Theoretical models of directional proton molecular transport

Ibon Alkorta* and José Elguero

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The important topic of proton transport through molecular wires is usually associated with the Grotthuss mechanism. In this paper we propose an alternative conductor based on chains of lone pairs. B3LYP/6–31+G** and PW91 DFT calculations on model compounds (1,2,3,4-tetrasubstituted benzenes) show that these compounds could play the role of proton conductors.

Introduction

Chemistry today has two main avenues: biological and materials sciences. In both, proton transport is fundamental. The transport of protons across membranes is an essential process for the bioenergetics of cells as well as for the origin of cellular life. All living systems make use of proton gradients across cell walls to convert environmental energy into a high-energy chemical compound, adenosine triphosphate (ATP), synthesized from adenosine diphosphate (ADP). ATP, in turn, is used as a source of energy to drive many cellular reactions. In cells, proton transfer is assisted by large, complex proteins embedded in membranes.[1] Protonic conduction in liquid electrolytes, such as polymer electrolyte membranes (PEM), is commonplace but is relatively rare in solids. There is currently much interest worldwide in proton conducting solids, both from the scientific aspect, as materials with novel properties, and also for their possible applications in high density solid-state batteries, sensors and other electrochemical devices.[2,3]

As early as 1806, von Grotthuss proposed a mechanism which is still in use.[4] The Grotthuss mechanism, also known as "hopping" or a "hop-turn" mechanism, is represented in Fig. 1 for the case of an alcohol, a phenol or water. On the top is a lateral view and on the bottom a perpendicular one. Water is a good conductor of protons, because of the H-bonded networks between water molecules that give water its liquid properties in the physiological range. In ice, the H-bonded networks are more extensive, and ice is a better proton conductor than liquid water.

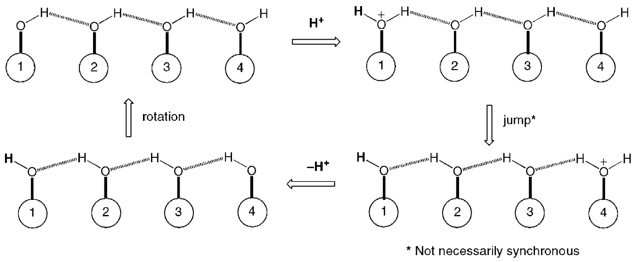


Fig. 1 The Grotthuss mechanism.

Many experimental and theoretical papers have been devoted to the conduction of protons along HBs, starting from the classical works of Bernal and Fowler,[5] Conway *et al.*,[6] and Eigen and DeMaeyer,[7] to a series of recent books and reviews.[8–12] Relevant experimental studies are those reporting proton transfer of phenols in ammonia as solvent,[13] the nature of proton wires in proteins,[14] the proton transfer and reorientation in an imidazole melt,[15] and the use of ultrafast IR spectroscopy to study the mechanism of proton transfer.[16] The theoretical studies, partly already cited,[1c,1d,4b,4d] concern proton tunnelling,[17] proton transport in water,[18] and the discussion of the Grotthuss mechanism in ammonia–ammonium mixtures.[19]

Of particular relevance for the present paper are those of Brédas *et al.*[20,21] In the first one, they propose a model of soliton formation and reorientation (Fig. 2). The conductivity along the HB chain is protonic in nature and the mechanism implies successive (**1**, **2**, ·) reorientations about the C2–C4/C5 axis. The proton transfer changes positions 4 and 5 of the imidazole ring (tautomerism). The reorientation process could thus correspond to the limiting step for the protonic conductivity in imidazole crystals.[20]

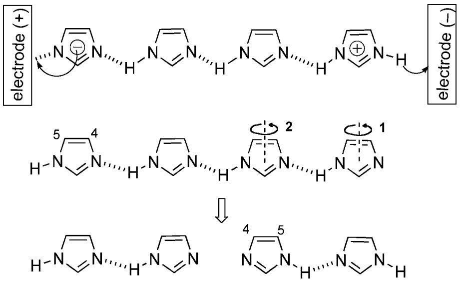


Fig. 2 The Brédas mechanism for poly[4(5)-vinylimidazole].

