$$C_{31}H_{27}NO_2P_2.C_2H_6O.2\cdot5H_2O$$

was $w = [\sigma^2(F_o) + gF_o^2]^{-1}$, where $g = 3\cdot37 \times 10^{-3}$. The final values of R and wR were 0·073 and 0·077, respectively. The largest shift/e.s.d. in the last cycle was 0·235. A final difference Fourier synthesis had a maximum peak of 0·54 and a minimum of $-0\cdot50$ e Å^{-3} and was featureless. All calculations were carried out using the *SHELXTL* program (Sheldrick, 1986) on a Data General Eclipse Model 30 computer. The scattering factors used in the *SHELXTL* program are the analytical form given in *International Tables for X-ray Crystallography* (1974). The final atomic coordinates are given in Table 1.* Selected bond lengths, bond angles and torsion angles are given in Table 2. The molecule with the atomic numbering scheme is shown in Fig. 1. The poorly defined solvent molecules are probably related to the decrease in the standard reflections during data collection. The result is a somewhat higher R value.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51791 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Related literature. The P—O distances of 1·474 (6) and 1·485 (7) Å are similar to the P—O distances in triphenylphosphine oxide (Brock, Schweizer & Dunitz, 1985) and related species (Bye, Schweizer & Dunitz, 1982). The various P—C, C—C and C—N distances are similar to those reported in other phosphinomethyl-pyridines by McNair & Pignolet (1986).

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Tetraphenylphosphonium Chloride Monohydrate, Tetraphenylphosphonium Bromide and Tetraphenylphosphonium Iodide

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Abstract. [C$_{24}$H$_{20}$P]Cl.H$_2$O, (1), $M_r = 392\cdot84$, triclinic, $P\bar{1}$, $a = 10\cdot837$ (3), $b = 10\cdot996$ (3), $c = 18\cdot399$ (5) Å, $\alpha = 77\cdot28$ (2), $\beta = 76\cdot45$ (2), $\gamma = 85\cdot69$ (2)°, $V = 2078\cdot5$ (8) Å^3, $Z = 4$, 2·0 molecules/asymmetric unit, $D_x = 1\cdot26$ g cm^{-3}, λ(Mo Kα) = 0·71073 Å, $\mu = 2\cdot7$ cm^{-1}, $F(000) = 824$, $T = 296$ K, $R_F = 5\cdot79\%$ for 3663 reflections and 391 parameters. The two independent cations are chemically indistinguishable, but produce two clearly resolved signals by ^{31}P solid-state NMR spectroscopy owing to small differences in the cation–anion interactions. Although all were prepared and recrystallized identically, only (1), the chloride, acquired adventitious water. Weak hydrogen bonding links the Cl$^-$ ions and the water molecules. [C$_{24}$H$_{20}$P]Br, (2), $M_r = 419\cdot27$, triclinic, $P\bar{1}$, $a = 10\cdot031$ (3), $b = 10\cdot688$ (3), $c =$ 10·678 (3) Å, $\alpha = 77\cdot45$ (2), $\beta = 83\cdot27$ (2), $\gamma = 71\cdot87$ (2)°, $V = 1060\cdot5$ (5) Å^3, $Z = 2$, $D_x = 1\cdot31$ g cm^{-3}, λ(Mo Kα) = 0·71073 Å, $\mu = 20\cdot0$ cm^{-1}, $F(000) = 428$, $T = 296$ K, $R_F = 5\cdot75\%$ for 2659 reflections and 198 parameters. [C$_{24}$H$_{20}$P]I, (3), $M_r = 466\cdot28$, tetragonal, $I\bar{4}$, $a = 11\cdot9785$ (14), $c = 6\cdot9809$ (9) Å, $V = 1001\cdot7$ (2) Å^3, $Z = 2$, $D_x = 1\cdot55$ g cm^{-3}, λ(Mo Kα) = 0·71073 Å, $\mu = 16\cdot63$ cm^{-1}, $F(000) = 464$, $T = 296$ K, $R_F = 3\cdot68\%$ for 624 reflections and 81 parameters. A curious feature of these three tetrahedral tetraphosphonium halides is that no two are isomorphous.

