

Solid-state conformations of 2,6-*cis*- and 2,6-*trans*-substituted dihydropyran-3-ones ^{*,†}

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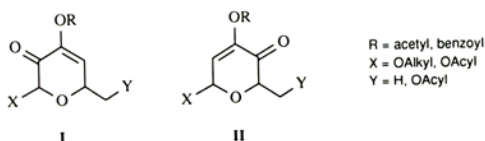
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ABSTRACT

2,6-Dihydropyran-3-ones carrying substituents at C-2 and C-6 in *cis*-arrangement invariably adopt half-chair conformations in which the ring oxygen and the carbon atom next to the carbonyl group are above and below, respectively, the plane formed by the other four carbon atoms, i.e., the 2H_0 or 0H_2 conformation. In the case of a *trans*-arrangement of 2,6-substituents, the geometry of the pyranoid ring falls into the $B_{0,6} \rightleftharpoons E_0 \rightleftharpoons {}^2H_0$ or the inverse ${}^0,6B \rightleftharpoons {}^0E \rightleftharpoons {}^0H_2$ section of the conformational cycle, depending on the absolute configuration of the compound; for two of the dihydropyranones, **4B** and **6**, a unique skew-boat ($SB_{0,6}$) conformation, fixed between the $B_{0,6}$ and E_0 geometries, was ascertained, which previously has only been observed for pyranoid enolactones.

INTRODUCTION

Of the various sugar-derived dihydropyranones with one or two chiral centers, those of type **I** and **II**, obtainable in enantiopure form, have turned out to be particularly important in both the efficiency with which they may be prepared from simple, bulk-scale-accessible sugars and the scope of the ensuing chemistry^{1,2}.



The enolone structural element of these dihydropyranones is flanked by chiral centers whose substituents exert a strong directing influence on the steric course of addition reactions; preparatively useful regio- and diastereo-selectivities are to be

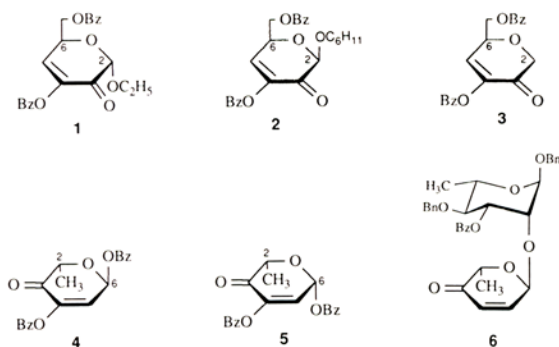
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* Enantiopure Building Blocks from Sugars, Part 16. For Part 15, see ref 1.

[†] Dedicated to Professor Erich R. Wölfel on the occasion of his 70th birthday.

expected, and are actually observed². Their established utility as highly versatile six-carbon building blocks for the construction of non-carbohydrate natural products would be further enhanced if the stereoselectivities attainable could be reliably predicted. This, in turn, requires a detailed knowledge of the molecular geometry of the pyranoid ring in relation to its substituents. Derivation of such information from ¹H NMR data is rather limited; the enolone ester unit is devoid of hydrogen atoms, and the two hydrogens next to the ring oxygen are not very informative probes for unravelling conformational features.

Detailed insights into the molecular geometries were to be expected from X-ray structural analyses, with the reasonable assumption that the solid-state conformations found are also applicable to the state in solution, since the enone grouping substantially restricts the flexibility of the pyranoid ring. We therefore now report on the X-ray structures of five dihydropyranones, three of type **I** (**1**, **2**, and **3**) and two of type **II** (**4** and **5**), whose pyran conformations are discussed in relation to the known³ analogue **6**.



RESULTS AND DISCUSSION

The molecular geometries found for dihydropyranones **1–5** in the solid state are depicted in Figs. 1–5, together with the respective preferred conformation of the pyranoid ring. In each case, the bond lengths and bond angles are within the expected ranges⁴, as indicated by the relevant examples collected in Tables I and II.

Of greater significance for elucidating the ring conformations adopted are the torsional angles in the pyranoid ring (Tables III and IV) and the puckering parameters according to Cremer and Pople⁵ (Table V). Their implications are discussed individually in the sequel.

The ring torsional angles in dihydropyranone **1** and the two forms appearing in the crystal lattice of **3** (**3A** and **3B**) (cf. Table III) vary within only a few degrees; in each case, the five ring carbons form a plane from which the ring oxygen stands out, thus resulting in an envelope (*E*) arrangement of the ^o*E* type. This is

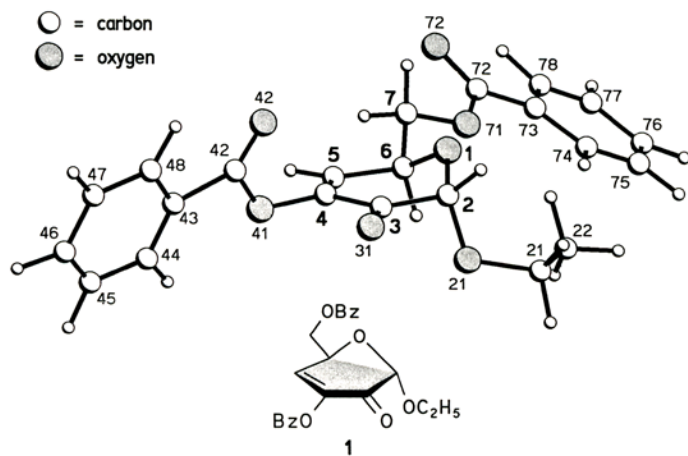


Fig. 1. Perspective drawing of the molecular structure of (2*S*,6*S*)-4-benzoyloxy-6-benzoyloxymethyl-2-ethoxy-2*H*-pyran-3(6*H*)-one (1). The presentation depicts carbon atoms as empty circles and the oxygen atoms as shaded circles, which allows the omission before numbers of the C and O specifications that would overload the drawing; the numbering follows pyran nomenclature starting with the ring oxygen such that the carbonyl group receives the lowest possible number.

