry optimization is carried out on the BSSE-corrected Born−Oppenheimer surface by using the new feature provided by the *Gaussian03* package.[30] For trimers, the reported H-bond energies correspond to the average of the energy of the two hydrogen bonds formed in these quasi-linear systems.

The results for H-bonded dimers and trimers of 3-aminopropenal and 3-aminopropenthial are presented in Table 4. These data, in addition to the H-bond energies, include also some selected geometry parameters for both the proton donor (HD) and proton acceptor (HA) molecules in dimers and for the central (donor−acceptor, DA) monomer in trimers. They follow from the optimization on the BSSE-corrected surface and will be used to discuss similarities and differences between intra- and intermolecular hydrogen bonds. Both 3-aminopropenal and 3-aminopropenthial form dimers and trimers of approximately the same shape, which is schematically presented in Figure 2.

Of some interest also is the distance between the H^1 atom of the proton donor and the proton acceptor atom. In the dimer of 3-aminopropenal, this distance is equal to 2.007 Å, whereas in the 3-aminopropenthial dimer, its value is 2.455 Å. Both these distances are considerably longer than the corresponding values in ZZ monomers. In the case of the trimer of 3-aminopropenal, the two $H^1\cdots O$ distances are almost the same and equal to 1.964 Å for the HA molecule bonded to the central DA system and 1.970 Å for the HD molecule on the other side of the trimer. These values are intermediate between those for ZZ monomers and EE dimers. The respective numbers for the trimer of 3-aminopropenthial are equal to 2.547 and 2.546 Å. A detailed discussion of all these features will be carried out in section IV.

III. Estimating the Intramolecular H-Bond Energy

To estimate the energy of the intramolecular hydrogen bond in ZZ, we assume the approximate additivity of intramolecular energies and define the total energy of the ZZ form, E^{ZZ}, as the difference of the electronic energy $E^{ZZ,f}$ of the fictitious ZZ system (ZZ, *f*) without the hydrogen bond and the energy E_{HB} supplied by this bond

$$E^{ZZ} \approx E^{ZZ,f} - E_{HB} \tag{6}$$

The E_{HB} energy is defined as a positive number and according to the first-order perturbation theory formulas[35,36] can be understood as arising from the balance between attractive (electrostatic) and repulsive (exchange) forces acting in the (S)O$\cdots$HN bridge. The model structure (ZZ, *f*) is used as a reference, and all its geometry parameters are the same as those in the real structure ZZ.

Suppose that ZZ undergoes rotation about the CC double bond which leads to the EZ structure. The total energy change follows from breaking the H-bond ($+E_{HB}$), and the geometry changes. The latter contribution is assumed to be expressible in terms of some "geometry change" increment $\Delta_g^{ZZ\rightarrow EZ}$ and permits to approximate the total energy of the EZ form by

$$E^{EZ} \approx E^{ZZ} + E_{HB} + \Delta_g^{ZZ\rightarrow EZ} = E^{ZZ,f} + \Delta_g^{ZZ\rightarrow EZ} \tag{7}$$

TABLE 4: Intermolecular H-bond Energies and Selected Bond Distances in All-Trans Dimers and Trimers of the EE forms of 3-Aminopropenal and 3-Aminopropenthial[a]

	3-aminopropenal			3-aminopropenthial		
	dimer		trimer	dimer		trimer
	HD[b]	HA	DA	HD	HA	DA
E_{HB}[c]	7.32		8.09	5.00		5.73
C^1N[d]	1.349	1.352	1.342	1.348	1.350	1.342
C^1C^2	1.359	1.357	1.363	1.365	1.364	1.369
C^2C^3	1.442	1.439	1.429	1.421	1.420	1.414
C^3X[e]	1.231	1.234	1.240	1.640	1.640	1.645

