Acetic Acid Molecular Aggregates: Energy and Softness of Hydrogen Bonding

Gloria I. Cárdenas-Jirón*,† and Fernando Zuloaga‡

Departamento de Química de los Materiales, Facultad de Química y Biología, Universidad de Santiago de Chile, Casilla 40, Correo 33, Santiago, Chile, and Departamento de Química Física, Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 306, Correo 22, Santiago, Chile

Received: April 6, 1999; In Final Form: June 30, 1999

We present a theoretical study of global and local energetic and electronic properties to rationalize the formation process of molecular aggregates of acetic acid. Total energy, electronic chemical potential (μ), hardness (η), and softness (S) are determined as a function of the size of the aggregate. We show that μ, η, and S are observable properties to indicate structural changes occurring along the aggregation process. From the local point of view, the hydrogen bonding is characterized by making use of the energy and softness ($S_{\mathrm{O\cdots H}}$) associated with that interaction. In relation to the determination of $S_{\mathrm{O\cdots H}}$ we propose an analytic form to obtain the hydrogen bonding *fukui* function. The excellent results obtained indicate that our model is useful for characterizing local intermolecular interactions and provides a starting point to determine indexes of local reactivity in these molecular systems. A global and local Principle of Minimum Softness is shown to be occurring when the aggregate is growing.

1. Introduction

The manner in which molecules nucleate and crystallize remains a very important problem in solid-state organic chemistry. Crystal engineering or the ability to predict the structures of crystalline materials can have important implications for the development of new materials. Theoretical study of various sized aggregates of molecules allow us to better understand the kinds and magnitudes of the intermolecular interactions that bind the growing aggregates and crystals.[1]

In this paper, we are interested in the theoretical study of acetic acid aggregates from the global and local hydrogen bonding point of views, and on the energetics and electronic properties. For this, we make use of chemical concepts already established by density functional theory (DFT) such as electronic chemical potential, molecular hardness and softness, and their local counterparts. From the global point of view, we are going to rationalize the formation of acetic acid aggregates, whereas from the local point of view we will characterize the hydrogen bonding intermolecular interaction for each of the aggregates.

DFT has provided solid and quantitative foundations to electronegativity and hardness in molecules.[2−5] In particular, electronegativity measures the escaping tendency of electrons in atoms and molecules and as such, it has been used extensively to study the charge-transfer phenomena during molecule formation until electronegativity equalization among atoms forming the molecule is satisfied. This principle of electronegativity equalization proposed intuitively some time ago[5,6] has been formally formulated through DFT.[7] Thus, today we have rigorous quantum mechanical methods to calculate it for many-electron systems in molecules.

Although electronegativity has been a highly valuable guide, it does not provide us with enough information of site reactivity in molecules, as required in acid−base reactions. However, its rate of change against charge flow (normally called hardness) is also a molecular index with local information about site reactivity. To the empirical rule "hard likes hard and soft likes soft" proposed by Pearson[8] and used extensively,[9] quantitative information has evolved for it.[10] Moreover, continuous work by Parr et al.[11] has laid down the basis for a local hardness definition,[12−14] the softness concepts,[15] and a theoretical formulation for the HSAB principle.[16] Thus, we plan to use all these concepts together with the Principle of Maximum Hardness[17,18] explained beautifully by Pearson[19] and verified to be valid for several cases.[20,21−25]

Various analytical relations have been proposed in the literature for the determination of local electronic properties.[5,26,27] Ghosh[5] has derived analytical relations connecting the energy with the electronic chemical potential and hardness to study the chemical binding in a molecular system. Since molecular softness is approximately equal to the arithmetic mean of atomic softnesses,[28] he proposed for simplicity that the bond hardness η_{AB} should be given also by a similar expression since molecular hardness is the inverse of softness. This modeling is not unique and other alternatives (e.g., explicit functions of the internuclear distance) are known.[29] However the description of η_{AB} only in terms of the atomic hardness and no adjustable parameter is the simplest.[5] On the other hand, Komorowski et al.[27,30] derived analytical relations for electronegativity and hardness of groups making use of the *fukui* function. Using these local reactivity indexes, these authors found a correlation between the charge-transfer affinity (polar binding energy) and the field Hammett constant. In relation to molecular systems with hydrogen bonding, Arulmozhiraja and Kolandaivel have published results concerning the study of profiles of electronic chemical potential and hardness for complexes such as $\mathrm{HF\cdots HCN}$, $\mathrm{HF\cdots HCl}$, and $\mathrm{CH_3OH\cdots H_2O}$.[31]

In this paper, we will make use at all these DFT theoretical frameworks to study molecular aggregates. To our knowledge, this is the first time that chemical potential, hardness, and softness concepts are used for the study of the formation of

---

* Author to whom correspondence should be addressed: E-mail: gcardena@lauca.usach.cl.

† Universidad de Santiago de Chile.

‡ Pontificia Universidad Católica de Chile.

