



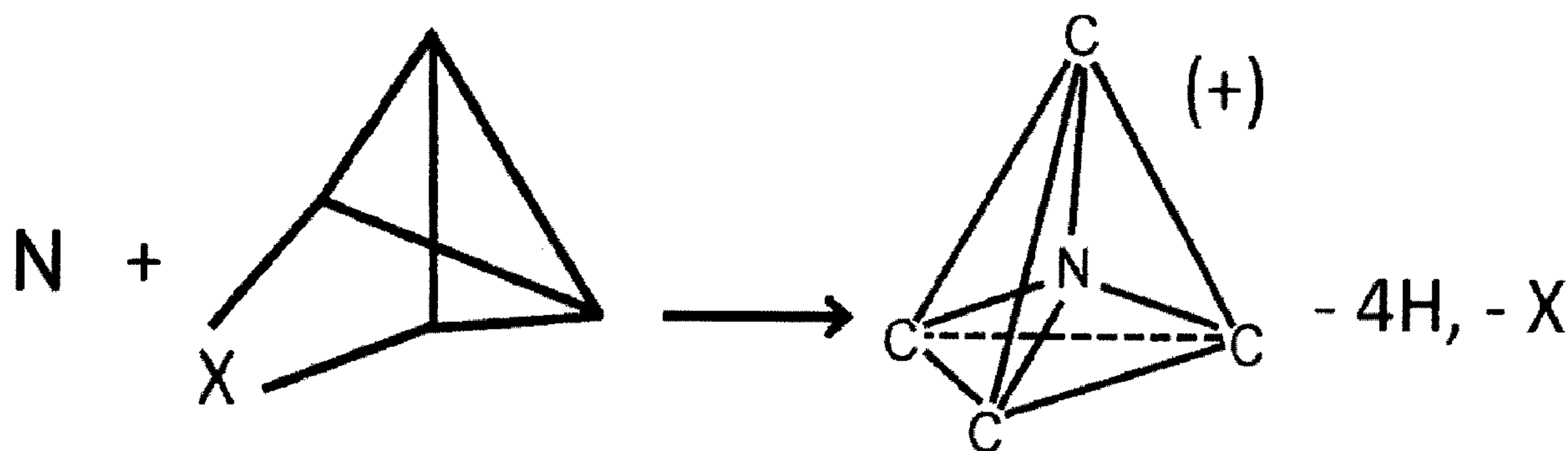
(12) **DEMANDE DE BREVET CANADIEN  
CANADIAN PATENT APPLICATION**

(13) **A1**

(86) Date de dépôt PCT/PCT Filing Date: 2016/11/03  
(87) Date publication PCT/PCT Publication Date: 2017/05/11  
(85) Entrée phase nationale/National Entry: 2018/04/25  
(86) N° demande PCT/PCT Application No.: US 2016/060249  
(87) N° publication PCT/PCT Publication No.: 2017/079388  
(30) Priorité/Priority: 2015/11/06 (US14/934,679)

(51) Cl.Int./Int.Cl. *B01J 19/00* (2006.01),  
*B01J 12/02* (2006.01), *B01J 19/08* (2006.01),  
*C01B 21/02* (2006.01), *C01B 32/25* (2017.01),  
*C01B 32/26* (2017.01)  
(71) Demandeur/Applicant:  
UNIT CELL DIAMOND LLC, US  
(72) Inventeurs/Inventors:  
NEWMAN, ARNOLD, US;  
HODES, DANIEL, US  
(74) Agent: KERR & NADEAU

(54) Titre : PROCEDES DE PRODUCTION D'HETERODIAMANT ET APPAREIL ASSOCIE  
(54) Title: METHODS OF PRODUCING HETERODIAMOND AND APPARATUS THEREFOR



$$\text{X} = -\text{CH}=\text{CH}-, \text{CO}, \text{ or } -\text{N}=\text{N}-$$

**FIG. 3B**

(57) Abrégé/Abstract:

A combinatorial synthesis of a heterodiamond unit cell, which entails a step of reacting a tetrahedranoidal molecule with a heteroatom to form heterodiamond unit cell and then heterodiamond mass.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property

Organization

International Bureau

(43) International Publication Date

11 May 2017 (11.05.2017)



(10) International Publication Number

WO 2017/079388 A1

## (51) International Patent Classification:

B01J 19/00 (2006.01) C01B 32/25 (2017.01)

B01J 19/08 (2006.01) C01B 32/26 (2017.01)

C01B 21/02 (2006.01) B01J 12/02 (2006.01)

## (21) International Application Number:

PCT/US2016/060249

## (22) International Filing Date:

3 November 2016 (03.11.2016)

## (25) Filing Language:

English

## (26) Publication Language:

English

## (30) Priority Data:

14/934,679 6 November 2015 (06.11.2015) US

(71) Applicant: UNIT CELL DIAMOND LLC [US/US]; P.O. Box 52, Cabin John, MD 20818-0052 (US).

(72) Inventors: NEWMAN, Arnold; 8220 Hamilton Spring Court, Bethesda, MD 20817 (US). HODES, Daniel; 8220 Hamilton Spring Court, Bethesda, MD 20817 (US).

(74) Agent: BEAUMONT, William E.; Juneau &amp; Mitchell PLLC, 1727 King St., Suite 300, Alexandria, VA 22314 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM,

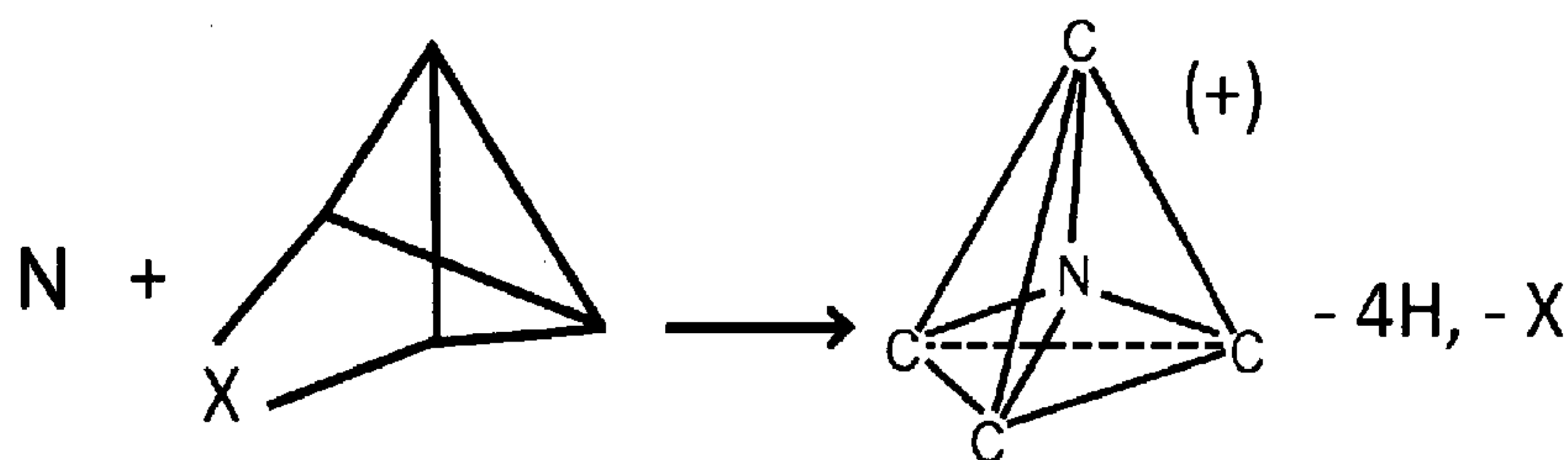
AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

## Published:

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))

(54) Title: METHODS OF PRODUCING HETERODIAMOND AND APPARATUS THEREFOR



$$X = -\text{CH}=\text{CH}-, \text{CO}, \text{ or } -\text{N}=\text{N}-$$

FIG. 3B

(57) Abstract: A combinatorial synthesis of a heterodiamond unit cell, which entails a step of reacting a tetrahedranoid molecule with a heteroatom to form heterodiamond unit cell and then heterodiamond mass.

## TITLE OF THE INVENTION

## **METHODS OF PRODUCING HETERODIAMOND AND APPARATUS THEREFOR**

## **FIELD OF THE INVENTION**

The present invention relates to methods and apparatus for performing the combinatorial synthesis of the heterodiamond unit cell and a heterodiamond mass therefrom.

More particularly, it relates to methods and apparatus for controllably producing a heterodiamond molecule having the tetrahedral structure of the diamond unit cell with a heteroatom controllably, and with precise stoichiometry, substituted into the diamond unit cell thereby replacing a carbon atom.

## **BACKGROUND OF THE INVENTION**

The term "heterodiamond" is conventionally defined to mean a super hard material containing boron, carbon and nitrogen (BCN). It is formed at high temperatures and high pressures, e.g., by application of an explosive shock wave to a mixture of diamond and cubic boron nitride." In contrast, the heterodiamond of the present invention is produced using combinatorial

synthesis reactions at or around ambient pressure. Furthermore, the heterodiamond of the present invention, synthesized controllably and with precise stoichiometry, can be exclusively either aza-diamond or bora-diamond. This is the definition and meaning of the term "heterodiamond" as used in the present specification, which is not to be confused with the conventionally used term "heterodiamond," which is BCN as already noted.

In addition, the term "diamond molecule" has been incorrectly used for diamondoid molecules and masses of diamondoid molecules such as adamantane. In fact, adamantane is a hydrocarbon whose structure is unrelated to that of the diamond unit cell: the diamond molecule.

Zhao et al., in US 7,938,997, disclose the preparation of a bulk superhard B-C-N nanocomposite compact. This is done by first ball-milling a mixture of graphite and hexagonal boron nitride, which is then encapsulated in a pressure range of 15 GPa to about 25 GPa and sintered at a temperature ranging from 1,800 to 2,500 K. These compacts include both boron and nitrogen. The heterodiamond of the present invention, however, is produced by a combinatorial synthesis reaction at generally ambient conditions. Furthermore, the present invention controllably yields either bora-diamond or aza-diamond individually with precise stoichiometries.

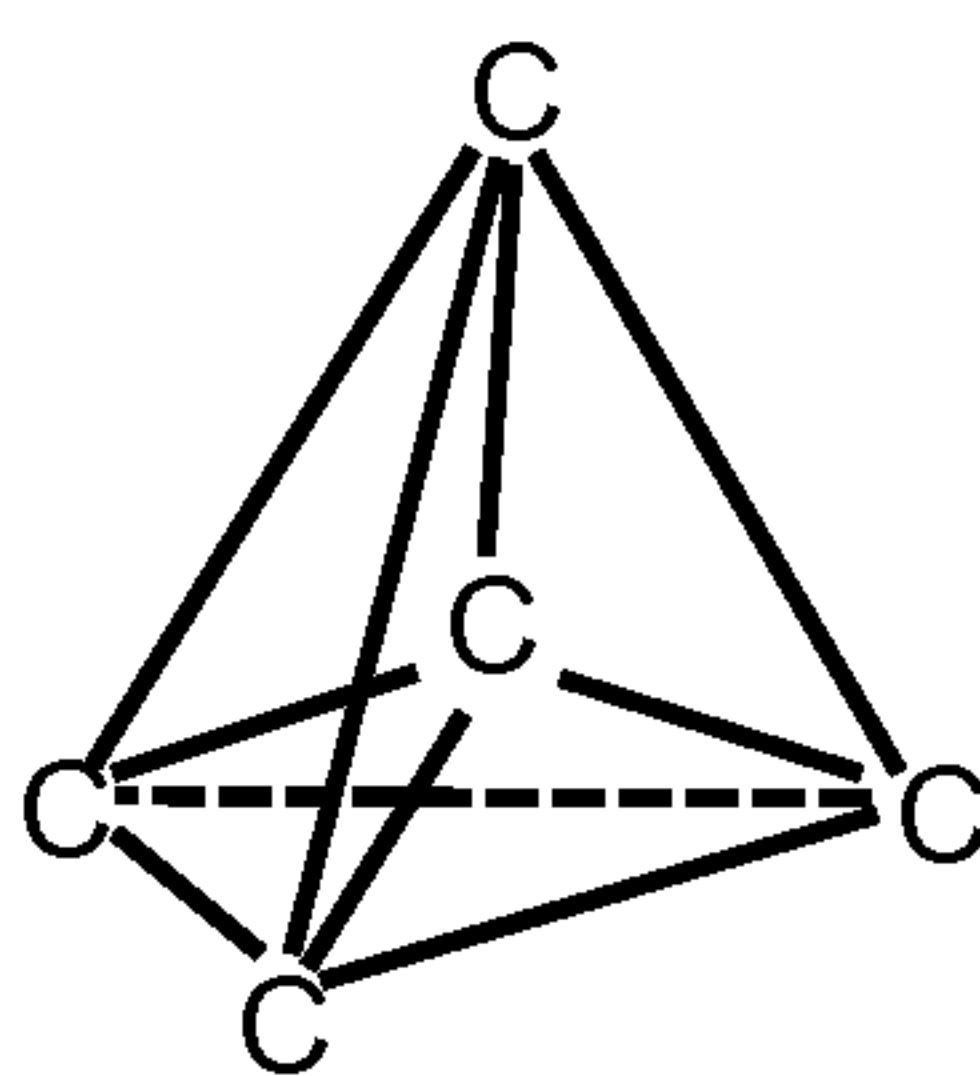
Popov et al. in their article "Deposition of BCN Films by Laser Ablation," describe the deposition of BCN films on silicon substrates by laser ablation. The films were deposited at 600°C and 950°C. In contrast, the present invention produces aza-diamond and bora-diamond with precise stoichiometries under generally ambient conditions using a combinatorial synthesis of heterodiamond unit cells.

Goglio et al. disclose the decomposition of commercial thiosemicarbazide at 600°C under nitrogen flow to produce carbon nitrides. This is different from the present invention wherein a carbon of the diamond unit cell is substituted with a heteroatom to produce a heterodiamond unit cell using a combinatorial synthesis.

In the published patent application, US 2015/0240381, Linares et al. disclose a boron doped single crystal diamond electrochemical synthesis electrode. They dope diamond with boron and thus do not controllably and precisely introduce a boron atom as a heteroatom that substitutes for a carbon atom in the diamond unit cell. This is different from the present invention, which produces heterodiamond wherein a heteroatom becomes an integral atom in the unit cell, occupying either an apical position or center, "cage," position of the unit cell.

The diamond unit cell is the smallest assembly of carbon atoms that make up diamond. It is, essentially, the diamond molecule. The diamond unit cell is a

tetrahedral structure comprising five carbon atoms with a carbon atom at each of the four apices and one in the center, “cage” position. Each carbon atom is bonded to each other carbon atom of the diamond unit cell. The bonds in diamond are short, strong  $sp^3$  bonds, which render the three-dimensional, solid structure of diamond, as opposed to graphite, another allotrope of carbon, which has  $sp^2$  bonds and is planar. The preparation of the diamond unit cell, whose structure is shown below, is described in U.S. 8,778,295 and U.S. 9,061,917:



The diamond unit cell

Conventional ways of fabricating diamond generally rely on the use of high pressure/high temperature or chemical vapor deposition methods. Diamond produced conventionally has several disadvantages including the following three. First, the high temperature processing of conventional methods precludes the use of many deposition substrates. Second, lengthy processing times make conventional diamond production uneconomical for many potential applications. Third, impurities produced by conventional methods require additional, expensive purification steps before the diamond product can be used in high precision applications such as semiconductor electronics and optics.

