The Crystal Structures of Four 2,2-R,R'-4-Benzyl-4-phenylbutanoic 1,4-Lactones: (I) R=R'=H; (II) R=CH₃, R'=H, Z-Configuration; (III) R=H, R'=CH₃, E-Configuration; and (IV) R=R'=CH₃, All at −40°C
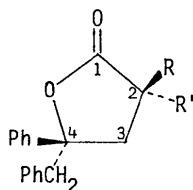
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The structures of four 1,4-lactones, all substituted at the 4-position with a phenyl and benzyl group, and successively substituted with from zero to two methyl groups at the 2-position, have been determined by X-ray diffraction methods. In the order listed in the title, these compounds are abbreviated as BPL, Z-MBPL, E-MBPL, MMBPL. The intensity data were collected on a Syntex diffractometer with the respective crystals cooled to − 40 °C. Positional and thermal parameters of both non-hydrogen (aniso-tropic) and hydrogen (isotropic) atoms were refined by full-matrix least squares. The conventional *R* index in each case was less than 4 %, except for *E*-MBPL where the presence of a small amount of the *Z*-isomer as a contaminant in the crystal resulted in a somewhat higher *R* value of 4·8 %. The four lactone rings exist in the 'envelope' conformation, the C–(CO)–O–C moiety being nearly planar and the carbon atom in the 3-position deviating considerably from this plane. The benzyl and phenyl groups are found in equatorial and axial positions, respectively, in BPL, *E*-MBPL (methyl group is equatorial), and MMBPL, but this reverses in the case of *Z*-MBPL in order to place the lone methyl group in an equatorial position. Increasing substitution of –CH₃ for –H on the carbon atom at the 2-position produces a shift in this atom away from the center of the lactone ring.

Introduction

2,2-R,R'-4-Benzyl-4-phenylbutanoic 1,4-lactones reported herein have the general formula

and have the following substitutions: R=R'=H (compound abbreviated as BPL); R=CH₃ and R'=H, Z-configuration (Z-MBPL); R=H and R'=CH₃, E-configuration (E-MBPL); R=R'=CH₃ (MMBPL). All

of the compounds are synthetic intermediates in the production of substituted alkyl chlorides which in turn have been used in a systematic study of Friedel–Crafts cycloalkylation reactions. The two diastereomer-ic pairs of enantiomers, Z-MBPL and E-MBPL, are of particular importance because they yield, as a result of stereospecific reactions, the individual diastereomer-ic alkyl chlorides which behave differently under Friedel–Crafts conditions. These two lactones were pre-pared by a non-stereoselective reaction, and although the configuration of each could be deduced from their chemical and physical properties, a definite assignment could not be made (Khalaf & Roberts, 1973). The other two lactones, BPL (Chayasirisophon, 1975) and MMBPL (Low, 1970), were used as part of the same general study and serve here to compare the geome-tries of the four lactones.

Table 1. *Crystal data*

	BPL	Z-MBPL	E-MBPL	MMBPL
Formula	C₁₇H₁₆O₂	C₁₈H₁₈O₂	C₁₈H₁₈O₂	C₁₉H₂₀O₂
F.W.	252·31	266·34	266·34	280·37
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$P2_1$

Unit-cell parameters at −40°C, Mo Kα, λ=0·71069 Å

	BPL	Z-MBPL	E-MBPL	MMBPL
a	10·149 (1) Å	9·982 (2) Å	8·320 (1) Å	16·506 (4) Å
b	9·537 (1)	19·395 (2)	13·958 (2)	7·651 (2)
c	14·305 (2)	7·516 (1)	6·692 (1)	6·057 (2)
α			98·00 (2)°	
β	107·92 (1)°	96·79 (1)°	103·17 (1)	98·37 (3)°
γ			79·63 (1)	
V	1317·4 Å³	1445·0 Å³	740·4 Å³	756·8 Å³
Z	4	4	2	2
Dₓ	1·272 g cm⁻³	1·224 g cm⁻³	1·195 g cm⁻³	1·230 g cm⁻³

Experimental

Crystals of the four compounds were obtained by slow evaporation of methanol solutions. Preliminary unit-cell parameters and space-group information were obtained from oscillation and Weissenberg photographs. The lattice parameters at $-40\,^\circ$C were refined by least squares using Bragg angles measured with the centering routine associated with the Syntex $P2_1$ diffractometer. At least 49 reflections ($18 < 2\theta < 28^\circ$) were included in each refinement. Table 1 summarizes the crystal data for the four lactones.

Intensity data were collected on a Syntex diffractometer with the crystal in each case maintained at

Table 2. *Details of intensity measurements and structure refinements*

	BPL	Z-MBPL	E-MBPL	MMBPL
(a) Data collected at $-40\,^\circ$C, Syntex $P2_1$ diffractometer, $1\cdot0^\circ$ ω-scans, Mo $K\alpha$ radiation				
Crystal dimensions	Sphere, $r=0\cdot17$ mm	Sphere, $r=0\cdot20$ mm	Plate, $0\cdot24\times0\cdot41\times0\cdot53$ mm	Plate, $0\cdot21\times0\cdot55\times0\cdot62$ mm
2θ range	4–50°	4–50°	4–55°	4–55°
Reflections measured	2323	2531	3404	1860

(b) Full-matrix least-squares refinement of all positional and thermal (anisotropic for non-hydrogen atoms; isotropic for hydrogen atoms) parameters

	BPL	Z-MBPL	E-MBPL	MMBPL
Reflections refined $I > 2\sigma(I)$	1824	1945	2712	1762
Variables	236	253	253	269
$R = \sum||F_o| - |F_c||/\sum|F_o|$	0·033	0·038	0·048	0·035
Largest parameter shift in final cycle	$0\cdot1\sigma$	$0\cdot3\sigma$	$0\cdot3\sigma$	$0\cdot1\sigma$
Largest peak in final difference Fourier map	0·09 e Å^{-3}	0·10 e Å^{-3}	0·46 e Å^{-3}	0·12 e Å^{-3}

Table 3. *Positional and thermal parameters for* 4-benzyl-4-phenylbutanoic 1,4-lactone *(BPL)*

Estimated standard deviations are given in parentheses.

