the length was 1.386 Å. The increase in length with MP2 is typical.

In Schulman & Disch's (1991) work on [18]-annulene, RMP2 geometries were not optimized but were taken from the best 6–31 G* geometries. Thus, the D_{6h} annulene theoretical bond lengths may need increasing by approximately 0.01 Å. For comparable 6–31 G* calculations, the mean C—C length in [18]-annulene is 1.392 Å compared with 1.386 Å in benzene, so theoretically the C—C bond length may be marginally longer in [18]-annulene. With the librational correction of 0.001 Å, the mean experimental length in [18]-annulene is 1.393 Å, marginally below 1.398 Å of benzene. The important point, however, is that theory and experiment both show that *the mean* C—C *length in* [18]-*annulene is close to that in benzene.*

In summary, the present work confirms the $4n+2$ π-electron molecule [18]-annulene as having an essentially planar aromatic structure in the crystal.

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Structural Properties of Synthetic Ionophore GL_2E_4 Diastereomers, 18-Membered Cyclic Lactone Tetraepoxides, by X-ray Crystal Analyses: Possible Relation Between Crystal Structure and Ca^{2+}-Transportation Ability

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Abstract

GL_2E_4s, $C_{20}H_{28}O_8$, $M_r = 396.2$, synthetic cyclic lactone tetraepoxides, are classified into six diastereomers according to the relative configuration of four epoxy groups and exhibit the Ca^{2+} ion-transport activity in membranes with each different potential. Three crystal structures of these diastereomers have been analyzed by

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X-ray diffraction and respective conformational features are described. Different molecular puckerings and crystal packings, which primarily resulted from different configurations of epoxy groups, are discussed in relation to their ion-transport activities. The possible interaction mode of GL_2E_4 with Ca^{2+} ions could be proposed based on the crystal packing.

Introduction

Antibiotics have been isolated from natural sources, of which some compounds are carriers of sodium, potassium or calcium ions, through hydrophobic membranes (Pressman, 1976; Kimura, Ishikawa, Tamura & Shiono, 1984; Scharff, Foder & Skibsted, 1983). These compounds, known as 'ionophores', strongly transport respective ions against the natural control in membranes and finally cause bioactivities on organs, like merremoside (Kitagawa *et al.*, 1986) and theonellapeptolide (Kitagawa *et al.*, 1988).

The cyclic polyether compounds (Pederson, 1976), as synthetic ionophores, have been investigated in various fields on the host–guest chemistry. Kitagawa and coworkers synthesized a series of dimeric geranyl lactone tetraepoxides (GL_2E_4), as shown in Fig. 1, and examined their ionophoretic abilities by the assay system using membranes (Kitagawa, Ohashi, Kawanishi *et al.*, 1989; Kitagawa, Ohashi, Koyama *et al.*, 1989; Shibuya *et al.*, 1990; Shibuya, Ohashi, Narita, Ishida & Kitagawa, 1994). These compounds consist of 18-membered rings and are classified as six diastereomers according to the relative configuration of the four epoxy groups. Each diastereomer shows the ion-transport activity for Ca^{2+} in membranes with different potentials: (4) > (6) > (2) > [mixture of diastereomers] > (3) > (5) > (1) (Shibuya, Ohashi, Narita, Ishida & Kitagawa, 1994). The difference in ion-transport activity seems to be closely related with their three-dimensional structures. Therefore, the X-ray analyses of these GL_2E_4 diastereomers were carried out hoping the elucidation of possible relationships between the ion-transport activity and the conformation of the ionophore, which might be helpful for further development of the chemically synthesized ionophore. The preliminary structure has been reported by Shibuya, Ohashi, Narita, Ishida & Kitagawa (1994).

