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Graphical Enumeration of Hydrogen-Bonded Structures

BY L. N. KULESHOVA AND P. M. ZORKY

Chemistry Department, Moscow State University, Moscow 117234, *USSR*

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Abstract

A classification of hydrogen-bonded structures (H structures) which is based on the representation of these structures as graphs has been developed. Statistical data on the distribution of 776 homomolecular H structures are given in the form of graphs. The most common modes of H-structure formation and some anomalous H structures are described.

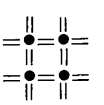
When molecules in crystals are joined by H bonds the aggregates so formed may be (1) dimers, trimers and some other finite clusters (islands), (2) infinite chains, (3) layers, or (4) frameworks. We designate such molecular aggregates as H aggregates and hydrogen-bonded structures as H structures. The H-aggregate type present in the structure has an obvious influence on the physicochemical properties of the crystals. This is why this aspect of H structures is of special interest.

Some attempts to classify the different types of hydrogen-bonded networks have been made by Wells (1962). For this purpose he used two parameters for the H aggregates: the number of H bonds formed by one molecule (n), and the number of molecules to which a given molecule is hydrogen bonded (m). Thus it was possible to divide the H aggregates into classes with appropriate symbols n_m.

A similar scheme has been given by Hamilton & Ibers (1968). They used a symbol (N,M), where $N = n/2$ is the number of H bonds per molecule and $M = m$. In describing the system of intermolecular H bonds, they considered each molecule as a single point with lines representing hydrogen bonds extending from it. This meant that an H aggregate was represented as a graph (Harary, 1967; Harary & Palmer, 1973) (though Hamilton & Ibers did not use this term). It should be remembered that the term 'graph' is applied to a system of *points*, some of which (or all of which) are connected by *lines*. The number of lines extending from a point is called the *degree* of this point.

In the present work the classification of H structures based on the representation of H aggregates as graphs is continued. We have taken into consideration only homonuclear crystals built up from symmetrically related molecules. Such crystals are described as graphs with topologically equivalent points. Like other authors, we have used the parameters n and m. The first is the degree of the point. We also call it the firmness of the H aggregate, because it shows how many H bonds must be broken to release a molecule. It is clear that for the structures considered here, n is always even. m is the number of points with which every point of the graph is directly joined. We also take into account the dimension (k) of the rings present in the graph, considering only those rings which do not overlap.

In general, a graph symbol may be written as $G_m^n(k)$. In particular cases we write I, C, L or F. These letters correspond to islands, chains, layers and frameworks respectively. For instance, the hydrogen-bonded layer



which is present in the *meso*-tartaric acid structure (Butsma & Schoone, 1967) is described by the symbol $L_4^8(2,4)$. It should be noted from Table 1 that these symbols are not completely adequate. For example, there are two different graphs represented by the symbols $C_4^6(2,3)$. Nevertheless, these symbols are sufficiently informative to classify H structures.

In order to determine the most common modes of H-structure formation and to investigate the variety of these modes (including rare and unique variants), we have statistically processed the data in the literature. Only those H bonds which were indicated by the authors were taken into account. Bifurcated H bonds were considered as two bonds.

As the source for the data we used Vols 1 and 2 of *Structure of Organic Substances* (Kitaigorodsky, Zorky & Belsky, 1980*a*,*b*). The data cover the period from 1929 to 1974 (inclusive).

The number of hydrogen bonds formed by different molecules for the 960 structures derived from this source is distributed as follows:

n	2	4	6	8	10	12	14	16	24
Number of structures	445	255	91	113	29	21	4	1	1

Table 1. *The distribution of* H *aggregates in the form of graphs*

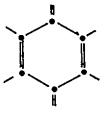
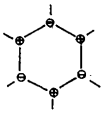
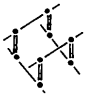
Note: the sign ⊕ (or ⊖) meant that there is a line directed up (or down) which is not represented in the graph of the framework.

