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Competition in structural analysis—old wine in new skins

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At the beginning of the 1980s, A. Zschunke devised a competition in molecular structure determination, which was first organized by the Sektion Chemie of Martin Luther University Halle and later by Humboldt University Berlin. Each of the five departments of chemistry in the former East Germany at that time could send two students. Further participants were recruited from other countries of the former Eastern bloc. The goals of this event were:

- To test the performance in structural analysis
- To compare the levels of performance at the different universities
- An international comparison, albeit restricted to eastern European countries

Astonishingly, this competition turned out to be a very popular event. Routinely, the number of students who desired to participate was greater than the number that could be accommodated, and an enormous amount of time was spent on the preparation for the event. A strong motivation for the participants was, beyond any doubt, that prizes were awarded to the winners. Unquestionably, the competition stimulated the involvement in structural analysis of both teachers and students. The competition was also used by the advisors of the groups to exchange experiences and discuss further improvements as well as the optimization of the courses on structural analysis, of special interest in this regard were the pulse NMR techniques, which were being transformed into routine methods at that time.

Since we were committed to the importance of such an event and since we wanted to promote analytics, we reestablished the competition and assigned the organization to the Jungchemikerforum Jena ("Young Chemists Association Jena," a subdivision of the German Chemical Society, GDCh, especially for student members). Although the competition was now open to participation by students from all German universities, initially only participants from the new German states could be welcomed. The reason might have been a suboptimal announcement policy in the western states. Nevertheless, in the following 2 years participants from the western states (from the universities of Darmstadt, Göttingen, Paderborn, and Duisburg-Essen) were able to participate in the event.

In a 3-h examination, the participants had to determine the structure of an unknown component based on a set of spectra (see Table 1). The composition of the set depended on the compound and could consist of the following spectra, for which the ability to interpret them should nowadays be mandatory for a chemist: electron ionization mass spectrometry, IR, UV, ^{1}HNMR, ^{13}CNMR, distortionless enhancement by polarization transfer, ^{1}H,^{1}H correlation spectroscopy, heteronuclear single quantum coherence, heteronuclear multiple bond correlation, and nuclear Overhauser effect spectroscopy spectra. Besides the spectra, each student received printed forms to be completed with the interpretation of the spectra. To allow there to be a uniform evaluation, some information and hints were given. Some examples are:

- Determination of the sum formula and the number and assignment of the double-bond equivalents.
- UV/vis: Calculation and evaluation of the molecular absorptivity at λ_{max} of the longest-wavelength absorption band and the assignment of this electronic transition to the respective chromophore. Which structural element is recognized?

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Table 1 Types of spectra provided for the three compounds, on the basis of which structure determination had to be done

Structure	Spectra
1	70-eV EI-MS, IR, UV (spectral data), 400-MHz ^{1}H NMR, 100-MHz ^{13}C NMR, (^{1}H,^{1}H) COSY, HSQC, HMBC
2	70-eV EI-MS, IR, 400-MHz ^{1}H NMR, 100-MHz ^{13}C NMR, (^{1}H,^{1}H) COSY, DEPT90, DEPT135, HSQC, HMBC, NOESY
3	14-eV EI-MS, IR, 400-MHz ^{1}H NMR, 100-MHz ^{13}C NMR, (^{1}H,^{1}H) COSY, DEPT90, DEPT135, HSQC, HMBC, NOESY

EI-MS electron ionization mass spectrometry, *COSY* correlation spectroscopy, *HSQC* heteronuclear single quantum coherence, *HMBC* heteronuclear multiple bond correlation, *DEPT90* distortionless enhancement by polarization transfer with a 90° pulse, *DEPT135* distortionless enhancement by polarization transfer with a 135° pulse, *NOESY* nuclear Overhauser effect spectroscopy

- IR: Assignment of the characteristics, the structure-specific coupled vibrations, etc., of the fingerprint region. Listing of the recognized functional groups and structural elements.
- ^{1}HNMR: Relative number of hydrogen atoms and the multiplet of the signals, calculation and assignment of the coupling constants, assignment of the signals, and so on.

You can obtain detailed information on the forms in the solution of Challenge 5.1 in *Challenges in molecular structure determination* by Reichenbächer and Popp [1]. Note that any books can be used.

The works are graded employing a point scoring system and awards are given to the works with the highest number of points. The spectra and the solution provided are returned to each participant. The results are presented in oral form by the leader of the competition so that each participant can recognize his or her performance level and know what needs to be improved.

To prepare for the event, two books, *Strukturanalytik organischer und anorganischer Verbindungen* [2] and *Challenges in molecular structure determination*, [1] both by Reichenbächer and Popp, were recommended. Both books show by examples of different degrees of difficulty the way to proceed to an unambiguous molecular structure determination.

Three competitions took place between 2009 and 2011, each at the beginning of October. The problems that were to be solved are presented in Fig. 1. The kinds of spectra that were provided to the participants are compiled in Table 1.

To find the right solution, it was essential to extract the structural information from all kinds of spectra, compile the information into a solution, and present conclusive evidence for it.

