

MEETING REPORT

Hydrogen bonding and other molecular interactions*

The International Union of Pure and Applied Chemistry (IUPAC) formed a task group of fifteen international experts to categorize hydrogen bonding and other molecular interactions, co-chaired by E. Arunan (Indian Institute of Science (IISc), Bangalore, India) and S. Scheiner (Utah State University, USA). This followed the initiative by Arunan and appears to be the first IUPAC project initiated from India. The details about the project and task group members may be found in the IUPAC website: <http://www.iupac.org/projects/2004/2004-026-2-100.html>. The objective of the task group is 'To take a comprehensive look at intermolecular interactions and classify them, and to give a modern definition of the hydrogen bond, taking into account all current experimental and theoretical information, and including hydrogen bonded systems both in gaseous and condensed phases as well as in chemical and biological systems'. A workshop was held in Pisa, Italy during 5–9 September 2005, in which 11 task group members and 11 other experts each gave a 30-minute presentation on their recent work relevant to the project. The details of this workshop are available in the website: http://institut.physiochem.uni-bonn.de/IUPAC_Pisa2005/Workshop.html. R. A. Klein (University of Bonn, Germany) and B. Mennucci (University of Pisa, Italy) from the task group took care of the local organization and Klein and Arunan put together the programme. A report from the meeting was submitted to IUPAC earlier and is available at the IUPAC website: <http://www.iupac.org/projects/2004/2004-026-2-100.html>.

A core group consisting of Arunan, G. R. Desiraju (Hyderabad University), R. A. Klein and J. Sadlej (University of Warsaw, Poland) met in Bangalore on 17 and 18 September 2006 to finalize the recommendation. Co-chairman Scheiner was available through video-conferenc-

ing. Along with the core group meeting, a one-day Discussion Meeting on Hydrogen Bonding and Other Molecular Interactions was held at the Department of Inorganic and Physical Chemistry, IISc on 18 September 2006. This included talks by the core group members and five other experts.

The meeting began with the welcome address by K. L. Sebastian (IISc). V. Krishnan (Chairman of the IUPAC operations in India), briefly summarized the activities of IUPAC and also informed the audience about the project mode of IUPAC. He also pointed out the contributions from India to IUPAC. C. N. R. Rao (JNCASR, Bangalore) had served as the President of IUPAC and G. Mehta (IISc) is currently serving as the President of the International Council of Scientific Unions. P. Balaram (IISc) gave a brief inaugural address. He pointed out the complex nature of hydrogen bonding and sympathized with the efforts of the task group. He also pointed out that G. N. Ramachandran had discussed the C–H...O interactions in its early days.

Arunan gave a brief introduction to the project and pointed out the diverse views existing in the literature on the definition of hydrogen bonding and on van der Waals interactions. It appears that there is an overwhelming opinion in the literature that these two interactions are different. However, there is no consensus on the definition of either one of them. Desiraju gave the first talk titled 'The C–H...O and other weak hydrogen bonds: From crystal engineering to virtual screening'. His talk summarized the voluminous literature existing in the domain of 'weak' hydrogen bonds. In particular, he pointed out that C–H...F interactions can be unambiguously identified from the Cambridge Crystal Structure Database, if the search is limited to fluorobenzenes rather than all molecules containing C–H and F, and other atoms. Guru Row presented results on experimental electron densities on substituted coumarins. Using Koch and Popelier's criteria (Koch, U. and Popelier, P. L. A., *J. Phys. Chem.*, 1995, **99**, 9747), he showed that the C–H...O interactions found in these systems could be classified as hydrogen bonding but the

C–H... π interactions would be van der Waals. The key criterion that leads to this difference is the mutual penetration of atoms which depends crucially on the assumed van der Waals radii of the two bonding partners. He also presented results on organic fluorine compounds that show a bond critical point between C and F groups implying C–F...F–C contacts.

Sadlej presented theoretical results on IR and NMR spectral properties of water clusters as a doorway to the mysteries of liquid water. She presented the OH stretching frequencies for (H₂O)_n ($n = 3 = 12$) and compared them with available experimental results. Sadlej also presented ¹⁷O and ¹H chemical shifts and ¹J_{OH} and ²J_{OO} spin–spin coupling constants for several clusters. She ended her talk with a question: Do these clusters really exist in liquid water? Sathyamurthy gave a talk entitled 'Hydrogen bonding without borders'. He showed that the binding energies for dimers have a linear relationship with the electron densities and the Laplacian at the bond critical points for hydrogen-bonded complexes, from Ar-CH₄ to (H₃O)⁺H₂O. He discussed the π – π interactions in a series of aromatic compounds with and without permanent dipole moments. Jemmis gave the last lecture in the morning session titled 'The long and short of weak hydrogen bonds'. He presented electronic structure calculations on several C–H...Y hydrogen-bonded systems. Optimization of C–H distance and energy as a function of H...Y distance revealed that the minimum in binding energy need not be at the minimum for the C–H distance. Hence, the C–H bond length at the energy minimum could be longer, shorter or unchanged compared to the C–H distance in the unperturbed monomer. This could explain both red and blue shifting of C–H groups that are observed in hydrogen-bonded systems.

