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Acta Cryst. (1995). C51, 1209-1211

1,1-Dichloro-3,3,5,5-tetraphenyl- $1\lambda^4$,2,6, $3\lambda^5$, $5\lambda^5$ -selenadiazadiphosphorin

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(Received 3 May 1994; accepted 15 July 1994)

Abstract

The first X-ray structure of a six-membered ring containing the structural unit N-SeCl₂-N is presented. The heterocycle in the title compound (as the trichloromethane solvate), C25H22Cl2N2P2Se.2CHCl3, adopts a boat conformation with the C and Se atoms deviating from the P₂N₂ plane. The two Se-Cl bonds differ markedly. Disorder of one of the phenyl groups may be explained in terms of the crystal packing.

Comment

The reaction leading to the title compound presents a new method for the synthesis of cyclic metallophosphazenes (Seseke, 1986). The reaction of (I) with WF_6 and WCl₆ yields analogous products which have been characterized by NMR spectroscopy. Compounds of type (I) with one, two and three methylene groups bridging the two P atoms have been investigated by Appel & Ruppert (1974), who showed the possibility of transforming (I) into cyclic products.



The title compound, (II), crystallizes with two chloroform molecules in the asymmetric unit. The heterocycle adopts a boat conformation with Se and C(1) deviating [by 0.32 (1) and 0.64 (1) Å, respectively] from the P_2N_2 plane ($\sigma = 0.023 \text{ Å}$).

Taking into account the free electron pair, the Se coordination geometry can be described as trigonal bipyramidal with the lone pair and the two N atoms in the equatorial plane, while the Cl atoms occupy the axial positions. The Se-N bond lengths are shortened compared with an Se-N single bond. The two Se-Cl bonds differ by nearly 0.5 Å. Both P-N double bonds display typical values. The phenyl rings C11-C16 and C21-C26 are approximately parallel, the angle between them being $19.7(6)^{\circ}$.

Inspection of the crystal packing reveals that the disordered phenyl ring is surrounded by other disordered phenyl rings and chloroform molecules, while the ring C11'-C16' lies in the vicinity of the nearly parallel aromatic rings which restrict its degrees of freedom. Therefore, it seems obvious that the crystal packing allows different orientations of one phenyl group while keeping the other in a more fixed position.



Fig. 1. View of $C_{25}H_{22}Cl_2N_2P_2Se.2CHCl_3$ showing the labelling of the non-H atoms. Displacement ellipsoids are plotted at the 30% probability level.

Experimental

Crystal data

a 40
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Acta Crystallographica Section C ISSN 0108-2701 ©1995

