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COMBINATORIAL ENUMERATION OF HETEROCYCLIC DIAMANTANE ANALOGS. PART I: APPLICATION OF THE OBLIGATORY MINIMUM VALENCY RESTRICTION

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ABSTRACT

A combinatorial enumeration under the obligatory minimum valency (OMV) restriction is carried out for the series of diamanane analogs where hetero atoms replacing carbon atoms in the parent diamantane are N or O. The pattern inventory includes an indirect subduction of the Coset Representations (CRs) D_{3d} ($/C_{3v}$) and D_{3d} ($/C_s$) assigned, respectively to bridgehead and bridge carbon atoms followed by symmetry adapted calculations using the unit subduced cycle index approach.

Key words: Obligatory minimum valency, Diamantane, Orbits, Coset representation, Unit-subduced-cycle index, Generating function.

INTRODUCTION

Diamantane or Congressane[1-2] also known as pentacyclo [$7.3.1.1^{4,12}.0^{2,7}.0^{6,7}$] tetradecane according to the Von Baeyer systemic nomenclature is a cage shaped hydrocarbon which consists of 2 adamantane units fused together at inverse position along 2 hexagonal faces in chair conformation. It belongs to the family of diamondoïds whose syntheses and numerous applications in nanotechnology, drug delivery and medicine are largely presented in the literature[3-8].

In a recent study, Nemba et al.[9] have developed an algorithm for direct combinatorial enumeration of chiral and achiral homopolysubstituted diamantane derivatives. The present work is focused on combinatorial enumeration of the first members of the series of oxo, aza-or oxoaza-diamantane analogs taking account of the obligatory minimum valencies (OMVs) of atoms and the Fujita's scheme of unit subduced cycle indices[10-15].

The hydrogen depleted diamantane skeleton (Fig. 1) has 8 bridgehead and 6 bridge carbon atoms. Each bridgehead position can take as substituent an atom having three or more valency (for instance C and N) and cannot accept a monovalent or a divalent atom. On the other hand, a bridge position can take an atom possessing a valency equal to 2 (like O) or more but cannot accept a monovalent atom. Throughout this study, we assume the OMV = 3 for bridgehead and OMV = 2 for bridge positions, respectively.

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Mathematical formulation and computational method

Let us consider the hydrogen depleted stereograph of Diamantane ($C_{14}H_{20}$) in D_{3d} symmetry shown in Fig. 1 where C atoms are indicated by numerical labels. The 8 bridgehead carbon atoms are partitioned into two orbits

$\Delta_1 = \{4,9\}$ and

$\Delta_3 = \{1,2,6,7,11,12\}$

while the bridge carbons form a single orbit

$\Delta_2 = \{3,5,8,10,13,14\}$

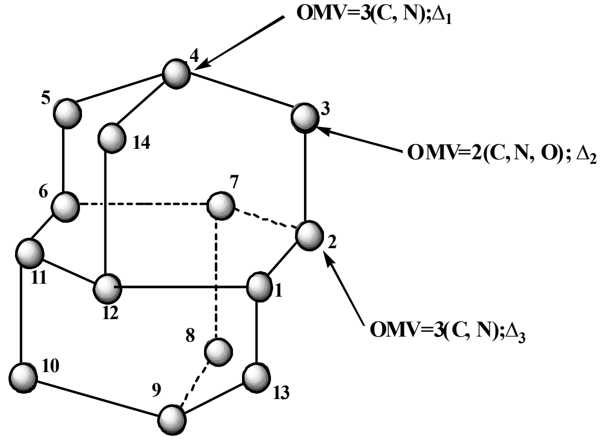


Fig. 1: Hydrogen depleted stereograph of diamantane with arrows reporting the OMV restriction

The D_{3d} symmetry point group of diamantane includes 12 symmetry operations detailed in Eq. 1:

$$D_{3d} = \left\{E, C_3, C_3^2, C_{2(1)}, C_{2(2)}, C_{2(3)}, \mathrm{i}, S_6, S_6^5, \sigma_{d(1)}, \sigma_{d(2)}, \sigma_{d(3)}\right\} \quad \ldots(1)$$

The right hand side elements of Eq. 1 form six equivalence classes given in Eq. 2:

$$\{E\}, \left\{C_3, C_3^2\right\}, \left\{C_{2(1)}, C_{2(2)}, C_{2(3)}\right\}, \{i\}, \left\{S_6, S_6^5\right\}, \left\{\sigma_{d(1)}, \sigma_{d(2)}, \sigma_{d(3)}\right\} \quad \ldots(2)$$

whose elements combine and generate a non redundant set of subgroups[15-16] for D_{3d} denoted $SSG_{D_{3d}}$ given in Eq. 3:

$$SSG_{D_{3d}} = \{C_1, C_2, C_i, C_s, C_3, C_{2h}, D_3, C_{3v}, S_6, D_{3d}\} \quad \ldots(3)$$

