A Molecular Dynamics Study of the Structure and Evolution of the 4,4′-Bis(diphenylhydroxymethyl)biphenyl/Acetone Host – Guest System

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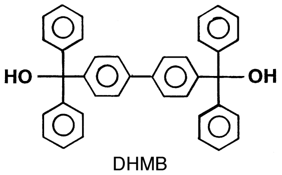
Abstract: The 4,4′-bis(diphenylhydroxymethyl)biphenyl/acetone (DHMB-Ac) system was studied by NPT molecular dynamics (MD) calculations; the study was prompted by the availability of X-ray single-crystal diffraction and calorimetric data (L. Johnson, L. Nassimbeni, E. Weber and K. Skobridis, *J. Chem. Soc. Perkin Trans. 2*, **1992**, 2131). Potential energies were calculated by using the UNI-FF or the OPLS all-atom force fields. The kinetics of formation of hydrogen-bonded aggregates between the DHMB molecule and acetone was sampled, and the persistence and fluxionality of the O–H⋯O=C hydrogen bond are clearly revealed. Extensive MD runs at variable temperature on the inclusion compound in its crystalline state allow a description of the thermal motion and eventual reorientation within its cavity of the acetone molecule; the host crystalline matrix does not survive when guests are removed. The dynamic evolution of a slab of 60 DHMB and 120 acetone molecules, which has the experimental crystal structure, was also simulated at the temperature experimentally observed for guest desorption, and the loss of solvent molecules was monitored. Crystalline order is very quickly lost; then, guest molecules can easily diffuse away from the surface without a noticeable swelling of the material. The molecular reorganization of the remaining host liquid back to the crystal structure of one of the two polymorphs of pure DHMB could not be observed, owing to the short simulation times and to the smallness of the computational sample.

Keywords: computer chemistry · inclusion compounds · molecular dynamics

Introduction

Molecular dynamics (MD) offers a unique opportunity to simulate the behaviour of organic phases at a molecular level. Although phase changes occur over macroscopic times and amounts of matter, some elementary molecular evolution steps may involve just a few molecules or a few pico- or nanoseconds; thus, in spite of orders of magnitude differences between the overall real and simulated sizes and timescales, scraps of information can be gathered from relatively straightforward computational protocols. In our line of research, aimed at the study of crystal construction and of the paths through which molecules find their way to crystal order,[1] attempts have been made to use MD to investigate molecular aggregation in solution[2] and molecular disaggregation when a crystal melts.[3]

Finding a system which at the same time has been characterized by significant experimental data and is computationally tractable is always a problem. We became recently acquainted with the multiform solid-state behaviour of the title compound: pure DHMB crystallizes in two polymorphs.[4] Also it can incorporate a number of different guest molecules to yield crystalline inclusion compounds,[5] which may revert to the pure crystal when heated, upon loss of the guests. While X-ray structural characterizations and thermal analysis give a wealth of information on the interconversions, the problem is at the borderline of computational affordability, due to the size and shape of the DHMB host molecule. With a little adjustment, however, we found that even such a system could be amenable to treatment by the OPLS-AA force field.[6] Acetone was chosen as the simplest guest, and also because the host – guest complex crystallizes in an orthorhombic space group, thus facilitating the MD treatment. The elementary recognition step in solution, the hydrogen bonding between host and guest, and the dynamics of guest reorientation and eventual escape from the crystal lattice could be simulated for times long enough to recognize some of the key structural and energetic aspects of these processes.



DHMB

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Results and Discussion

Crystal structures and thermodynamic data: The pure host compound crystallizes in two polymorphic forms,[4] α_1 and α_2. The first melts at 186.8 °C with an enthalpy of melting of 36.6 kJ mol^{-1}, with some differential scanning calorimetry (DSC) features that may suggest a phase change. α_2 melts at 180.4 °C with an enthalpy of melting of 49.7 kJ mol^{-1}. Interestingly, there is no hydrogen bonding in the crystal with the lower melting enthalpy, while molecules in the α_2 phase are held together in hydrogen-bonded dimers. The inclusion compounds were obtained by simply dissolving the host crystal into the guest liquid.[5] Table 1 has the relevant crystal data. X-ray studies of acetone, benzophenone, dioxane and *p*-xylene inclusion compounds reveal that the host is invariably hydrogen-bonded to the guests, when these have an acceptor atom, or are capable, when the guest is *p*-xylene, of folding the hydrogen-bonding pattern into host tetramers. Thus, the system shows a wide range of possible intermolecular interaction types, thanks also to the conformational flexibility of the host.

