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ORGANOMETALLIC COMPOUNDS
XVI*. MATRIX REPRESENTATIONS OF TRIGONAL-BIPYRAMIDAL STRUCTURES AND OF THE PSEUDO-ROTATIONS DESCRIBING THEIR INTRAMOLECULAR REARRANGEMENTS

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SUMMARY

Matrix representations are given for five-coordinate structures (product matrices P) and for the intramolecular isomerization reactions of these complexes (reaction matrices R) via pseudo-rotation processes. Matrix transformations are also described, which allow to deduce from the general case the subset of rearrangements generated by various constraints (using constraint matrices C). Several examples are depicted and compared with previous descriptions.

INTRODUCTION

Non-topological[1] and topological[2,3] representations have been given to describe the isomerization paths of trigonal-bipyramidal molecules via pseudo-rotation processes. It seemed interesting to see whether matrix representations might also be found to represent these structures and their intramolecular rearrangements.

RESULTS AND DISCUSSION

Matrix representation of bipyramidal structures

It is possible to represent the twenty trigonal-bipyramidal isomers of a pentacoordinate complex 12,345[†] by a matrix which relates the relative position of the ligand to the name (or symbol) of the different isomers. The function used here will be the apical (A) configuration of a given substituent.

If one uses the numbering which has been suggested in ref. 1 to describe the different ML_5[3], isomers, one has a = 12,345; b = 34,125; c = 35,142; d = 45,123; e = 25,134; f = 15,243; g = 14,235; h = 24,153; i = 13,254 and j = 23,145.

The p_{kl} coefficients of matrix P describe then the different isomers having ligands k and l in *trans* (or apical AA) position.

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[*] For Part XV see ref. 1.
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[†] For the numbering convention and symbolism, see ref. 2 and 3.

$$P=\begin{array}{c|ccccc|} & 1 & 2 & 3 & 4 & 5 \\ \hline 1 & 0 & \bar{a} & i & \bar{g} & f \\ 2 & a & 0 & \bar{j} & h & \bar{e} \\ 3 & \bar{i} & j & 0 & \bar{b} & c \\ 4 & g & \bar{h} & b & 0 & \bar{d} \\ 5 & \bar{f} & e & \bar{c} & d & 0 \end{array}$$

Since all five ligands in 12,345 are different, the diagonal elements p_{kk} are zero.

Matrix transformations

This matrix P gives thus immediately all the structures which have a given ligand (k) in an apical position (p_{kx} and p_{xk} for all allowed values of x: eight possibilities, two series of enantiomers).

Let us define a matrix C(kE)* which is a p by p unit matrix whose *k*th column has been replaced by a column of zero's; the operation

$$\tilde{C}(\text{kE})\times P\times C(\text{kE})=P(\text{kE})$$

changes the original matrix P into the particular one P(kE), which describes the case where ligand k *may not* be apical**.

The matrix transformation of P for the particular case where ligand k *must* be apical is simply

$$P-P(\text{kE})=P(\text{kA})$$

The same may be done for two ligands; if k and l *must both* be apical, one has

$$\tilde{C}(\text{kA,lA})\times P\times C(\text{kA,lA})=P(\text{kA,lA})$$

where C(kA,lA) is a p by p zero matrix where c_{kk} and c_{ll} have been replaced by 1.

Similarly, if k and l must both be equatorial, the transformation matrix C(kE,lE) is formed from a unit matrix where columns k and l are replaced by zero's

$$P(\text{kE,lE})=\tilde{C}(\text{kE,lE})\times P\times C(\text{kE,lE})$$

When $\overline{\text{kl}}$ is a chelating ligand, k and l cannot both be apical and one finds

$$P(\text{kl},\overline{\text{AA}})=P-P(\text{kA,lA})$$

If, for reasons of angular strain for instance, k and l may not be both apical or both equatorial (see ref. 2, example 5), the result is clearly

$$P(\text{kAE,lEA})=P-P(\text{kA,lA})-P(\text{kE,lE})$$

The changes which occur when two ligands (say k and l) are identical, are the following:

a. the six (kE, lE) isomers are converted into three inactive structures, having a plane of symmetry containing the central atom, the two A ligands and the third E one.