$n = 2$ (445 H structures)

Type of H aggregate					
Symbol	$C_2^2(0)$	$I_1^2(2)$	$I_2^2(3)$	$I_2^2(4)$	$I_2^2(6)$
Number of structures	270	172	1	1	1

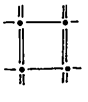
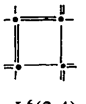
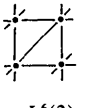
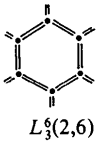
$n = 4$ (255 H structures)

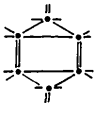
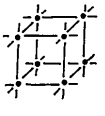
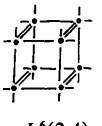
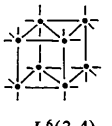
Type of H aggregate				
Symbol	$I_1^4(2)$	$C_2^4(2)$	$C_3^4(2,4)$	$C_4^4(3)$
Number of structures	5	105	18	10

Type of H aggregate				
Symbol	$L_4^4(4)$	$L_3^4(2,6)$	$F_4^4(6)$	$L_3^4(2,8)$
Number of structures	56	47	13	1

$n = 6$ (48 H structures)

Type of H aggregate				
Symbol	$C_2^6(2)$	$C_4^6(2,3)$	$C_4^6(2,3)$	$C_3^6(2,4)$
Number of structures	2	1	1	3

Type of H aggregate				
Symbol	$L_4^6(2,4)$	$L_4^6(2,4)$	$L_6^6(3)$	$L_3^6(2,6)$
Number of structures	12	5	1	1

Type of H aggregate				
Symbol	$L_5^6(2,3,4)$	$F_6^6(4)$	$L_5^6(2,4)$	$L_6^6(3,4)$
Number of structures	4	4	2	2

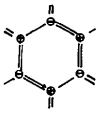
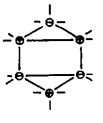
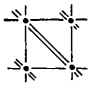
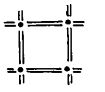
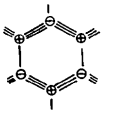
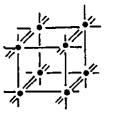
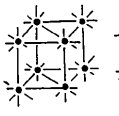
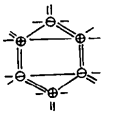
Type of H aggregate		
Symbol	$F_4^6(2,6)$	$F_6^6(3,4)$
Number of structures	4	6

Table 1 (*cont.*)

$n = 8$ (28 H structures)

Type of H aggregate				
Symbol	$C_2^8(2)$	$L_6^8(2,3)$	$L_4^8(2,4)$	$F_4^8(2,6)$
Number of structures	1	3	15	1

Type of H aggregate			
Symbol	$F_6^8(2,4)$	$F_8^8(3,4)$	$F_5^8(2,3,4)$
Number of structures	1	1	5

It is of interest to point out those structures with very large n values: cyclobutanoctol (Bock, 1968) where $n = 16$, and 1-kestose (Jeffrey & Park, 1972) where $n = 24$.

776 of these structures have been represented as graphs (all structures with $n = 2$ and 4 and some of those structures with $n = 6$ and 8). The results are summarized in Table 1.

It should be noted that the most common H aggregate is $C_2^2(0)$, the frequency of its occurrence being 28%. The second most common mode of H structure is $I_1^2(2)$ (19%), and the third is $C_2^4(2)$ (11%). The list of the more common H aggregates is completed by layers $L_4^4(4)$ (6%) and $L_3^4(2,6)$ (5%). These five modes of H bonding cover ~69% of H structures. All other H aggregates are encountered far less frequently (less than 2%). Examples of the most common H aggregates are: $C_2^2(0)$, 2,5-dimethylphenol (Neuman & Gillier-Pandraud, 1973); $I_1^2(2)$, propionic acid (Strieter, Templeton, Scheuerman & Sass, 1962); $C_2^4(2)$, dihydrouracil (Rohrer & Sundaralingam, 1970); $L_4^4(4)$, chloranilic acid (Andersen, 1967); $L_3^4(2,6)$, *o*-dihydroxybenzene (Brown, 1966).

We now consider some examples of the unusual modes of H aggregates. In some cases H bonding leads to the cyclic aggregates $I_2^2(3)$, $I_2^2(4)$ and $I_2^2(6)$ present in the structures of acetone oxime (Bierlein & Lingafelter, 1951), *anti*-α-bromoacetophenone oxime (Wetherington & Moncrief, 1973), and (±)-β-promedol alcohol (De Camp & Ahmed, 1972). The unique H-bonded layer $L_3^4(2,8)$ occurs in the structure of methyl 5-thio-β-D-ribopyranoside (Girling & Jeffrey, 1973). Sometimes a system of H bonds in a crystal is similar to a diamond structure, its graph being $F_4^4(6)$. Such a system occurs in 6-azauracil (Singh & Hodgson, 1974). The symbol $F_4^4(6)$ can also be applied

to the structure of hexagonal diamond (Ergun & Alexander, 1962). However, so far we have not detected any example of such a graph. It is interesting to consider structures of the type $F_5^8(2,3,4)$; these contain a diamond-like system of H bonds, but some lines of the graph are doubled by additional H bonds, and the six-membered rings are divided into three- and four-membered ones. Such a structure occurs, for example, in L-tyrosine (Mostad, Nissen & Rømming, 1972).