Actually, the $\Delta_g^{ZZ\rightarrow EZ}$ term simultaneously absorbs the energy contributions arising from the difference in nonbonded interactions between all atoms which are not involved directly in the hydrogen bond. Obviously, there is no formal method to separate the latter from the contribution from the plain geometry change. However, upon inspecting the data of Tables 2 and 3, one finds that the geometry changes upon passing from ZZ to either EZ or EE forms are similar. Hence, one can assume that the contribution due to nonbonded interactions resulting from the change ZZ → EE will be similar to that occurring in the ZZ → EZ process. This suggests the approximation in which eq 7 and

$$E^{EE} \approx E^{ZZ} + E_{HB} + \Delta_g^{ZZ\rightarrow EE} = E^{ZZ,f} + \Delta_g^{ZZ\rightarrow EE} \qquad (8)$$

are combined together to give the average value Δ_g^{av} of the contribution due to geometry changes

$$\Delta_g^{av} = \frac{1}{2}(E^{EZ} + E^{EE}) - E^{ZZ,f} \qquad (9)$$

With the aid of eq 6, this approximation leads to

$$E_{HB} + \Delta_g^{av} \approx \frac{1}{2}(E^{EZ} + E^{EE}) - E^{ZZ} \qquad (10)$$

where the two terms in the left-hand side (lhs) of this expression are formally inseparable. However, the averaging of the contribution due to the geometry change gives the possibility to evaluate eq 9 from the computed data for fictitious structures (EZ, *f*) and (EE, *f*).

The (EZ, *f*) structure is defined as the counterpart of the EZ conformer with all bond distances and planar bond angles the same as in the fully optimized ZZ conformer. Similarly, (EE, *f*) corresponds to the planar EE conformer with the geometry parameters frozen at the values appropriate for the fully optimized ZZ form. Under these assumptions

$$E^{EZ} = E^{EZ,f} + \Delta_g^{ZZ\rightarrow EZ} \approx E^{EZ,f} + \Delta_g^{av} \qquad (11)$$

$$E^{EE} = E^{EE,f} + \Delta_g^{ZZ\rightarrow EE} \approx E^{EE,f} + \Delta_g^{av} \qquad (12)$$

and the average correction for the geometry change can be approximated by

$$\Delta_g^{av} \approx \frac{1}{2}(E^{EZ} - E^{EZ,f}) + \frac{1}{2}(E^{EE} - E^{EE,f}) \qquad (13)$$

This gives the following estimate (approximation A) of the energy of the intramolecular hydrogen bond

$$E_{HB}^{A} \approx \frac{1}{2}(E^{EZ,f} + E^{EE,f}) - E^{ZZ} \qquad (14)$$

whose deficiencies will reflect the impossibility the exact partition of the total molecular energy into contributions of different bonds. All intermediate energy data and energies of (EZ, *f*) and (EE, *f*) are given in Table 5 and correspond to MP2/6-31G** and MP2/6-311++G** levels of approximation.

The difference of the ZPE contributions (E_{zpe}^{V} for the conformer V, V = ZZ, EZ, EE, and ZE) to relative energies of different conformers may also to some extent affect the estimate of the (electronic) hydrogen bond energy (eq 14). If these ZPE corrections to electronic energies in eq 10 are taken into account, they will lead to the ZPE-corrected expression for the estimate A of the intramolecular hydrogen bond energy

$$E_{HB,zpe}^{A} \approx E_{HB}^{A} + \Delta_{zpe}^{A} \qquad (15)$$

where

$$\Delta_{zpe}^{A} = \frac{1}{2}(E_{zpe}^{EZ} + E_{zpe}^{EE}) - E_{zpe}^{ZZ} \qquad (16)$$

All data necessary for the calculation of Δ_{zpe}^{A} are also given in Table 5.