The $SSG_{D_{3d}}$ is used to construct the sequence of coset representations for D_{3d} denoted $SCR_{D_{3d}}$ listed in Eq. 4:

$$SCR_{D_{3d}} = \left\{\begin{array}{l} D_{3d}(/C_1), D_{3d}(/C_2), D_{3d}(/Ci), D_{3d}(/C_s), D_{3d}(/C_3), D_{3d}(/C_{2h}), \\ D_{3d}(/D_3), D_{3d}(/C_{3v}), D_{3d}(/S_6), D_{3d}(/D_{3d}) \end{array}\right\} \quad \ldots(4)$$

The explicit forms of these different coset representations (CRs) are given as follows:

$$D_{3d}\ (/C_1) = C_1\ E + C_1C_3 + C_1C_3^2 + C_1C_{2(1)} + C_1C_{2(2)} + C_1C_{2(3)} + C_1i + C_1S_6 + C_1S_6^5 + C_1\sigma_{d(1)} + C_1\sigma_{d(2)} + C_1\sigma_{d(3)} \quad ...(5)$$

$$D_{3d}\ (/C_2) = C_2\ E + C_2\ C_{2(2)} + C_2\ C_{2(3)} + C_2i + C_2S_6 + C_2S_6^5 \quad ...(6)$$

$$D_{3d}\ (/C_s) = C_sE + C_sC_3 + C_sC_3^2 + C_sC_{2(1)} + C_sC_{2(2)} + C_sC_{2(3)} \quad ...(7)$$

$$D_{3d}\ (/C_i) = C_iE + C_iC_3 + C_iC_3^2 + C_iC_{2(1)} + C_iC_{2(2)} + C_iC_{2(3)} \quad ...(8)$$

$$D_{3d}\ (/C_3) = C_3E + C_3C_{2(1)} + C_3S_6 + C_3\sigma_{d(1)} \quad ...(9)$$

$$D_{3d}\ (/C_{2h}) = C_{2h}\ E + C_{2h}\ C_3 + C_{2h}\ C_3^2 \quad ...(10)$$

$$D_{3d}\ (/D_{3d}) = D_3\ E + D_3\ S_6 \quad ...(11)$$

$$D_{3d}\ (/C_{3v}) = C_{3v}\ E + C_{3v}\ C_{2(1)} \quad ...(12)$$

$$D_{3d}\ (/S_6) = S_6\ E + S_6\ C_{2(1)} \quad ...(13)$$

$$D_{3d}\ (/D_{3d}) = D_{3d}E \quad ...(14)$$

To permute the elements of each CR, we multiply the right hand side terms of Eqs. 5-14 by each symmetry operation of D_{3d}. Such operations allow obtaining a row vector of marks (i.e. numbers of invariant elements) assign to each CR. The ten row vectors of marks generated by these operations form the table of marks for D_{3d} denoted $M_{D_{3d}}$ given hereafter:

$$M_{D_{3d}} = \begin{pmatrix} 12 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 6 & 2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 6 & 0 & 2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 6 & 0 & 0 & 6 & 0 & 0 & 0 & 0 & 0 & 0 \\ 4 & 0 & 0 & 0 & 4 & 0 & 0 & 0 & 0 & 0 \\ 3 & 1 & 1 & 3 & 0 & 1 & 0 & 0 & 0 & 0 \\ 2 & 0 & 2 & 0 & 2 & 0 & 2 & 0 & 0 & 0 \\ 2 & 2 & 0 & 0 & 2 & 0 & 0 & 2 & 0 & 0 \\ 2 & 0 & 0 & 2 & 2 & 0 & 0 & 0 & 2 & 0 \\ 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \end{pmatrix}$$

The inverse of this mark table denoted $M_{D_{3d}}^{-1}$ is derived from Eq. 15:

$$M_{D_{3d}} \times M_{D_{3d}}^{-1} = I \quad ...(15)$$

where I represents the 10 x 10 identity matrix.

$$M^{-1}_{D_{3d}} = \begin{pmatrix} \frac{1}{12} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -\frac{1}{4} & \frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -\frac{1}{4} & 0 & \frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -\frac{1}{12} & 0 & 0 & \frac{1}{6} & 0 & 0 & 0 & 0 & 0 & 0 \\ -\frac{1}{12} & 0 & 0 & 0 & \frac{1}{6} & 0 & 0 & 0 & 0 & 0 \\ \frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} & 0 & 1 & 0 & 0 & 0 & 0 \\ \frac{1}{4} & 0 & -\frac{1}{2} & 0 & -\frac{1}{4} & 0 & \frac{1}{2} & 0 & 0 & 0 \\ \frac{1}{4} & -\frac{1}{2} & 0 & 0 & -\frac{1}{4} & 0 & 0 & \frac{1}{2} & 0 & 0 \\ \frac{1}{12} & 0 & 0 & -\frac{1}{6} & -\frac{1}{4} & 0 & 0 & 0 & \frac{1}{2} & 0 \\ -\frac{1}{2} & \frac{1}{2} & \frac{1}{2} & \frac{1}{2} & \frac{1}{2} & -1 & -\frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} & 1 \end{pmatrix}$$

