Structural Database, 1989). Although the lattice constants are comparable, it is not a monoclinic distortion of the orthorhombic potassium hydrogen phthalate type (Okaya, 1965). In this structure, the hydrogen phthalate residues form dimers *via* intermolecular hydrogen bonds instead of chains. All calculations were carried out on a MicroVAX and on the PDP 10 at the Rechenzentrum der Universität Kiel.

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Structures of Novel Calmodulin Inhibitors KS504a, KS504b and KS504e

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Abstract. (I) KS504a: (1R^*,3S^*)-2,2,4,4-tetrachloro-5-dichloromethylene-3-hydroxycyclopentane-1-spiro-2′-(3′R^*)-3′-chlorooxirane, $C_7H_3Cl_7O_2$, $M_r = 367{\cdot}27$, monoclinic, $P2_1/n$, $a = 9{\cdot}247$ (1), $b = 16{\cdot}593$ (1), $c = 8{\cdot}351$ (1) Å, $\beta = 100{\cdot}65$ (1)°, $V = 1259{\cdot}1$ (3) Å^3, $Z = 4$, $D_x = 1{\cdot}94$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 15{\cdot}7$ cm^{-1}, $F(000) = 720$, $T = 293$ K, $wR = 0{\cdot}078$ for 2264 observed reflections. (II) KS504b, (1S,3S)-2,2,4,4-tetrachloro-5-dichloromethylene-3-hydroxycyclopentane-1-spiro-2′-(3′R)-3′-chlorooxirane, $C_7H_3Cl_7O_2$, $M_r = 367{\cdot}27$, orthorhombic, $P2_12_12_1$, $a = 15{\cdot}543$ (2), $b = 36{\cdot}509$ (3), $c = 6{\cdot}793$ (1) Å, $V = 3855$ (1) Å^3, $Z = 12$, $D_x = 1{\cdot}27$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 10{\cdot}3$ cm^{-1}, $F(000) = 1440$, $T = 293$ K, $wR = 0{\cdot}054$ for 1567 observed reflections. (III) KS504e: (4S^*)-3,3,5,5-tetrachloro-4-hydroxy-2-trichloromethyl-1-cyclopentenecarbaldehyde, $C_7H_3Cl_7O_2$, $M_r = 367{\cdot}27$, monoclinic, $P2_1$, $a = 8{\cdot}861$ (2), $b = 11{\cdot}892$ (3), $c = 6{\cdot}121$ (3) Å, $\beta = 90{\cdot}15$ (3)°, $V = 644{\cdot}9$ (6) Å^3, $Z = 2$, $D_x = 1{\cdot}89$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 15{\cdot}3$ cm^{-1}, $F(000) = 360$, $T = 293$ K, $wR = 0{\cdot}051$ for 1449 observed reflections. The structures of these three compounds are novel and have not previously been observed in natural products from microorganisms. The absolute configuration of (II) was determined by the Bijvoet method. The five-membered rings adopt envelope conformations.

Introduction. Ca^{2+} acts as a second messenger in the control of a variety of cell functions and many of the effects of the ion are transmitted by calmodulin. In the course of studies on inhibitors or antagonists of the Ca^{2+}-messenger system, Nakanishi, Ando, Kawamoto, Yasuzawa, Sano & Kase (1989) found a novel group of calmodulin inhibitors, (I) and (II), from *Mollisia ventosa* KAC-1148. When (I) is heated at 333 K in acidic ethyl acetate solution with hydrochloric acid it yields (III), which shows a similar activity to (I). (II) does not yield (III) under the same conditions (Nakanishi *et al.*, 1989). (I), (II) and (III) inhibit Ca^{2+}/calmodulin-dependent cyclic nucleotide phosphodiesterases. The I_{50} values for the effect of the enzyme from bovine brain are 98, 93 and 133 μM, respectively. Usual chemical and spectroscopic methods suggested that the three compounds have novel structures as implied by their formulae of $C_7H_3Cl_7O_2$ but could not determine the structures

