

Role of the C–H···O Hydrogen Bonds in Liquids: A Monte Carlo Simulation Study of Liquid Formic Acid Using a Newly Developed Pair-Potential

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We performed a Monte Carlo simulation study on liquid formic acid employing a recently developed five-site pair-potential. We found that similarly to the crystalline phase, besides the strong O–H···O interactions, C–H···O hydrogen bonds are also present in the liquid and play an important role in the hydrogen-bonding structure. The presence of C–H···O hydrogen bonds is manifest in the results of the structural analysis based on the partial pair correlation functions, the pair-energy distribution function, and the statistical examination of the hydrogen-bonding network. Although, the C–H···O bonds are weaker than the O–H···O interactions and their geometry is somewhat more distorted, the basic geometric preferences are the same for all hydrogen bonds: the X–H···O (X = C, O) bonds tend to be linear in the plane of the acceptor molecule. On the other hand, the hydrogen bond donor molecule appears to rotate freely around the hydrogen bond. Interestingly enough, the acceptor atom both in the O–H···O and in the C–H···O hydrogen bonds is the carbonyl oxygen, the participation of the hydroxylic oxygen as hydrogen bond acceptor being negligible. The liquid structure of formic acid is significantly different from that in the gas phase. The role of the cyclic dimers, characteristic of the gas phase with two O–H···O hydrogen bonds, is minor (7% of the molecules) in the liquid. The liquid structure can be best described as a two-level hydrogen-bonding network. The liquid phase consists mainly of small, often branching oligomers held together by O–H···O hydrogen bonds. The small hydrogen-bonding oligomers are also connected to each other by weaker C–H···O interactions forming space-filling networks of hydrogen bonds. The two-level hydrogen-bonding network of the liquid shows little resemblance to the infinite hydrogen-bonded chains of the crystal containing both O–H···O and C–H···O hydrogen bonds. The experimental C···O separation of the crystal structure and recent results of high-quality *ab initio* calculations, however, correlate well with the position of the first hydrogen-bonding peak of the carbon–carbonyl oxygen partial pair correlation function of the liquid simulation.

Introduction

Aggregation of molecules is an issue of intense scientific interest. Although the basic physical laws of the interactions between molecules are understood in terms of quantum mechanics, the rigorous theoretical treatment of large clusters of molecules is still beyond the realm of reality. Of the many possible approximate ways to tackle the problem, one involves high-quality quantum chemical calculations on aggregates of growing size. In this “traditional” approach the focus is on understanding the properties of the characteristic interactions and the manner in which these interactions are modified by the increasing size of the cluster. Crystalline materials with regularly repeating molecular motifs are obvious candidates in such investigations. Previous molecular orbital (MO) studies on the crystal formation of selected organic molecules (1,3-diones,¹ nitroanilines,² and acetic acid³), for example, pointed to the possibly crucial role of hydrogen-bonding cooperativity and the presence of weaker hydrogen bonds, such as C–H···O interactions, in determining the structure of the crystalline phase.

Conclusions drawn from quantum chemical calculations on molecular aggregates are, however, difficult to apply and generalize for the liquid phase. It is clear that different methodology is needed to obtain insight into the nature of the

molecular interactions of the liquids. Classical liquid simulation techniques⁴ may offer a reasonable alternative to MO calculations for condensed phase problems. Due to the limitations inherent in most liquid simulation methods (e.g. classical approximation), the results of such investigations must be interpreted with sufficient care. The use of pairwise potentials, for example, neglects many-body interactions and ultimately cooperativity, which can be of central importance in the process of crystal formation.⁵ Furthermore, the united-site approach⁴ often used in the models of even simpler molecules may disregard such interactions in the liquid phase as the C–H···O hydrogen bonds, playing a vital role in many crystal structures, among others those of *m*- and *p*-nitroanilines.² Nevertheless, carefully devised effective pair-potentials based on high-quality quantum chemical calculations can provide an informative picture about the most important interactions and energetics of the liquid. In this sense, the interplay between the two powerful theoretical methods, the quantum chemical calculations and the liquid simulation techniques, may result in deeper understanding of molecular interactions and aggregation in the liquid phase.

During the course of our investigations on the structures of different organic molecules, we turned our attention to the aggregates of formic acid. Formic acid is a relatively simple, computationally tractable molecule. Formic acid, like acetic acid, but unlike other carboxylic acids, crystallizes forming long

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chains involving both O—H···O and C—H···O hydrogen bonds.⁶ The crystal structure is completely different from that of the gas phase structure consisting predominantly of cyclic C_{2v} dimers with two equivalent O—H···O H-bonds.⁷ Similar experimental observations for acetic acid were confirmed by ab initio calculations.³

An ab initio study on the formic acid dimers performed by one of us concluded that besides the most stable cyclic dimer other formic acid dimers with various O—H···O and C—H···O interactions may play important roles in condensed phases.⁸ The challenge of these conclusions subsequently led us to investigate the liquid phase of formic acid. In a previous paper,⁹ we published an improved five-site parameter set, based on correlated ab initio dimer potential surface, for formic acid to be used in classical liquid simulations. The new model explicitly includes all classical interaction sites of a formic acid molecule and, thus, is capable of properly modeling all possible interactions (including C—H···O hydrogen bonds) in condensed phases. Monte Carlo liquid simulation using the new parameter set reproduced the experimental structural and thermodynamical quantities significantly better than in previous models.⁹ The proposed model locates all seven minima on the dimer potential surface found in high-quality ab initio calculations.⁸ The promising results of the preliminary liquid simulation encouraged us to further investigate the liquid structure of formic acid.

In this paper, we present results of a Monte Carlo simulation performed on liquid formic acid. First, we examine the structure of the liquid phase in general and compare our results to the available data from experimental and other simulation studies. Next, we focus on the energetics and structure of the individual hydrogen-bonding interactions. These investigations can answer whether there exist C—H···O interactions in the liquid phase (similarly to the crystalline phase) and what is their contribution in determining the hydrogen-bonding network of the liquid. We also address another interesting, related question: what is the energetic and geometric relation of the C—H···O interactions to stronger hydrogen bonds? Finally, we attempt to compare the H-bonding network of the liquid phase of formic acid to that of the gas and crystalline phases.