(a) Non-hydrogen atoms (parameters $\times 10^4$)

Anisotropic thermal parameters are in the form $\exp[-2\pi^2(h^2a^{*2}U_{11}+\ldots+klb^*c^*U_{23})]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	6587 (1)	1452 (1)	9817 (1)	384 (5)	378 (5)	350 (5)	16 (5)	130 (3)	39 (4)
O(2)	5865 (1)	842 (1)	1075 (1)	606 (7)	573 (7)	386 (6)	−95 (5)	187 (5)	36 (6)
C(1)	5677 (2)	1512 (2)	331 (1)	420 (8)	418 (8)	366 (8)	−77 (7)	145 (7)	−65 (8)
C(2)	4510 (2)	2479 (2)	9839 (1)	406 (10)	587 (11)	532 (11)	9 (9)	203 (8)	−14 (9)
C(3)	4653 (2)	2695 (2)	8828 (2)	361 (9)	501 (11)	444 (9)	26 (8)	84 (7)	25 (9)
C(4)	6206 (1)	2434 (1)	8989 (1)	351 (8)	374 (8)	297 (7)	26 (7)	77 (6)	44 (6)
C(5)	6447 (2)	1665 (2)	8113 (1)	424 (9)	387 (9)	328 (8)	−44 (8)	79 (7)	−34 (7)
C(11)	7056 (1)	3760 (1)	9291 (1)	309 (7)	340 (8)	323 (7)	60 (6)	117 (6)	1 (6)
C(12)	7853 (2)	4008 (1)	252 (1)	402 (9)	379 (9)	344 (8)	31 (7)	71 (7)	34 (7)
C(13)	8582 (2)	5247 (2)	517 (1)	432 (9)	437 (9)	403 (9)	7 (8)	45 (7)	−46 (8)
C(14)	8540 (2)	6256 (2)	9824 (1)	427 (9)	359 (9)	546 (10)	−22 (8)	186 (8)	−53 (8)
C(15)	7753 (2)	6027 (2)	8862 (1)	560 (10)	355 (9)	445 (9)	27 (8)	240 (8)	39 (8)
C(16)	7014 (2)	4797 (2)	8596 (1)	472 (9)	390 (9)	315 (8)	65 (7)	127 (7)	6 (7)
C(21)	7922 (2)	1281 (1)	8217 (1)	460 (8)	320 (8)	280 (8)	−12 (7)	117 (6)	−79 (6)
C(22)	8499 (2)	53 (2)	8685 (1)	635 (12)	375 (10)	515 (10)	39 (9)	278 (9)	34 (8)
C(23)	9850 (2)	9693 (2)	8781 (1)	699 (13)	477 (11)	529 (10)	206 (10)	238 (9)	59 (9)
C(24)	653 (2)	540 (2)	8402 (1)	463 (11)	581 (11)	485 (10)	79 (9)	146 (8)	−161 (9)
C(25)	92 (2)	1758 (2)	7928 (1)	522 (10)	458 (10)	523 (10)	−44 (9)	260 (9)	−103 (8)
C(26)	8745 (2)	2127 (2)	7839 (1)	531 (10)	353 (9)	380 (8)	18 (8)	187 (7)	−31 (7)

(b) Hydrogen atoms (parameters $\times 10^3$)

	x	y	z	U_{iso}		x	y	z	U_{iso}
H(2A)	361 (2)	205 (2)	983 (1)	54 (5)	H(14)	908 (2)	714 (2)	3 (1)	49 (4)
H(2B)	466 (2)	337 (2)	25 (1)	59 (5)	H(15)	771 (2)	673 (2)	837 (1)	49 (5)
H(3A)	409 (2)	197 (2)	835 (1)	45 (4)	H(16)	643 (2)	463 (2)	790 (1)	42 (4)
H(3B)	439 (2)	364 (2)	855 (1)	43 (4)	H(22)	795 (2)	947 (2)	894 (1)	50 (5)
H(5A)	606 (1)	227 (2)	754 (1)	39 (4)	H(23)	24 (2)	884 (2)	913 (1)	59 (5)
H(5B)	587 (2)	81 (2)	801 (1)	40 (4)	H(24)	159 (2)	30 (2)	846 (1)	47 (4)
H(12)	791 (2)	331 (2)	74 (1)	48 (5)	H(25)	65 (2)	233 (2)	765 (1)	45 (4)
H(13)	915 (2)	538 (2)	119 (1)	47 (4)	H(26)	837 (2)	300 (2)	751 (1)	42 (4)

Table 4. *Positional and thermal parameters for (Z)-2-methyl-4-benzyl-4-phenylbutanoic 1,4-lactone (Z-MBPL)*

(a) Non-hydrogen atoms (parameters × 10⁴)