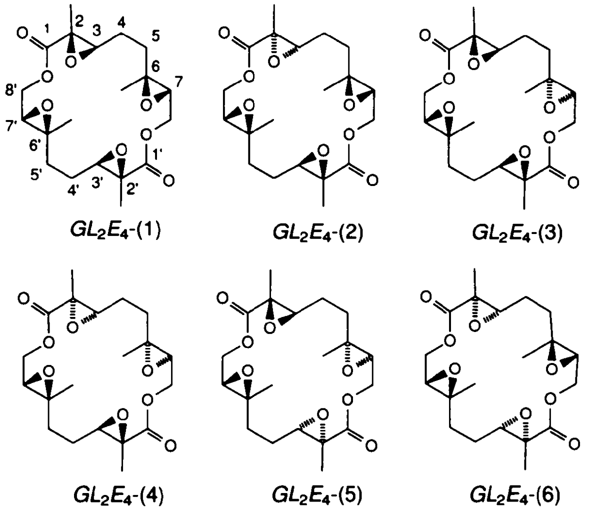
Experimental

The GL_2E_4 diastereomers have a formula of $C_{20}H_{28}O_8$ ($M_r = 396.2$), and crystals of each diastereomer were obtained from ethylacetate and hexane solution. The intensity data were measured on a Rigaku AFC-5 spectrophotometer using graphite-monochromated Cu$K\alpha$ radiation ($\lambda = 1.5418$ Å). The cell dimensions were determined by a least-squares fitting of 20 centered reflections. Intensity data were collected by the ω–2θ scan mode. The standard reflections were monitored and showed no significant decay of the crystal during the measurement. The data were corrected for Lorentz and polarization effects, but not for absorption. Table 1 summarizes details of the structural refinement. The structures were solved by direct methods using *MULTAN*88 (Debaerdemaeker *et al.*, 1988), and refined by the full-matrix least-squares method using *SHELXL*93 (Sheldrick, 1993) on *F*. The H atoms were assigned at geometrically calculated positions and then refined by the 'ride-on' method. In the diastereomer (2), the absolute structure had been determined by matching the spectroscopic data of isolated diastereomers with those of synthetic fragments (Shibuya, Ohashi, Narita, Ishida & Kitagawa, 1994). The final refinements were made with anisotropic and isotropic temperature factors for non-H and H atoms, respectively. The final coordinates of each diastereomer are listed in Table 2. The selected geometrical parameters concerning the conformation of the ring are listed in Table 3. No abnormal values were observed.*

Results and discussion

Molecular structure and crystal packing

The GL_2E_4 diastereomers are composed of the chemically equivalent components and form a symmetrical structure concerning the 18-membered ring. Fig. 2, the projections on the backbone rings, shows that the GL_2E_4 molecules take various ring-puckerings depending on the relative configuration of four epoxy groups. In



GL_2E_4-(1) GL_2E_4-(2) GL_2E_4-(3)

GL_2E_4-(4) GL_2E_4-(5) GL_2E_4-(6)

Fig. 1. Chemical structures and epoxy configurations of GL_2E_4 diastereomers.

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the IUCr. Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Experimental details*

