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Space Group $R\bar{3}c$ = $R\bar{3}2/c$(167) and the Crystal Structure of Tris(1,2,3,4-tetraphenylbuta-1,3-dienyl)cyclotriphosphazene

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Space Group $R\bar{3}c$ = $R\bar{3}2/c$(167)과 Tris(1,2,3,4-tetraphenylbuta-1,3-dienyl)cyclotriphosphazene의 結晶構造

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Abstract

There are 25 space groups in the trigonal system. Eighteen out of them have a lattice letter *P* displaying only hexagonal axes, whereas the remaining seven rhombohedral space groups *R*3(146), $R\bar{3}$(148), *R*32(155), *R*3*m*(160), *R*3*c*(161), $R\bar{3}m$(166) and $R\bar{3}c$(167) are described with two coordinate systems, first with hexagonal axes having three lattice points (0, 0, 0), (2/3, 1/3, 1/3), (1/3, 2/3, 2/3) and second with primitive rhombohedral axes. In this paper, the space group $R\bar{3}c$ is discussed and the crystal structure of a compound, tris(1,2,3,4-tetraphenylbuta-1,3-dienyl)cyclotriphosphazene, $C_{84}H_{60}N_3P_3$, belonging to the space group $R\bar{3}c$ is elucidated with both hexagonal and rhombohedral cells.

概 要

Trigonal system에 屬한 25個 space group들 中 18個는 hexagonal axes만을 나타내는 lattice letter *P*로 表示되고, 나머지 7個의 rhombohedral space groups *R*3(146), $R\bar{3}$(148), *R*32(155), *R*3*m*(160), *R*3*c*(161), $R\bar{3}m$(166), $R\bar{3}c$(167)은 첫째 3개의 lattice points (0, 0, 0), (2/3, 1/3, 1/3), (1/3, 2/3, 2/3)를 갖는 hexagonal cell in obverse setting과 둘째 primitive rhombohedral cell의 두 가지로 表示된다. 本 論文에서는 space group $R\bar{3}c$(167)에 대하여 論한 後 이 space group에 屬한 化合物인 tris(1,2,3,4-tetraphenylbuta-1,3-dienyl)cyclotriphosphazene, $C_{84}H_{60}N_3P_3$의 構造를 hexagonal 및 rhombohedral cell 의 양쪽으로 糾明하여 發表하였다.

(1) $R\bar{3}c$(R)

Space group $R\bar{3}c$는 Laue group $\bar{3}m$의 *m* 代身에 *c*-glide plane을 代入하고 primitive lattice를 의미하는 *R*를 붙인 것이다. 따라서 Space group $R\bar{3}c$(R)는 Laue point group $\bar{3}m$에 屬한다.

$R\bar{3}c$(R)의 full symbol은 $R\bar{3}2/c$이다. 여기서 $\bar{3}$는 [111] 방향으로 있고 c-glide plane은 [1$\bar{1}$0] 방향에 있으며 이 glide vector는 [111] 방향을 따르는 1/2($\vec{a}$ + $\vec{b}$ + $\vec{c}$)이고 2-fold rotation symmetry는 z = 1/4에서 [1$\bar{1}$0] 方向에 있다.[1)]

Rhombohedral cell과 hexagonal cell in obverse setting 間 그리고 rhombohedral cell과 hexagonal cell in reverse setting 間의 軸 및 座標變換 matrix는 Table 1 및 2와 같다.

Table 1. Rhombohedral cell과 hexagonal cell in obverse setting間의 軸 및 座標變換 matrix M와 $[M^T]^{-1}$

rhombohedral에서 hexagonal cell in obverse setting으로의 axes transformation matrix M	座標變換 matrix $[M^T]^{-1}$	hexagonal cell in obverse setting에서 rhombohedral로의 axes transformation matrix M^{-1}	座標變換 matrix $[[M^{-1}]^T]^{-1}$
$\begin{pmatrix} 1 & -1 & 0 \\ 0 & 1 & -1 \\ 1 & 1 & 1 \end{pmatrix}$	$\frac{1}{3}\begin{pmatrix} 2 & -1 & -1 \\ 1 & 1 & -2 \\ 1 & 1 & 1 \end{pmatrix}$	$\frac{1}{3}\begin{pmatrix} 2 & 1 & 1 \\ -1 & 1 & 1 \\ -1 & -2 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 1 \\ -1 & 1 & 1 \\ 0 & -1 & 1 \end{pmatrix}$

Table 2. Rhombohedral cell과 hexagonal cell in reverse setting間의 軸 및 座標變換 matrix M와 $[M^T]^{-1}$

rhombohedral에서 hexagonal cell in reverse setting으로의 axes transformation matrix M	座標變換 matrix $[M^T]^{-1}$	hexagonal cell in reverse setting에서 rhombohedral로의 axes transformation matrix M^{-1}	座標變換 matrix $[[M^{-1}]^T]^{-1}$
$\begin{pmatrix} 1 & 0 & -1 \\ -1 & 1 & 0 \\ 1 & 1 & 1 \end{pmatrix}$	$\frac{1}{3}\begin{pmatrix} 1 & 1 & -2 \\ -1 & 2 & -1 \\ 1 & 1 & 1 \end{pmatrix}$	$\frac{1}{3}\begin{pmatrix} 1 & -1 & 1 \\ 1 & 2 & 1 \\ -2 & -1 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & -1 & 1 \\ 0 & 1 & 1 \\ -1 & 0 & 1 \end{pmatrix}$