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Table 1. *Experimental and refinement details*

	(I)	(II)	(III)
Crystal size (mm)	0·4 × 0·4 × 0·3	0·4 × 0·3 × 0·15	0·4 × 0·4 × 0·3
2θ range of reflections for cell determination (°)	$16 < \theta < 21$	$14 < \theta < 17$	$17 < \theta < 24$
No. of reflections to determine cell	23	25	25
Range of h	−12 to 11	0 to 20	−11 to 11
k	0 to 21	0 to 47	0 to 15
l	0 to 10	0 to 5	0 to 7
No. of unique reflections	2439	3707	1535
No. of data with $I > 3\sigma(I)$	2264	2567	1449
Empirical isotropic extinction coefficient	$1·489 \times 10^7$	$5·424 \times 10^8$	$6·659 \times 10^7$
Final R	0·059	0·042	0·038
Final wR	0·078	0·54	0·051
S	2·89	2·02	2·09
Max. Δ/σ	0·01	0·12	0·01
$\Delta\rho_{\max}$(e Å^{-3})	0·7 (2)	0·43 (8)	0·60 (9)
$\Delta\rho_{\min}$(e Å^{-3})	−0·64 (4)	−0·32 (9)	−0·41 (8)

Table 2. *Positional and equivalent isotropic temperature factors* (Å^2) *for* (I)

$$B_{\rm eq} = (4/3)\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
Cl(1)	0·7488 (1)	0·85201 (6)	−0·1590 (1)	4·70 (2)
Cl(2)	0·9249 (1)	0·84421 (6)	0·2385 (2)	4·65 (2)
Cl(3)	0·61622 (9)	0·801	0·1668 (1)	3·50 (2)
Cl(4)	0·5829 (1)	0·60309 (7)	0·2573 (1)	4·25 (2)
Cl(5)	0·8772 (1)	0·54337 (6)	0·3670 (1)	4·45 (2)
Cl(6)	0·7485 (2)	0·47011 (5)	0·0229 (2)	5·36 (3)
Cl(7)	0·8200 (1)	0·57275 (7)	−0·2222 (1)	5·16 (2)
O(1′)	0·9437 (2)	0·7365 (2)	−0·0326 (3)	3·43 (5)
O(2)	0·7709 (3)	0·7216 (2)	0·4699 (3)	3·71 (5)
C(1)	0·8202 (3)	0·7151 (2)	0·0404 (3)	2·23 (5)
C(2)	0·7992 (3)	0·7636 (2)	0·1920 (4)	2·53 (6)
C(3)	0·8252 (4)	0·7015 (2)	0·3305 (4)	2·70 (6)
C(3′)	0·8018 (4)	0·7514 (2)	−0·1221 (4)	3·24 (6)
C(4)	0·7715 (4)	0·6206 (2)	0·2504 (4)	2·62 (6)
C(5)	0·7952 (3)	0·6280 (2)	0·0764 (4)	2·32 (5)
C(6)	0·7905 (4)	0·5661 (2)	−0·0267 (4)	3·14 (7)

and the stereochemical relationships among them. Therefore we have undertaken X-ray analyses of (I), (II) and (III), respectively.

Experimental. Colourless crystals of (I), (II) and (III) obtained from cyclohexane at 278 K. Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation, ω–2θ scan technique, $1 \leq \theta \leq 27·5°$. Crystals decayed rather quickly under X-ray irradiation. Total losses in intensities of three reference reflections of (I), (II), and (III) were 32·2 (35), 29·1 (38·9) and 11·7% (36 h), respectively (exposure time in parentheses). Anisotropic decay correction and normal Lp corrections were made. No absorption correction. A secondary-extinction correction (Zachariasen, 1963) was applied. Experimental and refinement details are listed in Table 1.

