CURRENT SCIENCE

Volume 104 Number 5 **10 March 2013**

EDITORIAL

Bonds: Chemical, Hydrogen and Others

The chemical bond is central to chemistry. The line that connects the symbols for the elements signifies a profound and intimate union of atoms to create molecules. Chemical imagery conjures up the 'electron pair bond', an idea, due to G. N. Lewis, whose appearance in 1916 dramatically transformed 20th century chemistry. Bonds could now be made, broken and moved about by agile electron pairs, as molecules transformed and reacted. At times, pairs bound in covalent union could be separated; a divorce that created free radicals – singles searching for partners. For students of chemistry a course on 'chemical bonding' seems almost as essential as 'classical and quantum mechanics' for physicists and genetics for biologists. Curiously, a couple of years ago the journal *Nature* ushered in the 'Year of Chemistry' with a provocative commentary, catchily headlined 'Beyond the bond'. Readers were attracted with the declaration that 'new techniques show the bond to be a convenient fiction, albeit one that holds the field of chemistry together'. The author, Philip Ball, quoted Charles Coulson whose 1952 text *Valence* was required reading for those seeking a theoretical understanding of chemistry's most enduring image: 'A chemical bond is not a real thing: it does not exist: no one has ever seen it, no one ever can. It is a figment of our own imagination' (*Nature*, 2011, **469**, 26). Why do chemists persist with an idea that theoreticians caution is a poor representation of reality? Ball answers: 'The bond is literally the glue that makes the entire discipline cohere; to consider it an objective reality is necessary for any kind of discourse on chemistry'. In raising questions about chemistry's theoretical foundations, Ball adds: 'The discipline is in fact riddled with such convenient (and contested) fictions, such as electronegativity, oxidation state, tautomerism and acidity'. Having studied and taught many of these 'convenient fictions', I was consoled by the thought that drifting away into the fuzzier world of biology had provided me with some relief, from the predatory assault of theoreticians and sophisticated experimentalists, who seemed intent on destroying a familiar and comfortably fuzzy view of chemistry. My spirits further lifted when I came across a 'definition of the hydrogen bond' by an international team of 14 chemists, who had been commissioned by the International Union of Pure and Applied Chemistry (IUPAC). For the general reader, I might add that IUPAC is to chemistry what FIFA is to football and the ICC to cricket. Even as Ball was raising doubts about the covalent chemical bond, here was chemistry's highest body laying down definitions of a much weaker bond in a magisterial report, suggesting that chemistry's fictions were here to stay (Arunan, E. *et al.*, *Pure Appl. Chem.*, 2011, **83**, 1619–1636; *ibid*, 2011, **83**, 1637–1641).

The 'hydrogen bond' is an old concept which is crucial to our understanding of the properties of substances as diverse as water and DNA. The chemistry of heredity is determined by the hydrogen bonds that hold DNA strands together in the double helix; Watson–Crick base pairs are now common knowledge even in high school. The historical origins of the hydrogen bond have always been the subject of debate. Most students of chemistry associate the idea of the hydrogen bond with Linus Pauling, arguably the most influential chemist of the 20th century. Pauling's 1939 classic, *The Nature of the Chemical Bond* taught generations of students everything that seemed worth knowing about chemical bonds, strong and weak. His success in using hydrogen bonds as a dominant force in determining fibrous protein structures revealed the helical structures of polypeptides, a forerunner of the DNA structure. But, Pauling was not the man behind the idea of the hydrogen bond. A perceptive colleague drew my attention to a recent 'thesis' by Patrick Goymer, which appeared to mark an anniversary – '100 years of the hydrogen bond'. The author notes that Pauling drew attention to an 'unremarkably sounding study' that appeared in 1912 (Goymer, P., *Nature Chemistry*, 2012, **4**, 863). My curiosity was aroused, prompting a quick search that led me to the paper by T. S. Moore and T. F. Winmill modestly titled 'The state of amines in aqueous solution' (*J. Chem. Soc. Trans*., 1912, **101**, 1635). This long and detailed study of the ionic conductivity of amines in water is filled with forbidding tables and has no specific mention of a 'hydrogen bond'. But there is a structure and a mention of a 'union', both of which suggest that these uncelebrated authors were indeed on the verge of uncovering a weak interaction between molecular species. Could the 'hydrogen bond' have met with a warm reception even before the Lewis electron pair covalent bond? Probably not. Inevitably, the origins of the hydrogen bond are traced today to a 1920 paper by Latimer and Rodebush (*J. Am. Chem. Soc.*, 1920, **42**, 1419), which appeared from the chemistry department at Berkeley. A footnote in this paper tantalisingly provides an earlier reference to unpublished work by Maurice Huggins, then a first year graduate student. A wonderfully readable account of the reception of the concept of hydrogen bonding by the chemical community between 1920 and 1937 by Denis Quane, notes that this 'unpublished work' was actually an undergraduate 'term paper' written in May 1919 (Quane, D., *Bull. Hist. Chem*., 1990, **7**, 3). In later years Huggins would indeed attempt to provide his version of the historical record (Huggins, M. L., *Angew. Chem. Int. Ed. Engl*., 1971, **10**, 147). Quane notes that the first use of the term 'hydrogen bond' may have appeared in G. N. Lewis' 1923 book, *Valence and the Structure of Atoms and Molecules*. The emerging New World ideas on bonding in chemistry were not always welcomed in the Old World. Quane notes that Henry Armstrong, a conservative British chemist, was scathing in a letter to *Nature* in 1926, describing the hydrogen bond as a formula in which 'hydrogen figures as a bigamist'. He dismisses G. N. Lewis as a 'Californian thermodynamiter, who has chosen to disregard the fundamental canons of chemistry – for no obvious reason other than that of indulging in premature speculation upon electrons as the cause of valency'. Between 1920 and 1937 bonds in molecules were debated intensely, with Pauling emerging by the end of the 1930s as the figure who unified and clarified many disparate ideas of molecular structure.

