

groupement amidique N(1)–H(N1) se trouve alors libre de toute interaction.

La conformation décrite est différente de celle des deux conformères reconnus en solution diluée dans un solvant inerte (Marraud & Neel, 1972) où le radical hydroxyle est engagé dans une chélation intramoléculaire avec l'un ou l'autre des groupements carbonyle. Cependant, l'association de deux molécules par deux liaisons hydrogène N(2)···O(1) a déjà été observée dans les agrégats des dipeptides dérivés de la glycine et de la L-alanine en solution (Cung, Marraud, Neel & Aubry, 1976) et dans la structure cristalline de la *N*-pivalyl-glycyl-isopropylamide (Aubry, Marraud, Protas & Neel, 1973).

Enfin les valeurs de χ_1 voisines de 60° semblent être assez caractéristiques de la conformation du résidu séryle à l'état solide.

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Very Short Hydrogen Bonds and Crystallographic Symmetry

BY MICHELE CATTI AND GIOVANNI FERRARIS

Istituto di Mineralogia, Cristallografia e Geochimica

'G. Spezia' dell'Università, Via S. Massimo 24, 10123 Torino, Italy

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From data on very short hydrogen bonds, the symmetrical location of the proton is shown to be only apparent in disordered structures, and to be doubtful in some other cases (ambiguity of the space group, twin peaks in the electron density map). Analyses of the thermal motion and of the O–H vs O···O distances suggest that the chemical–physical properties of both symmetrical and asymmetrical very short hydrogen bonds are basically the same; bond symmetry should then merely be a crystallographic event due to a peculiar arrangement of the neighbourhood.

Introduction

The concept of a symmetrical hydrogen bond A···H···A has concerned crystallographers since the fifties for KHF₂ (Peterson & Levy, 1952) and investigations have continued by diffraction (Speakman, 1972) and spectroscopic (Novak, 1974) methods. However, one characteristic has always been perplexing: the proton is normally required to lie on a crystallographic element of symmetry [type *A* (Currie & Speakman, 1970) or symmetry-restricted (SR) hydrogen bonds (Catti & Ferraris, 1974)].* Since simulation of higher

symmetry in crystal structures is not rare, chemical results which arise directly from crystallographic constraints should be considered very cautiously.

Disordered structures*

Let us consider a system which is shown by diffraction analysis to be B–A···H···A–B, where A···H···A is a SR hydrogen bond and B represents one or more atoms, which, at least in part, are disordered over positions related by the symmetry element on which H is supposed to lie. The symmetry element is then true

* Only one symmetry free (SF) hydrogen bond is known, which is symmetrical within the e.s.d.'s (Ellison & Levy, 1965).

* The concept of static disorder is used here in a pragmatic sense; the effect could be simulated, e.g. by undetected superstructures or twinnings by merohedry (Catti & Ferraris, 1976).

only for the average structure, but is false locally and the hydrogen bond is not very likely to be symmetrical because of the unbalancing action of the group B; *e.g.* in a cell (or domain) the system B-A...H-A, and in the next one the system A-H...A-B could exist. Diffraction methods might fail to detect the disorder of the H atom because its two extreme positions are too close.

CaHPO₄ (monetite) (Catti, Ferraris & Filhol, 1975), the high-temperature phase of YH(C₂O₄)₂·3H₂O (Brunton & Johnson, 1975), CaHAsO₄ (weilite) (Ferraris & Chiari, 1970) and [(C₉H₁₈)₃(NH)₂Cl]⁺Cl⁻[H₁₃O₆]⁺Cl⁻ (Bell, Christoph, Fronczek & Marsh, 1975) are cases of disordered structures with very short hydrogen bonds which should be only apparently symmetrical.

Ambiguous symmetry

Space group

Screw axes and glide planes can be detected from diffraction effects with much greater certainty than their equivalents without translations. Analysis shows that about 75% of the structures containing SR hydrogen bonds have been solved and refined in space groups not unambiguously determined. Then, two alternatives arise: refinement of the structure (i) in a lower-symmetry space group and (ii) in the higher-symmetry space group, but with a disordered model for the hydrogen bond. Convergence can often be reached in different space groups (Parthasarathy, Sime & Speakman, 1969), and with both an ordered and a disordered model for the hydrogen bond (Lehmann & Larsen, 1971; Prelesnik, Herak, Manojlović-Muir & Muir, 1972); in another case, the hydrogen bond proved to be asymmetrical by removal of the mirror plane on which the bond was supposed to lie (Bartl & Küppers, 1975).

Unfortunately, least-squares refinement presents difficulties in cases of 'quasi-symmetry' (Rae, 1974), and results for (i) and (ii) are often unsatisfactory, from a mathematical point of view. In default of objective results, the choice of the best model has to be based on questionable chemical considerations.

KKM effect

This effect (Macdonald, Speakman & Hadži, 1972) means a pair of electron-density peaks astride the position expected for the H atom of SR hydrogen bonds. A corresponding phenomenon has not been observed so far with neutron diffraction data; therefore, proton disorder does not seem to be a satisfactory explanation. However, by taking into account the polarization of the electron density of H towards A in the bond A-H, the hypothesis of static proton disorder over two very close positions (not resolved by neutron diffraction) can be accepted; the two corresponding maxima of electron densities would in fact be much more distant, and might be resolved by X-ray measurements.