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	4064 (1)	7269 (1)	7579 (1)	409 (6)	359 (6)	400 (6)	−37 (5)	−35 (5)	−10 (5)
O(2)	3471 (1)	6173 (1)	7152 (2)	791 (9)	463 (7)	547 (8)	−199 (7)	−8 (7)	−39 (6)
C(1)	4230 (2)	6584 (1)	7913 (2)	591 (11)	382 (10)	341 (9)	−30 (9)	84 (8)	1 (8)
C(2)	5424 (2)	6468 (1)	9301 (2)	641 (12)	411 (10)	340 (9)	86 (9)	60 (9)	29 (8)
C(3)	6207 (2)	7132 (1)	9230 (3)	474 (11)	430 (10)	375 (10)	94 (8)	−56 (9)	−31 (8)
C(4)	5123 (2)	7670 (1)	8621 (2)	354 (8)	368 (9)	355 (9)	21 (7)	−49 (7)	−54 (7)
C(5)	4533 (2)	7979 (1)	247 (2)	498 (11)	424 (10)	358 (10)	42 (9)	−10 (8)	−20 (8)
C(6)	6197 (3)	5809 (1)	9037 (3)	887 (17)	446 (12)	531 (14)	203 (12)	101 (13)	54 (10)
C(11)	5580 (2)	8224 (1)	7416 (2)	339 (9)	334 (9)	398 (9)	19 (7)	18 (7)	−69 (7)
C(12)	4857 (2)	8394 (1)	5794 (2)	439 (10)	438 (10)	425 (10)	−59 (9)	−23 (8)	2 (8)
C(13)	5285 (2)	8920 (1)	4747 (3)	707 (14)	484 (11)	467 (12)	−39 (10)	63 (10)	49 (9)
C(14)	6442 (2)	9275 (1)	5295 (3)	712 (14)	495 (11)	660 (14)	−131 (11)	197 (12)	18 (11)
C(15)	7166 (2)	9114 (1)	6902 (3)	565 (13)	595 (14)	870 (17)	−239 (11)	66 (12)	−27 (12)
C(16)	6748 (2)	8590 (1)	7969 (3)	513 (12)	567 (12)	585 (13)	−79 (10)	−93 (10)	−30 (10)
C(21)	3334 (2)	8440 (1)	9791 (2)	476 (10)	414 (10)	290 (8)	85 (8)	59 (7)	−8 (7)
C(22)	2038 (2)	8173 (1)	9556 (2)	540 (12)	599 (12)	374 (10)	29 (11)	106 (8)	−43 (9)
C(23)	935 (2)	8601 (1)	9148 (3)	478 (13)	1066 (20)	419 (11)	158 (13)	76 (9)	−145 (12)
C(24)	1120 (3)	9297 (2)	8962 (3)	789 (18)	1025 (20)	407 (12)	551 (17)	26 (11)	−81 (12)
C(25)	2390 (3)	9570 (1)	9177 (3)	1037 (20)	533 (13)	476 (12)	331 (14)	135 (12)	35 (10)
C(26)	3493 (2)	9145 (1)	9593 (2)	655 (13)	451 (11)	467 (11)	80 (11)	109 (10)	−14 (9)

(b) Hydrogen atoms (parameters × 10³)

	x	y	z	U_{iso}		x	y	z	U_{iso}
H(2)	501 (2)	643 (1)	44 (2)	47 (5)	H(13)	477 (2)	903 (1)	362 (3)	73 (7)
H(3A)	673 (2)	726 (1)	41 (2)	55 (5)	H(14)	676 (2)	965 (1)	453 (3)	64 (6)
H(3B)	687 (2)	710 (1)	832 (2)	37 (4)	H(15)	800 (2)	938 (1)	738 (3)	75 (6)
H(5A)	527 (2)	823 (1)	94 (2)	44 (5)	H(16)	725 (2)	849 (1)	915 (3)	67 (6)
H(5B)	426 (2)	759 (1)	105 (2)	58 (5)	H(22)	195 (2)	768 (1)	965 (2)	49 (5)
H(6A)	693 (2)	570 (1)	8 (3)	62 (6)	H(23)	3 (2)	839 (1)	904 (3)	67 (6)
H(6B)	554 (2)	543 (1)	896 (3)	75 (7)	H(24)	33 (2)	957 (1)	871 (3)	82 (7)
H(6C)	657 (2)	582 (1)	793 (3)	64 (6)	H(25)	250 (2)	6 (1)	906 (3)	67 (6)
H(12)	405 (2)	814 (1)	540 (2)	48 (5)	H(26)	437 (2)	933 (1)	976 (2)	51 (5)

Table 5. *Positional and thermal parameters for (E)-2-methyl-4-benzyl-4-phenylbutanoic 1,2-lactone (E-MBPL)*

(a) Non-hydrogen atoms (parameters × 10⁴)

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	4987 (1)	6701 (1)	4722 (1)	536 (6)	467 (6)	311 (5)	−147 (5)	78 (4)	18 (4)
O(2)	3796 (2)	6024 (1)	6698 (2)	792 (9)	668 (8)	364 (6)	−180 (6)	179 (5)	83 (5)
C(1)	3782 (2)	6247 (1)	5024 (2)	490 (9)	358 (7)	356 (8)	−39 (6)	141 (6)	8 (6)
C(2)	2515 (2)	6119 (1)	3047 (2)	504 (9)	471 (9)	425 (8)	−111 (7)	106 (7)	51 (7)
C(3)	3513 (2)	6152 (1)	1446 (2)	582 (10)	448 (9)	323 (8)	−196 (7)	178 (7)	−5 (6)
C(4)	4761 (2)	6844 (1)	2538 (2)	487 (8)	382 (7)	291 (7)	−109 (6)	106 (6)	9 (6)
C(5)	6479 (2)	6534 (1)	1974 (3)	535 (9)	365 (8)	443 (9)	−45 (7)	178 (7)	9 (7)
C(7)	1667 (3)	5230 (1)	2886 (3)	562 (11)	577 (11)	567 (11)	−219 (9)	128 (9)	72 (9)
C(11)	4092 (2)	7915 (1)	2246 (2)	359 (7)	395 (8)	387 (8)	−107 (6)	86 (6)	9 (6)
C(12)	3913 (2)	8616 (1)	3890 (3)	449 (8)	418 (8)	433 (9)	−107 (7)	97 (7)	−30 (7)
C(13)	3318 (2)	9586 (1)	3559 (3)	515 (10)	431 (9)	652 (11)	−74 (7)	128 (8)	−89 (8)
C(14)	2935 (2)	9868 (1)	1610 (3)	632 (12)	391 (9)	794 (13)	−14 (8)	70 (10)	94 (9)
C(15)	3135 (3)	9182 (1)	9958 (3)	816 (14)	553 (11)	565 (11)	−15 (9)	61 (10)	175 (9)
C(16)	3694 (2)	8207 (1)	267 (3)	676 (11)	463 (9)	427 (9)	−53 (8)	99 (8)	45 (7)
C(21)	7728 (2)	7209 (1)	2957 (2)	394 (8)	364 (8)	552 (9)	8 (6)	177 (7)	44 (7)
C(22)	8453 (2)	7238 (1)	5047 (3)	502 (10)	505 (10)	586 (10)	−81 (8)	165 (8)	78 (8)
C(23)	9559 (2)	7882 (1)	5962 (3)	468 (10)	656 (12)	658 (12)	−92 (9)	120 (9)	−36 (10)
C(24)	9964 (2)	8505 (1)	4795 (4)	430 (10)	515 (10)	959 (16)	−102 (8)	178 (10)	−22 (10)
C(25)	9291 (2)	8473 (1)	2723 (4)	489 (10)	547 (11)	967 (16)	−92 (9)	193 (10)	243 (10)
C(26)	8176 (2)	7833 (1)	1806 (3)	444 (9)	530 (10)	673 (12)	−32 (8)	140 (8)	188 (8)