(1-1) $R\bar{3}c/2$(R)의 general coordinates의 誘導

(1-1-1) Rhombohedral의 body-diagonal을 따르는 $\bar{3}$//[111]에서 다음의 6개 좌표가 얻어진다. General coordinates의 위에 있는 숫자(n : integer)는 IT Vol. A에 있는 座標의 番號이다.[1]

$$\begin{matrix} & & & (1) & & (8) & & (3) & & (7) & & (2) & & (9) & \\ \begin{bmatrix} 0 & 0 & -1 \\ -1 & 0 & 0 \\ 0 & -1 & 0 \end{bmatrix} & \begin{bmatrix} x \\ y \\ z \end{bmatrix} & = & \begin{bmatrix} -z \\ -x \\ -y \end{bmatrix} & = & \begin{bmatrix} y \\ z \\ x \end{bmatrix} & = & \begin{bmatrix} -x \\ -y \\ -z \end{bmatrix} & = & \begin{bmatrix} z \\ x \\ y \end{bmatrix} & = & \begin{bmatrix} -y \\ -z \\ -x \end{bmatrix} & = & \begin{bmatrix} x \\ y \\ z \end{bmatrix} \end{matrix}$$

(1-1-2) 상기 6개 좌표에 c-glide plane//[$\bar{1}$10]을 조작하면 나머지 6개의 座標가 追加된다.

$$\begin{matrix} & & & (1) & & & (10) \\ \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} & \begin{bmatrix} x \\ y \\ z \end{bmatrix} & + & \begin{bmatrix} 1/2 \\ 1/2 \\ 1/2 \end{bmatrix} & = & \begin{bmatrix} y \\ x \\ z \end{bmatrix} + \begin{bmatrix} 1/2 \\ 1/2 \\ 1/2 \end{bmatrix} \end{matrix}$$

$$\begin{matrix} & & & (2) & & & (11) \\ \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} & \begin{bmatrix} z \\ x \\ y \end{bmatrix} & + & \begin{bmatrix} 1/2 \\ 1/2 \\ 1/2 \end{bmatrix} & = & \begin{bmatrix} x + 1/2 \\ z + 1/2 \\ y + 1/2 \end{bmatrix} \end{matrix}$$

$$\begin{matrix} & & & (3) & & & (12) \\ \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} & \begin{bmatrix} y \\ z \\ x \end{bmatrix} & + & \begin{bmatrix} 1/2 \\ 1/2 \\ 1/2 \end{bmatrix} & = & \begin{bmatrix} z + 1/2 \\ y + 1/2 \\ x + 1/2 \end{bmatrix} \end{matrix}$$

$$\begin{matrix} & & & (7) & & & (10) \\ \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} & \begin{bmatrix} -y \\ -z \\ -x \end{bmatrix} & + & \begin{bmatrix} 1/2 \\ 1/2 \\ 1/2 \end{bmatrix} & = & \begin{bmatrix} -z \\ -y \\ -x \end{bmatrix} + \begin{bmatrix} 1/2 \\ 1/2 \\ 1/2 \end{bmatrix} \end{matrix}$$

$$\begin{matrix} & & & (8) & & & (5) \\ \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} & \begin{bmatrix} -z \\ -x \\ -y \end{bmatrix} & + & \begin{bmatrix} 1/2 \\ 1/2 \\ 1/2 \end{bmatrix} & = & \begin{bmatrix} -x \\ -z \\ -y \end{bmatrix} + \begin{bmatrix} 1/2 \\ 1/2 \\ 1/2 \end{bmatrix} \end{matrix}$$

$$\begin{matrix} & & & (9) & & & (6) \\ \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} & \begin{bmatrix} -y \\ -z \\ -x \end{bmatrix} & + & \begin{bmatrix} 1/2 \\ 1/2 \\ 1/2 \end{bmatrix} & = & \begin{bmatrix} -z \\ -y \\ -x \end{bmatrix} + \begin{bmatrix} 1/2 \\ 1/2 \\ 1/2 \end{bmatrix} \end{matrix}$$

(1-1-3) 2//[$\bar{1}$10] at z = 1/4은 다음과 같이 同一한 座標를 提供하므로 不必要하다.

$$\begin{matrix} & & & (1) & & & (6) \\ \begin{bmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix} & \begin{bmatrix} x \\ y \\ z \end{bmatrix} & + & \begin{bmatrix} 1/2 \\ 1/2 \\ 1/2 \end{bmatrix} & = & \begin{bmatrix} -y \\ -x \\ -z \end{bmatrix} + \begin{bmatrix} 1/2 \\ 1/2 \\ 1/2 \end{bmatrix} \end{matrix}$$

$$\begin{matrix} & & & (2) & & & (5) \\ \begin{bmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix} & \begin{bmatrix} z \\ x \\ y \end{bmatrix} & + & \begin{bmatrix} 1/2 \\ 1/2 \\ 1/2 \end{bmatrix} & = & \begin{bmatrix} -x \\ -z \\ -y \end{bmatrix} + \begin{bmatrix} 1/2 \\ 1/2 \\ 1/2 \end{bmatrix} \end{matrix}$$

(1-2) Structure Factor[2]

위에서 얻은 12個 座標: ± | x, y, z; $\bar{y}, z, x$; $z, x, \bar{y}$; $y, \bar{x}, z$; $\bar{x}, \bar{z}, \bar{y}$; $\bar{z}, \bar{y}, \bar{x}$ |

y; 1/2 + y, 1/2 + x, 1/2 + z; 1/2 + z, 1/2 + y, 1/2 + x; 1/2 + x, 1/2 + z, 1/2 + y]를 structure factor 式에 代入하면 $R\bar{3}c$(R)의 structure factor 式은 다음과 같다.

