

Chapter 7.2

XYHDEX

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7.2.1. Introduction

XHYDEX is a program written in a simple subset of Fortran (designed to be reasonably machine independent) which uses crystallographically determined molecular parameters to infer the positions of hydride ligands in metal cluster complexes. The procedure is of special interest for cluster compounds of 2nd and 3rd row transition elements where direct X-ray location of hydrogen atoms is very difficult and qualitative indirect hydride location sometimes ambiguous. The program finds optimised hydride positions, given X-ray structural parameters for non-hydrogen atoms, such that the hydride is bonded to 1, 2 or 3 atoms (usually metals) at user specified bond lengths. The optimised positions are at suitable minima of a potential energy defined by intra- molecular non-bonded interactions between the postulated hydride position and other atoms subject to the appropriate bond length constraints. The optimised sites thus located agree well with those found by neutron diffraction methods for almost all cases in the literature (r.m.s. error ca. 0.05 Å). When more than one hydride is known to be present in the cluster the non-bonded interactions between hydride sites can be taken into account in order to ensure the compatibility of proposed sites. A picture of the molecule projected onto a user specified plane through the unit cell, and a map of the appropriate potential energy function in this plane may be obtained. This facility is especially useful in checking for multiple hydride sites on a cluster edge or around a metal centre. The program thus provides an easily used semi-quantitative procedure for inferring hydride positions inaccessible from single crystal X-ray data alone.

7.2.2. Program Specifications and Installation

The program consists of about 1040 FORTRAN statements contained in a main program and subroutines. It is supplied together with three test jobs checking features of the program and listings of the output produced by these jobs by electronic means. Documentation is provided separately. The program has been extensively tested on a variety of computers and should prove readily adaptable. The main aspect requiring attention when installing concerns contour map plotting. This is carried out using CALCOMP subroutines BRKPLT and PLOT at or near line 611 of the main program and in subroutine XPLOD respectively. These routines will need to be replaced with others should you wish to exploit this aspect of the program.

The Fortran unit numbers used by READ and WRITE statements are specified as integers NIN and NOUT in the DATA statement of the main program. The program assumes there to be at least 110 line printer characters available across the page, the number of characters per inch across and down the page may be specified as real variables HA and HD in the main program DATA statement. The program

requires at least 24 bit integer word length. Default settings of NIN, NOUT, HD and HA are 5, 6, 8 and 10 respectively.

Three test jobs are supplied with the program. The output from these jobs should be as in the output listings provided, and is discussed in the Examples section. Users of the program should refer to the literature description of the program and its use:

A.G. Orpen, *J. Chem. Soc., Dalton Trans.*, **1980**, 2509.

7.2.3. Using the program

The examples in the test data provided show typical use of the program. Given X-ray structural parameters for the non-hydrogen atoms in a cluster compound it is possible to conduct initial searches for hydride sites on edges and faces of the cluster as well as in terminal positions, using the TERM, EDGE AND FACB instructions as appropriate. A conjugate-gradient technique is used - derived from that of Fletcher and Reeves [2] - which finds local minima of the potential energy function (including the bond length constraints) appropriate to the hydride specified. In an initial search, interactions are evaluated for all atoms within a restricted 'search radius' - see test output - of an initial estimate of the hydride position. Twenty-six starting hydride positions around this estimate are refined and each optimised position checked for suitability. Positions too close to a non-bonded atom are rejected, as are those where the M-H bond length is too far from that specified. When convergence of a particular optimisation is slow and therefore incomplete, a message to that effect is output. The unique 'suitable' positions are further refined and their coordinates and potential energies (excluding the bond length term) output. This technique ensures location of separated multiple hydride sites in cases where more than one hydride is bound to a vertex, edge or face of a cluster. The output table of inter-minima distances enables the user to check for short hydride-hydride contacts (inter-hydride distances as short as 1.85 Å apart, are known). The co-refinement of hydride positions is possible using the HLOC command and is recommended in cases where the hydrides are sufficiently close to one another to have significant non-bonded interactions (less than 3 Å apart, say). Multiple hydride sites may well not be detected in an initial search and only be revealed by use of the PLOT command. They are typified by abnormally low potential energy minima and/or unusually diffuse or extended potential minimum shape (see examples). Typical hydride site energies are in the range 0-3.5 units whereas false minima have higher energies greater than 10 units. Energies are not on an absolute scale but show relatively little variation between different molecules and site types. Thus typically terminal sites are of slightly higher energy than edge bridging or triply bridging sites. The program has been widely used in the past 25 years. Initial testing was done against neutron diffraction data and showed r.m.s. disagreement with neutron determined hydride position of ca. 0.05 Å - see A.G. Orpen [1]. Difficulties are most likely to arise when the non-hydride ligand framework is sparse (i.e. polyhydrides) or the