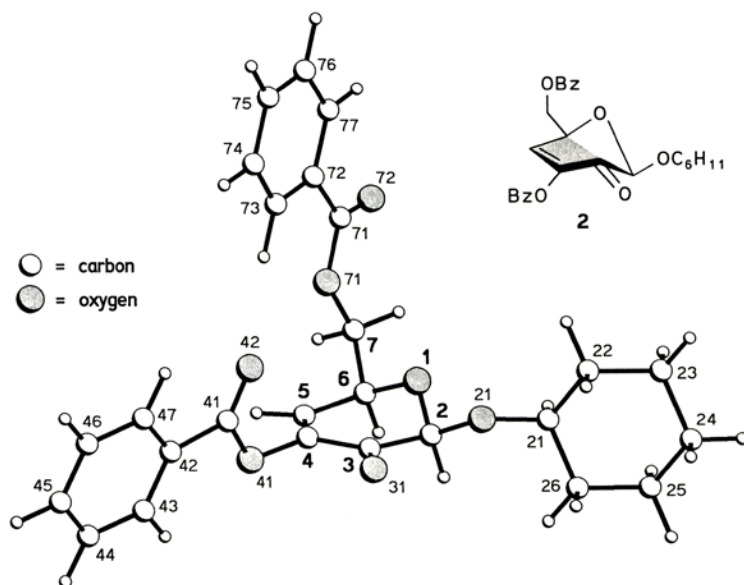


Fig. 2. Molecular structure of (2*R*,6*S*)-4-benzoyloxy-6-benzoyloxymethyl-2-cyclohexyloxy-2*H*-pyran-3(6*H*)-one (2).

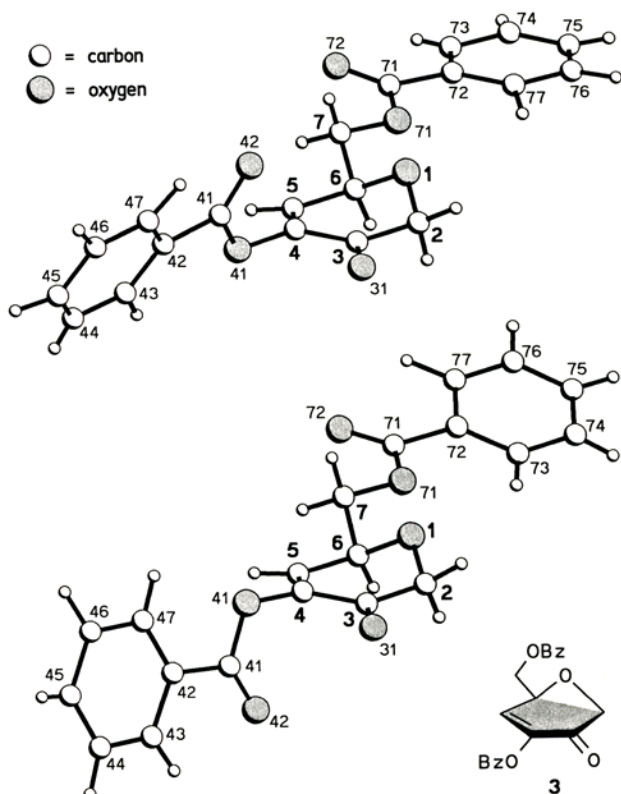


Fig. 3. Perspective drawing of the two forms, **A** and **B**, of (6*S*)-4-benzoyloxy-6-benzoyloxymethyl-2*H*-pyran-3(6*H*)-one (**3**); both showed nearly identical ${}^{\circ}E$ -conformations in the pyranoid ring, the major differences lying in the orientation of the two aromatic rings.

illustrated by the deviations of the oxygen from the best plane for the five carbon atoms (dotted area in Fig. 6): 0.58 Å in the case of **1**, and 0.61 and 0.63 Å for **3A** and **3B**, respectively.

Configurational inversion of the C-2 ring substituent in **1**, as in the case of the 2,6-*cis*-disubstituted dihydropyranone **2**, shifts the ring geometry: the best plane turns out to be one formed by carbons C-3 to C-6 (dotted area in Fig. 6), from which the ring oxygen projects by a sizeable 0.5 Å upwards, versus a smaller downward deflection of C-2 (0.19 Å). The preferred pyran-ring geometry of **2** is, therefore, best described as a non-ideal half-chair conformation ${}^{\circ}H_2$. The same conformation, in the mirror image version 2H_0 , is realized in the other 2,6-*cis*-disubstituted dihydropyranone **5** in a somewhat more idealized form: the ring oxygen is located above the four-carbon plane by 0.24 Å versus 0.32 Å for C-2 in the other direction (Table VI, Fig. 6). The alternative five-carbon-plane approximation (i.e., E_0 conformation) is clearly a less adequate possibility as indicated by the deviations given in Table VI. On the basis of these data, it may safely be concluded that