As a material, diamond has many desirable properties that make it ideal for microelectronic, optics, and other technological applications. These include extreme hardness, high index of refraction, high dielectric constant, extremely broad transparency bandwidth, band gap energy of around 5.45 eV, and others. Additionally, while diamond is an excellent electrical insulator, it is also one of the best heat conductors, more than four times better than copper. Unfortunately, because of their disadvantages, conventional methods of producing diamond have not been able to exploit these properties sufficiently to meet the large potential industrial demand that diamond, as a technological material, deserves. Furthermore, no method and apparatus to date has been able to produce reliably and controllably an identifiable diamond unit cell wherein a carbon atom is substituted by a heteroatom to produce "heterodiamond" as defined herein.

A diamond p-type semiconductor can be produced by doping diamond with boron. For example, when diamond is produced by conventional chemical deposition methods, boron is introduced into the gas stream of the reactor to form a boron impurity (i.e., dopant) that is incorporated into the diamond. This boron, however, is not controllably substituted for a carbon of the diamond unit cell, thus controllably and predictably yielding a heterodiamond unit cell. Rather, as an impurity, it is essentially a useful defect in the diamond crystal lattice.

It is also known that nitrogen can be contained within CVD-produced diamond. Indeed, nitrogen vacancies in diamond are currently an active area of research because they have the potential to yield a spintronic material that can be used as quantum electronic devices with qubits and quantum logic gates. This work is described in an article titled "The Diamond Age of Spintronics" (David D. Awschalom, et al., Scientific American, October, 2007, pp. 84-91.) The nitrogen of nitrogen vacancies in diamond and nitrogen-doped diamond, however, do not reliably and controllably substitute for a carbon atom of the diamond unit cell to yield a heterodiamond unit cell.

The term "heterodiamond" has been used conventionally, albeit incorrectly, for a very hard material containing boron, carbon and nitrogen (BCN) usually formed by applying a shock wave to a mixture of diamond and cubic boron nitride. Another variety is cubic BC<sub>2</sub>N, which is produced at very high pressures from a graphite-like BC<sub>2</sub>N. Thus, heterodiamond has been used conventionally to describe a ceramic material, which is not structurally related to diamond. These ceramic materials do not reliably, controllably, and consistently comprise a diamond unit cell that has been modified to include a heteroatom such as boron or nitrogen substituting for a carbon atom of the diamond unit cell to produce a heterodiamond unit cell. In contrast the present invention is directed to a diamond unit cell having a carbon replaced by a single heteroatom such as nitrogen or boron resulting in a heterodiamond unit cell. Thus, for the purposes of this specification, the term "heterodiamond" is used to mean a material

comprising at least one diamond unit cell wherein a heteroatom, such as nitrogen or boron, replaces a carbon atom: the heterodiamond unit cell. For the purposed of the present invention, the homo-penta-atomic molecule having five carbon atoms in a tetrahedral configuration with one carbon atom occupying the center “cage” position and four carbon atoms deployed apically, is designated the “homodiamond unit cell.”

It is important to distinguish between the use of boron and nitrogen as diamond dopants and the use of those elements in the present invention wherein nitrogen and boron are incorporated as structural members of the diamond unit cell.

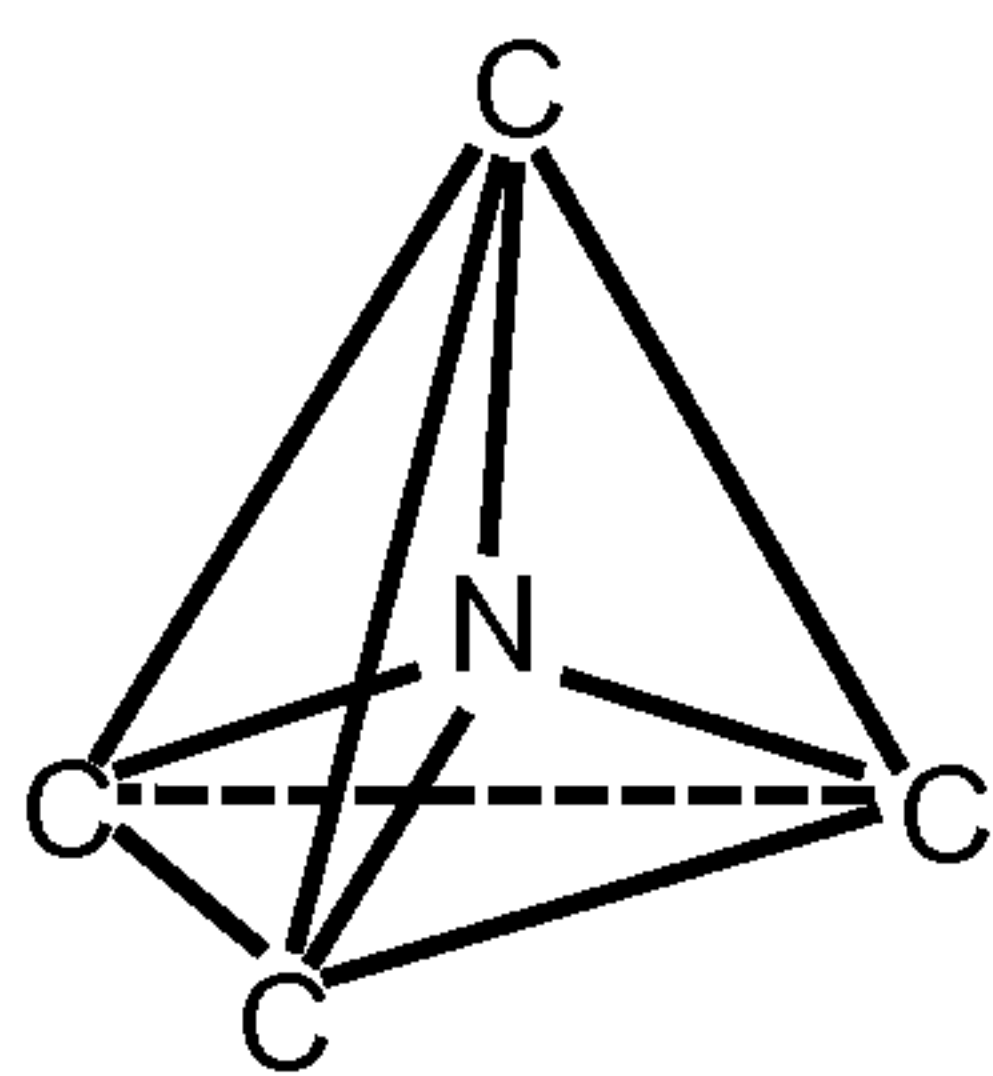
When nitrogen, boron, or other elements are used as diamond dopants, they are infiltrated into the lattice of the diamond mass. They are not chemically a part of the structure of the diamond unit cell in that they are not bonded to the carbon atoms that comprise the diamond unit cell. They are, rather, intervening impurities that become defects in the diamond crystal lattice that render the diamond a semiconductor. In contrast to doped diamond, the heteroatoms of the present invention are structurally a part of the crystal lattice because they are structural elements of the heterodiamond unit cells and of the heterodiamond mass which they comprise.

A heteroatom can occupy one of two positions of the heterodiamond unit cell, the center “cage” position or an apex position of the tetrahedron. A geometric

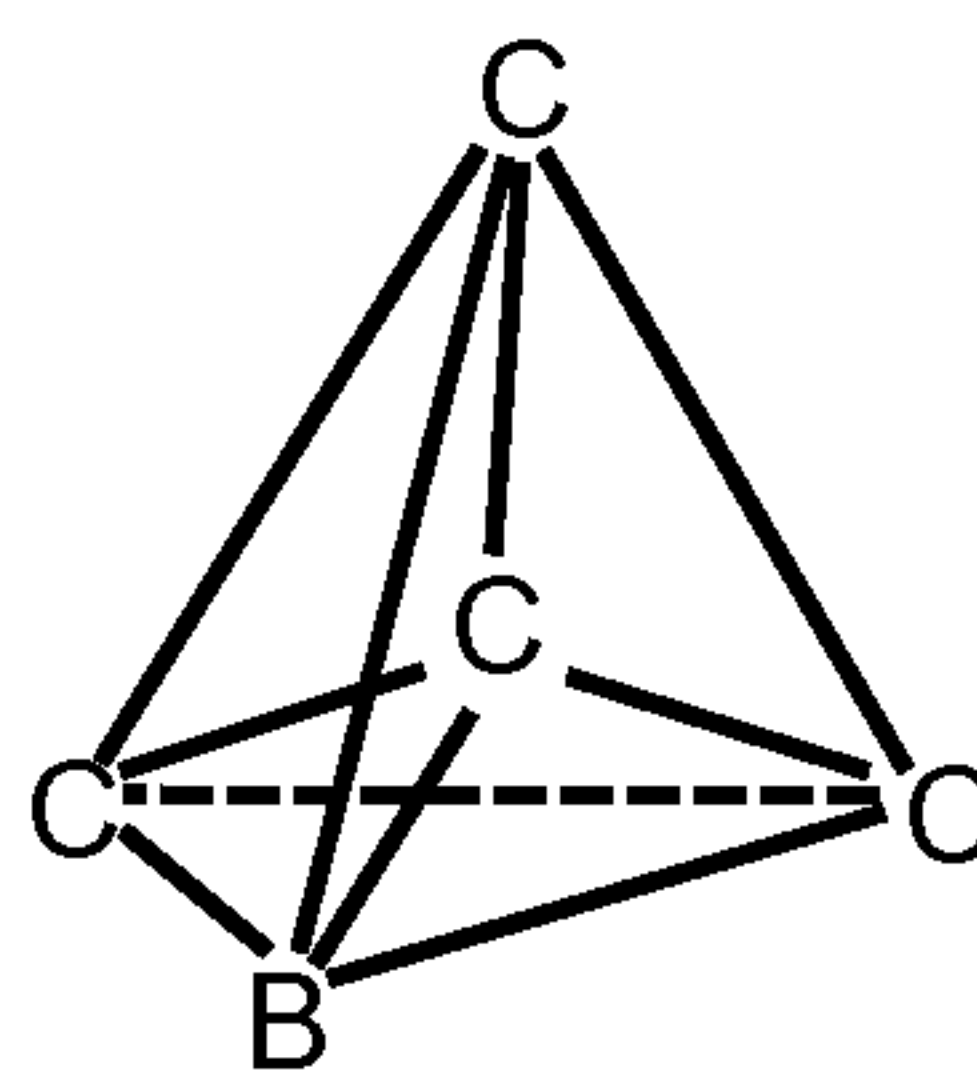
analysis can be performed relating to atoms with sizes that are close to that of carbon. In the periodic chart, carbon is flanked by the III, V elements boron and nitrogen, respectively. Carbon has an atomic radius of 70 pm, while boron and nitrogen have atomic radii of 85 pm and 65 pm, respectively. The covalent radii of carbon, boron and nitrogen, are 77 pm, 83 pm, and 75 pm, respectively. Thus, the practitioner will recognize that nitrogen is small enough to occupy the center “cage” position of the diamond unit cell. The atomic radius and covalent radius of boron are such that it can occupy an apical position of the heterodiamond unit cell.

Thus, the skilled practitioner might recognize that boron or nitrogen as a substitute element for carbon in a diamond unit cell is possible if a mechanism for their incorporation could be implemented. Heterodiamond unit cells, which are the subject of the present invention, include aza-diamond, in which the heteroatom is nitrogen, and bora-diamond, in which the heteroatom is boron.

These are shown below:

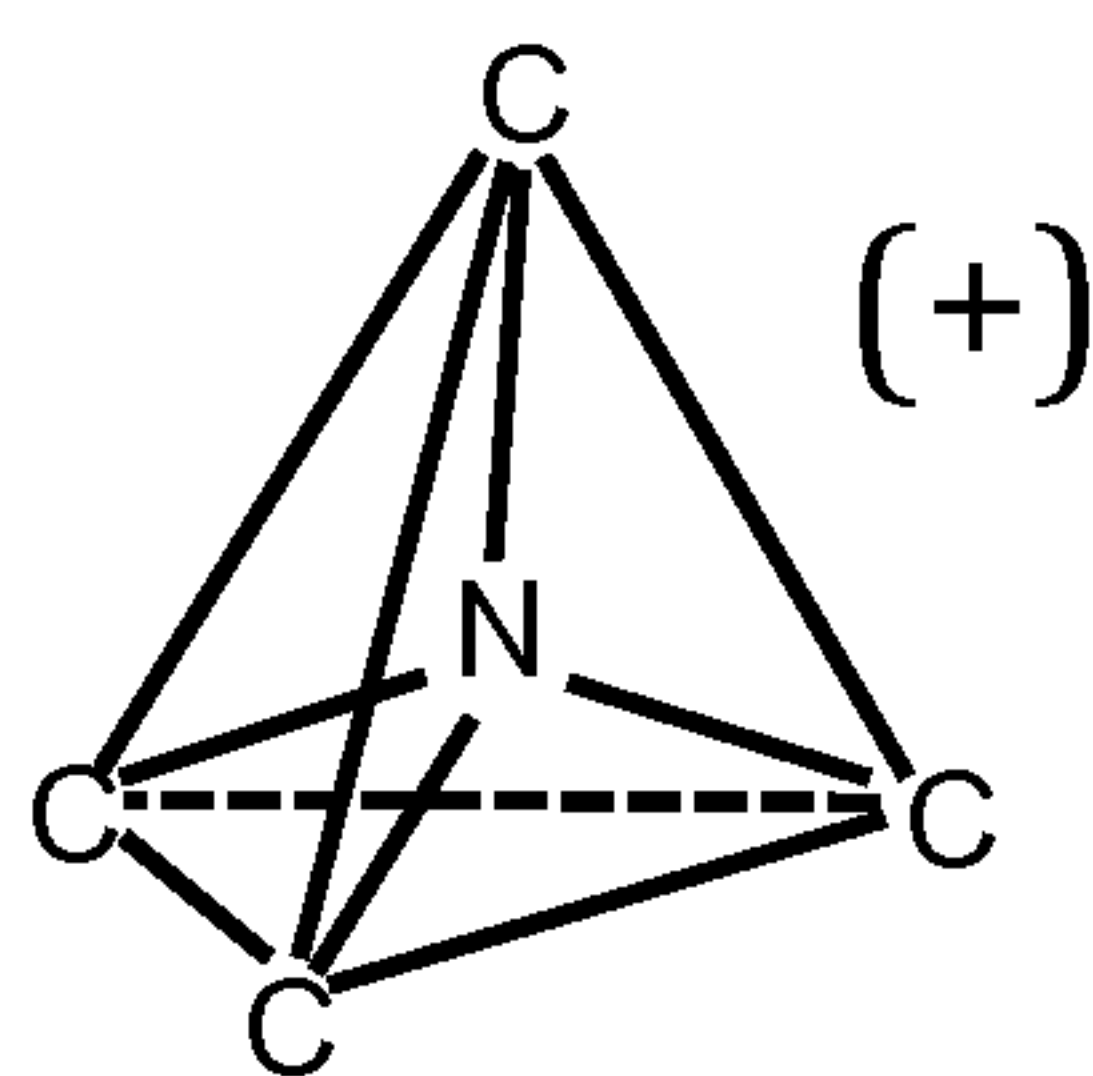


aza-diamond

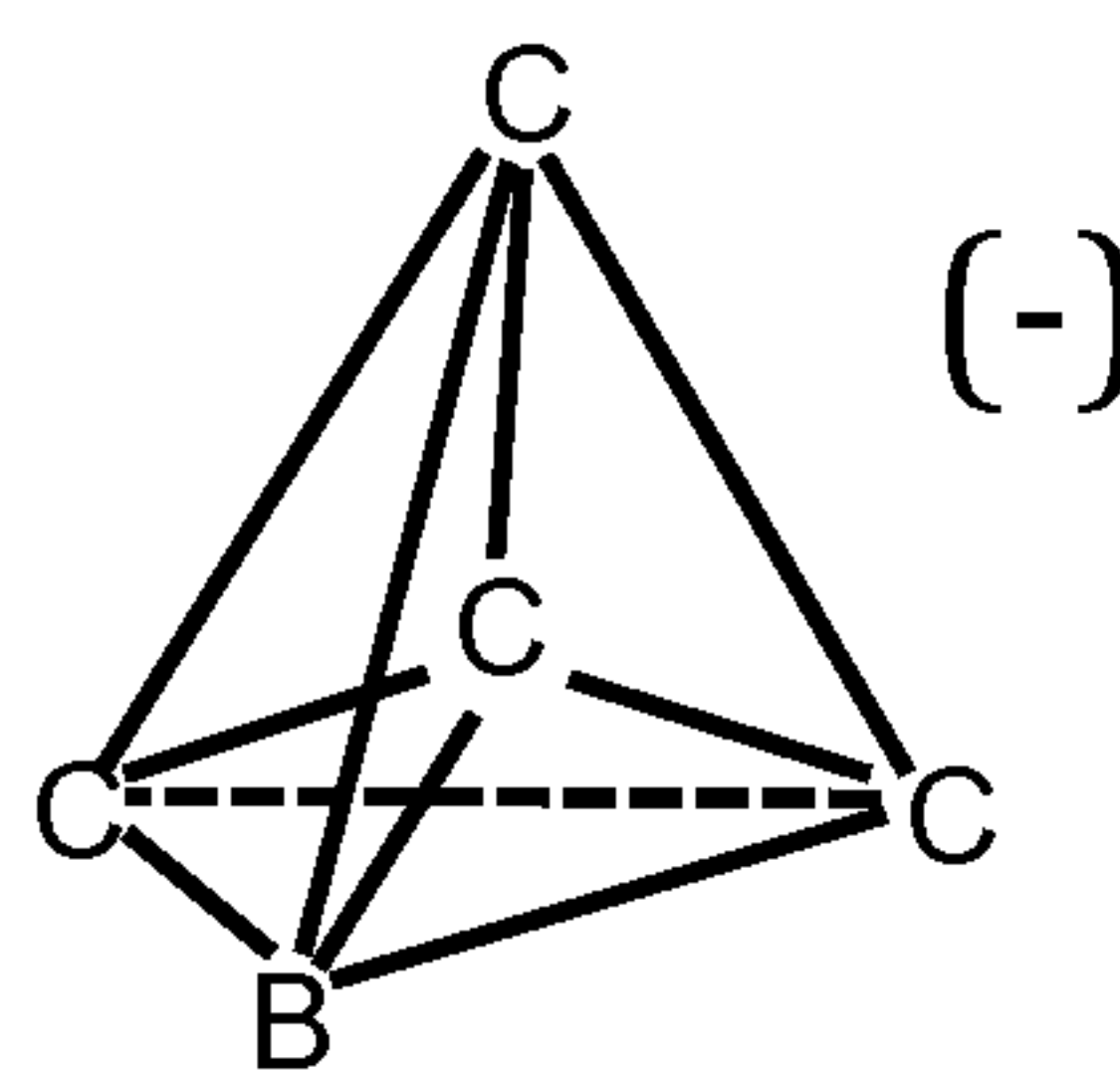


bora-diamond

The skilled practitioner will also recognize that aza-diamond and bora-diamond, once formed, are charged monopoles, that is, species bearing charge with no counter charge.



aza-diamond



bora-diamond

However, to date, neither of the above compounds have been formed, let alone used to form masses of aza-diamond and bora-diamond.

## SUMMARY OF THE INVENTION

Accordingly, it is an object of the present invention to substitute a heteroatom for a carbon atom in the diamond unit cell thereby producing a heterodiamond unit cell.

It is a further object of the present invention to produce a diamond unit cell that includes a non-carbon atom structurally incorporated into the unit cell, thus producing the heterodiamond unit cell.

It is yet another object of the present invention to produce a plurality of heterodiamond unit cells.

Still another object of the invention is producing a heterodiamond unit cell by a vapor phase reaction.

Another object of the invention is to produce a heterodiamond unit cell by a solid state reaction.

A further object of the present invention is to produce a mixture comprising both homodiamond unit cells and heterodiamond unit cells.

Yet a further object of the present invention is an apparatus that can produce homodiamond unit cells, heterodiamond unit cells, and any combinations thereof.

The above objects and others can be accomplished by methods and apparatus previously disclosed for forming the diamond unit cell (homodiamond unit cell), which methods and apparatus are modified to react a heteroatom with a tetrahedranoidal molecule.

## **BRIEF DESCRIPTION OF THE DRAWINGS**

Figure 1(A)-(B): (A) shows a vapor phase reaction for producing homodiamond using tetrahedrane as the tetrahedranoidal reactant. (B) shows a vapor phase

reaction that produces homodiamond using three other tetrahedranoidal reactants.

Figure 2 shows three reactions for producing excited state atomic nitrogen and one reaction for producing excited state atomic boron.

Figure 3(A)-(B): (A) shows a vapor phase reaction for producing aza-diamond using tetrahedrane as the tetrahedranoidal reactant. (B) shows a vapor phase reaction that produces aza-diamond using three other tetrahedranoidal reactants.

Figure 4(A)-(B): (A) shows a vapor phase reaction for producing bora-diamond using tetrahedrane as the tetrahedranoidal reactant. (B) shows a vapor phase reaction that produces bora-diamond using two other tetrahedranoidal reactants.

Figure 5 depicts a solid state reaction for forming aza-diamond.

Figure 6 is a schematic diagram of an integrated, controlled system for producing heterodiamond and homodiamond unit cells and a mixture of any combination thereof.

Figure 7 is a schematic diagram with added detail of a portion of the integrated, controlled system for producing heterodiamond and homodiamond unit cells and a mixture of any combination thereof.

Figure 8 is a schematic diagram of a deposition chamber adapted to receive heterodiamond and homodiamond unit cells and a mixture of any combination thereof from the integrated, controlled system of Figures 6 and 7.

Figure 9 illustrates a process for producing an aza-diamond mass using a solid state reaction.

## **DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS**

### **Term Definitions:**

Field measurements: as used herein means measurements of experimental variables, such as temperature, pressure, reactant flow rates and nozzle sizes, for example, that may be adjusted with routine skill in the art to achieve best results.

Tetrahedranoidal molecules: as used herein means benzvalene, 3,4-diazabenzvalene and 2,3,4-methynyl-cyclobutanone. One or more of these molecules may be preferred in the reactions as described hereinbelow.

Combinatorial syntheses of the diamond unit cell are disclosed in US 8,778,295 and US 9,061,917, which are fully incorporated herein by reference in their entirety. These syntheses proceed by the reaction of an excited state carbon atom with a tetrahedranoidal molecule with concomitant ejection of leaving groups to form the diamond unit cell. The diamond unit cell produced by these combinatorial reactions is a homo-penta-atomic molecule being comprised of 5 carbon atoms. While not intending to be bound by theory, it is believed that the excited state carbon atom "inserts" into the unit cell cage position. Figures 1(A) and 1(B) illustrate the diamond unit cell forming reactions of the above cited references.

As disclosed in U.S. 8,778,295 and 9,061,917, the conditions under which the diamond unit cell, and consequently a diamond mass containing these unit cells, form are mild and altogether different from conventional diamond forming methods such as high pressure, high temperature (HPHT) and chemical vapor deposition. The disclosure of US 2015/0259213 is directed to means of exploiting the combinatorial syntheses of the diamond unit cell to produce diamond masses comprising diamond unit cells and articles comprised of such diamond masses

that have been previously unavailable by conventional diamond forming methods due to the strenuous conditions of these conventional methods. US 2015/0259213 is also fully incorporated herein by reference in the entirety.

Insertion of an excited state heteroatom into a tetrahedral molecule can be accomplished by adapting the methods of diamond unit cell synthesis described in the above cited references by substituting a heteroatom for a carbon atom in the diamond unit cell. There are two requirements for the hetero-atom to be substituted for carbon. First, the atomic radius of the hetero-atom must be similar to that of carbon. Second, the heteroatom must be capable of forming four sigma bonds (bond order of 4). Both nitrogen and boron have such capability. The atomic radius of carbon is 70 picometers (pm). The nitrogen atom has a radius of 65 pm, and the boron atom has a radius of 85 pm. When the heteroatom is nitrogen, the heterodiamond unit cell so produced is aza-diamond. When the heteroatom is boron, the heterodiamond unit cell so produced is bora-diamond. Both are hetero-penta-atomic molecules having the tetrahedron structure of diamond. The heterodiamond unit cells as discussed are charge monopoles in that they bear a charge without a species bearing a charge of opposite sign. The aza-diamond unit cell bears a positive charge because nitrogen must donate its lone pair of electrons to form the fourth sigma bond to a carbon atom of the tetrahedral molecule. The bora-diamond unit cell bears a negative charge because the vacant orbital of the boron atom receives electron density from a carbon atom of the tetrahedral molecule to form the fourth

sigma bond between carbon and boron. Quaternary ammonium compounds of nitrogen such as tetramethyl ammonium salts are well known to organic chemists. Quaternary boride anions such as the tetraphenyl boride anion are also well known to organic chemists. Unipolar molecules have been well studied.

### **Vapor Phase Aza-Diamond**

The vapor phase reactions for the production of the homodiamond unit cell and the aza-diamond unit cell are substantially the same as those of US 9,061,917 (fully incorporated herein by reference), which details temperatures, pressures, and other reaction conditions for effecting the synthesis of homodiamond. However, in aza-diamond unit cell synthesis, cubane is replaced by a source of excited state nitrogen atoms. With reference to Figure 2, reactions 1-3, three nitrogen atom sources may be used: dinitrogen, ammonia, and hydrazine, respectively. The microwave discharge used for obtaining excited state carbon atoms from vapor phase cubane may be used to obtain excited state nitrogen atoms from ammonia and hydrazine. To derive atomic nitrogen from dinitrogen gas, a high voltage discharge is used (Rayleigh). The same method may also be used with ammonia and hydrazine (reactions 2 and 3). All these sources must be delivered to the system as a vapor in an inert carrier gas (He, Ar, Ne, Kr, Xe). Care must be taken to ensure that the nitrogen atoms so produced are delivered to the reaction zone in such a manner that their reaction with the tetrahedranoidal molecule does occur because nitrogen atoms recombine to dinitrogen at an

extremely high rate. Thus, the dispensing nozzle must be located within the “cloud” of vaporous tetrahedranoidal compound. The kinetically and thermodynamically favored recombination of nitrogen atoms to form dinitrogen is also advantageous because excess atomic nitrogen will recombine rather than deposit into the diamond mass so produced. The stoichiometric considerations required for the heterodiamond unit cell forming reaction are exactly opposite of those for the homodiamond unit cell forming reaction. For the heterodiamond unit cell reaction, an excess of the excited state atom to be cage inserted relative to the tetrahedranoidal reactant is required. In the homodiamond unit cell reaction, an excess of the tetrahedranoidal compound relative to the excited state carbon atom is required.

The reactions for forming the aza-diamond unit cell are shown in Figure 3. The excited state nitrogen atoms in inert carrier gas are delivered by a nozzle disposed within the volume of the vaporous tetrahedranoidal molecule “cloud,” and this nozzle is also the high energy discharge apparatus that is a conduit comprising an electrical insulator within which are a discharge electrode pair. Such an apparatus, into which are disposed the discharge electrodes (these can be metal foils such as Cu, Pt, Pd, Au, etc.), may comprise diamond prepared by the diamond unit cell forming methods disclosed by Newman et al. in US 2015/0259790. The nozzle material may also comprise glass or ceramic, but diamond by the unit cell process is preferred owing to its electrical insulating properties unavailable by diamond produced by conventional processes.

Nitrogen atom flow rates, dispensing nozzle dimensions and geometry are best determined by field measurements for preferred results and control by appropriate hardware and software. The same is done when the tetrahydronoidal molecule reactant is used.

Pressures and temperatures of the vapor phase reaction for forming the aza-diamond unit cell are preferentially maintained to deter the rearrangement or decomposition of the tetrahydronoidal molecule. Benzvalene is vaporized between 77 and 80°C at 760 mm pressure at a rate of not more than 5°C per minute. Reduced pressure may be used for benzvalene vaporization with concomitant decrease in vaporization temperature, but the rate of heating should not be altered from that which is used for atmospheric vaporization of benzvalene. Reduced pressure reaction conditions using benzvalene are preferably determined by field measurements. Tetrahydronone may be used as the tetrahydronoidal reactant, but it should only be vaporized at atmospheric pressure and at about 37°C to avoid autogenous ejection of CO which leads to decomposition of tetrahydronone.

Externally applied heating to the reaction zone provides no advantage with respect to driving the reaction of the tetrahydronoidal molecule and an excited state nitrogen atom. In fact, heat other than that used to vaporize the nitrogen

atom source and the tetrahedranoidal molecule should not be applied to the reaction zone.

### **Solid State Aza-Diamond**

As disclosed in US 9,061,917, the solid state homodiamond unit cell forming reaction proceeds by forming a homogeneous blend of benzvalene and cubane in an 8:1 benzvalene : cubane ratio having high stoichiometric precision to prevent the formation of carbonaceous impurities in the mass of diamond unit cells so produced due to an excess (or deficiency) of either cubane or benzvalene. Care must be taken during preparative manipulations of the homogeneous blend of reactants such that this precise stoichiometric ratio is not altered by the vapor pressures of the two blend constituents. Accordingly, the preparative manipulations and the actual reaction by exposure to a high energy discharge are conducted at temperatures that substantially prevent mass loss due to vapor pressures of the blend constituents. Similar precautions must be exercised for solid state heterodiamond unit cell forming reactions. Hydrazine is the most convenient source of reactive nitrogen atoms. Ultrapure and military propellant grade hydrazine is available commercially eliminating the need to remove water from the mono-hydrate or neutralize HCl associated with the mono-hydrochloride. Literature methods for obtaining pure hydrazine from the hydrate or the hydrochloride may be also used by the skilled practitioner. Hydrazine freezes at 2.0°C, boils at 113.5°C, and has a vapor pressure of 10mm

at 30.7°C. Following the procedures of US 9,061,917, stock solutions of benzvalene and hydrazine (substituted for cubane) in a solvent such as diethyl ether are prepared having a high degree of stoichiometric precision with respect to molar concentration. These solutions are combined in a ratio of 2:1 benzvalene to hydrazine, and the solution so obtained is freed of solvent under reduced pressure and temperature to produce the homogeneous solid reaction blend for exposure to a microwave discharge under an inert atmosphere with appropriate cooling to eliminate mass losses due vapor pressure of the blend components. Despite the fact that nitrogen atoms readily recombine to form dinitrogen gas, it is not recommended that the stoichiometric precision prescription be relaxed in a favor of a slight excess of nitrogen atom source for the sake of manipulative convenience as this may lead to the possibility of impurity formation.

A charge of opposite sign to that of the aza-diamond unit cell may be impressed upon the reaction vessel to mitigate like charge repulsions between the aza-diamond unit cells formed. However, the effect of a static electric field upon benzvalene has not been studied, to date. Accordingly, the reaction should be conducted in a sealed tube type of apparatus.