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* The C matrices used in the present paper describe the reduction of original matrices under the influence of special constraints. The type of constraint is represented in the parentheses.

** $\tilde{C}$(kE) is the transposed of C(kE); in this particular case, $\tilde{C}$(kE) = C(kE).

For these six (kE,lE) isomers, one has thus $p_{mn}=p_{nm}$ (if m, n$\neq$k, l)

b. the two (kA,lA) enantiomers become identical, symmetrical with respect to the plane of the three equatorial ligands

c. each of the six original (kA,lE) or (kE,lA) isomers become identical to one of the other AE or EA structures.

These changes are summarized by the following successive matrix transformations: we first define

$$I = P+\tilde{P}(\mathrm{kE,lE})$$

and the final matrix $P(\mathrm{k=l})$ is formed by

$$P(\mathrm{k=l}) = \tilde{C}(\mathrm{k=l})\times I\times C(\mathrm{k=l})$$

where $C(\mathrm{k=l})$ is a rectangular matrix constructed from a (p−1) by (p−1) unit matrix by inserting between lines (l−1) and l, a row which is identical to line k.

For example, if ligands 4 and 5 are identical

$$P(4=5)=\begin{pmatrix} 0 & (a+\bar{a}) & (i+\bar{i}) & (\bar{g}+f) \\ (a+\bar{a}) & 0 & (j+\bar{j}) & (h+\bar{e}) \\ (i+\bar{i}) & (j+\bar{j}) & 0 & (\bar{b}+c) \\ (g+\bar{f}) & (e+\bar{h}) & (b+\bar{c}) & (d+\bar{d}) \end{pmatrix}$$

The elements $(a+\bar{a})$, $(i+\bar{i})$, $(j+\bar{j})$ and $(d+\bar{d})$ represent inactive isomers. Elements such as $(g+\bar{f})$ show that g and $\bar{f}$ have merged into one single compound, which is the enantiomer of $(\bar{g}+f)$.

If more than two ligands are made identical to one another, all the structures become optically inactive, for the reason that one necessarily finds two equivalent groups either in EE or in AA position, which implies the existence of a symmetry plane. In these cases, one has thus to consider $P+\tilde{P}$ instead of P.

Matrix representation of intramolecular rearrangements via pseudo-rotations of trigonal-bipyramidal structures

It is also possible to represent the isomerization reactions of these pentacoordinate structures by a square 20×20 matrix R representing the possible isomers of 12,345, whose coefficients r_{kl}, r_{km} and r_{kn} are 1 if isomer k may be converted into the isomers l, m and n by the three possible pseudo-rotations[2,3] and 0 otherwise. As a given isomer may only be converted into three isomers of the enantiomorph series by a single step process if the modified numbering is used[1,*], the matrix describing the rearrangements is of the type

$$R=\begin{array}{ccc} & a\ \cdots\ j & \bar{a}\ \cdots\ \bar{j} \\ \begin{array}{c} a\\ \vdots\\ j\end{array} & O & A \\ \begin{array}{c} \bar{a}\\ \vdots\\ \bar{j}\end{array} & \tilde{A} & O \end{array}$$

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[*] With this numbering, the topological representation is alternate.

and may be formally reduced to a 10 × 10 symmetrical one A. This sub-matrix A can be used instead of the topological graphs to find isomerization paths, the non-zero elements being the turning-points (or transition states) to go from one isomer to another.