The crystal of the DHMB-Ac inclusion compound has two acetone molecules in the asymmetric unit,[5] with host–guest O–H⋯O=C hydrogen-bonding distances of 1.876 and 2.021 Å, against 1.879 Å for the host–host hydrogen bond in the pure host crystal (all these distances refer to renormalized[7] H-atom positions). There are no channels in this crystal, guests being included in cavities. The DSC analysis reveals that acetone molecules are desorbed at 74 and 94 °C, then the material undergoes an endothermic process postulated as a phase change and finally shows an endotherm at the melting temperature of the pure host crystal. The interpretation of these features is made more difficult by the fact that the area of the “phase change” peak is much larger than that of the “melting” peak.

A standard packing analysis of these compounds was carried out by using UNI-FF potentials.[7] Relaxation of the crystal structures under the action of the potentials never changed cell parameters by more than 2%. The lattice enthalpies are 221 (α_1) and 234 kJ mol^{-1} (α_2), matching the order of stability and even reproducing exactly (by accident, no doubt) the difference in melting enthalpies. The calculated lattice energy for the acetone inclusion compound is 297.5 kJ mol^{-1} (or a sublimation enthalpy of 310 kJ mol^{-1}, after compensation for the effects of cutoff[7]), and the acetone desorption enthalpies, or $[E(\text{host–guest}) - E(\text{host})]/2$ since there are two solvate molecules, are calculated[8] as 39 and 32 kJ mol^{-1} with respect to each of the two polymorphs. While no experimental value is accessible, this result is at least in line with the visual evidence that the area of the desorption peaks is of the same order of magnitude as that of the melting peaks.[5]

Adaptation of the OPLS force field: There is no well-established force field for the dynamic simulation of such a large molecule as DHMB. The UNI force field has been shown to perform rather well,[2] but is not entirely satisfactory as it has been developed on static simulations. The OPLS all-atom (OPLS-AA) force field[6] is preferable to the less accurate UNI force field for small molecules;[3] its extension to larger molecular systems with possibly high intramolecular strain has not been extensively tested so far. Besides, since the GROMOS[9] molecular dynamics architecture was adopted (OPLS was developed and used mostly in an AMBER environment) some modifications had to be introduced.

For the host DHMB molecule, the bond lengths and angles were taken from the X-ray geometry, as constraints (SHAKE procedure[9]) for the bond lengths and as reference values for angle bending potentials. One improper dihedral was imposed at each phenyl ring carbon atom ($E = 0.051\,\phi^2$,or $E = 0.102\,\phi^2$ over ring and ring fusion carbons, respectively); proper torsions were imposed over each C-C-C-C group $[E = 50(1-\cos 2\phi)]$, to further enforce planarity in the phenyl rings. A proper torsion was also calculated over the central C–C bond in the biphenyl system, with $E = 10(1-\cos 2\,\phi)$ and over the C-C-O-H group, with $E = 1.40(1+\cos 3\,\phi)$.[10]

The OPLS-AA non-bonded interaction and atomic charge parameters were employed without modification (Table 2).

Table 2. The non-bonded force-field parameters.[a]

	R^0 [Å]	ε [kJ mol^{-1}]	atomic charge [e$^-$]
H(aromatic)	2.42	0.1255	0.115
O(alcohol)	3.12	0.7113	−0.683
C(aromatic)	3.55	0.2929	−0.115
H(alcohol)	0.0	0.0	0.418
C(ring fus.)	3.55	0.3180	0.0
C(OH)	3.50	0.2761	0.265
Ac-methyl	3.91	0.6694	0.0
Ac–C	3.75	0.4393	0.50
Ac–O	2.96	0.8786	−0.50

[a] Van der Waals intermolecular potential $E = AR^{-12} - BR^{-6}$, where $A = 4\varepsilon(R^0)^{12}$, $B = 4\varepsilon(R^0)^6$. Mixed interactions use the geometrical mean for ε and R^0.

All atoms within the same phenyl ring were declared excluded neighbours (no non-bonded energy terms), while for 1–4 interactions the non-bonded energy contribution was halved. Each phenyl C–H group and the COH group were taken as GROMOS charge groups. All non-bonded energy summations were extended to 10–17 Å, cutoff problems being somewhat mitigated by the GROMOS artifice of using summations over neutral domains.

The minor modifications introduced in the intramolecular part of the OPLS-AA force field are justified by the resulting very reasonable intramolecular dynamics at all temperatures.

