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Dedicated to Professor Alexandru T. Balaban
on the occasion of his 85th anniversary

ALEXANDRU T. BALABAN'S SYMMETRY: AN APPRECIATION

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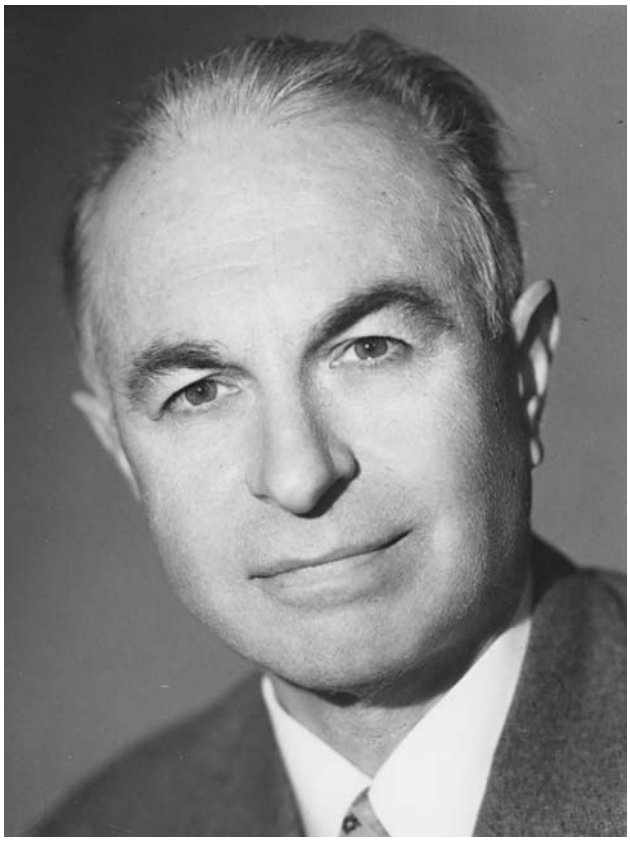

Alexandru T. Balaban (courtesy of Alexandru T. Balaban).

The symmetry concept – explicitly or implicitly – has informed Alexandru T. Balaban's oeuvre as a guiding thread. It provided a great utility in his multifaceted activities embracing many areas of chemistry. It has also formed a link to other branches of science and other aspects of human endeavors.

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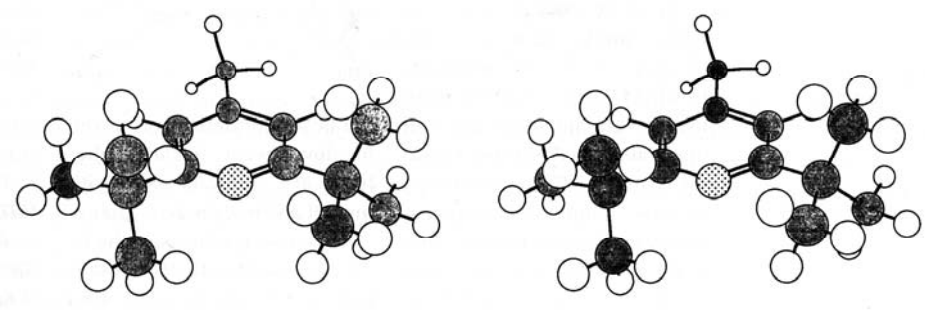
Alexandru T. Balaban's fairly detailed biographical account available on the Internet enumerates his principal areas of activity as Experimental Organic Chemistry, Theoretical Chemistry, Graph Theory, and Philosophy of Chemistry.[1] Even this terse biographical note conveys the riches of Balaban's multifaceted achievements.

Balaban's fascination with science and his joy of chemistry shine through every page of his publications. When one of us (BH) initiated a column "Beautiful Molecules" in the now defunct magazine of chemical culture, *The Chemical Intelligencer*,[2] Balaban was a dedicated contributor.



Stereoview of the molecular model of 2,6-di-*t*-butyl-4-methylpyrylium (Ref. 3).

He wrote about 2,6-di-*t*-butyl-4-methylpyrylium, and not only its structure, but also about its production.[3] As it turned out there were two simultaneous and independent discoveries of obtaining pyrylium salts. The starting points were different, but the results the same. One laboratory in London and another in Bucharest were involved. Molecular beauty, as any other beauty, is in the eye of the beholder, and there may be millions of other beautiful molecules beside 2,6-di-*t*-butyl-4-methylpyrylium. It was the process of discovery and especially how Balaban wrote about this molecule that made us all appreciate its beauty!