(b) Hydrogen atoms (parameters × 10³)

	x	y	z	U_{iso}		x	y	z	U_{iso}
H(2)	159 (2)	677 (1)	302 (3)	66 (5)	H(13)	321 (2)	4 (1)	320 (3)	60 (5)
H(3A)	414 (2)	542 (1)	126 (3)	67 (5)	H(14)	254 (2)	54 (1)	139 (3)	63 (5)
H(3B)	285 (2)	634 (1)	14 (3)	49 (4)	H(15)	293 (2)	940 (1)	860 (3)	72 (6)
H(5A)	688 (2)	586 (1)	239 (2)	48 (4)	H(16)	385 (2)	772 (1)	909 (3)	63 (5)
H(5B)	628 (2)	650 (1)	48 (3)	46 (4)	H(22)	818 (2)	681 (1)	586 (3)	54 (5)
H(7A)	122 (3)	525 (1)	410 (3)	73 (6)	H(23)	5 (2)	788 (1)	738 (3)	65 (6)
H(7B)	251 (3)	459 (2)	288 (3)	96 (7)	H(24)	75 (3)	895 (1)	542 (3)	72 (6)
H(7C)	85 (3)	521 (2)	163 (4)	90 (7)	H(25)	958 (3)	887 (2)	187 (3)	80 (6)
H(12)	423 (2)	843 (1)	526 (2)	41 (4)	H(26)	768 (2)	783 (1)	32 (3)	59 (5)

−40 °C. ω-Scans of 1·0° were used throughout (accumulating P counts) with the scan rate, S, varying from 1·0 to 5·0° min^{-1} depending on the number of counts measured in a rapid preliminary scan. Background counts, B_1 and B_2, were collected at both ends of the scan with ω displaced 1·0° from the $K\alpha$ peak; each was taken for half the scan time. The intensities of four standard reflections were monitored after every 96 reflections and only statistical variations were noted. The net intensity, I (relative to a 1·0° scan rate), and its estimated standard deviation, $\sigma(I)$, were calculated as follows: $I = S(P - B_1 - B_2)$; $\sigma^2(I) = S^2(P + B_1 + B_2) + pI^2$, where p was assigned a judicious value of 0·03. Lorentz and polarization factors were applied, but absorption corrections were not made in the conversion to structure amplitudes. Values of $\sigma(F_o)$ were derived directly from $\sigma(I)$ taking into account the various corrections that were made. Details on the individual data collections for the four lactones are given in Table 2(a).

All of the structures were solved by direct methods (*MULTAN*),* and refined by the full-matrix least-

* The structure of BPL was initially solved and refined by Pathipvanich (1975) using room-temperature data.

squares technique, the general results of which are listed in Table 2(b). The final positional and thermal parameters are listed in Tables 3–6 for BPL, Z-MBPL, E-MBPL, and MMBPL respectively.* The computational details can be found elsewhere (Harlow, Loghry, Williams & Simonsen, 1975).

All solutions and refinements proceeded in an uneventful manner except for E-MBPL. In the final difference map, a peak with a height of 0·46 e Å^{-3} appeared at approximate coordinates of 0·68, 0·44, and 0·72. A close examination of this peak showed that the crystal of the (E)-isomer was evidently contaminated with a small amount (5–10%) of the (Z)-isomer (the isomerization evidently occurred during recrystallization when the methanol solution was heated to effect dissolution). This peak, representing atom C(2) of the (Z)-isomer, was the only significant manifestation of the contamination; the remainder of the non-hydrogen atoms of this isomer must superimpose

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31646 (47 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 6. *Positional and thermal parameters for 2,2-dimethyl-4-benzyl-4-phenylbutanoic 1,4-lactone (MMBPL)*

(a) Non-hydrogen atoms (parameters × 10⁴)