C₂₅H₂₂Cl₂N₂P₂Se.2CHCl₃

Data collection						Cl3A	C13A 0.4533 (11) 0.2435 (11) 0.0262 (5) 0.430				0.436 (12)
Stoe four-circle diffractom-			$R_{\rm int} = 0.0736$			CIB CIIB	0.8989 (7)	0.1930 (1	B)	0.0695 (5)	0.133 (7)
eter			$\theta_{\rm max} = 25^{\circ}$			C12B	0.9963 (12)	0.0972 (7	7)	0.0119 (4)	0.304 (6)
$\omega/2\theta$ scans, profile fitting			$h = -12 \rightarrow 2$			C13 <i>B</i>	1.0675 (15)	0.2484 (1	11) -	-0.0112 (6)	0.426 (11)
(Cleg	g, 1981)		$k = 0 \rightarrow 18$			† Site occupancy factor = 0.55.‡ Site occupancy factor = 0.45.					
Absorption correction:			l = -24	$4 \rightarrow 24$							
ψ scans			3 standa	ard reflection	IS					•	
$T_{\min} = 0.36, T_{\max} = 0.41$ monitored every 100						Table 2. Selected geometric parameters (A, °)					
8144 measured reflections reflection					11.11.1	Se-N1		1.716 (9)	C21C	226	1.365 (15)
6084 independent renections			intensity decay: negligible			Se—N2		1.730 (8)	C21C	222	1.401 (15)
						Se-Cll		2.390 (4)	C22C	23 Ma	1.40(2)
[l > l]	$2\sigma(I)$					N1-P1		1.618 (9)	C24C	225	1.36 (2)
Refinement						N2—P2		1.603 (9)	C25-C	226	1.39 (2)
D.6	E^2		Δ.	- 0.002 - Å	-3	PICII PICI		1.770 (10)	C21'-	C22 C26'	1.40
Remember on F^- $B(E^2) = 0.1049$			$\Delta \rho_{\rm max} =$	= 0.903 e A	% -3	PI-CII'		1.817 (10)	C22'—	C23'	1.39
$R[F^{-} > 2\sigma(F^{-})] = 0.1048$ $mP(F^{2}) = 0.2524$			$\Delta \rho_{\min} =$	= -0.095 e	1 n: none	P2-C21''		1.768 (9)	C23'	-C24'	1.40
WR(r) = 0.2324 S = 1.278			Atomic	scattering f	n. none	P2C21'		1.768 (9)	C24'	-C25' -C26'	1.39
5 - 1.27	flections		from	Internation	al Tables	P2-C1		1.798 (9)	C21''-	-C21''	1.39
328 par	ameters		for C	rvstallooran	hv (1992	C11-C16		1.384 (14)	C21''-	C21''	1.39
w = 1/1	$r^{2}(F^{2}) \pm (0.146)$	$(P)^2$	Vol C Tables 4268 and			C11-C12		1.386 (14)	C21''-	C21''	1.40
where	$P = (F_{1}^{2} + 2F_{2})$	$(2^{2})/3$	6 1 1 4)			C12 - C13 C13 - C14		1.37 (2)	C21'' - C21'	-C21''	1.39
$(\Delta/\sigma)_{-}$	$\sim 1 - (1_0 + 21)$	<i>c </i>	0.1.1.4)			C14-C15		1.36 (2)	C21''-	-C21''	1.39
						C15-C16		1.37 (2)	CIA-4	C13A	1.60 (2)
Table 1 Fractional atomic coordinates and equivalent						CITCI2 CI1'C16'		1.373 (15)			1.03 (3)
isotronic displacement parameters $(Å^2)$						C12'-C13'		1.386 (15)	C1B	C13 <i>B</i>	1.60 (2)
isotropic displacement parameters (A)						C13'-C14'	,	1.37 (2)	C1 <i>B</i>	C1B	1.62 (2)
$U_{\rm eq} = (1/3) \Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$						C14'-C15'	,	1.37 (2)	CIB	CI2B	1.67(2)
	r	ν	-	7	Um		2	112.6 (4)	C11′	C12'_C13'	1191(11)
Se	0.09771 (9)	0.15020 (6) ().25122 (6)	0.0567 (4)	N1—Se—C	11	98.2 (3)	C14'-	-C13'-C12'	120.1 (12)
CI1	-0.0789 (3)	0.1253 (2) (0.3027 (2)	0.1031 (14)	N2—Se—C	11	97.6 (3)	C13'-	-C14'C15'	120.8 (12)
Cl2	0.2740 (3)	0.2343 (2) ().1843 (2)	0.0695 (9)	N1—Se—C	12	91.7 (3)	C14'-	-C15'C16'	120.2 (12)
N2	0.2149 (8)	0.1191 (5) ().3155 (4)	0.055 (2)	N2-Se-C	12 112	93.0 (3) 161.35 (12)	C11	$C_{10} = C_{13}$	119.5 (11)
P1	0.0890 (2)	-0.0268 (2	.) (0.20428 (14)	0.0450 (7)	PI-NI-S	e	124.0 (6)	C26	C21—P2	121.9 (8)