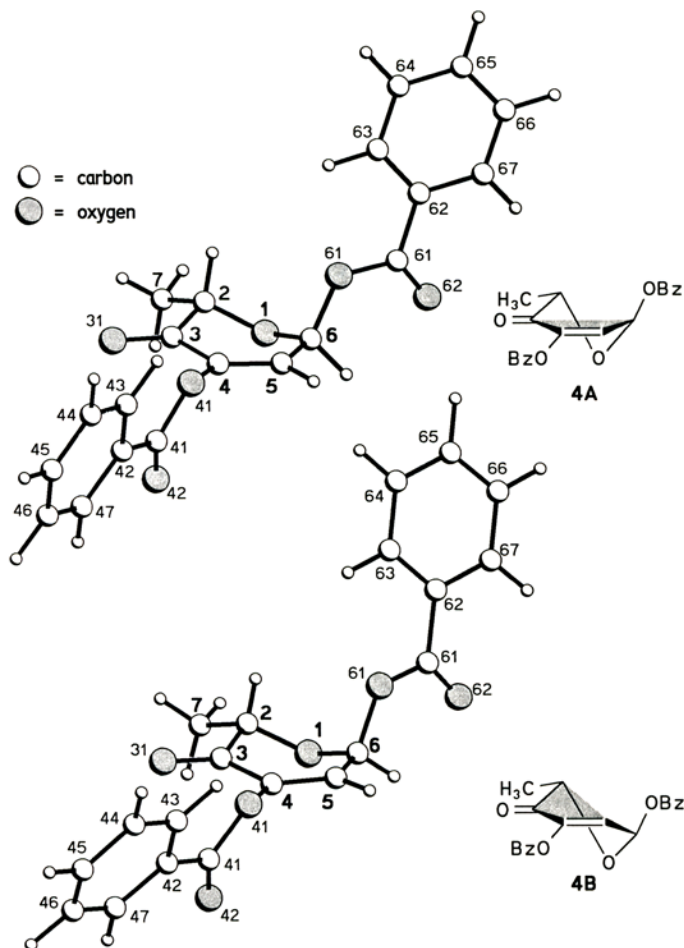


Fig. 4. Perspective drawing of the two molecular geometries, **A** and **B**, realized in the crystal lattice of (2*S*,6*S*)-4,6-dibenzoyloxy-2-methyl-2*H*-pyran-3(6*H*)-one (**4**).

2,6-*cis*-disubstituted dihydropyran-3-ones, in general, approximate to either the 2H_0 or the (enantiomeric) 0H_2 conformation in the solid state, and, conceivably, also in solution (cf. below).

The 2,6-*trans*-disubstituted pyrans clearly present a larger conformational variety. In contrast to **1** crystallizing in the 0E conformation with respect to the pyranoid ring, **4** gives two forms in the crystal lattice (Fig. 4), in which the ring torsional angles (Table IV) and puckering parameters (Table V) are quite different. Calculation of the various possible best planes (cf. Table VI) results in a 2H_0 conformation for **4a** (cf. Fig. 6) due to a four-carbon plane C-3 to C-6 with C-2 and the ring oxygen above and below, respectively. The conformation adopted in **4b** is less apparent; of the three “best” planes calculated, those approximating to the 2H_0 and E_0 conformations are not the best, but, unequivocally, the one formed by

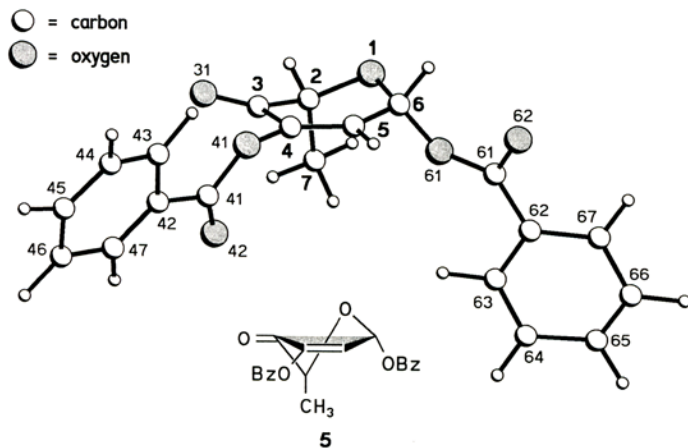


Fig. 5. Molecular plot of (2*S*,6*R*)-4,6-dibenzoyloxy-2-methyl-2*H*-pyran-3(6*H*)-one (**5**) as determined by X-ray analysis.

TABLE I

Selected bond lengths (Å) and bond angles (°) for the dihydropyran-3-ones **1**, **2**, and **3**

	1	2	3A	3B
Bond length ^a				
O-1-C-2	1.41(1)	1.416(3)	1.415(5)	1.425(6)
C-2-C-3	1.53(2)	1.538(3)	1.421(6)	1.509(6)
C-3-C-4	1.50(2)	1.460(4)	1.466(5)	1.468(6)
C-4-C-5	1.29(1)	1.314(4)	1.303(5)	1.306(6)
C-5-C-6	1.54(2)	1.496(3)	1.514(6)	1.512(6)
C-6-O-1	1.40(1)	1.417(3)	1.409(5)	1.445(5)
C-2-O-21	1.41(1)	1.365(3)		
C-3-O-31	1.17(2)	1.198(3)	1.210(5)	1.224(5)
C-4-O-41	1.41(1)	1.405(2)	1.408(4)	1.440(7)
C-6-C-7	1.52(1)	1.501(4)	1.490(6)	1.511(7)
Bond angles ^a				
O-1-C-2-C-3	112(1)	109.3(2)	113.2(3)	113.1(4)
C-2-C-3-C-4	114(1)	113.8(2)	114.0(3)	114.3(4)
C-3-C-4-C-5	124(2)	122.6(2)	122.5(3)	123.1(4)
C-4-C-5-C-6	119(1)	120.7(2)	120.2(4)	120.3(4)
C-5-C-6-O-1	112(1)	111.7(2)	111.8(3)	110.3(3)
C-6-O-1-C-2	113(1)	113.5(2)	112.5(3)	112.6(3)
C-1-C-2-O-21	113(1)	109.8(2)		
C-3-C-2-O-21	104(1)	107.6(2)		
C-2-C-3-O-31	124(1)	122.2(2)	121.7(4)	121.1(4)
C-4-C-3-O-31	122(2)	123.9(2)	124.2(4)	124.5(4)
C-3-C-4-O-41	117(1)	116.0(2)	116.2(3)	115.5(3)
C-5-C-4-O-41	120(2)	120.9(2)	120.8(3)	121.4(4)
C-5-C-6-C-7	110(1)	112.1(2)	108.9(4)	108.5(4)
O-1-C-6-C-7	107(1)	107.3(2)	110.4(4)	105.3(4)