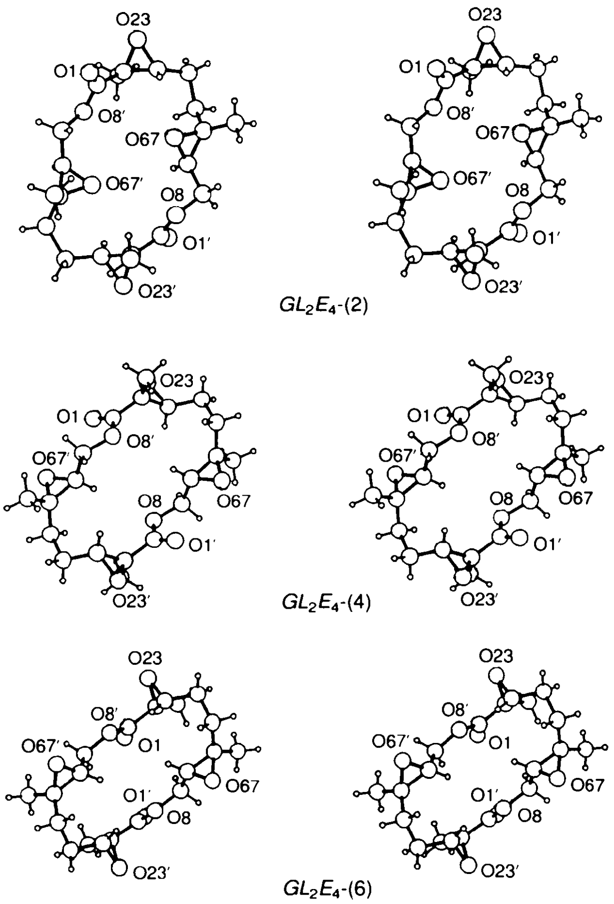
	(2)	(4)	(6)
Crystal data			
Chemical formula	$C_{20}H_{28}O_8$	$C_{20}H_{28}O_8$	$C_{20}H_{28}O_8$
Chemical formula weight	396.42	396.42	396.42
Cell setting	Orthorhombic	Triclinic	Orthorhombic
Space group	$P2_12_12_1$	$P\bar{1}$	*Pbca*
a (Å)	6.372 (1)	10.649 (4)	8.669 (2)
b (Å)	10.206 (2)	8.559 (4)	20.847 (4)
c (Å)	31.085 (5)	5.734 (2)	21.746 (4)
α (°)	90.00	107.76 (3)	90.00
β (°)	90.00	91.13 (3)	90.00
γ (°)	90.00	100.56 (3)	90.00
V (Å^3)	2021.5 (6)	487.7 (3)	3930.0 (14)
Z	4	1	8
D_x (Mg m^{-3})	1.303	1.350	1.340
Radiation type	Cu $K\alpha$	Cu $K\alpha$	Cu $K\alpha$
Wavelength (Å)	1.54180	1.54180	1.54180
No. of reflections for cell parameters	20	20	20
θ range (°)	21.3–29.7	20.7–28.5	23.2–27.0
μ (mm^{-1})	0.841	0.871	0.865
$F(000)$	848	212	1696
Temperature (K)	293 (2)	293 (2)	293 (2)
Crystal form	Plate	Plate	Plate
Crystal size (mm)	0.7× 0.2× 0.2	0.4× 0.4× 0.1	0.6× 0.2× 0.2
Crystal color	Clear	Clear	Clear
Data collection			
Diffractometer	Rigaku AFC-5	Rigaku AFC-5	Rigaku AFC-5
Data collection method	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
Absorption correction	None	None	None
No. of measured reflections	2029	1793	3352
No. of independent reflections	2029	1669	3352
No. of observed reflections	1703	1563	2238
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
$R_{\rm int}$	–	0.0080	–
$\theta_{\rm max}$ (°)	65.11	65.12	65.09
Range of h, k, l	$0 \rightarrow h \rightarrow 7$ $0 \rightarrow k \rightarrow 12$ $0 \rightarrow l \rightarrow 36$	$-12 \rightarrow h \rightarrow 12$ $-10 \rightarrow k \rightarrow 0$ $-6 \rightarrow l \rightarrow 6$	$0 \rightarrow h \rightarrow 10$ $0 \rightarrow k \rightarrow 24$ $0 \rightarrow l \rightarrow 25$
No. of standard reflections	4	4	4
Frequency of standard reflections	100	100	100
Intensity decay (%)	0.962	0.978	0.997
Refinement			
Refinement on	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$	0.0488	0.0482	0.0893
$wR(F^2)$	0.1092	0.1245	0.1945
S	0.964	1.091	1.034
No. of reflections used in refinement	2029	1669	3352
No. of parameters used	258	130	258
H-atom treatment	'Ride on' method	'Ride on' method	'Ride on' method
Weighting scheme	$w = [\sigma^2(F_o^2) + (a^*p)^2 + b^*p]^{-1}, \quad p = (\max(F_o^2, 0) + 2^*F_c^2)/3$		
a	0.0630	0.0668	0.0752
b	0.4507	0.1889	2.2127
$(\Delta/\sigma)_{\rm max}$	0.055	<0.001	0.004
$\Delta\rho_{\rm max}$(e Å^{-3})	0.146	0.201	0.279
$\Delta\rho_{\rm min}$(e Å^{-3})	−0.171	−0.259	−0.261
Extinction correction method	None	None	None
Source of atomic scattering factors	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Computer programs			
Data reduction	*MSC/AFC* Software (MSC, 1988)	*MSC/AFC* Software (MSC, 1988)	*MSC/AFC* Software (MSC, 1988)
Cell refinement	*MSC/AFC* Software (MSC, 1988)	*MSC/AFC* Software (MSC, 1988)	*MSC/AFC* Software (MSC, 1988)
Data reduction	*MSC/AFC* Software (MSC, 1988)	*MSC/AFC* Software (MSC, 1988)	*MSC/AFC* Software (MSC, 1988)
Structure solution	*MULTAN*88 (Debaerdemaeker, 1988)	*MULTAN*88 (Debaerdemaeker, 1988)	*MULTAN*88 (Debaerdemaeker, 1988)
Structure refinement	*SHELXL*93 (Sheldrick, 1993)	*SHELXL*93 (Sheldrick, 1993)	*SHELXL*93 (Sheldrick, 1993)
Preparation of material for publication	*APATHLATH*	*APATHLATH*	*APATHLATH*