Regardless of whether the vapor phase or solid state reaction is used to form aza-diamond unit cell and/or diamond mass, neither reaction uses a diamond

seed or heterodiamond seed, and neither the aza-diamond unit cell nor diamond mass contain any boron nitride.

### **Bora-Diamond**

The boron atomic radius is 85 pm and thus is unlikely to occupy the cage position of the diamond unit cell. Furthermore, anions are well known by both chemists and physicists to have radii larger than their neutral atom counterparts owing to the presence of excess electrons constituting the “noble gas shell.” Accordingly, a synthetic strategy for inserting a boron atom into the cage position of a tetrahedranoidal molecule should not be used. A different strategy is required because a different kind of heterodiamond unit cell is produced relative to the homodiamond unit cell or the aza-diamond unit cell.

The bora-diamond unit cell must be prepared using an apical insertion strategy. This is unlikely to proceed using the method of US 9,061,917 using benzvalene. Referring to US 9,061,917, two other tetrahedronoidal reactants are disclosed: 3,4-diazabenzvalene and 2,3,4-methynyl-cyclobutanone (“tetrahedranone”). While their tetrahedronoidal structures are closely related to that of benzvalene structure, their stability is different. Both tetrahedranone and diazabenzvalene can decompose autogenously if care is not taken in storage and manipulations.

Benzvalene does not decompose in the strict sense; rather, it re-arranges to benzene, which can be removed from benzvalene under reduced pressure. The other two tetrahydronoid molecules decompose because their “leaving groups,” or ejection products, are thermodynamically stable species (dinitrogen for 3,4-diazabenzvalene; carbon monoxide (C=O) for tetrahydronone). The decomposition product of both of these tetrahydronoid molecules is a transient di-radical.

This extremely unstable structure produces dicyclobutadiene, which presumably results from the initial decomposition product, cyclobutadiene, an extremely unstable species. The formation of cyclobutadiene requires an intra-molecular re-arrangement. The synthesis of the bora-diamond unit cell exploits this decomposition and intra-molecular re-arrangement in that it “traps” the unstable initial product formed by ejection product release and provides a thermodynamically more stable re-arrangement product than cyclobutadiene. This produces the bora-diamond unit cell by incorporating the boron atom apically. The preferred tetrahydronoid molecule for this reaction is 2,3,4-methynyl-cyclobutanone because its counterpart, 3,4-diazabenzvalene, is only stable below -60°C.

To exploit the decomposition of tetrahydronone and trap its decomposition product by a boron atom, it is crucial to exercise control over this decomposition,

and this places limits upon the conditions of this reaction. Tetrahdranone cannot be allowed to decompose autogenously; rather, this decomposition must be a result of the chemical interaction between tetrahdranone and an excited state boron atom. It is highly unlikely that an excited state boron atom will be able to react with an autogenous tetrahdranone decomposition transient. Thus, the conditions of the reaction must preserve the integrity of tetrahdranone in the vapor phase. This requires very gentle heating to no more than about 40°C, and this heating must not be rapid. Autogenous decomposition of tetrahdranone occurs by loss (ejection) of CO, which is a very stable leaving group. Thus, to deter ejection of CO, reduced pressures cannot be tolerated. It is recommended that the reaction be conducted at not less than 1 atmosphere and not more than two atmospheres. Reduced pressure favors the loss of CO. Excessive overpressure hinders the vaporization of tetrahdranone. Accordingly, bora-diamond must be prepared in the vapor phase following the procedures for vapor phase homodiamond unit cell synthesis of US 9,061,917 using tetrahdranone as the tetrahdranoidal compound and substituting diborane for cubane but maintaining temperature and pressure of the reaction within the narrow ranges detailed above to deter autogenous decomposition of tetrahdranone in favor of (excited state) boron atom interaction with tetrahdranone to form bora-diamond.

Bora-diamond should preferably be formed by the reaction of tetrahdranone and an excited state boron atom. Accordingly, heat other than that used to vaporize the atomic boron source and tetrahdranone should not be applied to the

reaction zone. Tetrahdranone is best vaporized at atmospheric pressure and at its vaporization temperature which is approximately 37°C. Higher temperatures are counter-indicated because tetrahdranone decomposes thermally. Pressures higher than one atmosphere would require a higher vaporization temperature for tetrahdranone which is likely to lead to autogenous and thermally induced decomposition of tetrahdranone. Reduced pressure can be used to reduce the heat required to vaporize tetrahdranone, but this increases the likelihood of ejection of CO and concomitant decomposition of tetrahdranone. Thus, the proper use of reduced pressure to vaporize tetrahdranone to form the bora-diamond unit cell by the reaction of an excited state boron atom with vaporous tetrahdranone is preferably set by field measurements.

With reference to Figure 2, reaction 4, the boron atom source may be diborane. The microwave discharge used for obtaining excited state carbon atoms from vapor phase cubane may be used to obtain excited state boron atoms from diborane.

Reactions for forming the bora-diamond unit cell are shown in Figure 4. The boron source must be delivered to the system as a vapor in an inert carrier gas such as argon, helium, etc. Care must be taken to ensure that the boron atoms so produced are delivered to the reaction zone. Thus, the dispensing nozzle must be located within the "cloud" of vaporous tetrahdranoidal compound. The

stoichiometric considerations required for the heterodiamond unit cell forming reaction using boron as the heteroatom are the same as those for the homodiamond unit cell forming reaction. An excess of tetrahydronoidal molecules relative to the excited state boron atoms is necessary to insure that all boron atoms delivered to the reaction zone are consumed by their reaction with the tetrahydronoidal molecules so that contamination of the heterodiamond deposited upon the deposition substrate by unreacted boron atoms does not occur.

The excited state boron atoms in inert carrier gas are delivered by a nozzle disposed within the volume of the tetrahydronoidal molecule vapor.

Boron atom flow rates, dispensing nozzle dimensions and geometry are determined by field measurements for optimization and control by appropriate hardware and software. The same optimizations are done for the tetrahydronoidal molecule reactant to be used within the temperature and pressure ranges detailed above.

The synthesis of the bora-diamond unit cell is limited to the vapor phase reaction. Synthetic chemists are well aware of the behavior of boron hydrides with carbonyl compounds. In synthetic organic chemistry, boranes are reducing agents for aldehydes and ketones. Hence, a blend of diborane and tetrahydronone prepared at even very low temperatures will not serve as a solid

state precursor for preparing the bora-diamond unit cell. Accordingly, bora-diamond must be prepared in the vapor phase following the procedures for vapor phase diamond unit cell synthesis of US 9,061,917 substituting tetrahedranone for the tetrahedranoidal compound and diborane for cubane.

The vapor phase synthesis of bora-diamond uses neither diamond nor heterodiamond seed, nor does the produced bora-diamond unit cell and/or diamond mass contain any boron nitride.

### **Apparatus for Producing Homodiamond Unit Cells and Heterodiamond Unit Cells**

Figure 6 shows an apparatus configured to produce homodiamond unit cells and heterodiamond unit cells. For the purposes of the present invention, the term “line” can mean one line or a plurality of lines. Reaction chambers **102**, **104**, and **106** are for producing bora-diamond, homodiamond, and aza-diamond, respectively. Thus, reaction chambers **102** and **106** are for producing heterodiamond unit cells and reaction chamber **104** is for producing homodiamond unit cells. There is one input port for the atomic reactant (i.e., B, C, N) and another for the tetrahedranoidal compound reactant. Tetrahedranoidal reactant conduits **210**, **212**, and **214** define tetrahedranoidal reactant input ports into reaction chambers **102**, **104**, and **106**, respectively.

Reaction chambers **102**, **104**, and **106** receive boron, carbon, and nitrogen through conduit nozzles **200**, **204**, and **208**, respectively, which define atomic reactant input ports. Inert gas source **126** provides, for example, argon as a carrier gas to the reaction chambers **102**, **104**, and **106** through carrier gas conduits **194**, **202**, and **196**, respectively. Another inert gas (excluding nitrogen) such as helium can be used. The inert gas is also provided to boron source container **120**, carbon source container **122** and nitrogen source container **124**. Details (e.g., conduits and flow control, etc.) for providing the inert gas to the source containers are not shown in Figure 6.

Diborane is subjected to a high energy discharge (e.g., microwave discharge) within the boron source container **120** to produce excited state boron atoms. This is reaction 4 of Figure 2. As shown, a microwave discharge is provided by microwave source **134**, within boron source container **120**. Microwave source **134** is controlled by control line **174**, which connects through to the systems controller **390** via the main system bus **392** and controller bus **391**. The excited state boron atoms exit the boron source container **120** through boron flow control valve **140**. Boron flow control valve **140** is controlled by system controller **390** via valve control line **142**, which connects to system controller **390** through main system bus **392** and controller bus **391**. Additional inert gas (as shown, argon) flows from inert gas source **126** through carrier gas conduit **194** controlled by

carrier gas valve **152** and converges and mixes with the excited state boron atom stream controllably flowing through boron flow control valve **140**. Inert gas valve **152** is controlled by control line **154**, which connects to system controller **390** through main system bus **392** and controller bus **391**. The excited state boron atom and argon mixture flow through conduit nozzle **200**, which serves as an input port into reaction chamber **102**. Tetrahedranoidal molecule source container **108** provides tetrahedranoidal molecules to reaction chamber **102** through tetrahedranoidal reactant conduit **210**, which flow is controlled by valve **168**. Valve **168** is controlled by control line **170**, which is connected to system controller **390** through main system bus **392** and controller bus **391**. For the synthesis of the bora-diamond unit cell, the preferred tetrahedranoidal molecule is 2,3,4-methynyl-cyclobutanone ("tetrahedranone").

The bora-diamond unit cell reaction of Figure 4(B) occurs in reaction chamber **102**. Within reaction chamber **102**, excited state boron atom cloud **201** is shown mixing and reacting with tetrahedranone vapor **211**. The resulting bora-diamond unit cells are conducted out of reaction chamber **102** through bora-diamond output conduit **216**. The output flow of the bora-diamond unit cells through bora-diamond output conduit **216** is controlled by bora-diamond output valve **186**, which is regulated by the systems controller **390** via control line **176**, which connects to the systems controller **390** through main system bus **392** and controller bus **391**. Bora-diamond unit cells are provided through bora-diamond output conduit **216** to manifold **112**.

The apparatus of Figure 6 is also configured to produce homodiamond unit cells. This is achieved with the reaction shown in Figure 1(B). Cubane is subjected to a high energy discharge (e.g., microwave discharge) within the carbon source container **122** to produce excited state carbon atoms. This reaction is disclosed in US 9,061,917, which is incorporated fully herein by reference. As shown, a microwave discharge is provided by microwave source **132**, within carbon source container **122**. Microwave source **132** is controlled by control line **172**, which connects through to the systems controller **390** via the main system bus **392** and controller bus **391**. The excited state carbon atoms exit the carbon source container **122** through carbon flow control valve **144**. Carbon flow control valve **144** is controlled by system controller **390** via valve control line **146**, which connects to system controller **390** through main system bus **392** and controller bus **391**. Additional inert gas (as shown, argon) flows from inert gas source **126** through carrier gas conduit **202**, controlled by carrier gas valve **184** and converges and mixes with the excited state carbon atom stream controllably flowing through carbon flow control valve **144**. Carrier gas valve **184** is controlled by control line **179**, which connects to system controller **390** through main system bus **392** and controller bus **391**. The excited state carbon atom and argon mixture flow through conduit nozzle **204**, which serves as an input port into reaction chamber **104**. Tetrahedranoidal molecule source container **110** provides tetrahedranoidal molecules to reaction chamber **104** through tetrahedranoidal reactant conduit **212**, which flow is controlled by valve **160**.

Valve **160** is controlled by control line **162**, which is connected to system controller **390** through main system bus **392** and controller bus **391**. For the synthesis of the homodiamond unit cell, the preferred tetrahedranoidal molecule is benzvalene.

The homodiamond unit cell reaction of Figure 1(B) occurs in reaction chamber **104**. Within reaction chamber **104**, excited state carbon atom cloud **205** is shown mixing and reacting with benzvalene vapor **213**. The resulting homodiamond unit cells are conducted out of reaction chamber **104** through homodiamond output conduit **218**. The output flow of the homodiamond unit cells through homodiamond output conduit **218** is controlled by homodiamond output valve **188**, which is regulated by the systems controller **390** via control line **178**, which connects to the systems controller **390** through main system bus **392** and controller bus **391**. Homodiamond unit cells are provided through homodiamond output conduit **218** to manifold **112**.

The apparatus of Figure 6 is also configured to produce aza-diamond unit cells. This is achieved with the reaction shown in Figure 3(B). A nitrogen source is subjected to a high energy discharge (e.g., electrostatic discharge) to produce excited state nitrogen atoms. The Figure 2 reactions 1, 2, or 3, which produce atomic nitrogen from molecular nitrogen, ammonia, and hydrazine, respectively,

can be used to yield the excited state nitrogen atoms for synthesizing aza-diamond.

As shown in Figure 6, hydrazine is used as a nitrogen atom source. Hydrazine exits nitrogen source container **124** through nitrogen flow control valve **148**. Nitrogen flow control valve **148** is controlled by system controller **390** via valve control line **150**, which connects to system controller **390** through main system bus **392** and controller bus **391**. Additional inert carrier gas (as shown, argon) flows from inert carrier gas source **126** through carrier gas conduit **196** controlled by carrier gas valve **156** and converges and mixes with the excited hydrazine stream controllably flowing through nitrogen flow control valve **148**. Inert gas valve **156** is controlled by control line **158**, which connects to system controller **390** through main system bus **392** and controller bus **391**.

The hydrazine mixed with the argon carrier gas mixture passes between electrostatic discharge electrode pair **182**, which are powered by high voltage source **130** through power lines **181**, of which there are two (i.e., one line per electrode). High voltage source **130** is controlled by systems controller **390** through control line **131**, which connects through to systems controller **390** via main system bus **392** and controller bus **391**. The electrodes of the discharge electrode pair **182**, are located within conduit nozzle **208** and, when energized by voltage source **130**, produce an electrostatic discharge between them. This

electrostatic discharge causes hydrazine within conduit nozzle **208** to dissociate according to reaction 3 of Figure 2, thereby producing excited state nitrogen atoms, which flow into reaction chamber **106**.

Tetrahedranoidal molecule source container **110** provides tetrahedranoidal molecules to reaction chamber **106** through tetrahedranoidal reactant conduit **214**, which flow is controlled by valve **164**. Valve **164** is controlled by control line **166**, which is connected to system controller **390** through main system bus **392** and controller bus **391**. For the synthesis of the aza-diamond unit cell, the preferred tetrahedranoidal molecule is benzvalene.

The aza-diamond unit cell reaction of Figure 3(B) occurs in reaction chamber **106**. Within reaction chamber **106**, excited state nitrogen atom cloud **209** is shown mixing and reacting with benzvalene vapor **215**. The resulting aza-diamond unit cells are conducted out of reaction chamber **106** through aza-diamond output conduit **220**. The output flow of the aza-diamond unit cells through aza-diamond output conduit **220** is controlled by aza-diamond output valve **190**, which is regulated by the systems controller **390** via control line **180**, which connects to the systems controller **390** through main system bus **392** and controller bus **391**. Aza-diamond unit cells are provided through aza-diamond output conduit **220** to manifold **112**.

Manifold **112** can receive bora-diamond unit cells, homodiamond unit cells, and aza-diamond unit cells, singularly, or in any predetermined combinations of controlled proportions. During operation, concentrations of any of these three products can be kept constant or controllably varied in a predetermined sequence, according a program stored in the systems controller. The output of manifold **112** is through manifold output conduit **114**, which control there through is regulated by manifold output valve **192**. Manifold output valve **192** is controlled by the systems controller **390** via control line **198**, which connects to the systems controller **390** through main system bus **392** and controller bus **391**. Flow of unit cells out of manifold **112** can be stopped immediately by diverting the gaseous stream away from manifold output conduit **114** with a diversionary stream of inert gas (e.g., argon) that enters manifold output conduit **114** through diversion input port **116** and exits through diversion output port **118**.