10.1021/jp991152n CCC: $18.00

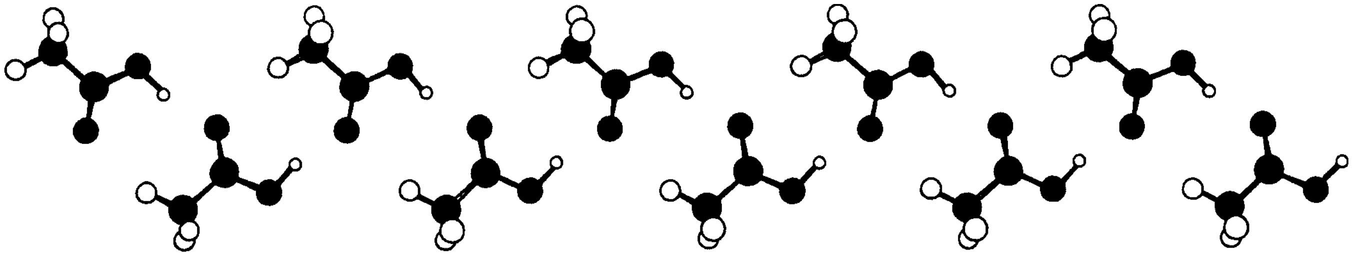

Figure 1. Structural view of an aggregate of 10 acetic acid molecules.

organic molecular aggregates. This paper describes the energetics of the aggregation process of acetic acid and the behavior of their electronic properties such as electronic chemical potential, molecular hardness, and molecular softness associated with the aggregation.

In Section 2 we see the theoretical aspects involved in this work, and Section 3 describes our results focusing on the properties of interest from a global and local point of view. Finally, Section 4 contains our conclusions.

2. Theoretical Aspects

Aggregates of different size starting from one acetic acid unit (monomer) up to 10 acetic acid units (decamer), as shown in Figure 1, were studied. The atom position coordinates used for the acetic acid monomer were taken from the Crystallographic Structural Database of Cambridge.[32] Ab initio restricted Hartree−Fock SCF/MO calculations using the D95* basis set have been carried out to study all of the acetic acid aggregates. These calculations were performed using the *GAUSSIAN94* program.[33]

The electronic chemical potential (μ) and the hardness (η) for a finite molecular system are related to the total energy by

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{v(r)},\ \eta = \frac{1}{2}\left(\frac{\partial \mu}{\partial N}\right)_{v(r)} \tag{1}$$

In a finite difference approximation the above equations are written as $\mu = 1/2(I + A)$ and $\eta = 1/2(I - A)$ where I is the ionization potential and A is the electron affinity. Softness $S = (\partial N/\partial \mu)_{v(r)}$, the reciprocal of hardness, has been also used as descriptor of chemical reactivity. So, the most reactive species shows the highest softness value.

In this article, hardnesses and electronic chemical potentials for all aggregates are calculated as a difference of two SCF calculations for the total energy for I and A.

The softness of a molecule can be decomposed into contributions from the component fragments:

$$S = \sum_{x}^{n_f} S_x \tag{2}$$

with n_f as the number of fragments of the molecule and S_x being the softness associated to a local region like atoms, bonds, and hydrogen bonding:

$$S = \sum_{\alpha}^{\text{atoms}} \int [S(r)\,\mathrm{d}r]_\alpha + \sum_{\beta}^{\text{bonds}} \int [S(r)\,\mathrm{d}r]_\beta + \sum_{\gamma}^{\text{O}\cdots\text{H's}} \int [S(r)\,\mathrm{d}r]_\gamma \tag{3}$$

where $S(r)=f(r)S$ is a regional softness obtained from the *fukui* function $f(r)$ at the atoms, bonds, and hydrogen bonding regions in the aggregate. Since in this paper we are interested in characterizing the last hydrogen bond formed in the aggregate, a more specific notation for the $S_{\text{O}\cdots\text{H}}$ region should be introduced:

$$\sum_{\gamma}^{\text{O}\cdots\text{H's}} \int [S(r)\,\mathrm{d}r]_\gamma = \sum_{\gamma}^{(\text{O}\cdots\text{H})-1} \int [S(r)\,\mathrm{d}r]_\gamma + \{\int [S(r)\,\mathrm{d}r]_{\text{H}\epsilon(\text{O}\cdots\text{H})} + \int [S(r)\,\mathrm{d}r]_{\text{O}\epsilon(\text{O}\cdots\text{H})} + \int [S(r)\,\mathrm{d}r]_{(\text{O}\cdots\text{H})}\} \tag{4}$$