Structures solved by direct methods using *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). *DIRDIF* (Beurskens, Van den Hark & Beurskens, 1976) was also applied to solve the structure of (I). Refinement using the *SDP* package (Frenz, 1983), full-matrix

Table 3. *Positional and equivalent isotropic temperature factors* (Å^2) *for* (II)

$$B_{\rm eq} = (4/3)\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
Molecule A				
Cl(1)	0·9931 (1)	0·65634 (5)	0·6920 (4)	5·01 (6)
Cl(2)	1·1268 (1)	0·76293 (6)	0·9201 (4)	6·23 (6)
Cl(3)	1·1418 (1)	0·78745 (5)	0·5203 (4)	5·29 (5)
Cl(4)	0·9361 (1)	0·80137 (5)	0·3318 (4)	6·33 (6)
Cl(5)	0·8280 (1)	0·75920 (5)	0·5924 (5)	6·81 (7)
Cl(6)	0·8780 (2)	0·72249 (6)	0·1506 (4)	6·85 (6)
Cl(7)	1·0223 (2)	0·67684 (5)	0·2228 (4)	5·37 (6)
O(1′)	1·1197 (3)	0·7016 (1)	0·5699 (8)	4·2 (1)
O(2)	0·9893 (3)	0·8212 (1)	0·723 (1)	4·9 (1)
C(1)	1·0528 (4)	0·7272 (2)	0·609 (1)	3·2 (2)
C(2)	1·0750 (4)	0·7644 (2)	0·692 (1)	3·6 (2)
C(3)	0·9863 (4)	0·7830 (2)	0·705 (1)	3·7 (2)
C(3′)	1·0641 (4)	0·6939 (2)	0·723 (1)	3·6 (2)
C(4)	0·9368 (4)	0·7681 (2)	0·523 (1)	4·0 (2)
C(5)	0·9824 (4)	0·7335 (2)	0·461 (1)	3·0 (2)
C(6)	0·9635 (4)	0·7136 (2)	0·305 (1)	4·2 (2)
Molecule B				
Cl(1)	0·5977 (1)	0·95899 (5)	0·0480 (4)	4·68 (5)
Cl(2)	0·7472 (1)	0·85583 (6)	0·2654 (4)	5·53 (6)
Cl(3)	0·7726 (1)	0·83472 (5)	−0·1398 (4)	5·40 (5)
Cl(4)	0·9060 (1)	0·90107 (5)	−0·3603 (4)	4·80 (5)
Cl(5)	0·8844 (1)	0·96343 (4)	−0·1041 (4)	5·11 (5)
Cl(6)	0·7712 (1)	0·96054 (6)	−0·5348 (4)	5·66 (6)
Cl(7)	0·6062 (1)	0·93490 (7)	−0·4197 (4)	6·05 (6)
O(1′)	0·6167 (3)	0·8886 (1)	−0·0679 (9)	4·4 (1)
O(2)	0·9280 (3)	0·8732 (1)	0·0356 (9)	4·5 (1)
C(1)	0·7033 (4)	0·8998 (2)	−0·046 (1)	2·9 (2)
C(2)	0·7693 (4)	0·8720 (2)	0·027 (1)	3·8 (2)
C(3)	0·8521 (4)	0·8941 (2)	0·022 (1)	3·2 (2)
C(3′)	0·6360 (4)	0·9140 (2)	0·078 (1)	3·5 (2)
C(4)	0·8443 (3)	0·9188 (2)	−0·161 (1)	3·0 (2)
C(5)	0·7483 (4)	0·9207 (2)	−0·210 (1)	3·4 (2)
C(6)	0·7138 (4)	0·9363 (2)	−0·366 (1)	3·9 (2)
Molecule C				
Cl(1)	0·4068 (1)	0·94814 (8)	0·3732 (4)	6·92 (7)
Cl(2)	0·1189 (1)	0·95020 (6)	0·5742 (4)	5·73 (6)
Cl(3)	0·0695 (1)	0·94881 (5)	0·1672 (4)	5·35 (6)
Cl(4)	0·1326 (1)	0·86446 (6)	−0·0294 (4)	5·92 (6)
Cl(5)	0·2655 (1)	0·84022 (5)	0·2369 (5)	6·34 (6)
Cl(6)	0·3252 (1)	0·87896 (6)	−0·1942 (4)	6·33 (6)
Cl(7)	0·3614 (1)	0·95303 (6)	−0·0985 (4)	5·19 (5)
O(1′)	0·2583 (3)	0·9770 (1)	−0·2427 (9)	4·1 (1)
O(2)	0·0623 (3)	0·8734 (1)	0·364 (1)	4·5 (1)
C(1)	0·2342 (4)	0·9403 (2)	0·269 (1)	3·1 (2)
C(2)	0·1431 (4)	0·9317 (2)	0·343 (1)	3·5 (2)
C(3)	0·1446 (4)	0·8895 (2)	0·348 (1)	4·1 (2)
C(3′)	0·2965 (4)	0·9582 (2)	0·400 (1)	4·7 (2)
C(4)	0·1997 (4)	0·8780 (2)	0·170 (1)	4·1 (2)
C(5)	0·2537 (4)	0·9114 (2)	0·118 (1)	3·4 (2)
C(6)	0·3054 (4)	0·9144 (2)	−0·036 (1)	4·6 (2)