In the more recent paper,[21] they explain why the proton conductivity of poly[4(5)-vinyl-1*H*-1,2,3-triazole] is about 10^5 times higher than that of poly[4(5)-vinylimidazole] by the mechanism represented in Fig. 3, where instead of a perpendicular 180° rotation only a lateral rotation of about 70° is involved.

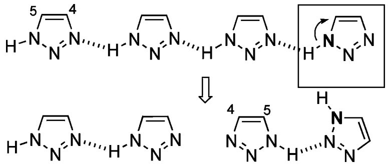


Fig. 3 The Liu–Brédas mechanism for poly[4(5)-vinyl-1*H*-1,2,3-triazole].

Instituto de Química Médica (CSIC), Juan de la Cierva 3, E-28006, Madrid, Spain

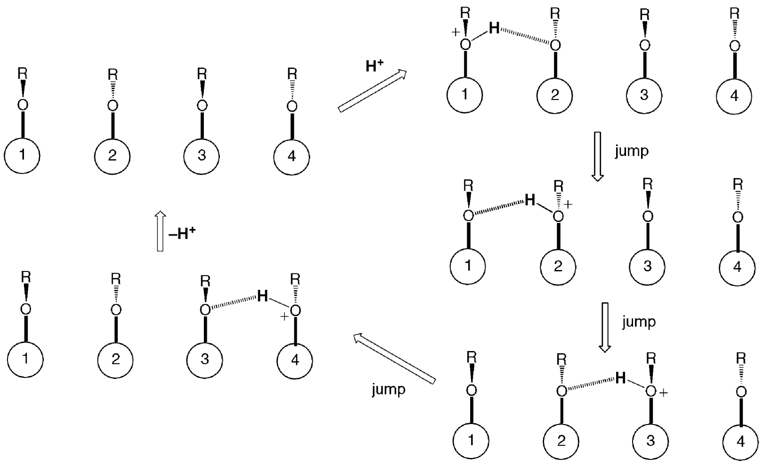


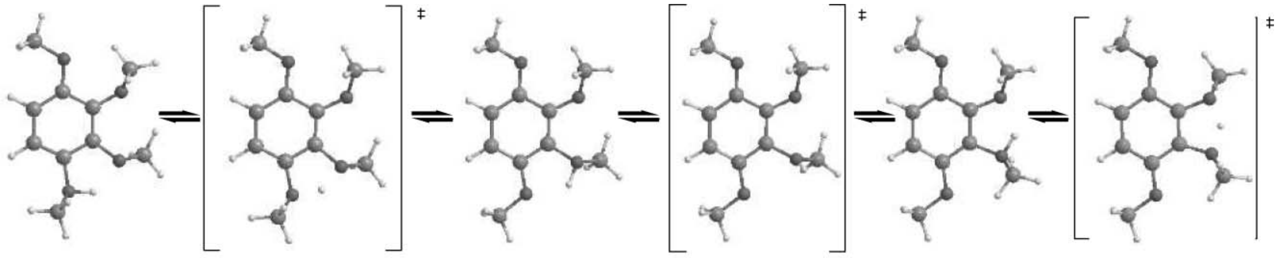
Fig. 4 The "caterpillar" proton conduction.

Results and discussion

All these mechanisms without exception involve a HB chain, and the proton that enters the chain does not exit until it has covered the whole of the chain length. We would like to propose a new type of proton conductor without protons on the wire, where the proton that enters the wire is the same as that which exits at the end of the course (Fig. 4). The only requirement is a series of lone pairs conveniently disposed.

To theoretically explore this possibility we have chosen two models. In both cases, the rigid framework that put all the lone pairs in the adequate position and proximity is a benzene ring bearing four substituents at the 1,2,3,4 positions. These substituents are in one case methoxy groups **1** and in the other 2*H*-1,2,3-triazolyl residues **2**. DFT calculations have been carried out using the B3LYP and PW91 functionals and the 6-31+G** basis set. All structures of the minima and the transition states have either no imaginary frequencies or one imaginary frequency, respectively.