Figure 7 provides greater detail of a portion of the apparatus of Figure 6. The reaction between a highly excited boron, carbon, or nitrogen atom and a tetrahedranoidal molecule, such as benzvalene or tetrahedranone, occurs in reaction chamber **404**. Atomic reactant source container **410** provides boron, carbon or nitrogen as highly excited atoms **530** to reaction chamber **404** through atomic reactant flow control valve **430** into conduit nozzle **406** where it converges and mixes with an inert carrier gas such as argon, which is introduced into conduit nozzle **406** through carrier gas conduit **402**. Reaction chamber **404** can be flushed of all reactants and reaction byproducts by closing atomic reactant

flow control valve **430** and allowing inert carrier gas to flow into reaction chamber **404**. Inlet port **516**, provides for an inflow of inert carrier gas (e.g., argon), which is provided to reaction chamber **404** under controlled flow and pressure by inlet pump **518**. Inlet pump **518** is controlled by the systems controller **390** via control lines **520**, which connects to the systems controller **390** through main system bus **392** and controller bus **391**. Effluent leaves reaction chamber **404** through effluent port **504**. As shown, effluent pump **506** controls flow of effluent from reaction chamber **404**. There may be circumstances when effluent pump **506** is not used, and, thus, effluent exits reaction chamber **404** through effluent port **506** passively (e.g., due to the pressure from inlet pump **518**) but through a controllable valve (not shown). Effluent pump **506** connects through to GC-MS **508** (gas chromatograph in tandem with a mass spectrometer), for effluent analysis. Effluent pump **506** may be separate from, or integrally a part, of GC-MS **508**. When separate from mass GC-MS **508**, effluent pump **506** is controlled by the system controller **390** through effluent pump control lines **512**. When integrally a part of GC-MS **508**, effluent pump **506** may be directly or indirectly controlled through GC-MS bus **510**, which connects communicatively through to system controller **390** through main system bus **392** and controller bus **391**.

Conduit nozzle **406** functions as an input port into reaction chamber **404** for highly excited boron, carbon, or nitrogen atoms within an inert carrier gas flow. Atomic reactant flow control valve **430**, is controlled by systems controller **390** via

control line **498**, which connects to systems controller **390** through controller bus **391** and main system bus **392**.

Tetrahedranoidal molecule source container **408** provides tetrahedranoidal molecules **532** in vapor phase to reaction chamber **404** through tetrahedranoidal reactant conduit **420** the flow of which is regulated by valve **422**. Valve **422** is controlled by systems controller **390** via control line **492**, which connects to systems controller **390** through controller bus **391** and main system bus **392**. Product **428** of the reaction in reaction chamber **404**, i.e., bora-diamond, homodiamond, or aza-diamond unit cells, exits through output conduit **424**, which flow is regulated by output valve **426**. Output valve **426** is controlled by systems controller **390** via control line **490**, which connects communicatively to systems controller **390** through controller bus **391** and main system bus **392**.

Reaction chamber **404** provides a controlled environment specifically intended to maintain the physical and chemical conditions conducive to the production of homodiamond and heterodiamond unit cells invention and to eliminate impurities formed by autogenous processes. Furthermore, physical and chemical conditions within tetrahedranoidal molecule source container **408** and atomic reactant source container **410** are also maintained so as to be conducive to the unit cell reactions of the present invention.

The physical and chemical conditions within reaction chamber **404** are maintained by sensor/actuator suite **444**, which is controlled by the systems controller **390**. Sensor/actuator suite **444** communicatively connects through to systems controller **390** via sensor/actuator bus **494**, main system bus **392**, and controller bus **391**.

The physical and chemical conditions within tetrahedranoidal molecule source container **408** are maintained by sensor/actuator suite **412**, which is controlled by systems controller **390**. Sensor/actuator suite **412** communicatively connects through to systems controller **390** via sensor/actuator bus **500**, main system bus extension **392a**, main system bus **392**, and controller bus **391**.

The physical and chemical conditions within atomic reactant source container **410** are maintained by sensor/actuator suite **414**, which is controlled by systems controller **390**. Sensor/actuator suite **414** communicatively connects through to systems controller **390** via sensor/actuator bus **502**, main system bus extension **392a**, main system bus **392**, and controller bus **391**.

If it is desired to use the apparatus of Figures 6 and 7 with the reactions of Figures 1A, 3A, and 4A, that is, reactions that include what we believe to be tetrahdrane (as the tetrahedranoidal molecule), some modifications to the

apparatus are necessary. In particular, tetrahedranoidal reactant conduits **210**, **212**, and **214** of Figure 6 and tetrahedranoidal reactant conduit **420** of Figure 7 must be modified to include a heated catalytic frit so that acetylene can be converted to what we believe to be tetrahedrane. Thus, acetylene is sourced to the heated catalytic frit from tetrahedranoidal molecule source containers **108** and **110** of Figure 6 and tetrahedranoidal molecule source container **408** of Figure 7. The acetylene is provided within an inert carrier gas such as argon.

Reaction chambers **104** and **106** of Figure 6 are shown sharing the same tetrahedranoidal molecule source container **110**. If it is desired to use a different tetrahedranoidal molecule in reaction chamber **104** from that of reaction chamber **106**, each chamber can be provided with its own tetrahedranoidal molecule source container and tetrahedranoidal reactant conduit.

Particularly in the case where more than one type of unit cell (bora-diamond, aza-diamond, homodiamond, or any mixture thereof) is produced using the apparatus of Figures 6 and 7, manifold **112** can be adapted to perform mixing to provide a uniform mixture of the unit cells. Alternatively, other means known in the gas mixing art can be used.

Figure 8 shows an exemplary use of the homodiamond unit cell and heterodiamond unit cell products of the apparatus of Figures 6 and 7. Deposition chamber **610** provides a controlled environment specifically intended to maintain the physical and chemical conditions conducive to the production of molecular diamond (i.e., the homodiamond unit cell and the heterodiamond unit cell) to yield useful, shapeable diamond masses that can be components of products or products themselves. As shown, work piece holder **640** supports deposition substrate **604**. Although only one work piece holder **640**, is shown, a plurality of work piece holders with associated deposition substrates in a single deposition chamber **610** can be accommodated by the present invention. Work piece holder **640** includes a means for locally controlling the temperature and charge of the deposition substrate **604**, the details for which are not shown. Temperature control lines **642** communicate data to and from the system controller **390** through sensor/actuator suite and interface **644**, through sensor bus **645**, main system bus **392**, and controller bus **391**. Sensor/actuator suite and interface **644**, contains one or more temperature sensors and one or more pressure sensors. It can accommodate additional sensors. Although sensor/actuator suite and interface **644** is shown as a single, integrated module at one location in deposition chamber **610**, alternatively, the sensors can be placed at disparate locations within deposition chamber **610**. Sensor/actuator suite and interface **644** communicates data to and from the system controller **390** through sensor/actuator bus **645**, main system bus **392**, and controller bus **391**. Inlet port **684** provides for an inflow of inert carrier gas **652**. Deposition chamber **610** may

be pressurized by inlet pump **686** under the control of inlet pump control lines **688**. Inlet pump **686** may be provided with dedicated flow sensor or sensors (preferably non-contact sensors) and/or pressure sensors that are not shown. Inlet pump control lines **688** communicate with system controller **390** through main system bus **392** and controller bus **391**. It is also possible to maintain desired flow and pressure in deposition chamber **610** using the pressure of the inert carrier gas **652** storage tank and its regulator alone, making the inlet pump **686** unnecessary.

Effluent leaves deposition chamber **610** through effluent port **660**. As shown, effluent pump **662** controls flow of effluent from deposition chamber **610**. There may be circumstances when effluent pump **662** is not used, and, thus, effluent exits deposition chamber **610** through effluent port **660** passively (e.g., due to the pressure) but through a controllable valve (not shown). Effluent pump **662** connects through to GC-MS **666** (gas chromatograph in tandem with a mass spectrometer) for effluent analysis. Effluent pump **662** may be separate from or integrally a part of GC-MS **666**. When separate from mass GC-MS **666**, effluent pump **662** is controlled by the system controller **390** through effluent pump control lines **664**. When integrally a part of GC-MS **666**, effluent pump **662** may be directly or indirectly controlled through GC-MS bus **667**, which connects communicatively through to system controller **390** through main system bus **392** and controller bus **391**.

Unit cell inlet **614** provides homodiamond unit cells and/or heterodiamond unit cells, or any combination thereof, to deposition chamber **610**. As shown, unit cell inlet **614** is an extension of manifold output conduit **114** of Figure 6 or output conduit **424**, of Figure 7. The unit cells passing through unit cell inlet **614** are provided to delivery apparatus **612** through which they pass and are controllably directed at a predetermined location on deposition substrate **604**. Unit cell stream **616** deposits unit cell mass **608** on deposition substrate **604**. Unit cell stream **616** can comprise homodiamond unit cells, heterodiamond unit cells, or a mixture thereof. Unit cell mass **608** can be a localized mass (as shown) or a diffuse, uniform mass such as a thin film on deposition substrate **604**. The relative position of delivery apparatus **612** is controlled by three dimensional position controller **694** (details not shown). Three dimensional position controller **694** is, in turn, controlled through position control lines **696**, which communicate through to the systems controller **390** through main system bus **392** and controller bus **391**. A single deposition chamber **610** can also accommodate multiple reactant delivery apparatuses. Delivery apparatus **612** can be configured as a simple port to deliver a generally diffuse cloud of unit cells within deposition chamber **610** for a uniform deposition of homodiamond unit cells, heterodiamond unit cells, or a mixture thereof on one or more deposition substrates **604**.

The solid state reaction formula shown in Figure 5 uses hydrazine as the source for highly excited nitrogen atoms. Figure 9 is a schematic that shows the formation of aza-diamond using this solid state reaction. A solution of benzvalene **700** and a solution of hydrazine **702** are combined to form a homogeneous solution **704** of benzvalene and hydrazine in a proportion of benzvalene to hydrazine of 2:1. The solutions can be made in an organic solvent such as diethyl ether. The homogeneous solution **706** undergoes evaporation to form a homogeneous solid mixture **708** of benzvalene and hydrazine in a proportion of 2:1 respectively. Homogeneous solid mixture **708** is subjected to a high energy discharge (e.g., microwave) to yield aza-diamond mass **710**. Once removed from its container, aza-diamond mass **712** retains the shape defined by the container. This reaction can be adapted for use with apparatus similar to that shown in Figures 8 and 10 of US 2015/0259790, which is fully incorporated herein by reference. For example, this can be achieved by substituting a homogeneous solution of hydrazine and benzvalene for the homogeneous solution of cubane and benzvalene, which is disclosed in US 2015/0259790. When using this apparatus to produce aza-diamond using the solid state reaction, sensors, actuators and control parameters of the systems controller are adjusted to be conducive to the reaction.

The disclosed apparatus for producing bora-diamond, aza-diamond, and homodiamond unit cells is versatile. For example, unit cells exiting from manifold output conduit **114** of Figure 6 or output valve **426** of Figure 7 can be used to

build up thin films or layers of bora-diamond, aza-diamond, and homodiamond masses or masses comprising any combination mixed heterodiamond and/or homodiamond unit cells on a deposition substrate such as deposition substrate **604** of Figure 8. Another exemplary use of bora-diamond, aza-diamond, and homodiamond unit cells, or various combinations thereof of the present invention, is as a dopant for other materials such as silicon, compound semiconductors, etc. As a dopant, it is the heterodiamond or homodiamond unit cell that is the dopant species, not the heteroatom *per se*. For example, the bora-diamond unit cell and/or the aza-diamond unit cell can be the dopant species.

As in US 8,778,295 and US 9,061,917, the choice of substrate is not critical, and it is not necessary to heat the substrate as the energy of the substrate does not participate in the heterodiamond unit cell reaction. However, the heterodiamond unit cells so produced are charge monopoles (unipolar) having no associated species bearing charges of opposite sign (counter charges). For this reason, it can be beneficial to impress a charge of opposite sign onto the deposition substrate to minimize the potential for like charge repulsion phenomenon. Impressing a charge on a deposition substrate, that is, biasing a substrate is known in the art of semiconductor manufacturing. For example, in US 5,145,712, Jesser et al. disclose the chemical deposition of diamond crystals on a substrate whose positive charge is achieved with a substrate bias supply. In US 5,310,703, Visser et al. disclose a method of manufacturing a semiconductor device in which photoresist on a silicon oxide layer on a semiconductor substrate

is stripped using an oxygen plasma afterglow and a biased substrate. In JP 2001148487, Nishioka et al. disclose a manufacturing method for silicon thin film solar batteries wherein a substrate can be biased negatively or positively.

## **The Control System**

The control system of the apparatus comprises a computer system in combination with hardware interfaces for sensor input data and output control signals for actuators. Control system software for the computer is designed with a modular structure, although other schemes are also possible. Process control can employ previously determined, preferred parameters that are stored in memory maps for use with process control strategies such as closed-loop, fuzzy logic, etc., which are commercially available. The general structure applies to both vapor phase and solid state embodiments of the present invention.

Generally, data are received from sensors in the apparatus and processed by the control system. When data indicate that a specific parameter's value has diverged from the desired set point, control signals are generated by the computer and routed through the control system interface to actuators in the apparatus. These signals correct for the difference between the actual measured parameter value and the target or desired value for that parameter.

Thus, for example, the internal temperature and pressure of a reaction chamber or deposition chamber can be set to preferred values by adjusting the inert

carrier gas temperature and/or flow rate based on the data received from temperature and pressure sensors. The inert gas can be, for example, argon gas with less than three parts per million O<sub>2</sub>, which is commercially available. Thus, the gas entering a reaction chamber first passes through a refrigeration device that includes a pump and one or more heat exchangers. The temperature of the inert gas is controlled by varying the heat exchanger's refrigerant temperature, which is managed by the system controller. The reaction chamber temperature is measured by one or more temperature sensors and the temperature data are provided to the system controller. One temperature sensor can be placed on a wall of the reaction chamber. Another one or two can be placed on or near the gas input port or ports of the reaction chamber. Depending on the embodiment, temperature can also be measured with a temperature sensor disposed on or near the reactant nozzle or dispenser. If additional temperature control is desired, the work piece holder that holds the deposition substrate can be placed in intimate contact with a dedicated heat exchanger for heating and cooling the deposition substrate as required by the chosen process. Such a dedicated heat exchanger can have its own thermal fluid that is separate from that of the inert gas heat exchanger. Such apparatuses and their associated control systems are commercially available. The associated control system of the substrate heat exchanger is under the command and control of the general system controller.

The pressure in a reaction chamber and deposition chamber can be controlled over a very wide range of values from fractions of an atmosphere up to many

atmospheres. This is achieved by a combination of options that include using the high pressure of the inert gas in its storage cylinder or tank (passive pressure control) and/or an additional pressure pump in combination with a vacuum pump at the effluent port of the reaction chamber (active pressure control). Typically, when pressurized gas from a high pressure tank is provided to the reaction chamber or deposition chamber, it flows through a gas pressure regulator, which provides a “step-down” in pressure as a first order of pressure control. Additional control is achieved through the use of a pressure sensor or sensors that are disposed within the reaction chamber. For example, one pressure sensor can be placed on the reaction chamber wall but local to the general deposition area. In the placement of sensors, care is taken to avoid gas currents. If the reaction is performed at sub-atmospheric temperatures, a vacuum pump is used to maintain the lower pressure at the same time that inert gas continues to flow into the reaction chamber. If the reaction is performed above atmospheric pressures, passive pressure control (e.g., regulated tank pressure) and/or in combination of passive and active pressure control can be used. A valve can be used at the effluent port to control egress of the effluent gas.