Table 4. *Positional and equivalent isotropic temperature factors* (Å^2) *for* (III)

$$B_{\rm eq} = (4/3)\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
Cl(1)	0·5985 (1)	0·3607 (1)	−0·2519 (2)	4·13 (2)
Cl(2)	0·5516 (1)	0·169	0·0292 (2)	3·37 (2)
Cl(3)	0·2752 (1)	0·0050 (1)	−0·2301 (2)	3·19 (2)
Cl(4)	0·2101 (1)	0·1136 (1)	−0·6431 (2)	3·30 (2)
Cl(5)	0·0028 (2)	0·3547 (2)	−0·4320 (2)	5·78 (3)
Cl(6)	−0·0102 (2)	0·2975 (2)	0·0217 (2)	6·07 (3)
Cl(7)	−0·0666 (1)	0·1307 (2)	−0·2970 (4)	6·52 (4)
O(1)	0·3654 (5)	0·3978 (3)	0·1720 (6)	4·76 (8)
O(2)	0·5588 (3)	0·0931 (3)	−0·4429 (5)	3·07 (5)
C(1)	0·3189 (5)	0·2884 (3)	−0·1411 (6)	2·71 (7)
C(2)	0·2139 (4)	0·2280 (3)	−0·2464 (6)	2·42 (6)
C(3)	0·2866 (4)	0·1340 (3)	−0·3775 (6)	2·35 (6)
C(4)	0·4519 (4)	0·1742 (3)	−0·3999 (6)	2·45 (6)
C(5)	0·4753 (4)	0·2476 (3)	−0·1919 (6)	2·51 (6)
C(6)	0·2996 (6)	0·3881 (4)	0·0033 (9)	3·91 (9)
C(7)	0·0443 (4)	0·2492 (4)	−0·2400 (7)	3·22 (8)

Table 5. *Bond lengths* (Å) *and angles* (°)

Numbers in parentheses are e.s.d.'s in the least significant digits.