The relative energies are reported in Table 1 and the different structures depicted in Fig. 5 and 6. Once the last transition state is attained (on the right), the inverse path leads to the starting material. Obviously, the driving force should be an excess of proton

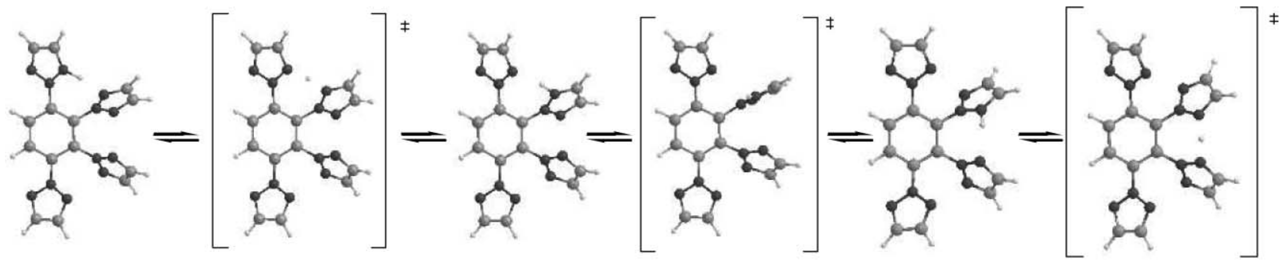


1a **1b** **1c** **1d** **1e** **1f**

Fig. 5 The case of 1,2,3,4-tetramethoxybenzene **1**.

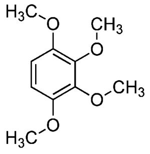
Table 1 Relative energies (E_{rel}/kJ mol^{-1}) of the different structures for compounds **1**, **2** and **3** with different corrections

Compound	E_{rel}	B3LYP E_{rel} + ZPE	ΔG°_{298}	E_{rel}	PW91 E_{rel} + ZPE	ΔG°_{298}
1a	16.54	14.50	12.58	15.58	13.34	11.65
1b	24.40	13.48	13.69	17.26	8.63	8.61
1c	4.67	4.70	3.26	8.57	9.52	7.02
1d	27.09	23.83	21.52	34.92	33.41	30.09
1e	**0.00**	**0.00**	**0.00**	**0.00**	0.00	0.00
1f	10.77	1.24	4.92	3.29	−4.22	−1.03
2a	10.32	8.49	8.79	6.89	4.48	4.30
2b	16.67	5.39	7.15	8.68	−0.69	0.21
2c	7.19	6.18	5.81	5.49	3.84	3.26
2d	10.86	10.85	11.67	15.35	16.80	16.62
2e	**0.00**	**0.00**	**0.00**	**0.00**	0.00	0.00
2f	13.70	2.84	5.14	4.99	−3.87	−2.26
3a	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**
3b	22.42	14.00	16.28	11.56	4.21	6.64
3c	5.49	4.00	2.44	7.11	5.92	2.73
3d	35.18	25.33	27.04	24.89	16.34	18.31



2a **2b** **2c** **2d** **2e** **2f**

Fig. 6 The case of 1,2,3,4-tetra(2*H*-1,2,3-triazolyl)benzene **2**.



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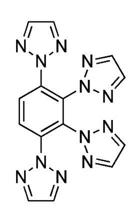

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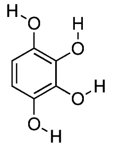

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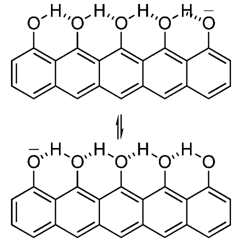

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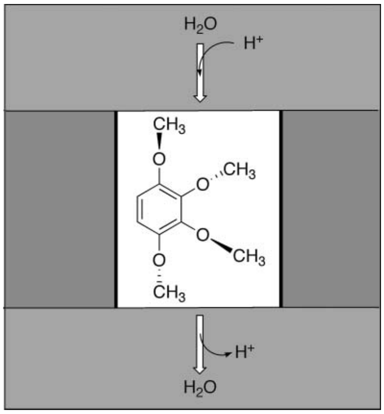