Klein gave the first talk in the afternoon titled 'Characterizing hydrogen bonding: Creation and genesis'. He argued that a bond critical point must be present between the H and the acceptor atom. He pointed out the inadequacy of single van der Waals radii of atoms in confirming/ruling out hydrogen bonding. He also showed that the attractive hyper-conjuga-

*Report of a one-day Discussion Meeting on the Hydrogen Bonding and Other Molecular Interactions held at the Inorganic and Physical Chemistry Department, Indian Institute of Science, Bangalore, as part of an IUPAC Project.

tive effects exceed Pauli exchange (steric) repulsion at the optimum geometry for hydrogen-bonded systems. Naresh Patwari presented a talk titled 'Is dihydrogen bonding analogous to hydrogen bonding?' He showed the strong correlation between proton affinity of the acceptor and the shift observed in O–H stretching frequency in a series of hydrogen-bonded complexes. However, for dihydrogen-bonded complexes, this correlation worked only with an empirical correction of 0.84, i.e. dihydrogen-bonded systems are similar to hydrogen bonds, but 16% weaker.

Viswanathan spoke about hydrogen bonds in cryogenic matrices. He presented infrared spectra of several hydrogen-bonded complexes observed in a matrix and showed that the experimental frequency shifts had a good correlation with the computed frequency shifts and also the binding energies of the hydrogen-bonded complexes. Arunan gave the last talk of the day titled 'Hydrogen bond radii: From microwave spectroscopic, *ab initio* and AIM studies'. He presented microwave spectroscopic results on several H₂O and H₂S complexes and showed the structural similarities between these complexes. He also showed that the H...Y distance could be written as a sum of hydrogen bond radius for X–H donor and an acceptor radius for Y. He presented theoretical results from *ab initio* and AIM calculations and showed that both the donor and acceptor radii increase from strong to medium to weak hydrogen bonds. He presented a set of 'hydrogen bond radii' that may be used instead of the single set of van der Waals radii for all atoms in

confirming/ruling out the presence of hydrogen bonds.

There was panel discussion at the end that involved all the participants (about 100). The discussion centred around the use of experimental and theoretical electron density topology in confirming/ruling out hydrogen bonds. Arunan presented the evolving definition of hydrogen bonding and sought comments from everyone. After the meeting, the core group finalized the recommendation and started working on a manuscript that will justify their recommendation. This recommendation was circulated within the task group and was revised based on suggestions/criticisms.

There was a unanimous view among the task group and the participants in both meetings that there is no single physical force that can be characterized as hydrogen bonding or van der Waals interaction. This may be contrasted with covalent bonding (as in H₂ molecule), ionic bonding (as in KCl molecule in the gas phase) and London dispersion forces (as in Ar₂). Hydrogen bonding is used by various scientists to describe interactions in extremes that can be well summarized by an isoelectronic series, (FHF)[−], HF...HF and Ne...HF, suggested by A. C. Legon (member of the task group from University of Bristol). In (FHF)[−], we have a very strong hydrogen bond with a binding energy of 167 kJ mol^{−1} (Elgobashi, N. and González, L., *J. Chem. Phys.*, 2006, **124**, 174308) that borders a covalent bond. In HF...HF, we have a typical hydrogen bond with a binding energy of 19 kJ mol^{−1} (Klopper, W., Quack, M. and Suhm, M. A., *J.*

Chem. Phys., 1998, **108**, 10096) that is dominated by electrostatic forces. Finally in Ne...HF, we have a weak interaction with a binding energy of 1 kJ mol^{−1} (Meuwly, M. and Hutson, J. M., *J. Chem. Phys.*, 1999, **110**, 8338) dominated by dispersive and inductive forces.

For hydrogen bonding, the proposed definition follows closely the one given by Pimentel and McClellan (Pimentel, G. C. and McClellan, A. L., *The Hydrogen Bond*, W. H. Freeman and Co, San Francisco, 1960). It was decided to propose a short definition and a list of criteria and characteristics for hydrogen bonding. The short definition would be: The hydrogen bond is an attractive interaction between the hydrogen from a group X–H and an atom or a group of atoms Y, in the same or different molecule(s), where there is evidence of bond formation'. The most important criteria for a hydrogen bond are: (i) the H in the X–H group is more electropositive than X and (ii) the physical forces involved in hydrogen bonding should include attractive electrostatic forces, i.e. it should not be primarily dispersive forces. A detailed recommendation for classification of intermolecular forces and the rationale for the proposed definition of hydrogen bonding will be submitted to IUPAC shortly. Any comments/criticism can be sent to arunan@ipc.iisc.ernet.in or scheiner@cc.usu.edu.

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