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Crystalline-State Reaction of Cobaloxime Complexes. 17. Requirements for Racemization of the Bulky Dimethoxycarbonylethyl Group

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Abstract

Two crystal structures, [(*R*)-1,2-dimethoxycarbonylethyl]bis(dimethylglyoximato)(*R*)-phenylethylamine]cobalt(III) (*R*-pea) and [(*R*)-1,2-dimethoxycarbonylethyl]bis(dimethylglyoximato)(1-propylamine)cobalt(III) methanol solvate (pa), have been determined. *R*-pea: [Co(C₄H₇N₂O₂)₂(C₆H₉O₄)(C₈H₁₁N)], *M_r* = 555.5, monoclinic, *P*2₁, *a* = 9.125 (1), *b* = 15.820 (2), *c* = 9.348 (1) Å, β = 102.57 (1)°, *V* = 1317.0 (1) Å³, *Z* = 2, *D_x* = 1.40 g cm⁻³, λ(Mo *K*α) = 0.71069 Å, μ = 7.32 cm⁻¹, *F*(000) = 584, *T* = 298 K, *R* = 0.055 and *wR* = 0.049 for 2208 observed reflections. pa: [Co(C₄H₇N₂O₂)₂(C₆H₉O₄)(C₃H₉N)].CH₃OH, *M_r* = 525.4, monoclinic, *P*2₁, *a* = 9.803 (3), *b* = 15.554 (3), *c* = 9.267 (3) Å, β = 117.24 (2)°, *V* = 1255.4 (7) Å³, *Z* = 2, *D_x* = 1.39 g cm⁻¹, λ(Mo *K*α) = 0.71069 Å, μ = 7.66 cm⁻¹, *F*(000) = 556, *T* = 298 K, *R* = 0.070 and *wR* = 0.076 for 1699 observed reflections. Neither crystal was racemized on exposure to X-rays or visible light without crystal degradation. The structures are compared with those of crystals which contain the same chiral alkyl group but a different axial base ligand. Non-reactivity of the two crystals

may be due to the fact that the chiral dimethoxycarbonylethyl groups of the two crystals have too small a cavity for racemization to take place and are not in contact with each other.

Introduction

In serial studies of crystalline-state racemization of bis(dimethylglyoximato)cobalt(III) (cobaloxime) complexes, two kinds of chiral alkyl groups bonded to the Co atom have been found to be racemized on exposure to X-rays or visible light. One group is the (*R*)-1-cyanoethyl (ce) group, [—CH(CH₃)CN] (Ohashi, 1988), while the other is the (*R*)-1-methoxycarbonylethyl (mce) group, [—CH(CH₃)-CO₂CH₃] (Kurihara, Ohashi, Sasada & Ohgo, 1983; Kurihara, Uchida, Ohashi, Sasada & Ohgo, 1984). Recently several cobaloxime complexes have been prepared which contain the bulkier (*R*)-1,2-dimethoxycarbonylethyl (dmce) group (Ohgo, Arai & Takeuchi, 1991). Although the dmce group is much bulkier than the ce and mce groups, the dmce complexes with diphenylmethylphosphine (dpmp) and pyridine (py) as axial base ligands exhibit crystalline-state racemization (Sekine, Sakai, Uchida, Ohashi, Arai, Ohgo, Kamiya & Iwasaki, 1990; Sakai,

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Table 1. Crystal data and details of data collection and refinement

	<i>R</i> -pea	pa
Crystal size (mm)	0.30 × 0.25 × 0.20	0.40 × 0.20 × 0.20
Method of measuring intensities	$\omega/2\theta$	$\omega/2\theta$
Scan speed (° min ⁻¹)	32	16
Scan width (°)	0.945 + 0.350tan θ	1.628 + 0.350tan θ
No. and 2 θ range (°) of reflections used for refining lattice parameters	25 24–30	25 28–31
2 θ_{max} (°)	55	50
Range of		
<i>h</i>	0–12	0–12
<i>k</i>	0–21	0–18
<i>l</i>	–12–12	–11–11
ΔI for standard reflections (%)	2.5	2.6
No. of reflections		
Measured	3323	2381
Unique	3137	2245
Observed	2208 [$I > 3\sigma(I)$]	1699 [$ F_o > 3\sigma(F_o)$]
<i>R</i> _{int}	0.032	0.031
No. of parameters refined	324	289
<i>w</i>	$\sigma^{-2}(I)$	$[\sigma(F_o)]^2 + 0.004F_o^2$
Goodness of fit, <i>S</i>	1.34	0.887
(Δ/σ) _{max}	0.04	0.12
$\Delta\rho_{max}$ (e Å ⁻³)	0.42	0.72
$\Delta\rho_{min}$ (e Å ⁻³)	–0.36	–0.59