Experimental. For (1), colorless crystals from methylene chloride/hexane (0·36 × 0·26 × 0·30 mm); Nicolet R3m diffractometer with graphite monochromator; ω scans; lattice parameters from least-squares fit of 25 reflections (20 < 2θ < 25°); an absorption correction

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Table 1. *Atomic coordinates* (× 10⁴) *and equivalent isotropic thermal parameters* ($\mathring{A}^2$ × 10³) *for* (1)

	x	y	x	U*
Cl(1)	4327 (1)	1193 (1)	2463 (1)	49 (1)
Cl(2)	5309 (1)	3710 (1)	7797 (1)	55 (1)
P(1)	1612 (1)	2219 (1)	5217 (1)	33 (1)
P(2)	1573 (1)	2160 (1)	231 (1)	34 (1)
C(1)	3039 (3)	402 (3)	−464 (1)	43 (2)
C(2)	3806 −	−674	−477	50 (2)
C(3)	4031	−1405	204	47 (2)
C(4)	3490	−1060	898	50 (2)
C(5)	2722	16	911	46 (2)
C(6)	2497	747	230	35 (2)
C(11)	2062 (2)	3241 (3)	−1302 (2)	52 (2)
C(12)	1756	3631	−2014	67 (3)
C(13)	536	3463	−2095	73 (3)
C(14)	−379	2907	−1463	75 (3)
C(15)	−73	2517	−751	50 (2)
C(16)	1147	2685	−670	37 (2)
C(21)	3236 (3)	3045 (2)	911 (2)	41 (2)
C(22)	3861	3977	1078	51 (2)
C(23)	3691	5222	733	60 (2)
C(24)	2894	5535	221	65 (3)
C(25)	2269	4603	53	55 (2)
C(26)	2439	3358	398	36 (2)
C(31)	−346 (3)	699 (2)	1224 (2)	54 (2)
C(32)	−1525	526	1735	66 (3)
C(33)	−2204	1545	1982	69 (3)
C(34)	−1704	2735	1719	64 (2)
C(35)	−525	2907	1208	51 (2)
C(36)	154	1889	961	39 (2)
C(1')	3109 (3)	473 (3)	4518 (1)	40 (2)
C(2')	3847	−621	4507	48 (2)
C(3')	4011	−1390	5191	47 (2)
C(4')	3437	−1065	5886	54 (2)
C(5')	2699	29	5897	46 (2)
C(6')	2534	798	5213	34 (2)
C(11')	2155 (2)	3396 (3)	3701 (2)	54 (2)
C(12')	1899	3782	2976	65 (3)
C(13')	722	3553	2856	74 (3)
C(14')	−200	2937	3462	73 (3)
C(15')	56	2550	4187	56 (2)
C(16')	1234	2780	4307	37 (2)
C(21')	2264 (3)	4640 (3)	5109 (2)	53 (2)
C(22')	2878	5557	5299	66 (3)
C(23')	3697	5218	5797	58 (2)
C(24')	3903	3962	6104	51 (2)
C(25')	3289	3045	5914	44 (2)
C(26')	2469	3384	5417	36 (2)
C(31')	−334 (3)	748 (2)	6169 (2)	54 (2)
C(32')	−1517	561	6675	63 (2)
C(33')	−2202	1567	6935	65 (3)
C(34')	−1704	2759	6690	61 (2)
C(35')	−522	2946	6184	47 (2)
C(36')	163	1940	5924	37 (2)
O(1)	4018 (3)	1322 (3)	7477 (2)	72 (2)
O(2)	5402 (4)	3471 (4)	2950 (2)	80 (2)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. *Atomic coordinates* (× 10⁴) *and equivalent isotropic thermal parameters* ($\mathring{A}^2$ × 10³) *for* (2)