Methods

Monte Carlo simulation of liquid formic acid has been performed on the (N, p, T) ensemble. The basic simulation box contained 500 rigid planar molecules at 298 K and 10^5 Pa. As in our earlier studies, we considered only *cis*-formic acid, assuming the role of the *trans* conformer to be negligible.^{8,9} The geometry of the formic acid molecules was taken from ab initio MP2/6-31G(d) calculations.^{8,9} The bond lengths of the molecules are 1.213, 1.096, 1.350, and 0.980 Å for C=O_c, C—H_f, C—O_h, and O_h—H_a bonds, whereas the H_f—C=O_c, O_c=C—O_h, and C—O_h—H_a bond angles are 125.5°, 125.1°, and 106.1°, respectively.¹⁰ The interactions of the molecules are assumed to be pairwise additive, described by a sum of Lennard-Jones and Coulombic interactions between the atoms. The long-range part of the Coulombic interaction is taken into account using the reaction field method.^{11,12} Thus, the interaction energy of molecules i and j with molecular centers (arbitrarily chosen as the C atoms) closer than R_c is calculated as

$$U_{ij} = \frac{1}{4\pi\epsilon_0} \sum_{\alpha} \sum_{\beta} \left[\frac{q_{\alpha} q_{\beta}}{r_{i\alpha, j\beta}} \left\{ 1 + \frac{\epsilon_{\text{RF}} - 1}{2\epsilon_{\text{RF}} + 1} \left(\frac{r_{i\alpha, j\beta}}{R_c} \right)^3 \right\} + 4\epsilon_{\alpha\beta} \left\{ \left(\frac{\sigma_{\alpha\beta}}{r_{i\alpha, j\beta}} \right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r_{i\alpha, j\beta}} \right)^6 \right\} \right] \quad (1)$$

TABLE 1: Parameters of the Pair Potential of Formic Acid Used in the Present Simulation

	O _c	C	H _f	O _h	H _a
σ (Å)	2.674	3.727	0.800	3.180	0.994
ϵ (kJ/mol)	5.079	1.573	0.084	1.640	0.418
q (e)	−0.432 36	+0.444 69	+0.107 32	−0.552 96	+0.433 31

where the summation runs over all sites a of molecule i and all b sites of molecule j . The fractional charges of sites a and b are denoted by q_a and q_b , respectively. Further notation of eq 1 is straightforward: $r_{i\alpha, j\beta}$ is the distance between sites a on molecule i and b of molecule j ; R_c is the cutoff distance of the molecular centers beyond which all interactions are truncated to zero; ϵ_0 is the permittivity of vacuum; ϵ_{RF} is the dielectric constant of the background continuum beyond R_c , whereas $\epsilon_{\alpha\beta}$ and $\sigma_{\alpha\beta}$ are the Lennard-Jones parameters.

Table 1 contains the numerical values of the Lennard-Jones parameters and fractional charges for liquid formic acid optimized by us in a recent paper.⁹ The $\epsilon_{\alpha\beta}$ and $\sigma_{\alpha\beta}$ parameters are obtained from ϵ_{α} and ϵ_{β} and from σ_{α} and σ_{β} by using the Lorentz–Berthelot combining rules:

$$\epsilon_{\alpha\beta} = (\epsilon_{\alpha} \epsilon_{\beta})^{1/2} \quad \sigma_{\alpha\beta} = \frac{\sigma_{\alpha} + \sigma_{\beta}}{2} \quad (2)$$

The reaction field dielectric constant was set to infinite (conducting boundary condition), whereas the value of R_c was 15 Å in the simulation. The long-range part of the Lennard-Jones interactions is estimated by assuming that all partial pair correlation functions are equal to unity beyond R_c .⁴

In the simulation, volume changing steps of maximum 400 Å³ were performed after every N th particle displacement step. In a particle displacement step the randomly selected particle was translated randomly by no more than 0.3 Å followed by a random rotation by no more than 10° around an axis parallel to one of the edges of the simulation box. The ratio of the accepted moves to the total number of steps was about 1:2 for the particle displacement and about 1:3 for the volume change steps. At the beginning of the simulation the system was equilibrated for 1000N particle displacement steps. After equilibration 100 independent configurations, separated by 100N particle displacement steps each, were collected for further evaluation. The resulting energy and molecular number density of the simulated system (39.46 kJ/mol and 0.015 69 Å^{−3}) compare well with the experimental results (38.96 kJ/mol and 0.015 88 Å^{−3}).^{13,14}

Results and Discussion

Partial Pair Correlation Functions. Some of the partial pair correlation functions calculated from the Monte Carlo simulation are presented in Figure 1. Results of an analysis of a previous reverse Monte Carlo (RMC) simulation are also shown for comparison.^{15,16} The strong hydrogen-bonding nature of the liquid is clearly indicated by the pronounced first peak of $g_{\text{O}_h\text{H}_a}(r)$ at 1.8 Å. Integration of the first peak up to the first minimum at 2.5 Å results in a coordination number of 1. However, unlike in the RMC results, the first peak is very small in the $g_{\text{O}_h\text{H}_a}(r)$ function, confirming that, similarly to the gas phase, the role of the hydroxylic oxygens as H-bonding acceptors is minor in the liquid phase. This observation is underlined by the small coordination number of about 0.15 for $g_{\text{O}_h\text{H}_a}(r)$. The lack of the secondary peak at about 3 Å on $g_{\text{O}_h\text{H}_a}(r)$ (present on the RMC function) also shows that the ability of the hydroxylic oxygens to accept hydrogen bonds is not significant, since this peak could be assigned to the non-hydrogen-bonding O_h···H_a atom pairs in molecule pairs connected by O_h—H_a···O_h hydrogen bonds. The deviation from