12,345

$$A=\begin{array}{c|cccccccccc|}
 & \bar{a} & \bar{b} & \bar{c} & \bar{d} & \bar{e} & \bar{f} & \bar{g} & \bar{h} & \bar{i} & \bar{j} \\
a & 0 & 1 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
b & 1 & 0 & 0 & 0 & 1 & 1 & 0 & 0 & 0 & 0 \\
c & 1 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 0 & 0 \\
d & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 \\
e & 0 & 1 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 \\
f & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 \\
g & 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 1 \\
h & 0 & 0 & 1 & 0 & 0 & 1 & 0 & 0 & 1 & 0 \\
i & 0 & 0 & 0 & 1 & 1 & 0 & 0 & 1 & 0 & 0 \\
j & 0 & 0 & 0 & 1 & 0 & 1 & 1 & 0 & 0 & 0
\end{array}$$

Matrix transformations

The introduction of a chemical bond between two ligands[3] or any other constraint[2] such as having two identical ligands reduces the number of possible isomers (*vide supra*), and this reduces also the size of the isomerization matrix R.

Chelating groups

The introduction of a bond between two ligands k and l* restricts the number of possible isomers [the structures p_{kl} and p_{lk} are impossible, see matrix $P(\mathrm{kl},\overline{\mathrm{AA}})$]. These structures have thus to be excluded from matrix R by eliminating the rows and columns corresponding to p_{lk} and p_{kl}.

This can be done by the following matrix transformation

$$\tilde{C}(p_{kl}=p_{lk}=0)\times R\times C(p_{kl}=p_{lk}=0)=R(p_{kl}=p_{lk}=0)$$

If R is a r by r matrix, $C(p_{kl}=p_{lk}=0)$ has (r−2) columns and r rows and is constructed from a (r−2) × (r−2) unit matrix by inserting two lines of zero's which will become the p_{kl}th and p_{lk}th ones.

$$\begin{array}{c|ccccccccc|}
 & \bar{a} & \bar{b} & \bar{c} & \bar{d} & \bar{e} & \bar{f} & \bar{g} & \bar{h} & \bar{i} \\
a & 0 & 1 & 1 & 1 & 0 & 0 & 0 & 0 & 0 \\
b & 1 & 0 & 0 & 0 & 1 & 1 & 0 & 0 & 0 \\
c & 1 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 0 \\
d & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\
e & 0 & 1 & 0 & 0 & 0 & 0 & 1 & 0 & 1 \\
f & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\
g & 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 \\
h & 0 & 0 & 1 & 0 & 0 & 1 & 0 & 0 & 1 \\
i & 0 & 0 & 0 & 1 & 1 & 0 & 0 & 1 & 0
\end{array}=A(1\overline{2,3}45)$$

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* The case of structures which contain two chelating groups will be discussed elsewhere[4].

It is thus possible to transform the matrix R of the 12,345 system into another one for $1\overline{2,3}45$ for instance $[R(\mathrm{j}=\bar{\mathrm{j}}=0)]^{\star}$. The obtained matrix corresponds to the topological description given before[3].

Identity of ligands

If the isomers m and n become identical when ligand k = ligand l, one has to replace in matrix R every r_{mx} by $\mathrm{r}_{\mathrm{mx}}+\mathrm{r}_{\mathrm{nx}}$ and r_{xm} by $\mathrm{r}_{\mathrm{xm}}+\mathrm{r}_{\mathrm{xn}}$, and to suppress row and column n.

This can also be done by the following matrix transformation

$$\tilde{C}(\mathrm{m}=\mathrm{n})\times R\times C(\mathrm{m}=\mathrm{n})=R(\mathrm{m}=\mathrm{n})$$

where $C(\mathrm{m}=\mathrm{n})$ has $(\mathrm{r}-1)$ columns and r rows and is constructed from a unit matrix with $(\mathrm{r}-1)$ columns and lines by inserting one line, which is identical to row m, between the $(\mathrm{n}-1)$th and nth line of the unit matrix.

