Statistical analysis of C–H···N hydrogen bonds in the solid state: there*are* real precedents

Mark Mascal*

Department of Chemistry, University of Nottingham, Nottingham, UK NG7 2RD

A survey of the Cambridge Structural Database reveals hundreds of C–H··N contacts which are significantly shorter (< 2.45 Å) than the sum of the van der Waals radii (2.75 Å), effectively refuting recent claims to the contrary and supporting the description of this interaction as a hydrogen bond.

The nature of nonbonded C–H··N interactions has been called into question in the form of a recent publication which has appeared in this Journal.[1] Based on a self-declared 'superficial check of the literature', the authors of this work manage to discredit certain observations of C–H··N hydrogen bonds, while at the same time putting forward their own example of an apparently uncommon and authentic case of this phenomenon. A more thorough search however indicates that the published structure is not extraordinary, rather only one among nearly a thousand such cases.

We were first alerted to problems with the aforementioned paper by simple comparison with some of our own work. The authors make two major assertions, that: (i) 'in most, if not all, of the previously claimed examples of C–H··N "hydrogen bonds" the contact is little (or no) different from that expected for an ordinary, classic van der Waals contact,' and (ii) the C–H··N distance in $Co(dpa)_2$ 'is among the shortest of the C–H··Y, Y = N or O distances'. The $Co(dpa)_2$ complex has a C–H··N distance of 2.44 Å and C–H–N angle of 177°.[1] By way of comparison, the triazine–$2Br_2$ complex[2] has a C–H··N distance of 2.42 Å and a C–H–N angle of 180°, and, indeed, even this is not a particularly remarkable example of such nonbonded contact when the literature on the matter is properly consulted. A statistical analysis of the problem using the Cambridge Structural Database[3] currently indicates no less than 967 observations of intermolecular C–H··N contact with distances (r) less than 2.45 Å and C–H–N angles (α) between 120 and 180°, as identified using the query dialogue within QUEST3D[3] represented in Fig. 1. Histograms for both variables r and α are illustrated in Figs. 2 and 3. The mean C–H···N separation within the sample taken is 2.38 Å,[4] effectively disputing point (ii). Yet another claim, that 'the angles at the H atom are well below (often far below) 180°'[1] is also called into question by the data in Fig. 3, which show that over 100 entries have C–H–N angles between 170 and 180°. In fact, the mean α value of 155° is not far off that for classic N–H··O interactions, which is 161°.[5]

Another difficulty with such a sweeping statement as (i) above is that it entirely ignores the fact that C–H bonds can under some circumstances be as polar as a hydroxy group, whose capacity to participate in hydrogen bonding is not in question. A good example of an interaction involving an acidic C–H is seen in the crown ether **1**–nitromethane complex[6] (Fig. 4) with its C–H··N distance of 2.21 Å and C–H–N angle of 178°.

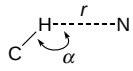

Fig. 1 The QUEST3D query, with conditions $r \leqslant 2.45$ Å and $120 \leqslant \alpha \leqslant 180°$

An entirely systematic study of this phenomenon would involve sampling the nearest neighbour contacts for every (C–)H atom in every structure containing C, H and N and demonstrating that the proportion of close approaches to nitrogen is statistically greater than the stoichiometric content of N in the database. In consideration of the number of structures involved this is clearly not practicable. However, in ground-breaking work, Taylor and Kennard,[7] using a small but representative subset of the databse (relevant neutron diffraction structures), were able to show that 'counterintuitive' C–H··C and C–H··H close contacts are comparatively rare,[8] and one could reason that the profusion of short C–H··N distances strongly implies a tendency for (C–)H to interact with nitrogen in preference to non-H-bond acceptors. Because such a strong case for C–H··O hydrogen bonding has already been made,[8,9] it is logically contentious to challenge the existence of C–H··N hydrogen bonds, since N is generally a more effective hydrogen acceptor than O.[10] Thus, although it is not possible to

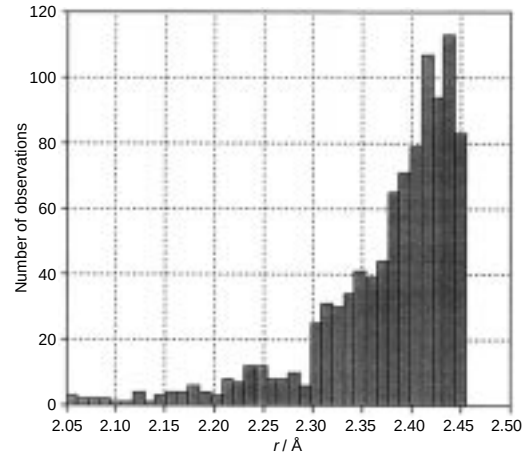

Fig. 2 Histogram for r (C–H···N)