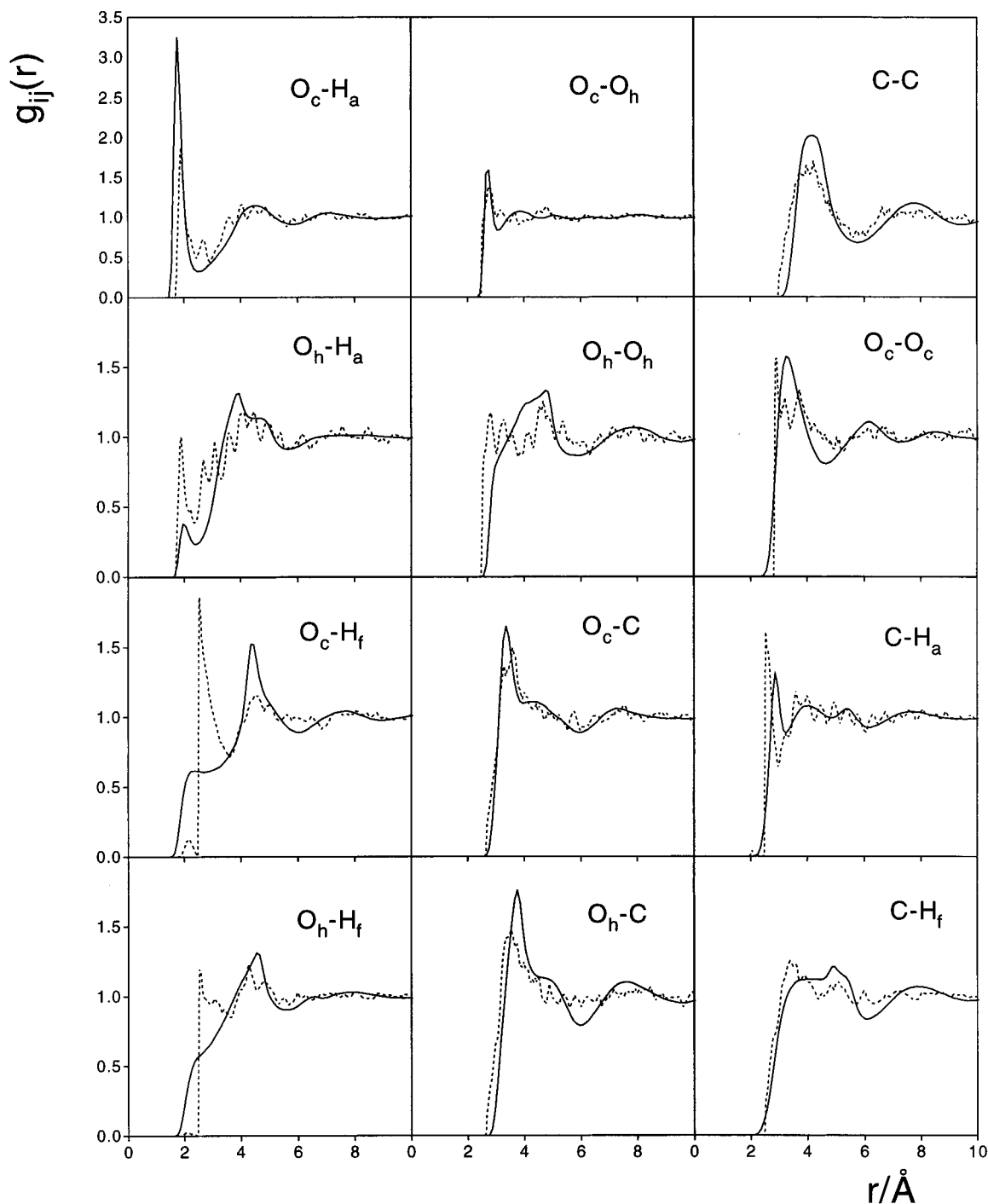


Figure 1. Calculated partial pair correlation functions of liquid formic acid for 12 different atom pairs. Solid lines: present results. Broken lines: results of a previous RMC simulation.¹⁵

the RMC results probably stems from the fact that the RMC method is unable to distinguish directly between the two different oxygen atoms since their scattering amplitudes are equivalent. Furthermore, although the pair correlations in liquid formic acid can be fully described by 15 independent pair correlation functions or structure factors, only two of them were used in the RMC fitting procedure.¹⁵ Thus, the resulting pair correlation functions of the RMC procedure might be related to the fact that RMC has a tendency to find the most disordered configuration within the limits of the given constraints as has been documented in the literature.^{17,18}

The comparison of the $g_{O_cO_h}(r)$ and $g_{O_hO_h}(r)$ functions parallels the observations made above. The $g_{O_cO_h}(r)$ function has a sharp first peak at 2.7 Å, corresponding to the hydrogen-bonding atom pairs in the $O_h-H_a\cdots O_c$ type hydrogen bonds. The integration

of this peak up to 3.05 Å, the position of the first minimum, gives a coordination number of 1, consistent with the $g_{O_cH_a}(r)$ function. On the other hand, a similar peak is missing in $g_{O_hO_h}(r)$; only a shoulder at about 3.5 Å can be observed. Closer inspection of the $g_{O_cO_h}(r)$ and $g_{O_hO_h}(r)$ functions shows that the oxygen atoms can approach each other as close as 2.5 Å in both cases. This verifies that the relatively small coordination number of the hydroxyl oxygen in the hydrogen-bonding region is *not* simply a computational artifact due to the difference in the σ Lennard-Jones parameters of the two different oxygen atoms.

Thinking about the reasons of the insignificance of the O_h oxygen as a hydrogen bond acceptor, it is probably energetics that answer the question. The interaction energies of the hypothetical individual H-bonding interactions examined in our

previous studies clearly indicate that the $O_h-H_a\cdots O_c$ type hydrogen bonds are significantly stronger (by about 10–12 kJ/mol) in formic acid dimers than the $O_h-H_a\cdots O_h$ interactions.^{8,9} Although energetics provide a plausible explanation for the above problem, we cannot exclude the possibility that entropy also contributes to the preference of $O_h-H_a\cdots O_c$ interactions.