^a Standard deviations are given in parentheses.

TABLE II

Selected bond lengths (Å) and bond angles (°) of the 6-epimeric dihydropyran-3-ones **4** and **5**

	4A	4B	5
Bond lengths ^a			
O-1-C-6	1.392(3)	1.391(3)	1.39(1)
C-6-C-5	1.493(3)	1.477(4)	1.44(2)
C-5-C-4	1.307(4)	1.332(3)	1.29(2)
C-4-C-3	1.478(4)	1.477(4)	1.51(2)
C-3-C-2	1.506(4)	1.510(4)	1.50(1)
C-2-O-1	1.439(4)	1.441(3)	1.44(1)
C-6-O-61	1.443(3)	1.456(3)	1.48(1)
C-4-O-41	1.388(3)	1.386(4)	1.41(1)
C-3-O-31	1.209(3)	1.209(3)	1.22(1)
C-2-C-7	1.501(4)	1.510(5)	1.52(2)
Bond angles ^a			
O-1-C-6-C-5	113.9(2)	114.4(2)	114(1)
C-6-C-5-C-4	121.5(3)	120.1(2)	124(1)
C-5-C-4-C-3	121.4(2)	121.4(3)	120(1)
C-4-C-3-C-2	114.8(2)	114.9(2)	114(1)
C-3-C-2-O-1	110.7(3)	110.3(2)	110(1)
C-2-O-1-C-6	115.2(2)	114.1(3)	119(1)
C-1-C-6-O-61	110.1(2)	109.4(2)	109(1)
C-5-C-6-O-61	105.7(2)	106.3(3)	110(1)
C-5-C-4-O-41	121.7(2)	122.4(2)	123(1)
C-3-C-4-O-41	116.6(2)	115.3(2)	117(1)
C-4-C-3-O-31	122.2(2)	121.7(3)	121(1)
C-2-C-3-O-31	122.9(3)	123.2(2)	123(1)
C-3-C-2-C-7	113.4(2)	112.7(2)	112(1)
O-1-C-2-C-7	107.5(3)	108.8(3)	113(1)

^a Standard deviations in parentheses.

the four carbon atoms C-2-C-3-C-4-C-5 (cf. Table VI); each of the other ring atoms, O-1 and C-6, lies below this nearly perfect plane, by 0.22 and 0.72 Å, respectively (Fig. 6).

Inspection of the literature with respect to analogies revealed that another dihydropyranone shows the very same conformation in the solid state, although this was not realized³: the disaccharide-derived **6** carries a hydrogen atom in place of the 4-benzoyloxy group but is otherwise a close structural analogue of **4**. A recalculation of the dihedral angles in the pyranoid ring, the puckering parameters, and the best planes from the configurationally inverted * data reported³ shows a pronounced similarity to **4B**. Compound **6** does not adopt a “sofa conformation (*E*) deformed towards the half-chair (*H*)”³, but one lying between

* In this paper³, instead of dihydropyranone **6** with the (2*S*,6*R*)-configuration (corresponding to α -L), the enantiomer with the α -D configuration is depicted in the ORTEP diagram; correspondingly, all signs of the positional parameters, the angles, and the best planes have to be inverted. In Tables IV–VI, this has already been done.

TABLE III

Selected torsional angles (°) in dihydropyranones **1**, **2**, and **3**

Torsional angles ^a	1	2	3A	3B
Pyranoid ring				
O-1-C-2-C-3-C-4	27	35.2	26	24
C-2-C-3-C-4-C-5	-1	-2.5	4	7
C-3-C-4-C-5-C-6	1	-6.8	-6	-7
C-4-C-5-C-6-O-1	-28	-17.2	-23	-24
C-5-C-6-O-1-C-2	57	52.9	54	55
C-6-O-1-C-2-C-3	-57	-61.7	-57	-56
Ring substituent				
C-6-O-1-C-2-O-21	60	180.0		
C-4-C-3-C-2-O-21	-95	154.4		
C-1-C-2-C-3-O-31	-159	-147.7	-158	-159
C-5-C-4-C-3-O-31	-175	180.0	-171	-170
C-2-C-3-C-4-O-41	174	169.5	176	-174
C-6-C-5-C-4-O-41	-173	-178.5	-178	175
C-2-C-1-C-6-C-7	178	176.2	176	172
C-4-C-5-C-6-C-7	-147	-137.7	-145	-139
O-1-C-6-C-7-O-71	78	69.1	64	62
C-5-C-6-C-7-O-71	-161	53.9	-173	180
Ring conformation	^o E	^o H ₂	^o E	^o E

^a Standard deviations: ca. 3° for **1**, 0.8° for **2**, and 1° for **3A** and **3B**.