Ohashi, Arai & Ohgo, 1992). Three other dmce complexes, with (*S*)-1-phenylethylamine (*S*-pea), (*R*)-1-phenylethylamine (*R*-pea) and 1-propylamine (pa) as axial base ligands, however, were not racemized and retained the single-crystal form. The structure of the *S*-pea complex has already been reported (Sakai, Tamura, Uchida, Ohashi, Hasegawa, Arai & Ohgo, 1991). This paper reports the structures of two dmce crystals, *R*-pea and pa, and discusses the requirements necessary for the racemization process to retain the single-crystal form, based on the structures of five dmce crystals.

Experimental

The complexes were prepared as reported previously (Ohgo, Arai & Takeuchi, 1991). Orange plate-like crystals of *R*-pea and pa were obtained from aqueous methanol solutions. The X-ray work was performed on a Rigaku AFC-5R diffractometer equipped with a graphite monochromator at room temperature. Crystal data and experimental details are listed in Table 1. Corrections for absorption and extinction were not applied. Both structures were solved using the *TEXSAN* program package (Molecular Structure Corporation, 1985). All non-H atoms were refined with anisotropic thermal parameters using the *TEXSAN* program package and the H atoms were calculated geometrically and not refined for the *R*-pea crystal. In the refinement of the pa crystal, using the program *SHELX76* (Sheldrick, 1976), all non-H atoms except the solvent molecule were refined with anisotropic thermal parameters and the solvent *O*(*M*) and *C*(*M*) atoms and the two hydrogen atoms, H(10) and H(30), were refined isotropically. The other H atoms were located geometrically and not refined. Bonds other than those

Table 2. Fractional coordinates and *B*_{eq} or *B*_{iso} (Å²) for non-H atoms, with *e.s.d.*'s in parentheses