			(II)	
	(I)	*A*	*B*	*C*
Cl(1)—C(3′)	1·750 (4)	1·772 (7)	1·759 (7)	1·761 (7)
Cl(2)—C(2)	1·768 (3)	1·744 (9)	1·754 (9)	1·747 (9)
Cl(3)—C(2)	1·779 (3)	1·772 (8)	1·768 (8)	1·765 (8)
Cl(4)—C(4)	1·779 (3)	1·776 (8)	1·778 (8)	1·778 (9)
Cl(5)—C(4)	1·788 (3)	1·782 (6)	1·785 (6)	1·774 (7)
Cl(6)—C(6)	1·708 (4)	1·720 (8)	1·700 (9)	1·708 (9)
Cl(7)—C(6)	1·708 (4)	1·716 (6)	1·712 (7)	1·710 (7)
O(1′)—C(1)	1·435 (4)	1·423 (7)	1·413 (7)	1·404 (8)
O(1′)—C(3′)	1·407 (4)	1·379 (9)	1·385 (9)	1·40 (2)
O(2)—C(3)	1·390 (4)	1·401 (8)	1·406 (8)	1·413 (7)
C(1)—C(2)	1·542 (4)	1·511 (9)	1·526 (9)	1·533 (9)
C(1)—C(3′)	1·465 (5)	1·46 (1)	1·44 (1)	1·47 (2)
C(1)—C(5)	1·504 (4)	1·50 (1)	1·51 (2)	1·50 (2)
C(2)—C(3)	1·533 (5)	1·539 (9)	1·519 (9)	1·541 (9)
C(3)—C(4)	1·540 (5)	1·55 (1)	1·54 (2)	1·54 (1)
C(4)—C(5)	1·514 (5)	1·507 (9)	1·529 (8)	1·523 (9)
C(5)—C(6)	1·335 (5)	1·32 (2)	1·31 (1)	1·32 (1)
C(1)—O(1′)—C(3′)	62·1 (3)	62·3 (4)	61·8 (4)	63·2 (5)
O(1′)—C(1)—C(2)	116·8 (2)	119·5 (5)	118·8 (5)	118·9 (5)
O(1′)—C(1)—C(3′)	58·0 (3)	57·3 (4)	58·1 (4)	58·3 (5)
O(1′)—C(1)—C(5)	119·1 (3)	120·6 (6)	120·6 (6)	121·9 (6)
C(2)—C(1)—C(3′)	122·3 (3)	121·8 (7)	122·5 (7)	120·2 (7)
C(2)—C(1)—C(5)	106·9 (3)	106·0 (5)	105·3 (5)	105·5 (5)
C(3′)—C(1)—C(5)	125·8 (3)	125·0 (5)	125·5 (6)	126·5 (5)
Cl(2)—C(2)—Cl(3)	109·6 (2)	109·0 (3)	109·6 (4)	109·2 (4)
Cl(2)—C(2)—C(1)	113·4 (2)	114·1 (5)	113·1 (6)	114·3 (5)
Cl(2)—C(2)—C(3)	109·8 (3)	112·1 (6)	111·3 (6)	111·7 (6)
Cl(3)—C(2)—C(1)	110·2 (2)	108·5 (6)	108·9 (5)	107·8 (5)
Cl(3)—C(2)—C(3)	109·7 (2)	110·6 (6)	111·8 (6)	112·3 (5)
C(1)—C(2)—C(3)	104·0 (3)	102·4 (5)	102·0 (6)	101·4 (6)
O(2)—C(3)—C(2)	116·0 (3)	114·6 (6)	114·8 (5)	113·9 (5)
O(2)—C(3)—C(4)	115·9 (3)	115·8 (6)	115·8 (6)	116·9 (6)
C(2)—C(3)—C(4)	105·4 (3)	104·0 (6)	105·2 (6)	105·3 (7)
Cl(1)—C(3′)—O(1′)	117·7 (3)	117·2 (6)	118·1 (5)	115·8 (6)
Cl(1)—C(3′)—C(1)	122·5 (3)	120·7 (5)	121·1 (5)	119·0 (6)
O(1′)—C(3′)—C(1)	59·9 (2)	60·3 (5)	60·0 (4)	58·6 (5)
Cl(4)—C(4)—Cl(5)	107·8 (2)	108·1 (4)	108·0 (3)	108·4 (4)
Cl(4)—C(4)—C(3)	111·6 (2)	109·9 (4)	110·9 (5)	110·4 (4)
Cl(4)—C(4)—C(5)	111·2 (3)	111·9 (6)	112·1 (6)	111·5 (6)
Cl(5)—C(4)—C(3)	106·8 (2)	108·9 (6)	109·6 (5)	109·5 (6)
Cl(5)—C(4)—C(5)	114·8 (2)	111·5 (4)	110·2 (4)	111·5 (4)
C(3)—C(4)—C(5)	104·8 (2)	106·5 (5)	106·2 (5)	105·8 (6)
C(1)—C(5)—C(4)	108·9 (3)	106·6 (6)	105·6 (6)	106·9 (6)
C(1)—C(5)—C(6)	126·8 (3)	127·9 (6)	128·2 (6)	127·3 (6)
C(4)—C(5)—C(6)	124·3 (3)	125·6 (6)	126·2 (7)	125·8 (7)
Cl(6)—C(6)—Cl(7)	112·1 (2)	111·2 (5)	112·5 (5)	112·2 (6)
Cl(6)—C(6)—C(5)	122·9 (3)	123·8 (5)	123·7 (6)	122·9 (5)
Cl(7)—C(6)—C(5)	125·0 (3)	125·0 (6)	123·9 (6)	124·9 (6)