P2	0.2532 (2)	0.0220 (2) (0.33248 (14)	0.0493 (7)	P2N2S	e	124.1 (5)	C22—	C21P2	118.7 (9)
	0.1381 (8)	-0.0512 (0) () (0.2900 (5) 0.1594 (5)	0.048(3) 0.047(2)	NI-PI-C	11	109.6 (5)	C21-4	C22-C23	118.8 (12)
C12	0.2696 (11)	-0.0062 (9	ý (0.1290 (7)	0.083 (4)	C11-P1-C	C1	112.2 (5)	C24-	C23C25	119.9 (13)
C13	0.3516 (13)	-0.0338 (1	1) (0.0908 (8)	0.100 (5)	N1P1C	'11'	109.8 (5)	C24	C25—C26	120.9 (14)
C14 C15	0.3732 (13)	-0.1201(1 -0.1763(9	1) (1) (0.0834 (8) 0.1163 (7)	0.094 (5)	C11—P1—C	C11'	108.8 (5)	C21-4	C26C25	119.7 (12)
C16	0.2271 (11)	-0.1493 (8	i) (0.1529 (6)	0.067 (3)	$N_2 - P_2 - C_2$	21''	108.7 (5)	C22	-C21' - P2	124.8 (8)
C11′	-0.0575 (9)	-0.0847 (7) (0.1778 (5)	0.052 (3)	N2-P2-C	21'	108.7 (5)	C26'-	-C21'-P2	115.4 (8)
C12'	-0.0699(11)	-0.1668 (7	') (') (0.1983 (7) 0.1772 (7)	0.071 (4)	N2—P2—C	21	111.1 (5)	C23'-	-C22'C21'	120.1
C13	-0.2800(12)	-0.1698 (9) (0.1368 (7)	0.085 (4)	C21 [°] P2		111.2 (5)	C22	-C23 - C24 -C24' - C23'	120.0
C15′	-0.2676 (12)	-0.0881 (1	0) (0.1164 (7)	0.094 (5)	N2-P2-C	1	112.0 (4)	C24'-	-C25'-C26'	120.0
C16'	-0.1546 (9)	-0.0431 (8	6) (1) (0.1377 (6)	0.066 (3)	C21''P2-	C1	106.5 (5)	C25'-	-C26'C21'	120.1
C21 C22	0.4708 (10)	0.0620 (8) () (0.2881 (6)	0.073 (4)	$C21^{-}-P2^{-}$	-01	106.5 (5)	C21"-	-C21' - C21' - C21' - C21' - C21' - C21' - C21'' - C	120.2
C23	0.5850 (11)	0.0418 (1	1) (0.2689 (8)	0.100 (5)	P2C1P	1	113.5 (5)	C21''-	-C21''-P2	119.5 (7)
C24	0.6299 (12)	-0.0377 (1	0) (0.2733 (7)	0.083 (4)	C16-C11-	-C12	117.3 (11)	C21''-	-C21'' - C21''	119.9
C25	0.4476 (10)	-0.0846 (8	i) (0.3139 (6)	0.066 (3)	CI6CII	PI PI	122.4 (8)	C21 -	$-C_{21} - C_{21}$	120.0
C21'†	0.2582 (10)	0.0052 (7	ý (0.4166 (4)	0.062 (3)	C12-C11-	-C11	120.9 (13)	C21''-	C21''C21''	120.0
C22'†	0.3633 (11)	-0.0245 (1	1) (0.4605 (7)	0.115 (10)	C12-C13-	C14	120.9 (13)	C21''-	C21''C21''	119.9
$C_{23'}^{\dagger}$	0.3559 (20)	-0.0382(1 -0.0221(1	(4) (3) (0.5256(6)	0.160 (15)	C15-C14-	-C13	118.0 (13)	Cl3A-	-C1A $-C12A$	112.3 (16)
C25'†	0.1381 (19)	0.0076 (1	3) (0.5034 (8)	0.131 (12)	C14-C15-	-C10 -C11	121.3 (13)	CI3A-	-C1AC11A	111.0 (11)
C26′†	0.1455 (10)	0.0213 (1	1) (0.4382 (7)	0.108 (10)	C12'-C11'	′—C16′	121.9 (10)	Cl3 <i>B</i> —	-C1 <i>B</i> Cl1 <i>B</i>	115.4 (16)
C21''‡	0.2582 (10)	0.0052 (7) () (0.4166 (4) 0.4594 (7)	0.062 (3)	C12'-C11'	'—P1	120.3 (9)	C13B-	-C1 <i>B</i> C12 <i>B</i>	103.4 (13)
$C_{23''}^{\pm}$	0.2888 (20)	0.0740 (7	, (2) (0.5262 (6)	0.092 (11)	C16	11	117.8 (8)	UI <i>B</i>	-0180128	107.2 (12)
C24''‡	0.2765 (21)	-0.0210 (1	5) (0.5501 (4)	0.084 (13)	H atoms	of ordered	d phenyl ri	ngs an	d the methyl	ene group
C25''‡	0.2550 (22)	-0.0898 (1	1) (0.5071 (8)	0.118 (13)	were loca	ited by a d	ifference sy	nthesis	; others were	positioned
C26 ‡	0.2458 (17)	-0.0766 (6	99 (901 (0.4403(7) 0.1008(11)	0.098 (11) 0.169 (10)	with idea	al geometr	y. All Ha	toms v	were treated	with fixed
CIIA	0.6034 (6)	0.3214 (6	i) (0.1300 (4)	0.214 (3)	individua	l displacen	nent parame	eters [L	$U(\mathbf{H}) = 1.2U_{eq}$	(C)] using
Cl2A	0.6104 (11)	0.1452 (6	5) (0.1102 (6)	0.288 (6)	a riding	model wit	h C—H(ter	tiary (CH group) 0.9	98 A, C—