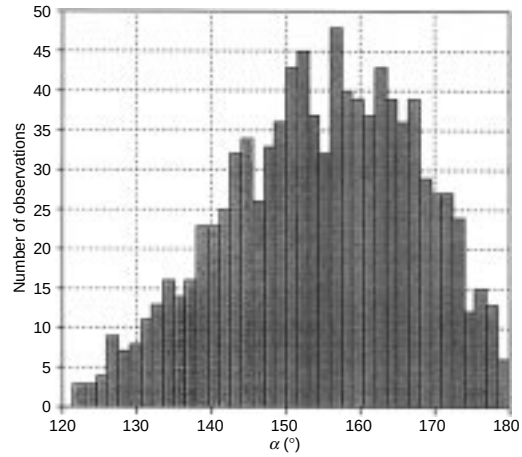

Fig. 3 Histogram for α (C–H–N)

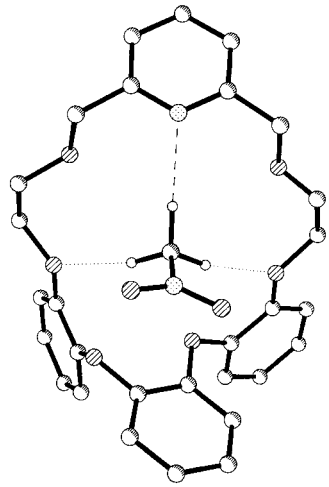

Fig. 4 Crystal structure of the **1**–$MeNO_2$ complex (ref. 6). The C–H··N distance (2.21 Å, dashed line) is actually shorter than the C–H··O distances (2.39 and 2.44 Å, dotted lines).

deliberate over the precise nature of these contacts without individually examining the many hundred occurrences of C–H··N relationships in the literature, the fact that such a large number are significantly shorter than the 2.75 Å sum of the van der Waals radii[11] indicates that the distinction between the classical van der Waals interaction and the hydrogen bond is not necessarily being 'blurred',[1] at least not when all of the available data are taken into consideration.

Dr A. J. Blake is thanked for helpful discussions, and the use of the EPSRC's Chemical Database Service[12] at Daresbury is gratefully acknowledged.

Notes and References

* E-mail: pczmm@vax.ccc.nottingham.ac.uk

1 F. A. Cotton, L. M. Daniels, G. T. Jordan IV and C. A. Murillo, *Chem. Commun.*, 1997, 1673.
2 M. Mascal, J. L. Richardson, A. J. Blake and W.-S. Li, *Tetrahedron Lett.*, 1996, **37**, 3505.
3 Version 5.13 (167 797 structures, April 1996 update): F. H. Allen and O. Kennard, *Chemical Design Automation News*, 1993, **8**, 31.
4 Twenty-one entries with r values between 1.47 and 1.99 Å were found dubious and therefore not used in the final analysis. If the range is increased to $r \leqslant 2.50$ Å with $120 \leqslant \alpha \leqslant 180°$, a total of 1841 observations are found with $r = 2.42$ and $\bar{\alpha} = 154°$. An identical search involving neutron diffraction structures (in which all protons are accurately located) produces 13 observations with $\bar{r} = 2.43$ Å (range 2.32–2.50 Å) and $\bar{\alpha} = 150°$ (range 139–166°).
5 R. Taylor and O. Kennard, *Acc. Chem. Res.*, 1984, **17**, 320.
6 E. Weber, S. Franken, H. Puff and J. Ahrendt, *J. Chem. Soc., Chem. Commun.*, 1986, 467.
7 R. Taylor and O. Kennard, *J. Am. Chem. Soc.*, 1982, **104**, 5063.
8 (C–)H atoms did however show a significant tendency to form close intermolecular contacts to oxygen (see also ref. 9). Due to the limited amount of data in this study, no real conclusions were drawn concerning C–H··N contact.
9 J. A. R. P. Sarma and G. R. Desiraju, *Acc. Chem. Res.*, 1986, **19**, 222; G. R. Desiraju, *Acc. Chem. Res.*, 1991, **24**, 290.
10 M. H. Abraham, *Chem. Soc. Rev.*, 1993, **22**, 73.
11 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441. A recent revision of the van der Waals radius of nitrogen to 1.60 Å would actually put the H to N contact distance at 2.80 Å (see S. C. Nyburg and C. H. Faerman, *Acta Crystallogr., Sect. B*, 1985, **41**, 274), while the Pauling radius of N (1.5 Å) gives a total of 2.7 Å (see L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithica, 1942, p. 192).
12 The United Kingdom Chemical Database Service: D. A. Fletcher, R. F. McMeeking and D. Parkin, *J. Chem. Inf. Comput. Sci.*, 1996, **36**, 746.

Received in Liverpool, UK, 24th October 1997; 7/07702E