	$B_{eq} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$			<i>B</i> _{eq} or <i>B</i> _{iso}
	<i>x</i>	<i>y</i>	<i>z</i>	
<i>R</i> -pea				
Co	0.6724 (1)	0.2662	0.5900 (1)	2.27
N(1)	0.8742 (6)	0.3010 (4)	0.6164 (7)	2.6
N(2)	0.7281 (6)	0.2546 (5)	0.7946 (6)	2.7
N(3)	0.4687 (6)	0.2349 (4)	0.5618 (7)	2.8
N(4)	0.6181 (6)	0.2769 (5)	0.3833 (6)	2.9
O(1)	0.9397 (5)	0.3196 (4)	0.5050 (6)	3.7
O(2)	0.6338 (6)	0.2253 (3)	0.8739 (5)	3.4
O(3)	0.4062 (6)	0.2097 (4)	0.6730 (6)	4.0
O(4)	0.7184 (6)	0.2944 (4)	0.3006 (5)	4.1
C(1)	0.9489 (8)	0.3045 (5)	0.7500 (8)	3.0
C(2)	0.8643 (7)	0.2787 (6)	0.8567 (7)	2.8
C(3)	0.3886 (9)	0.2356 (5)	0.431 (1)	3.6
C(4)	0.4783 (8)	0.2608 (7)	0.3226 (7)	3.5
C(5)	1.112 (1)	0.3324 (6)	0.786 (1)	4.4
C(6)	0.921 (1)	0.2732 (9)	1.0193 (9)	4.7
C(7)	0.227 (1)	0.2124 (8)	0.390 (1)	5.6
C(8)	0.4124 (9)	0.2698 (9)	0.1610 (8)	5.1
C(9)	0.6184 (8)	0.3900 (4)	0.6280 (8)	2.7
C(10)	0.5621 (9)	0.4330 (5)	0.4863 (8)	3.0
O(5)	0.4306 (7)	0.4426 (4)	0.4276 (6)	5.2
O(6)	0.6732 (7)	0.4605 (4)	0.4259 (6)	5.0
C(11)	0.632 (1)	0.4911 (7)	0.278 (1)	7.4
C(12)	0.5076 (9)	0.4006 (5)	0.7265 (9)	3.4
C(13)	0.490 (1)	0.4913 (6)	0.7700 (8)	3.6
O(7)	0.5448 (7)	0.5515 (4)	0.7259 (7)	5.3
O(8)	0.4052 (7)	0.4959 (4)	0.8690 (7)	5.4
C(14)	0.381 (1)	0.5806 (6)	0.921 (1)	6.6
N(5)	0.7223 (7)	0.1401 (4)	0.5589 (7)	3.1
C(15)	0.8803 (9)	0.1070 (5)	0.5785 (9)	3.5
C(16)	0.9430 (9)	0.0821 (5)	0.735 (1)	3.7
C(17)	1.083 (1)	0.1092 (6)	0.810 (1)	5.3
C(18)	1.145 (2)	0.082 (1)	0.953 (2)	9
C(19)	1.065 (2)	0.031 (1)	1.017 (2)	11
C(20)	0.932 (2)	0.002 (1)	0.949 (2)	8.3
C(21)	0.870 (1)	0.0269 (7)	0.808 (1)	5.9
C(22)	0.886 (1)	0.0316 (7)	0.474 (1)	5.4
pa				
Co	0.4883 (2)	0.25000	0.2585 (2)	3.38
N(1)	0.460 (1)	0.2855 (8)	0.051 (1)	4.5
N(2)	0.637 (1)	0.3378 (8)	0.325 (1)	4.2
N(3)	0.519 (1)	0.2116 (8)	0.465 (1)	3.7
N(4)	0.345 (1)	0.1600 (8)	0.194 (1)	3.8
O(1)	0.357 (1)	0.246 (1)	–0.087 (1)	6.0
O(2)	0.730 (1)	0.3558 (9)	0.484 (1)	6.4
O(3)	0.631 (1)	0.245 (1)	0.607 (1)	5.3
O(4)	0.261 (1)	0.1368 (8)	0.038 (1)	5.7
C(1)	0.546 (2)	0.344 (1)	0.049 (2)	4.7
C(2)	0.654 (2)	0.377 (1)	0.203 (2)	5.1
C(3)	0.440 (2)	0.149 (1)	0.470 (2)	4.5
C(4)	0.331 (2)	0.118 (1)	0.310 (2)	4.3
C(5)	0.543 (2)	0.375 (1)	–0.108 (2)	7.5
C(6)	0.775 (3)	0.441 (1)	0.233 (3)	8
C(7)	0.442 (3)	0.110 (1)	0.622 (2)	7.4
C(8)	0.225 (2)	0.045 (1)	0.277 (3)	7.0
C(9)	0.3339 (9)	0.3411 (9)	0.260 (1)	4.0
C(10)	0.176 (1)	0.3117 (8)	0.1646 (9)	4.5
O(5)	0.108 (1)	0.2768 (8)	0.229 (1)	7.2
O(6)	0.108 (1)	0.3210 (7)	0.0027 (8)	6.1
C(11)	–0.041 (1)	0.286 (2)	–0.096 (3)	12
C(12)	0.370 (2)	0.3777 (8)	0.427 (1)	5.3
C(13)	0.295 (1)	0.4599 (7)	0.423 (1)	4.4
O(7)	0.347 (1)	0.5072 (7)	0.540 (1)	6.5
O(8)	0.171 (1)	0.4829 (7)	0.287 (1)	6.2
C(14)	0.098 (2)	0.5627 (8)	0.287 (2)	5.8
N(5)	0.655 (1)	0.1640 (8)	0.276 (2)	4.0
C(15)	0.650 (3)	0.127 (1)	0.130 (2)	7.2
C(16)	0.788 (3)	0.066 (2)	0.183 (3)	12
C(17)	0.781 (4)	0.025 (2)	0.030 (4)	15
O(<i>M</i>)	–0.023 (2)	0.228 (1)	–0.579 (2)	11.8 (5)
C(<i>M</i>)	0.071 (4)	0.269 (3)	–0.427 (4)	20 (1)

around the Co atoms and in the cobaloxime moieties were constrained to have fixed values during refinement. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Table 3. Selected bond distances (Å) and angles (°)