TABLE IV

Relevant torsional angles (°) in the dihydropyranone epimers **4** and **5**, and the known³ analogue **6**

Torsional angle	4A ^a	4B ^a	5 ^a	6 ^b
Pyranoid ring				
O-1-C-6-C-5-C-4	-15.1	-15.0	12	18.3
C-6-C-5-C-4-C-3	-3.0	-8.3	-2	6.2
C-5-C-4-C-3-C-2	-8.2	-1.7	15	-1.1
C-4-C-3-C-2-O-1	36.0	33.1	-37	-27.3
C-3-C-2-O-1-C-6	-56.2	-57.9	51	53.1
C-2-O-1-C-6-C-5	45.6	49.2	-38	-48.4
Ring substituents				
C-2-O-1-C-6-O-61	-72.9	-70.0	84	70.9
C-4-C-5-C-6-O-61	106.0	105.9	-110	-104.5
C-6-C-5-C-4-O-41	-176.1	-177.5	-177	
C-2-C-3-C-4-O-41	165.2	168.2	-170	
C-5-C-4-C-3-O-31	175.6	-176.9	-177	174.3
O-1-C-2-C-3-O-31	-174.8	-151.7	155	157.3
C-6-C-1-C-2-C-7	180.0	178.1	-75	176.6
C-4-C-3-C-2-C-7	157.0	155.0	90	-147.7
Ring conformation	^o H ₂	^{o(6)} SB	² H _o	^{o(6)} SB

^a Standard deviations for **4A** and **4B**, 0.6°; for **5**, 2°. ^b Values calculated from the structural data of Krajewski et al.³

TABLE V

Puckering parameters ^a, according to Cremer and Pople⁶, for dihydropyranones 1–6

Compound	ϕ	θ	Q
1	359.0(4)	52.0(3)	0.440(3)
2	16.6(9)	56.0(8)	0.470(6)
3A	2.4(9)	58.0(7)	0.452(5)
3B	358.4(9)	59.7(7)	0.467(6)
4A	23.5(4)	52.8(4)	0.415(3)
4B	18.1(4)	57.9(3)	0.444(3)
5	215.0(4)	132.0(4)	0.370(2)
6	189.4	122.5	0.413

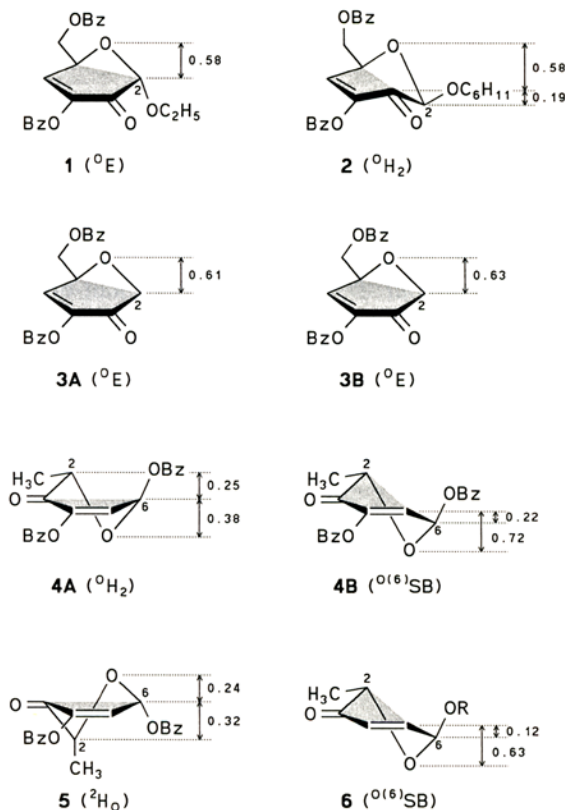
^a The program of Luger and Bülow⁷ was used for the calculations. Standard deviations in parentheses.

Fig. 6. Graphic representation of the molecular geometries preferred by dihydropyran-3-ones 1–6, and deviations of the ring atoms, in Å, from the calculated best planes (indicated by dotting). To emphasize their derivation from sugars, and for reasons of clarity, all conformations are presented in the sugar mode of orienting a pyranoid ring, i.e., with the ring oxygen at the right rear corner. Since pyran numbering starts with the ring oxygen such that the carbonyl group receives the lowest possible number, compounds 1–3 are to be numbered clockwise, and 4–6, accordingly, in an anticlockwise fashion. Thus, for 4–6, the conformational indices for the respective *H* and *SB* forms are to be derived from the formula drawings in inverted form.

the envelope E_o and a boat ($B_{o,6}$); this is clearly borne out by the nearly perfect four-atom plane made up of carbons 2, 3, 4, and 5 (Table VI), which is decisively better than the two others also considered. The conformation is thus clearly the one depicted in Fig. 6.

As of now, no specific designatory name or abbreviation exists for such a conformation, despite the fact, that, on closer inspection of the literature, it is quite common. About 40 enelactones (of types **III** and **IV**^{8–28}, and even complex structures with one or two rings annellated in the 4,5- and 5,6-positions^{29–41}), which have been studied by X-rays, adopt this molecular geometry, as indicated by a detailed comparison of pyranoid ring torsional angles and deviations from the four-carbon plane C-1–C-2–C-3–C-4²⁸.