	(III)
Cl(1)—C(5)	1·771 (5)
Cl(2)—C(5)	1·776 (4)
Cl(3)—C(3)	1·782 (4)
Cl(4)—C(3)	1·777 (4)
Cl(5)—C(7)	1·758 (5)
Cl(6)—C(7)	1·770 (4)
Cl(7)—C(7)	1·753 (5)
O(1)—C(6)	1·190 (6)
O(2)—C(4)	1·378 (5)
C(1)—C(5)	1·501 (5)
C(1)—C(6)	1·490 (6)
C(1)—C(2)	1·339 (5)
C(4)—C(5)	1·557 (5)
C(3)—C(4)	1·547 (5)
C(2)—C(3)	1·520 (5)
C(2)—C(7)	1·525 (5)
C(5)—C(1)—C(6)	119·2 (4)
C(2)—C(1)—C(5)	111·6 (3)
C(2)—C(1)—C(6)	129·3 (4)
Cl(1)—C(5)—Cl(2)	108·9 (3)
Cl(1)—C(5)—C(1)	111·6 (3)
Cl(1)—C(5)—C(4)	109·7 (3)
Cl(2)—C(5)—C(1)	111·2 (3)
Cl(2)—C(5)—C(4)	112·2 (3)
C(1)—C(5)—C(4)	103·3 (3)
O(2)—C(4)—C(5)	117·4 (4)
O(2)—C(4)—C(3)	116·8 (3)
C(3)—C(4)—C(5)	103·1 (3)
O(1)—C(6)—C(1)	122·5 (4)
Cl(3)—C(3)—Cl(4)	109·0 (2)
Cl(3)—C(3)—C(4)	111·5 (3)
Cl(3)—C(3)—C(2)	109·9 (3)
Cl(4)—C(3)—C(4)	108·7 (2)
Cl(4)—C(3)—C(2)	115·0 (3)
C(2)—C(3)—C(4)	102·9 (3)
C(1)—C(2)—C(3)	110·7 (3)
C(1)—C(2)—C(7)	125·6 (4)
C(3)—C(2)—C(7)	123·7 (3)
Cl(5)—C(7)—Cl(6)	108·4 (3)
Cl(5)—C(7)—Cl(7)	108·9 (2)
Cl(5)—C(7)—C(2)	107·8 (3)
Cl(6)—C(7)—Cl(7)	106·7 (2)
Cl(6)—C(7)—C(2)	110·4 (3)
Cl(7)—C(7)—C(2)	114·4 (3)

least-squares refinement on F, with non-H atoms having anisotropic temperature factors. H atoms not refined. Weight $w = 4F_o^2/[\sigma(I_o)^2 + (0{\cdot}04I_o)^2]^{1/2}\mathrm{Lp}$. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). The absolute configuration of (II) was determined by Bijvoet difference analysis (Bijvoet, Peerdeman & van Bommel, 1951) using Cu $K\alpha$ radiation (λ = 1·5418 Å). The absolute configurations of (I) and (III) could not be determined. Computers used: VAX 11/750 and VAX 8550.