			<i>R</i> -pea	pa
Co	N(1)		1.886 (6)	1.90 (1)
Co	N(2)		1.878 (6)	1.88 (1)
Co	N(3)		1.887 (6)	1.89 (1)
Co	N(4)		1.895 (5)	1.88 (1)
Co	C(9)		2.069 (7)	2.08 (1)
Co	N(5)		2.081 (6)	2.06 (1)
N(1)	O(1)		1.340 (9)	1.35 (1)
N(1)	C(1)		1.287 (9)	1.24 (2)
C(1)	C(2)		1.45 (1)	1.43 (2)
C(1)	C(5)		1.51 (1)	1.52 (3)
C(9)	C(10)		1.48 (1)	1.46 (1)
C(9)	C(12)		1.52 (1)	1.53 (2)
C(10)	O(5)		1.215 (9)	1.21 (2)
C(10)	O(6)		1.34 (1)	1.34 (1)
O(6)	C(11)		1.44 (1)	1.43 (2)
C(12)	C(13)		1.51 (1)	1.47 (2)
C(13)	O(7)		1.19 (1)	1.21 (1)
C(13)	O(8)		1.33 (1)	1.34 (1)
O(8)	C(14)		1.46 (1)	1.43 (2)
N(1)	Co	N(2)	81.7 (3)	81.4 (5)
N(1)	Co	N(3)	178.2 (2)	178.3 (6)
N(1)	Co	N(4)	97.9 (3)	98.9 (5)
N(1)	Co	C(9)	87.9 (3)	92.3 (5)
N(1)	Co	N(5)	93.5 (2)	90.5 (6)
N(2)	Co	N(3)	99.0 (3)	99.1 (5)
N(2)	Co	N(4)	179.3 (3)	178.2 (5)
N(2)	Co	C(9)	86.5 (3)	87.8 (5)
N(2)	Co	N(5)	91.7 (3)	88.8 (6)
N(3)	Co	N(4)	81.4 (3)	80.5 (5)
N(3)	Co	C(9)	90.5 (3)	89.3 (5)
N(3)	Co	N(5)	88.1 (2)	87.9 (6)
N(4)	Co	C(9)	94.1 (3)	93.9 (5)
N(4)	Co	N(5)	87.7 (3)	89.5 (5)
C(9)	Co	N(5)	177.6 (3)	175.1 (4)
Co	N(1)	O(1)	123.4 (4)	122 (1)
Co	N(1)	C(1)	115.8 (6)	116.0 (9)
O(1)	N(1)	C(1)	120.8 (6)	122 (1)
N(1)	C(1)	C(2)	114.1 (6)	117 (2)
N(1)	C(1)	C(5)	121.1 (7)	121 (1)
C(2)	C(1)	C(5)	124.9 (6)	122 (2)
Co	C(9)	C(10)	109.3 (5)	110.9 (9)
Co	C(9)	C(12)	115.0 (5)	115.4 (7)
C(10)	C(9)	C(12)	110.2 (6)	115 (1)
C(9)	C(10)	O(5)	125.3 (8)	120.8 (8)
C(9)	C(10)	O(6)	112.4 (6)	119 (1)
O(5)	C(10)	O(6)	122.3 (7)	120.1 (9)
C(10)	O(6)	C(11)	116.9 (7)	121 (1)
C(9)	C(12)	C(13)	113.0 (7)	114.8 (9)
C(12)	C(13)	O(7)	126.3 (8)	120.6 (9)
C(12)	C(13)	O(8)	110.5 (7)	118.9 (9)
O(7)	C(13)	O(8)	123.2 (8)	120 (1)
C(13)	O(8)	C(14)	115.8 (7)	118 (1)