Note that the last three terms to the right side of eq 4 correspond to the softness associated with the hydrogen and oxygen atoms participating in the last hydrogen bond of the aggregate and the softness of the intermolecular hydrogen bond. In this paper, we propose that $S_{\text{O}\cdots\text{H}}$ of the last hydrogen bond formation may be obtained from these last three terms of eq 4:

$$S_{\text{O}\cdots\text{H}} = S\int [f(r)\,\mathrm{d}r]_{\text{H}\epsilon(\text{O}\cdots\text{H})} + S\int [f(r)\,\mathrm{d}r]_{\text{O}\epsilon(\text{O}\cdots\text{H})} + S\int [f(r)\,\mathrm{d}r]_{(\text{O}\cdots\text{H})} = f_\text{H}S + f_\text{O}S + f_{\text{O}\cdots\text{H}}S \tag{5}$$

Our second proposal in this paper is that the *fukui* function in eq 5 be determined from a difference of the values of the charge density ρ in the last formed aggregate with hydrogen bond and the previous aggregate for the oxygen atom, and with respect to the monomer for the hydrogen atom of the $O\cdots H$ bonding. This leads to a new formulation for eq 5:

$$S_{\text{O}\cdots\text{H}} = (\rho_\text{H}^n - \rho_\text{H}^1)S + (\rho_\text{O}^n - \rho_\text{O}^{n-1})S + (\rho_{\text{O}\cdots\text{H}}^n)S \tag{6}$$

where the superscripts refer to the number n of fragments of the aggregate, and ρ_atom is the electron density at that atomic site suffering hydrogen bonding in the corresponding aggregate. In particular, we used the Mulliken electronic population analysis to obtain the different values of ρ. Since the term $\rho^n{}_{\text{O}\cdots\text{H}}$ in eq 6 is small in comparison with corresponding ones for atoms we will approximate the softness for the hydrogen bonding region by

$$S_{\text{O}\cdots\text{H}} \approx (\rho_\text{H}^n - \rho_\text{H}^1)S + (\rho_\text{O}^n - \rho_\text{O}^{n-1})S \tag{7}$$

which is our final working formula for $S_{\text{O}\cdots\text{H}}$. Thus, f_O is determined from the difference between the oxygen electronic population when forming hydrogen bonding (aggregate with n fragments) and that one when it does not (aggregate with $n - 1$ fragments). In the case of hydrogen atom, f_H is obtained as a difference between ρ_H when participating in the hydrogen bonding (n fragments) and ρ_H when it does not (monomer). The chemical picture that best illustrates this procedure is to consider the monomer at infinite distance of the $n - 1$ aggregate.

It is important to mention that local hardness suffers from the drawback of ambiguity in its definition.[12,26] Some more conditions are needed to resolve this problem. Local softness, however, does not face this trouble. Among the different indexes

TABLE 1: Values of Energy (*E*), Electronic Chemical Potential (μ), and Hardness (η) of Aggregates of Acetic Acid Obtained at the Calculation Level HF/D95* [a]

	E	μ	η	*S*
2	−455.720915	−0.10264	0.21290	4.69704
3	−683.589021	−0.12164	0.22443	4.45573
4	−911.457274	−0.12084	0.22048	4.53556
5	−1139.325824	−0.12512	0.22307	4.48290
6	−1367.194247	−0.12428	0.22124	4.51998
7	−1595.062880	−0.12413	0.22042	4.53679
8	−1822.931348	−0.10453	0.20037	4.99077
9	−2050.800007	−0.10469	0.20018	4.99550
10	−2278.668493	−0.10458	0.19981	5.00475

[a] We have also included the resulting values of global softness (*S*). *E*, μ, and η are given in au and *S* in au^{-1}.

of reactivity defined by DFT, the local softness seems to contain maximum information. To obtain insights into the chemical reactivity, chemisorption, and catalysis, local softness is expected to be the most important local index.[12,26]

In the next section we present the results obtained for the global and local electronic properties and discuss their differences for aggregates of different size. We will see how these properties allow us to rationalize the aggregation process in acetic acid.

3. Results and Discussion

3.1. Global Properties (*E*, μ, η). Calculated values of total energy, electronic chemical potential and molecular hardness of aggregates for different numbers of fragments of acetic acid are shown in Table 1 and depicted in Figure 2. Figure 2a shows the total energy variation against fragment number and Figure 2b displays the results determined for μ and η. In Figure 2a we see that, as expected, the total energy of the aggregate decreases as this continues to grow. It is interesting to note that this behavior is linear, indicating that each additional molecule of acetic acid has the same general effect on the electronic energy. The same behavior linear is observed for the different components of the total energy like the nuclei−nuclei repulsion energy, electron−electron repulsion energy and the nuclei−electron atraction energy. On the other hand, Figure 2 shows that *E* is not a mirror image of η which may be due to the fact that the asymmetric variation of the growing, essential condition for *E* and η be opposite,[20,34] become numerically large and this leads to important energy changes.