To assign an appropriate CR to Δ_1, Δ_2 and Δ_3, we find the largest subgroup that keeps the elements of each orbit invariant. The elements of Δ_1 are invariant under the C_{3v} subgroup action and similarly those of the orbits Δ_2 and Δ_3 are kept unchanged by C_s. The coset representation assigned to Δ_1 is therefore D_{3d} ($/C_{3v}$) and that one governing Δ_2 and Δ_3 is denoted D_{3d} ($/C_s$).

RESULTS AND DISCUSSION

In this work, we have used Fujita's[10-15] mathematical approach to calculate the subduction of coset representations D_{3d} ($/C_{3v}$) and D_{3d} ($/C_s$) by all subgroups of D_{3d}. These operations are symbolized by Eq. 16-18:

$$D_{3d}\,(/C_{3v}) \downarrow G_i = \beta_{ij} G_i\,(/G_j) \qquad \ldots(16)$$

$$D_{3d}\,(/C_s) \downarrow G_i = \beta_{ik} G_i\,(/G_k) \qquad \ldots(17)$$

$$D_{3d}\,(/C_s) \downarrow G_i = \beta_{ij} G_i\,(/G_j) + \beta_{il} G_i\,(/G_l) \qquad \ldots(18)$$

where $(G_i, G_k, G_l) \in SSG_{D_{3d}}$. Then the right hand side terms of Eqs. 16-18 are transformed into unit subduced cycle indices (USCIs) $S_{d_i}^{\beta_i}$, $f_{d_i}^{\beta_i}$ and $f_{d_{ij}}^{\beta_{ij}} \times f_{d_{il}}^{\beta_{il}}$ given in Eqs. 19-21, respectively.

$$D_{3d}\,(/C_{3v}) \downarrow G_i = \beta_{ij} G_i\,(/G_j) \rightarrow S_{d_{ij}}^{\beta_{ij}} \quad \text{for } \Delta_1 \qquad \ldots(19)$$

$$D_{3d}\,(/C_s) \downarrow G_i = \left\{ \begin{matrix} \beta_{ir} G_i\,(/G_r) \rightarrow f_{d_{ir}}^{\beta_{ir}} \\ \beta_{ik} G_i\,(/G_k) + \beta_{il} G_i\,(/G_l) \rightarrow f_{d_{ir}}^{\beta_{ik}}\ f_{d_{il}}^{\beta_{il}} \end{matrix} \right\} \quad \text{for } \Delta_2 \qquad \ldots(20)$$

$$D_{3d}\ (/C_s) \downarrow G_i = \begin{Bmatrix} \beta_{ir} G_i\ (/G_r) \rightarrow S_{d_{ir}}^{\beta_{ir}} \\ \beta_{ik} G_i\ (/G_k) + \beta_{il} G_i\ (/G_l) \rightarrow S_{d_{ir}}^{\beta_{ik}}\ S_{d_{il}}^{\beta_{il}} \end{Bmatrix} \text{ for } \Delta_3 \quad \ldots(21)$$

The superscripts β_{ij}, β_{ik}, β_{ir} and β_{il} in eqs. 16-21 are subduction's coefficients and the subscripts are derived from the ratios $d_{ij} = \frac{|G_i|}{|G_j|}$, $d_{ik} = \frac{|G_i|}{|G_k|}$, $d_{ir} = \frac{|G_i|}{|G_r|}$ and $d_{il} = \frac{|G_i|}{|G_l|}$, where $|G_i|$, $|G_j|$, $|G_k|$, $|G_k|$, $|G_r|$ and $|G_l|$ are the cardinalities of the respective subgroups. The subductions and the USCIs obtained are reported in Table 1 for the orbits Δ_1, Δ_2 and Δ_3. Note that global USCIs are derived from Eq. 22 :

$$S_{d_{ij}}^{\beta_{ij}+} \times S_{d_{ik}}^{\beta_{ik}} \times f_{d_{il}}^{\beta_{il}} = S_{d_{ij}}^{\beta_{ij}+\beta_{ik}} \times f_{d_{il}}^{\beta_{il}} \text{ if } d_{ij} = d_{ik} \quad \ldots(22)$$

For example the global USCI for the subsymmetry C_1 is : $S_1^2 \times f_1^6 \times S_1^6 = S_1^8 f_1^6$