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
(2)				
C1	0.0091 (5)	0.5565 (3)	0.69199 (9)	0.0472 (7)
O1	0.1431 (5)	0.6128 (2)	0.71139 (8)	0.0733 (8)
C2	−0.1346 (5)	0.6174 (3)	0.65950 (10)	0.0471 (7)
C2*M*	−0.3525 (6)	0.5635 (4)	0.65547 (12)	0.0660 (10)
C3	−0.0210 (6)	0.6829 (3)	0.62428 (9)	0.0503 (8)
O23	−0.1157 (4)	0.7584 (2)	0.65839 (7)	0.0605 (7)
C4	−0.1119 (7)	0.6953 (3)	0.57977 (10)	0.0604 (9)
C5	−0.0908 (6)	0.5666 (3)	0.55462 (10)	0.0543 (8)
C6	0.1323 (5)	0.5242 (3)	0.54614 (8)	0.0457 (7)
C6*M*	0.2551 (8)	0.6118 (3)	0.51666 (12)	0.0729 (11)
C7	0.1850 (5)	0.3855 (3)	0.55252 (9)	0.0479 (7)
O67	0.2434 (4)	0.4808 (2)	0.58419 (6)	0.0581 (6)
C8	0.3581 (6)	0.3183 (3)	0.52932 (10)	0.0577 (9)
O8	0.4598 (4)	0.2232 (2)	0.55718 (7)	0.0546 (6)
C1′	0.3684 (6)	0.1058 (3)	0.56047 (9)	0.0492 (8)
O1′	0.2145 (5)	0.0733 (3)	0.54113 (8)	0.0672 (7)
C2′	0.4814 (5)	0.0218 (3)	0.59304 (10)	0.0483 (7)
C2′*M*	0.7026 (6)	0.0563 (4)	0.60408 (12)	0.0656 (10)
C3′	0.3393 (5)	−0.0500 (3)	0.62179 (10)	0.0495 (8)
O23′	0.4394 (4)	−0.1160 (2)	0.58670 (7)	0.0636 (7)
C4′	0.3925 (6)	−0.0919 (3)	0.66691 (10)	0.0554 (8)
C5′	0.2633 (6)	−0.0150 (3)	0.69987 (10)	0.0530 (8)
C6′	0.3006 (5)	0.1310 (3)	0.69934 (9)	0.0427 (7)
C6′*M*	0.5141 (6)	0.1755 (4)	0.71369 (14)	0.0727 (11)
C7′	0.1188 (5)	0.2180 (3)	0.70154 (10)	0.0504 (8)
O67′	0.2215 (4)	0.1956 (2)	0.66122 (6)	0.0506 (5)
C8′	0.1298 (6)	0.3531 (3)	0.71863 (10)	0.0579 (9)
O8′	−0.0256 (4)	0.4284 (2)	0.69461 (7)	0.0550 (6)
(4)				
O1	0.45712 (13)	0.7396 (2)	1.0589 (2)	0.0585 (4)
C1	0.3821 (2)	0.6808 (2)	0.8825 (3)	0.0388 (4)
C2	0.2483 (2)	0.5832 (2)	0.8720 (3)	0.0378 (4)
C2*M*	0.1463 (2)	0.6530 (2)	0.7738 (4)	0.0520 (5)
O23	0.22025 (13)	0.5293 (2)	1.0813 (2)	0.0511 (4)
C3	0.2337 (2)	0.4054 (2)	0.8525 (3)	0.0414 (4)
C4	0.1177 (2)	0.2785 (2)	0.7223 (4)	0.0453 (5)