	x	y	z	U*
Br	621·1 (7)	2554·3 (7)	1223·2 (7)	51·1 (3)
Br'	669 (6)	5744 (6)	1666 (5)	97 (3)
P	5645 (2)	2636 (1)	3421 (1)	45·2 (6)
C(1)	3866 (4)	2826 (4)	5571 (3)	58 (3)
C(2)	2555	3193	6233	69 (3)
C(3)	1351	3356	5605	74 (3)
C(4)	1458	3251	4315	69 (3)
C(5)	2769	2984	3653	58 (3)
C(6)	3972	2822	4281	46 (2)
C(7)	7212 (4)	3136 (3)	5099 (4)	65 (3)
C(8)	8080	2748	6131	82 (4)
C(9)	8675	1389	6628	93 (4)
C(10)	8403	419	6093	90 (4)
C(11)	7535	808	5061	65 (3)
C(12)	6940	2166	4563	49 (2)
C(13)	5140 (4)	599 (4)	2466 (4)	65 (3)
C(14)	5485	−361	1688	82 (4)
C(15)	6740	−574	936	82 (4)
C(16)	7651	175	963	74 (3)
C(17)	7307	1135	1741	63 (3)
C(18)	6051	1347	2492	49 (2)
C(19)	4397 (3)	5130 (4)	1977 (4)	59 (3)
C(20)	4413	5287	1076	73 (3)
C(21)	5690	6504	581	76 (4)
C(22)	6951	5563	986	68 (3)
C(23)	6935	4407	1887	60 (3)
C(24)	5659	4190	2383	48 (2)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3. *Atomic coordinates* (× 10⁴) *and equivalent isotropic thermal parameters* ($\mathring{A}^2$ × 10³) *for* (3)

	x	y	z	U*
I	0	0	0	78 (1)
P	0	5000	2500	28 (1)
C(1)	1007 (3)	4325 (3)	978 (6)	34 (1)
C(2)	615 (4)	3556 (5)	−334 (8)	52 (2)
C(3)	1349 (5)	3024 (5)	−1586 (8)	57 (2)
C(4)	2464 (5)	3298 (5)	−1546 (8)	55 (2)
C(5)	2860 (4)	4049 (4)	−222 (14)	57 (2)
C(6)	2146 (4)	4564 (4)	1074 (8)	44 (1)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4. *Bond lengths* ($\mathring{A}$) *and angles* (°) *for* (1)

P(1)–C(6')	1·790 (3)	Cl(1)···O(1)	3·177 (3)
P(1)–C(16')	1·783 (4)	Cl(1)···O(2)	3·216 (3)
P(1)–C(26')	1·786 (4)	Cl(2)···O(1)	3·289 (3)
P(1)–C(36')	1·787 (3)	Cl(2)···O(2)	3·218 (3)
P(2)–C(6)	1·785 (3)	P(1)···Cl(1)	5·534 (2)
P(2)–C(16)	1·787 (4)	P(2)···Cl(1)	5·500 (2)
P(2)–C(26)	1·792 (3)	P(2)···Cl(2)	5·342 (2)
P(2)–C(36)	1·783 (3)		

C(6')–P(1)–C(16')	109·8 (2)	P(2)–C(16)–C(11)	119·2 (1)
C(6')–P(1)–C(26')	110·8 (2)	P(2)–C(16)–C(15)	120·8 (1)
C(16')–P(1)–C(26')	108·8 (2)	P(2)–C(26)–C(21)	119·4 (1)
C(6')–P(1)–C(36')	109·7 (1)	P(2)–C(26)–C(25)	120·5 (1)
C(16')–P(1)–C(36')	108·4 (2)	P(2)–C(36)–C(31)	120·8 (1)
C(26')–P(1)–C(36')	109·3 (2)	P(2)–C(36)–C(35)	118·9 (1)
C(6)–P(2)–C(16)	109·8 (2)	P(1)–C(6')–C(1')	119·5 (1)
C(6)–P(2)–C(26)	111·1 (1)	P(1)–C(6')–C(5')	120·5 (1)
C(16)–P(2)–C(26)	108·7 (1)	P(1)–C(16')–C(11')	119·2 (1)
C(6)–P(2)–C(36)	109·6 (1)	P(1)–C(16')–C(15')	120·7 (1)
C(16)–P(2)–C(36)	108·6 (2)	P(1)–C(26')–C(21')	119·8 (1)
C(26)–P(2)–C(36)	109·0 (2)	P(1)–C(26')–C(25')	120·1 (1)
P(2)–C(6)–C(1)	119·4 (1)	P(1)–C(36')–C(31')	120·5 (1)
P(2)–C(6)–C(5)	120·6 (1)	P(1)–C(36')–C(35')	119·3 (1)