In order to solve our enumeration problem let us consider L={C, N, O} as a set of ligands to be put in distinct ways among the bridgehead and bridge positions of diamantane. According to the OMV restriction of the orbits we attribute to these ligands the following weights:

$$\omega_{\Delta_1}(\mathrm{C}) = 1,\ \omega_{\Delta_1}(\mathrm{N}) = x \text{ and } \omega_{\Delta_1}(\mathrm{O}) = 0 \text{ for } \Delta_1$$

$$\omega_{\Delta_2}(\mathrm{C}) = 1,\ \omega_{\Delta_2}(\mathrm{N}) = x \text{ and } \omega_{\Delta_2}(\mathrm{O}) = y \text{ for } \Delta_2$$

$$\omega_{\Delta_3}(\mathrm{C}) = 1,\ \omega_{\Delta_3}(\mathrm{N}) = x \text{ and } \omega_{\Delta_3}(\mathrm{O}) = 0 \text{ for } \Delta_3$$

We have considered the following ligand inventories:

$$S_d = 1 + x^d \text{ for } \Delta_1 \text{ and } \Delta_3$$

and

$$f_d = 1 + x^d + y^d \text{ for } \Delta_2$$

Table 1: Subductions of CRs D_{3d} (/C_{3v}) and D_{3d} (/C_s) and their resulting USCIs

Δ_1	$\Delta_2 = \Delta_3$	Δ_1	Δ_2	Δ_3	Global USCIs
D_{3d} (/C_{3v}) $\downarrow C_1 = 2C_1$ (/C_1)	D_{3d} (/C_s) $\downarrow C_1 = 6C_1$ (/C_1)	S_1^2	f_1^6	S_1^6	$S_1^8\ f_1^6$
D_{3d} (/C_{3v}) $\downarrow C_2 = C_2$ (/C_1)	D_{3d} (/C_s) $\downarrow C_2 = 3C_2$ (/C_1)	S_2^1	f_2^3	S_2^3	$S_2^4\ f_2^3$

Cont…

Δ_1	$\Delta_2 = \Delta_3$	Δ_1	Δ_2	Δ_3	Global USCIs
D_{3d} (/C_{3v}) ↓ C_s = 2C_s (/C_s)	D_{3d} (/C_s) ↓ C_s = 2C_s (/C_s) + 2C_s (/C_1)	s_1^2	$f_1^2 f_2^2$	$s_1^2 s_2^2$	$s_1^4 s_2^2 f_1^2 f_2^2$
D_{3d} (/C_{3v}) ↓ C_i = C_i (/C_1)	D_{3d} (/C_s) ↓ C_i = 3C_i (/C_1)	s_2^1	f_2^3	s_2^3	$s_2^4 f_2^3$
D_{3d} (/C_{3v}) ↓ C_3 = 2C_3 (/C_3)	D_{3d} (/C_s) ↓ C_3 = 2C_3 (/C_1)	s_1^2	f_3^2	s_3^2	$s_1^2 s_3^2 f_3^2$
D_{3d} (/C_{3v}) ↓ C_{2h} = C_{2h} (/C_s)	D_{3d} (/C_s) ↓ C_{2h} = C_{2h} (/C_1) + C_{2h} (/C_s)	s_2^1	$f_2^1 f_4^1$	$s_2^1 s_4^1$	$s_2^2 s_4^1 f_2^1 f_4^1$
D_{3d} (/C_{3v}) ↓ C_{3v} = 2C_{3v} (/C_{3v})	D_{3d} (/C_s) ↓ C_{3v} = 2C_{3v} (/C_s)	s_1^2	f_3^2	s_3^2	$s_1^2 s_3^2 f_3^2$
D_{3d} (/C_{3v}) ↓ D_3 = D_3 (/C_3)	D_{3d} (/C_s) ↓ D_3 = D_3 (/C_1)	s_2^1	f_6^1	s_6^1	$s_2^1 s_6^1 f_6^1$
D_{3d} (/C_{3v}) ↓ S_6 = S_6 (/C_3)	D_{3d} (/C_s) ↓ S_6 = S_6 (/C_1)	s_2^1	f_6^1	s_6^1	$s_2^1 s_6^1 f_6^1$
D_{3d} (/C_{3v}) ↓ D_{3d} = D_{3d} (/C_{3v})	D_{3d} (/C_s) ↓ D_{3d} = D_{3d} (/C_s)	s_2^1	f_6^1	s_6^1	$s_2^1 s_6^1 f_6^1$

To convert the global USCIs shown in table 2 into generating functions of type *F(x,y)* related to each subsymmetry $G_i \subset D_{3d}$ as follows:

$$s_{d_{ij}}^{\beta_{ij}} + \times s_{d_{ik}}^{\beta_{ik}} \times f_{d_{il}}^{\beta_{il}} \rightarrow F(x,y) = \left(1+x^{d_{ij}}\right)^{\beta_{ij}} \left(1+x^{d_{ik}}\right)^{\beta_{ik}} \left(1+x^{d_{il}}+y^{d_{il}}\right)^{\beta_{il}} = \sum_{q_1,q_2} A_{q_1,q_2} x^{q_1} y^{q_2} \quad \ldots(23)$$

