Adamantane Essay, Research Paper

The unique nature of diamond is heavily dependent upon its composition, crystal structure, and mechanical, thermal, and electromagnetic properties.1 Of those dependencies, composition exacts the most influence over the characteristics. Crystal structure is the repeating pattern of diamond?s composition, and each of the properties are the result of molecular interaction which is determined by composition. Therefore, composition is paramount in the determination of the qualities of diamond.

Before its discovery, adamantane was known as decaterpene, the name applied by Decker to his tricyclic hydrocarbon. Decker believed that his decaterpene was similar in structure as the diamond lattice. Decaterpene, as in diamond, was proposed by Decker to be highly structured and strain free.2

Decker proposed decaterpene in 1924, but that was all it was until 1933 when the structure was proven to exist. Isolated in the petroleum of Hodinin, Czechoslovakia by Landa and Machachaeck, decaterpene became incarnate.3 However, the fact that they found the structure Decker predicted did not mean that his nomenclature would be used to identify the compound. That honor was bestowed upon its discoverers Landa and Machcahcaeck who used the Greek translation of diamond, adamantane, to identify the compound.2

Crude petroleum is separated into its component compounds by fractional distillation. The procedure involves a sample of the petroleum to be heated until the sample is vaporized leaving behind any solid impurities. The resulting steam enters a fractional distillation column in which a temperature gradient had been instilled. The temperature of the column decreases as the steam rises through the column. The idea is that, as the temperature of the column decreases, the vapor temperature will decrease. When the boiling point of a compound is passed, the compound will condense on the sides of the column and be collected in the fraction well at that point. Thus the mixture is separated into fractions of compounds with similar boiling points in a mixture.4 Adamantane?s high boiling point caused it to be one of the initial compounds to condense with the kerosene fraction in the 190o C cut.5

The only problem with the fractional distillation method is that adamantane cannot be extracted in large quantities because it exists in only a small quantity in petrol. The presence of adamantane was found to be only 0.0004% of the composition of petroleum by the fractional distillation method.2 Adamantane is not alone in the petroleum distillate in which it is present. Alkylated adamantane derivatives also show up in adamantane containing distillate. (II, III, IV) The output of adamantane is capable of being increased if the thiourea adduct method is employed on the petroleum. Landa and Hale were able to isolate complexes of adamantane from crude petroleum that had bonded to thiourea.5

Now that the natural product has been discovered, the next logical step would be to formulate the natural process in which the compound was made. As of 1964, the natural method that creates the adamantane compound had not been found. The natural process that was attempted was to bombard adamantane-free petroleum with catalysts in an attempt to initiate the formation of adamantane. The resulting mixture was fractioned and analyzed to see if any extra adamantane was created. In most cases, the catalyst failed to produce any adamantane. However, many of the catalysts produced derivatives that had the ring structure but with extra components attached.5 The only catalyst shown to make a significant amount was AlCl3, but not enough was created for the catalyst to be considered for mass production of adamantane. Catalysts that failed were: oil-bearing stone from Hodin with and without HF, aluminum silicate, aluminum oxide, concentrated sulfuric acid, zinc chloride, iron(III) chloride, tin(IV) chloride, antimony(V) chloride.5 It is believed that the reason many of the catalysts did not work, even though they are present in natural petroleum, is that the conditions that they were subjected to were experimental in nature. The creation of adamantane is thought to be a biogenesis of petroleum under a set of conditions that is not able to be recreated in the lab.2

With the natural mechanism a mystery, a synthetic method to create the compound was sought after to allow the study of adamantane to proceed. After all, with Landa in complete control of the slim supply of adamantane, the cost of adamantane skyrocketed.6 Two methods were investigated to be able to create the natural adamantane structure: ring closure and isomerization.