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	3390 (1)	3760*	4910 (2)	400 (7)	396 (7)	231 (5)	32 (6)	39 (5)	17 (5)
O(2)	4417 (1)	2109 (3)	6524 (2)	635 (9)	614 (11)	290 (7)	184 (8)	−7 (6)	96 (7)
C(1)	4050 (1)	2718 (3)	4850 (3)	393 (9)	313 (10)	298 (9)	−14 (8)	33 (7)	5 (8)
C(2)	4220 (1)	2462 (3)	2465 (3)	337 (9)	328 (10)	276 (8)	10 (8)	45 (7)	3 (7)
C(3)	3742 (1)	3997 (3)	1283 (3)	354 (9)	368 (11)	255 (8)	−2 (8)	61 (7)	39 (8)
C(4)	3047 (1)	4348 (3)	2666 (3)	348 (9)	330 (10)	216 (8)	15 (8)	36 (7)	48 (7)
C(5)	2871 (1)	6311 (3)	2823 (3)	358 (9)	322 (10)	334 (10)	−6 (8)	33 (7)	49 (8)
C(6)	3883 (1)	667 (3)	1652 (4)	435 (12)	353 (11)	383 (11)	−10 (10)	85 (9)	−35 (9)
C(7)	5137 (1)	2552 (4)	2367 (4)	347 (10)	464 (13)	422 (11)	12 (10)	68 (8)	−11 (11)
C(11)	2270 (1)	3321 (3)	1862 (3)	329 (9)	300 (9)	304 (8)	26 (7)	75 (7)	−20 (7)
C(12)	1917 (1)	2202 (3)	2202 (4)	388 (10)	376 (11)	401 (10)	26 (9)	126 (8)	43 (9)
C(13)	1176 (1)	1386 (4)	2479 (5)	423 (11)	405 (12)	686 (15)	−53 (10)	241 (11)	−23 (12)
C(14)	774 (1)	1722 (4)	360 (4)	351 (10)	518 (15)	687 (15)	−55 (11)	85 (10)	−208 (13)
C(15)	1130 (1)	2824 (4)	−1033 (4)	443 (11)	534 (14)	442 (12)	0 (11)	−17 (9)	−126 (11)
C(16)	1873 (1)	3609 (4)	−310 (3)	428 (10)	410 (11)	310 (9)	−16 (10)	43 (8)	−24 (9)
C(21)	2256 (1)	6867 (3)	4326 (3)	359 (9)	277 (9)	359 (9)	59 (8)	14 (8)	44 (8)
C(22)	2506 (1)	7890 (4)	6192 (3)	397 (10)	378 (11)	395 (10)	42 (9)	−36 (8)	−16 (9)
C(23)	1953 (1)	8462 (4)	7555 (4)	549 (13)	439 (12)	362 (10)	93 (11)	7 (9)	−24 (10)
C(24)	1139 (2)	7973 (4)	7111 (4)	522 (12)	448 (13)	470 (12)	133 (11)	143 (10)	33 (10)
C(25)	881 (1)	6954 (4)	5260 (4)	347 (10)	466 (13)	625 (13)	58 (10)	56 (9)	−2 (11)
C(26)	1426 (1)	6431 (4)	3862 (4)	367 (10)	397 (11)	457 (11)	55 (9)	−20 (8)	−56 (10)

* Defines origin, not refined.

(b) Hydrogen atoms (parameters × 10³)

	x	y	z	U_{iso}		x	y	z	U_{iso}
H(3A)	353 (1)	378 (3)	−29 (3)	29 (5)	H(12)	217 (1)	198 (4)	470 (4)	44 (6)
H(3B)	410 (1)	506 (3)	142 (4)	40 (6)	H(13)	94 (1)	60 (4)	352 (4)	49 (6)
H(5A)	268 (1)	667 (3)	140 (4)	32 (5)	H(14)	25 (1)	111 (4)	−18 (4)	49 (7)
H(5B)	339 (1)	690 (3)	340 (3)	24 (5)	H(15)	86 (1)	305 (3)	−253 (4)	48 (7)
H(6A)	416 (1)	−31 (3)	246 (4)	32 (5)	H(16)	214 (1)	434 (3)	−131 (4)	35 (6)
H(6B)	333 (1)	52 (3)	189 (3)	32 (5)	H(22)	308 (1)	830 (3)	644 (4)	39 (6)
H(6C)	393 (1)	55 (4)	6 (5)	59 (7)	H(23)	212 (1)	919 (4)	883 (4)	47 (6)
H(7A)	542 (2)	157 (4)	317 (4)	53 (7)	H(24)	75 (1)	832 (3)	808 (4)	40 (6)
H(7B)	523 (1)	247 (4)	85 (4)	56 (7)	H(25)	32 (1)	658 (4)	496 (4)	51 (7)
H(7C)	537 (1)	247 (4)	301 (4)	42 (6)	H(26)	125 (1)	574 (3)	257 (4)	36 (6)

or nearly superimpose on their conterparts in the (E)-molecule. The contamination was later confirmed when the melting point of crystals from the same recrystallization batch was found to be slightly lower than that of the pure substance. No attempt to include this