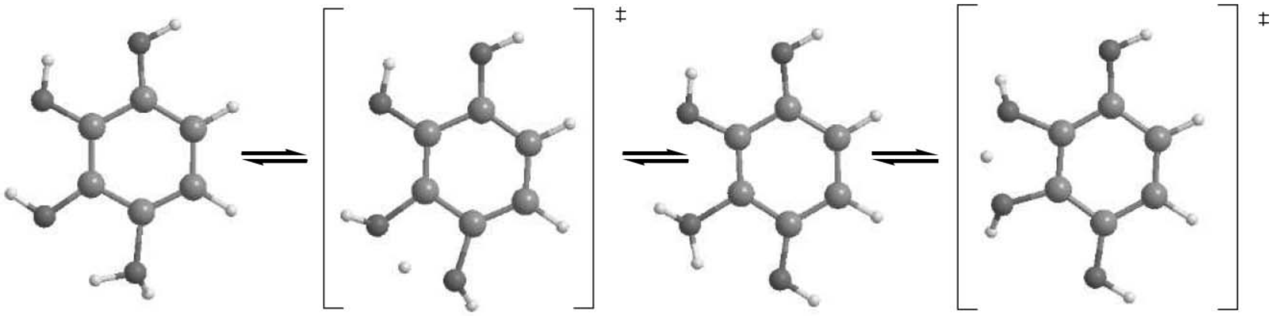
Fig. 7 1,2,3,4-Tetramethoxybenzene in an interphase.

in one extremity and a deficiency in the other, *e.g.* a gradient of pH (Fig. 7).

For comparative purposes we have studied the "classical" case of benzene-1,2,3,4-tetraol **3** (Fig. 8) where the proton transfer should occur by the Grotthuss mechanism forcing the OH groups to rotate to come back to the starting structure. Note that Brzezinski and Zundel[9c,9d] have studied experimentally by FTIR the related case of pentacene anion **4** (tetrabutylammonium salt) where the proton motion is coupled to an electron motion.

We have represented in Fig. 9 the profiles corresponding to E_{rel} (Table 1). In the case of the B3LYP/6-31+G** calculation and for compound **1**, the structure of minimum energy is **1e** and the highest TS (transition state) is **1d**. The relative effect of the ZPE (zero point energy) correction is very marked in **1b** (45%) and **1f** (88%) but very small in **1a** (12%), **1c** (<1%) and **1d** (12%). Similarly, in the case of **2**, the structure of minimum energy is **2e** and the highest TS depends on the ZPE correction, without it is **2b** and with it is **2d**. The relative effect of the ZPE correction is very marked in **2b** (68%) and **2f** (79%) but very small in **2a** (18%), **2c** (14%) and **2d** (<1%). Note that cases **b** and **f** correspond to proton-transfer TSs.

In both cases, and in the absence of a pH gradient, the prototropy would stop in the middle, **1e** and **2e**. Otherwise, the process will occur with an activation barrier of 24–27 kJ mol^{-1} for **1** and 11–17 kJ mol^{-1} for **2**. Thus the second model is much more efficient as proton wire. The classical tetraol **3** has its minimum not



3a **3b** **3c** **3d**

Fig. 8 The case of benzene-1,2,3,4-tetraol **3**.