The centenary of the largely unknown Moore–Winmill paper has passed unnoticed. Can chemists and chemistry find a more appealing cause to celebrate? After all, this is a discipline sorely in need of favourable public attention. 2016 which marks 100 years of the most enduring 'fiction' in chemistry, the electron pair bond, may be a strong candidate. Bonds of every kind – covalent, ionic, hydrogen and even the recently suggested 'halogen' bond – could be highlighted in a celebration of the way in which atoms unite in molecules and molecules unite in chemistry and biology. In reading about the hydrogen bond I was reminded of a commentary that addressed 'the precise chemical nature of this unique interaction'. This essay has a striking title: 'The name is bond – H bond' (Martin, T. W. and Derewenda, Z. S., *Nature Structural Biology*, 1999, **6**, 403). The line is, of course, a variation from a(nother) work of fiction: 'The name's Bond. James Bond.' Curiously, even as we wonder whether chemists have allowed a 'hydrogen bond centenary' to pass unnoticed, the world of entertainment celebrated the 'Bond' golden jubilee with considerable fan fare. A new James Bond film, an interlude at the Oscars ceremony and saturation screening of Bond films on television marked the 50th anniversary of the appearance of the first movie, *Dr. No* in 1962. Another anniversary can be celebrated this year; the 60th year since the first of Ian Fleming's books, *Casino Royale*, appeared in 1953. Considering these dates reminded me that a long time ago, in my youth, chemistry's 'bonds' seemed hard to understand and, at times, forbiddingly dull; a characteristic that seemed to be shared with works of non-fiction that students were compelled to read as part of general education. Fleming's fictional 'Bond' was infinitely more entertaining. In writing this column I cannot help a feeling of guilt; is even a mention of James Bond appropriate on the generally stodgy pages of a scientific journal? Was Fleming's work even appropriate for scholarly study by social scientists and those concerned with popular literature. I was heartened to note that Indiana University, Bloomington, far removed from the glamorous locales where Bond practiced his craft, hosted a symposium titled, 'Ian Fleming and James Bond: The Cultural Politics of 007' (Hitchens, C., *The Atlantic*, April 2006). Is there any connection between the most 'fictional Bond' and science, apart from the unending stream of 'innovative technology for spies' that appear in the films? A quick search on the internet produced Richard Zare, a Stanford physical chemist of considerable distinction and infectious enthusiasm, explaining Bond's preference for dry martinis, 'shaken not stirred'. The physical chemistry of mixing ice cubes and alcohol left me, a teetotaller, mildly bemused. A more direct connection may be found in the origin of 007's name. Fleming, a bird watcher, borrowed the name of a decorated, ornithologist, James Bond (1900–1989), an authority on Caribbean birds and author of a 1936 book on the *Birds of the West Indies*. His obituary in the *New York Times* (17 February 1989) quotes Fleming: 'It struck me that this brief, unromantic Anglo-Saxon and yet masculine name was just what I needed and so a second James Bond was born.'

Hunting for the origins of names and terms can be an entertaining exercise. Even the apparently prosaic 'fictions' of covalent bonds and hydrogen bonds provide human drama as we trace their roots. Maurice Huggins, fifty years after his undergraduate term paper, lectured at the Royal Swedish Academy in Stockholm in 1969. G. N. Lewis died mysteriously in his laboratory in 1946, his body found next to a leaking hydrogen cyanide line. He had returned from lunch with a long time rival Irving Langmuir, who received a Nobel Prize in 1934. Lewis was nominated over 30 times but never rewarded. A 2006 study that revisits the circumstances of Lewis' death, concludes that he died of a 'broken heart'. Is there a moral to the story? Michael Kasha, a student of Lewis in the 1940s provides one: 'We try to teach our students to be generous, to be honest, to give other people credit and don't expect any prizes – because you're not likely to get them' (Delvecchio, R., *San Francisco Chronicle*, 5 April 2006). Pauling's wife, Ava Helen, said it well at an International Congress in Yugoslavia in 1957: 'The only bond more important than the hydrogen bond is the human bond.'

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