distribution of ligand atoms is far from spherical (e.g. in locally square planar environments).

7.2.4. Input to the program

All instructions are read as 80 character instructions and supply the program with information regarding unit cell dimensions, atomic positions and types, potential energy parameters and define which calculations are to be carried out. The first four characters define the type of instruction. An instruction is assumed to be an 'atom instruction' if not recognised by the program to be otherwise. The remaining 76 characters are used to convey numerical information in machine-independent free format with blanks separating the numbers. Faulty or illegal instructions are either ignored or cause the program to halt further execution of instructions and return an error message. The first and second instructions of any job must be the TITL and CELL instructions respectively, the last must be the END instruction. Instructions with the first four characters blank are ignored and may be used to include comments, all input instructions are reflected in the lineprinter output before being obeyed. Reading END or END+ causes the program to execute the preceding instructions.

7.2.5 Instructions

TITL *followed by a title of up to 40 characters.*

CELL *a, b, c. alpha, beta, gamma in Å and degrees.*

PARM *n, A, B, C, D.*

Where n is the atom type number and A, B, C, D are potential energy parameters appropriate for to describe the non-bonded interaction of the hydride with atoms of type n. The potential energy function used in the program is: $V(r) = A \exp(-Br)/r^D - C/r^6$. See the Appendix for suitable values for A,B,C and D. Default values for A, B, C and D are those given for carbon atoms in the Appendix, inter-hydride terms required when using the HLOC instruction are calculated using the parameters given for hydrogen atoms.

TERM *n1, d, sd, ni*

This initiates a search for terminal hydride sites at a bond length dÅ from the n1th atom in the atom list input. Sd is the permitted 'uncertainty' in this bond length, a constraint is applied to the minimisation process by adding a term equal to $\text{mod}(\text{observed bond length} - d)/(sd*sd)$ to the potential energy function to be minimised. This ensures that the minima found by the program are at suitable bond lengths. The minimised potential energies output after the completion of the calculations exclude this term. ni sets an upper limit on the number of potential

energy function evaluations which may be made during the minimisation process. Default values of *d*, *sd* and *ni* are 1.60, 0.05 and 250.

EDGE *n1, n2, d1, d2, sd1, sd2, ni*

As for the TERM instruction, this causes a search for a hydride bonded to atoms *n1*th and *n2*th in the atom list at bond lengths *d1*, *d2* respectively. Default settings of *d*, *sd*, and *ni* are 1.85, 0.05 and 250. If *d2* is not given (i.e. *sd*, *sd2* and *ni* are also omitted) then *d2* is assumed equal to *d1*.

FACB *n1, n2, n3, d1, d2, d3, sd1, sd2, sd3, ni*

As for EDGE and TERM instructions, this causes a search for a hydride bonded to the *n1*th, *n2*th and *n3*th atoms in the atom list at bond lengths *d1*, *d2* and *d3* Å respectively. Default settings of *d*, *sd* and *ni* are 1.95, 0.05 and 250. If *d2*, *d3* etc. are omitted then *d2* = *d3* = *d1* is assumed.

MATR *p11, p12, p13, p21, p22, p23, p31, p32, p33*

Defines an orientation matrix *P*, such that *P* gives plot coordinates from orthogonal coordinates *XO*, *YO*, *ZO* (where the *XO* axis is parallel to *x**, *YO* parallel to *zXx** and *ZO* to *z*). *X'*, *Y'*, *Z'* are the coordinates for 'plots' requested by subsequent PLOT instructions (where $X' = p11 \times XO + p12 \times YO + p13 \times ZO$ etc., see J.S. Rollett, Computing Methods in Crystallography, Pergamon (1965) p. 22.) *X'* runs down the page, *Y'* across the page and *Z'* vertically out of the paper. This convention is used in the Siemens proprietary program XP and its forbears (such as XMOL).