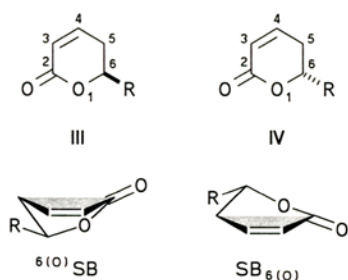


Fig. 7. Ring conformations adopted by pyranoid enelactones of types **III** and **IV**.

The ring conformation has been designated as “*distorted boat*”⁴², “*modified skew-boat*”⁸, “*distorted envelope*”⁹, and “*half-boat*”¹⁰. The designation half-boat appears inappropriate since, unlike the pictorially discerning designation half-chair, it neither makes sense stereochemically nor visually. Also, the description used for the boat (“*B*”) conformation comprises a plane made up of opposite pairs of adjacent atoms separated by two other atoms that *both* lie either above or below this plane and are designated as, for example, the ^{2,5}*B* form in Fig. 8. The

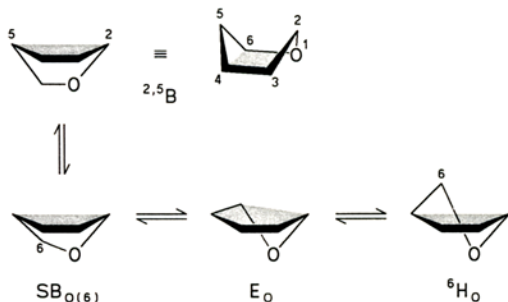


Fig. 8. Sector of the boat/envelope/half-chair pseudorotational itinerary of the ring conformations pertinent to dihydropyranones. An enone (or enelactone) structural element in a pyranoid ring does not allow the adoption of a perfect boat; the compounds crystallize in a half-chair (*H*) form, an envelope (*E*) form, or in a form between envelope and boat, i.e., the skew-boat (*SB*) conformation.

TABLE VI
 Dihydropyranones **4–6**: deviations (Å) from the least-square planes formed by four atoms (half-chair *H* or skew-boat conformations *SB*) or, alternatively, one formed by five atoms (envelope conformation *E*)

Atom	4A		4B		5		6^a			
O-1	0.380	0.536	0.462	0.582	0.715	-0.239	-0.443	0.503	0.629	
C-6	0.006 *	0.064 *	0.016 *	0.062 *	0.219	0.003 *	-0.069 *	0.012 *	0.033 *	
C-5	-0.013 *	-0.053 *	-0.035 *	-0.067 *	0.004 *	-0.007 *	0.043 *	-0.026 *	-0.043 *	
C-4	0.013 *	-0.017 *	0.035 *	0.013 *	-0.008 *	0.007 *	0.047 *	0.026 *	0.019 *	
C-3	-0.006 *	0.077 *	-0.017 *	0.047 *	0.007 *	-0.003 *	-0.109 *	-0.012 *	0.015 *	
C-2	-0.250	-0.071 *	-0.195	-0.055 *	-0.004 *	0.322	0.089 *	-0.089 *	-0.024 *	
Conformation	^o H ₂	(^o E)	(^o H ₂)	(^o E)	α(⁶)SB	² H ₀	(E ₀)	(^o H ₂)	(^o E)	α(⁶)SB

* Atoms defining the plane. ^a Data calculated from literature³.

molecular geometry adopted by **4B**, **6**, and a host of pyranoid enelactones, however, is neither a boat nor an envelope, but a conformation in between, i.e., between $B_{o,6}$ and oE , or alternatively, between $B_{o,6}$ and 2E . Such an intermediate conformation is best visualized by “pushing in” or denting one of the four atoms making up the “keel bottom” of a boat, a *skew-boat* so to speak. This designation, first used by Clarke and Pauling⁸, appears to us a most appropriate visual concept, and we here propose to use it with the descriptor *SB*, indexing the two atoms involved with the one dented in parentheses. This leads to an $SB_{o(6)}$ conformation (cf. Fig. 8) as the intermediate geometry between ${}^{2,5}B$ and E_o forms for dihydropyran-3-ones.