The proposed method of estimating the energy of intramolecular hydrogen bonds in 3-aminopropenal and 3-aminopropenthial can be compared with the results of other approaches.[14−16,37,38] The simplest route leading to crude estimates of the intramolecular hydrogen bond energy can be based on the data for the highest energy conformer ZE.[12] This conformer can be obtained from its H-bonded counterpart by the s-cis → s-trans (ZZ → ZE) isomerization. Hence, a very crude estimate (B) of the intramolecular hydrogen bond energy is given by the difference of the E^{ZE} and E^{ZZ} energies (see Table 1)

$$E_{HB}^{B} = E^{ZE} - E^{ZZ} \qquad (17)$$

Its ZPE-corrected counterpart reads

$$E_{HB,zpe}^{B} = E_{HB}^{B} + \Delta_{zpe}^{B} \qquad (18)$$

where

$$\Delta_{zpe}^{B} = E_{zpe}^{ZE} - E_{zpe}^{ZZ} \qquad (19)$$

and can be calculated from the data of Table 5. As compared to the previous estimates based on eqs 14 and 15, the estimate B completely neglects all contributions due to the change of molecular geometries which accompanies the transition from ZZ to ZE.

Another method for the estimation of the intramolecular hydrogen bond energy has been recently used by Alkorta et al.[14] and is based on the consideration of isodesmic reactions which are assumed to produce the quasi-cyclic form without the hydrogen bond. In the present case, the corresponding isodesmic reaction is shown in Scheme 1, and structure **1** vaguely resembles the fictitious (ZZ, *f*) system introduced in our estimation method A. However, the energy of **1**

$$E(\mathbf{1}) = E(\mathbf{3}) + E(\mathbf{4}) - E(\mathbf{2}) \approx E^{ZZ,f} \qquad (20)$$

and the estimated (C) energy of the intramolecular hydrogen bond

$$E_{HB}^{C} = E(\mathbf{1}) - E^{ZZ} \qquad (21)$$

completely neglects all corrections for the possible change of geometries. All energies in the right-hand side (rhs) of eq 20 are assumed to correspond to fully optimized geometries of the pertinent molecules. Although the isodesmic approach of Alkorta

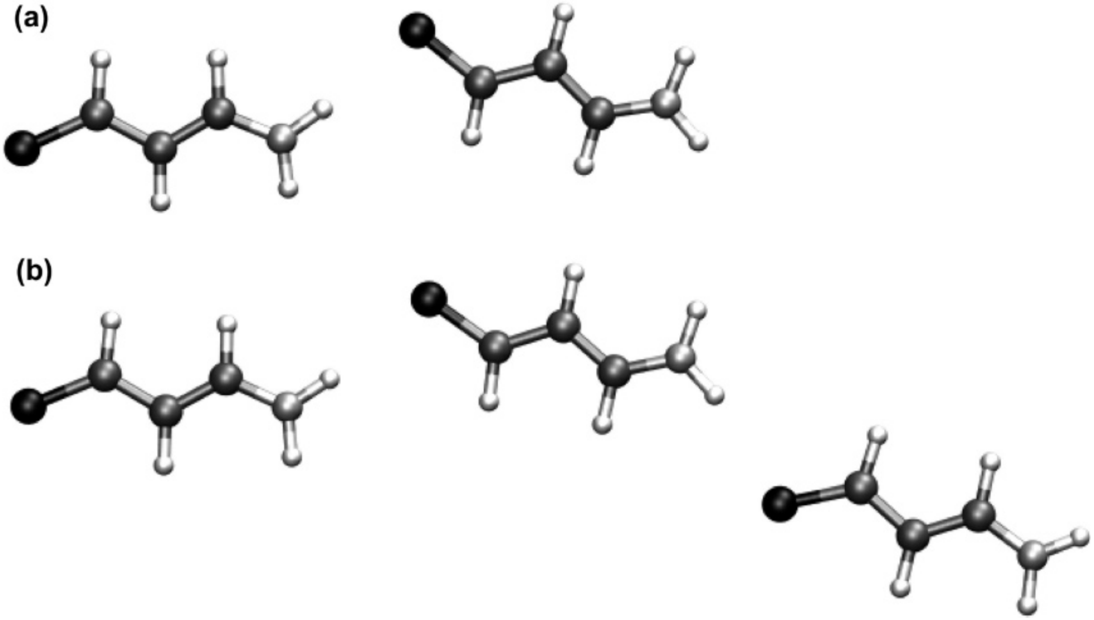


Figure 2. Schematic drawing of the optimized structures of the dimer (a) and trimer (b) for 3-aminopropenal and 3-aminopropenthial. For both molecules, their multimers have essentially the same shape.

