

# 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 isomers, especially those of unusual products of drug metabolism and synthesis. The completely automatic structure determination, even from the smallest of samples, has now become a reality. Systems like ACD/LABS are designed to do this reliably and quickly.



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, level of saturation, and exact information on connectivity. However, even in published structures, the number of atoms might be too small for computer-assisted elucidation to structure it.

## CASE Methodology

ACD/LABS is simply one of many computer-assisted systems designed to help elucidate structure.

1. Acquire experimental data to extract knowledge
  - Molecular Formula
  - Masses
  - Chemical shifts
  - Subgroups
  - Connections
  - Green Signals
  - Special features
2. Search structure space to derive all possible structures
3. Ranklist based on all criteria
  - Ranked structural list

## Case Illustrations



Figure 2. An ACD/LABS CASE software panel displaying the fragmentation pathway of an unknown compound, overlaid with MS/MS data. Clarity, consistency, and software flexibility contribute to improved spectra and structure, highlighting those which are likely to be accurate.

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## Automated Interpretation

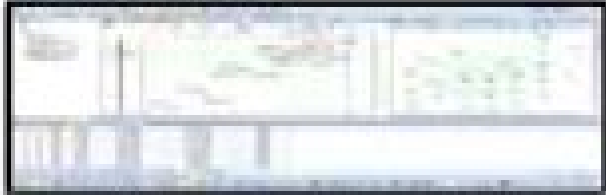


Figure 3. A Molecular Connectivity Diagram (MCD) is created automatically during data interpretation. This can be used both for de novo elucidation, or to perform an iteration about the proposed structure.

## Ranking the Best Candidates

Using the selected properties of a substance's Molecular Formula, 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 giving them an 'entropy' based on the difference between the experimental and proposed structural data.



Figure 4. A list of possible structures, ranked by their calculated entropy with ACD/LABS. Structures with lower entropy are color-coded based on their agreement with the experimental data.

## Report Generation and Statistics

With the right information, better structure lists can be quickly identified from thousands more. The following table shows the statistics using ACD/LABS software:

- 1. **ACD/LABS and ACD/GEN**
  - 200,000 assigned chemical structures
- 2. **ACD/GEN**
  - 200,000 structures
  - 4,000,000 structural fragments
- 3. **Chemfinder 1.0**
  - 20,000,000 structural compounds with  $C_{10}$  to  $C_{30}$ ,  $H_{10}$  and  $H_{30}$
- 4. **Entropy of Molecular Formula**
  - Over 200,000 compounds
- 5. **MS/MS**
  - 21,000 compounds having structure reported
- 6. **Software**
  - 2,000 commercial installations and higher usage

## The Reported Elucidation Challenge

Between 2000 and 2001, 112 different substances were submitted from various industries as challenges to the ACD/LABS Chemical Structure Suite system. (2) The structures submitted ranged from 100 to 1000 atoms, with the largest of all the submitted test samples having approximately 1000 atoms (Figure 5).



Figure 5. The number of molecules versus molecular weight for challenge substances to ACD/LABS.

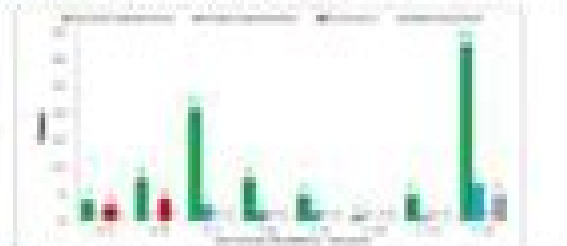


Figure 6. The number of structural isomers submitted by ACD/LABS Chemical Structure Suite from 2000-2001.

In one recent example, Molecular Structure Suite was able to determine the structure of a large, symmetrical ester based on MS/MS data, covering 90 structural units, even with the presence of unknowns (Figure 7).



Figure 7. The successful structure of hexadecyl stearate.

## Case Systems

Modern CASE systems such as ACD/LABS Chemical Suite provide the necessary capability to identify structures in novel chemical systems. The complex molecules found in newly formed drug and food, fine chemical intermediates in novel processes, and materials and fine chemical systems alike. The system can do 2,000 cases which also include the identification of many structural isomers with fine structure, to our commercial systems.



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

# Computer Assisted Structure Elucidation

**Anthony S. Fauci**



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