peak in the refinement was made because the disorder did not appear to otherwise seriously affect the refinement of the (E)-molecule. The contamination did, of course, lead to a higher R index for this structure than for the other three.
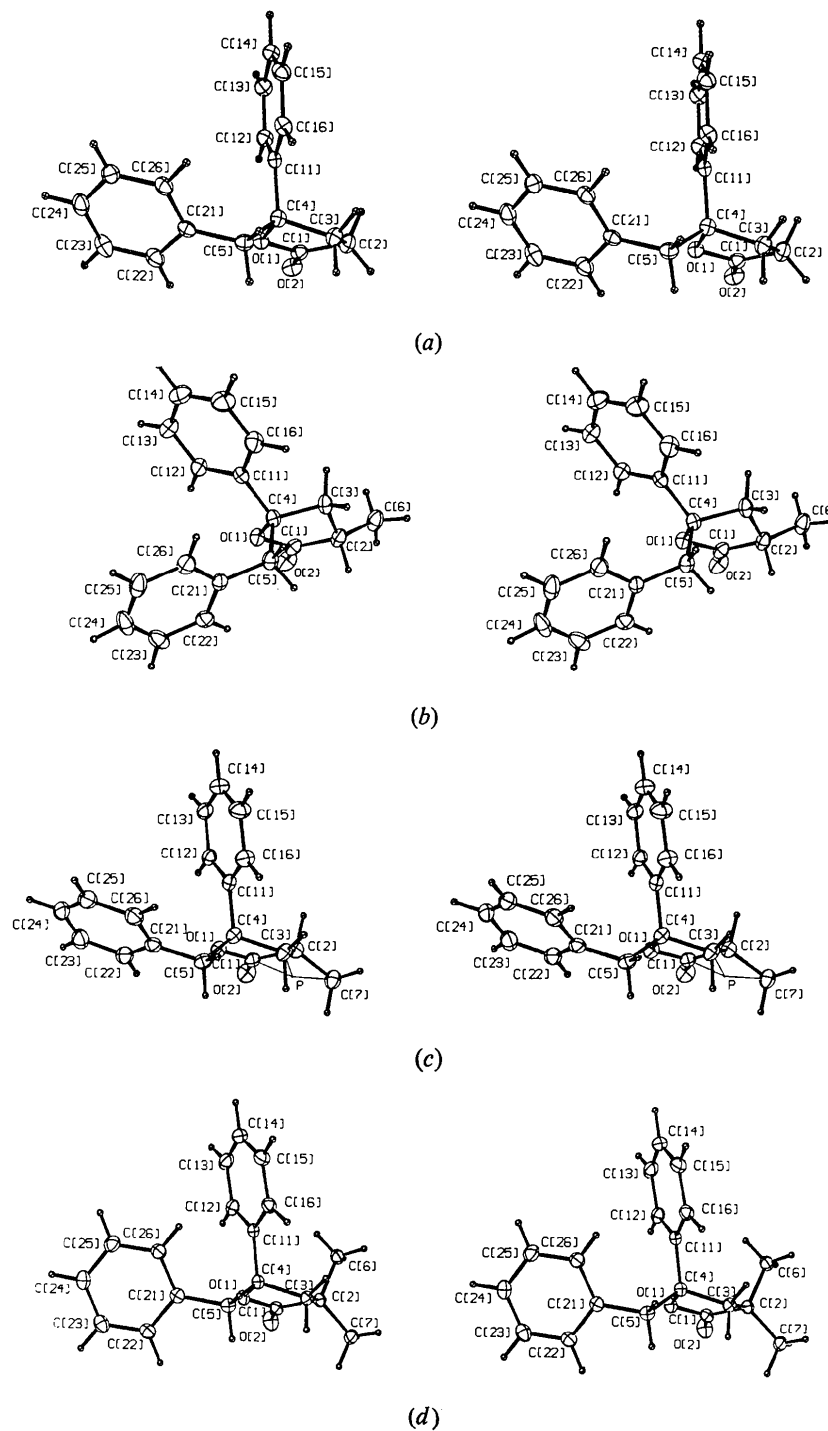

Fig. 1. Stereo drawings of the four molecules with the view standardized with respect to the atoms associated with the carbonyl moiety. (a) BPL. (b) Z-MBPL. (c) E-MBPL, point P is the extraneous peak found in the final difference map (see text). (d) MMBPL.

Table 7. *Results of least-squares mean-plane calculations*

	BPL	Z-MBPL	E-MBPL	MMBPL

(a) Carbonyl plane, atoms O(1), O(2), C(1), and C(2).
Deviations from the plane (sign of deviation is such that the phenyl group [C(11)–C(16)] is above the plane, *i.e.* positive).

	BPL	Z-MBPL	E-MBPL	MMBPL
O(1)	0·000 (1) Å	0·001 (1) Å	0·003 (1) Å	0·001 (1) Å
O(2)	0·000 (1)	0·001 (1)	0·004 (1)	0·001 (2)
C(1)	0·000 (2)	−0·003 (2)	−0·009 (2)	−0·004 (2)
C(2)	0·000 (2)	0·001 (2)	0·003 (2)	0·001 (2)
C(3)	−0·361 (2)	0·487 (2)	−0·570 (2)	−0·467 (2)
C(4)	0·109 (1)	0·041 (2)	−0·099 (1)	−0·011 (2)

(b) Phenyl group containing atoms C(11), C(12), C(13), C(14), C(15), and C(16).
Maximum deviation from any of the four planes is 0·013 (3) Å.

	BPL	Z-MBPL	E-MBPL	MMBPL
C(4)	0·043 (2)	0·038 (2)	−0·099 (1)	−0·130 (2)

(c) Phenyl group containing atoms C(21), C(22), C(23), C(24), C(25), and C(26).
Maximum deviation from any of the four planes is 0·015 (3) Å.

	BPL	Z-MBPL	E-MBPL	MMBPL
C(5)	−0·009 (2)	0·008 (2)	0·053 (2)	0·016 (2)

Dihedral angles

	BPL	Z-MBPL	E-MBPL	MMBPL
a–b	84·4°	38·2°	74·1°	70·4°
a–c	31·0	32·7	19·5	57·1
b–c	71·0	49·9	54·8	59·4

Table 8. *Selected torsion angles* (°)

	BPL	Z-MBPL	E-MBPL	MMBPL
(a) Lactone ring				
C(4)–O(1)–C(1)—C(2)	4·5	2·1	−5·1	−0·9
O(1)–C(1)–C(2)—C(3)	14·3	−19·6	23·7	18·4
C(1)–C(2)–C(3)–C(4)	−25·9	28·3	−31·4	−27·6
C(2)–C(3)–C(4)—O(1)	28·4	−27·6	29·1	28·0
C(3)–C(4)–O(1)—C(1)	−21·0	16·2	−15·3	−17·2
(b) Atoms bonded directly to the lactone ring				
C(2)–C(3)–C(4)—C(5)	142·5e*	88·2a*	143·7e	142·8e
C(2)–C(3)–C(4)—C(11)	−88·0a	−144·8e	−88·8a	−90·4a
C(1)–O(1)–C(4)—C(5)	−138·6e	−101·2a	−134·1e	−135·2e
C(1)–O(1)–C(4)—C(11)	97·9a	137·7e	105·2a	103·9a
O(1)–C(1)–C(2)—C(6)		−146·1e		−101·0a
O(1)–C(1)–C(2)—C(7)			151·0e	138·5e
C(4)–C(3)–C(2)—C(6)		153·4e		87·8a
C(4)–C(3)–C(2)—C(7)			−155·9e	−145·9e
(c) Other				
O(1)–C(4)–C(11)–C(12)	−9·9	14·1	5·6	7·9
C(4)–C(5)–C(21)–C(22)	85·1	88·3	72·6	115·9
O(1)–C(4)–C(5)—C(21)	−64·7	−59·1	−69·4	−61·6

* The last atom in the set is an axial substituent (a) or an equatorial substituent (e).