C5	0.1279 (2)	0.2172 (2)	0.4445 (3)	0.0444 (4)
C6	0.2398 (2)	0.1329 (2)	0.3694 (3)	0.0367 (4)
C6*M*	0.2431 (2)	−0.0187 (2)	0.4477 (4)	0.0474 (5)
O67	0.26984 (12)	0.1177 (2)	0.1184 (2)	0.0470 (4)
C7	0.3585 (2)	0.2298 (2)	0.3172 (3)	0.0387 (4)
C8	0.4838 (2)	0.1822 (2)	0.3527 (3)	0.0438 (4)
O8	0.59518 (12)	0.3020 (2)	0.3362 (2)	0.0479 (4)
(6)				
C1	0.8956 (3)	0.79003 (13)	0.69393 (12)	0.0452 (7)
O1	0.9270 (4)	0.81701 (12)	0.74072 (12)	0.0877 (9)
C2	0.9685 (4)	0.72681 (12)	0.67649 (13)	0.0459 (7)
C2*M*	1.0900 (5)	0.7055 (2)	0.72032 (14)	0.0670 (10)
C3	0.9610 (3)	0.70583 (13)	0.61184 (14)	0.0473 (7)
O23	0.8599 (3)	0.67840 (10)	0.65727 (12)	0.0692 (7)
C4	1.0790 (4)	0.66410 (14)	0.58181 (14)	0.0536 (8)
C5	1.1799 (4)	0.70215 (14)	0.53741 (13)	0.0517 (7)
C6	1.2714 (3)	0.75587 (12)	0.56640 (11)	0.0414 (6)
C6*M*	1.4101 (4)	0.73682 (15)	0.6038 (2)	0.0581 (8)
C7	1.1941 (3)	0.81770 (12)	0.57580 (12)	0.0407 (6)
O67	1.2980 (3)	0.80978 (9)	0.52506 (9)	0.0558 (6)
C8	1.2395 (3)	0.86452 (12)	0.62482 (12)	0.0433 (6)
O8	1.1547 (2)	0.92301 (9)	0.61170 (8)	0.0501 (5)
C1′	1.1320 (3)	0.96348 (13)	0.65801 (12)	0.0409 (6)
O1′	1.1828 (3)	0.95556 (11)	0.70823 (10)	0.0790 (8)
C2′	1.0361 (3)	1.02085 (13)	0.64058 (12)	0.0439 (7)
C2′*M*	0.9715 (5)	1.0572 (2)	0.6942 (2)	0.0743 (11)
C3′	0.9709 (3)	1.02392 (12)	0.57821 (12)	0.0418 (6)
O23′	1.1070 (3)	1.05903 (9)	0.59276 (11)	0.0608 (6)
C4′	0.8274 (3)	1.05969 (13)	0.56013 (13)	0.0495 (7)
C5′	0.7001 (3)	1.01368 (14)	0.54099 (12)	0.0484 (7)
C6′	0.6453 (3)	0.96997 (13)	0.59182 (12)	0.0428 (6)
C6′*M*	0.5518 (4)	1.0009 (2)	0.64153 (15)	0.0603 (9)
C7′	0.7278 (3)	0.90963 (12)	0.60249 (12)	0.0428 (6)
O67′	0.5845 (2)	0.90914 (10)	0.57015 (10)	0.0566 (6)
C8′	0.7374 (4)	0.87654 (13)	0.66343 (12)	0.0488 (7)
O8′	0.8006 (3)	0.81319 (9)	0.65195 (9)	0.0552 (6)