In Figure 2b we present the results for μ and η as a function of the number of fragments in the aggregate. The calculated values are represented as points appearing in the figure and the lines are spline interpolations which obviously have not a physical meaning. Here, we see that the ΔSCF calculations predict an oscillatory behavior for μ and η as the aggregate becomes larger. It is interesting to note that similar results have been published in the framework of lithium clusters[35] where chemical hardness results obtained as ($I - A$) for clusters containing a number of atoms in the range of 2−67 show that for a specific number of lithium atoms hardness deviates from an otherwise smooth curve showing distinct peaks. These peaks or oscillations would be associated with the electronic shell structure. In our case, the results of μ and η suggest that the aggregation in acetic acid is being marked by some electronic or structural effect producing an oscillatory behavior on these electronic properties. Since the theoretical calculations used in obtaining μ and η were performed by using the crystallographic geometry and the aggregation process of acetic acid is periodic, it is natural to obtain these fluctuations.

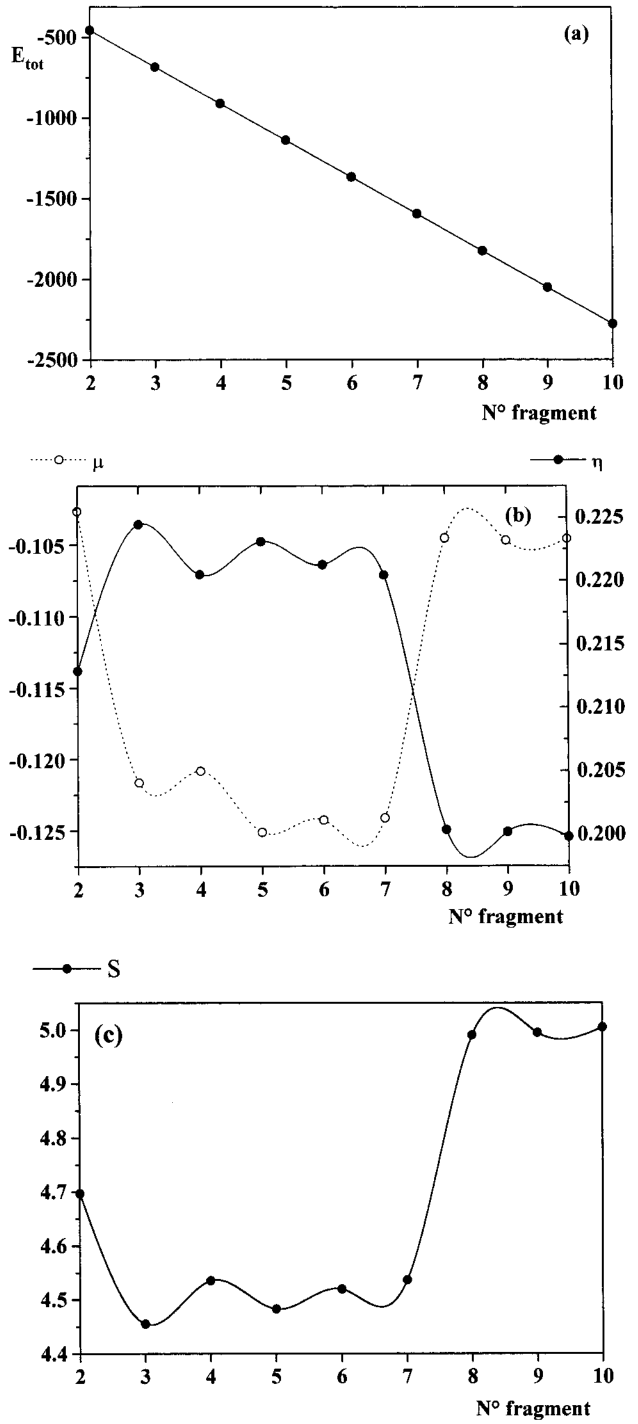

Figure 2. (a) Total energy (*E*) for each of the aggregates; (b) electronic chemical potential (μ) (···) and hardness (η) (—) as a function of the number of fragments of the aggregate; (c) Softness (*S*) for each of the aggregates. Values of *E*, μ, and η are given in *au*, *S* is given in *au*$^{-1}$.

On the other hand, from Figure 2b we find that μ and η show a completely opposite behavior, a maximum in μ is accompanied with a minimum in η and vice versa. This result may be understood from symmetry considerations.[20,34] An asymmetric variation (e.g., aggregation process) about a symmetric nuclear configuration (e.g., acetic acid unit) predicts that μ and η be extreme. Although the acetic acid aggregation process is periodic the external potential is changing during the growing and the symmetry is broken during this process. This leads to extremum for μ and η. On the other hand, although the condition that *E* and η be opposite is necessary to say a Principle of Maximum