Costin D. Nenitzescu in his fifties (courtesy of Alexandru T. Balaban).

Balaban has valued both molecular qualities and human qualities. The way he remembered his mentor, Costin D. Nenitzescu, was exemplary for how a grateful pupil can pay tribute to a remarkable teacher.[4]

In our note, we propose to look at his oeuvre from a point of view different from the above quoted Internet account. We are taking an alternative cross section using the symmetry principle as a reference point. In doing so, we rely on two of Balaban's comprehensive overviews published in two edited

interdisciplinary volumes on *Symmetry*. These are not broadly known publications. We label one as ATB1[5] and the other as ATB2.[6] Although Balaban's activities throughout his career involved intimately the symmetry concept, both as a tool and as a target, the term does not even occur in the above-cited biographical overview of his activities.

We are going to examine these two comprehensive articles; we refer to some of their sections and statements and add our commentaries to them. Our purpose is to illustrate the universality and eminently interdisciplinary character of Balaban's approach to research, his science, and his outlook on life. It is inevitable that our coverage will be eclectic, but even from mosaic components an enjoyable impression of the wholeness may emerge.

In ATB1, Balaban takes the reader to a comprehensive journey, from the atomic to the molecular, then, to the supramolecular level, on to polymers, and to chemical reactions. He moves from the ideal to the real, which is a fruitful approach in general and when discussing symmetry in particular. What is especially refreshing is his directness with which he connects the universe and the objects of physical chemistry, and makes it clear that the same approach is applicable to the two. He says, "In order to arrive at an understanding of, and to be able to live in, a crooked world, human reason needs the representation of perfection in the universe; likewise, in order to understand the behavior of real gases, physical-chemists had first to discover the laws of perfect or ideal gases. Perfection involves, in many cases, higher symmetry than the extant one."

Eugene P. Wigner and Istvan Hargittai in 1969 at the University of Texas at Austin.

Here, it is possible to discover the resonance between Balaban's approaches to nature in utilizing the symmetry concept with Eugene P. Wigner's views.[7] Wigner pointed out the semantic connection between the term invariances, used much in physics, with the word symmetry that we are much more accustomed to as being applied in everyday language. Wigner stressed that the observation of invariances makes it possible to formulate the laws of nature and he described the consecutiveness of invariances, laws of nature, and the events we observe and experience, that is, the physical phenomena:

Invariances	→	Laws of Nature	→	Physical Phenomena
(Symmetries)				(Events)

Wigner saw in this the profound unity of nature, which he pronounced eloquently in the following way: "[T]he function of the invariance principles [is] to provide a structure or coherence to the laws of nature just as the laws of nature provide a structure and coherence to the set of events."[8]

Balaban draws a panoramic picture of the utility of the symmetry concept in ATB1 as he discusses symmetry at the atomic level, involving atoms, electrons, and the periodic system. He then extends his considerations to the molecular level and to the entirety of chemistry. Just as he was writing this contribution, one of the present authors (IH) was being involved in creating a comprehensive presentation of symmetry in chemistry.[9] This is one of several meeting points of our interests and activities, adding so much to the rewarding pleasure of the overview of Sandy's (Sandy for Alexandru for his friends) works.

Ronald J. Gillespie's valence shell electron pair repulsion (VSEPR) model is another area where our interests overlap.[10] The model predicts the geometry of a molecule considering the repulsions of all electron pairs in the valence shell of its central atom, assuming that this valence shell retains its spherical symmetry. The total energy of repulsions to be minimized may be expressed through the potential energy terms, $V_{ij} = k/(r_{ij})^n$, where k is a constant and r_{ij} is the distance between the charge centroids of the electron pairs i and j. The exponent n is large for strong repulsions and small for weak repulsions, but it is not known to any accuracy. The beauty of the model is that in making reliable predictions for molecular geometry, for the range where n is larger than three, the actual value of n need not be known, because the results become insensitive to the value of n.

Our first instinct would suggest that the most symmetrical geometries should be predicted, but this is mostly valid only when all ligands are the same, and even then, this is not always so. When not all ligands are the same about the central atom, the VSEPR model provides great utility in making reliable predictions. Balaban recognized early on the structural variability of structures that fall into the scope of validity of the VSEPR model [ATB1].