$$A = 4\left\{\cos\pi\left[(h+k)(x+y)+2lz+\frac{h+k+l}{2}\right]\cos\pi\left[(h-k)(x-y)-\frac{h+k+l}{2}\right]\right.$$
$$+\cos\pi\left[(k+l)(x+y)+2hz+\frac{h+k+l}{2}\right]\cos\pi\left[(k-l)(x-y)-\frac{h+k+l}{2}\right]$$
$$\left.+\cos\pi\left[(l+h)(x+y)+2kz+\frac{h+k+l}{2}\right]\cos\pi\left[(l-h)(x-y)-\frac{h+k+l}{2}\right]\right\}$$

$$B = 0$$

(1-3) Reflection conditions[1,2]

(1-3-1) (hhl) : $l = 2n$

$$A = 4\left\{\cos\pi\left[2h(x+y)+2lz+\frac{2h+l}{2}\right]\cos\pi\left[-\frac{2h+l}{2}\right]\right.$$
$$+\cos\pi\left[(h+l)(x+y)+2hz+\frac{2h+l}{2}\right]\cos\pi\left[(h-l)(x-y)-\frac{2h+l}{2}\right]$$
$$\left.+\cos\pi\left[(l+h)(x+y)+2hz+\frac{2h+l}{2}\right]\cos\pi\left[(l-h)(x-y)-\frac{2h+l}{2}\right]\right\}$$

(1-3-2) (hhh) : $h = 2n$

$$A = 4\left\{\cos\pi\left[2h(x+y)+2lz+\frac{3h}{2}\right]\cos\pi\left[-\frac{3h}{2}\right]\right.$$
$$+\cos\pi\left[2h(x+y)+2hz+\frac{3h}{2}\right]\cos\pi\left[-\frac{3h}{2}\right]$$
$$\left.+\cos\pi\left[2h(x+y)+2hz+\frac{3h}{2}\right]\cos\pi\left[-\frac{3h}{2}\right]\right\}$$

(1-4) Patterson function[3]

Heavy atom method에 사용되는 다음의 Patterson function에는

$$P(uvw) = \frac{1}{V}\sum_{hkl=-\infty}^{\infty}|F(hkl)|^2\cos2\pi(hu+kv+lw)$$

phase를 알 수 없는 $|F(hkl)|$가 使用된다.

Point group $\bar{3}m(R)$에서는 다음의 intensity 관계가 성립한다.

$$|F(hkl)| = |F(\bar{h}\bar{k}\bar{l})| \neq |F(\bar{h}kl)| \neq |F(h\bar{k}l)| \neq |F(hk\bar{l})|$$

이를 윗식에 代入하면 Patterson function은 다음과 같다.

$$P(uvw) = \frac{2}{V}\sum_{hkl=0}^{\infty}\{|F(hkl)|^2\cos2\pi(hu+kv+lw)$$
$$+|F(\bar{h}kl)|^2\cos2\pi(-hu+kv+lw)$$
$$+|F(h\bar{k}l)|^2\cos2\pi(hu-kv+lw)$$
$$+|F(hk\bar{l})|^2\cos2\pi(Ihx+ky-lz)\}$$

이 式은 space group No. 2, $P\bar{1}$의 electron density 式과 類似하며 unit cell의 半에 해당하는 區間 即 (u, v, w) 중 1개는 0.0~0.5까지 그리고 나머지 2개는 0.0~1.0까지가 非對稱單位이다.

(1-5) Electron Density Equation[2]

$$\rho(XYZ) = \frac{2}{V}\sum_{0}^{\infty}\sum_{0}^{\infty}\sum_{0}^{\infty}\{F(hkl)\cos2\pi(hX+kY+lZ)$$
$$+F(\bar{h}kl)\cos2\pi(-hX+kY+lZ)$$
$$+F(h\bar{k}l)\cos2\pi(hX-kY+lZ)$$
$$+F(hk\bar{l})\cos2\pi(hX+ky-lZ)$$

(2) $R\bar{3}c$(H)(167)

Laue group $\bar{3}m$은 rhombohedral lattice 뿐만 아니라 hexagonal lattice에도 적용되는데 hexagonal lattice에서는 다시 2個로 나누어져 mirror plane의 方向이 [100] 방향을 向할 때 $\bar{3}m1$이고, mirror plane의 方向이 [210]을 향할 때 $\bar{3}1m$로 된다.[4]

Space group $R\bar{3}c$(H)는 Laue group $\bar{3}m$의 m대신에 c-glide plane을 대입한 것에 lattice letter R를 붙인 것으로 3個의 lattice points (0, 0, 0), (2/3, 1/3,

1/3), (1/3, 2/3, 2/3)를 갖는 hexagonal cell이다.

따라서 Space group $R\bar{3}c$(H)의 point group은 $\bar{3}m1$이며 Patterson symmetry도 $P\bar{3}m1$이어야 한다.

$R\bar{3}c$(H)의 full symbol은 $R\bar{3}2/c$이다. 여기서 $\bar{3}$는 [001] 방향으로 있고 c-glide plane은 [100] 방향에 있으며 2-fold symmetry는 z = 1/4에서 [100] 方向에 있다.