TABLE 5: Intermediate Energy Data (in kcal/mol) Used to Estimate the Intramolecular Hydrogen Bond Energy in 3-Aminopropenal and 3-Aminopropenthial[a]

	basis set	3-aminopropenal			3-aminopropenthial		
		EZ	EE	ZE	EZ	EE	ZE
$E^{V,f}$ [b]	b	6.43	6.26	10.42	7.08	6.29	8.22
	c	5.91	4.65	8.37	7.58	6.34	7.88
$\Delta_g^{ZZ\to V}$ [c]	b	−1.32	−1.45	−2.51	−1.30	−1.99	−1.70
	c	−1.14	−1.28	−1.87	−1.51	−2.25	−1.86
E_{zpe}^{V} [d]	b	50.87	50.76	50.71	49.49	49.50	49.48
	c	49.94	49.93	49.91	48.64	48.68	48.67

[a] Calculations at MP2/6-31G** (a) and MP2/6-311++G** (c) levels of approximation. [b] The energy (relative to ZZ) of fictitious structures, V = EZ, EE, and ZE, with bond distances and planar bond angles from the ZZ form. [c] See eqs 11 and 12. The correction term $\Delta_g^{ZZ\to ZE}$ corresponds to the energy difference between (ZE, *f*) and ZE structures. [d] The MP2/6-311++G** ZPE energies for the ZZ form of 3-aminopropenal and 3-aminopropenthial are equal to 50.26 kcal/mol and 48.99 kcal/mol, respectively. For the 6-31G** basis set, the corresponding entries are 51.04 kcal/mol and 49.84 kcal/mol, respectively.

et al.[14] looks quite appealing, its results may heavily depend on the geometry change contributions.

The ZPE-corrected result, which corresponds to eq 21, will be

$$E_{HB,zpe}^{C} = E_{HB}^{C} + \Delta_{zpe}^{C} \tag{22}$$

where

$$\Delta_{zpe}^{C} = E(\mathbf{1})_{zpe} - E_{zpe}^{ZZ} = E(\mathbf{3})_{zpe} + E(\mathbf{4})_{zpe} - E(\mathbf{2})_{zpe} - E_{zpe}^{ZZ} \tag{23}$$

and the relevant energy data are collected in Table 6. Similarly to calculations carried out for estimates A and B, the energy data in Table 6 correspond to both MP2/6-31G** and MP2/6-311++G** levels of approximation.

IV. Discussion and Conclusions

The final results for the estimated values of the intramolecular hydrogen bond energy in ZZ conformers of the investigated two molecules are presented in Table 7. Both the pure electronic and ZPE-corrected energies are given. The latter are systematically lower than the pure electronic values. Including the ZPE correction does not affect relations between different estimates.

Let us begin by discussing the intramolecular hydrogen bond energies obtained according to the scheme B. This is the easiest and supposedly the crudest[14,37,38] estimate of the intramolecular hydrogen bond energy which follows from eqs 17 and 18. The magnitude of the estimate B is of the order characteristic for moderately strong intermolecular hydrogen bonds and is close to the values obtained for dimers and trimers (see Table 4). According to the estimate B, the intramolecular hydrogen bond to sulfur is a little weaker than that to oxygen. The difference in the intramolecular hydrogen bond energy depends on the basis set and amounts to about 1.5 kcal/mol for basis b and about 0.5 kcal/mol for basis c.