PLOT *x, y, z, h, n1 ... nh, s, d1, ... dh, sd, ... sdh*

This causes a line-printer plot of the molecule, size $2 \times s \times HA/HD$ along *X1* by $2 \times s$ Å along *Y1* centered on *x*, *y*, *z* and projected onto a plane defined by *x*, *y*, *z* and the orientation matrix *P*, (set by a preceding MATR instruction) and an identically scaled plot of the potential energy function in this plane suitable for hand contouring. This may be as for terminal, edge-bridging or face capping hydride (*h* = 1, 2 or 3 respectively) bonded to atoms *n1*, ... *nh* in the atom list at bond length(s) *d1*, ... *dh* uncertainty *sd1*, ... *sdh* (if only one of *d1*, *d2* is given when *h* = 2 then *d2* is assumed = *d1*, likewise if *d2* and *d3* is not given when *h* = 3 then *d3* = *d2* = *d1* is assumed for *sd1*, ... *sdh*).

CONT *n, co, c1, ... cn*

This instruction specifies the contour levels to be used in the contouring *g* of the potential energy function in the specified plane. There will be *n* contours and those below *co* will be broken lines, and levels at which contours are to be drawn will be *c1*, *c2*, ... *cn*. Both the potential energy contours and a stick drawing of the molecule projected in to the plane are drawn.

HLOC *x, y, z, h, n1 ... nh, d1, ... dh, sd, ... sdh*

Is used to refine a hydride position as determined by initial use of TERM, EDGE or FACB instructions. Up to 10 HLOC instructions may be used in one job to co-refine

hydride positions at x, y, z (as for the PLOT instruction), at bond lengths d1 ... dh from the n1th ... nth atoms in the atom list (uncertainty sd1, ... sdh Å). Inter-hydride potential energy terms are evaluated using the parameters given in the Appendix for hydrogen atoms, the hydrides refined are included at the end of the atom list with atom names HLn (n = 1, ... 10)

atom instructions *name (4 characters), type, x, y, z*

these are recognised as atom instructions if the given name does not correspond to a permitted instruction, the atom type corresponds to the appropriate PARM instruction (where given). Further numbers on this instruction e.g. Uij etc. are ignored.

END+

Indicates the end of a segment of a job and initiates execution of preceding instructions, and is followed by further instructions to be executed.

END

Is the obligatory final instruction of a job.

7.2.6. Examples

Three test jobs illustrating the use of all the commands available in the program are included with the program provided. For discussion of the outcomes of these hydride location attempts see A.G. Orpen [1].

JOB 1.

This job is typical initial hydride search on a tetrahedral osmium cluster compound $\text{H}_3\text{Os}_4(\text{CO})_{11}\text{C}_6\text{H}_9$. All non-hydrogen atoms have been located from an X-ray study and are included in the input deck with the appropriate TITL and CELL instructions. Suitable potential energy parameters are used for the various atom types present and four of the edges and two of the triangular faces of the cluster are searched for minima. The output from this job reflects all the input instructions and gives details of the results of the various minima searches carried out. Each search is preceded by a heading indicating the type of hydride being searched for, and the bond lengths (and uncertainties) to be used, in addition to the search radius within which non-bonded potential energies will be evaluated (usually 3.5-4.0Å). 26 attempts are made to locate the minima and optimised positions are output after each attempt together with their potential energies and a comment on their suitability, the unique solutions are then further refined. This process is repeated for all 6 requested searches and the summary of refined hydride sites at the end of the output shows all minimum energies and the inter-minima distances as well as bonded and non-bonded distances to other atoms. In this case three edges of the cluster show how single low energy minima typical of hydrides bridging edges of a carbonyl cluster. The remaining faces and edges

tested clearly are not bridged as indicated by either no suitable sites being located or only high energy minima being found.

JOB 2.