Discussion. Atomic parameters are given in Tables 2, 3 and 4,* bond lengths and angles in Table 5. The atomic numbering system and the chemical structures of (I), (II) and (III) are shown in Fig. 1. The absolute configurations of (I) and (III) are tentatively assigned on the assumption that the absolute configurations around the C(3) atom in (I) and (II), and the C(4) atom in (III) are all the same. *ORTEP* (Johnson, 1976) drawings of the compounds are shown in Fig. 2. The chemical structures of the compounds are novel and have not been observed in any natural products so far. On the assumption of the absolute configurations described above, (I) is thought to be an epimer of (II) with respect to the C(1) atom. It is noteworthy that although these three compounds are relatively simple and have the same formula, normal spectroscopic and chemical methods can determine neither the structures nor even the stereochemical interrelationships between them, obviously because of the lack of H atoms which are usually important clues for non-X-ray structure determination methods.

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and ring-puckering details have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52844 (41 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Bond lengths and angles are within normal ranges. The five-membered rings adopt envelope conformations. The C(3), C(2) and C(4) atoms are at the flap positions in (I), (II) and (III), respectively, and the remaining four atoms in each ring are coplanar (within 0·025 Å). The three crystallographically independent molecules in (II) adopt essentially the same envelope conformation.

The torsion angle C(6)—C(5)—C(1)—C(2) is 174·1 (3)° in (I) and the corresponding angle in (III), C(7)—C(2)—C(1)—C(5), is −177·3 (4)°. In (II), however, the average angle is 151·8 (8)°. The angles indicate that the exocyclic double bond in (I) can migrate more easily into the five-membered ring than that in (II). The C(1)—O(1′) bond length of 1·435 (2) Å in (I) is significantly longer than the average value of 1·413 (7) Å in (II). This indicates that the bond in (I) is more scissile than that in (II).

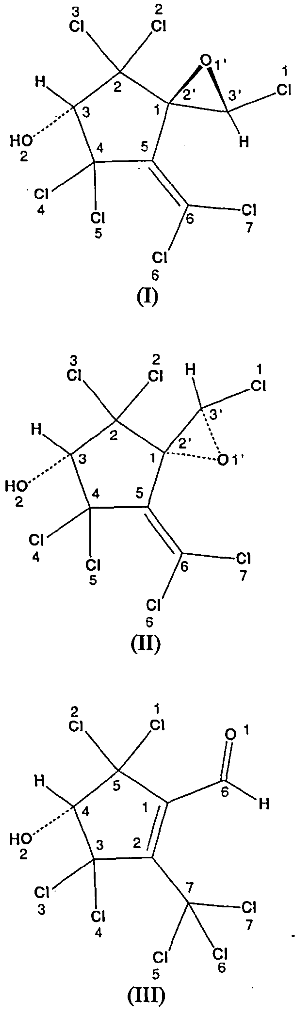

Fig. 1. Chemical structures and atomic numbering.

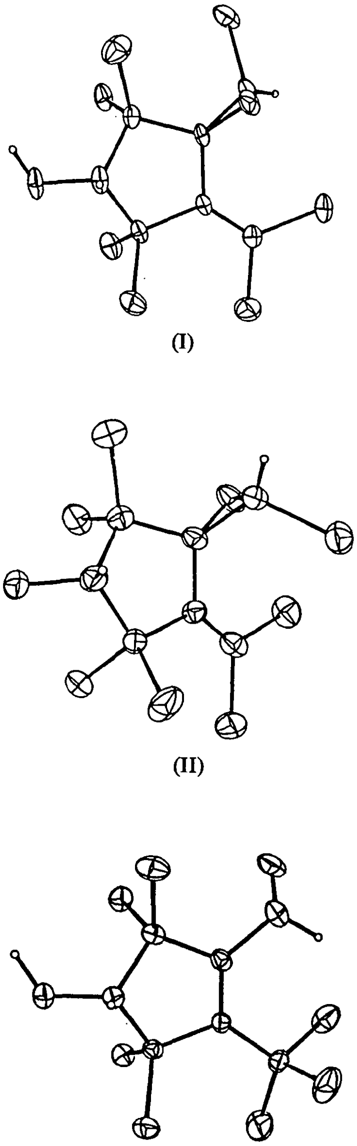

Fig. 2. *ORTEP* drawings of (I), (II) (molecule *A*) and (III) with thermal ellipsoids at 30% probability.