Table 1. Crystal data (cell parameters in Å and degrees).

	a	*b*	*c*	α	β	γ	ρ [g cm^{-3}]	space group
DHMB, α_1	16.827	15.212	10.708	–	97.01	–	1.27	$C2/c$, $Z = 4$
DHMB, α_2	8.807	10.687	16.263	100.97	91.47	113.02	1.25	$P\bar{1}$, $Z = 2$
DHMB-2 Ac	29.169	8.046	15.235	–	–	–	1.18	$Pna2_1$, $Z = 4$

The intermolecular part was used without modifications, and its performance on such a large molecular system is validated by the present results, especially with respect to the reproduction of the crystal density at room temperature. Besides, OPLS-AA had already been used profitably in crystal calculations.[3]

The acetone molecule was treated as a solvent in MD simulations, hence with rigid geometry (planar, C=O = 1.21 Å, C–methyl = 1.50 Å, C-C-C angle 119°). The OPLS united-atom (OPLS-UA) potentials (see ref. [11] and references cited therein) were used, so that the solvent is a four-atom molecule.

The systems investigated: In simulations of the perfect crystal, periodic boundary conditions were applied, and in the resulting NPT ensemble (constant number of particles, pressure and temperature) T was fixed by separately coupling the internal and center-of-mass degrees of freedom to a thermal bath, while pressure was constrained at 1 atm by isotropic coupling. The temperature and pressure weak-coupling constants[9] were 0.1 and 0.5 ps, respectively. Since crystal structures are already at, or very close to, a minimum in potential energy, their simulations were started abruptly by assigning Boltzmann velocities at any given temperature (below 300 K). Periodic boundary conditions were of course preserved in simulations of molten states arising from the collapse of the corresponding crystalline system. Other calculations were done without periodic boundaries, and suffer from surface tension effects.

The host matrix: A set of calculations was performed on a crystal made of 60 molecules (15 unit cells) of the host DHMB alone, assigning velocities at 100 K and then running 120 ps at 330 K, with isotropic periodic boundary conditions. The starting coordinates were obtained from the crystal structure of the inclusion compound, by deleting the guest molecules. The host matrix with empty guest cavities is unstable and quickly collapses to a semi-liquid, or glassy structure: the density rises from 1.09 to a steady 1.12 gmL^{-1} after about 80 ps, as empty cavities are filled, while traces of order of the host molecules are still present. Recrystallization to one of the two polymorphs of pure DHMB could not be observed, since boundary conditions do not allow changes in cell shape. However, this calculation demonstrates that solvent loss must lead to destruction of the host structure.

Hydrogen-bonding in solution: The host–guest hydrogen-bonding equilibrium was then studied in solution. A 500 molecule liquid acetone computational box was equilibrated at 300 K, by using the OPLS-UA force field. One DHMB molecule was then solvated within the bulk liquid, in a niche obtained by deleting 17 acetone molecules, and we checked that no strongly repulsive contacts arose. The simulation was run for 100 ps, with periodic boundary conditions and a cutoff of 17 Å for the non-bonded contributions. The initial configuration had no hydrogen-bonding host–guest contacts.

Figure 1 shows the time evolution of some key energetic parameters. The solute–solvent interaction energies drop to more stabilizing values just after the start of the simulation, while the stiffness of the artificial starting box is released and the first hydrogen bonds form. After a short equilibration time, the energies level off and the average solute–solvent non-bonded energy is about 300 kJ mol^{-1}, of which only about one third is ascribed to electrostatic contributions by the OPLS force field. Figure 2 confirms that hydrogen-bonding contacts are formed almost immediately, with a typical dynamic bond length of 1.7–2.5 Å. The DHMB molecule

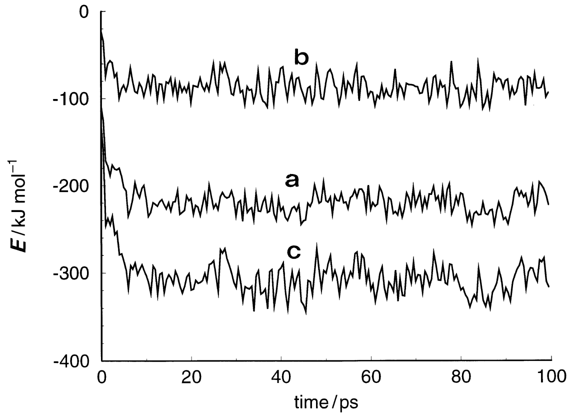

Figure 1. Solute–solvent interaction energies for one DHMB molecule (solute) in 483 acetone molecules (solvent) at 300 K. Dispersive (a) and coulomb-type (b) energies add up to the total energy (c).