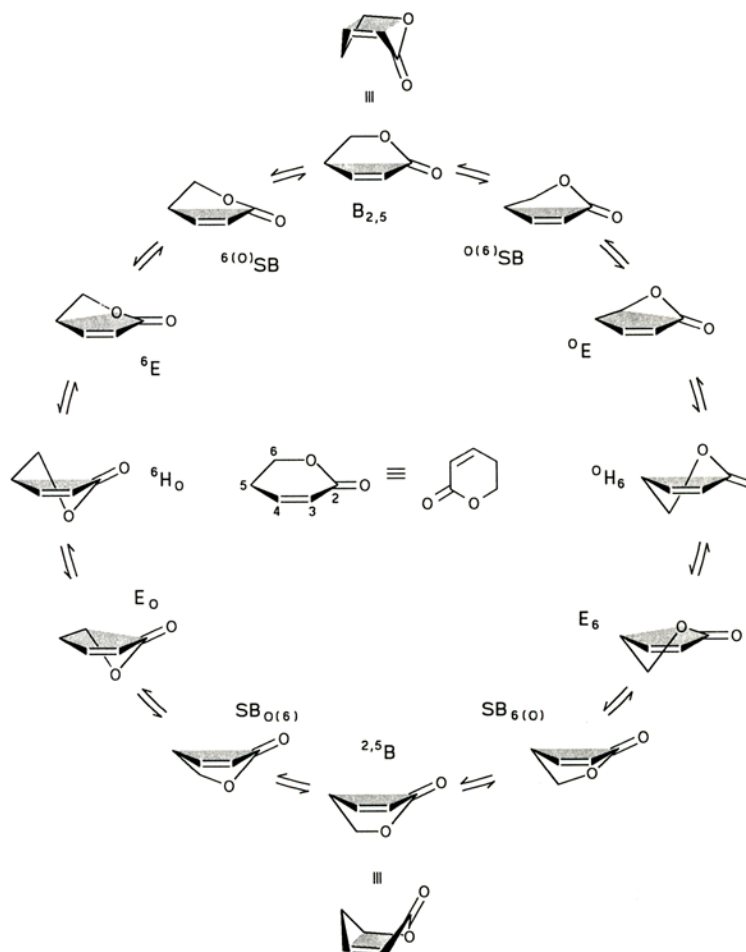


Fig. 9. The boat/skew boat/envelope/half-chair pseudorotational itinerary for pyranoid enelactones. The conformations preferred in the solid state are the ${}^{6(o)}SB$ and $SB_{6(o)}$ forms.

Using this nomenclature, the results of this paper may be summarized as follows: 2,6-disubstituted dihydropyran-3-ones, in the solid state, adopt half-chair conformations, e.g., the oH_2 form for **2** and **5** (Fig. 6); analogues with a 2,6-*trans*-substitution pattern show a broader range of conformations, the pyranoid ring adopting either half-chair (2H_o for **4A**), envelope (oE for **1** and **3**), or skew-boat geometries ($SB_{o(6)}$ for **4B** and **6**). However, dihydropyran-1-ones, i.e., pyranoid enelactones of type **III** (or **IV**, if configurationally inverted), invariably adopt the skew-boat conformations ${}^{6(o)}SB$ or $SB_{6(o)}$, as indicated by numerous examples in the literature^{8–41}. When considering the entire conformational cycle for such enelactones, as illustrated in Fig. 9, their distinct preference for the two mirror-image skew-boat conformations, ${}^{6(o)}SB$ and $SB_{6(o)}$, becomes particularly apparent.

EXPERIMENTAL

The five dihydropyranones for which the X-ray structural analysis is described here are all accessible from simple sugars in a few, preparatively satisfactory steps: compounds **1–3**, for example, from the D-glucose-derived 3,4,6-tri-*O*-benzoyl-2-benzoyloxy-D-glucal⁴³; the three-step sequence hydrolytic chlorination, β -elimination, and HBr treatment smoothly elaborates the (2*R*,6*S*)-4-benzoyloxy-6-benzoyloxymethyl-2-bromo-2*H*-pyran-3(6*H*)-one⁴⁴ (in carbohydrate nomenclature: 3,6-di-*O*-benzoyl-4-deoxy- α -D-glycero-hex-3-enopyranosyl-2-ulose bromide), which is either subjected to direct acid-catalyzed ethanolsis to give a mixture of **1** and its 2-epimer (cf. below), or to Ag₂CO₃-promoted alcoholysis with cyclohexanol to yield exclusively **2**; another reaction sequence, hydroxylaminolysis \rightarrow deoximation \rightarrow β -elimination, converts the hydroxyglycal ester into **3**^{45,46}. The 6-epimeric dihydropyranones **4** and **5** were prepared⁴⁷ from L-rhamnose by a sequence involving selective benzylation, oxidation, and β -elimination.

With respect to nomenclature and numbering, the compounds are, in accordance with Chemical Abstracts usage, considered to be 2*H*-pyran derivatives, for which numbering starts at the ring oxygen in such a sense that the carbonyl function receives the lowest possible number. Although this pyran-based designation does not lead to shorter names, it is retained here on the premise that a dihydropyranone with one or two chiral centers is no longer a sugar. Nevertheless, in compliance with the suggestion of a referee, the names based on carbohydrate nomenclature are also given, separately rather than in brackets behind the pyran-derived names to avoid confusion (sugar numbering entails C-1 for the “anomeric” center, which becomes C-2 or C-6 in a dihydropyran-3-one): **1**, ethyl 3,6-di-*O*-benzoyl-4-deoxy- α -D-glycero-hex-3-enopyranosid-2-ulose; **2**, cyclohexyl 3,6-di-*O*-benzoyl-4-deoxy- β -D-glycero-hex-3-enopyranosid-2-ulose; **3**, 1,5-anhydro-3,6-di-*O*-benzoyl-4-deoxy-D-glycero-hex-3-en-2-ulose; **4**, 1,3-di-*O*-benzoyl-2,6-dideoxy- α -L-glycero-hex-2-enopyranos-4-ulose; **5**, 1,3-di-*O*-benzoyl-2,6-dideoxy- β -L-glycero-hex-2-enopyranos-4-ulose.

The crystallographic data of dihydropyranones **1–5** are listed in Table VII. The structures * were solved by direct methods and anisotropic refinement of the carbon and oxygen atoms with fixed positions of hydrogen atoms, utilizing the programs SHELX-86⁴⁸ and SHELX-76⁴⁹. The positional parameters of the heavy atoms are listed in Tables VIII–XII.