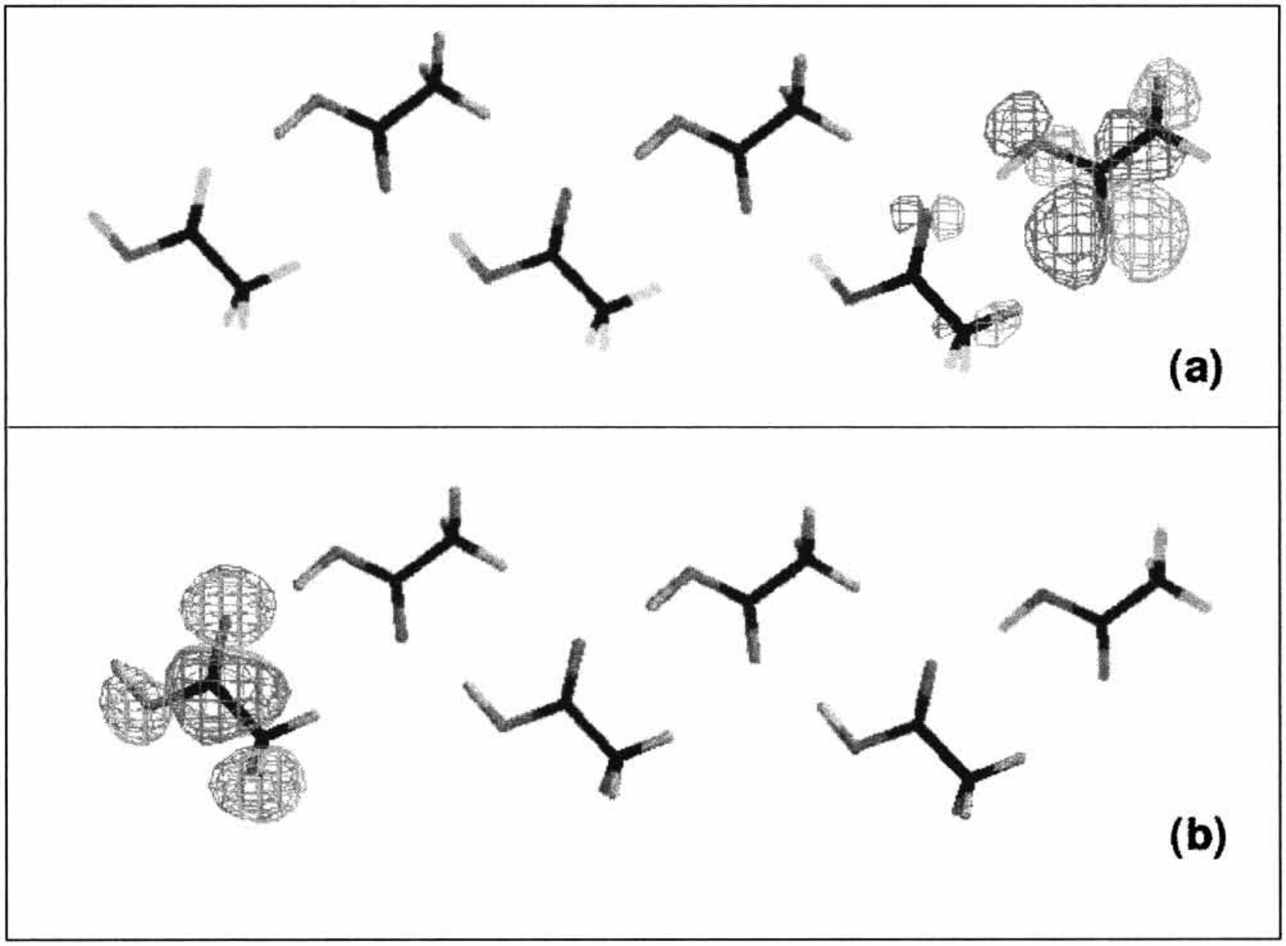

Figure 3. Molecular surface of the (a) HOMO with $\epsilon_{\mathrm{HOMO}} = -0.4227$ au and (b) LUMO with $\epsilon_{\mathrm{LUMO}} = 0.1536$ *au*, both calculated for an aggregate containing six acetic acid units.

Hardness (PMH) is fulfilled,[17,18] we may not discard that it is also present in these systems. PMH states that "... molecules arrange themselves so as to be as hard as possible" and is strictly applicable to the change in a system when it evolves from one ground state to another. Thus, according to this principle for a given molecular system the larger the value of η, is the more stable it is.

The results shown in Figure 2b seem to support the existence of a PMH in our systems. Two regions are clearly defined. One of them is the aggregates of acetic acid up to seven units that show high hardness values and low μ values. The other region starts at the eight-unit aggregate and one observes a sudden increase for the chemical potential value asociated with a sudden decrease for the corresponding chemical hardness values. Thus the stability decreases when more than seven fragments are present in the aggregate. These results may be related to the fact that acetic acid crystallizes with four units of acetic acid in each unit cell. The difference between η_8 and η_7 amounts to 12.6 kcal/mol, a significant quantity that permits the division of these two regions. Furthermore, it is important to point out at this moment that the chain of acetic acid was grown along only one direction (*x*-axis), thereby the results obtained for μ and η uniquely represent the chemical interactions along the *x* direction and conclusions about the reactivity of bidimensional or tridimensional may differ. For those cases it should be necessary to grow along *y* and *z* directions (stacking and microcrystal) to better conclude on this matter. Figure 2c shows the resulting values of the molecular softness for each of the aggregates of acetic acid. As may be seen, the behavior is exactly opposite to the molecular hardness and follow the trend of the electronic chemical potential.