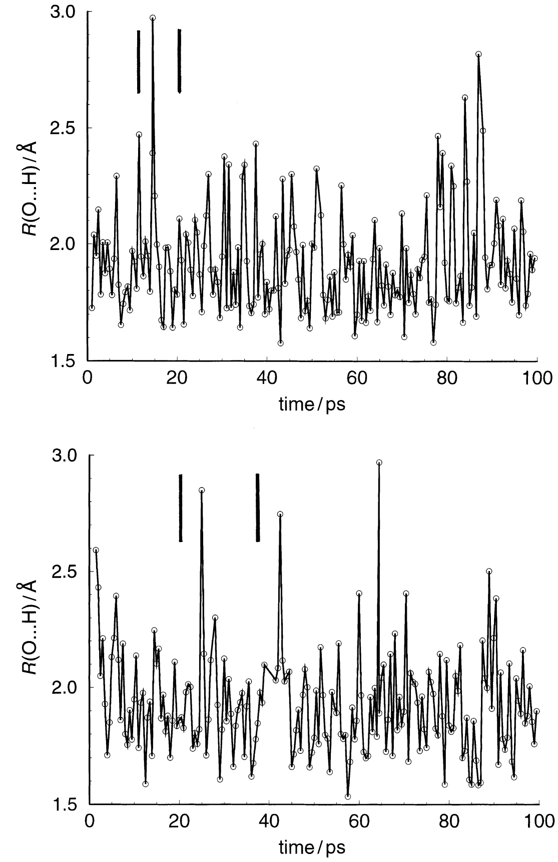

Figure 2. Distance between each of the two donor DHMB hydroxyl hydrogens (upper and lower frame) and the closest acceptor acetone oxygen in solution. The hydrogen bond forms almost immediately, but is fluxional; the acetone partner molecule changes at times denoted by a vertical bar.

captures at once two acetone molecules, and remains H-bonded to the solvent throughout the simulation, although the partners can change. Even in the relatively short simulation time, the average life of a hydrogen bond between DHMB and acetone is seen to go from 5 to 80 ps. Thus, host–guest hydrogen bonding is extremely persistent, although fluxional. Figure 3 shows a typical snapshot of the solvated DHMB molecule.

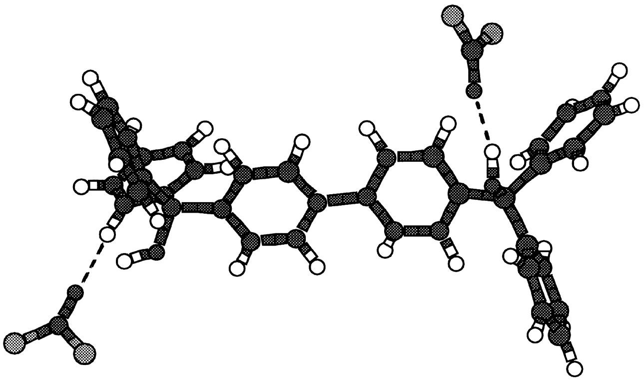

Figure 3. A snapshot of the DHMB-2 Ac complex in solution, with hydrogen bonding distances of 1.8 and 1.9 Å . United-atom methyl groups.

Dynamics of guest molecules: The next set of calculations was planned in order to probe the dynamic behaviour of guest molecules within their cavities. A slab of the inclusion compound crystal was obtained by 1 × 3 × 5 repetition of the unit cell contents (see cell parameters in Table 1), for a total of 60 DHMB and 120 acetone molecules. Periodic boundary conditions were imposed, and the temperature was increased in a stepwise manner from 270 to 407 K. A 14 Å cutoff was used. From an MD estimate of the total energy of the DHMB gas-phase molecule and an estimated equipartition kinetic energy of a rigid acetone molecule with six degrees of freedom and $E(\text{pot}) = 0$, the estimated enthaply of sublimation at 270 K is 360 kJ mol^{-1}, against a static UNI-FF estimate of 310 kJ mol^{-1} (see above). The 14 % difference is within the usual range between force fields that do or do not include electrostatic terms. At 270 K, the calculated cell volume is 3590 Å^3 (experimental 3576 Å^3 at room temperature).