Discussion

Final atomic parameters for non-H atoms of *R*-pea and pa are given in Table 2.* *ORTEP* (Johnson, 1976) plots, showing the molecular structures together with the atomic numbering, are shown in Fig. 1. The crystal structures are shown in Fig. 2. There is no unusually short contact in *R*-pea. The pa molecules are linked by hydrogen bonds, N(5)—H(51N)⋯O(7) [N(5)⋯O(7) 2.98 (2) Å], which form a ribbon along the *b* axis, and which are connected by

* Lists of structure factors, anisotropic thermal parameters for non-H atoms, positional and thermal parameters for H atoms, and bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71278 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS0638]

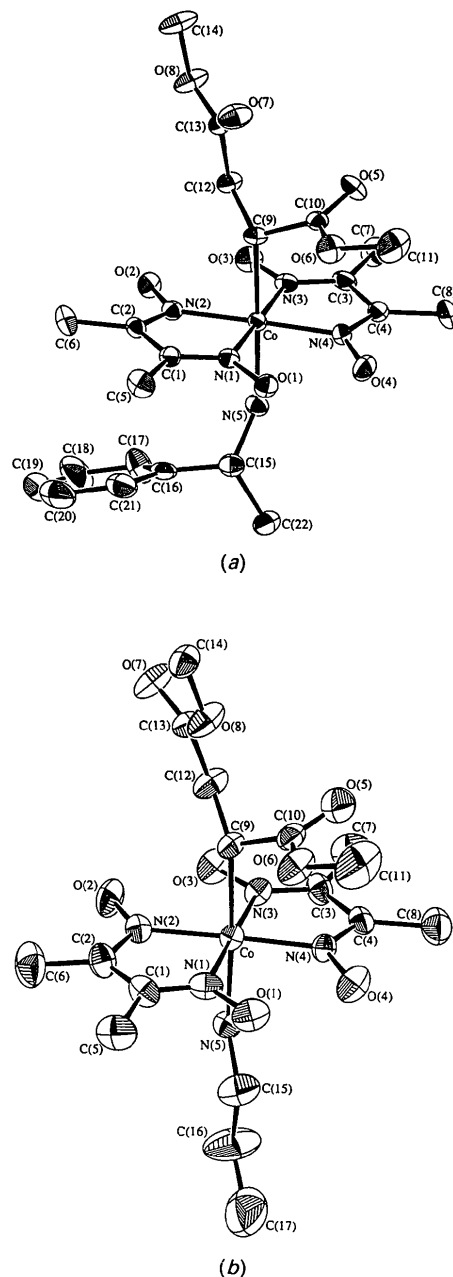
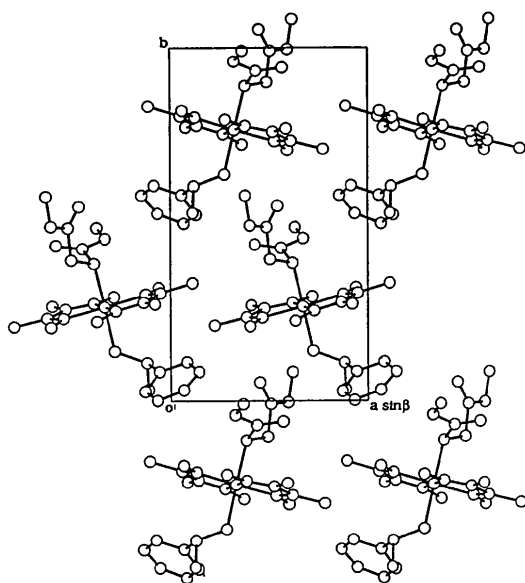