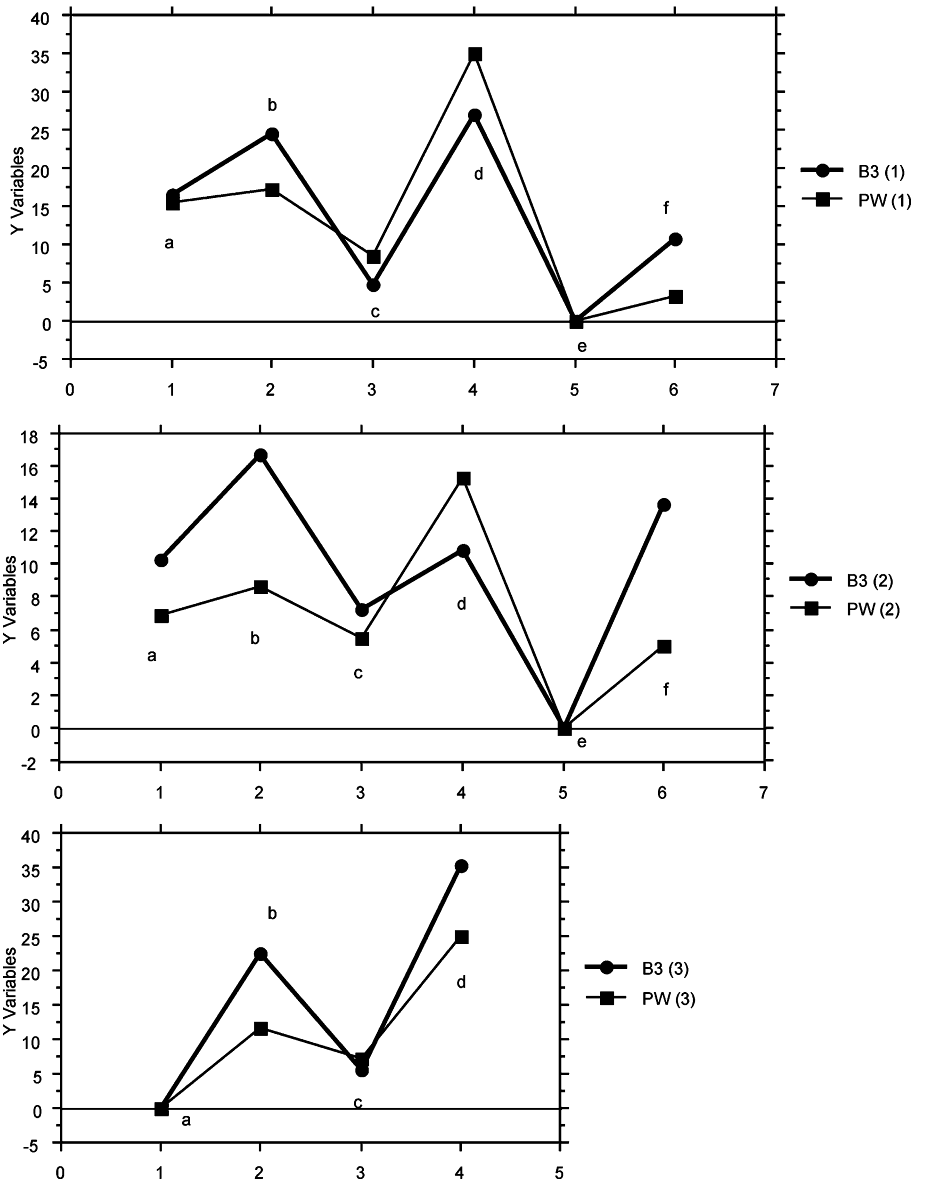


Fig. 9 The energy profiles for molecules **1**, **2** an **3** (B3 stands for B3LYP and PW for PW91). The Y axis corresponds to the relative energies (kJ mol^{-1}) of Table 1 and the X axis numbers to 1 = **a**, 2 = **b**, 3 = **c**, 4 = **d**, 5 = **e**, 6 = **f** for compounds **1**, **2** and **3**.

in the middle of the path but at the beginning, **3a**, and the transition state in the middle **3d** (22–35 kJ mol^{-1}), is thus comparable in efficiency to **1** but worse than **2**.

Concerning the PW91 calculations, if the ZPE correction is not considered, the analogy between both functionals is clearly apparent in Fig. 9. With both B3LYP and PW91, the tetratriazolyl derivative **2** is more efficient (lower activation barriers) than the tetramethoxy one **1** (compare Table 1, 15 with 35 kJ mol^{-1}). The inclusion of the ZPE correction in the case of the PW91 functional led to the result that some TSs (**1f**, **2f**) are more stable than the minima **1e** and **2e**, as an indication of the effective absence of barrier for these transformations that correspond to low-barrier hydrogen bonds (LBHB).

Table 1 also reports Gibbs free energies, but these are strictly proportional to the ZPE corrected values of E_{rel}:

B3LYP: $\Delta G^\circ_{298} = (1.006 \pm 0.038)*E_{\mathrm{rel}} + \mathrm{ZPE}, n = 16, r^2 = 0.98$

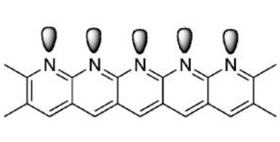
PW91: $\Delta G^\circ_{298} = (0.925 \pm 0.036)*E_{\mathrm{rel}} + \mathrm{ZPE}, n = 16, r^2 = 0.98$

Therefore, the ΔG°_{298} values are qualitatively similar to those of the ZPE corrected energies indicating that all structures for each molecule have similar thermal and entropic corrections.