3.2. Molecular Orbital Characterization of the Aggregates. To characterize the reactivity sites of these aggregates we have analyzed orbital energies and surface maps of HOMO and LUMO. The surfaces obtained for frontier orbitals of the aggregate containing six units of acetic acid are depicted in Figure 3 and similar trends are also observed for all the other aggregates: The HOMO orbital is mainly localized on the last bonded acetic acid unit, whereas the LUMO orbital appears on the first acetic acid unit of the aggregate. These results show that the last acetic acid unit contains one carbonyl group free of hydrogen bonding and therefore constitutes a nucleophilic site available to form a new hydrogen bond. In the case of LUMO, Figure 3 shows that the first acetic acid molecule is an electrophilic site. In summary, the first and the last acetic acid units of the aggregate are important sites for its growing process. Thus, for the hydrogen bonding study in these aggregates one finds that only the first and the last O···H bonds formed are important to this study. In the next Section about local properties we will discuss the properties of the last hydrogen bonding.

In addition to this, Figure 4 shows the electrostatic potential for the same six acetic acid molecules aggregate mapped into the charge density iso surface at the 0.002 e/bohr^3 value. The color map provides information about preferential reactivity sites toward electrophiles and nucleophiles. This figure shows quantitatively that the most nucleophilic site is the carbonyl oxygen of the last acetic acid unit of the chain and the most electrophilic site is the hydroxyl hydrogen for the first acetic

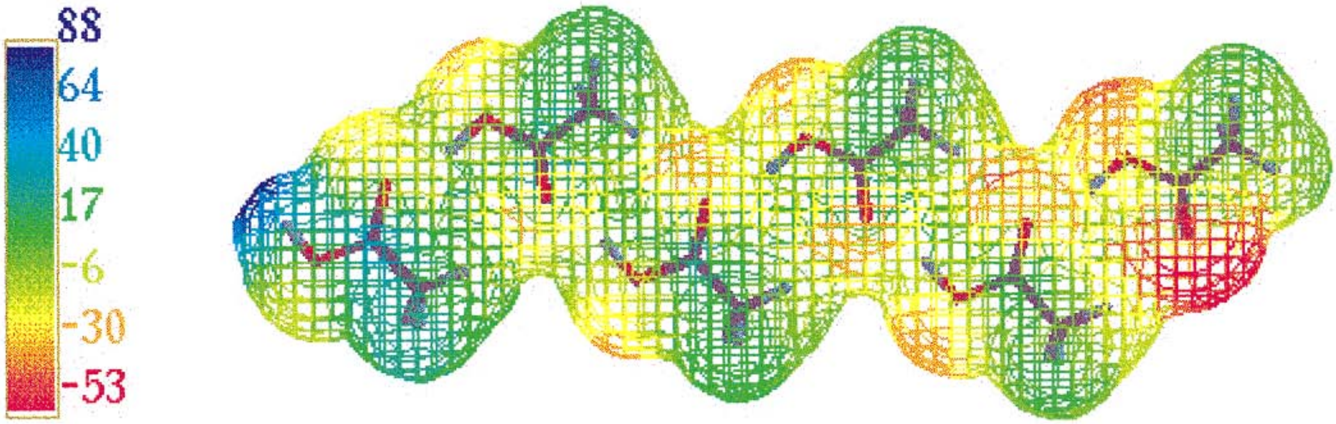

Figure 4. Molecular electrostatic potential mapped into the charge density iso surface of 0.002 e/bohr^3 calculated for an aggregate containing six acetic acid units.

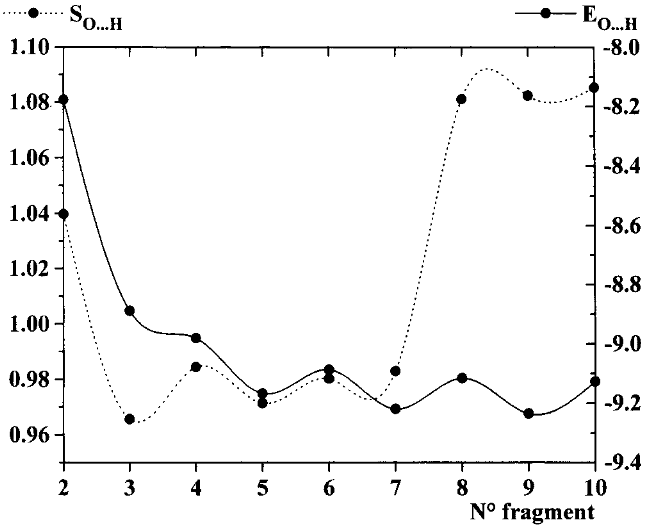

Figure 5. $E_{O\cdots H}$ (—) (kcal/mol) and $S_{O\cdots H}$ (···) (au^{-1}) as a function of the number of fragments of the aggregate.

acid unit of the chain. It is interesting to mention that these results are in perfect agreement with the HOMO and LUMO results already discussed, though the electrostatic potential clearly shows the specific atomic sites involved for the chemical attack. In conclusion, the extremes of the chain constitute important sites for the reactivity of the aggregate. Moreover, similar results for the molecular electrostatic potential are observed for other aggregates of different size.