It is thus possible to examine the case of 12,245 structures for instance, defining first $P(2\mathrm{E},3\mathrm{E})$:

$$\begin{bmatrix} 10000\\ 00000\\ 00000\\ 00010\\ 00001 \end{bmatrix}\times P\times\begin{bmatrix} 10000\\ 00000\\ 00000\\ 00010\\ 00001 \end{bmatrix}=P(2\mathrm{E},3\mathrm{E})$$

One may now calculate I

$$I=P+\tilde{P}(2\mathrm{E},3\mathrm{E})=\begin{bmatrix} 0 & \bar{\mathrm{a}} & \mathrm{i} & \mathrm{g}+\bar{\mathrm{g}} & \mathrm{f}+\bar{\mathrm{f}}\\ \mathrm{a} & 0 & \bar{\mathrm{j}} & \mathrm{h} & \bar{\mathrm{e}}\\ \bar{\mathrm{i}} & \mathrm{j} & 0 & \bar{\mathrm{b}} & \mathrm{c}\\ \mathrm{g}+\bar{\mathrm{g}} & \bar{\mathrm{h}} & \mathrm{b} & 0 & \mathrm{d}+\bar{\mathrm{d}}\\ \mathrm{f}+\bar{\mathrm{f}} & \mathrm{e} & \bar{\mathrm{c}} & \mathrm{d}+\bar{\mathrm{d}} & 0 \end{bmatrix}$$

The final matrix $P(2=3)$ is formed by

$$P(2=3)=\tilde{C}(2=3)\times I\times C(2=3)=\begin{pmatrix} 10000\\ 01100\\ 00010\\ 00001 \end{pmatrix}\times I\times\begin{pmatrix} 1000\\ 0100\\ 0100\\ 0010\\ 0001 \end{pmatrix}$$

$$P(2=3)=\begin{array}{c|cccc} & 1 & 2=3 & 4 & 5\\ \hline 1 & 0 & \bar{\mathrm{a}}+\mathrm{i} & \mathrm{g}+\bar{\mathrm{g}} & \mathrm{f}+\bar{\mathrm{f}}\\ 2=3 & \mathrm{a}+\bar{\mathrm{i}} & \mathrm{j}+\bar{\mathrm{j}} & \mathrm{h}+\bar{\mathrm{b}} & \bar{\mathrm{e}}+\mathrm{c}\\ 4 & \mathrm{g}+\bar{\mathrm{g}} & \bar{\mathrm{h}}+\mathrm{b} & 0 & \mathrm{d}+\bar{\mathrm{d}}\\ 5 & \mathrm{f}+\bar{\mathrm{f}} & \mathrm{e}+\bar{\mathrm{c}} & \mathrm{d}+\bar{\mathrm{d}} & 0 \end{array}$$

★ $p_{23}=\mathrm{j}$ (see matrix P).

$P(2=3)$ shows how $a=\bar{i}$, $b=\bar{h}$, $c=\bar{e}$, $d=\bar{d}$, $e=\bar{c}$, $f=\bar{f}$, $g=\bar{g}$, $h=\bar{b}$, $i=\bar{a}$ and $j=\bar{j}$.

It is now possible to determine $R(2=3)=R(12{,}245)$ using the suitable transformation matrix defined from $P(2=3)$ which will have ten columns less than R. The matrix $C(a=\bar{i},\ b=\bar{h},\ c=\bar{e},\ d=\bar{d},\ e=\bar{c},\ f=\bar{f},\ g=\bar{g},\ h=\bar{b},\ i=\bar{a},\ j=\bar{j})$ may thus be written

$$\tilde{C}(a=\bar{i},\ b=\bar{h},\ c=\bar{e},\ d=\bar{d},\ e=\bar{c},\ f=\bar{f},\ g=\bar{g},\ h=\bar{b},\ i=\bar{a},\ j=\bar{j})=$$