was not necessary; $2\theta_{max} = 48°$ ($h = \pm 13$, $k = \pm 13$, $l = +22$); standard reflections $\overline{6}20$, $\overline{1}60$, $0,1,10$ (≤2%). 6755 reflections collected, 6525 independent ($R_{int} = 0·7\%$), 3663 observed with $F_o > 5\sigma(F_o)$, 2862 unobserved reflections. Direct-methods (*SOLV*) structure solution; least-squares refinement on 391 parameters; all non-H atoms anisotropic, H atoms idealized and updated (C—H = 0·96 Å, $U = 1·2U$ of attached C). $R_F = 5·79\%$, $wR_F = 6·12\%$, $S = 1·30$, $w^{-1} = \sigma^2(F_o) + gF_o^2$, $g = 0·001$; $(\Delta/\sigma)_{max} = 0·075$; $\Delta\rho_{max} = 0·29$, $\Delta\rho_{min} = -0·52$ e Å⁻³; atomic scattering factors from *International Tables for X-ray Crystallography* (1974); *SHELXTL* computer program (Sheldrick, 1984).

For (2), colorless crystals from methylene chloride/hexane (0·18 × 0·18 × 0·30 mm); lattice parameters

Table 5. Bond lengths (Å) and angles (°) for (2)

P—C(6)	1·792 (4)	P—C(12)	1·768 (5)
P—C(18)	1·787 (5)	P—C(24)	1·788 (4)
P···Br (2—x, 1—y, 1—z)	5·835 (2)	P···Br	5·244 (3)
C(6)—P—C(12)	107·7 (2)	C(6)—P—C(18)	112·0 (2)
C(12)—P—C(18)	107·7 (2)	C(6)—P—C(24)	109·6 (2)
C(12)—P—C(24)	110·5 (2)	C(18)—P—C(24)	109·3 (2)
P—C(6)—C(1)	118·7 (1)	P—C(6)—C(5)	121·0 (1)
P—C(12)—C(7)	120·3 (1)	P—C(12)—C(11)	119·0 (1)
P—C(18)—C(13)	122·3 (1)	P—C(18)—C(17)	117·6 (1)
P—C(24)—C(19)	120·0 (1)	P—C(24)—C(23)	119·7 (1)

Table 6. Bond lengths (Å) and angles (°) for (3)

P—C(1)	1·799 (4)	C(1)—P—C(1a)	110·4 (1)
P—C(1a)	1·799 (4)	C(1)—P—C(1b)	107·6 (3)
P—C(1b)	1·799 (4)	C(1a)—P—C(1b)	110·4 (1)
P—C(1c)	1·799 (4)	C(1)—P—C(1c)	110·4 (1)
C(1)—C(2)	1·382 (7)	C(1a)—P—C(1c)	107·6 (3)
C(1)—C(6)	1·395 (6)	C(1b)—P—C(1c)	110·4 (1)
C(2)—C(3)	1·394 (8)	P—C(1)—C(2)	117·6 (3)
C(3)—C(4)	1·376 (9)	P—C(1)—C(6)	122·4 (3)
C(4)—C(5)	1·374 (10)	C(2)—C(1)—C(6)	120·1 (4)
C(5)—C(6)	1·390 (9)	C(1)—C(2)—C(3)	120·4 (5)
P···I	6·238 (1)	C(2)—C(3)—C(4)	119·4 (5)
		C(3)—C(4)—C(5)	120·4 (5)
		C(4)—C(5)—C(6)	121·0 (5)
		C(1)—C(6)—C(5)	118·7 (5)

Table 7. Inter-phenyl-ring torsional angles (°) for (1), (2) and (3) (centroids identified by ipsoid carbon atom)

(1) Molecule A

	C(6)	C(16)	C(26)
C(6)			
C(16)	70·6		
C(26)	59·8	86·5	
C(36)	56·5	100·0	108·4

(1) Molecule B

	C(6')	C(16')	C(26')
C(6')			
C(16')	75·1		
C(26')	64·8	77·6	
C(36')	58·1	91·2	102·1

(2)