Regardless of the pressure conditions chosen for a particular reaction, flow into, through, and out of a reaction chamber or deposition chamber must be maintained. A controllable manifold can be used to provide kinetic energy to the gases to drive the heterodiamond and homodiamond forming reactions. By manipulating the gas regulator, inert gas pump, vacuum pump, and/or effluent

valve based on temperature and pressure sensor data, the control system is able to set the preferred conditions for heterodiamond and homodiamond unit cell formation.

In vapor phase embodiments of the present invention, flow control may be achieved with a non-contact flow sensor or sensors (e.g., ultrasonic flow sensor) in the inert gas input port or ports of reaction chamber. These sensors can be embedded in the walls of the conduits or nozzles. The feedback control loop for controlling flow is regulated by the system controller through a reactant gas pump and/or a throttling valve. In solid state embodiments, precise amounts of homogeneous reactant solution can be delivered or dispensed by the use of well-calibrated metering pumps.

Effluent ports are generally attached to the input port of a GC-MS spectrometer, which often has its own controllable pump system. The GC-MS spectrometer can monitor effluent either continually or periodically and provide effluent content data to the system controller. Process control may be based upon compositional data, physical parameter data, relative positional data, morphological data of the molecular diamond mass, etc. Mass spectrometer software is available both commercially and as open source programs that can be easily used in combination with the control system of the present invention.

For solid state embodiments of the present invention, three-dimensional positioning of dispensers (e.g., automated pipetting systems), printing devices and other actuators and control systems therefor are well-developed technologies. A wide range of products for accomplishing the manufacturing processes shown in FIGS. 6-8 of US 2015/0259790, which is fully incorporated herein by reference, are available commercially and can be adapted to work in combination, and interface, with the control system of the present invention. For example, the reactant delivery apparatuses of FIGS. 6-8 of US 2015/0259790 can be achieved using three-dimensional positioning devices (e.g., a 3 D printer gantry, etc.) and their associated control software.

The control system software for the present invention not only maintains preferred reaction conditions but also controls the proper sequence of events. For example, the switchable high-energy discharge apparatus can be actuated on and off depending on the effluent data provided by the mass spectrometer. The control system software can be written in a variety of programming languages, but it is particularly useful to use languages that provide bit-level addressing and manipulation, such as C or C++, because these allow for easy interfacing with input and output ports (e.g., reading from or writing to A/D and D/A converters directly, respectively). Otherwise, interface routines can be coded in assembly language and control processing can be done in a higher level language. Alternatively, instrument control software development systems are available commercially (e.g., LabVIEW or LabWindows/CVI from National

Instruments) that can be adapted to develop the control system software for the present invention.

What Is Claimed Is:

1. A combinatorial synthesis of a heterodiamond unit cell, which comprises a step of reacting a tetrahydronoidal molecule with a heteroatom.
2. The combinatorial synthesis of claim 1, wherein the tetrahydronoidal molecule is benzvalene, 3,4-diazabenzvalene or 2,3,4-methynylcyclobutane.
3. The combinatorial synthesis of claim 1, wherein said heteroatom species is atomic nitrogen.
4. The combinatorial synthesis of claim 3, wherein atomic nitrogen is obtained from a nitrogen-containing species in the vapor phase by exposing said species to a high energy discharge which nitrogen containing species is hydrazine, ammonia, or dinitrogen.
5. The combinatorial synthesis of claim 1, wherein the heteroatom is atomic boron.

6. The combinatorial synthesis of claim 5, wherein wherein atomic boron is obtained from a boron-containing species in the vapor phase by exposing said species to a high energy discharge which boron containing species is diborane.
7. The combinatorial synthesis of claim 1, wherein a heterodiamond mass is formed from an assembly of a plurality of heterodiamond unit cells.
8. The combinatorial synthesis of claim 1, which is conducted in vapor phase.
9. The combinatorial synthesis of claim 1, which is conducted in solid state.
10. The combinatorial synthesis of the heterodiamond unit cell of claim 9, wherein a homogeneous blend of a tetrahedranoidal molecule and a heteroatom source is subjected to a high energy discharge.
11. The combinatorial synthesis of the heterodiamond unit cell of claim 9, wherein the heteroatom source is hydrazine or ammonia.

12. The combinatorial synthesis of claim 1, which comprises obtaining heteroatoms from a heteroatom source by vaporizing said heteroatom source in an inert carrier gas and exposing said heteroatom source in an inert carrier gas to a high energy discharge, directing the heteroatoms so obtained to a reaction chamber, directing a flow of tetrahedranoidal molecules in an inert carrier gas into said reaction chamber, combining said heteroatoms with said tetrahedranoidal molecules to form heteroatom unit cells.

13. The combinatorial synthesis of claim 12, which further comprises forming heterodiamond mass from a plurality of the heterodiamond unit cells.

14. The combinatorial synthesis of claim 1, wherein a stoichiometric excess of tetrahedranoidal molecules with respect to heteroatom-containing species is used to ensure that all of the heteroatoms from the heteroatom-containing species are consumed by formation of heterodiamond unit cells.

15. The combinatorial synthesis of claim 1, which does not use diamond seed or heterodiamond seed.

16. The combinatorial synthesis of claim 10, wherein the inert gas is a noble gas.
17. The combinatorial synthesis of claim 16, wherein the noble gas is argon.
18. Boron-containing heterodiamond unit cell made by the combinatorial synthesis of claim 1.
19. The boron-containing heterodiamond unit cell of claim 18, which does not contain boron nitride.
20. Boron-containing heterodiamond mass formed from a plurality of the boron-containing heterodiamond unit cells of claim 18.
21. Nitrogen-containing heterodiamond unit cell made by the combinatorial synthesis of claim 1.
22. The nitrogen-containing heterodiamond unit cell of claim 21, which does not contain boron nitride.

23. Nitrogen-containing heterodiamond mass formed from a plurality of the nitrogen-containing heterodiamond unit cells of claim 21.

24. The combinatorial synthesis of claim 1, which is conducted using the apparatus of Figure 6.

25. The combinatorial synthesis of claim 1, which is conducted using the apparatus of Figure 7.

26. The combinatorial synthesis of claim 1, which is conducted using the apparatus of Figure 8.

27. Heterodiamond unit cells made using the apparatus of Figure 6.

28. Heterodiamond unit cells made using the apparatus of Figure 7.

29. Heterodiamond unit cells made using the apparatus of Figure 8.

30. Heterodiamond mass formed from a plurality of the heterodiamond unit cells of claim 27.

31. The heterodiamond mass of claim 30, which is a boron-containing heterodiamond mass.

32. The heterodiamond mass of claim 30, which is nitrogen-containing heterodiamond mass.

33. An apparatus for forming heterodiamond unit cell, which is depicted in Figure 6.

34. An apparatus for forming heterodiamond unit cell, which is depicted in Figure 7.

35. An apparatus for forming heterodiamond unit cell, which is depicted in Figure 8.

36. An apparatus for forming homodiamond and heterodiamond unit cells, comprising a reaction chamber, a means for providing tetrahedranoidal reactant molecules to said reaction chamber, a means for providing an excited state atomic reactants to said reaction chamber wherein said tetrahedranoidal reactant molecules and said excited state atomic reactants react to form unit cells of heterodiamond or homodiamond.

37. The apparatus of claim 36, further comprising sensors and actuators for maintaining reaction conditions conducive to the formation of unit cells of heterodiamond or homodiamond, wherein information derived from said sensors is processed by a systems controller, said systems controller providing signals to said actuators to maintain said reaction conditions within a predetermined range of parameters.

38) The apparatus of claim 36, further comprising sensors and actuators wherein said sensors send information to said systems controller, said systems controller processing said information and sending control signals to said actuator for producing a controlled reactant flow, temperature and pressure into, out of, and within said reaction chamber according to a predetermined range of parameters according to a predetermined sequence.

39. The apparatus of claim 36, wherein said actuators include valves controlled by said systems controller.

40. The apparatus of claim 36, further comprising means for producing a high energy discharge for providing excited state atomic reactants.

41. The apparatus of claim 40, wherein said excited atomic reactants are atomic boron, carbon, or nitrogen.

42. The apparatus of claim 40, wherein said means for producing a high energy discharge includes a microwave source, a radio frequency source, a laser, or an electrode pair for producing an electrostatic discharge.

1/9

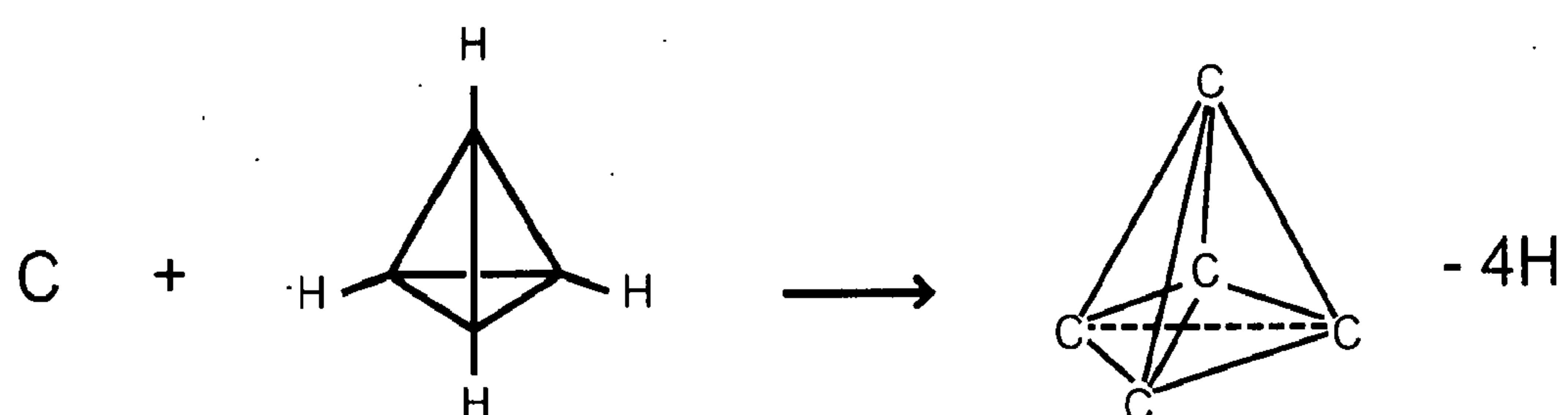
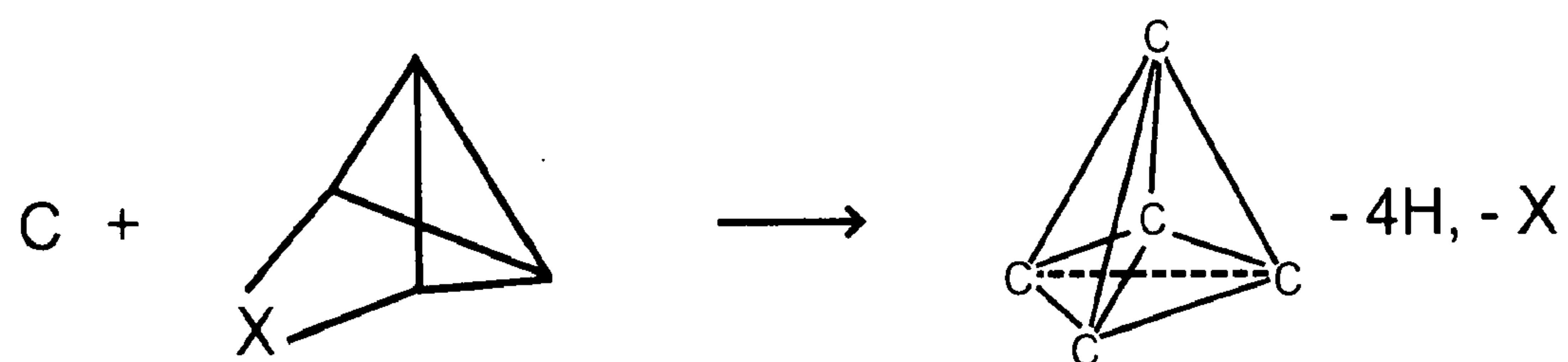