(2-1) Rhombohedral cell을 hexagonal cell로의 軸變換

Rhombohedral cell을 triple hexagonal cell in obverse setting으로의 transformation은 다음같이 Table 1의 matrix M을 사용하여 수행 할 수 있다.

$$\begin{matrix}\text{hex}\\ \begin{bmatrix}\vec{A}_1\\ \vec{A}_2\\ \vec{C}\end{bmatrix}\end{matrix} = \begin{bmatrix}1 & -1 & 0\\ 0 & 1 & -1\\ 1 & 1 & 1\end{bmatrix} \begin{matrix}\text{rhomb}\\ \begin{bmatrix}a_1\\ a_2\\ a_3\end{bmatrix}\end{matrix} = \begin{bmatrix}\vec{a}_1 - \vec{a}_2\\ \vec{a}_2 - \vec{a}_3\\ \vec{a}_1 + \vec{a}_2 + \vec{a}_3\end{bmatrix}$$

(2-2) Hexagonal cell內에 있는 3個 lattice point 誘導

Rhombohedral cell을 이룬 8개 lattice point들을 Table 1에 있는 $[M^T]^{-1}$에 代入하면 hexagonal cell 內의 lattice point를 얻는다.

$$\frac{1}{3}\begin{bmatrix}2 & -1 & -1\\ 1 & 1 & -2\\ 1 & 1 & 1\end{bmatrix}\begin{bmatrix}0\\0\\0\end{bmatrix} = \begin{bmatrix}0\\0\\0\end{bmatrix}$$

$$\frac{1}{3}\begin{bmatrix}2 & -1 & -1\\ 1 & 1 & -2\\ 1 & 1 & 1\end{bmatrix}\begin{bmatrix}1\\0\\0\end{bmatrix} = \begin{bmatrix}2/3\\1/3\\1/3\end{bmatrix}$$

$$\frac{1}{3}\begin{bmatrix}2 & -1 & -1\\ 1 & 1 & -2\\ 1 & 1 & 1\end{bmatrix}\begin{bmatrix}0\\1\\0\end{bmatrix} = \begin{bmatrix}-1/3\\1/3\\1/3\end{bmatrix}$$

$$\frac{1}{3}\begin{bmatrix}2 & -1 & -1\\ 1 & 1 & -2\\ 1 & 1 & 1\end{bmatrix}\begin{bmatrix}0\\0\\1\end{bmatrix} = \begin{bmatrix}-1/3\\-2/3\\1/3\end{bmatrix}$$

$$\frac{1}{3}\begin{bmatrix}2 & -1 & -1\\ 1 & 1 & -2\\ 1 & 1 & 1\end{bmatrix}\begin{bmatrix}1\\1\\0\end{bmatrix} = \begin{bmatrix}2/3-1/3\\1/3+1/3\\1/3+1/3\end{bmatrix} = \begin{bmatrix}1/3\\2/3\\2/3\end{bmatrix}$$

$$\frac{1}{3}\begin{bmatrix}2 & -1 & -1\\ 1 & 1 & -2\\ 1 & 1 & 1\end{bmatrix}\begin{bmatrix}1\\0\\1\end{bmatrix} = \begin{bmatrix}2/3-1/3\\1/3-2/3\\1/3+1/3\end{bmatrix} = \begin{bmatrix}1/3\\-1/3\\2/3\end{bmatrix}$$

$$\frac{1}{3}\begin{bmatrix}2 & -1 & -1\\ 1 & 1 & -2\\ 1 & 1 & 1\end{bmatrix}\begin{bmatrix}0\\1\\1\end{bmatrix} = \begin{bmatrix}-1/3-1/3\\1/3-2/3\\1/3+1/3\end{bmatrix} = \begin{bmatrix}-2/3\\-1/3\\2/3\end{bmatrix}$$

$$\frac{1}{3}\begin{bmatrix}2 & -1 & -1\\ 1 & 1 & -2\\ 1 & 1 & 1\end{bmatrix}\begin{bmatrix}1\\1\\1\end{bmatrix} = \begin{bmatrix}2/3-1/3-1/3\\1/3+1/3-2/3\\1/3+1/3+1/3\end{bmatrix} = \begin{bmatrix}0\\0\\1\end{bmatrix}$$

Rhombohedral cell을 hexagonal cell로 변환하면 unit cell 內에 3개의 lattice point (0, 0, 0), (2/3, 1/3, 1/3), (1/3, 2/3, 2/3)를 갖는 triple hexagonal cell이 된다.

(2-3) $R\bar{3}c$/2(H)의 general coordinates의 誘導

(2-3-1) $\bar{3}$//[001]으로부터 다음의 6개 좌표가 얻어지며

$$\begin{matrix}(1)\\ \end{matrix}\quad\begin{matrix}(8)\\ \end{matrix}\quad\begin{matrix}(3)\\ \end{matrix}\quad\begin{matrix}(7)\\ \end{matrix}\quad\begin{matrix}(2)\\ \end{matrix}\quad\begin{matrix}(9)\\ \end{matrix}$$

$$\begin{bmatrix}0 & 1 & 0\\ -1 & -1 & 0\\ 0 & 0 & -1\end{bmatrix}\begin{bmatrix}x\\y\\z\end{bmatrix} = \begin{bmatrix}-y\\-x+y\\-z\end{bmatrix} = \begin{bmatrix}-x+y\\-x\\z\end{bmatrix} = \begin{bmatrix}-x\\-y\\-z\end{bmatrix} = \begin{bmatrix}-y\\x-y\\z\end{bmatrix} = \begin{bmatrix}x-y\\x\\-z\end{bmatrix}$$

(2-3-2) 上記 6個 座標에 c//[100]를 操作하므로서 다음의 6個 座標를 얻는다.