	C(6)	C(12)	C(18)
C(6)			
C(12)	100·0		
C(18)	48·0	78·6	
C(24)	114·9	114·3	108·8

(3)

	C(1a)	C(1b)
C(1a)		
C(1b)	63·4	
C(1c)	83·9	63·4

from least-squares fit of 25 reflections ($20 < 2\theta < 25°$); empirical absorption correction (6 reflections, 216 data), $2\theta_{max} = 53°$ ($h = \pm13$, $k = \pm14$, $l = +14$); standard reflections $\overline{6}11$, $\overline{3}51$, $\overline{2}05$. 4651 reflections collected, 4404 independent ($R_{int} = 1·8\%$), 2659 observed with $F_o > 5\sigma(F_o)$, 1745 unobserved reflections. Least-squares refinement on 198 parameters; all non-H atoms anisotropic, H atoms idealized and updated (C—H = 0·96 Å, $U = 1·2$ U of attached C); disordered Br⁻ ion at two sites: Br at 84% occupancy, Br' at 16%; $R_F = 5·75\%$, $wR_F = 8·33\%$, $S = 1·37$, $w^{-1} = \sigma^2(F_o) + gF_o^2$, $g = 0·0002$; $(\Delta/\sigma)_{max} = 0·022$; $\Delta\rho_{max} = 0·72$, $\Delta\rho_{min} = -0·48$ e Å⁻³.
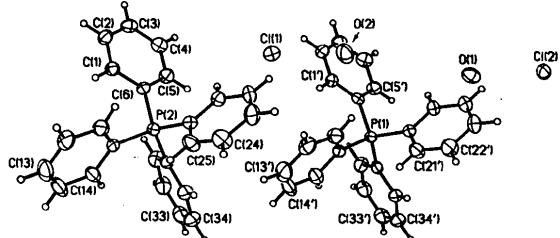
Fig. 1. Molecular structure and labeling scheme for (1).
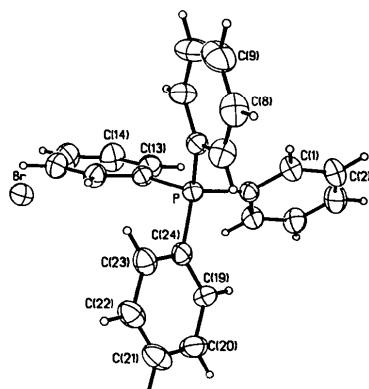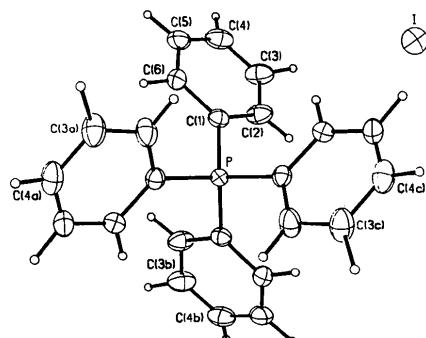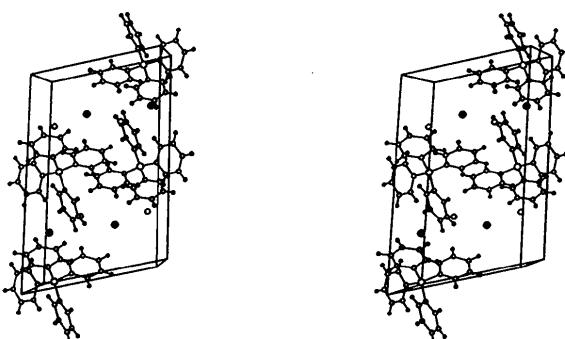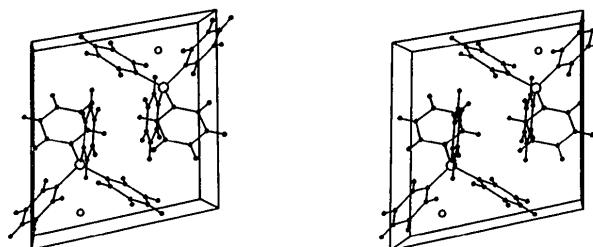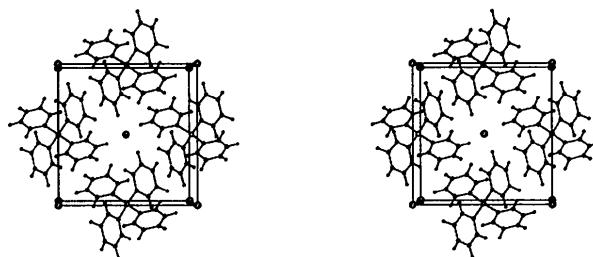
Fig. 2. Molecular structure and labeling scheme for (2). The Br⁻ ion is disordered at two sites; only the major-occupancy site (84%) is depicted.