Conclusions

1) If a chain of HBs is a necessary condition for the Grotthuss mechanism, the one proposed here is compatible with HBs but it is unlikely that it will be operative in these conditions because the HB network would prevent the adequate disposition of the remaining lone pairs.

2) The electronic wire formed by a chain of lone pairs (LP) is present in many systems, some examples are depicted below (**5**–**8**):



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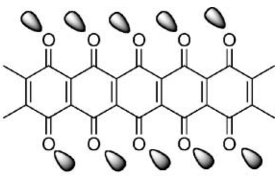

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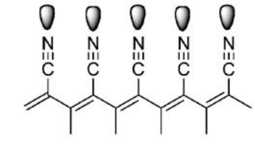

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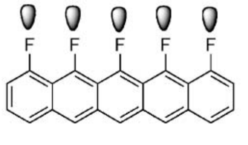

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The efficiency of these systems should be related to their basicity but mainly to the activation barriers to proton transfer.

3) Although some conformational changes intervene, the absence of large movements (rotations) makes these systems particularly attractive for solid state proton conduction.

4) For long arrays of LPs it should not be necessary that the first proton has left the wire for a new one to enter the first link of the chain.

5) The importance and the widespread use of the Grotthuss mechanism could lead some people to assume that an "internal proton" (a proton belonging to the molecule) is a necessary condition for proton transfer. Although the mechanism proposed here (more a model for material physics surfaces than for realistic biological systems) has not yet been discovered, it shows that other possibilities could exist.

Computational details

Geometries of all the stationary structures of **1**, **2** and **3** were fully optimised using the B3LYP[22,23] and PW91[24] functionals, with the 6-31+G** basis set[25] as implemented in the Gaussian 03 program.[26] Harmonic frequency calculations[27] verified the nature of the stationary points (all real frequencies) and TSs (only one imaginary frequency). According to Gill,[28] despite the added complexity of the Perdew-Wang 91 functional, energies obtained from it are seldom an improvement over B3LYP. The functional has also been shown to violate the original condition upon which B3LYP was developed.

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References

1 (*a*) L. Saiz and M. L. Klein, *Acc. Chem. Res.*, 2002, **35**, 482–489; (*b*) A. Sapronova, V. S. Bystrov and M. E. Green, *Front. Biosci.*, 2003, **8**, 1356–1370; (*c*) R. Pomès and B. Roux, *Biophys. J.*, 1998, **75**, 33–40; (*d*) R. Pomès and B. Roux, *Biophys. J.*, 2002, **82**, 2304–2316.

2 (*a*) *Proton Conductors: Solids, Membranes and Gels—Materials and Devices. Series: Chemistry of Solid State Materials (No. 2)*, ed. P. Colomban, Cambridge University Press, 1992; (*b*) *Conjugated Polymeric Materials: Opportunities in Electronics, Optoelectronics and Molecular Electronics, Vol. 182 of NATO Advanced Study Institute, Series E*, ed. J. L. Breadas and R. R. Chance, Kluwer Academic Publishers, Dordrecht, 1990.

3 Z. Zhou, S. Li, Y. Zhang and M. Liu, *J. Am. Chem. Soc.*, 2005, **127**, 10824–10825.

4 (*a*) C. J. D. von Grotthuss, *Ann. Chim. (Paris)*, 1806, **58**, 54–74; (*b*) M. E. Tuckerman, K. Laasonen, M. Sprike and M. Parrinello, *J. Chem. Phys.*, 1995, **103**, 150–161; (*c*) N. Agmon, *Chem. Phys. Lett.*, 1995, **244**, 456–462; (*d*) N. Agmon, *J. Chim. Phys. Phys.-Chim. Biol.*, 1996, **93**, 1714–1736; (*e*) K. D. Kreuer, *Solid State Ionics*, 2000, **136**, 149–160; (*f*) G. A. Voth, *Acc. Chem. Res.*, 2006, **39**, 143–150.

5 J. D. Bernal and R. H. Fowler, *J. Chem. Phys.*, 1933, **1**, 515–548.

6 B. E. Conway, J. O. Bockris and H. Linton, *J. Chem. Phys.*, 1956, **24**, 834–850.

7 (*a*) M. Eigen and L. DeMaeyer, *Proc. R. Soc. London, Ser. A*, 1958, **247**, 505–533; (*b*) M. Eigen, *Angew. Chem., Int. Ed. Engl.*, 1964, **3**, 1–19.