$$\begin{bmatrix}-1 & 1 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{bmatrix}\begin{bmatrix}x\\y\\z\end{bmatrix} + \begin{bmatrix}0\\0\\1/2\end{bmatrix} = \begin{matrix}(1)\\ \end{matrix}\begin{bmatrix}-x+y\\y\\z+1/2\end{bmatrix}\begin{matrix}(11)\\ \end{matrix}$$

$$\begin{bmatrix}-1 & 1 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{bmatrix}\begin{bmatrix}-x\\x-y\\z\end{bmatrix} + \begin{bmatrix}0\\0\\1/2\end{bmatrix} = \begin{matrix}(2)\\ \end{matrix}\begin{bmatrix}x\\x-y\\z+1/2\end{bmatrix}\begin{matrix}(12)\\ \end{matrix}$$

$$\begin{bmatrix}-1 & 1 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{bmatrix}\begin{bmatrix}-x+y\\-x\\z\end{bmatrix} + \begin{bmatrix}0\\0\\1/2\end{bmatrix} = \begin{matrix}(3)\\ \end{matrix}\begin{bmatrix}-y\\-x\\z+1/2\end{bmatrix}\begin{matrix}(10)\\ \end{matrix}$$

$$\begin{bmatrix}-1 & 1 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{bmatrix}\begin{bmatrix}-x\\-y\\-z\end{bmatrix} + \begin{bmatrix}0\\0\\1/2\end{bmatrix} = \begin{matrix}(7)\\ \end{matrix}\begin{bmatrix}x-y\\-y\\-z+1/2\end{bmatrix}\begin{matrix}(5)\\ \end{matrix}$$

$$\begin{bmatrix}-1&1&0\\0&1&0\\0&0&1\end{bmatrix}\begin{bmatrix}y\\-x+y\\-z\end{bmatrix}+\begin{bmatrix}0\\0\\1/2\end{bmatrix}=\begin{bmatrix}-x\\-x+y\\-z+1/2\end{bmatrix}\quad(8)\qquad(6)$$

$$\begin{bmatrix}-1&1&0\\0&1&0\\0&0&1\end{bmatrix}\begin{bmatrix}x-y\\x\\-z\end{bmatrix}+\begin{bmatrix}0\\0\\1/2\end{bmatrix}=\begin{bmatrix}y\\x\\-z+1/2\end{bmatrix}\quad(9)\qquad(4)$$

(2-3-3) 2//[100] at z = 1/4으로부터는 다음과 같이 同一한 座標들이 얻어진다.

$$\begin{bmatrix}1&-1&0\\0&-1&0\\0&0&-1\end{bmatrix}\begin{bmatrix}x\\y\\z\end{bmatrix}+\begin{bmatrix}0\\0\\1/2\end{bmatrix}=\begin{bmatrix}x-y\\-x\\-z+1/2\end{bmatrix}\quad(1)\qquad(5)$$

$$\begin{bmatrix}1&-1&0\\0&-1&0\\0&0&-1\end{bmatrix}\begin{bmatrix}-x\\x-y\\z\end{bmatrix}+\begin{bmatrix}0\\0\\1/2\end{bmatrix}=\begin{bmatrix}-x\\-x+y\\-z+1/2\end{bmatrix}\quad(2)\qquad(6)$$

$$\begin{bmatrix}1&-1&0\\0&-1&0\\0&0&-1\end{bmatrix}\begin{bmatrix}-x+y\\-x\\z\end{bmatrix}+\begin{bmatrix}0\\0\\1/2\end{bmatrix}=\begin{bmatrix}y\\x\\-z+1/2\end{bmatrix}\quad(3)\qquad(4)$$

$$\begin{bmatrix}1&-1&0\\0&-1&0\\0&0&-1\end{bmatrix}\begin{bmatrix}-x\\-y\\-z\end{bmatrix}+\begin{bmatrix}0\\0\\1/2\end{bmatrix}=\begin{bmatrix}-x+y\\y\\z+1/2\end{bmatrix}\quad(7)\qquad(11)$$

$$\begin{bmatrix}1&-1&0\\0&-1&0\\0&0&-1\end{bmatrix}\begin{bmatrix}y\\-x+y\\-z\end{bmatrix}+\begin{bmatrix}0\\0\\1/2\end{bmatrix}=\begin{bmatrix}x\\x-y\\z+1/2\end{bmatrix}\quad(8)\qquad(12)$$

$$\begin{bmatrix}1&-1&0\\0&-1&0\\0&0&-1\end{bmatrix}\begin{bmatrix}-y\\-x\\z+1/2\end{bmatrix}+\begin{bmatrix}0\\0\\1/2\end{bmatrix}=\begin{bmatrix}x-y\\x\\-z\end{bmatrix}\quad(10)\qquad(9)$$

위의 12個 座標 各各에 lattice point (0, 0, 0), (2/3, 1/3, 1/3), (1/3, 2/3, 2/3)를 加하면 모두 36個의 座標가 얻어진다.