Fig. 3. Molecular structure and labeling scheme for (3).

Fig. 4. Unit-cell packing diagram for (1) as viewed down the a axis.

Fig. 5. Unit-cell packing diagram for (2) as viewed down the c axis.

Fig. 6. Unit-cell packing diagram for (3) as viewed down the a axis.

For (3), yellow crystals from methylene chloride/hexane $(0.26 \times 0.30 \times 0.36$ mm); lattice parameters from least-squares fit of 25 reflections $(20 < 2\theta < 25°)$; empirical absorption correction (6 reflections, 216 data); $2\theta_{max} = 48°$ $(h = +15, k = +15, l = +9)$; standard reflections 222, 123, 321 $(\leq 1\%)$. 675 reflections collected, 667 independent $(R_{int} = 2.7\%)$, 624 observed with $F_o > 5\sigma(F_o)$, 43 unobserved reflections. Least-squares refinement on 81 parameters; all non-H atoms

anisotropic, H atoms were refined $(C-H = 0.96 Å)$. $R_F = 3.68\%$, $wR_F = 5.63\%$, $S = 1.28$, $w^{-1} = \sigma^2(F_o) + gF_o^2$, $g = 0.001$; $(\Delta/\sigma)_{max} = 0.044$; $\Delta\rho_{max} = 0.55$, $\Delta\rho_{min} = -0.28$ e Å^{-3}.

Atomic coordinates and equivalent isotropic thermal parameters for (1), (2), and (3) are given in Tables 1, 2 and 3, respectively.* Bond lengths and angles for (1) are given in Table 4, for (2) in Table 5, and for (3) in Table 6. Phenyl-ring torsional angles for (1), (2) and (3) are given in Table 7. Figs. 1, 2 and 3 show the labeled molecular structures for (1), (2) and (3), respectively. Unit-cell packing diagrams for (1), (2) and (3) are shown in Figs. 4, 5 and 6, respectively.

Related literature. To our knowledge, there has been only one previous report of the structure of a tetraphenyl cation halide of a group-15 element: tetraphenylphosphonium dibromoiodide (Muller, 1979).

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Structure of 8-Methoxy-5-methyl-3,4-cis-diphenylisochroman-1-one

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Abstract. $C_{23}H_{20}O_3$, $M_r = 344.4$, monoclinic, $P2_1/c$, $a = 6.254$ (6), $b = 18.266$ (3), $c = 15.536$ (3) Å, $\beta = 93.35$ (1)°, $V = 1771.7$ (4) Å^3, $Z = 4$, $D_x = 1.29$ g cm^{-3}, $\lambda(Mo K\alpha) = 0.71073$ Å, $\mu = 0.79$ cm^{-1}, $F(000) = 728$, $T = 295$ K, final $R = 0.044$ for 1023 observed reflections. The bond distances are C=O $= 1.196$ (11), O—C (cyclic, av.) $= 1.405$ (10), O—C (benz.) $= 1.364$ (8), O—CH$_3 = 1.417$ (7), C—C (benz., av) $= 1.382$ (12), C—C (aliph.—aliph.) $= 1.535$ (6) and C—C (benz.—aliph., av.) $= 1.512$ (9) Å. The X-ray structure shows the half-boat conformation of the six-membered lactone ring and confirms the cis disposition of the 3- and 4-phenyl groups.

Experimental. The title compound (1) was prepared by an intramolecular addition of the lithio salt obtained by the reaction of 6-benzyl-α-lithio-5-methyl-o-anisonitrile and benzaldehyde at 195 K to room temperature (18 h)

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