Another indication of the presence of the strong $O_h-H_a\cdots O_c$ hydrogen bonds is the first peak of the $g_{CH_a}(r)$ function at 2.85 Å (corresponding to the most probable distance of the C atom of the acceptor molecule and the hydrogen-bonding H_a atom) with a coordination number of 1.3 up to the first minimum of the pair correlation function at 3.25 Å.

Besides the obvious presence of strong hydrogen bonds, such as the $O_h-H_a\cdots O_c$ interactions, interesting features can be observed on the $g_{O_Hf}(r)$ and $g_{CH_f}(r)$ functions. These functions are usually not evaluated in liquid simulations mainly because of the theoretical approximations in the molecular model (united site). The present five-site pair-potential, on the other hand, offers an excellent opportunity to explicitly analyze the interactions the formic hydrogen participates in. In this sense, to our best knowledge, this is the first work in the literature that examines the role of the $C-H\cdots O$ interactions in liquid phase.

Both the $g_{O_Hf}(r)$ and $g_{CH_f}(r)$ functions exhibit distinct peaks between 2 and 3 Å and between 3 and 4 Å, respectively. Integration of the $g_{O_Hf}(r)$ function up to 3 Å gives a coordination number of 0.9. The presence of these peaks is strong evidence of a hydrogen bond-like interaction between the formic hydrogen and the carbonyl oxygen atoms. The position of the peak also compares favorably with the $H_f\cdots O_c$ distance of 2.6 Å of the $C-H_f\cdots O$ hydrogen bonds in crystalline formic acid^{6b} and the similar value of 2.4 Å of ab initio dimer calculations.⁸ (Note that these latter partial pair correlation functions are not reliable in the previous RMC simulation due to the negligible experimental coherent scattering amplitude of the formic H atom used in the simulation.¹⁵) Comparing the first peak of the $g_{O_Hf}(r)$ function to the hydrogen-bonding peak of the $g_{O_cH_f}(r)$ function, it is evident that the $C-H_f\cdots O_c$ interaction is significantly weaker than the ordinary $O_h-H_a\cdots O_c$ hydrogen-bonding interaction, since the position of the O_c-H_f peak can be found at about 0.7 Å higher r value than the O_c-H_a peak and is also much smaller. However, the agreement of the coordination numbers of the two peaks also suggests that the $C-H_f\cdots O_c$ interaction present in liquid formic acid is a type of weak hydrogen bond. The featureless $g_{O_hH_f}(r)$ function underscores our earlier observations regarding the weak ability of the O_h atoms to accept hydrogen bonds.

The center-center pair correlation function of the formic acid molecules can be estimated by the $g_{CC}(r)$ partial pair correlation function. This function seems to overestimate the long-range structure of liquid formic acid to some extent, consistent with the fact that the present potential model slightly overestimates the long-range structure of the liquid as seen from comparisons of the total pair correlation functions with experimental ones.⁹ However, the first-shell coordination number of 12.5, resulting from the integration of the first peak of $g_{CC}(r)$ up to 5.85 Å, is consistent with previous RMC simulation results.¹⁵ The integration of the first peak of other partial pair correlation functions (or the first and second peaks in those cases when the first peak describes hydrogen bonds and the second peak corresponds to the full first coordination shell) results in various coordination number values scattered around the C–C coordination number of 12.5. These coordination numbers are 14.5, 14, 14, 14, 13, 12.5, 12.5, 11 and 6 for $g_{CH_f}(r)$, $g_{O_cH_f}(r)$, $g_{CH_a}(r)$, $g_{O_hC}(r)$, $g_{O_cC}(r)$, $g_{O_cH_a}(r)$, $g_{O_hO_h}(r)$, $g_{O_hH_f}(r)$, and $g_{O_cO_c}(r)$, respectively.

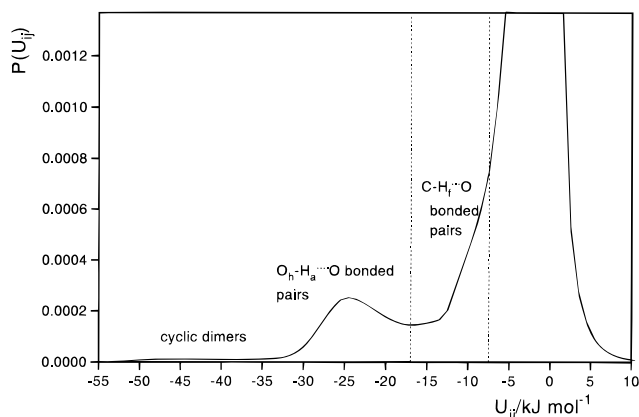


Figure 2. Distribution of the pair interaction energy of the molecules. The dashed vertical lines correspond to the U_{lim} limiting energy values used in the analysis of the hydrogen-bonded clusters (see the text).

In summary, on one hand, a formic acid molecule has two strong hydrogen bond accepting sites (on the O_c atom) and two weakly accepting sites (on the O_h atom). On the other hand, the number of hydrogen atoms to be donated in hydrogen-bonding interactions is only two: one “textbook case” $O-H$ hydrogen and a weaker $C-H$ hydrogen. It is, thus, reasonable to assume that, besides the stronger $O-H\cdots O$ hydrogen bonds, the molecules tend to form weaker hydrogen bonds, as well, namely, $C-H\cdots O$ interactions. This qualitative picture is strongly supported by the general characteristics of the partial pair correlation functions. Examination of the pair energy distribution function and statistical analyses of the hydrogen-bonding network will provide more quantitative details of the structure in the following sections.