$$\begin{array}{c|cccccccccccccccccccc|}
 & a & b & c & d & e & f & g & h & i & j & \bar{a} & \bar{b} & \bar{c} & \bar{d} & \bar{e} & \bar{f} & \bar{g} & \bar{h} & \bar{i} & \bar{j} \\
a & 1&0&0&0&0&0&0&0&0&0&0&0&0&0&0&0&0&0&1&0 \\
b & 0&1&0&0&0&0&0&0&0&0&0&0&0&0&0&0&0&1&0&0 \\
c & 0&0&1&0&0&0&0&0&0&0&0&0&0&0&1&0&0&0&0&0 \\
d & 0&0&0&1&0&0&0&0&0&0&0&0&0&1&0&0&0&0&0&0 \\
\bar{c} & 0&0&0&0&1&0&0&0&0&0&0&0&1&0&0&0&0&0&0&0 \\
f & 0&0&0&0&0&1&0&0&0&0&0&0&0&0&0&1&0&0&0&0 \\
g & 0&0&0&0&0&0&1&0&0&0&0&0&0&0&0&0&1&0&0&0 \\
\bar{b} & 0&0&0&0&0&0&0&1&0&0&0&1&0&0&0&0&0&0&0&0 \\
\bar{a} & 0&0&0&0&0&0&0&0&1&0&1&0&0&0&0&0&0&0&0&0 \\
j & 0&0&0&0&0&0&0&0&0&1&0&0&0&0&0&0&0&0&0&1
\end{array}$$

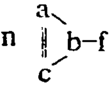
$\tilde{C}\times R\times C=R(2=3)=R(12{,}245)$ and $R(12{,}245)$ is analogous to A, the reduced form of R

$$\begin{array}{c|cccccccccc|}
 & a & b & c & d & \bar{c} & f & g & \bar{b} & \bar{a} & j \\
a & 0&1&1&1&0&0&0&0&0&0 \\
b & 1&0&0&0&1&1&0&0&0&0 \\
c & 1&0&0&0&0&0&1&1&0&0 \\
d & 1&0&0&0&0&0&0&0&1&1 \\
\bar{c} & 0&1&0&0&0&0&1&0&1&0 \\
f & 0&1&0&0&0&0&0&1&0&1 \\
g & 0&0&1&0&1&0&0&0&0&1 \\
\bar{b} & 0&0&1&0&0&1&0&0&1&0 \\
\bar{a} & 0&0&0&1&1&0&0&1&0&0 \\
j & 0&0&0&1&0&1&1&0&0&0
\end{array}\times 2=R(12{,}245)$$

From this particular case (12,245), one can deduce, by an analogous way, the 12,225 system, setting $4=2$. This gives finally

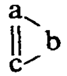
12,225

$$\begin{array}{c} \\ a \\ b \\ c \\ f \end{array}\begin{array}{c} a\ b\ c\ f \\ \begin{pmatrix} 0&1&2&0 \\ 1&0&1&1 \\ 2&1&0&0 \\ 0&1&0&0 \end{pmatrix}\end{array}\times 6=R(12{,}225)$$

This matrix is equivalent to the following topological description 

One may also deduce the matrix description of the $\overbracket{12,225}$ system from the former one. One gets

$$\begin{array}{c|ccc} & a & b & c \\ \hline a & 0 & 1 & 2 \\ b & 1 & 0 & 1 \\ c & 2 & 1 & 0 \end{array} \times 6 = R(\overbracket{12,225})$$

which gives topologically 

Other constraints

One may finally examine some of the examples given by Lauterbur and Ramirez[2].

Example 1: *Substituent* 1 *can be equatorial but not apical.*

$$\tilde{C}(1E) \times P \times C(1E) = P(1E)$$

and, as

$$C(1E) = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}, \qquad P(1E) = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \bar{j} & h & \bar{e} \\ 0 & j & 0 & \bar{b} & c \\ 0 & \bar{h} & b & 0 & \bar{d} \\ 0 & e & \bar{c} & d & 0 \end{bmatrix}$$

$$\begin{aligned} R(1E) &= R(a=\bar{a}=i=\bar{i}=g=\bar{g}=f=\bar{f}=0) \\ &= \tilde{C}(a=\bar{a}=i=\bar{i}=g=\bar{g}=f=\bar{f}=0) \times R \times C(a=\bar{a}=i=\bar{i}=g=\bar{g}=f=\bar{f}=0) \end{aligned}$$