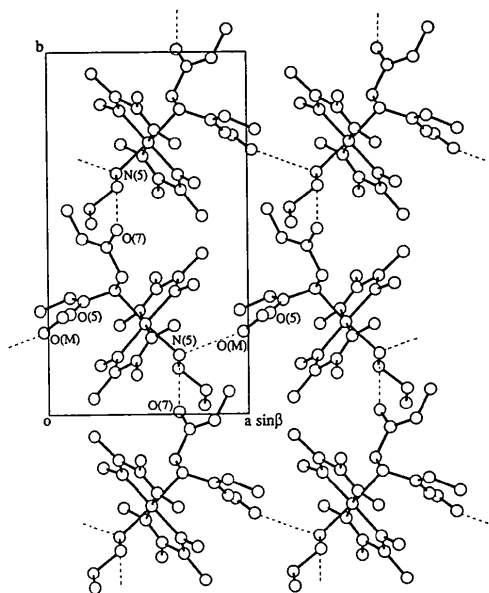
Fig. 1. *ORTEP* (Johnson, 1976) plots of the molecules, with 30% probability thermal ellipsoids for (a) *R*-pea and (b) pa.

two types of hydrogen bonds, N(5)—H(52N)⋯O(*M*) and O(*M*)—H(*MO*)⋯O(5), along the *a* axis. The N(5)⋯O(*M*) and O(*M*)⋯O(5) distances are 2.98 (2) and 2.73 (3) Å, respectively.

Selected bond distances and angles are listed in Table 3. The Co—C(9) and Co—N(5) distances are 2.069 (7) and 2.081 (6) Å for *R*-pea and 2.08 (1) and 2.06 (1) Å for pa. These values are approximately the same as those found in *S*-pea, which are 2.062 (5)



(a)



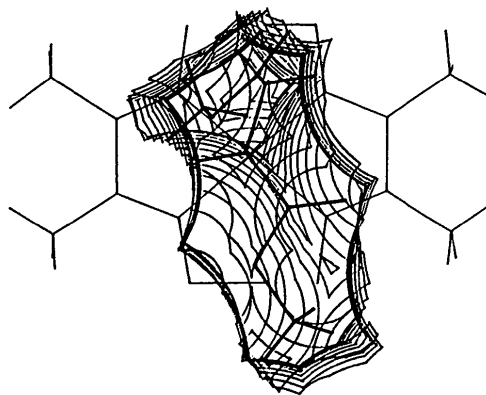
(b)

Fig. 2. Packing diagrams for (a) *R*-pea and (b) *pa*. Intermolecular hydrogen bonds are indicated by dashed lines.

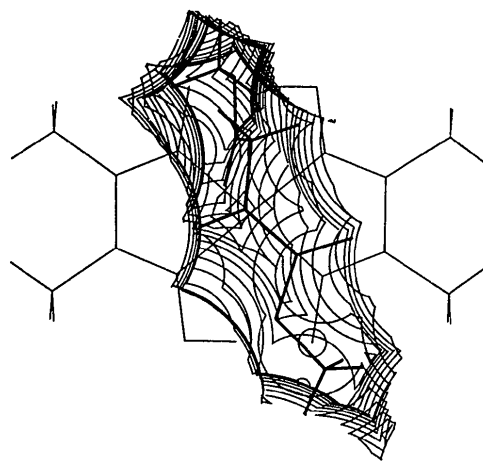
and 2.074 (4) Å, respectively (Sakai, Tamura, Uchida, Ohashi, Hasegawa, Arai & Ohgo, 1991). The other distances and angles are not significantly different from those found in other related complexes.

Selected torsion angles for the five dmce complexes are listed in Table 4. The torsion angles C(10)—

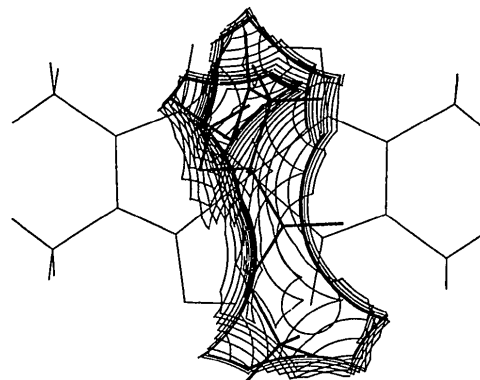
C(9)—C(12)—C(13) lie in the narrow range -77 (2) to -58.4 (8) $^\circ$, which is responsible for the L-type conformation of the dmce group in each of the complexes. Steric repulsion between the ester group composed of O(5), C(10), O(6) and C(11) and the cobaloxime moiety forces the torsion angle C(12)—



(a)



(b)



(c)

Fig. 3. Cavities for the dmce group for (a) *S*-pea, (b) *R*-pea and (c) *pa*. Contours are drawn in sections separated by 0.2 Å.