Pair Energy Distribution. An alternative way of analyzing the interactions between the molecules in the liquid is the calculation of the distribution of the U_{ij} pair interaction energies. The resulting distribution function for liquid formic acid is presented in Figure 2. The shape of the distribution is typical of hydrogen-bonded liquids,^{19–21} since, besides the trivial peak at zero energy of the distant molecules, another strong peak appears at about −25 kJ/mol, corresponding to the hydrogen-bonding molecular pairs. The energy of the peak at around the maximum correlates well with the energy of a single $O_h-H_a\cdots O_c$ hydrogen bond.^{8,9} At the same time, the high-energy tail of the band extending approximately to above 30 kJ/mol can hardly be explained exclusively by the presence of single $O_h-H_a\cdots O_c$ interactions. It appears that additional weaker interactions, such as the $C-H\cdots O$ interactions, contribute to the hydrogen-bonding stabilization in this regime. Approximately at the double of the maximum of the $O-H\cdots O$ hydrogen-bonded energy, between −35 and −55 kJ/mol, a small and rather diffuse peak is observed, corresponding to the cyclic hydrogen-bonded dimers with two $O_h-H_a\cdots O_c$ hydrogen bonds. These configurations are around the global minimum on the dimer potential energy surface,⁸ the dominant form of molecular clusters of formic acid in the gas phase.⁷ A similar cyclic dimer peak was found in liquid acetic acid by Briggs et al.¹⁹ Integration of this peak up to the minimum of the distribution function at −38.5 kJ/mol reveals that only about 7% of the molecules participate in such cyclic dimers.

The presence of $C-H\cdots O$ interactions manifests in an interesting property of the pair energy distribution. In addition to the two characteristic hydrogen-bonding peaks, the pronounced shoulder at the attractive side of the trivial peak, seen in Figure 2 between −7 and −13 kJ/mol, is a definite sign of weaker interactions. This shoulder can be attributed to the $C-H_f\cdots O_c$ hydrogen bonds present in liquid formic acid. A

similar shoulder appears in the pair energy distribution function of relatively strongly associating aprotic dipolar liquids (e.g., acetonitrile,²² acetone²³) at about the same energies. This feature of the latter liquids has been interpreted as originating from the dipolar association of the molecules.^{22,23} Recent investigations indicate that C-H \cdots O interactions may also play an important role in determining the liquid structure of acetone.²⁴ Nevertheless, the strength of the weak C-H \cdots O interactions in liquid formic acid, giving a rather small contribution to the total energy of the system, is comparable to the stabilization of the strongest molecular associates in aprotic dipolar liquids.

Hydrogen Bond Analyses. Hydrogen bonds are defined in computer simulations in two different ways. While the first approach is *geometric*, the second is of *energetic* nature. In the former case, two molecules are considered to be hydrogen-bonded if the hydrogen atom of one molecule is closer to the acceptor atom of the other molecule than a given distance (usually taken as the position of the first minimum on the corresponding partial pair correlation function). This condition is often combined with an angular criterion; for example, the X-H \cdots O angle should be larger than a previously fixed α_{lim} limiting value, where X stands for the donor atom. In the definition of *energetic* type, two molecules are hydrogen-bonded if their pair interaction is stronger than a given U_{lim} energy limit. The obvious choice for U_{lim} is usually the position of the minimum of the pair energy distribution function between the hydrogen-bonding peak and the trivial peak at zero energy.

In the following analysis we employ both definitions. First, we examine the average geometry of the hydrogen bonds and the relative orientation of the hydrogen-bonded molecules. In this analysis the geometric definition of the hydrogen bond is the most suitable. Then, topological and statistical properties of the hydrogen-bonded clusters are discussed at various values of the α_{lim} limiting angle. The analysis is then repeated using the energetic hydrogen bond definition. The comparison of the two analyses can provide the most reasonable value of the α_{lim} limiting angle. The analyses are performed for both the C-H \cdots O and the O-H \cdots O types of hydrogen bonds separately and also for all types of hydrogen bonds without distinguishing them according to the donor atom type.

Geometry of the Hydrogen Bonds. Investigating the geometry of the hydrogen bonds in liquid formic acid, we defined two molecules to be hydrogen-bonded if the interacting H atom and the acceptor atom are closer than 2.5 Å, the first minimum of $g_{\text{O}_c\text{H}_d}(r)$. Although this distance does not coincide with the position of the first minimum of $g_{\text{O}_c\text{H}_d}(r)$ at 3 Å, which would characterize the C-H \cdots O type hydrogen bonds, we found it more sensible to treat all hydrogen bonds in the system according to a common criterion and not using more and less permissive definitions for various types of hydrogen bonds.

Figure 3 shows the cosine distribution of three angles characterizing the hydrogen bonds: the X-H \cdots O angle (α), the angle between the H \cdots O hydrogen bond and the plane of the acceptor molecule (β), and the angle between the planes of the two interacting molecules (γ). All three distributions are shown for all hydrogen bonds in the system (dots) and for the O-H \cdots O (solid line) and C-H \cdots O (broken line) type hydrogen bonds.

As is apparent, the most favored arrangement of two hydrogen-bonded molecules in each case corresponds to a linear hydrogen bond in the plane of the acceptor molecule. This preference is stronger for the O-H \cdots O interactions than for the C-H \cdots O type of hydrogen bonds in the case of α , whereas only slight differences appear between the three distributions in the case of β . The integration of the distribution functions

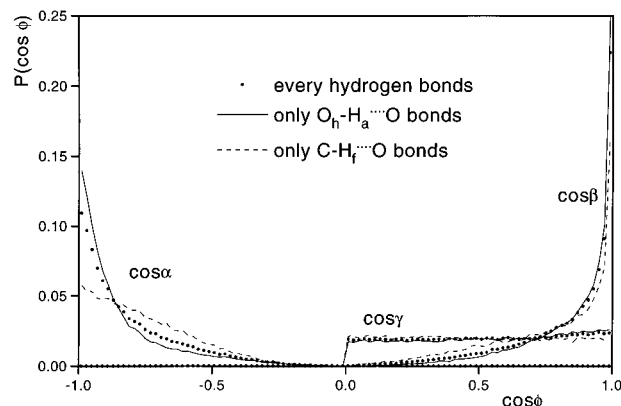


Figure 3. Cosine distribution of three different angles characterizing the geometry of the hydrogen bonds. α is the X-H \cdots O hydrogen bond angle (X = O, C), β is the angle between the O \cdots H hydrogen bond and the plane of the acceptor molecule, and γ is the angle between the planes of the two molecules. Solid lines: distributions of the O-H \cdots O type hydrogen bonds. Dashed lines: distributions of the C-H \cdots O type hydrogen bonds. Dots: distributions of all types of hydrogen bonds.