Table 2: Generating functions derived from global USCIs related to the subsymmetries of D_{3d}

Subsymmetries	Global USCIs	Generating function *F(x,y)*
C_1	$s_1^8 f_1^6$	$(1+x)^8 (1+x+y)^6$
C_i, C_2	$s_2^4 f_2^3$	$\left(1+x^2\right)^4 \left(1+x^2+y^2\right)^3$
C_s	$s_1^4 s_2^2 f_1^2 f_2^2$	$(1+x)^4 \left(1+x^2\right)^2 (1+x+y)^2 \left(1+x^2+y^2\right)^2$
C_3, 3v	$s_1^2 s_3^2 f_3^2$	$(1+x)^2 \left(1+x^3\right)^2 \left(1+x^3+y^3\right)^2$
C_{2h}	$s_2^2 s_4^1 f_2^1 f_4^1$	$\left(1+x^2\right)^2 \left(1+x^4\right)\left(1+x^2+y^2\right)\left(1+x^4+y^4\right)$
D_3, S_6, D_{3d}	$s_2^1 s_6^1 f_6^1$	$\left(1+x^2\right)\left(1+x^6\right)\left(1+x^6+y^6\right)$

The expansion of F(x, y) yields for each term $x^{q_1} y^{q_2}$ the coefficients A_{q_1,q_2}, which are collected to form a fixed point matrix FPM ($x^{q_1} y^{q_2}$) shown below:

$$FPM\left(x^{q_1} y^{q_2}\right) = \begin{array}{c} \\ x \\ y \\ x^2 \\ y^2 \\ x^3 \\ y^3 \\ x^4 \\ y^4 \\ xy \\ x^2y^2 \end{array} \begin{array}{c} \begin{array}{cccccccccc} \mathbf{C_1} & \mathbf{C_2} & \mathbf{C_i} & \mathbf{C_s} & \mathbf{C_3} & \mathbf{C_{2h}} & \mathbf{C_{3v}} & \mathbf{D_3} & \mathbf{S_6} & \mathbf{D_{3d}} \end{array} \\ \begin{pmatrix} 14 & 0 & 6 & 0 & 2 & 0 & 2 & 0 & 0 & 0 \\ 6 & 0 & 2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 91 & 7 & 19 & 7 & 1 & 3 & 1 & 1 & 1 & 1 \\ 15 & 3 & 3 & 3 & 0 & 1 & 0 & 0 & 0 & 0 \\ 364 & 0 & 44 & 0 & 4 & 0 & 4 & 0 & 0 & 0 \\ 20 & 0 & 4 & 0 & 2 & 0 & 2 & 0 & 0 & 0 \\ 1001 & 21 & 81 & 21 & 8 & 5 & 8 & 0 & 0 & 0 \\ 15 & 3 & 3 & 3 & 0 & 1 & 0 & 0 & 0 & 0 \\ 78 & 0 & 0 & 10 & 0 & 0 & 0 & 0 & 0 & 0 \\ 990 & 18 & 46 & 18 & 0 & 2 & 0 & 0 & 0 & 0 \end{pmatrix} \end{array}$$

To obtain the isomer count matrix ICM ($x^{q_1} y^{q_2}$) we multiply FPM ($x^{q_1} y^{q_2}$) by $M^{-1}_{D_{3d}}$ the inverse of the mark table for D_{3d}:

$$ICM\left(x^{q_1} y^{q_2}\right) = FPM\left(x^{q_1} y^{q_2}\right) \times M^{-1}_{\mathbf{D_{3d}}} \qquad \ldots(24)$$

The rows and columns of the ICM ($x^{q_1} y^{q_2}$) are numbers of hetero diamantane isomers given with respect to the symmetry and the degrees of substitution q_1 and q_2. These results depict compounds where the diamantane carbon skeleton (C_{14}) has been transformed into $C_{14-q_1-q_2}N_{q_1}O_{q_2}$ and such series are presented in the right hand side of the *ICM* together with their corresponding mathematical expression ($x^{q_1} y^{q_2}$) in the left hand side.

$$ICM\left(x^{q_1} y^{q_2}\right) = \begin{array}{c} \\ x \\ y \\ x^2 \\ y^2 \\ x^3 \\ y^3 \\ x^4 \\ y^4 \\ xy \\ x^2y^2 \end{array} \begin{array}{c} \begin{array}{cccccccccc} \mathbf{C_1} & \mathbf{C_2} & \mathbf{C_s} & \mathbf{C_i} & \mathbf{C_3} & \mathbf{C_{2h}} & \mathbf{C_{3v}} & \mathbf{D_3} & \mathbf{S_6} & \mathbf{D_{3d}} \end{array} \\ \begin{pmatrix} 0 & 0 & 2 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 2 & 2 & 8 & 0 & 0 & 2 & 0 & 0 & 0 & 1 \\ 0 & 1 & 1 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 20 & 0 & 20 & 0 & 0 & 0 & 2 & 0 & 0 & 0 \\ 1 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 60 & 8 & 34 & 1 & 0 & 5 & 4 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 4 & 0 & 5 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 66 & 8 & 22 & 2 & 0 & 2 & 0 & 0 & 0 & 0 \end{pmatrix} \end{array} \begin{array}{l} \\ \mathbf{C_{13}N} \\ \mathbf{C_{13}O} \\ \mathbf{C_{12}N_2} \\ \mathbf{C_{12}O_2} \\ \mathbf{C_{11}N_3} \\ \mathbf{C_{11}O_3} \\ \mathbf{C_{10}N_4} \\ \mathbf{C_{10}O_4} \\ \mathbf{C_{12}NO} \\ \mathbf{C_{10}N_2O_2} \end{array}$$