3.3. Local Properties ($E_{O\cdots H}$, $S_{O\cdots H}$). The rationalization of global electronic properties in terms of the corresponding values associated with atoms or fragments in molecules has been an important task since the foundation of DFT. A free atom or fragment possesses an undisturbed pattern of electronic density for which hardness and chemical potential can be identified by using eq 1 together with experimental or theoretical values of ionization potentials and electron affinities. However, these properties are modified by the bonding of the atom or fragment to a target molecule. Here we want to obtain the local softness $S_{O\cdots H}$ associated with the hydrogen bonding region in the sense of eq 5 for a given molecular aggregate. Although some analytical relations for local softness have been proposed already in the literature,[5,18] to our knowledge this is the first time that local softness is applied to chemical systems with hydrogen bonding.

In Figure 5 we show the results obtained for $S_{O\cdots H}$ and for the hydrogen bonding interaction energy $E_{O\cdots H}$ for the last bond formed, calculated under the same conditions. For example, the formation of the trimer of acetic acid gives rise to the hydrogen bonding formed of the dimer and the monomer of acetic acid, thereby the results shown in Figure 5 are referred to the same kind of hydrogen bond.

Figure 5 shows an oscillatory behavior for $E_{O\cdots H}$ and $S_{O\cdots H}$. We note that adding molecules to the aggregate stabilizes it showing an incremental in the hydrogen bonding strength. This mean that each additional molecule of acetic acid interacts more strongly than the previous one. It is interesting to note that the fluctuations observed for $S_{O\cdots H}$ follow the same trend found for the global softness (the inverse of global hardness) of Figure 2b.

Equation 5 provides an explanation to the oscillatory behavior of O···H. The last term to the right side in eq 5 contains the local contribution associated with all the O···H hydrogen bonding to the global softness. Obviously, this term contains the last formed O···H that we have taken into account to deduce the value for $S_{O\cdots H}$. Thus, if one represents in a graph the evolution S_{atoms}, S_{bonds}, and $S_{O\cdots H\text{'s}}$ against the aggregate number in separate form, one find that all the contributions to S follow the same trend, that is, where a maximum exists for S_{atoms} it also exists for S_{bonds} and for $S_{O\cdots H\text{'s}}$ and the same situation is applicable for a minimum. Here the more relevant result is that $S_{O\cdots H}$ in Figure 5 was obtained using an atomic *fukui* function for O and for H participating in the last O···H bond. The use of $S(r) = fS$ is a good way to study the local softness of the hydrogen bonding in general.

On the other hand, if one considers the inverse of the hydrogen bonding softness, $[S_{O\cdots H}]^{-1}$, as occurs with the global definition of η, our results for aggregates from 2 to 7 acetic acid units predict a Local Principle of Minimum Softness (LPMS) when confronting results of the n and the $n - 1$ units: A minimum hydrogen bond softness (or maximum hydrogen bonding $[S_{O\cdots H}]^{-1}$) is obtained for a lower value of $E_{O\cdots H}$, in the same spirit for hardness. Now it is necessary state that a minimum softness value—or a maximum $[S_{O\cdots H}]^{-1}$ value—implies a high stability for the aggregate. In summary, the excellent results obtained for $S_{O\cdots H}$ suggest that eq 5 is valid in general for its use when studying hydrogen bonding in organic molecular aggregates.

4. Conclusions

In this paper, we have done a theoretical study of global and local properties in acetic acid molecular aggregates to rationalize their formation process. Total energies, electronic chemical potential, and hardness have been determined as functions of the size of the aggregate. We have shown that μ and η are observable properties to study when structural changes occur along the aggregation process. From the local point of view, hydrogen bonding has been characterized by making use of the energy and softness associated with that specific interaction. An analytic form to obtain the hydrogen bonding *fukui* function for the determination of $S_{\mathrm{O}\cdots\mathrm{H}}$ is proposed here. The excellent results imply that this modeling for hydrogen bonding is useful for characterizing local intermolecular interactions and provides a starting point to discover local reactivity indexes for these molecular systems. A global and local Principle of Minimum Hydrogen Bonding Softness is shown to exist for the growing process of the aggregate. We may conclude now that ΔSCF calculations are a good procedure to rationalize the aggregation process of acetic acid. It is clear now the importance of the last hydrogen bonding present in each aggregate.

Acknowledgment. This work was supported by FONDECYT Project No. 3980031. G.I.C.J. acknowledges Conicyt, Sociedad Chilena de Química, and American Chemical Society for a fellowship to visit The City University of New York—Hunter College and The Graduate School where this work was begun. Further, G.I.C.J. acknowledges Professor J. J. Dannenberg for providing the crystallographic geometric parameters of acetic acid.