Figure 4 shows the fundamental energetics of the simulation. The host–guest DHMB-2 Ac cohesive energy in the crystal, almost entirely owing to two hydrogen bonds, is about 110 kJ mol^{-1} at 300 K, compared with 300 kJ mol^{-1} for the solute–solvent (solvation) energy, as from Figure 1. These data allow a rough partition of the interaction energy in solution, that is, 55 kJ mol^{-1} for the hydrogen bond and 95 kJ mol^{-1} for purely non-bonding solvation energy. The relative importance of coulombic terms is, as expected, much higher in the hydrogen bond than in the comprehensive host–guest interaction in solution. Even at the highest temperature in this simulation, the host matrix is still quite ordered and host molecules are relatively undistorted.

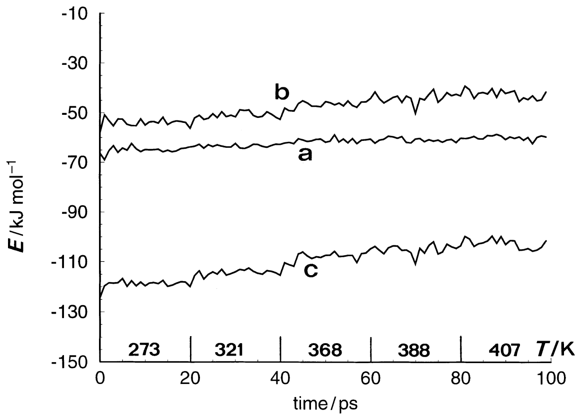

Figure 4. Host–guest interaction energy for the ordered crystal of the inclusion compound (the temperature of the simulation is shown). Dispersive (a) and coulomb-type (b) energies add up to the total energy (c). The temperature was increased every 20 ps, as shown.

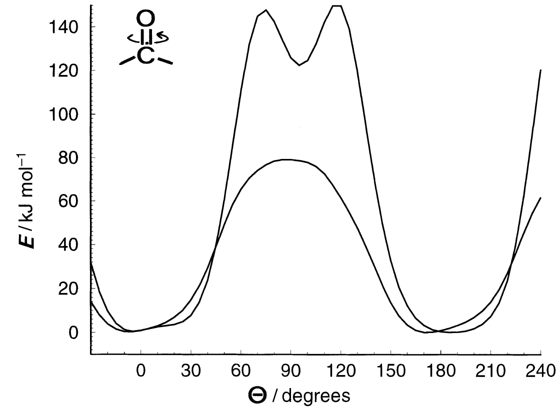

Figure 5. Potential energy barriers for the rotation of each of the two acetone molecules in an undistorted environment within the ordered crystal of the inclusion compound.

The solvent (guest) dynamic was then explored. Figure 5 shows the results of UNI-FF potential energy calculations on a static, undeformed crystal environment.[12]. The bottom of the potential energy well for libration of the guest molecules around the C=O axis is very flat, and a ± 25° libration is within the *RT* range at room temperature. Even complete reorientation jumps are likely, since the barriers calculated with a rigid crystalline environment without intermolecular cooperation largely overestimate the true values.[12] Details of the energy curves far from minima do not deserve a special discussion, being oversensitive to minute changes in the environment, which was not relaxed here.

The MD simulation allows, however, a deeper insight. In the analysis of vibrational trajectories, the guest molecular motion was decomposed into a "swinging" and a "rotation" component. The first is described by the angle the C=O bond vector forms, at any time in the simulation, with the original C=O bond vector in the starting crystal structure; the second is described in the same manner by the vector joining the two methyl groups (approximately the same rotational coordinate as in Figure 5). Although these two coordinates are not strictly orthogonal, the decomposition may serve to give a rough idea of the main librational modes of the guest molecules in the crystal. Figure 6a shows a spread of the swinging component