Table 9. *Bond distances* (Å) *with estimated standard deviations*

	BPL	Z-MBPL	E-MBPL	MMBPL
C(1)–O(1)	1·347 (2)	1·358 (2)	1·343 (2)	1·355 (2)
C(1)–O(2)	1·206 (2)	1·198 (2)	1·201 (2)	1·198 (2)
C(1)–C(2)	1·496 (2)	1·505 (2)	1·504 (2)	1·524 (2)
C(2)–C(3)	1·511 (2)	1·512 (2)	1·508 (2)	1·533 (3)
C(2)–C(6)		1·519 (3)		1·536 (3)
C(2)–C(7)			1·514 (3)	1·525 (3)
C(3)–C(4)	1·542 (2)	1·534 (2)	1·538 (2)	1·540 (3)
C(4)–O(1)	1·466 (2)	1·463 (2)	1·468 (2)	1·466 (2)
C(4)–C(5)	1·536 (2)	1·540 (2)	1·533 (2)	1·536 (3)
C(4)–C(11)	1·518 (2)	1·511 (2)	1·523 (2)	1·523 (3)
C(5)–C(21)	1·504 (2)	1·500 (2)	1·506 (2)	1·520 (3)

Table 9 (cont.)

Average bond distances for the two phenyl groups (e.s.d.'s calculated as $[\sum_{i=1}^{4}(\bar{D} - D_i)^2/3]^{1/2}$, where $\bar{D}$ is the average bond distance).

C(11)–C(12)	1·383 (2)	C(21)–C(22)	1·388 (2)
C(11)–C(16)	1·393 (6)	C(21)–C(26)	1·390 (5)
C(12)–C(13)	1·387 (3)	C(22)–C(23)	1·384 (4)
C(13)–C(14)	1·372 (7)	C(23)–C(24)	1·377 (5)
C(14)–C(15)	1·378 (6)	C(24)–C(25)	1·374 (7)
C(15)–C(16)	1·384 (5)	C(25)–C(26)	1·383 (3)

Average C–H bond distance is 0·98 (4) Å.

Results and discussion

Fig. 1 is an attempt to show the relative stereochemistry of the four compounds. The views are common with respect to the atoms associated with the carbonyl group [the horizontal direction was initially defined as the vector O(1)–C(2) with the view parallel to the C(1)–O(2) vector; several rotations were applied to eliminate some of the eclipsing of atoms and bonds]. The phenyl group [C(11)–C(16)] is thus always to the left of, and above, the plane of the atoms associated with the carbonyl moiety. The signs of the deviations from the mean planes calculated for the carbonyl group [Table 7(a)] have been altered where necessary so that the deviation of the phenyl group is always positive.

The general conformation of a 1,4-lactone ring is that of the 'envelope' form, where, because of the carbonyl group and the partial sp^2-character of the hetero-oxygen atom, atoms C(4), O(1), C(1), and C(2) are nearly planar, while C(3) deviates appreciably from this plane (Jeffrey, Rosenstein & Vlasse, 1967). Table 7(a) shows that such is the case for the four lactones presented here. While C(4) was not included in the mean-plane calculation, its largest deviation from the 'carbonyl plane' is only 0·109 Å. C(3), the 'flap' of the envelope, however, deviates considerably

from this plane, 0·361–0·570 Å. The torsion angles presented in Table 8 further demonstrate the point; the largest twist angle about the O(1)–C(1) bonds is only 5·1°, while angles O(1)–C(1)–C(2)–C(3) and C(1)–O(1)–C(4)–C(3) range between 14·3 and 23·7°.

The substituents on a 1,4-lactone ring can be classified as 'axial' or 'equatorial' by virtue of the resemblance between the envelope form of a five-membered ring system and the chair conformation of cyclohexane (Eliel, 1962). For BPL and MMBPL, where the competition between the phenyl and benzyl groups [both bonded to C(4)] determines the more stable conformer, the benzyl group is found to occupy the less sterically hindered equatorial position, leaving the phenyl group in the axial position. The implication is that the benzyl group is sterically 'bulkier' than the phenyl group. The presence of a single methyl substituent on C(2), considering now both Z- and E-MBPL, yields the more stable equatorial-equatorial-axial (as opposed to axial-axial-equatorial) conformer. The methyl group is in an equatorial position in both compounds; the (E)-isomer has the benzyl group in an equatorial position similar to the cases of BPL and MMBPL, while the phenyl group is equatorial in the (Z)-isomer. This reversal in the relative positions of the phenyl and benzyl groups is effectively brought about by the inversion of the 'flap' of the envelope, i.e. C(3), through the plane of the other four atoms in the ring. Thus, Table 7 shows that the deviation of C(3) from the 'carbonyl plane' is positive for Z-MBPL but negative for the remaining compounds. The torsion angles and the stereo drawings (Table 8 and Fig. 1) further illustrate the point.

