PL – 4

Fascinating serendipity some adventures in fullerene chemistry*

Tibor BRAUN

Institute of Inorganic and Analytical Chemistry, L.Eötvös University Budapest, 1443, P.O.Box 123, Hungary, e-mail: h1533bra@ella.hu

The lecture is divided into four chapters. Chapter one will give a short overview on the notion of serendipity and the serendipitous discovery of the fullerenes, the third allotropic form of carbon and will try to highlight why this discovery can be considered a revolution in chemistry. What do Velcro, penicillin, X rays, Teflon, dynamite, and the Dead Sea Scrolls have in common? Serendipity! These diverse things were discovered by accident, as were hundreds of other things that make everyday living more convenient, pleasant, healthy, or interesting. All have come to us as a result of serendipity – the gift of finding valuable or agreeable things not sought for or " the faculty of making fortunate and unexpected discoveries by accident" (dictionary definitions).

The word serendipity was coined by Horace Walpole in a letter to his friend Sir Horace Mann in 1754. Walpole was impressed by a fairy tale he had read about the adventures of "The Three Princes of Serendip" (or Serendib, an ancient name for Ceylon, now known as Sri Lanka), who "were always making discoveries, by accidents and sagacity, of things which they were not in quest of..."

The second and third chapters will present some results of the author's research group as outlined in the flow sheet of fig. 1. As visible, the research centers on the effect of two unconventional sources of energy (nuclear and mechanochemical) on the structure of three variants of solid C_{60} (polycrystals, monocrystals, and thin solid films) and uses instrumental analytical methods for detecting these effects, with the aim of obtaining new knowledge on the structure of the fullerenes. The results have shown that mechanochemical activation generates new mechanochemical structures which can lead to the mechanochemical synthesis of new supramolecular C_{60} compounds here exemplified by the synthesis of the C_{60}-gamma cyclodextrin host-guest complex.

*In cooperation with **Henrik Rausch**, Atomic Energy Research Institute (KFKI) of the Hungarian Academy of Sciences, Budapest

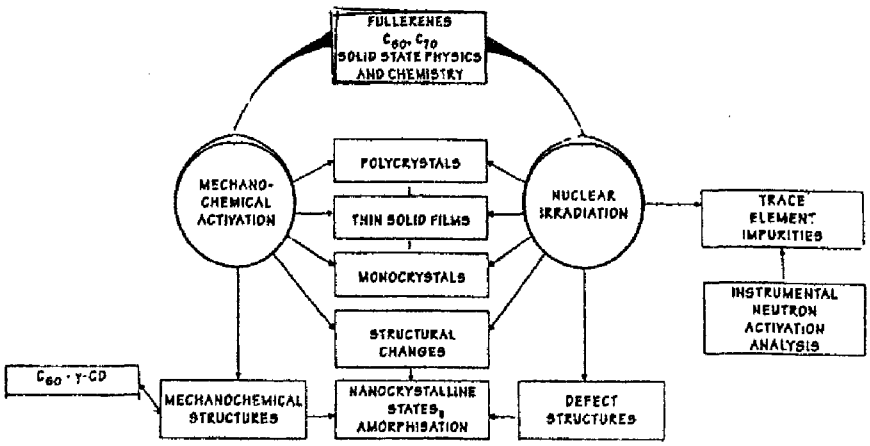

Fig. 1

The topic of our original investigations, started in fullerene research about ten years ago, has been an attempt to demonstrate the presence of the Wigner effect in polycrystalline C_{60} and C_{70}. In 1942 Eugene Wigner suggested that nuclear radiations might affect the graphite moderator of a nuclear reactor. He suggested that fast neutrons would displace atoms from their normal positions and so produce lattice defects in the form of holes in the graphitic network and interstitial atoms intercalated between the layer planes of the graphite. The interstitial atoms would cause an increase in the interlayer spacing and so cause the graphite to grow. Lattice strains produced by the defects would increase the internal energy of the graphite. This increase in internal energy stored energy might, if it were suddenly released, cause a spontaneous rise in temperature and is known as the Wigner effect. At that time, we have thought that the basic fullerenes having a similar all carbon structure, would be prone to manifest the same effect, which once revealed could bring some contribution to the better understanding of the solid state structure of crystalline fullerenes. Once more, the fullerenes being, as graphite, pure carbon structures and as carbon is a non activatable nuclide by neutron irradiation, we expected that irradiating it in a nuclear reactor will have as a consequence only purely structural effects, and the irradiated samples will emerge from the nuclear reactor without any induced radioactivity.

Much to our surprise, all our pure, polycristalline C_{60} and C_{70} samples have shown after the irradiation in a nuclear reactor an unexpected high gamma ray radioactivity, which at that time was of unknown origin. This has been a serendipitous result.