yielded that α is larger than 165° in 18% of the hydrogen bonds and 50% of the hydrogen bonds have $\alpha > 150^\circ$. The corresponding numbers are 22% and 60% for the O-H \cdots O hydrogen bonds and 9% and 34% for the C-H \cdots O interactions. The trends are similar for the planar preference of the hydrogen bond relative to the plane of the acceptor molecule: β is less than 15° and 30° in 29% and 55% of the hydrogen bonds (32% and 61% for O-H \cdots O, 21% and 44% for C-H \cdots O hydrogen bonds), respectively. The numbers indicate that planarity is a somewhat stronger requirement for hydrogen bonds than linearity in liquid formic acid. This result confirms previous observations obtained from RMC modeling of the structure of liquid formic acid.¹⁵

It is apparent from the cosine distributions that although the C-H \cdots O type hydrogen bonds deviate much stronger from linearity and slightly stronger from planarity than the O-H \cdots O hydrogen bonds, their preferred alignment basically exhibits the same tendencies. This fact is consistent with our previous observations that the close-contact H \cdots O \cdots C atom pairs form real hydrogen bonds, but these bonds are significantly weaker than the ordinary O-H \cdots O type hydrogen bonds. A short discussion of the problem and similar conclusions from the viewpoint of MO calculations can be found elsewhere.⁸

Unlike the cosine distribution of α and β , the distribution of $\cos \gamma$ is practically uniform in all three cases, showing no preferential alignment of the molecular planes. Considering the fact that the hydrogen bonds prefer to lie in the plane of the acceptor molecules, the uniform distribution of $P(\cos \gamma)$ indicates that the donor molecule can rotate freely around the hydrogen bond.

Hydrogen-Bonding Network. To analyze the connectivity of the hydrogen-bonded molecules in liquid formic acid, we calculated various topological and statistical properties of the hydrogen-bonded molecules and clusters. In our treatment, those groups of molecules are called hydrogen-bonded in which every pair of molecules is connected to each other by a chain of hydrogen bonds. In this section we use the same geometric condition for defining the hydrogen bonds as above (i.e., the intermolecular H \cdots O distance should be smaller than 2.5 Å) combined with an angular condition, that the α angle of the hydrogen bond should be larger than a given α_{lim} limiting value. Tables 2 and 3 summarize the calculated statistical properties at six different α_{lim} values. In Table 2 all possible hydrogen bonds are taken into account, whereas Table 3 shows the same

TABLE 2: Statistical Properties of the Hydrogen-Bonded Networks in Liquid Formic Acid Using the Geometric Hydrogen Bond Definition. Both C—H···O and O—H···O Types of Hydrogen Bonds Are Counted. α_{lim} Is the Limiting Angle of the Geometric Hydrogen Bond Definition; n_{HB} Is the Average Number of Hydrogen Bonds in Which a Molecule Participates; $\langle n \rangle$ Denotes the Average Size of the H-bonded Clusters; M Means the Average Number of H-bonded Clusters in a Configuration; f_i Is the Fraction of the Molecules Having Exactly i H-bonded Neighbors

α_{lim}	n_{HB}	$\langle n \rangle$	M	f_0	f_1	f_2	f_3	f_4	f_5
90°	3.46	245	2.04	0.001	0.025	0.177	0.338	0.284	0.129
120°	3.19	162	3.08	0.002	0.041	0.229	0.364	0.250	0.091
130°	2.85	77.8	6.43	0.006	0.075	0.301	0.366	0.191	0.052
140°	2.38	22.2	22.5	0.023	0.160	0.384	0.305	0.105	0.021
150°	1.76	5.19	96.3	0.088	0.321	0.384	0.168	0.035	0.004
165°	0.62	1.44	348	0.501	0.389	0.100	0.009	0.001	0

TABLE 3: Statistical Properties of the Hydrogen-Bonded Networks in Liquid Formic Acid Using the Geometric Hydrogen Bond Definition: Only O—H···O Types of Hydrogen Bonds Are Counted; for Definitions of the Various Quantities See Table 2 and the Text

α_{lim}	n_{HB}	$\langle n \rangle$	M	f_0	f_1	f_2	f_3	f_4	f_5
90°	2.14	13.57	36.8	0.009	0.181	0.522	0.238	0.045	0.005
120°	2.00	8.85	56.4	0.013	0.216	0.557	0.191	0.029	0.001
130°	1.85	6.16	81.1	0.025	0.265	0.558	0.142	0.011	0
140°	1.64	4.10	122	0.058	0.346	0.501	0.091	0.004	0
150°	1.29	2.56	195	0.153	0.449	0.356	0.042	0.001	0
165°	0.49	1.32	380	0.578	0.358	0.063	0.002	0	0

quantities for clusters connected by solely O—H···O hydrogen bonds. In the tables f_i is the fraction of molecules having exactly i hydrogen-bonded neighbors, n_{HB} is the average number of hydrogen bonds in which a molecule participates, M means the average number of hydrogen-bonded clusters in a configuration, and $\langle n \rangle$ is the average size of the hydrogen-bonded clusters (in other words, the average number of molecules in the clusters). Note that according to the above definition single molecules without hydrogen bonds to their neighbors are regarded as clusters of size 1.