The geometry of the phenyl and benzyl groups relative to the lactone rings is easily seen in Fig. 1. The phenyl ring C(11)–C(16) in all four lactones is situated so that C(12) eclipses the hetero-oxygen atom; the O(1)–C(4)–C(11)–C(12) torsion angles vary only from −9·9 to 14·1°. From models of the compounds, it is apparent that this conformation minimizes the

Table 10. Bond angles (°) with estimated standard deviations

	BPL	Z-MBPL	E-MBPL	MMBPL
C(1)–O(1)–C(4)	111·0 (1)	110·9 (1)	111·0 (1)	111·0 (1)
O(1)–C(1)–O(2)	120·7 (1)	120·4 (2)	120·9 (1)	121·1 (2)
O(1)–C(1)–C(2)	110·2 (1)	110·1 (1)	110·0 (1)	111·2 (1)
O(2)–C(1)–C(2)	129·1 (1)	129·5 (2)	129·0 (1)	127·8 (2)
C(1)–C(2)–C(3)	103·9 (2)	102·6 (1)	102·0 (1)	101·1 (2)
C(1)–C(2)–C(6)		114·1 (2)		108·1 (2)
C(1)–C(2)–C(7)			113·2 (1)	110·6 (2)
C(3)–C(2)–C(6)		116·1 (2)		113·5 (2)
C(3)–C(2)–C(7)			117·6 (1)	113·1 (2)
C(6)–C(2)–C(7)				110·0 (2)
C(2)–C(3)–C(4)	103·2 (1)	103·9 (1)	103·3 (1)	104·6 (2)
C(3)–C(4)–O(1)	103·2 (1)	103·8 (1)	103·1 (1)	103·5 (1)
C(3)–C(4)–C(5)	111·6 (1)	110·5 (1)	112·6 (1)	111·5 (2)
C(3)–C(4)–C(11)	112·0 (1)	114·2 (1)	113·1 (1)	113·3 (2)
O(1)–C(4)–C(5)	106·6 (1)	108·2 (1)	106·7 (1)	107·1 (1)
O(1)–C(4)–C(11)	108·5 (1)	107·9 (1)	109·2 (1)	109·4 (1)
C(5)–C(4)–C(11)	114·3 (1)	111·7 (1)	111·6 (1)	111·4 (2)
C(4)–C(5)–C(21)	116·1 (1)	114·9 (1)	114·4 (1)	117·4 (2)

Table 10 (cont.)

Average bond angles for the two phenyl groups

C(4)—C(11)–C(12)	122·3 (2)	C(5)—C(21)–C(22)	121·3 (6)
C(4)—C(11)–C(16)	119·2 (6)	C(5)—C(21)–C(26)	120·9 (6)
C(12)-C(11)–C(16)	118·5 (4)	C(22)-C(21)–C(26)	117·8 (2)
C(11)-C(12)–C(13)	120·7 (4)	C(21)-C(22)–C(23)	121·0 (2)
C(12)-C(13)–C(14)	120·4 (2)	C(22)-C(23)–C(24)	120·3 (4)
C(13)-C(14)–C(15)	119·4 (3)	C(23)-C(24)–C(25)	119·5 (6)
C(14)-C(15)–C(16)	120·6 (3)	C(24)-C(25)–C(26)	120·3 (3)
C(15)-C(16)–C(11)	120·3 (3)	C(25)-C(26)–C(21)	121·0 (2)

number of steric interactions between the phenyl group and neighbouring substituents regardless of whether the phenyl group is in an axial or an equatorial position on the lactone ring. C(21) of the benzyl group is likewise fixed by steric interactions and is found in a *gauche* conformation between C(11) and O(1) when viewed along the C(4)–C(5) bond; the O(1)–C(4)–C(5)–C(21) torsion angles range from −59·1 to −69·4°. The amount of twisting about C(5)–C(21), however, varies over a range of more than 40° (Table 8) and indicates, as might be expected, reasonable flexibility about this bond.

The bond distances and angles for the four compounds are listed in Tables 9 and 10, respectively, and are found to agree well with previously reported 1,4-lactones [Jeffrey, Rosenstein & Vlasse (1967), and references therein]. With the increasing number of methyl groups attached to atom C(2), there is a general increase in the bond lengths associated with C(2), a decrease in the C(1)–C(2)–C(3) angle, and an increase in the angles O(1)–C(1)–C(2) and C(2)–C(3)–C(4). These are consistent with a movement of C(2) out away from the center of the ring in an effort to minimize the steric effects of the methyl groups.

The angle C(4)–C(11)–C(12) is approximately 3° larger than the C(4)–C(11)–C(16) angle in all compounds, apparently as a result of the eclipsing between C(12) and O(1). The deviations from 120° of the angles within the phenyl groups [C(12)–C(11)–C(16) and C(22)–C(21)–C(26), for example, average 118·5 and 117·8° respectively] are well documented and are discussed by Domenicano, Vaciago & Coulson (1975). There do not appear to be any unusually short intermolecular contacts in any of the compounds.

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The Crystal and Defect Structures of W25O73, a Member of the Homologous Series WnO3n−2

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Reduced tungsten trioxide of approximate bulk composition WO2.92 has been studied by X-ray diffraction and electron microscopy. A crystal-structure investigation based on single-crystal diffractometer data has shown the existence of W25O73, a new member of the WnO3n−2 homologous series of {103} CS structures. The unit-cell parameters are a = 11·93, b = 3·82, c = 59·72 Å, β = 98·3° and the symmetry is P2/c. A puckered arrangement of tungsten atoms was found. Electron-diffraction studies of several crystal fragments have shown the existence of members of the series in the range n = 22 through n = 26, with n = 25 the most common. Lattice-image investigations have given further details of the defect structure of such crystals.

Introduction

The crystal structure of β-tungsten oxide was determined by Magnéli (1950). The phase is stoichiometric and has a unit-cell content of W20O58. The crystal structure consists of slabs of corner-sharing WO6 octahedra (ReO3-type) which have an infinite extension in two dimensions and a finite, characteristic width in a