One should note that the estimation method B does not take into account that simultaneously with the breaking the hydrogen bond the transformation ZZ → ZE dramatically changes the pattern of intramolecular interactions. The repulsion between H^1 and H^5, which would result from the intramolecular rotation of the −CH(X) group at frozen ZZ geometry, is to some extent balanced by changes in bond distances and bond angles (see Tables 2 and 3). According to the method used to define the estimation scheme A, the energy difference between ZE and ZZ structures can be represented by

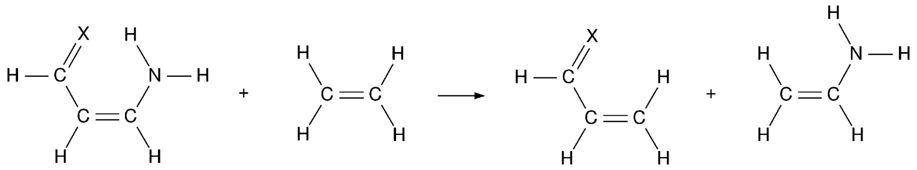
$$E^{ZE} - E^{ZZ} \approx E^{ZE,f} + \Delta_g^{ZZ\to ZE} - E^{ZZ} = E^{ZE,f} - E^{ZZ,f} + E_{HB} + \Delta_g^{ZZ\to ZE} \tag{24}$$

where the correction terms $\Delta_g^{ZZ\to ZE}$ for both molecules are shown in Table 5. However, as compared to $E^{V,f}$ for V = EZ and EE, the $E^{ZE,f}$ also involves the contribution due to repulsion between H^1 and H^5

$$E^{ZE,f} \approx E^{ZE,f\,\prime} + \Delta_{rep}^{ZE} \tag{25}$$

where (ZE, *f*′) denotes a fictitious structure which has all bond distances and planar bond angles equal to those in ZZ and is free of the H^1 and H^5 repulsion. Obviously, this structure neither exists nor can be calculated. Nonetheless, its energy should be

SCHEME 1



1 2 3 4

TABLE 6: Energy Data (in au) for Structures 1−4 Used to Estimate the Intramolecular Hydrogen Bond Energy in 3-Aminopropenal and 3-Aminopropenthial According to the Isodesmic Reaction Scheme[a]

	basis set	structure 1	2	3	4
		$X = O^b$			
$E^{\mathrm{el}\ c}$	b	−246.585076	−78.327231	−191.358533	−133.532925
	c	−246.672998	−78.346528	−191.423796	−133.579403
ZPE	b	0.081338	0.052413	0.062720	0.069568
	c	0.080101	0.050805	0.061075	0.069255
		$X = S^b$			
$E^{\mathrm{el}\ c}$	b	−569.181907	−78.327231	−513.953028	−133.532925
	v	−569.250827	−78.346528	−513.998893	−133.579403
ZPE	b	0.079561	0.052413	0.060625	0.069569
	c	0.078068	0.050805	0.059266	0.0695255

[a] Calculations at MP2/6-31G** (b) and MP2/6-311++G** (c) levels of approximation. [b] See Scheme 1. [c] The total electronic energy calculated at the level of the MP2 approximation with full geometry optimization. See text.

TABLE 7: Estimates of the Intramolecular Hydrogen Bond Energy (in kcal/mol) in 3-Aminopropenal and 3-Aminopropenthial from MP2/6-31G (b) and MP2/6-311++G** (c) Energy Data**

		estimate[a]					
molecule	basis set	A	A_{zpe}	B	B_{zpe}	C	C_{zpe}
3-aminopropenal (ZZ)	b	6.35	6.13	7.91	7.58	13.08	12.17
	c	5.28	4.96	6.50	6.15	10.24	9.88
3-aminopropenthial (ZZ)	b	6.69	6.34	6.52	6.16	14.55	13.37
	c	6.96	6.63	6.02	5.70	11.90	11.68