(2-4) Structure Factor[2)]

Hexagonal coordinates인 (0, 0, 0; 1/3, 2/3, 2/3; 2/3, 1/3, 1/3) ± | x, y, z; $\bar{y}, x-y, z$; $y-x, \bar{x}, z$; $\bar{y}, \bar{x}, z$; $x, x-y, z$; $y-x, y, z$ |를 structure factor 式에 代入하면 $R\bar{3}c$(H)의 structure factor 式은 다음과 같다.

$$\begin{aligned}A = 4\Big(1+2\cos 2\pi\frac{-h+k+l}{3}\Big)&\Big\{\cos\pi\Big[(h-k)(x-y)+2lz+\frac{l}{2}\Big]\cos\pi\Big[i(x+y)+\frac{l}{2}\Big]\\&+\cos\pi\Big[(k-i)(x-y)+2lz+\frac{l}{2}\Big]\cos\pi\Big[h(x+y)+\frac{l}{2}\Big]\\&+\cos\pi\Big[(i-h)(x-y)+2lz+\frac{l}{2}\Big]\cos\pi\Big[k(x+y)+\frac{l}{2}\Big]\Big\}\end{aligned}$$

$$B = 0$$

(2-5) Reflection conditions[3)]

(2-5-1) (hkl) : $-h+k+l = 3n$

(2-5-2) (hhl) : $l \neq 3n$

(2-5-3) $(h\bar{h}l)$: $h+l = 3n$, $l = 2n$

$$\begin{aligned}A = 4\Big(1+2\cos 2\pi\frac{-h-k+l}{3}\Big)&\Big\{\cos\pi\Big[(h+h)(x-y)+2lz+\frac{l}{2}\Big]\cos\pi\Big[i(x+y)+\frac{l}{2}\Big]\\&+\cos\pi\Big[(-h-0)(x-y)+2lz+\frac{l}{2}\Big]\cos\pi\Big[h(x+y)+\frac{l}{2}\Big]\\&+\cos\pi\Big[(0-h)(x-y)+2lz+\frac{l}{2}\Big]\cos\pi\Big[k(x+y)+\frac{l}{2}\Big]\Big\}\end{aligned}$$

(2-5-4) (001) : $l = 6n$

(2-6) Patterson function[3]

Heavy atom method에 사용되는 다음의 Patterson function에는

$$P(uvw) = \frac{1}{V}\sum_{hkl=-\infty}^{\infty} |F(hkl)|^2 \cos 2\pi(hu + kv + lw)$$

phase를 알 수 없는 $|F(hkl)|$가 使用된다.

Point group $\bar{3}m1$에서는 다음의 intensity 관계가 얻어진다.

$$|F(hkl)| = |F(\bar{h}\bar{k}l)| \neq |F(\bar{h}kl)|$$
$$\neq |F(\bar{h}kl)| \neq |F(h\bar{k}l)| \neq |F(hkl)|$$

이를 윗 式에 代入하면 Patterson function은 다음과 같다.

$$P(uvw) = \frac{2}{V}\sum_{hkl=0}^{\infty} |F(hkl)|^2 \cos 2\pi(hu + kv + lw)$$
$$+ |F(\bar{h}kl)|^2 \cos 2\pi(-hu + kv + lw)$$
$$+ |F(h\bar{k}l)|^2 \cos 2\pi(hu - kv + lw)$$
$$+ |F(hk\bar{l})|^2 \cos 2\pi(hx + ky - lz)$$

이 式은 space group No. 2, $P\bar{1}$의 electron density 式과 類似하며 unit cell의 半에 해당하는 區間 卽 (u, v, w) 中 1個는 0.0~0.5까지 그리고 나머지 2개는 0.0~1.0까지만이 非對稱單位이다.

(3) $R\bar{3}c$(H)의 實例

한 compound tris(1,2,3,4-tetraphenylbuta-1,3-dienyl) cyclotriphosphazene, $C_{84}H_{60}N_3P_3$의 구조를 밝힌 결과 그의 crystallographic data는 Table 3과 같다.: 구조해석 및 구조의 정밀화는 SHELX97[5]로 수행하였다.

한 分子의 1/6인 asymmetric unit $C_{14}H_{10}N_{0.5}P_{0.5}$의 3次元的構造가 Fig. 1이며 6개의 asymmetric unit가 모여 이루워진 한 分子의 構造가 Fig. 2이다.

$R\bar{3}c$(H)에는 Z = 36이며, asymmetric unit內에 있는 nitrogen과 phosphorus가 special position에 位置하고 있어 N-P group이 6개가 모여 하나의 cyclotriphosphazene ring을 이루므로 6개의 asym-

Table 3. Crystal data and structure refinement for $C_{84}H_{60}N_3P_3$ with $R\bar{3}c$ (H)

Empirical formula	$C_{14}H_{10}N_{0.5}P_{0.5}$
Formula weight	200.71
Temperature	293(2) K
Wavelength	0.71073
Crystal system, space group	Trigonal, $R\bar{3}c$(H) (167)
Unit cell dimensions	$a = b = 19.0620(9)$, $c = 30.5790(14)$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$, $V = 9622.4(6)$ Å^3
Z, Calculated density	36, 1.247 Mg/m^3
Absorption coefficient μ	0.143 mm^{-1}
F(000)	3780
Crystal size	0.23 × 0.23 × 0.17 mm
θ range for data collection	1.82 to 28.32°
Limiting indices	$-22 <= h <= 25$, $-25 <= k <= 15$, $-40 <= l <= 35$
Reflections collected/unique	16415/2524 [R(int) = 0.1785]
Completeness to θ = 28.32°	94.4%
Max. and min. transmission	0.9761 and 0.9676
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2524/0/147
Goodness-of-fit on F^2	0.877
Final R indices [I > 2σ(I)]	R1 = 0.0736, wR2 = 0.1605
R indices (all data)	R1 = 0.1397, wR2 = 0.1876
Largest diff. peak and hole	0.419 and −0.312 eÅ^{-3}

where $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$

$wR2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$

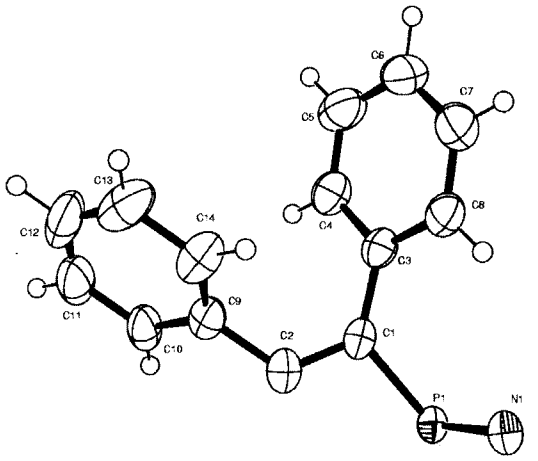

Fig. 1. ORTEP diagram showing the structure of an asymmetric unit, $C_{14}H_{10}N_{0.5}P_{0.5}$, with labelling of the atoms and displacement ellipsoids at the 30% probability level.