These geometrical prerequisites certainly favor the reaction from (I) to (III) but not from (II) to (III).

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Phosphorus–Nitrogen Compounds. I. Structure of 2,*cis*-4,*trans*-6,*trans*-8-Tetrachloro-2,4,6,8-tetrakis(diethylamino)cyclotetra(phosphazene)

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Abstract. $C_{16}H_{40}Cl_4N_8P_4$, $M_r = 610{\cdot}252$, monoclinic, $P2_1/c$, $a = 15{\cdot}374\,(5)$, $b = 9{\cdot}758\,(3)$, $c = 10{\cdot}117\,(3)$ Å, $\beta = 97{\cdot}41\,(2)°$, $V = 1505{\cdot}03\,(2)$ Å^3, $Z = 4$, $D_m = 2{\cdot}61$, $D_x = 2{\cdot}694$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 12{\cdot}505$ cm^{-1}, $F(000) = 1280$, $T = 293$ K, $R = 0{\cdot}042$ for 871 observed reflections. The structure consists of four chloro and four diethylamino groups connected to P atoms of the non-planar cyclotetra(phosphazene) ring.

Introduction. The investigation of cyclic phosphazenes has attracted great interest in their synthetic, spectroscopic and unusual structural properties and dramatic advances have been observed in this area during the past decade (Allcock, 1972; Shaw, 1980; Fincham, Hursthouse, Parkes, Shaw & Shaw, 1986; Krishnamurty & Woods, 1987).

Cyclophosphazenes are used in the production of phosphazene polymers for different purposes (Allcock, 1985) and some of them are thought to be useful as cancer chemotherapeutic agents (Chernov, Lytkina, Sergievskaya, Kropacheva, Parshina & Sventsitkaya, 1959; Huizen, 1984). A relationship has been observed between the structures of the cyclophosphazenes and cytostatic activity (van der Huizen, 1984) and for effective tumour growth inhibition, electron-donating groups (*e.g.* aziridine, pyrrolidine, primary and other secondary amines) in the P–N ring skeletons seem to be essential. The aminolyses of octachlorocyclotetra(phosphazene), $N_4P_4Cl_8$, with various primary and secondary alkylamines in different solvents, give partially or fully substituted aminotetra(phosphazenes), according to the reaction conditions (Contractor, Kılıç & Shaw, 1987; Katti & Krishnamurty, 1985).

The reaction in ether between $N_4P_4Cl_8$ and an excess of the diethylamine led to the isolation of tetrachlorotetrakisdiethylaminocyclotetra(phosphazene) which is the only major product (m.p. 409 K). Several types of isomerization, such as *cis-/trans-*, geminal-*cis-/trans-* and geminal-geminal can be expected for the structure of this compound.

The unknown isomer of $N_4P_4Cl_4(NEt_2)_4$ (m.p. 445 K) has been reported previously (Ray, Shaw & Smith, 1963), which is different from the title compound. A structure determination of the title compound was undertaken to permit a comparison of its structure with that of previously reported analogues.

Experimental. 240 mmol of freshly distilled anhydrous diethylamine in 50 cm^3 of anhydrous diethyl ether was cooled to 273 K and added dropwise to a stirred solution of 10 mmol $N_4P_4Cl_8$ in 200 cm^3 anhydrous diethyl ether cooled to 268 K. The reaction mixture was stirred for 3 h and then boiled under reflux for 24 h. After removal of diethylamine hydrochloride and of solvent the residue was subjected to column chromatography using tetrahydrofuran–dichloromethane mixture as eluant on silica gel to remove salt and coloured products. The resulting solid substance was crystallized from

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