The applications of the VSEPR model led to accurate predictions of this variability. They brought the first examples of convincing evidence to make the model broadly accepted not only as a tool of chemical education, but also as a tool of research. Thus, in spite of the availability of experimental data interpreted otherwise, the model correctly predicted C_s symmetry for $OClF_3$ (rather than the C_{3v} symmetry of the "analogous" OPF_3). Another celebrated case was the prediction of a distorted octahedral geometry for the XeF_6 molecule rather than a regular octahedral shape.[10]

Balaban discussed the structure of hydrocarbons having skeletons of the shape of Platonic solids. He recognized the special efforts necessitated in producing dodecahedrane, $(CH)_{20}$ [ATB1]. Balaban went on musing about the production of other polyhedral molecules, among them those having the shapes of truncated regular polyhedra. Of course, one of those shapes is the truncated icosahedron, the structure of C_{60}—buckminsterfullerene. Balaban was compiling the manuscript of ATB1 less than a year before the actual discovery of this chemical sensation.

The Jahn-Teller effect may be one of the few reasons causing a small molecule, consisting of a central atom and identical ligands, having lower than the highest possible symmetry. An example is the MnF_3 molecule in the gas phase. Balaban's discussion of the Jahn-Teller effect focuses on examples from organic chemistry [ATB1].

Balaban's considerations of chemical symmetries extend to linear macromolecules, to supramolecular systems, and to the conservation of orbital symmetry and the role of symmetry in chemical reactions. He has been a pioneer in chemical topology and graph theory and edited the first book in chemistry on graph theory.[11] Graphs can represent all molecular structures as far as the connectivity of atoms is concerned and provided the bonding is covalent in them. In the molecular or constitutional graphs, the points indicate the atoms and the lines represent the bonds. Application for nomenclature is one of the uses of graph theory in chemistry.

Vladimir Prelog wrote the Foreword to Balaban's graph theory book and Prelog figures in the ATB1 article in more than one place. Chemical chirality, or molecular handedness, has been an important topic in Balaban's science. Prelog was one of the pioneers in uncovering the role of chirality in stereochemistry and in chemical processes. Prelog's famous *ex libris* bookplate by the artist Hans Erni represented three basic ingredients of chirality: human intelligence, the left and right hands, and two enantiomorphous tetrahedra. Note that the tetrahedral shapes here are not regular because regular tetrahedra are not chiral due to their symmetry planes. In Erni's drawing, the two hands appear as if they were inverted – the person must have crossed his/her two arms. Erni made other drawings with non-inverted hands.[12]

Hans Erni's *ex libris* bookplate for Vladimir Prelog with Prelog's dedication to one of the authors.[12]

We make no attempt even approximately covering Balaban's two selected articles. We mention though one more item from the end of ATB1 where there is a brief section on spheres and chemistry. Balaban notes that the sphere is the most symmetrical object. Already Copernicus remarked in 1543, in his *De Revolutionibus Orbium Caelestium* that "… the spherical is the form of all forms most perfect …"[13] Balaban delves into the importance of the spherical shape in chemistry. Then, he expresses his fascination with increasing dimensionality. The inhabitants of a flatland[14] could not even visualize many of the objects that are natural for us. Balaban recognizes that extending our considerations to higher dimensions carries the promise of further scientific discoveries. It suffices to think of the so-called quasicrystals to recognize the validity of such expectations.

Balaban's other comprehensive article was entitled "Carbon and Its Nets" [ATB2]. This was another example of Balaban's pouring out a chemical cornucopia to the enjoyment of his readers. He calls carbon "the most precious atom in the universe," and justifiably, to be sure, yet the adjective is particularly appealing. Balaban discusses the uniqueness of the carbon-carbon bond and its significance for life. He then moves on to describing the softest crystal graphite and the hardest crystal diamond as the two known allotropic forms of carbon, until recently, that is.

Alexandru T. Balaban and Istvan Hargittai in Bucharest in 1987.

This was shortly after the discovery of buckminsterfullerene, C_{60}, but before this new allotropic form could have been actually produced and thus subjected to the usual analyses. Nonetheless, Balaban devotes a

subsection in his review to buckminsterfullerene. We note here that the next entry following Balaban's chapter in this edited volume was a contribution by H. W. Kroto about fullerenes.[15] Balaban was very open to the appearance and production of further allotropic forms of carbon, such as the linear carbine and other finite and infinite carbon forms. His whole discussion is an illustration and demonstration of the importance of symmetry for the stability of molecules.

We have been fortunate in some minor ways to be associated with Alexandru T. Balaban. One of us (IH) fondly remembers our personal meeting in fall 1987 in Bucharest, which served as an inspiration. Those were difficult times, yet Professor Balaban's demeanor and the attitude of his associates were exemplary, dignified, and forward looking, and, thus, inspiring.

On the occasion of your 85th birthday, we are congratulating you, Sandy, and wish you many happy returns to the joy of all of us!

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