Before adamantane was known to the world, the starting material commonly used to synthesize adamantane and its derivatives through ring closure was being developed. In 1922, Meerwein was investigating a way to remove the bridgehead carboxymethoxy group of ring compounds, and reseal the ring structure with diiodomethane(V) and sodium. His experiments failed because the malonic ester(VI) which he created forced the reactant groups too far apart for the recycling to occur.3,4 Despite his failures, Meerwein was able to inspire other advancements of his research through the malonic ester which came to bear his name as Meerwein?s ester.7 This became the common starting point for the search for the path to cyclic adamantane.

Bottger was the first to make great strides in the adamantane synthesis research following Meerwein?s lead. Starting with Meerwein?s ester Bottger was able to bring the ring together to create a cyclic product.6 The product was of the tricyclo-[3.3.1.13,7] decane ring system of which adamantane is a constituent, but Bottger?s product still had external functional groups around the ring instead of the only hydrogen around adamantane.5 As a result, what Bottger had synthesized was not adamantane, but a derivative of it.

The first synthesis of true adamantane did not occur until 1937 when Prelog and Seiworth were able to advance the work of Bottger, and decarboxylize the ring structure leaving behind only the basic ring.6 Adamantane was their final product, but that product still was not produced in large quantities. The system used by Prelog and Seiworth yielded an output of adamantane at 0.16% of the materials going into it.7

As often occurs in science, the advancements made by Prelog and Seiworth were furthered by the research of others. Landa reentered the adamantane research realm with Stetter. Together, they were able to improve the efficiency of Prelog and Seiworth?s overall synthesis. Decarboxylation yield was increased by the addition of the Heinsdecker pathway (11%), and the Hoffman reaction (24%). Even with the advancements, synthesis of adamantane by ring closure was never able to yield an output over 6.5% of the reactants.5 Nevertheless, the process developed by Bottger remained an efficient method for the synthesis of derivatives.

This left research of adamantane to be inferred through the experimentation of adamantane?s derivatives since it?s synthesis was not economical. This was true until 1957 when Paul von R. Schleyer accidentally synthesized adamantane. Schleyer was working on the inversion of reversible endo-exo isomerization of tetrahydrodicyclopentadiene.3 During his experimentation, he noticed that the reaction had a side product of a white crystalline compound. The compound was set aside and investigated later. The mysterious compound was found to have a melting point that matched the experimental adamantane melting point. Other adamantane-like characteristics later solidified his compound as a match.

Schleyer?s discovery of an isomerization method of adamantane synthesis rocked the scientific community, as it provided a more efficient method for adamantane production. Schleyer was able to increase the output of his adamantane synthesis to a 30% and 40% yield by exposing the tetrahydrodicyclopentadiene to an AlCl3-HCl mixture under 40 atms. of pressure of hydrogen and HF-BF3 catalyst respectively.7

When Schleyer focused his procedure on the retrieval of adamantane, he found that the synthesis was bountiful with the starting reactant dicyclopentadiene which is a common compound.3 Research into the enigmatic compound could then proceeded full force from this point on to examine the compound to its every minute detail. What they found confirmed their previous assertions that adamantane was unlike any carbohydrate known to man.

That carbohydrate was found to be a three fused chairs of cyclohexane rings bound only to hydrogen atoms. The crystallized structure of adamantane was studied in depth by X-ray diffraction. An X-ray diffraction pattern is created through the interaction of photons emitted from an excited metal atom with the crystal form of a compound. The photon either misses the crystal atoms or is deflected by the atom. Most photons miss the atoms, but those deflected do so in a regular pattern because of the repetitious nature of crystals. That pattern may be recorded through the use of a strip of photographic film or a two-dimensional array detector to provide a hard copy of the deflection pattern.8 Thus the crystalline lattice type, distance between atoms, and number of atoms per unit cell may be found by analysis of the diffraction pattern. The crystal orientation is a face centered cubic lattice that was completely separate from all known carbohydrate crystal orientation.6 Face centered cubic means that there are atoms centered at the faces of the cube as well as at the corners. Adamantane was derived to have a tetragonal space group with four molecules per unit cell, and the vector quantities a = 6.60A and c = 8.81A.7 The carbon bond lengths and angles were stereotypically sound as they were measured to be 1.54 \_ 0.01A and 109.5 \_ 1.5o respectively.6 This data showed proof that adamantane was a stable compound, but how stable they did not know until the physical qualities were determined.