It should be noted that for $q_2 = 0$ the rows (x^{q_1}) present the isomers numbers of azadiamantane series symbolized by the empirical formula $C_{14-q_1}N_{q_1}$. The calculations reveal that substitution under the OMV restriction of C atoms by N atoms among 8 bridgehead positions of diamantane skeleton generates for:

$q_1 = 1 \rightarrow 1C_s + 1C_{3v}$ ($C_{13}N$)

$q_1 = 2 \rightarrow 2C_1 + 2C_2 + 8C_s + 2C_{2h} + 1D_{3d}$ ($C_{12}N_2$)

$q_1 = 3 \rightarrow 20C_1 + 20C_s + 2C_{3v}$ ($C_{11}N_3$)

$q_1 = 4 \rightarrow 60C_1 + 8C_2 + 34C_s + 1C_i + 5C_{2h} + 4C_{3v}$ ($C_{10}O_4$)

For the sake of illustration figure 2 depicts chemical graphs of 3 mono and 15 di-azadiamantane skeletons predicted by the pattern inventory.

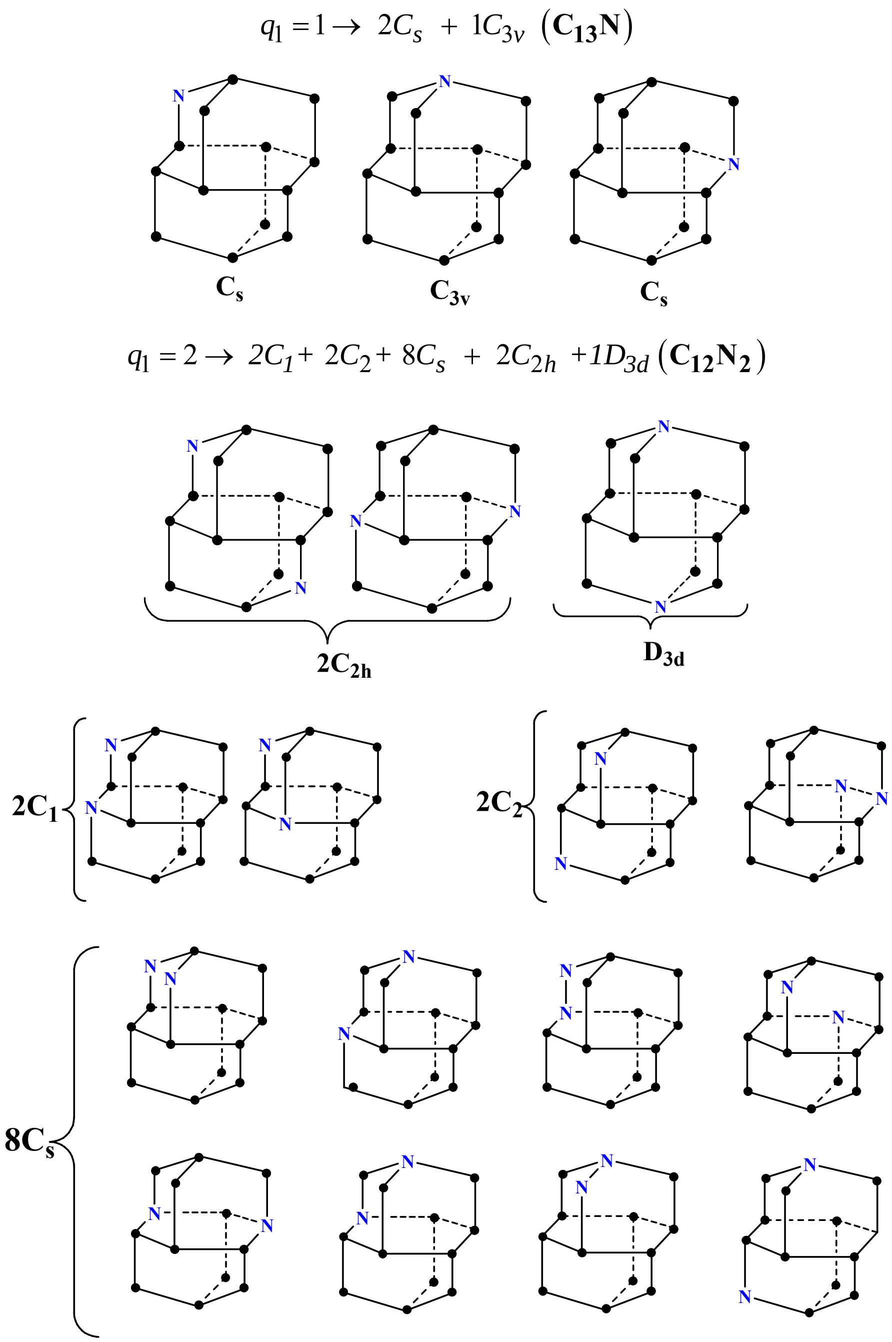


Fig. 2: Chemical graphs of mono- and di-azadiamantane derivatives

In the other hand, the substitution under the OMV restriction of C atoms by O atoms among 6 bridge positions of diamantane skeleton (see rows (y^{q_2})) generates for :

$q_2 = 1 \rightarrow 1C_s\ (C_{13}O)$