the diastereomer (2), the epoxy oxygens of O23 and O23′ are directed to the outside of the backbone ring and the O67 and O67′ atoms of the remaining epoxy groups face each other within the ring. The alternate disposition of the epoxy oxygens forms a relatively flat ring. The local asymmetric twisting is observed at the C2—C3—C4—C5 bond and its primed equivalent bonds (Table 3), and results in the disturbance of intramolecular symmetry. In contrast with (2), the diastereomer (4) was crystallized in the centrosymmetric space group $P\bar{1}$, the center of the molecule locates at a center of symmetry of the crystal. All epoxy oxygens are directed to the outside of the ring and four methyl groups of the C2, C6, C2′ and C6′ atoms are arranged



GL$_2$*E*$_4$-(2)

GL$_2$*E*$_4$-(4)

GL$_2$*E*$_4$-(6)

Fig. 2. Stereodrawing of GL_2E_4 diastereomers. Molecules are projected on the 18-membered ring. All O atoms are labeled. The chemically equivalent atoms are shown with primes.

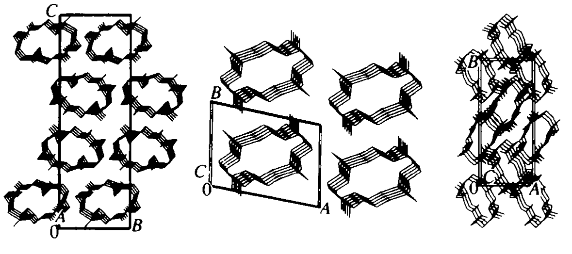
Table 3. *The selected parameters* (Å, °) *of* GL_2E_4 *structures**

	(2)	(4)	(6)
C2—C3	1.473 (4)/1.468 (4)	1.470 (3)	1.474 (4)/1.471 (4)
C2—O23	1.444 (4)/1.445 (4)	1.430 (2)	1.442 (4)/1.446 (4)
C3—O23	1.443 (4)/1.431 (4)	1.442 (2)	1.439 (4)/1.424 (3)
C6—C7	1.461 (4)/1.461 (4)	1.469 (2)	1.468 (4)/1.466 (4)
C6—O67	1.448 (4)/1.447 (4)	1.453 (2)	1.457 (3)/1.452 (3)
C7—O67	1.433 (4)/1.432 (4)	1.439 (2)	1.434 (3)/1.428 (3)
C3—C2—O23	59.3 (2)/58.9 (2)	59.6 (1)	59.1 (2)/58.4 (2)
C2—C3—O23	59.4 (2)/59.8 (2)	58.8 (1)	59.3 (2)/59.9 (2)
C2—O23—C3	61.3 (2)/61.4 (2)	61.6 (1)	61.5 (2)/61.7 (2)
C7—C6—O67	58.8 (2)/59.0 (2)	59.0 (1)	58.7 (2)/58.6 (2)
C6—C7—O67	59.9 (2)/60.0 (2)	59.9 (1)	60.3 (2)/60.2 (2)
C6—O67—C7	61.3 (2)/61.0 (2)	61.1 (1)	61.0 (2)/61.2 (2)
O8′—C1—C2—C3	−120.4 (3)/136.5 (3)	101.6 (2)	15.2 (3)/4.2 (2)
C1—C2—C3—C4	151.0 (3)/−152.1 (3)	−149.2 (2)	151.1 (3)/153.4 (3)
C2—C3—C4—C5	−78.2 (3)/111.4 (3)	82.7 (2)	−106.4 (3)/−112.9 (3)
C3—C4—C5—C6	−63.5 (3)/−61.6 (3)	60.9 (2)	60.9 (3)/63.7 (2)
C4—C5—C6—C7	136.4 (3)/135.6 (3)	−97.3 (2)	−83.3 (3)/−86.2 (3)
C5—C6—C7—C8	153.2 (4)/154.4 (4)	152.7 (2)	153.5 (3)/151.8 (3)
C6—C7—C8—O8	144.1 (3)/148.1 (3)	−169.9 (2)	170.1 (3)/168.6 (3)

* The equivalent parameters of the primed atoms are listed after the slashes.

alternatively above and below the backbone ring. On the other hand, the torsional angles of diastereomers (6) show an approximate *C*2-symmetry structure with small local deviations (Table 3). Its backbone ring takes a relatively compact rectangular or lozenge structure and results in the twisting and/or bending of the entire ring (Fig. 2). Although the spatial dispositions of epoxy oxygens are similar to each other between diastereomers (4) and (6), all methyl groups of GL_2E_4-(6) are located on the same side of the ring.

The molecular packing diagrams of GL_2E_4s are shown in Fig. 3. A major difference among three diastereomers is the overlapping mode of molecules. In the crystals of diastereomers (2) and (4), the molecules are piling up along the projection axis and construct a cylindrical structure. These packing diagrams are likely to simulate an ion-channel path-penetrating membrane. Indeed, this type of channel has been proposed for gramicidine antibiotics (Wallace & Ravikumar, 1988). On the other hand, the diastereomer (6) makes another type of molecular association in the crystal, in which two types of cylindrical structures are alternatively arranged along the *c*-axis.



GL_2E_4-(2) GL_2E_4-(4) GL_2E_4-(6)

Fig. 3. Packing diagrams of GL_2E_4 diastereomers.

Cavity space in 18-*membered ring*

The ion-free GL_2E forms cavities of various shapes and sizes depending on the conformation (Fig. 2). A very narrow space is observed in the molecule of diastereomer (4) and there is actually no space in diastereomer (6). The largest cavity is found in diastereomer (2), which is probably generated by the steric hindrance between the O67 and O67′ atoms. These inwardly directed chelating oxygens seem to be effective for trapping Ca^{2+} ions in the molecule. The dimension of the largest cavity of (2) is, however, less than 1 Å, and clearly not large enough to accommodate a Ca^{2+} ion (van der Waals radius = 1.97 Å). In contrast with the typical ionophores such as valinomycin (Karle & Flippen-Anderson, 1988) and crown ethers (Dalley, Smith, Izatt & Christensen, 1972), the present 18-membered ring is probably too small to accommodate the ion completely within the molecule.