The melting point was determined by sealed tube, and was found to be 269oC which is the melting point for adamantane exposed to the atmosphere as well as the highest melting point for a carbohydrate.9 It is unusual for such an occurrence, but adamantane has no end to its surprises. The exact boiling point of adamantane is impossible to be determined for it is incapable of being reached except by mixture with other carbohydrates at which time the boiling point is 190oC. It is this property that allowed adamantane to be discovered by fractionalization.6 The enigmatic nature of adamantane is reinforced by the fact that it has such a high melting and boiling point, yet it remains true that adamantane will sublime at room temperature and atmospheric pressure.

Now that adamantane?s crysatlline structure is known along with the physical properties, what remains is for technology to fill in the blanks as far as molecular interactions of the compound. Adamantane was subjected to NMR and IR(Fig 1,2) Each test produced results that were unique for any carbohydrate upon which the same conditions were exerted.5 The most probable reason for such unique results is the symmetrical nature of adamantane. In fact, adamantane has a symmetry number of twelve which is unheard of in a carbohydrate. This means that throughout the structure there exists a combination of planes and axes about which adamantane is symmetrical or identical that totals twelve. Many compounds, organic and inorganic, are symmetrical in one or two dimensions, but few are symmetrical in three dimensions as adamantane is.

NMR uses the magnetic nature of atom nuclei to its advantage. By surrounding a compound in a magnetic field, the nuclei become vulnerable to excitation by radiation in the radiofrequency range. The radiofrequency that the nuclei absorb is dependent upon the environment the nuclei are exposed to as far as the neighboring nuclei and those the nuclei are bonded to.10 In this case, a proton NMR showed adamantane as only a sharp doublet with a spacing of 0.95 ppm.(Fig 1) The symmetry of adamantane is perfectly supported by these NMR results because only a doublet means that all of the protons are identical in nature. This shows that each proton in the structure of adamantane is sharing each of the electrons equally creating a strong dependence of resonance by all protons.6 The singularity in the NMR result becomes an important diagnostic tool for determination of the purity of an adamantane perspective. Any substitution anywhere on the ring would unbalance resonance of the compound that would be picked up by the NMR in the form of another series of peaks indicating an adamantane derivative as long as the doublet remains present.

IR results are much the same as those of NMR in that adamantane itself gives a clear result while any impurity clouds those results. Specifically, adamantane gives a major doublet in the region of 2926 cm-1 with a 0.8983 transmittance, and other peaks shown on Figure 2. This means that around the adamantane compound exists methyl groups that are similar in nature and surrounding environment. Consequently, all bonds absorb the same wavelengths that suggests identical motion of each of the bonds whether that be stretching, scissoring, or other. Any variance in a functional group would result in the absorbance wavelength to change. Therefore, an increase in the number of peaks and a decrease in intensity of the existing peaks would occur because the change in bonding pattern would limit or expand the possible motions of the bonds. Each bond-motion type absorbs a different wavelength in the IR, so any change in the types changes the absorbances. IR translates the amount transmitted per wavelength to an electrical signal that is interpreted through fourier transform to an IR spectrogram.10 Absorbance is the inverse of transmittance, so any change in absorbance changes the transmittance and the ending spectrogram values.

Since adamantane is so symmetrical and stable, it becomes the perfect basis for many studies and research. In fact the universality of adamantane is so great that it is capable of being used for: structure reactivity relationships, development of empirical force field methods, orientation disorder probe model, and structure basis for drugs.5 The possibilities are endless for adamantane and its uses simply because of its simplicity in nature and structure allow for a structure that is one of the most unique and strong in nature.

Bibliography

Resources

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