References and Notes

(1) Turi, L.; Dannenberg, J. J. *J. Phys. Chem.* **1996**, *100*, 9638.

(2) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.

(3) Mulliken, R. S. *J. Chem. Phys.* **1934**, *2*, 782; Pritchard, H. O.; Skinner, H. A. *Chem. Rev.* **1955**, *55*, 745.

(4) *Electronegativity, Structure and Bonding*, Vol. 66; Sen, K. D., Jorgensen, C. K., Eds.; Springer—Verlag: Berlin, 1987.

(5) Ghosh, S. K. *Int. J. Quantum Chem.* **1994**, *49*, 239.

(6) Sanderson, R. T. *Chemical Bonds and Bond Energy*; Academic Press: New York, 1976; Sanderson, R. T. *Polar Covalence*; Academic Press: New York, 1983.

(7) Parr, R. G.; Donnelly, R. A.; Levy, M.; Palke, W. E. *J. Chem. Phys.* **1978**, *68*, 3801.

(8) (a) Pearson, R. G. *Hard and Soft Acids and Bases*; Dowden Hutchinson and Ross: Stroudsville, PA, 1973. (b) Pearson, R. G. *Coord. Chem. Rev.* **1990**, *100*, 403.

(9) Klopman, G. *J. Am. Chem. Soc.* **1968**, *90*, 223.

(10) Parr, R. G.; Pearson, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 7512.

(11) Parr, R. G. List of papers in *CIT—JHU—UNC QUANTA* Newsletter.

(12) Harbola, M. K.; Chattaraj, P. K.; Parr, R. G. *Isr. J. Chem.* **1991**, *31*, 395.

(13) Berkowitz, M.; Ghosh, S. K.; Parr, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 6811; Ghosh, S. K.; Berkowitz, M. *J. Chem. Phys.* **1985**, *83*, 2976.

(14) Ghosh, S. K. *Chem. Phys. Lett.* **1990**, *172*, 77.

(15) Yang, W.; Parr, R. G. *Proc. Natl. Acad. Sci. U.S.A.* **1985**, *82*, 6723.

(16) Chattaraj, P. K.; Lee, H.; Parr, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 1855.

(17) Parr, R. G.; Chattaraj, P. K. *J. Am. Chem. Soc.* **1991**, *113*, 1854.

(18) Chattaraj, P. K. *Proc. Indian Natl. Sci. Acad.* **1996**, *62A*, 513.

(19) Pearson, R. G. CHEMTRACTS: *Inorg. Chem.* **1991**, *3*, 317.

(20) Pearson, R. G.; Palke, W. E. *J. Phys. Chem.* **1992**, *96*, 3283; Galvan, M.; Pino, A. D.; Joannopoulos, J. D. *Phys. Rev. Lett.* **1993**, *70*, 21.

(21) Cárdenas—Jirón, G. I.; Lahsen, J.; Toro—Labbé, A. *J. Phys. Chem.* **1995**, *99*, 5325.

(22) Cárdenas—Jirón, G. I.; Toro—Labbé, A. *J. Phys. Chem.* **1995**, *99*, 12730.

(23) Cárdenas—Jirón, G. I.; Toro—Labbé, A. *J. Mol. Struct. (THEOCHEM)* **1997**, *390*, 79.

(24) Cárdenas—Jirón, G. I.; Gutiérrez, S.; Melin, J.; Toro—Labbé, A. *J. Phys. Chem. A* **1997**, *101*, 4621.

(25) Cárdenas—Jirón, G. I.; Letelier, J. R.; Toro—Labbé, A. *J. Phys. Chem. A* **1998**, *102*, 7864.

(26) Chattaraj, P. K. *J. Indian Chem. Soc.* **1992**, *69*, 173.

(27) Komorowski, L.; Lipinski, J.; Pyka, M. J. *J. Phys. Chem.* **1993**, *97*, 3166.

(28) Yang, W.; Lee, C.; Ghosh, S. K. *J. Phys. Chem.* **1985**, *89*, 5412.

(29) Ghosh, S. K.; Parr, R. G. *Theor. Chim. Acta* **1987**, *72*, 379.

(30) Parr, R. G.; Yang, W. *J. Am. Chem. Soc.* **1984**, *106*, 4049.

(31) Arulmozhiraja, S.; Kolandaivel, P. *Int. J. Quantum Chem.* **1997**, *64*, 231.

(32) Crystallographic Structural Database (CSD), with permission of J. J. Dannenberg, Hunter College and The Graduate School, The City University of New York.

(33) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *GAUSSIAN94*; Gaussian, Inc.: Pittsburgh, PA, 1995.

(34) Makov, G. *J. Phys. Chem.* **1995**, *99*, 9337.

(35) Harbola, M. K. *Proc. Natl. Acad. Sci. U.S.A.* **1992**, *89*, 1036.