This job illustrates use of the PLOT command to check for multiple minima undetected by an initial search. After TITL, CELL, atom and PARM instructions the TERM instruction is read in causing a search for a terminal hydride in the mononuclear compound $\text{H}_3\text{Re}(\text{dppe})_2$. The MATR instruction causes the plots to be in the equatorial plane of the pentagonal bipyramidally coordinated rhenium, with the plots centered on that atom. The plot shows two distinct minima associated with the three terminal hydrides known to be present, one a single well, the other a double well, as indicated by its extended shape. The degeneracy must be lifted by appropriate use of the HLOC command to insert two hydrides into this double minimum (see ref [1]). Note that the TERM search finds only a very low energy site in this pseudo-single minimum.

JOB 3.

This job illustrated use of the HLOC instruction when investigating a triangular cluster compound $\text{H}_3\text{Ru}_3(\text{CO})_9\text{CCH}_3$ where the hydrides have been located from initial EDGE searches as bridging each edge of the cluster on the opposite side of the triangle from the face-capping $\mu_3\text{-CCH}_3$ group. Three HLOC commands are used to allow for the non-bonded interactions between these hydrides enabling more accurate estimates of their positions to be made. Their positions are refined in turn and the refined position output in the usual way.

7.2.7. Rules

There are some rules which should be followed in order to use the program successfully:

1. Up to 150 atoms (including hydrides as input with HLOC) are permitted in the atom list.
2. Up to 9 different atom types are permitted.
3. Only one of EDGE, TERM or FACB is allowed per job segment i.e. before an END+ or END instruction.
4. PLOT instructions must be preceded by a MATR instruction (and all atom instructions).
5. Only up to 10 unique minima may be located per job using TERM, EDGE or FACB commands.
6. HLOC instructions may not be used in the same job as TERM, EDGE or FACB commands.

7.2.8. Appendix

7.2.8.1 Potential energy parameters,

These are taken from Pavel et al [3]. The expression used is : $V(r) = A\exp(-Br)r^D - C/r^6$

Atom type	A	B	C	D
H	6600	4.08	49.2	0
C	44800	2.04	125.0	6
N	52100	2.04	132.0	6
O	42000	2.04	132.7	6
S/Cl	40500	3.85	265.2	0
Me	49100	3.71	380.5	0
Br	25650	3.56	366.7	0
I	43400	3.54	527.8	0

I and Br serve as reasonable approximations for larger elements not listed e.g. the transition elements.

7.2.8.2 Metal-Hydride bond lengths

Accurate (neutron diffraction determined) bond length information on transition metal hydrides is relatively sparse but certain conclusions may be drawn about values suitable for use here.

- Terminal hydride bond lengths are 0.1-0.2 Å shorter than those for edge bridging hydrides which are probably slightly shorter than those of face capping hydrides.
- M-H distances follow fairly closely the trends in covalent radius shown by transition elements, i.e. bonds to 2nd and 3rd row elements of the same group are likely to be 0.1-0.2 Å longer than for the corresponding 1st row element, and a small drop in M-H bond length is likely on traversing a row of the Periodic Table from left to right.

7.2.8.3 Some Neutron Determined Bond Lengths (Å).

See A.G. Orpen *et al* [4] for another list.

Terminal: Mn-H 1.60, Pt-H 1.60, Ir-H 1.60, Os-H 1.66, W-H 1.73, Re-H 1.67, Ta-H 1.77

Edge Bridging: Os-H 1.81-1.86, W-H 1.86-1.89, Cr-H 1.72, Mo-H 1.86, Re-H 1.88, Ru-H 1.79, Rh-H 1.78, Fe-H 1.67

Face Capping Co-H 1.73, Ni-H 1.69, Os-H 1.93, Rh-H 1.8

References

1. A.G. Orpen, *J. Chem. Soc., Dalton Trans.*, **1980**, 2509.
2. Fletcher and Reeves, *Computer J.* **1964** *7*, 149.
3. N.V. Pavel, C. Quagliata and N. Scarcelli, *Z. Krist.* **1976**, *144*, 64.
4. A.G. Orpen et al, *J.Chem. Soc. Dalton Trans.*, **1989**, S1.