FIG. 1A



$\text{X} = -\text{CH}=\text{CH}-, \text{CO}, \text{ or } -\text{N}=\text{N}-$

FIG. 1B

2/9

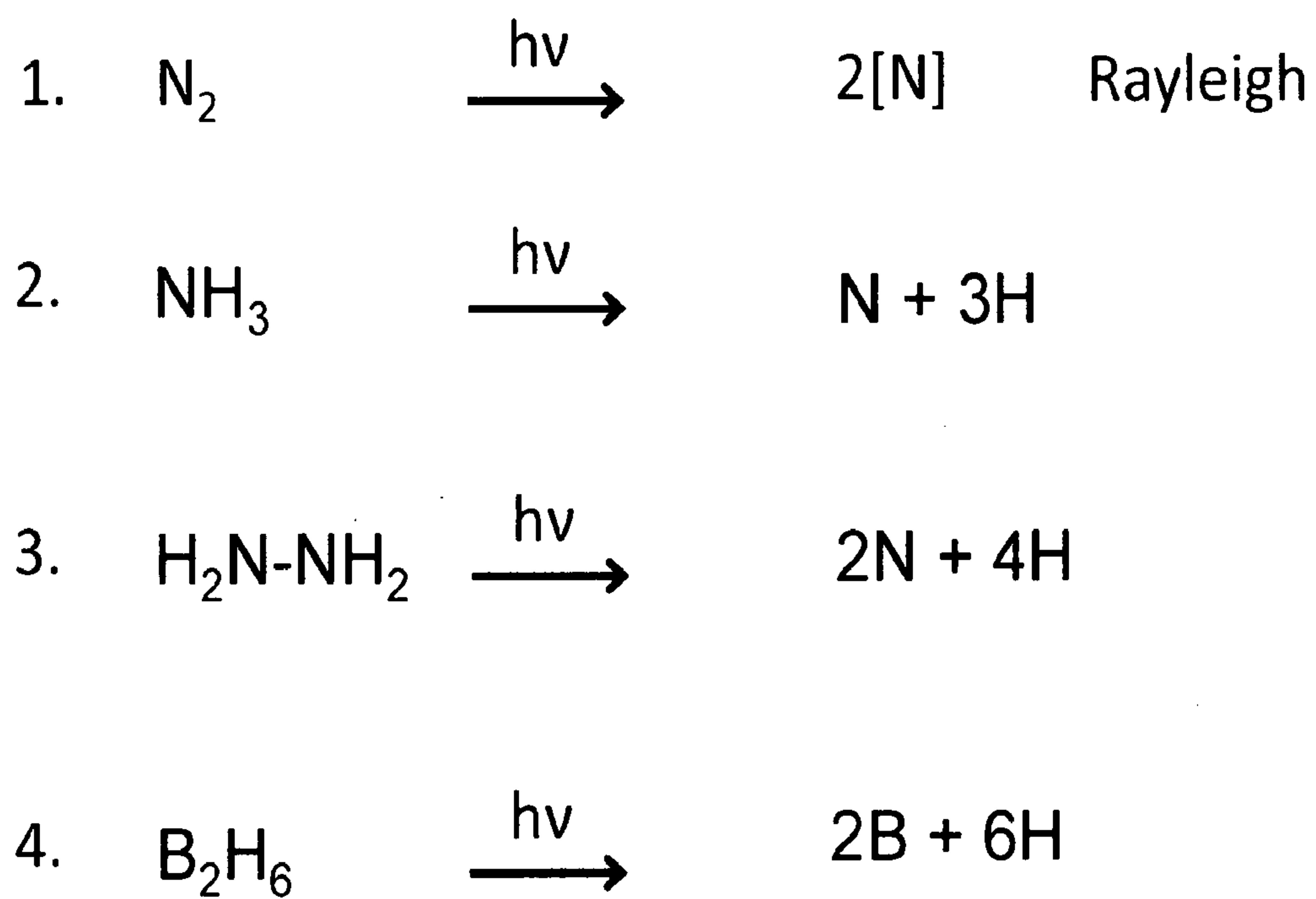


FIG. 2

3/9

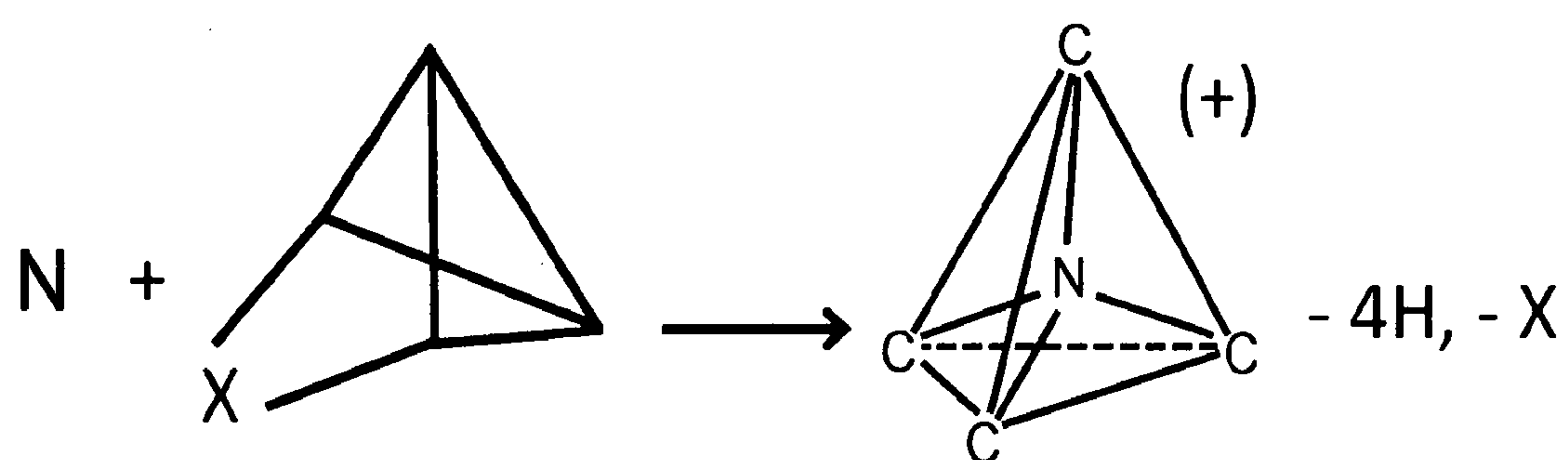
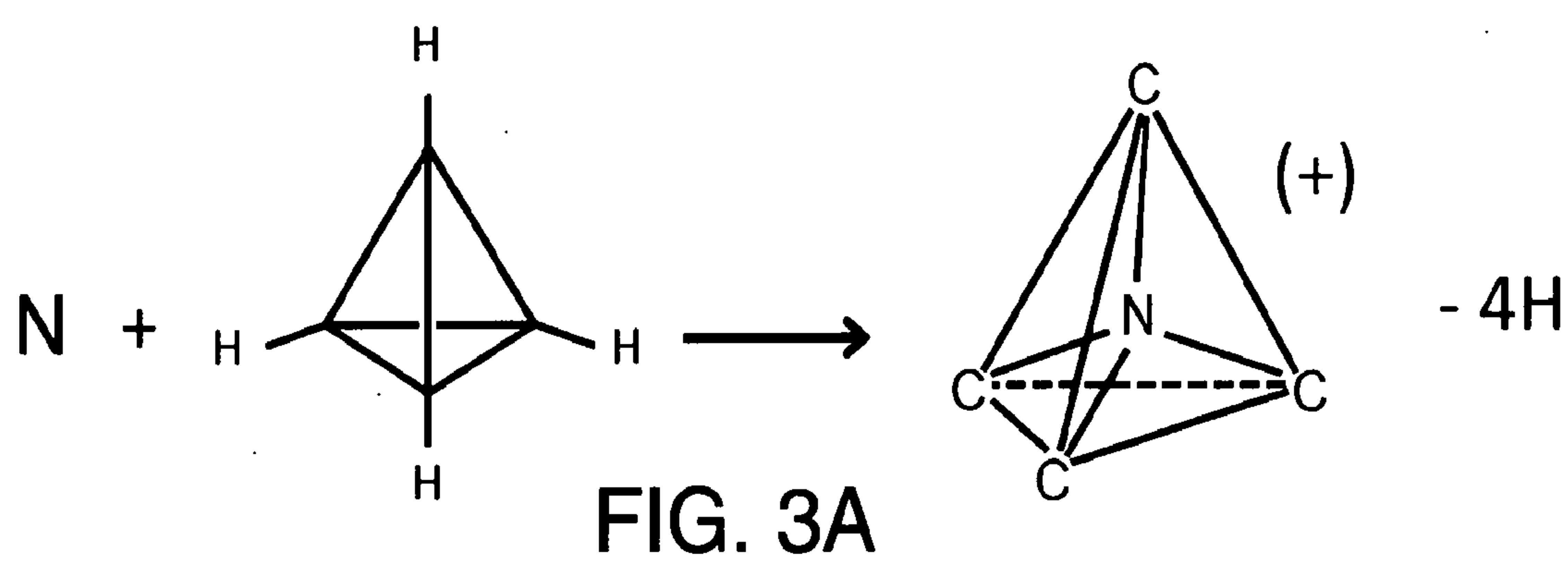

$$X = -CH=CH-, CO, \text{ or } -N=N-$$

**FIG. 3B**

4/9

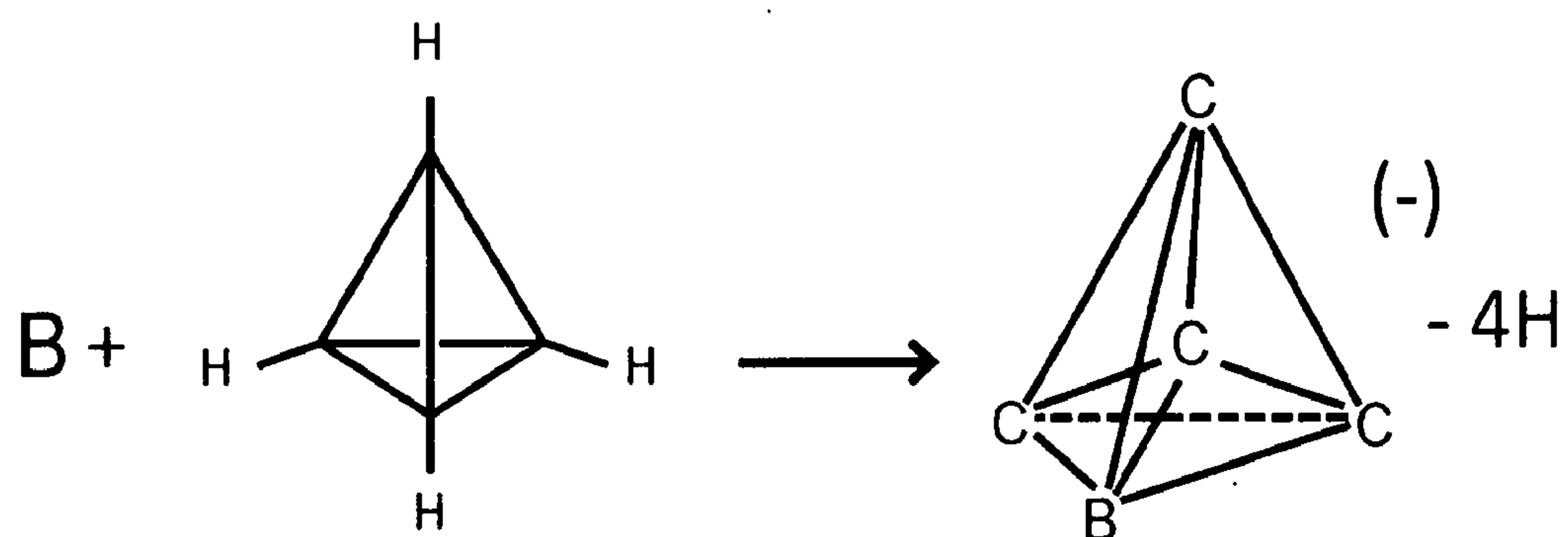


FIG. 4A

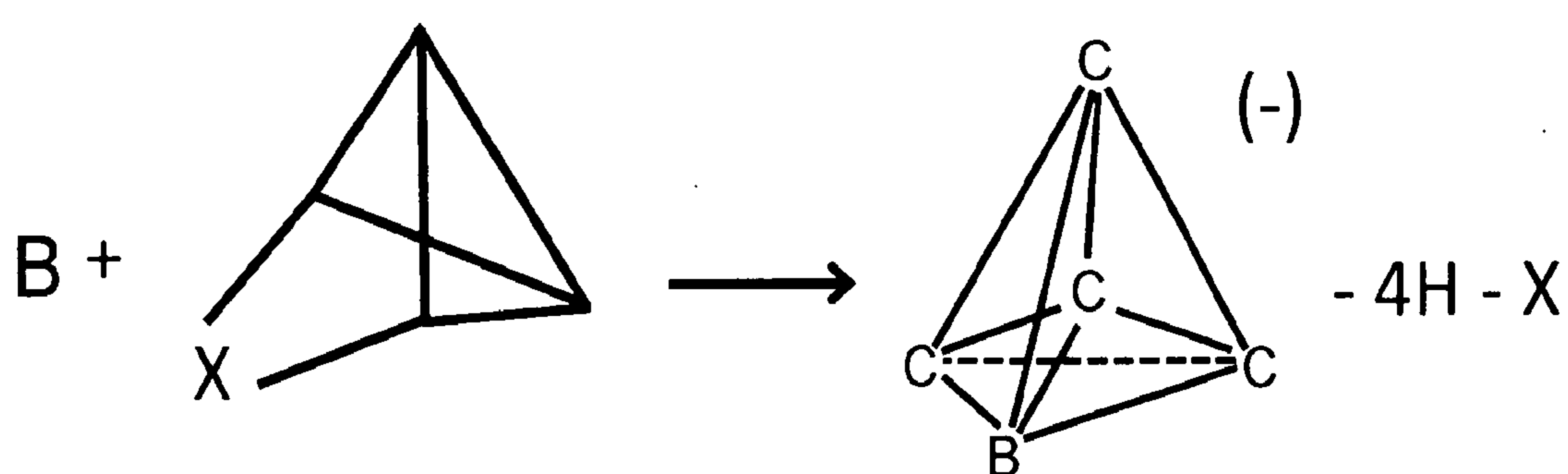
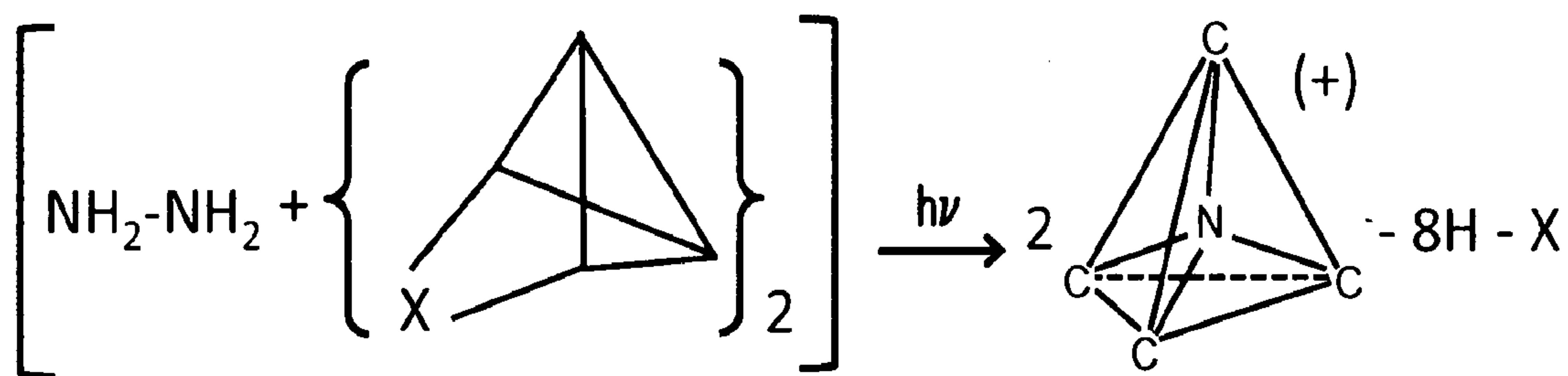