1210

H(secondary CH₂ group) 0.97 Å or C—H(aromatic) 0.93 Å. The disordered phenyl rings were refined as a rigid group applying the geometry of a regular hexagon with isotropic displacement parameters for the C atoms. The site occupancy factor of each of the two rings was refined as one additional variable by constraining the sum of the two values to 1.

Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993).

I thank Professor Dr H. W. Roesky, University of Göttingen, for providing the sample.

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Acta Cryst. (1995). C51, 1211-1213

3-(4-Butoxycarbonylphenyloxycarbonyl)xanthen-9-one

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(Received 4 July 1994; accepted 4 November 1994)

Abstract

The title compound, butyl 4-[(9-0x)(2-3y))carbonyloxy]benzoate, $C_{25}H_{20}O_6$, has been obtained as a product of the intramolecular cyclization of 2phenoxyterephthaloyl dichloride in the presence of butyl 4-hydroxybenzoate. The crystal and molecular structures are reported. The xanthone group is planar to within 0.084(1) Å. Molecules in the crystal are packed with planes of xanthone groups parallel to one another.

Comment

The title compound, (I), was obtained as a product (60% yield) of the reaction between 2-phenoxyterephthaloyl dichloride and butyl 4-hydroxybenzoate (mole ratio 2:1) in hot pyridine (2-phenoxyterephthaloyl dichloride was obtained by refluxing 2-phenoxyterephthalic acid with thionyl chloride and removing the excess thionyl chloride by distillation under reduced pressure; butyl 4-hydroxybenzoate was obtained by Fischer esterification of 4-hydroxybenzoic acid and *n*-butanol). The raw product, obtained after pouring the reaction mixture into an excess of ethanol, was purified by silica-gel chromatography, using chloroform as eluent, and finally recrystallized from chloroform-hexane solution (m.p. 403 K).



The proton NMR spectrum was not consistent with the structure of the expected product, i.e. bis(4butoxycarbonylphenyl)-2-phenoxyterephthalate, indicating the formation of a different compound. This seemingly unusual behaviour is actually consistent with previous observations (Kricheldorf, Schwarz & Ruhser, 1988). It was shown, in fact, that intramolecular cyclization of 2-phenoxyterephthaloyl dichloride (via Friedel-Crafts acylation) may also occur under rather mild conditions giving xanthone-3-carboxylic acid chloride. In our case, the formation of the title compound may be accounted for by intramolecular cyclization of 2phenoxyterephthaloyl dichloride followed by esterification with butyl 4-hydroxybenzoate. The X-ray analysis was undertaken for the definitive assignment of the molecular structure.

Bond lengths and angles in the molecule are all close to expected values. In particular, as far as the geometry of the xanthone moiety is concerned, the observed bond lengths and angles are in fair agreement with those previously reported for xanthone (Onuma, Iijima & Oonishi, 1990). A small, but probably statistically significant, spread of the bond lengths in the benzenoid rings of the xanthone group was observed, the shortest C— C distances being C17—C18 and C24—C25 [1.375 (1) and 1.377 (1) Å, respectively] and C13—C14 and C22— C23 [1.381 (1) and 1.380 (1) Å, respectively]. This is consistent with the central pyranoid ring having partial aromatic character (Lumbroso, Curé & Evers, 1986).

Lists of structure factors, anisotropic displacement parameters, Hatom coordinates and complete geometry have been deposited with the IUCr (Reference: SE1064). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.