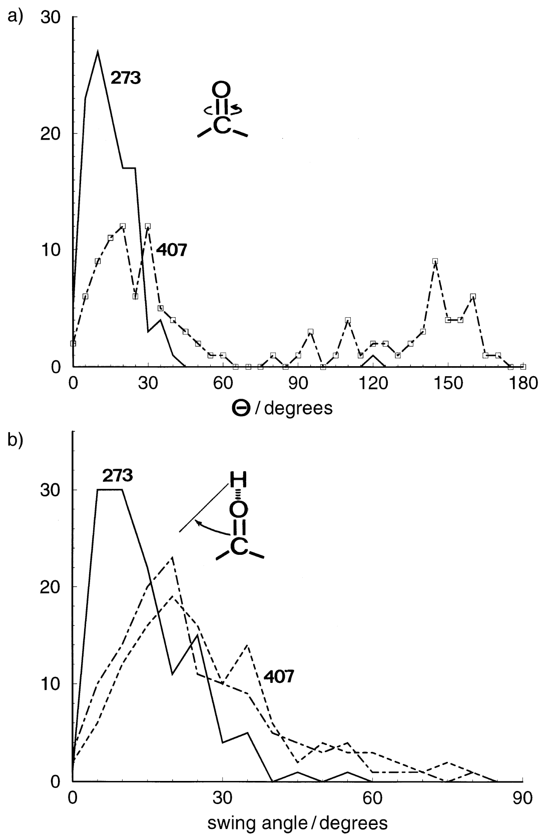

Figure 6. Distribution of a) "swinging" and b) "rotation" angles (shown in insets) during the simulation of the crystalline inclusion compound. Both angles are taken as zero in the X-ray structure of the perfect crystal. Each distribution curve refers to the temperature shown.

over a 60° range at the highest temperature reached in the simulation. Figure 6b shows a sudden drop of the population above 30° and 273 K, in good agreement with the potential curves in Figure 5; this indicates that UNI-FF and OPLS-AA intermolecular force fields yield consistent results. At 407 K a significant number of molecules has performed a complete rotational jump, as inferred by the height of the peak close to 180° in the angular distribution of Figure 6a.

The comparison between the two frames in Figure 7 illustrates the thermal libration and reorientation of guest molecules as the temperature rises. At 407 K the orientational order is almost completely lost, but translational order seems to be still preserved, since centers of mass of guest molecules cluster around the original lattice sites and there have been no real translational displacements. This is plausible since molecules are closely packed, there are no channels, and all cavities are occupied. As expected, the average value of the O···H hydrogen-bonding distance rises steadily from 1.8 to 2.0 Å on going from 300 to 407 K.

Desorption of guest molecules: DSC results[5] show that after guest desorption the material reorganizes to a crystalline state and then melts. Hoping to gain some insight into the molecular detail of this process, a computational system allowing guest escape from the lattice had to be prepared. The most obvious choice was a computational box as in perfect crystal calculations, but without periodic boundary conditions, at the price of generating a presumably very large surface tension on the resulting crystalline slab in vacuo, as well as an exceedingly high surface to bulk ratio. These two approximations certainly help in speeding up the desorption process, thus reducing the timescale of the calculations to be per-