 $X = \text{CO or } -\text{N}=\text{N}-$ 

FIG. 4B

5/9



X = -CH=CH-, CO, or -N=N-

FIG. 5

6/9

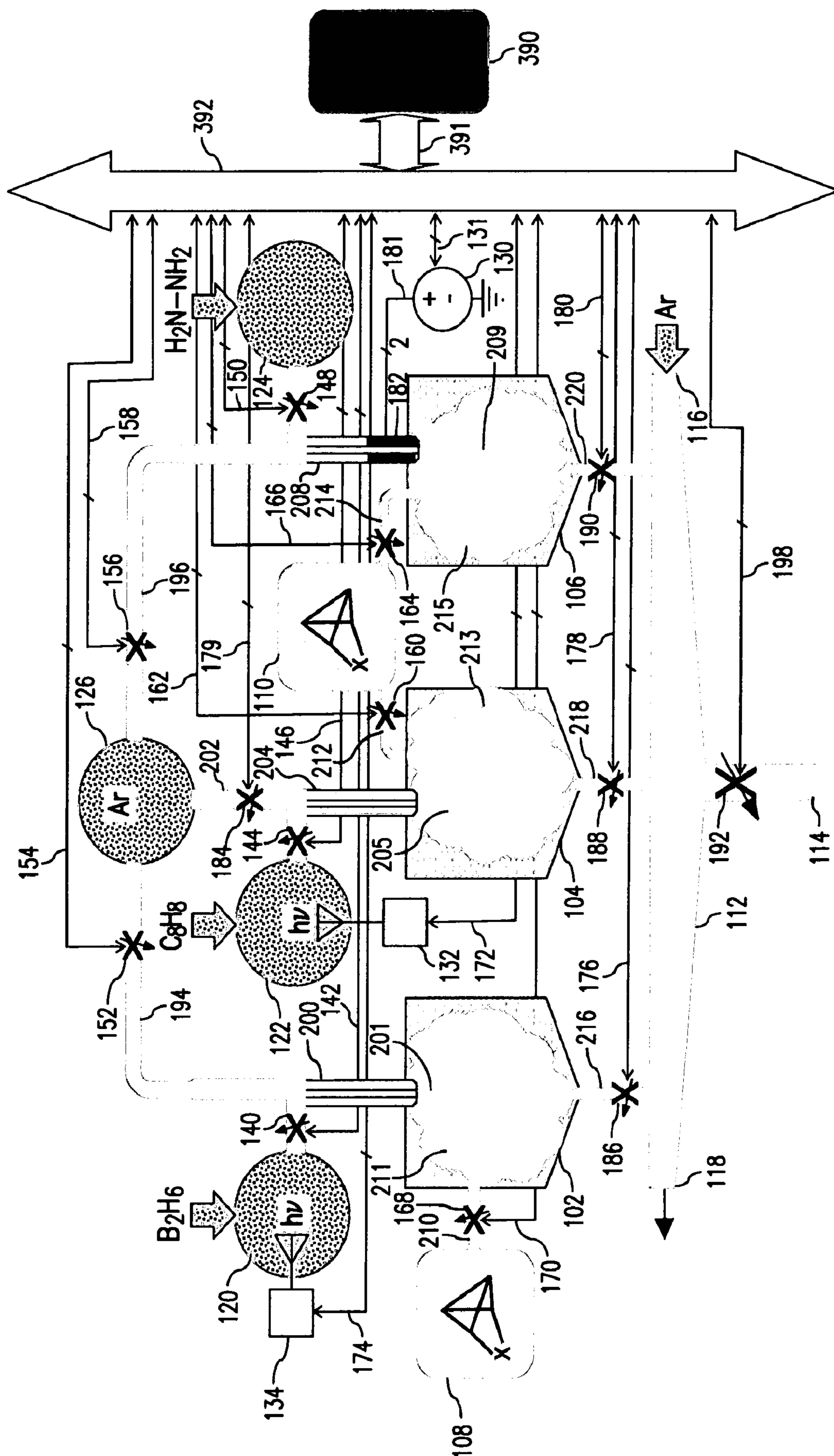


FIG. 6

7/9

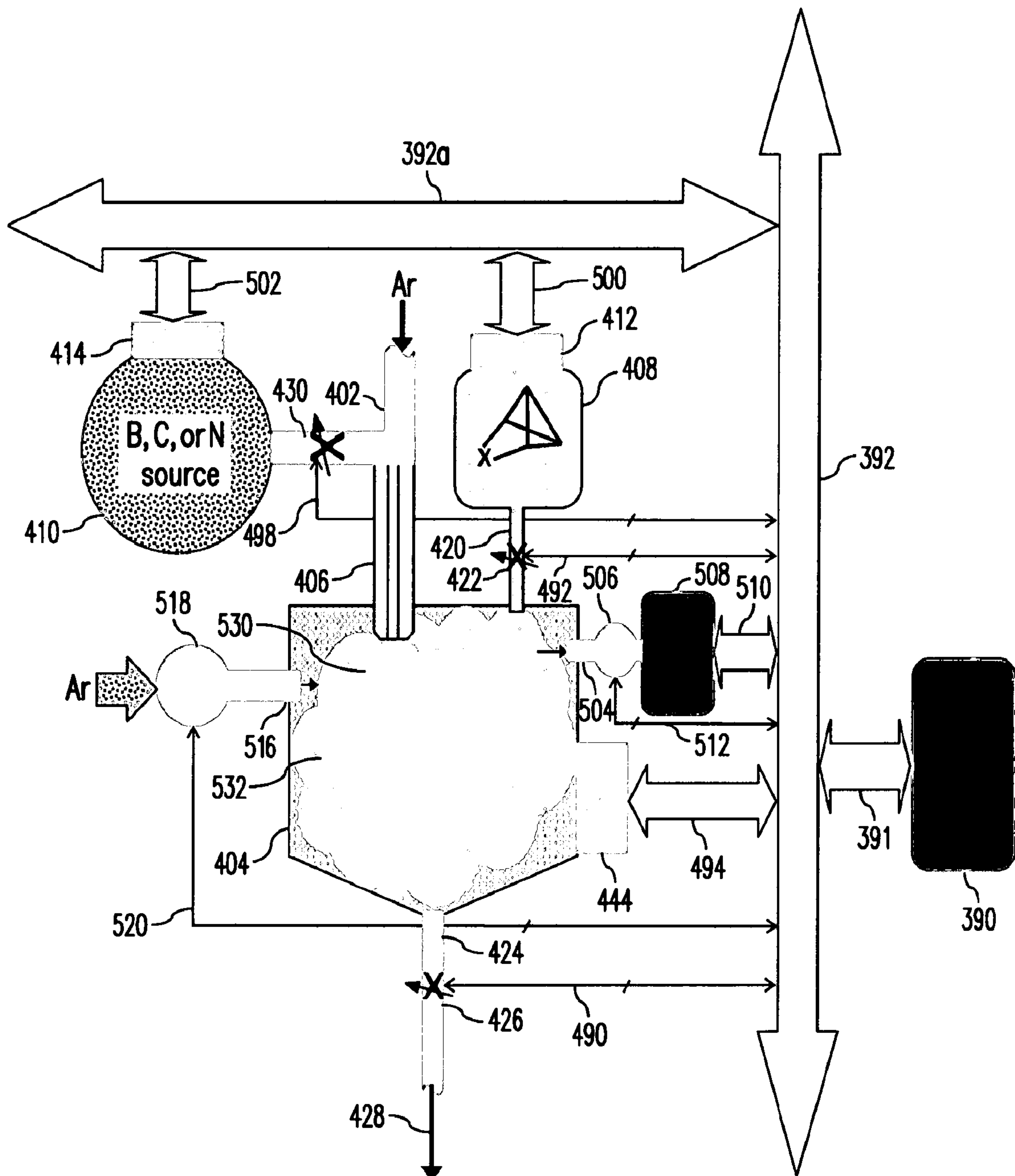


FIG. 7

8/9

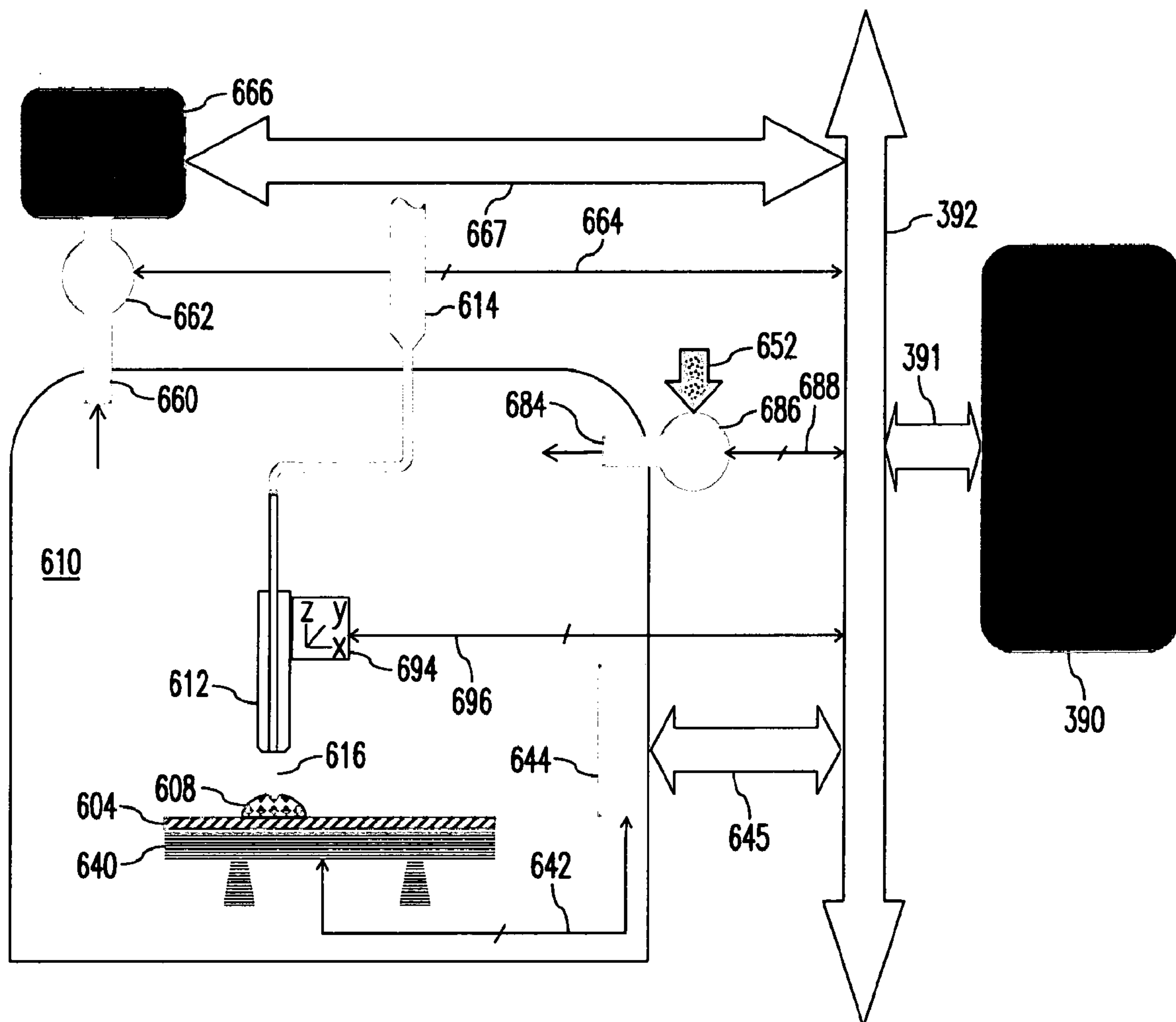


FIG. 8

9/9

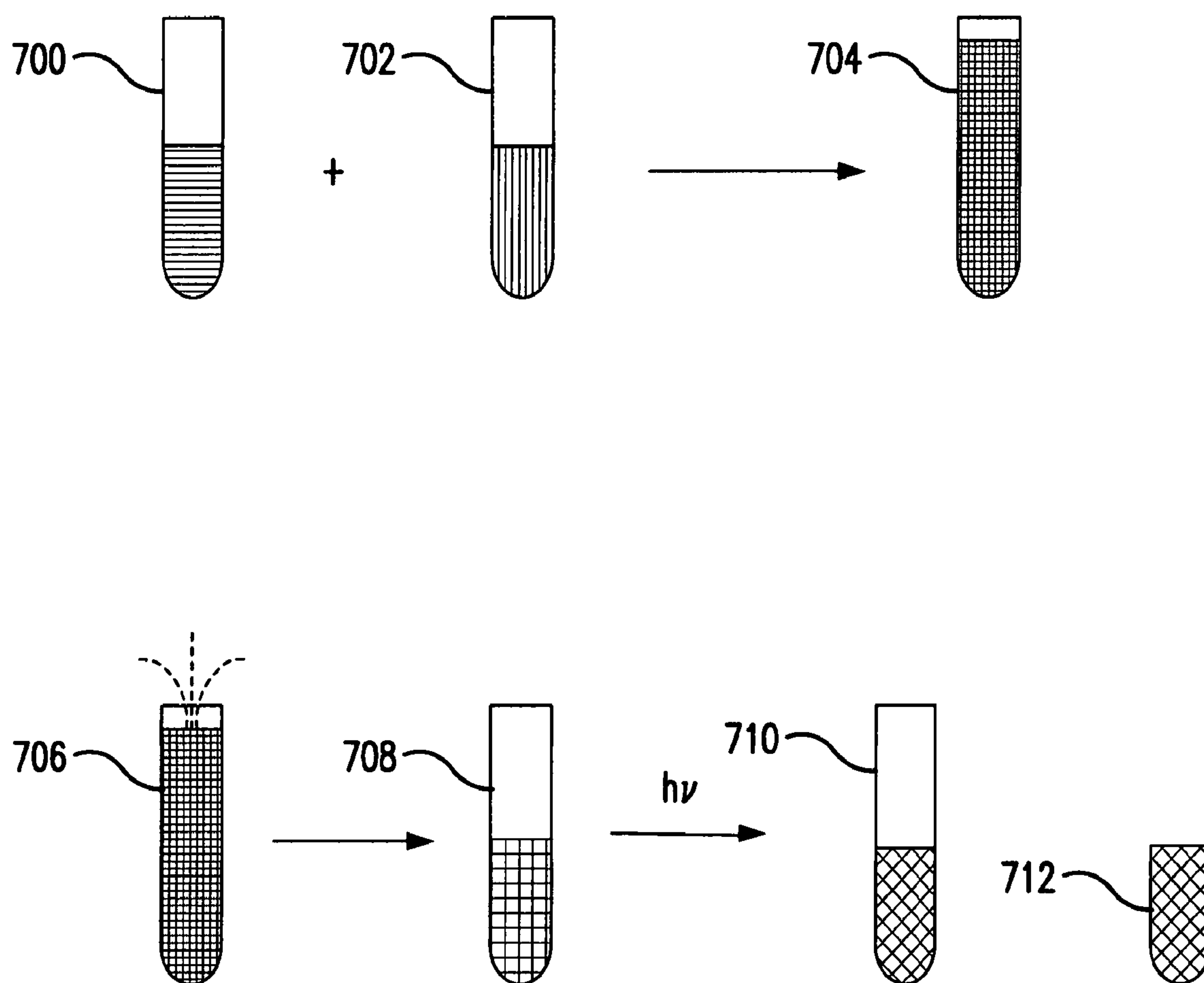
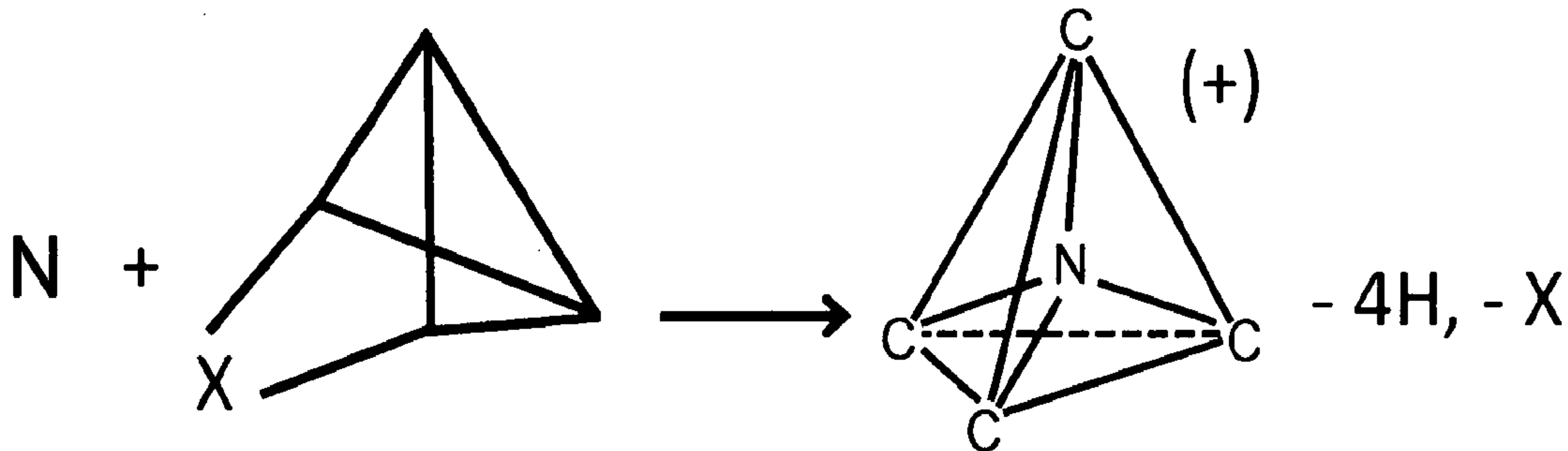


FIG. 9



$X = -CH=CH-, CO, \text{ or } -N=N-$

FIG. 3B