Fig. 1. shows that the nuclear irradiation of solid C_{60} generates deffect structures (on the crystal lattice and on the molecule itself). Additionally it was discovered that all the fullerenes and their precursors (graphite and soot) contain non-negligible amounts of about 30 trace element impurities, a fact that has been not known nor taken into account until quite recently. The detection and

determination of these trace element impurities has been made by using instrumental neutron activation analysis and gamma spectrometry. The neutron irradiation of C_{60} in a nuclear reactor has also made possible the serendipitous discovery of a new procedure for the synthesis of endohedral C_{60} compounds examplified by the synthesis of many endohedral radiofullerenes of $^{*}X@C_{60}$ type. The fourth chapter of the lecture deals with "Capturer-captive chemistry" as a new typology for molecular containers including fullerenes. (Fig. 2)

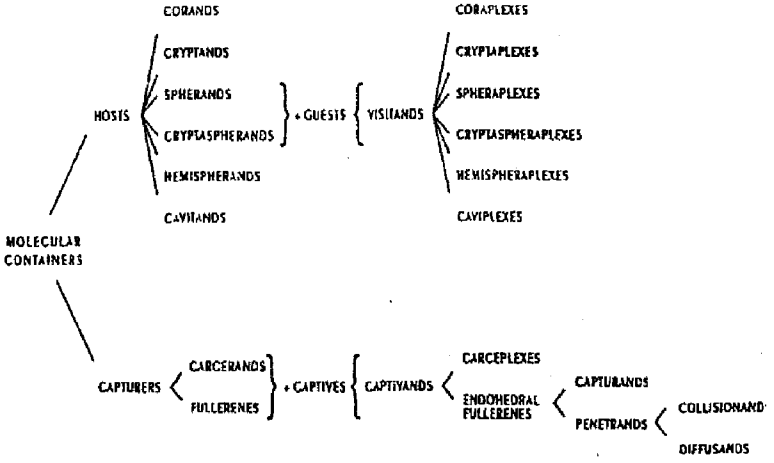

Fig. 2

In 1974 Donald and Jane M. Cram first used and defined a new concept they called "Host-Guest Chemistry. The concept has been based on a fascinating idea originating in Aeschylos's work, the Athenian poet-dramatist, who wrote 2500 years ago that the "pleasantest of all ties is the tie of host and guest." This later statement proved to be crystal clear and correct for a quite long period which extended approximately until 1988. But that year nomenclatural clouds began to accumulate on the heaven of host-guest chemistry. Namely that year, Cram et al., published their paper reporting on the first carcerands and carceplexes. "Absent among the millions of organic compounds hitherto reported are closed-surface hosts with enforced interiors large enough to imprison behind covalent bars guests the size of ordinary solvent molecules. The term carcerands was applied to this class of compounds ". Another event which has also contributed to the above-mentioned nomenclatural clouds in host-guest chemistry has been the discovery in 1985 of buckminsterfullerene and its oligomers, new carbon allotropes which are also closed-surface, hollow spheres with potentially enough internal volume to enclose small molecules or ions to result in so called endohedral fullerenes. The clouds came from the fact that in the case of carceplexes and endohedral fullerenes terms as "jailing", "incarceration" "prisoners", "guests behind bars" began to surface in the

literature of molecular container compounds. It does not need too much of explicative nomenclatural sophistication that this kind of relationship can no longer be considered to represent a "pleasant tie" in the sense of Aeschylos's host-guest relationship when the guest is not free to come and go at will being, in fact, "jailed" or "incarcerated" as a "prisoner".

The new approach presented in Fig. 2 has been outlined with the aim of preserving Cram's beautiful concept and reconciliating it with the advent of carcerands and fullerenes and with the "harsher ties" in carceplexes and endohedral fullerenes. Thus, the chemistry of molecular containers are, logically, split into a "host-guest" chemistry and "capturer-captive" chemistry.

As suggested, e.g., the coraplexes, cryptaplexes, sphereaplexes, crypta spheraplexes, hemispheraplexes, caviplexes, etc., are considered to be "visitand" compounds as a result of "pleasant ties" during their visiting "host-guest" relationship.

On the contrary, the carceplexes and endohedral fullerenes (Fig. 2) appear as "captivand" compounds, the captives being "captured" and irreversibly held behind covalent bars not as a result of "pleasant" but "harsh" ties, resulting in a "capturer-captive" relationship.

REFERENCES

1. T.Braun, A.Schubert, H.Maczelka, L.Vasvári: Fullerene Research 1985-1993, World Scientific, Singapore, London, 1995.

2. T.Braun, A.Schubert, G.Schubert, L.Vasvári,: Fullerene Research, 1994-1996, World Scientific, Singapore, London, 1997.

3. T.Braun, H.Rausch: Nuclear Recoil Implosion for Generating Radioisotopically. Labelled Fullerene Endohedrals and Cages, J.Radioanal. Nucl. Chem., 243(2000) 27.

4. K.Komatsu, K.Fujiwara, Y.Murata, T.Braun: Aqueos Solubilization of Crystalline Fullerenes by Supramolecular. Complexation with γ –Cyclodextrin and Sulfocalix[8]arene under. Mechanochemical High-Speed Vibration Milling, J.Chem.Soc.Perkin Trans. 1, (1999) 2963.

5. T.Braun (Ed.) Nuclear and Radiation Chemical Approaches to Fullerene Science, Kluwer Academic Publishers, Dordrecht, 2000.