8 P. Bell, *The Proton in Chemistry*, Chapman and Hall, London, 1960.

9 (*a*) P. Schuster, G. Zundel and C. Sandorfy, *The Hydrogen Bond—Recent Developments in Theory and Experiment*, North-Holland Publishing Co., Amsterdam, 1975; (*b*) G. Zundel, in Transport Through Membranes, *Carriers, Channels and Pumps*, ed. A. Pullman and J. Jortner, Kluwer Academic Publishers, Dordrecht, 1988, p. 409; (*c*) G. Zundel, *Adv. Chem. Phys.*, 2000, **111**, 1–217; (*d*) B. Brzezinski, G. Zundel and R. Krämer, *Chem. Phys. Lett.*, 1989, **157**, 512.

10 G. A. Jeffrey and W. Saenger, *Hydrogen Bonding in Biological Structures*, Springer, Berlin, 1994.

11 T. Bountis, *Proton Transfer in Hydrogen-Bonded Systems*, Plenum Press, New York, 1992.

12 A. Müller, H. Ratajczak, W. Junge and E. Diemann, *Electron and Proton Transfer in Chemistry and Biology*, Plenum Press, New York, 1992.

13 J. Steadman and J. A. Syage, *J. Phys. Chem.*, 1991, **95**, 10326–10331.

14 J. P. Cowin, A. A. Tsekouras, M. J. Iedema, K. Wu and G. B. Ellison, *Nature*, 1999, **398**, 405–407.

15 M. F. H. Schuster, W. H. Meyer, M. Schuster and K. D. Kreuer, *Chem. Mater.*, 2004, **16**, 329–327.

16 O. F. Mohammed, D. Pines, J. Dreyer, E. Pines and E. T. J. Nibbering, *Science*, 2005, **310**, 83–86.

17 (*a*) M. E. Tuckerman, D. Marx, M. L. Klein and M. Parrinello, *Science*, 1997, **275**, 817–820; (*b*) D. Marx, M. E. Tuckerman, J. Hutter and M. Parrinello, *Nature*, 1999, **397**, 601–604.

18 (*a*) R. G. Schmidt and J. Brickmann, *Ber. Bunsen-Ges. Phys. Chem.*, 1997, **101**, 1816–1827; (*b*) K. Ando and J. T. Hynes, *J. Phys. Chem. B*, 1997, **101**, 10464–10478; (*c*) D. E. Sagnella and M. E. Tuckerman, *J. Chem. Phys.*, 1998, **108**, 2073–2083; (*d*) U. W. Schmitt and G. A. Voth, *J. Phys. Chem. B*, 1998, **102**, 5547–5551.

19 D. T. Major, M. Garcia-Viloca and J. Gao, *J. Chem. Theory Comput.*, 2006, **2**, 236–245.

20 J. L. Brédas, M. P. Posin, J. Delhalle, J. M. André and H. Chojnacki, *J. Phys. Chem.*, 1984, **88**, 5882–5887.

21 Z. Zhou, R. Liu, J. Wang, S. Li, M. Liu and J.-L. Brédas, *J. Phys. Chem. A*, 2006, **110**, 2322–2324.

22 A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098–3100; A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648–5652; C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785–789.

23 R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules*, Oxford University Press, New York, 1989.

24 (*a*) J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh and C. Fiolhais, *Phys. Rev. B*, 1992, **46**, 6671–6687. Erratum: J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh and C. Fiolhais, *Phys. Rev. B*, 1993, **48**, 4978; (*b*) K. Burke, J. P. Perdew and Y. Wang, in *Electronic Density Functional Theory: Recent Progress and New Directions*, ed. J. F. Dobson, G. Vignale and M. P. Das, Plenum Press, New York, 1998.

25 W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257–2261; T. Clark, J. Chandrasekar and P. v. R. Schleyer, *J. Comput. Chem.*, 1983, **4**, 294–301.

26 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi,

C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *Gaussian 03*, Gaussian, Inc., Pittsburgh PA, 2003.

27 J. W. McIver and A. K. Komornicki, *J. Am. Chem. Soc.*, 1972, **94**, 2625–2633.

28 P. M. W. Gill, *Mol. Phys.*, 1996, **89**, 433–445.