Do Nitromethane and Malononitrile form C–H · · · O Hydrogen Bonds? Implications for Molecular Recognition by Crown Ethers

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Using *ab initio* methods at the 6-31G**//6-31G** level of sophistication, we demonstrate that while malononitrile is capable of forming C–H · · · O hydrogen bonds with a neutral oxygen donor, nitromethane shows no tendency to form this type of bonding interaction.

For over a decade, it has been hypothesized[1] that C–H · · · O hydrogen bonding[2]† is of major importance in determining the binding efficiency of simple organic molecules to host systems such as 18-crown-6.[1] Three particularly notable guest molecules for which such C–H · · · O hydrogen bonding has been suggested are acetonitrile, nitromethane (**1**), and malononitrile (**2**).[1] Previous studies from our laboratories[3] have shown that acetonitrile exhibits no tendency to form C–H · · · O hydrogen bonds. This interaction, therefore, cannot properly be considered important in determining the complexation efficiency of acetonitrile with 18-crown-6. The present study was undertaken in order to determine whether (**1**) and (**2**) are capable of forming C–H · · · O hydrogen bonds with simple neutral oxygen donors. The results of this work have direct implications for the molecular recognition of (**1**) and (**2**) by crown ether hosts.

In order to explore C–H · · · O hydrogen bonding in (**1**) and (**2**), we performed *ab initio* calculations at the 6–31G** level of sophistication using the program Gaussian 82 (G82).[4] This level of theory was chosen because of its well known ability to accurately represent intermolecular hydrogen bonding interactions.[5] Water was used as a model for the ether oxygens in 18-crown-6 since it has been previously demonstrated[6] that exchange of donor oxygen alkyl groups with hydrogens causes little perturbation on H · · · O hydrogen bond strengths. Since our objective was to determine whether (**1**) and (**2**) are capable of forming C–H · · · O hydrogen bonding interactions with a neutral oxygen donor, we employed one water donor molecule for this study. Water, (**1**), and (**2**) were optimized for C_{2v}, C_s, and C_{2v} symmetry, respectively. For both (**1**) and (**2**), 1 : 1 complexes with water were considered. To allow for the greatest possible C–H · · · O interaction, linear C–H · · · O arrangements were used as input. All complexes were completely optimized under C_s symmetry at the 6-31G** level (*i.e.*, 6-31G**//6-31G**). Figure 1 shows the input and optimized configurations for complexes of (**1**) and (**2**).

Nitromethane (**1**) forms a 2 : 1 complex with both 18-crown-6[1c,d] and dibenzo-18-crown-6[1e] in the solid state. Evidence for the formation of C–H · · · O hydrogen bonds between (**1**) and these crown ethers is based upon the close C · · · O contacts observed in the complexes. These C · · · O distances are typical for heavy atom separations in hydrogen bonded systems (av. 3.28 and 3.39 Å, respectively). Additional evidence for the formation of C–H · · · O hydrogen bonds by (**1**) has been obtained from liquid–vapour equilibria studies[7] that hypothesize C–H · · · O bonding interactions between the carbonyl oxygen of acetone and the C–H bonds of (**1**).

Since the close contacts observed in the crystal structures of complexes of (**1**) do not necessarily imply bonding interactions,[2d] we explored the possibility of C–H · · · O hydrogen bonding in (**1**) computationally. When (**1a**), the linear C–H · · · O structure for the 1 : 1 water–(**1**) complex (Figure 1), was subjected to full geometry optimization at the 6–31G** level, no potential energy minimum was found in the C–H region. Instead, structure (**1b**) (Figure 1), in which water and (**1**) are oriented in a 'side-by-side' configuration, was obtained. This structure has a binding energy of −5.6 kcal mol^{-1} (1 cal = 4.184 J) and is similar to the 'side-by-side' structure observed for the acetonitrile–water complex.[3] Repeated searches in the C–H region of (**1**) did not yield a C–H · · · O hydrogen bonded minimum for (**1**). For example, even when an input structure with a C–H · · · O angle of 175° (directed toward the cavity formed by the three C–H bonds of the methyl group) was employed, geometry optimization consistently yielded (**1b**).

We conclude from these studies that (**1a**) is not a minimum on the (**1**)–water potential energy surface. We see no evidence for the formation of C–H · · · O hydrogen bonds by (**1**) with this simple oxygen donor.‡ We therefore suggest that close contacts between the C–H groups of (**1**) and crown ether oxygens cannot reasonably be taken as indicative of C–H · · ·