Table 2 indicates that the average cluster size decreases rapidly with increasing α_{lim} , covering 2 orders of magnitude (considering all types of hydrogen bonds). Using the most permissive definition of $\alpha_{\text{lim}} = 90^\circ$ (which is, in practice, equivalent to the lack of the angular condition; see Figure 3), the system consists of only about two clusters on average. These clusters, thus, can be considered space-filling percolating networks. A more reasonable limiting angle, $\alpha_{\text{lim}} = 130^\circ$, still results in few, large clusters. More than 60% of the molecules have at least three neighbors, confirming that the clusters of the hydrogen bonds in this definition are still space-filling networks of the molecules. On the other hand, it is particularly noteworthy that the size of the O—H···O bonded clusters is considerably smaller, consisting of only a few molecules regardless of the angular condition (see Table 3). The average cluster size is still below 15 when hydrogen bonds are defined without angular conditions (i.e., $\alpha_{\text{lim}} = 90^\circ$), smaller than the $\langle n \rangle$ value corresponding to $\alpha_{\text{lim}} = 140^\circ$ with all types of hydrogen bonds included in the statistics. Applying angular conditions for the O—H···O interactions, small, often branching oligomers build up the system. For example, for $\alpha_{\text{lim}} = 130^\circ$, when the average cluster size is more than 4 (the smallest possible size of a branching cluster), 10% of the molecules are in a branching position participating in at least three hydrogen bonds. This means that more than 40% of the clusters are branching in this case. Furthermore, the number of branches increases rapidly with more permissive angular definitions of the hydrogen bonds.

TABLE 4: Statistical Properties of the Hydrogen-Bonded Networks in Liquid Formic Acid Using the Energetic Hydrogen Bond Definition. In the Table U_{lim} Is the Limiting Energy of the Energetic Hydrogen Bond Definition; for Definitions of the Various Quantities See Table 2 and the Text

U_{lim} (kJ/mol)	n_{HB}	$\langle n \rangle$	M	f_0	f_1	f_2	f_3	f_4	f_5
-7.5	2.82	125	4.01	0.002	0.068	0.325	0.377	0.179	0.043
-17	1.34	2.87	174	0.105	0.472	0.398	0.025	0	0

All of these observations indicate a two-level hydrogen-bonded structure of liquid formic acid. The molecules form small branching oligomers held together by strong O—H···O type hydrogen bonds, whereas these oligomers are connected to each other by weak C—H···O hydrogen bonds forming space-filling networks. Note, however, that the *geometric* definition of the hydrogen bonds based on the α_{lim} limiting angle is not unambiguous. Figure 3 illustrates that there is no obvious choice for α_{lim} , since the distribution of $\cos \alpha$ decreases monotonously. Therefore, we calculated all the hydrogen-bonding statistics as a function of the α_{lim} limiting angle instead.

The distribution of the molecular pair interaction energy (Figure 2) provides an alternative way of defining hydrogen bonds. According to the *energetic* definition, two molecules are hydrogen-bonded if their pair interaction energy is deeper than a given U_{lim} limiting value. The pair distribution function offers an evident choice for U_{lim} . As it has been discussed above, the peak at about -25 kJ/mol of the $P(U_{ij})$ function corresponds to the O—H···O bonded molecular pairs, while the shoulder on the attractive side of the trivial peak at about -10 kJ/mol originates from the C—H···O bonded molecules. Analyzing both C—H···O and O—H···O interactions, we employ -7.5 kJ/mol as U_{lim} , approximately the beginning of the shoulder on the trivial peak. Similarly, we choose $U_{\text{lim}} = -17$ kJ/mol, the position of the minimum before the O—H···O bonding peak at -25 kJ/mol when only O—H···O bonds are considered in the statistics. These two limiting energy values are indicated in Figure 2 by dashed vertical lines.

We computed the same statistical properties of the hydrogen-bonded molecules and clusters as in the geometric analysis using the energetic definition of hydrogen bonds with the above two limiting energy values. The results, summarized in Table 4, confirm our previous observations on the two-level hydrogen-bonded structure of the liquid. The average size of the O—H···O bonded clusters is about 3, whereas the C—H···O type hydrogen bonds connect these small clusters, forming space-filling percolating networks. The two-level hydrogen-bonding system of the liquid can be compared to the crystal structure of formic acid. The liquid phase contains short, often branching oligomers with O—H···O hydrogen bonds that are connected to each other mostly by C—H···O interactions. The basic units of the crystal structure are, on the other hand, long chains with both O—H···O and C—H···O hydrogen bonds. Thus, in our opinion, the hydrogen-bonding structures of the liquid and crystalline phases exhibit very important differences. Practically, the only significant, common thing in the structures of the two condensed phases of formic acid is the simultaneous presence of O—H···O and C—H···O interactions.

The consistency between the results based on the geometric and the energetic definitions is also illustrated in Figure 4, where the average cluster size $\langle n \rangle$ and the number of clusters M are plotted as a function of n_{HB} . Note that the use of n_{HB} as an independent variable instead of α_{lim} and U_{lim} has the advantage

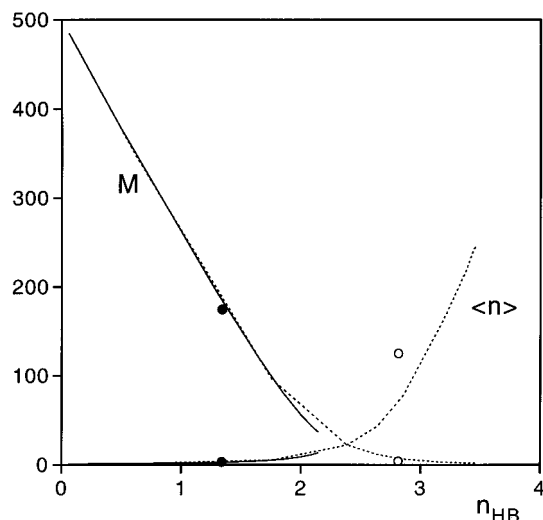


Figure 4. Average size of the hydrogen-bonded clusters, $\langle n \rangle$, and average number of hydrogen-bonded neighbors in a configuration, M , as a function of the average number of hydrogen-bonded neighbors of the molecules, n_{HB} . Solid lines: geometric definition considering only O—H···O type hydrogen bonds. Dashed lines: geometric definition, taking every hydrogen bond into account. Full circles: energetic definition with only O—H···O type hydrogen bonds. Open circles: energetic definition with every hydrogen bond taken into account. For the various definitions of the hydrogen bonds see the text.