[a] See eqs 14 and 15 for A, eqs 17 and 18 for B, and eqs 21 and 22 for C.

close to that of the (ZZ, *f*) structure, and thus

$$E_{\mathrm{HB}} \approx E^{\mathrm{ZE}} - E^{\mathrm{ZZ}} - \Delta_{\mathrm{rep}}^{\mathrm{ZE}} - \Delta_{\mathrm{g}}^{\mathrm{ZZ}\rightarrow\mathrm{ZE}} \tag{26}$$

This expression can be used to guess the possible violation of the estimation method B and the expected direction of changes in the estimate $E_{\mathrm{HB}}^{\mathrm{B}}$.

First, let us consider the $H^1 \cdots H^5$ distances in (ZE, *f*) forms of the two molecules. In the MP2/6-311++G** set, they are equal to 1.840 and 1.968 Å, respectively, as compared to the corresponding distances of 2.141 and 2.127 Å in fully optimized ZE conformers. The data obtained in the MP2/6-31G** approximation for the (ZE, *f*) forms of 3-aminopropenal and 3-aminopropenthial are equal to 1.803 and 1.985 Å, respectively. In fully optimized MP2/6-31G** ZE structures, the respective numbers are 2.141 and 2.130 Å. For both basis sets, this comparison shows that the repulsion term for 3-aminopropenal should be much larger than in 3-aminopropenthial. Hence, the B estimate of the hydrogen bond energy in the latter molecule should be more reliable than in 3-aminopropenal. The repulsion contribution $\Delta_{\mathrm{rep}}^{\mathrm{ZE}}$ is defined as positive. Therefore, at least for 3-aminopropenal, the B estimate of the intramolecular hydrogen bond energy in the ZZ conformer of 3-aminopropenal is concluded to overestimate its expected value. This is supported by the results of the estimation method A.

Indeed, method A, which is based on quite realistic assumptions concerning the partition of changes in the total molecular energy, gives the value of $E_{\mathrm{HB}}^{\mathrm{A}}$ (6.96 kcal/mol for basis c) in 3-aminopropenthial by less than 1 kcal/mol higher than the $E_{\mathrm{HB}}^{\mathrm{B}}$ result (6.02 kcal/mol for basis c), whereas the MP2/6-311++G** value of $E_{\mathrm{HB}}^{\mathrm{A}}$ in 3-aminopropenal (5.28 kcal/mol) is about 1.2 kcal/mol lower than the corresponding value of $E_{\mathrm{HB}}^{\mathrm{B}}$. Similar relations follow from the data calculated with basis set b (see Table 7). This makes the results of both approaches A and B mutually consistent and indicates that the first of them leads to reasonable estimates of what can be called the intramolecular hydrogen bond energy.

Method A is obviously limited to molecules of a particular class which supply more than just two conformers, and we do not pretend to propose it as a general scheme for the determination of the intramolecular hydrogen bond energy in arbitrary systems. The focus is rather on the distinction between intramolecular and intermolecular hydrogen bonds. The estimate A reflects the importance of the contribution due to geometry changes which have usually been discussed in terms of the "resonance enhancement" as measured for instance by the equalization of interatomic distances in the unsaturated skeleton.[9,38,39] These equalization parameters can be used to discuss the relative strength of intramolecular hydrogen bonds in different molecules.[38] However, at variance with the method proposed in this paper, they do not seem to provide numerical data for the corresponding energy contributions.