The method of H-bonded structure representation described here does not take into account the fact that one of the two molecules connected by a H bond is a donor and that the other is an acceptor. This shortcoming can be eliminated by using so-called *digraphs* which consist of points and directed lines.

We plan to apply the digraph concept to the further systematization of H structures.

References

ANDERSEN, E. K. (1967). *Acta Cryst.* **22**, 188–191.

BIERLEIN, T. K. & LINGAFELTER, E. C. (1951). *Acta Cryst.* **4**, 450–453.

BOCK, C. M. (1968). *J. Am. Chem. Soc.* **90**, 2748–2754.

BROWN, C. J. (1966). *Acta Cryst.* **21**, 170–174.

BUTSMA, G. A. & SCHOONE, J. C. (1967). *Acta Cryst.* **22**, 522–526.

DE CAMP, W. H. & AHMED, F. R. (1972). *Acta Cryst.* B**28**, 3484–3489.

ERGUN, S. & ALEXANDER, L. E. (1962). *Nature (London)*, **195**, 765–767.

GIRLING, R. L. & JEFFREY, G. A. (1973). *Acta Cryst.* B**29**, 1102–1111.

HAMILTON, W. C. & IBERS, J. A. (1968). *Hydrogen Bonding in Solids*, pp. 18–22. New York: Benjamin.

HARARY, F. (1967). *Graph Theory and Theoretical Physics*. New York, London: Academic Press.

HARARY, F. & PALMER, E. M. (1973). *Graphical Enumeration*. New York, London: Academic Press.

JEFFREY, G. A. & PARK, Y. J. (1972). *Acta Cryst.* B**28**, 257–267.

KITAIGORODSKY, A. I., ZORKY, P. M. & BELSKY, V. K. (1980*a*). *Structure of Organic Substances*. Vol. 1. Moscow: Nauka.

KITAIGORODSKY, A. I., ZORKY, P. M. & BELSKY, V. K. (1980*b*). *Structure of Organic Substances*. Vol. 2. Moscow: Nauka (in the press).

MOSTAD, A., NISSEN, H. M. & RØMMING, C. (1972). *Acta Chem. Scand.* **26**, 3819–3824.

NEUMAN, A. & GILLIER-PANDRAUD, H. (1973). *Acta Cryst.* B**29**, 1017–1023.

ROHRER, D. C. & SUNDARALINGAM, M. (1970). *Acta Cryst.* B**26**, 546–553.

SINGH, P. & HODGSON, D. J. (1974). *Acta Cryst.* B**30**, 1430–1435.

STRIETER, F. J., TEMPLETON, D. U., SCHEUERMAN, R. F. & SASS, R. L. (1962). *Acta Cryst.* **15**, 1233–1239.

WELLS, A. J. (1962). *Structural Inorganic Chemistry*, pp. 307–315. Oxford: Clarendon Press.

WETHERINGTON, J. B. & MONCRIEF, J. W. (1973). *Acta Cryst.* B**29**, 1520–1526.

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The Structure of 7-Chloro-1,3-dihydro-1-(*N*-methylacetamido)-5-phenyl-2*H*-1,4-benzodiazepin-2-one

BY PONGCHAN CHANANONT AND T. A. HAMOR

Department of Chemistry, University of Birmingham, Birmingham B15 2TT, England

AND I. L. MARTIN

MRC Neuropharmacology Unit, Department of Pharmacology, The Medical School, Birmingham B15 2TJ, England

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Abstract

$C_{18}H_{16}ClN_3O_2$ is monoclinic, space group $P2_1/c$, with $a = 4{\cdot}775\ (5)$, $b = 11{\cdot}74\ (1)$, $c = 30{\cdot}54\ (2)$ Å, $\beta = 91{\cdot}60\ (5)°$, $Z = 4$. Final $R = 6{\cdot}0\%$ for 1300 observed counter amplitudes $[I > 2{\cdot}5\sigma(I)]$. E.s.d.'s average 0·008 Å for bond lengths and 0·6° for bond angles not involving H atoms. The *N*-methylacetamido group is planar and oriented at an angle of 75·5° to the C(6)–(11) phenyl residue of the 1,4-benzodiazepine system. The angle between the two phenyl rings is 61·6°. Comparison of molecular parameters with those of diazepam indicates that the geometries of the 5-phenyl-1,4-benzodiazepine residues of the two molecules differ only slightly.

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