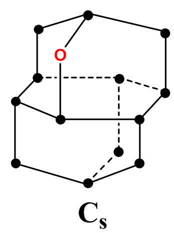
$q_2 = 2 \rightarrow 1C_2 + 1C_s + 1C_{2h}\ (C_{12}O_2)$

$q_2 = 3 \rightarrow 1C_1 + 1C_s + 1C_{2H}\ (C_{11}O_3)$

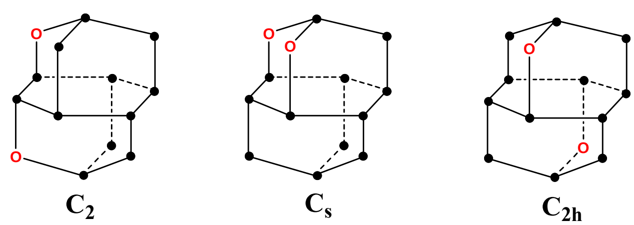
$q_2 = 4 \rightarrow 1C_2 + 1C_s + 1C_{2h}\ (C_{10}O_4)$

Fig. 3 depicts chemical graphs of 1 mono, 3 di-, 3tri- and 3 tetra- oxadiamantanes analogs $C_{14-q_2}O_{q_2}$.

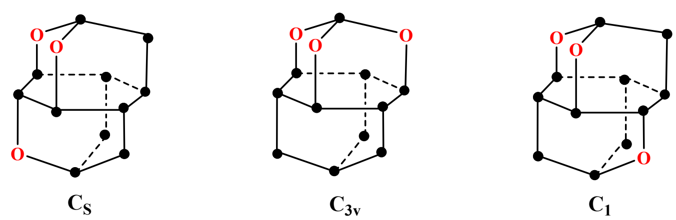
$q_2 = 1 \rightarrow 1C_s\ (C_{13}O)$



$q_2 = 1 \rightarrow 1C_s\ (C_{13}O)$



$q_2 = 3 \rightarrow 1C_1 + 1C_s + 1C_{2H}\ (C_{11}O_3)$



$q_2 = 4 \rightarrow 1C_2 + 1C_s + 1C_{2h}\ (C_{10}O_4)$

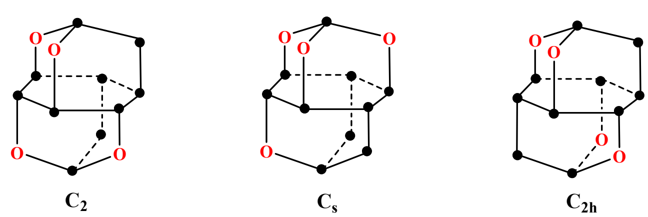


Fig. 3: Graphs of mono-, di, tri and tetraoxa-diamantanes with their respective symmetry

The simultaneous substitutions under the OMV restriction of C atoms by N and O atoms among 8 bridgehead and 6 bridge positions of diamantane skeleton (see rows ($x^{q_1}\ y^{q_2}$)) generate for $q_1 = 1$ and $q_2 = 1$, 9 oxa-aza-diamantanes ($C_{12}NO$) including 4 C_1 + 5 C_s (see Fig. 4).