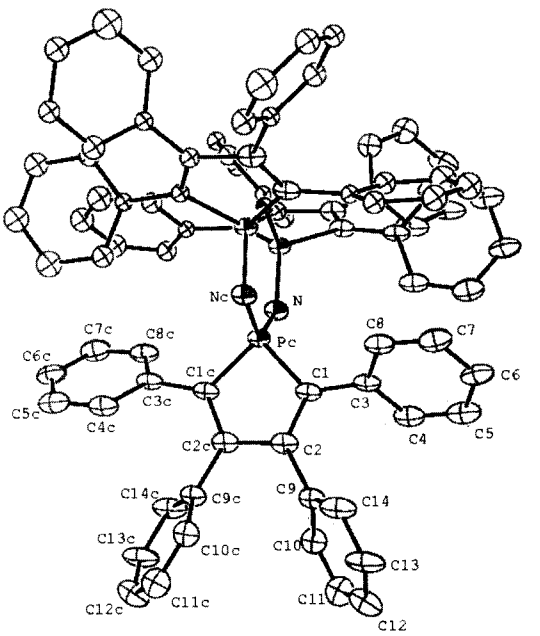

Fig. 2. A molecular structure of tris(1,2,3,4-tetraphenylbuta-1,3-dienyl)cyclotriphosphazene, $C_{84}H_{60}N_3P_3$.

metric unit가 모여서 한 個의 分子를 이루며 unit cell에는 6個 分子가 있다.

(4) $R\bar{3}c$(R)(167)의 實例

(4-1) Hexagonal unit cell dimensions $a = b =$ 19.0620(9), c = 30.5790(14) Å, $\alpha = \beta = 90°$, $\gamma = 120°$, V = 9622.4(6) Å^{3}을 上記 M의 inverse matrix

Table 4. Crystal data and structure refinement for $C_{84}H_{60}N_3P_3$ with $R\bar{3}c$ (R)

Empirical formula	$C_{14}H_{10}N_{0.5}P_{0.5}$
Formula weight	200.71
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Trigonal, $R\bar{3}c$(R)
Unit cell dimensions	$a = b = c$ = 15.0005(5) Å
	$\alpha = \beta = \gamma$ = 78.895(3)°
Volume	3207.46(19) Å^3
Z, Calculated density	12, 0.208 Mg/m^3
Absorption coefficient μ	0.024 mm^{-1}
F(000)	210
Crystal size	0.23 × 0.23 × 0.17
θ range for data collection	1.82 to 28.32°
Limiting indices	$-19 <= h <= 19$, $-19 <= k <= 13$, $-19 <= l <= 20$
Reflections collected/unique	16415/2524 [R(int) = 0.1785]
Completeness to θ = 28.32	94.4%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2524/0/137
Goodness-of-fit on F^2	0.702
Final R indices [I > 2σ(I)]	R1 = 0.0747, wR2 = 0.1722
R indices (all data)	R1 = 0.1389, wR2 = 0.2178
Largest diff. peak and hole	0.337 and −0.316 eÅ^{-3}

인 $M^{-1} = \frac{1}{3}\begin{pmatrix} 2 & 1 & 1 \\ -1 & 1 & 1 \\ -1 & -2 & 1 \end{pmatrix}$를 이용하여 rhombohedral cell, $a = b = c = 15.0005(5)$ Å, $\alpha = \beta = \gamma = 78.895(3)^{\circ}$, $V = 3207.5(2)$ Å로 transform하였다.[6]

(4-2) Hexagonal cell 內의 원자좌표들을 transformation matrix를 $[[M^{-1}]^T]^{-1}$ 사용하여 rhombohedral cell 내의 원자좌표로 변환하였다.[6]

(4-3) Hexagonal cell의 intensity data도 transformation matrix인 $M^{-1} = \frac{1}{3}\begin{pmatrix} 2 & 1 & 1 \\ -1 & 1 & 1 \\ -1 & -2 & 1 \end{pmatrix}$를 이용하여 변환한 後[6] rhombohedral cell의 intensity로 구조를 refine한 結果의 crystallographic data는 Table 4, 5, 6과 같다.

Rhombohedral cell의 [111] 방향으로 본 한 분자의 구조는 Fig. 3와 같다.

