

# The Case for CASE: Computer-Assisted Structure Elucidation



## Introduction

Computer-assisted structure elucidation (CASE) has been used to help identify compounds isolated by the detection of novel or difficult structural formulas, especially those of unusual products of drug metabolism and reactions. The completely automatic structure determination, even from the smallest of samples and very weak experimental spectra, is made possible by sophisticated CASE software designed to do this complex task.



Figure 1. The large number of possible isomers for some relatively small organic molecules.

Modern CASE algorithms give ever-increasing amounts of information about a substance's structure, such as its molecular weight, formula, and other information on composition. However, even in published structures the number of atoms might be too small for computer-assisted elucidation to structure it.

## CASE Methodology

CASE follows a simple set of steps to computer-assisted structure elucidation: generate possible structures.

1. Generate experimental data to extract knowledge
  - Molecular Formula
  - Masses
  - Chemical shifts
  - Subgroups
  - Connections
  - Green fragments
  - Special reactions
2. Search structure space to derive all possible structures
3. Ranklist based on all criteria
  - Molecular formula

## Case Illustrations



Figure 2. An ACQTOF and GC/MS collection, peak assignments, and fragmentation through a set of related ions, associated with 1,1,1,1-tetra, showing connections, the software displays relationships for assigned spectra and structure, highlighting those which are likely to be accurate.

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## Automated Generation



Figure 3. A Molecular Connectivity matrix helps to control automatically during their interpretation. This can be used both for the final structure, or to perform an iteration about its proposed structure.

## Ranking the Best Candidates

Using the selected properties of substructure Molecular Weights, the entropy of the structure space can be gained for possible structures which agree with the experimental data. The software automatically evaluates all structural possibilities, and then ranks the best candidates by using based on the difference between the experimental and proposed structural data.



Figure 4. A set of possible structures, ranked by their molecular formula and masses. Structure assignments are color-coded based on their agreement with the experimental data.

## Report Generation and Statistics

With the right information, better structure can also be easily identified from structure space. The following table shows the statistics using ACQTOF and GC/MS.

1. ACQTOF and GC/MS
  - 200,000 assigned chemical structures
2. Molecular Weights and
  - 200,000 structures
  - 4,400,000 structural fragments
3. Chemical Shift
  - 20,000,000 structural connections with  $^{13}C$ ,  $^{15}N$ ,  $^{17}O$ , and  $^{31}P$  NMR
4. Entropy of Molecular Formula
  - 200,000,000 comparisons
5. Masses
  - 2,000,000 comparisons between structure
6. Results
  - 2,000,000 experimental comparisons and higher range



## The Automatic Structure Elucidation Challenge

Between 2004 and 2011, 112 different datasets were submitted from various institutions as challenges to the ACQTOF and GC/MS software system. (1) The structures determined ranged from 100 to 1000, with the largest set and the smallest that contained complex structures and several isomers (Figure 5).



Figure 5. The number of structures per dataset challenge submitted to ACQTOF.



Figure 6. The number of structural assignments performed by ACQTOF and GC/MS from these 112 datasets.

In one recent example, Molecular Weights software was able to determine the structure of a large, symmetrical dimer based on 1000,000,000 comparisons of structural units with the presence of structures (Figure 7).



Figure 7. The successful structure of hexamer 4.

## Case Systems

Modern CASE systems such as Molecular Weights software (2) can identify rapidly and accurately structures in novel chemical libraries. The software is based on ready structure with data sets, five data structures in each structure, 100,000,000 and 100,000,000,000 comparisons. The system can of 2,000,000,000 comparisons and 100,000,000,000 comparisons of many structural units with the structure, to get structural results.



For more information, visit [www.acdlabs.com](http://www.acdlabs.com) or contact us at [info@acdlabs.com](mailto:info@acdlabs.com).

# Computer Assisted Structure Elucidation

**Hussin A.Rothana**



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