Surprisingly enough, method C adopted by Alkorta et al.[14] leads to H-bond energies almost twice as large as those obtained in the other two approximations. Although this method is based on reasonable general assumptions, it may not be able to handle relatively large changes in geometry and, in particular, in bond distances, which occur in the case of relatively strong hydrogen bonds. Alkorta et al.[14] applied their isodesmic reaction schemes to study relatively weak interactions which are not supposed to result in large contributions due to geometry changes. Their $E_{\mathrm{HB}}^{\mathrm{C}}$ values seem to show the right magnitude and direction of changes in the intramolecular hydrogen bond energies. However, depending on the system, the isodesmic energy values can be either larger or smaller than those obtained from the simplest method B.[14]

The present results can also be compared with the estimate of the intramolecular hydrogen bond energy in 3-aminopropenal obtained by Buemi and Zuccarello[15] from the study of barriers for the rotation of the end groups. From the rotation barriers for the $-NH_2$ groups, they obtained the H-bond energy in the range 11.6−18.2 kcal/mol. The rotation of the −CHO group leads to the H-bond energy of 10.2 kcal/mol. These results are considerably different from the present estimates A and B and seem to be affected by relatively large changes in bond distances which result from the rotation of the end groups. This factor is not accounted for in the method used by Buemi and Zuccarello.[15]

The estimation method used by Nowroozi et al.[16] is very similar to that of Buemi and Zuccarello[15] and includes the energy data for structures with a rotated $-NH_2$ group. The DFT calculations by Nowroozi et al. estimate the energy of the intramolecular hydrogen bond in ZZ 3-aminopropenal as equal to 8.35 kcal/mol. This result is based on the suggestion of Schuster et al.[7] that the reference system should have the least distorted geometry with respect to that of the H-bonded species. In the case of the present estimation method A, this factor is taken into account by introducing the correction for the change of geometry. By noting that the DFT results for E_{HB} are higher than those obtained in MP2 calculations,[15] one can conclude that the estimate produced by Nowroozi et al. is fully compatible with our estimate E_{HB}^{A} (Table 7).

With all reservation concerning to the possibility of defining and extracting the energy of intramolecular hydrogen bonds, we conclude that the likely H-bond contributions in ZZ structures of the two molecules investigated in this paper are of the order of 5−7 kcal/mol. Upon comparison of these data with intermolecular H-bond energies in dimers and trimers (see Table 4), one finds that in terms of their energies both inter- and intramolecular hydrogen bonds are not that much different. This already indicates that associating the benzene-like structure of ZZ conformers with particular “resonance” effects is likely to be rooted in the similarity of the corresponding structural formulas.[8−10]

The major difference between intramolecular and intermolecular hydrogen bonds is due to proximity of the proton donor and proton acceptor groups. In the ZZ chelate structure, the rigidity of the molecular skeleton makes the two groups approaching each other much closer than in the case of intermolecular hydrogen bonds. The condition of the total energy minimum leads to a certain balance between the energy gain due to proton donor−proton acceptor interaction and the energy loss because of the distortion of in-plane angles. In the case of the chelate structure, the shorter distance between the end groups increases their mutual interaction and enhances the polarization effects. In consequence, this leads to the change of bond distances in the molecular skeleton. Obviously, all these contributions are closely related to the sum of E_{RES} and E_{BP} in eq 1. However, a further separation of these two terms is rather unlikely. The present energy data give support to similar recent claims by Alkorta et al.[11,12,14]

One of the features frequently discussed in the context of intramolecular hydrogen bonds in conjugated systems is the so-called bond equalization.[8,40] Indeed, if one compares the values of the C^1N and C^2C^3 bond distances in the ZZ form with the corresponding data for other forms of the two molecules (see Tables 2 and 3), there is a visible shortening of these bonds in the H-bonded structure. Similarly, the C^1C^2 and C^3O distances become longer. If viewed as the result of the presence of the intramolecular hydrogen bond in the ZZ structure, this observation can be interpreted as some gain of the aromatic character in the chelate form.[8−10] However, despite significantly longer H-bond distances, the same pattern of changes is seen in dimers and trimers (Table 4), and for these systems, one would rather avoid addressing the possible resonance-assisted contributions to the H-bond energy. The change of the conjugation pattern is simply induced by the donor−acceptor interaction. In particular, the bond distance equalization in the central (DA) molecule of trimers approaches that in ZZ forms. This shows that the bond equalization results from the interaction between proton donor and proton acceptor groups. Their proximity in the chelate structure has the same effect as the proximity of the corresponding groups in the trimer.[12]