$$q_1 = 1,\ q_2 = 1 \rightarrow 4\ C_1 + 5\ C_s\ (C_{12}NO)$$

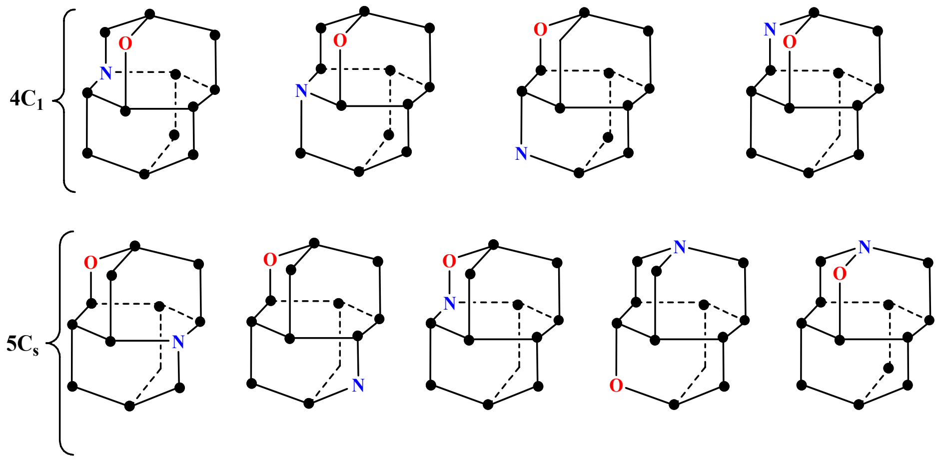


Fig. 4: Chemical graphs of 4 C_1 and 5 C_s oxa-aza diamantane analogs

In the case where $q_1 = q_2 = 2$ the calculations have predict :

$$66\ C_1 + 8\ C_2 + 22\ C_s + 2C_i + 2\ C_{2h}$$

Dioxa-diaza diamantanes ($C_{10}N_2O_2$). Fig. 5 presents for illustration chemical graphs for 2C_i, 2C_{2h} and 8 C_2 diamantane analog skeletons.

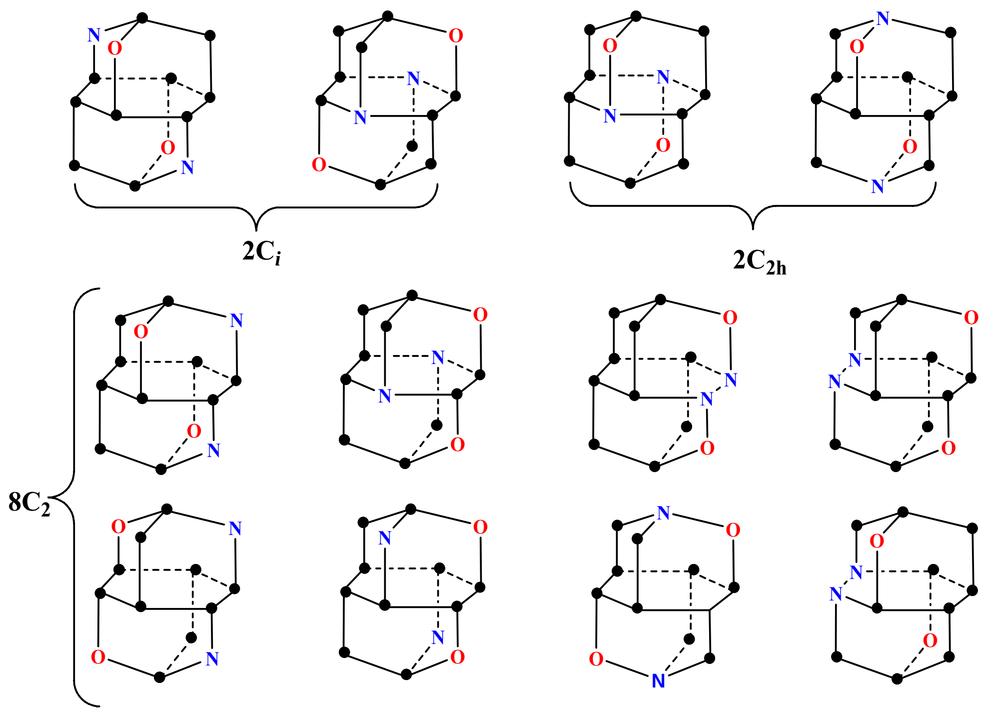


Fig. 5: Chemical graphs of 2 C_i, 2 C_{2h} and 8 C_2 dioxa-diaza diamantane analogs

CONCLUSION

The pattern inventory presented in this study is applicable to the enumeration of series of heterocyclic aza-, oxa- and oxa-aza-diamantane skeletons symbolized by the general empirical formula $C_{14-q_1-q_2}N_{q_1}O_{q_2}$. The results have shown that for fixed values of the degrees of substitutions q_1 and q_2 the numbers of heterocyclic isomers of aza-diamantane ($C_{14-q_1}N_{q_1}$) is higher than the number of oxadiamantane ($C_{14-q_2}O_{q_2}$) while a combined substitutions producing oxa-aza-diamantane analogs yields numbers of isomers intermediate to those of the 2 aforementioned series. These differences results from the OMV restriction. It is to be noticed that the sum of isomers numbers in each row of the ICM match up with the polya's coefficients[16] obtained from the direct subduction method presented in part II of this study.

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