Bond lengths and symmetry

Thermal motion

Very strong hydrogen bonds show quite peculiar vibrational features (Speakman, 1975a): the direction of largest thermal motion of the proton is along the bond, instead of being normal as in ordinary bonds. This behaviour appears to be shared by both symmetrical and asymmetrical hydrogen bonds, and is confirmed by the inversion between stretching and out-of-plane bending IR frequencies of the proton [Novak (1974), where unfortunately data are reported for symmetrical bonds only]. A reasonable explanation (Speakman, 1975a) is provided by assuming that the proton vibrates in a single, broad, flat potential-energy well. The vibrational properties of the hydrogen bond should then be affected by the length rather than by the symmetry of the bond.

Correlation of O-H vs O...O distances

It is instructive to compare an up-to-date graph (Lundgren, 1974) with previous versions (Hamilton & Ibers, 1968; Speakman, 1973). The extent of the curve for asymmetrical hydrogen bonds has increased in the course of time, so that the curve tends now to include also the values of symmetrical hydrogen bonds;* this effect is particularly noticeable for Speakman's (1973) graph, limited to results published in 1971-72. Two causes lead to the effect: (i) the range of symmetrical hydrogen bonds has shrunk from 2.40-2.55 Å (Hamilton & Ibers, 1968) to 2.40-2.47 Å (Lundgren, 1974), and even to 2.41-2.43 Å for partial data (Speakman, 1973); (ii) many new shorter asymmetrical hydrogen bonds have been added to the graph, with much longer O-H distances than previously suspected. From (i) it could be inferred that some of the longest supposed symmetrical bonds may still prove to be asymmetrical in the future; in agreement with vibrational considerations, (ii) would show that there is no gap of a chemical nature between symmetrical and asymmetrical very short bonds, but the former simply fit an appropriate crystallographic environment.

The peculiar behaviour of the O...O hydrogen bond in comparison, for example, with the N-H...O bond (Jönsson, 1973; Speakman, 1974) is to be noticed, however; the O-H vs O...O correlation (asymmetrical bonds) shows a negative slope much greater for short O...O distances, while the N-H vs N...O curve decreases linearly to a good approximation; this peculiarity might lead to a symmetrical or quasi-symmetrical bond as a limit for very short O...O lengths. It should be noted that the graph is linear also in the O...O case, if only hydrogen bonds donated by water molecules are taken into account (Ferraris & Franchini-Angela,

* The ν_{OH} vs O...O or O-H correlations are reported to be unambiguous (Novak, 1974); data are however lacking for O...O < 2.43 Å and for 1.1 ≤ O-H ≤ 1.2 Å.

1972); the above peculiarities must therefore be ascribed to acidic bonds only.

Conclusions

According to the analysis of thermal motion, hydrogen bonds should be divided into two groups: ordinary and very short hydrogen bonds. Their different chemical properties can be stressed by saying that, in the latter, the H atom shows a CN of two. For O...O lengths, the boundary between the two groups should lie in the range 2.50–2.45 Å; long symmetrical bonds are then likely to be more suspect, perhaps concealing some kind of disorder. A possible presence of crystallographic symmetry does not seem to change the basic nature of very short hydrogen bonds, which would be insensitive to the proton being located exactly on or slightly off the bond centre.

Hydrogen bonding is ruled not only by interactions with stronger bonds, but also by long-range perturbations. A potentially symmetrical hydrogen bond is then likely to be unbalanced by even the weakest asymmetrical perturbations (Kvick, Koetzle, Thomas & Takusagawa, 1974), and its existence could be only allowed by a perfect bilateral symmetry, such as required by a crystallographic symmetry element. If this hypothesis is accepted, the rule of equality between donor and acceptor atoms and between their first neighbourhoods (Olovsson, 1974; Speakman, 1975b) must be replaced by a rule of crystallographic equivalence. A suitable example is provided by the F...H...F hydrogen bond in the HF₂⁻ ion, which proves to be SR in KHF₂ (Ibers, 1964) and in NaHF₂ (McGaw & Ibers, 1963), but SF in C₇H₇NH₃⁺HF₂⁻ (Williams & Schneemeyer, 1973), with the same F...F bond length (2.26 Å) in all cases.

Finally, according to recent results, bond length and symmetry appear to be no longer unambiguously related, and it should be borne in mind that the following physical models could simulate a symmetrical hydrogen bond: the proton is (i) statically or (ii) dynamically disordered; (iii) the proton is off the centre of the bond but is not detected because of a strong crystallographic pseudosymmetry. Diffraction methods would not be *a priori* powerless in case (i) if the disorder is not perfect, or in case (iii); IR spectroscopy, too, should be able to detect these cases as shown by the study of RbHCO₃ quoted by Novak (1974). Case (ii) could be considered to be an effectively symmetrical hydrogen bond at least with respect to events with a life much longer than the tunnelling period.

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