$R\bar{3}c$(R)에는 Z = 12이며 6개 asymmetric unit가 모여 한 분자를 이루므로 Fig. 3에서 보인 바와 같이 unit cell 내에는 2개 분자가 있다. 여기서 6개 symmetry로 된 原子들의 좌표를 計算하여 한 分子를 만든 後 2個의 symmetry만을 利用하여 作圖

Table 5. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for $C_{84}H_{60}N_3P_3$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U(eq)
P	8357(1)	7500	6643(1)	49(1)
N	8322(2)	6678(2)	7500	53(1)
C(1)	8607(2)	7061(2)	5554(2)	53(1)
C(2)	9424(2)	7249(2)	5090(2)	54(1)
C(3)	8022(2)	6546(2)	5209(2)	57(1)
C(4)	7849(2)	6780(2)	4306(2)	70(1)
C(5)	7411(3)	6223(3)	3956(3)	88(1)
C(6)	7138(3)	5437(3)	4508(3)	95(1)
C(7)	7290(3)	5222(3)	5390(3)	94(1)
C(8)	7734(2)	5769(2)	5751(2)	71(1)
C(9)	9854(2)	6996(2)	4176(2)	60(1)
C(10)	10118(2)	7664(3)	3440(2)	76(1)
C(11)	10503(3)	7436(5)	2599(3)	103(2)
C(12)	10633(3)	6550(6)	2463(3)	117(2)
C(13)	10394(3)	5863(4)	3175(3)	105(2)
C(14)	9990(3)	6090(3)	4037(3)	81(1)

Table 6. Bond lengths [Å] and angles [°] for $C_{84}H_{60}N_3P_3$

P-N	1.6007(15)
P-N#1	1.6007(15)
P-C(1)#2	1.825(3)
P-C(1)	1.825(3)
N-P#3	1.6007(15)
C(1)-C(2)	1.339(4)
C(1)-C(3)	1.491(4)
C(2)-C(9)	1.486(4)
C(2)-C(2)#2	1.502(6)
C(3)-C(8)	1.378(4)
C(3)-C(4)	1.393(4)
C(4)-C(5)	1.386(5)
C(5)-C(6)	1.387(6)
C(6)-C(7)	1.352(6)
C(7)-C(8)	1.389(5)
C(9)-C(10)	1.392(5)
C(9)-C(14)	1.385(5)
C(10)-C(11)	1.361(6)
C(11)-C(12)	1.355(8)
C(12)-C(13)	1.379(8)
C(13)-C(14)	1.394(6)
N-P-N#1	115.87(19)
N-P-C(1)#2	112.42(11)
N#1-P-C(1)#2	111.19(10)
N-P-C(1)	111.19(10)
N#1-P-C(1)	112.42(11)
C(1)#2-P-C(1)	91.19(17)
P-N-P#3	124.13(19)
C(2)-C(1)-C(3)	123.2(2)
C(2)-C(1)-P	110.04(19)
C(3)-C(1)-P	126.7(2)
C(1)-C(2)-C(9)	125.3(3)
C(1)-C(2)-C(2)#2	114.37(16)
C(9)-C(2)-C(2)#2	120.37(16)
C(8)-C(3)-C(4)	119.3(3)
C(8)-C(3)-C(1)	119.8(3)
C(4)-C(3)-C(1)	120.5(3)
C(3)-C(4)-C(5)	120.0(4)
C(6)-C(5)-C(4)	119.8(4)
C(5)-C(6)-C(7)	120.0(3)
C(6)-C(7)-C(8)	121.0(4)
C(3)-C(8)-C(7)	119.8(3)
C(10)-C(9)-C(14)	118.7(3)
C(10)-C(9)-C(2)	120.8(3)
C(14)-C(9)-C(2)	120.5(3)
C(11)-C(10)-C(9)	120.9(4)
C(12)-C(11)-C(10)	120.3(5)
C(11)-C(12)-C(13)	120.8(4)
C(12)-C(13)-C(14)	119.4(5)
C(9)-C(14)-C(13)	119.8(4)

Symmetry transformations used to generate equivalent atoms: #1 z, x, y #2 $-z + 3/2, -y + 3/2, -x + 3/2$ #3 y, z, x

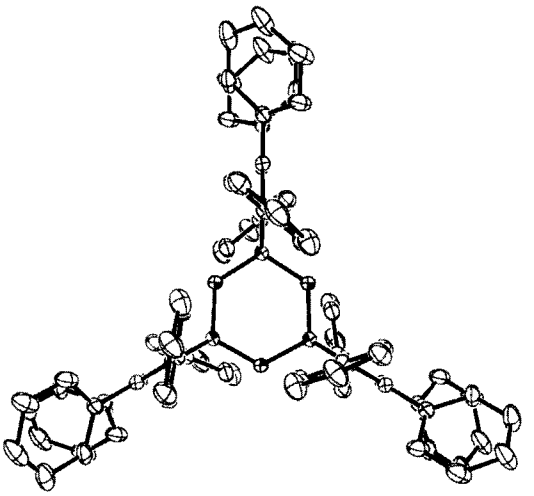

Fig. 3. A molecule viewed along [111] direction.

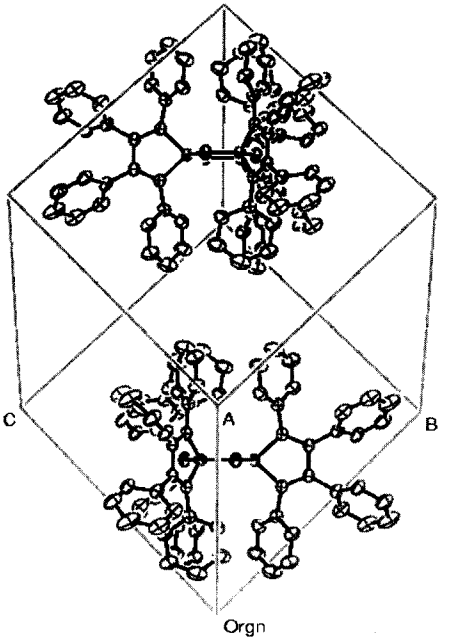

Fig. 4. There are two molecules in a rhombohderal unit cell.

하였다.

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