A proposed ion-transport model for GL_4E_2

It is well known that the ionophore is able to form the hydrophobic shell to transport ions in the membrane (Artarap, Chamberlin, Pinkerton & Steinrauf, 1967). Such a structure is also provided by the molecular association in GL_2E_4. As a possible way to explain the Ca^{2+}-transport activity, therefore, it would be reasonable to consider the molecular arrangement of GL_2E_4 to trap ions. Based on the observed molecular arrangements, possible multi-molecular interaction modes as shown in Fig. 4 were considered; each model postulates that the Ca^{2+} ion is trapped by two adjacent GL_2E_4 molecules.

As is obvious from Fig. 4(*a*), the symmetrical epoxy groups in diastereomer (4) are centrosymmetrically disposed on the twisted backbone and the molecular arrangement seems to be beneficial to trap the ions. In this model, the molecules are able to make a continuous layer consisting of alternative arrangements of the molecules and ions by using all chelating O atoms. A Ca^{2+} ion is trapped by four coordination bonds with the O atoms of two neighboring GL_2E_4 molecules and consequently, a higher potent ionophoretic activity of (4) would be expected. In the case of diastereomer (6), each of the two epoxy groups of a molecule are able to chelate to the Ca^{2+} ions (Fig. 4*b*). However, the twisted ring disturbs the effective molecular arrangement for trapping ions and the infinite linear complex formation would be impossible. In diastereomer (2) the Ca^{2+} ions would be trapped through the coordinations between the epoxy oxygens of O23 and O23′ of neighboring molecules (Fig. 4*c*). However, the coordinations of the inwardly directed oxygens and ions seem to result in the steric hindrance between adjacent molecules and consequently, the O67 or O67′ atoms cannot participate in the ion trapping (blanket model).

In conclusion, the coordination pattern of (4) appears to be more effective and compact than those of (2) and (6) and the diastereomer (6) is superior to (2) in ion-trapping ability. The GL_2E_4s, therefore, should be ranked as (4) > (6) > (2) in the ion-transport activity.

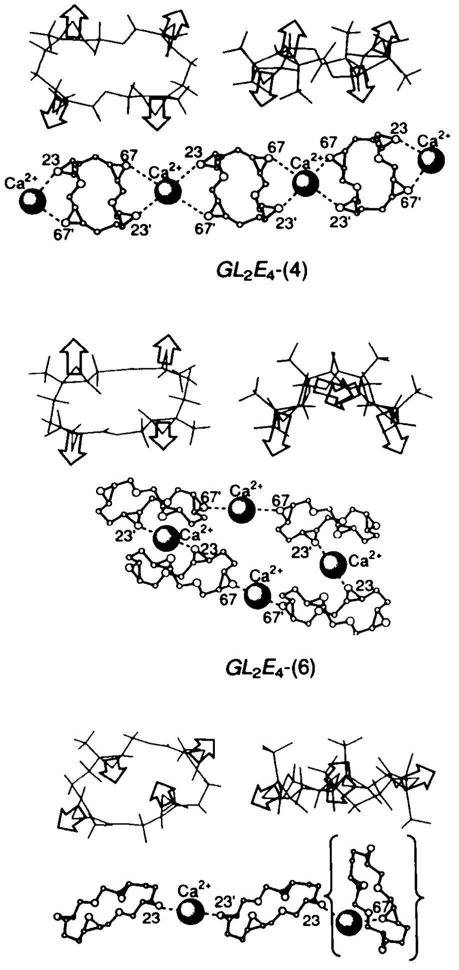


Fig. 4. Proposed interaction modes of GL_2E_4 molecules with calcium ions. Upper: The GL_2E_4 molecule is drawn by stick from two orthogonal directions (right and left sides). Arrows show the approximate direction of the epoxy group. Lower: The GL_2E_4 molecules are drawn by stick and ball, in which the methyl groups and H atoms are excluded for clarity. The calcium ion (shaded ball) is trapped by two neighboring GL_2E_4 molecules. Dotted lines indicate possible coordination bonds between the calcium ions and epoxy O atoms. The numbers indicate the positions of the epoxy groups.

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