Upon comparison of intra- and intermolecular hydrogen bonds, one needs to take into account that in the latter case the H-bond distances are much longer (see section II) than in ZZ forms of the respective molecules. The nonbonded repulsion between the hydrogen atom of the $-CXH$ group and the H^2 atom of the other molecule does not permit as close an approach of X and H^1 as in the case of the intramolecular hydrogen bond. The dimers and trimers show a much higher degree of flexibility that the ZZ monomers. The shorter intramolecular H-bonds result from the compensation between the energy gain due to a closer approach between X and H^1 and the loss of energy associated with the deformation of planar angles in the ZZ-shaped $X{=}C{-}C{=}C{-}N$ skeleton. The resulting net force pushes X and H^1 toward each other. This mechanism is completely irrelevant in the case of EE dimers and trimers. Yet, the proximity of proton donor and proton acceptor groups brings about the bond equalization. In general, as far as the H-bonding interaction is concerned, there does not seem to be too much difference between inter- and intramolecular hydrogen bonds.

There is one more feature of the two trimers which supports certain disbelief in the concept of the “resonance assistance”. One notes that the bond equalization in trimers approaches that in ZZ monomers. Since the increase of the bond equalization in the conjugated chain is approximately parallel to the increase of the strength of the intramolecular hydrogen bond,[42] one concludes that both intra- and intermolecular H-bonds in the studied systems should be of similar energy. This is supported by the comparison of our estimate A with the H-bond energies reported in Table 4. A simple model based on the donor−acceptor interactions can simultaneously elucidate the energetics of inter- and intramolecular hydrogen bonds.

The intramolecular hydrogen bond leads to the enhancement of the push−pull effect through the changes in the σ framework of the system. This, in turn, is reflected by some changes in the conjugation pattern in the monomer. There is essentially no redistribution of π electrons between monomers in the trimer, and there is no flow of π electrons through the hydrogen bridge in the ZZ conformer. This is also confirmed by calculations of currents,[41] which show no trace of paramagnetic contributions associated with the hydrogen bridge. Thus, the present results supplement the recent debate[12] concerning the “resonance-assisted” interpretation of the nature of intramolecular hydrogen bonds in conjugated systems. The interpretation proposed by Alkorta et al.[12] is strongly favored by our data and indicates that there is nothing particular concerning these bonds. The resulting chelate structure follows from the condition of the total energy minimum which is achieved through the balance of all possible energy contributions.

To conclude this paper, let us remark on the idea of the intramolecular hydrogen bond energy. Usually, the energy associated with the interaction through the $Y{\cdots}H{-}X$ bridge follows from considerations of intermolecular complexes. Then, the separated monomers are the natural reference, and the difference between the sum of their energies and the energy of the complex at their optimized geometry defines the energy of the intermolecular hydrogen bond. No such natural reference is available in the case of intramolecular hydrogen bonds, and there is no rigorous quantum mechanical formalism to define their energies. Hence, the energy of the intramolecular hydrogen bond becomes a rather qualitative notion, and its numerical value can be defined only with respect to a certain model of the total molecular energy partition.

Any partition scheme for intramolecular energies applied to the determination of the energy of relatively weak intramolecular interactions means stretching the concept of the interaction energy beyond the limits of its formal validity. These partition schemes may work reasonably well if used for the usual bonds with energies of the order of 100 kcal/mol. The errors of the partition schemes are then of the order of a few kilocalories per mole and are insignificant. If the estimated intramolecular bond energy is of the order expected for moderately strong hydrogen bonds, the inaccuracy of the adopted partition scheme strongly affects the final result. The relatively large values obtained from certain estimation schemes may easily lead to speculations concerning the origin (or nature) of different contributions arising from the given partition model.

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