Here, the transformation matrix $C(a=\bar{a}=i=\bar{i}=g=\bar{g}=f=\bar{f}=0)$ is given by

$$\begin{array}{c|cccccccccccccccccccc} & a & b & c & d & e & f & g & h & i & j & \bar{a} & \bar{b} & \bar{c} & \bar{d} & \bar{e} & \bar{f} & \bar{g} & \bar{h} & \bar{i} & \bar{j} \\ \hline b & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ c & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ d & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ e & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ h & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ j & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \bar{b} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \bar{c} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \bar{d} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ \bar{e} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ \bar{h} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ \bar{j} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{array} = \tilde{C}(a=\bar{a}=i=\bar{i}=g=\bar{g}=f=\bar{f}=0)$$

This gives $$R(1\mathrm{E}) = \left(\begin{array}{c|c} O & A(1\mathrm{E}) \\ \hline A(1\mathrm{E}) & O \end{array}\right)$$

with

$$\begin{array}{c|cccccc|} & \bar{\mathrm{b}} & \bar{\mathrm{c}} & \bar{\mathrm{d}} & \bar{\mathrm{e}} & \bar{\mathrm{h}} & \bar{\mathrm{j}} \\ \mathrm{b} & 0 & 0 & 0 & 1 & 0 & 0 \\ \mathrm{c} & 0 & 0 & 0 & 0 & 1 & 0 \\ \mathrm{d} & 0 & 0 & 0 & 0 & 0 & 1 \\ \mathrm{e} & 1 & 0 & 0 & 0 & 0 & 0 \\ \mathrm{h} & 0 & 1 & 0 & 0 & 0 & 0 \\ \mathrm{j} & 0 & 0 & 1 & 0 & 0 & 0 \end{array} = A(1\mathrm{E})$$

$R(1\mathrm{E})$ may thus be reduced to six one by one unit matrices

$$\begin{array}{cccccc} \bar{\mathrm{e}} & \bar{\mathrm{h}} & \bar{\mathrm{j}} & \bar{\mathrm{b}} & \bar{\mathrm{c}} & \bar{\mathrm{d}} \\ \mathrm{b}(1); & \mathrm{c}(1); & \mathrm{d}(1); & \mathrm{e}(1); & \mathrm{h}(1); & \mathrm{j}(1) \end{array}$$

which is analogous to Lauterbur and Ramirez's topological representation: only isolated pairs of isomers may interconvert[2].

Example 2: *Substituent* 1 *can be apical but not equatorial.*

$$P(1\mathrm{A}) = P - P(1\mathrm{E})$$

$$= \begin{bmatrix} 0 & \bar{\mathrm{a}} & \mathrm{i} & \bar{\mathrm{g}} & \mathrm{f} \\ \mathrm{a} & 0 & 0 & 0 & 0 \\ \bar{\mathrm{i}} & 0 & 0 & 0 & 0 \\ \mathrm{g} & 0 & 0 & 0 & 0 \\ \bar{\mathrm{f}} & 0 & 0 & 0 & 0 \end{bmatrix}$$

The suitable matrix transformation $C(\mathrm{j}=\bar{\mathrm{j}}=\mathrm{h}=\bar{\mathrm{h}}=\mathrm{e}=\bar{\mathrm{e}}=\mathrm{b}=\bar{\mathrm{b}}=\mathrm{c}=\bar{\mathrm{c}}=\mathrm{d}=\bar{\mathrm{d}}=0)$ changes R into $R(1\mathrm{A})$

$$R(1\mathrm{A}) = \left(\begin{array}{c|c} O & A(1\mathrm{A}) \\ \hline A(1\mathrm{A}) & O \end{array}\right) \text{ where } A(1\mathrm{A}) = \begin{array}{c|cccc|} & \bar{\mathrm{a}} & \bar{\mathrm{f}} & \bar{\mathrm{g}} & \bar{\mathrm{i}} \\ \mathrm{a} & 0 & 0 & 0 & 0 \\ \mathrm{f} & 0 & 0 & 0 & 0 \\ \mathrm{g} & 0 & 0 & 0 & 0 \\ \mathrm{i} & 0 & 0 & 0 & 0 \end{array}$$

so that no isomerizations at all can occur[2].