Table 4. Selected torsion angles (°)

	S-pea	R-pea	pa	py		dpmp	
				A	B	A	B
C(10) C(9) C(12) C(13)	-60.3 (5)	-64.9 (8)	-69 (2)	-64 (1)	-77 (2)	-58.4 (8)	-65.7 (7)
C(12) C(9) C(10) O(5)	-28.8 (6)	-30 (1)	-37 (2)	-31 (2)	-44 (2)	-32.6 (8)	-40.5 (8)
C(12) C(9) C(10) O(6)	149.0 (4)	150.6 (6)	146 (1)	140 (1)	138 (1)	146.1 (5)	144.0 (5)
C(9) C(12) C(13) O(7)	157.8 (6)	6 (1)	-158 (1)	-31 (2)	-18 (3)	-18 (1)	-24 (1)
C(9) C(12) C(13) O(8)	-22.6 (7)	-173.0 (6)	20 (2)	156.7 (9)	137 (2)	161.2 (6)	156.8 (7)

C(9)—C(10)—O(5) to lie in the narrow range $-44(2)$ to $-28.8(6)^\circ$. The hydrogen bond of O(5)⋯O(M), observed in the pa crystal, does not seem to influence the torsion angle. However, the torsion angle C(9)—C(12)—C(13)—O(7) adopts a variety of values. The ester group composed of C(13), O(7), O(8) and C(14) rotates easily around the C(12)—C(13) bond.

The dpmp and py crystals have two crystallographically independent molecules, *A* and *B*, in the asymmetric unit which are closely related by a pseudo-inversion centre. The *A* and *B* dmce groups face each other around the pseudo-inversion centre. When the dpmp and py crystals were exposed to X-rays or visible light at room temperature, only the *B* dmce groups were inverted to the opposite configuration and the pseudo-inversion centre in each crystal was changed to a crystallographic one. The chiral crystal was transformed to the racemic one (Sekine, Sakai, Uchida, Ohashi, Arai, Ohgo, Kamiya & Iwasaki, 1990; Sakai, Ohashi, Arai & Ohgo, 1992).

Chiral crystals of *R*-pea, pa and *S*-pea were not changed on exposure to X-rays or visible light, although powdered samples were changed, so as to racemize the dmce groups, on exposure to visible light (Ohgo, Arai & Takeuchi, 1991). To examine why the dmce groups of the *R*-pea, pa and *S*-pea crystals are not racemized with retention of the single crystal form, the reaction cavity for the dmce group was drawn for each crystal and its volume calculated in the same way as that reported previously (Ohashi, Uchida, Sasada & Ohgo, 1983). The cavities, shown in Fig. 3, have volumes of 34.2, 37.6 and 45.7 Å³ for pa, *R*-pea and *S*-pea, respectively. The corresponding values are 40.6 (*A*) and 43.9 (*B*) Å³ for py, and 47.8 (*A*) and 55.0 (*B*) Å³ for dpmp, respectively. Since the precise structure could not be determined for the py crystal at room temperature, the above value was deduced from the structure at 243 K (Sakai, Ohashi, Arai & Ohgo, 1992). The cavity volume of the *B* dmce group for the dpmp crystal is significantly greater than the corresponding ones in *R*-pea, pa and

S-pea. However, the cavity for the *B* dmce group in the py crystal may not be significantly different from those in *R*-pea, pa and *S*-pea, even if its thermal expansion were taken into account. This suggests that another factor is important. For the mce group, the cooperative motion of the two reactive groups, which face each other around a pseudo-inversion centre in the initial structure, seems to be essential for crystalline-state racemization (Kurihara, Uchida, Ohashi, Sasada & Ohgo, 1984). For the dmce group described here, the dpmp and py crystals have two crystallographically independent molecules and the two dmce groups face each other around a pseudo-inversion centre. The above results strongly suggest that bulky groups such as mce and dmce should face each other around a pseudo-inversion centre and move cooperatively when they are racemized so as to retain the single-crystal form.

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