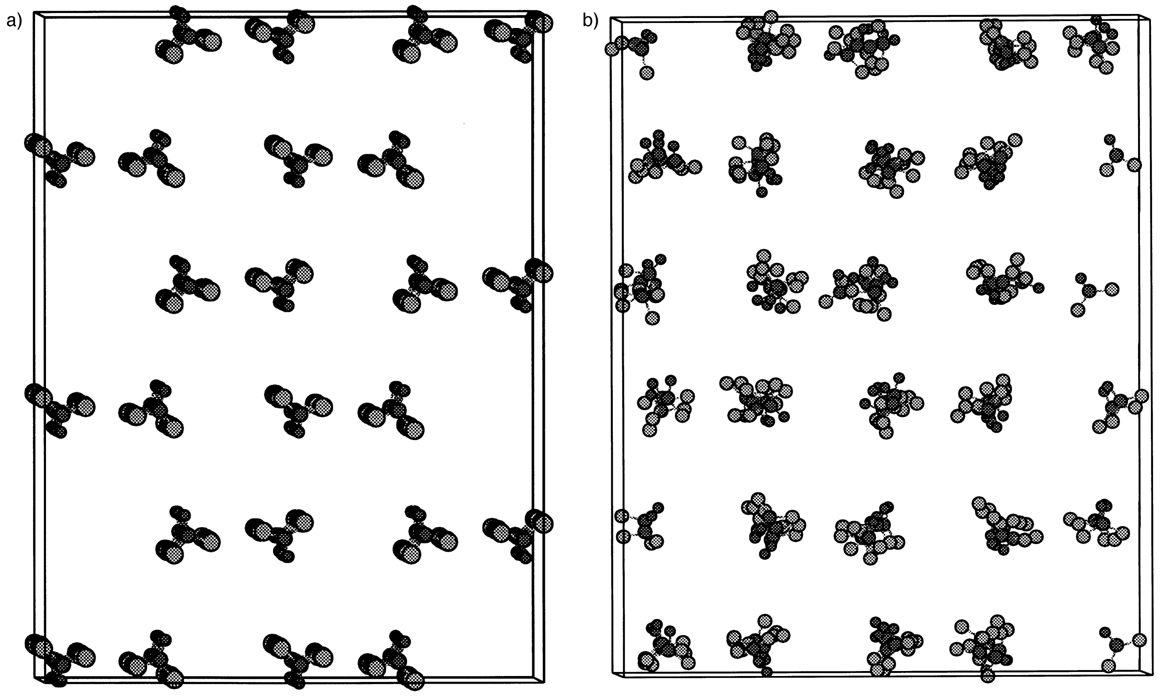

Figure 7. The arrangement of guest molecules in a) the X-ray structure and b) the crystal at the end of the 407 K simulation shown in Figure 4. Although atoms overlap, this picture clearly shows that translational disorder has not set in, since the centers of mass of guest molecules do not show large displacements.

formed, while, it is hoped, not altering substantially the picture of the fundamental molecular desorption process.

The temperature was set at 410 K, intermediate between desorption and melting temperatures, and a cutoff of 14 Å was imposed in intermolecular summations. The starting point for this simulation was the ordered crystal structure. Every 10 ps the simulation was stopped and guest molecules whose center of mass was at a distance greater than 10 Å from the center of mass of any other molecule in the cluster were considered as evaporated and manually removed from the computational box.

Figure 8 shows the energy evolution during the simulation. The traces show a decrease of the total kinetic energy, due to the loss of mass, and a rise of the potential energy, due to loss of cohesive energy as acetone molecules leave the system. The spikes in the kinetic energy curves are due to problems[2] with the distribution of kinetic energies after removal of mass at each restart, but have no influence here since the guest mass is much smaller than the mass of the host. Otherwise, the energetic picture is that of a quick melting of the crystalline slab, followed by a smooth transition toward the simulation of a pure DHMB liquid droplet.

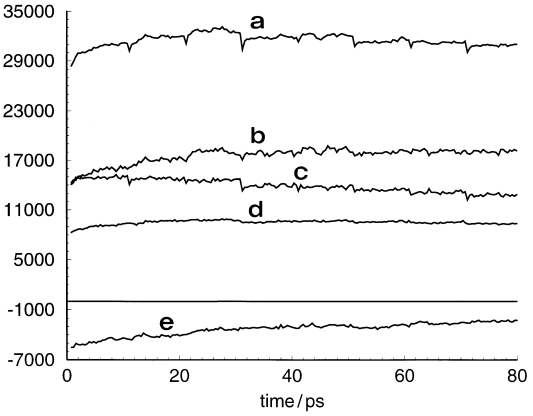

Figure 8. Simulation of the crystalline cluster without periodic boundary conditions. Energies shown are in kJ: a) total configurational, b) total potential, c) total kinetic, d) coulombic and e) dispersive energies. The last two terms include both intra- and intermolecular terms. Energies are not shown per mole because the mass is not constant during the simulation due to solvent loss. The number of remaining acetone molecules at 0, 20, 40, 60 and 80 ps is 120, 101, 61, 34 and 13, respectively.

Just 10 ps after the start of the simulation the initially crystalline system has already collapsed to an almost completely disordered state. This evolution is probably related to surface tension, but collapse to a liquid was observed also in simulations of the host matrix with periodic boundaries (see above). The breaking of the host–guest hydrogen bond at 410 K is almost instantaneous, and more than 50 % of such bonds have been destroyed after just 30 ps. Once the rigid crystalline structure has been distorted, diffusion of guest molecules through the slab and eventually out of the surface seems very easy, 80 ps being sufficient for a nearly complete removal of guests. Examination of graphical displays shows that the size of the main nucleus decreases substantially, while solvent molecules evaporate out. Taken together, the energetic and structural results provide a reasonable picture of the desorption process.

During this simulation, five host molecules evaporated out of the cluster. The dynamics of the 55 remaining DHMB molecules was then simulated for another 200 ps, cooling the system down to 370 K. The system, now a 100 % pure DHMB liquid droplet, did not recover any trace of order, nor could it reasonably have done so in such a short time, in spite of being well below the melting temperature of the host crystals. The simulation yields an approximate vaporization enthalpy of 130 kJ mol^{-1}, and a number of hydrogen bonds oscillating between 30 and 50 (Figure 9). The capability for hydrogen-bonding self-association of the DHMB molecule is remarkable, in spite of steric hindrance and shielding of the OH group by the phenyl rings, but the wide variation in the number of hydrogen bonds in the liquid is probably at the origin of the possible formation of two crystal structures, one with and one without hydrogen bonding. The intermolecular cohesive energy is almost entirely dispersive, in accordance with the overwhelming hydrocarbon character of the DHMB molecule.