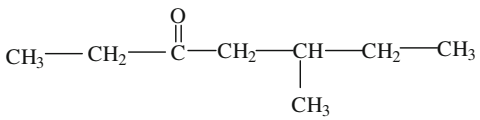
Essential to obtain the solution was:

- To detect heteroatoms and determine the chemical formula based on the isotopic ratio obtained by electron ionization mass spectrometry and information from IR, ^{1}H NMR, and ^{13}C NMR spectra
- Detection of rings based on the degree of unsaturation
- Detection of optically active centers
- Determination of structural elements (aromatics, alkynes, alkenes, alkanes) and functional groups
- Determination of structure proposals based on the individual information obtained from the spectra, selection of and evidence for the correct structure
- Assignment of all ^{1}H NMR and ^{13}C NMR signals
- Cross-check of the structure based on mass-spectrometric fragmentation, if possible.

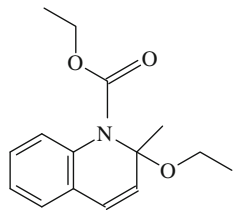
Each of the three compounds (Fig. 1) presented a specific challenge that had to be recognized, such as:

- Optically active centers (structures 1, 2, and 3)
- Several heteroatoms (structures 2 and 3)
- Nonaromatic rings (structures 2 and 3)
- Accidentally isochronous NMR signals (structure 2).

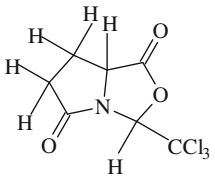
In the case of structure 3, it should have been realized by the participants that low-voltage spectra can be used to detect the molecular ion peak of compounds with many fragments. It goes without saying that the two possible diastereomers of structure 3 cannot be distinguished.



5-Methyl-heptanone-3 (structure 1)



N-Ethoxycarbonyl-2-ethoxy-1,2-dihydrochinoline (structure 2)



2-Trichlormethyl-1-aza-3-oxa-bicyclo[3,3,0]-octane-4,8-dione (structure 3)

Fig. 1 Structural formulas of the compounds that were to be identified in the three competitions of the new series

The results of the first competition were very divergent. There were good solutions, but some of the participants were not able to solve the problems satisfactorily. This was especially true for the interpretation of NMR correlation spectra, but also for the evaluation of IR spectra with respect to functional groups and structural elements. Often the evaluation of the latter spectra was limited to the detection of carbonyl groups without further attempts to be more specific. But these participants have been motivated to improve their performance. Several students took part repeatedly, showing a clear improvement, which can be taken as a sign that our intention to induce the acquisition of deeper understanding of structural analysis was successful. Accordingly, nearly all participants could present the correct or a nearly correct solution.

Later, the spectra of all three compounds which were the subject of the competitions were added to the book *Challenges in molecular structure determination* by Reichenbächer and Popp [1], and the full solutions to the problems are now accessible at http://extras.springer.com/2012/978-3-642-24389-9 (structure 1, Challenge 5.7; structure 2, Challenge 5.21; structure 3, Challenge 5.20).

In one of the supporting programs of the event, there was not only an opportunity to take a guided tour through the city of Jena, but also the possibility to obtain an inside view of scientific institutions such as the Institute of Forensics and its analytic capabilities following court standards. Additional social events such as a typical Thuringian barbecue in the evening served as a means to become better acquainted with each other and helped in the exchange of experiences and views.

Conclusion

We believe that the spectroscopic methods listed above should be the standard of performance of the modern chemist in the area of structural analysis. Doubtless, the performance of students is tested in each university, but this competition is a test of performance *between* universities on the basis of the standard of performance mentioned above. Therefore, a test between various universities should be obligatory; the competition we devised would be in our opinion an ideal candidate for this.

Although the competition has taken place only three times so far, the overall outcome is fairly positive; the competition is a stimulus to acquire deeper knowledge and abilities in the field of structural analysis, and the results allow a comparison between the success of different universities in this field.

There is enough capacity to increase the previous number of participants, which was between ten and 15. We therefore kindly ask our colleagues to encourage potential participants and explore opportunities to finance their travel costs.

A goal worth striving for would be to have at least one participant from each university. As already stated, this has already been possible, albeit on a small scale.

We are convinced that this competition would well fit with the demands of the Bologna Process of tuning the training of chemists in a European framework. Accordingly the "Communiqué of the Conference of European Ministers Responsible for Higher Education" (April 2012) focuses not only on the acceptance of academic achievements, the support of mobility within Europe, etc., but also on quality assurance, which also includes the check of these achievements on the European level. Especially, the field of structural analysis as a reasonably limited and well-defined field of knowledge as outlined above should be well suited. A competition on a national level would provide a good starting point for an extension to other European countries. A subdivision of the competition into two parts would be useful in this context. One group would be formed by bachelor students, where apart from classic spectra only distortionless enhancement by polarization transfer spectra but no NMR correlation spectra would be required to solve the problem at hand, and another group would be formed by master and doctoral students, where this limitation would be omitted.

Outlook

Owing to the very positive response, we will continue to organize the competition. Since it seems that the established date directly after the summer break might be unfavorable, we will move the date forward to the start of the summer semester. Furthermore, in accordance with the Young Chemists Association Jena, the competition will be implemented within the scope of the Spring Symposium for bachelor, master, and doctoral students organized by the GDCh. In this manner, the competition would be elevated to a European frame.

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Manfred Reichenbächer is the scientific organizer of the competition in structural analysis. He has expert knowledge of exercises, practical courses and lectures in structural analysis over more than 30 years.