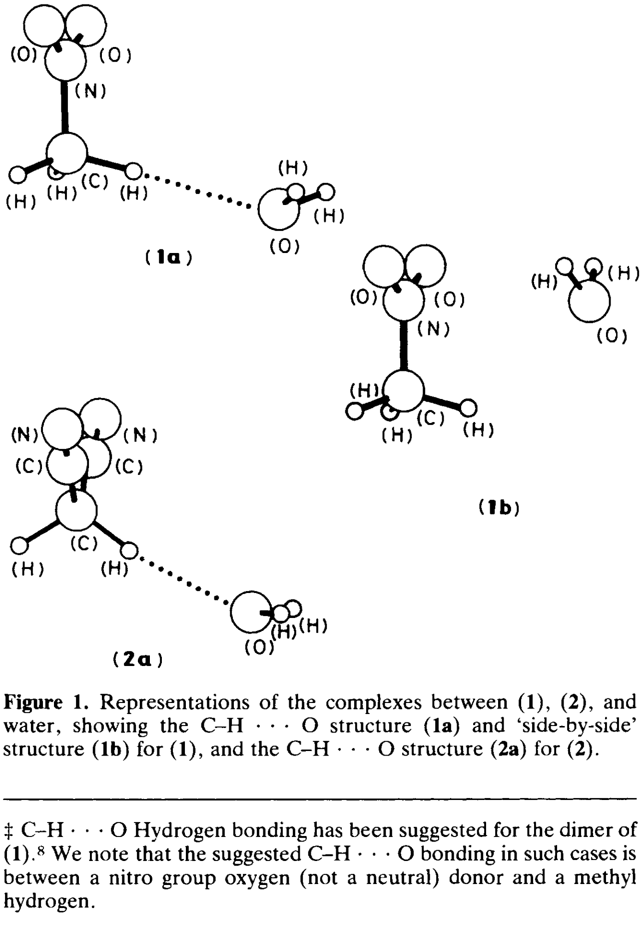

Figure 1. Representations of the complexes between (**1**), (**2**), and water, showing the C–H · · · O structure (**1a**) and 'side-by-side' structure (**1b**) for (**1**), and the C–H · · · O structure (**2a**) for (**2**).

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† We use the term hydrogen bonding to describe a directed (near linear), attractive C–H · · · O interaction at a potential energy minimum on the intermolecular hypersurface.

‡ C–H · · · O Hydrogen bonding has been suggested for the dimer of (**1**).[8] We note that the suggested C–H · · · O bonding in such cases is between a nitro group oxygen (not a neutral) donor and a methyl hydrogen.

O hydrogen bonding in these complexes. Evidently, these close contacts are the result of other favourable intermolecular interactions (such as dipole–dipole and Van der Waals interactions) being most favourable in this configuration.

The efficiency of malononitrile (**2**)–crown ether complexation has been attributed, in part, to the relatively strong C–H · · · O hydrogen bonds that form between the activated (polar) methylene group of (**2**) and the crown ether oxygens.[1] Crystallographic evidence supports this interpretation, with close C · · · O contacts in these complexes averaging 3.33 Å.[9] In addition, solution studies of the formation constant for the (**2**)–HMPA (HMPA = hexamethylphosphoramide) complex[10] ($K = 60.0 \pm 0.06$ M^{-1}) indicate that (**2**) forms one of the stronger C–H · · · O hydrogen bonds reported for neutral systems.

For the complex between (**2**) and water [(**2a**), Figure 1] we calculate a hydrogen bond strength of -5.4 kcal mol^{-1}. This remarkably strong, neutral C–H · · · O hydrogen bond is comparable in energy to the linear O–H · · · O hydrogen bond experimentally found for the water dimer (4.8—7.7 kcal mol^{-1}).[11] The structural details of (**2a**) are also consistent with the formation of a C–H · · · O hydrogen bond.† The C–H · · · O angle (170.3°) is nearly linear and strongly suggestive of significant bonding interactions.

Since there is strong evidence for C–H · · · O hydrogen bonding in (**2**), the question arises as to the importance of C–H · · · O hydrogen bonding in determining the efficiency of complexation of (**2**) with crown ethers. The binding enthalpy (ΔH) for 1:1 complexation of (**2**) with 18-crown-6 is -14.2 kcal mol^{-1}.[1c] While the C–H · · · O bond energy of -5.4 kcal mol^{-1} may seem large enough to account for a considerable portion of the binding energy (considering two C–H · · · O bonds), it is important to note that (**2a**) represents an optimal arrangement for C–H · · · O hydrogen bonding. The C–H · · · O assemblage is nearly linear, and each interaction is between a single donor and acceptor. Inspection of the crystal structure of complexes of (**2**)[9] indicates that C–H · · · O bonds to (**2**) can be non-linear and are often part of bifurcated hydrogen bonding arrangements. Since both of these factors may significantly reduce the hydrogen bond strengths from their optimal values (-5.4 kcal mol^{-1}), the binding energy calculated for (**2a**) serves as an upper limit to the C–H · · · O bond strengths in these complexes.§

In summary, we conclude that C–H · · · O hydrogen bonding with neutral oxygen donors is not important for (**1**). In contrast, we find that (**2**) is capable of forming C–H · · · O hydrogen bonds that may be as stable as -5.4 kcal mol^{-1}. These results imply that C–H · · · O hydrogen bonding may be important in the molecular recognition of (**2**) by crown ethers, however, for (**1**) this type of hydrogen bonding interaction is probably not involved. While greater for (**2**) than for (**1**), all experimental evidence to date[1] was consistent with both guests forming C–H · · · O hydrogen bonds with neutral oxygen donors such as the crown ethers. Computational techniques (in this case, *ab initio* calculations) made it possible to determine accurately whether C–H · · · O hydrogen bonding is important in the molecular recognition of these molecules.

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§ Assuming that there are no positive co-operativity effects involved in C–H · · · O hydrogen bond formation with more than one oxygen donor. Our preliminary investigations of hydrogen bonding between (**2**) and two water molecules supports this position.[12]