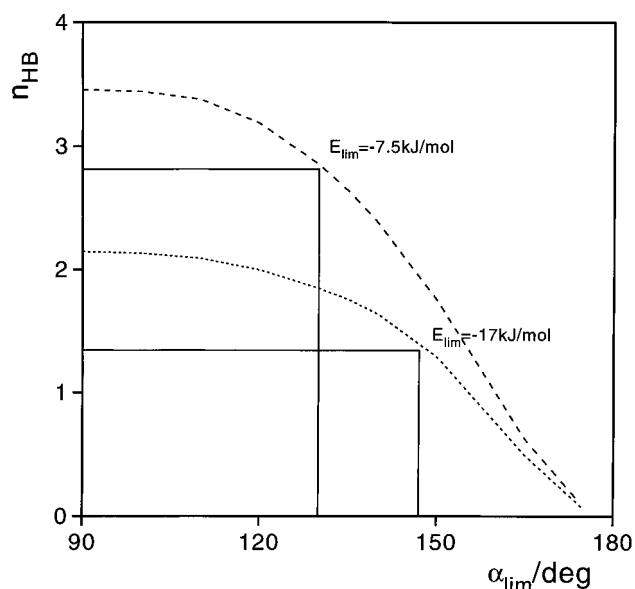


Figure 5. Average number of hydrogen-bonded neighbors of the molecules, n_{HB} , as a function of the α_{lim} limiting angle for the O—H···O type hydrogen bonds (dotted line) and for every hydrogen bond (dashed line). The n_{HB} values obtained with energetic hydrogen bond definitions and the corresponding α_{lim} values are also indicated (solid lines).

of allowing direct comparison between the numbers resulting from different definitions. A quantitative comparison of the results employing the two types of definition can also be performed by inspecting the n_{HB} values. Figure 5 shows n_{HB} as a function of the α_{lim} limiting angle both for the O—H···O types and for all kinds of hydrogen bonds. The n_{HB} values obtained by using the energetic definition are also indicated. As is evident, the energetic definition with $U_{lim} = -7.5$ kJ/mol corresponds to the geometric definition for all hydrogen bonds with the limiting angle $\alpha_{lim} = 130^\circ$, whereas the $U_{lim} = -17$ kJ/mol limiting energy choice yields results similar to those with the geometric definition with $\alpha_{lim} = 150^\circ$ for the O—H···O hydrogen bonds. The comparison of Table 4 with Tables 2 and 3 also shows that all calculated statistical results with α_{lim}

$= 130^\circ$ for all hydrogen bonds and $\alpha_{lim} = 150^\circ$ for the O—H···O hydrogen bonds are consistent with the corresponding quantities in the energetic treatment. The consistency of analyses based on different definitions of the hydrogen bond (geometric vs energetic) offers an excellent opportunity to choose and fix reasonable values for the α_{lim} limiting angles characterizing the hydrogen bonds in a geometric sense.

Conclusions

In the present study we analyzed the hydrogen-bonding structure of liquid formic acid by using Monte Carlo computer simulation. Analysis of the partial pair correlation functions and the distribution of the pair interaction energies of the molecules shows that not only are hydrogen bonds in liquid formic acid formed between an O—H group and an oxygen atom but the formic hydrogen in the C—H bond can also participate in hydrogen bonds. However, these C—H···O type hydrogen bonds are much weaker (being about half as strong or even less) than the O—H···O hydrogen bonds, and their geometry is usually more distorted. We also found that the acceptor atom of the hydrogen bonds in liquid formic acid is the carbonyl oxygen atom in most cases. Only about 10% of the O—H···O hydrogen bonds are located between two hydroxylic oxygen atoms, while the amount of the C—H···O_h hydrogen bonds is negligible relative to the C—H_f···O_c interactions.

The preferential geometry of the X—H···O ($X = O, C$) hydrogen bonds is found to be linear in the plane of the acceptor molecule. We pointed out that the latter preference is somewhat stronger than the former one. These geometrical preferences of the hydrogen bonds, especially that for linearity, are stronger for the O—H···O types of hydrogen bonds than for the C—H···O hydrogen bonds. Nonetheless, the C—H···O hydrogen bonds clearly exhibit both preferences in a weaker form. Although the hydrogen bond itself favors being in the plane of the acceptor molecule, the alignment of the two molecular planes has no preferential orientation, indicating that the donor molecule can rotate practically freely around the hydrogen bond.

In statistical treatments of the hydrogen-bonded networks of the molecules, we observed a two-level hydrogen-bonded structure in liquid formic acid. Small, often branching oligomers of a few molecules are formed by strong O—H···O types of hydrogen bonds. The O—H···O hydrogen-bonded oligomers are, in turn, connected to each other by weak C—H···O hydrogen bonds, forming space-filling hydrogen-bonding networks. The two-level hydrogen-bonded structure shows only little resemblance (simultaneous presence of O—H···O and C—H···O interactions) to the structure of the crystalline formic acid, in which the infinite O—H···O bonded chains are interconnected by weak C—H···O interactions. We also found that only about 7% of the molecules belong to cyclic dimers, indicating that the dominant cluster form of the gas phase formic acid plays only a minor role in forming the liquid structure.

Comparison of the various statistical properties of the hydrogen-bonded clusters using both a geometric and an energetic definition of the hydrogen bonds revealed that the most reasonable value of the limiting angle above which two molecules should be considered as hydrogen-bonded is 150° for the O—H···O type hydrogen bonds. Consistently with a previous observation that the preference of the C—H···O hydrogen bonds for linearity is not as pronounced as that of the O—H···O hydrogen bonds, the value of this angle is found to be only 130° when C—H···O bonds are also taken into account.

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