Example 5 (*which is analogous to example* 7 *ref.* 2): *Substituents* 1 *and* 2 *cannot be both apical or both equatorial.*

One has first to determine $P(\mathrm{kA},1\mathrm{A})$ and $P(\mathrm{kE},1\mathrm{E})$. In this case

$$P(1\mathrm{E},2\mathrm{E}) = \begin{bmatrix} 0&0&0&0&0\\ 0&0&0&0&0\\ 0&0&1&0&0\\ 0&0&0&1&0\\ 0&0&0&0&1 \end{bmatrix} \times P \times \begin{bmatrix} 0&0&0&0&0\\ 0&0&0&0&0\\ 0&0&1&0&0\\ 0&0&0&1&0\\ 0&0&0&0&1 \end{bmatrix} = \begin{bmatrix} 0&0&0&0&0\\ 0&0&0&0&0\\ 0&0&0&\bar{\mathrm{b}}&\mathrm{c}\\ 0&0&\mathrm{b}&0&\bar{\mathrm{d}}\\ 0&0&\bar{\mathrm{c}}&\mathrm{d}&0 \end{bmatrix}$$

$$P(1\mathrm{A},2\mathrm{A}) = \begin{bmatrix} 1&0&0&0&0\\ 0&1&0&0&0\\ 0&0&0&0&0\\ 0&0&0&0&0\\ 0&0&0&0&0 \end{bmatrix} \times P \times \begin{bmatrix} 1&0&0&0&0\\ 0&1&0&0&0\\ 0&0&0&0&0\\ 0&0&0&0&0\\ 0&0&0&0&0 \end{bmatrix} = \begin{bmatrix} 0&\bar{\mathrm{a}}&0&0&0\\ \mathrm{a}&0&0&0&0\\ 0&0&0&0&0\\ 0&0&0&0&0\\ 0&0&0&0&0 \end{bmatrix}$$

It is now possible to calculate $P(\mathrm{kAE},1\mathrm{EA})$:

$$P(1\mathrm{AE},2\mathrm{EA}) = P - P(1\mathrm{A},2\mathrm{A}) - P(1\mathrm{E},2\mathrm{E})$$

$$= \begin{bmatrix} 0&0&\mathrm{i}&\bar{\mathrm{g}}&\mathrm{f}\\ 0&0&\bar{\mathrm{j}}&\mathrm{h}&\bar{\mathrm{e}}\\ \bar{\mathrm{i}}&\mathrm{j}&0&0&0\\ \mathrm{g}&\bar{\mathrm{h}}&0&0&0\\ \bar{\mathrm{f}}&\mathrm{e}&0&0&0 \end{bmatrix}$$

$C(\mathrm{a}=\bar{\mathrm{a}}=\mathrm{b}=\bar{\mathrm{b}}=\mathrm{c}=\bar{\mathrm{c}}=\mathrm{d}=\bar{\mathrm{d}}=0)$ may thus be written and $R(\mathrm{a}=\bar{\mathrm{a}}=\mathrm{b}=\bar{\mathrm{b}}=\mathrm{c}=\bar{\mathrm{c}}=\mathrm{d}=\bar{\mathrm{d}}=0) = R(1\mathrm{AE},2\mathrm{EA})$ is equal to

$$\left(\begin{array}{c|c} O & A(1\mathrm{AE},2\mathrm{EA}) \\ \hline \tilde{A}(1\mathrm{AE},2\mathrm{EA}) & O \end{array}\right) = R(1\mathrm{AE},2\mathrm{EA})$$

where

$$A(1\mathrm{AE},2\mathrm{EA}) = \begin{bmatrix} 0&0&1&0&1&0\\ 0&0&0&1&0&1\\ 1&0&0&0&0&1\\ \hline 0&1&0&0&1&0\\ 1&0&0&1&0&0\\ 0&1&1&0&0&0 \end{bmatrix}.$$

The remaining isomers form two distinct and *unconnected* sets[2], which can be seen on the matrix or on Lauterbur and Ramirez's graph[2].

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