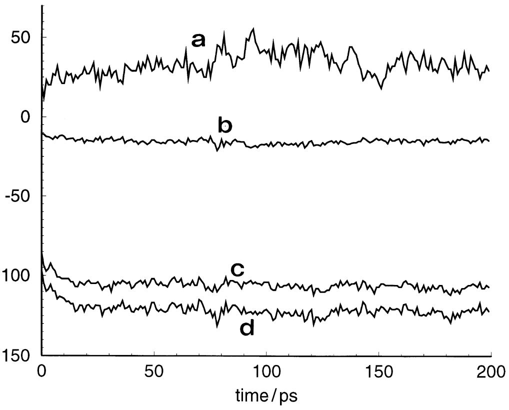

Figure 9. Top to bottom: a) number of hydrogen bonds, b) coulomb energy, c) dispersion energy and d) total intermolecular energy during a simulation of a cluster of 55 host molecules at 370 K with a liquid structure. Energies in kJ mol^{-1}.

Conclusion

1) The crystal structure of the host compound and of the acetone solvate were analyzed, and enthalpies of sublimation and of solvent desorption have been calculated, with good agreement with available thermochemical data.

   Within the usual limitations of molecular dynamics simulations, it appears that:
2) The host cage is not stable without the included guest.
3) The solvation of the host molecule in an acetone solution implies a substantial energetic contribution from bulk attractive solute–solvent intermolecular energies, plus solute–solvent hydrogen bonds, one for each donor H atom of DHMB. These bonds are easily formed and are fluxional, but extremely persistent. Accordingly, the formation of the inclusion compound in the solid state must be described as the crystallization of hydrogen-bonded

entities already present in solution. This could explain the experimental observation that in the crystalline inclusion compounds all guests with acceptor atoms hydrogen-bond to the host.

4) While the host scaffold is still ordered up to 400 K, guest molecules in the crystal have a high librational freedom, and as the temperature is increased full rotational jumps around the C=O axis of the acetone molecule are performed; these jumps have a low activation energy, and might be detected by solid-state variable-temperature NMR spectroscopy. Translational diffusion of guests among different cavities in the fully ordered crystal was not observed up to 400 K.
5) With the further limitations due to the restricted size of the model system—a droplet with high surface/bulk ratio and hence very high surface tension—it further appears that desorption of guest molecules readily occurs at 410 K and produces an almost immediate collapse of the host matrix so that further diffusion and escape of the guest is easy. Remarkably, guest escape does not require a swelling of the material, as the droplet is seen to contract during that process. The pure DHMB liquid resulting at the end of the simulation, when all the guest material had been removed, is moderately hydrogen-bonded: this finding is in agreement with the observation of two crystalline polymorphs of DHMB, one with and one without hydrogen bonding. More significantly perhaps, it should be noted that the non-hydrogen-bonded polymorph was crystallized from ethyl ether (an H-bonding acceptor substance) while the hydrogen-bonded polymorph was crystallized from o-xylene.

The picture that MD gives of the molecular recognition in solution and of the librational motions of the guest molecules in the crystal below the desorption temperature is consistent and convincing. Significantly, for some purposes the UNI-FF force field may compete with more sophisticated force fields as to the quality of results.

On the other hand, the interpretation of the above results along with thermal analysis data is not simple. Our simulations clearly suggest that guest desorption is followed by a liquid state of the host material. The fact that no recrystallization exotherm is observed in DSC after desorption may contradict this result, but it may be argued that the heat release as a result of crystallization is simultaneous to, and masked by, heat intake due to guest desorption. That a complex reorganization is taking place is indicated by the rounded shape and indentations of the DSC desorption peaks. There is no doubt that if a liquid phase is formed, it is metastable since the temperature of desorption is well below the melting temperature, so that the material must recrystallize. As usual, the MD simulation cannot indicate if or when a reorganization to a crystalline state may occur, due to severe limitations in its time span.

Our results demonstrate, we believe, that even size- and time-restricted molecular dynamics simulations can give a substantial help in the interpretation of evolution and phase changes in crystalline systems. Whether such studies may pave the way to prediction and control of crystal packing or of host–guest design remains to be seen. We suggest that for a better exploitation of the simulation techniques and, eventually, for the success of these predictive exercises what is needed is, rather than a manifold increase in computing power, a sound choice of the system and a clever design of the computational experiment.

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