(2*S*,6*S*)-4-Benzoyloxy-6-benzoyloxymethyl-2-ethoxy-2*H*-pyran-3-(6*H*)-one (**1**).—A suspension of 2.2 g (5 mmol) of (2*R*,6*S*)-4-benzoyloxy-6-benzoyloxymethyl-2-bromo-2*H*-pyran-3-(6*H*)-one⁴⁴ (the 2-bromo analogue of **1**) in abs EtOH (50 mL) was stirred for 3 h at 35°C. Although a clear solution was not obtained, ethanolysis had occurred. The crystals formed were collected by filtration to yield the 2*R*-epimer of **1** (1.1 g, 55%); mp 106°C; $[\alpha]_{\text{D}}^{22} - 108^\circ$ (*c* 1, CHCl₃); lit.⁴⁴ mp 106°C, $[\alpha]_{\text{D}}^{22} - 108.2^\circ$ (CHCl₃). The mother liquor was evaporated to dryness and the residue was recrystallized twice from EtOH, to give **1** (0.58 g, 28%) as long needles; mp 95–96°C; $[\alpha]_{\text{D}}^{20} + 22.3^\circ$ (*c* 1, CHCl₃); ¹H NMR (300 MHz, CDCl₃): δ 1.30 (t, 3 H, CH₂CH₃), 3.78 and 3.92 (2 dt, 1 H each, CH₂CH₃), 4.60 (ddd, 2 H, 2 H-7), 5.09 (s, 1 H, H-2), 5.18 (dt, 1 H, H-6), 6.87 (d, 1 H, H-5), 7.4–8.1 (m, 10 H, 2 C₆H₅), *J*_{5,6} 1.8, *J*_{6,7} 3.4 Hz. Anal. Calcd for C₂₂H₂₀O₇: C, 66.66; H, 5.09. Found: C, 66.62; H, 5.06.

A colorless needle of **1**, obtained by crystallization from 5:3:3 diethyl ether–EtOAc–hexane, was positioned along the *c*-axis. The preliminary lattice constants were refined by determination of the positions of the axis reflexes; those with $8^\circ \leq 2\theta \leq 120^\circ$ of layers *hk0* to *hk5* were used for anisotropic refinement of the heavy atoms. Due to the low scattering capacity of the crystal, only a data set of low quality could be obtained, which is reflected in the comparatively large standard deviations of the parameters (cf. Table VIII) and the high *R*-factor.

(2*R*,6*S*)-4-Benzoyloxy-6-benzoyloxymethyl-2-cyclohexyloxy-2*H*-pyran-3-(6*H*)-one (**2**).—A mixture of cyclohexanol (300 mg, 3 mmol), CH₂Cl₂ (10 mL), 3A molecular sieves, and silver carbonate (0.92 g, 3.3 mmol) was stirred for 30 min at ambient temperature in the dark with exclusion of moisture. Then, a solution of 1.29 g (3 mmol) of (2*R*,6*S*)-4-benzoyloxy-6-benzoyloxymethyl-2-bromo-2*H*-pyran-3-(6*H*)-one⁴⁴ (2-bromo analogue of **1**) in CH₂Cl₂ (15 mL) was added dropwise and stirring was continued for another 12 h. Filtration through silica gel and concentration of the filtrate under reduced pressure left a crystalline mass, which was recrystallized from MeOH, to give **2** (1.10 g, 81%) as colorless needles; mp 137–138°C; $[\alpha]_{\text{D}}^{20} - 115^\circ$ (*c* 0.9, CHCl₃); ¹H NMR (300 MHz, CDCl₃): δ 1.1–2.1 (m, 10 H, cyclohexyl-CH₂), 3.84 (ddd, 1 H, cyclohexyl-CH), 4.46 and 4.76 (2 dd, 1 H each, H-7a,7b), 5.08 (sx, 1 H, H-6), 5.24 (s, 1 H, H-2), 6.91 (d, 1 H, H-5), 7.4–8.2 (10 H, 2 C₆H₅); *J*_{5,6} 3.5, *J*_{6,7a} 6.3, *J*_{6,7b} 6.9, *J*_{7a,7b} 11.0 Hz. Anal. Calcd for C₂₆H₂₆O₇: C, 69.32; H, 5.82. Found: C, 69.30; H, 5.77.

* Atomic coordinates for these structures have been deposited with the Cambridge Crystallographic Data Centre. The coordinates may be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

TABLE VII
Crystallographic data from dihydroxyran-3-ones 1–5

Compound	1	2	3	4	5
Formula	$C_{22}H_{20}O_7$	$C_{26}H_{26}O_7$	$C_{20}H_{16}O_6$	$C_{20}H_{16}O_6$	$C_{20}H_{16}O_6$
Mol wt	396.38	450.47	352.33	352.33	352.33
Crystal size (mm)	$0.08 \times 0.20 \times 0.80$	$0.05 \times 0.12 \times 0.4$	$0.1 \times 0.1 \times 1.2$	$0.2 \times 0.3 \times 0.6$	–
Space group	$P2_12_12_1$ (Nr. 19)	$P2_1$ (Nr. 4)	$P1$ (Nr. 1)	$P1$ (Nr. 1)	$P2_1$ (Nr. 4)
Cell dimensions (\AA)					
<i>a</i>	24.80(9)	18.748(6)	13.068(5)	11.743(4)	11.43(1)
<i>b</i>	13.48(2)	5.455(2)	11.213(4)	11.579(4)	5.540(5)
<i>c</i>	5.80(1)	11.745(4)	6.062(3)	7.992(3)	13.46(1)
Angles (degrees)					
α	90	90	86.55(2)	71.409(3)	90
β	90	101.798(5)	79.75(2)	70.858(3)	91.32(5)
γ	90	90	86.37(2)	62.899(3)	90
V_{EZ} (\AA^3)	1939	1176	871	1770	852
<i>Z</i>	4	2	2	2	2
D_{calcd} (g/cm^3)	1.358	1.272	1.348	1.322	1.373
Diffractometer	STOE STADI2 (rot. Anode)	STOE STADI4	STOE STADI4	STOE STADI4	STOE STADI2
λ (\AA)	0.7107 (MoK α)	1.5418 (CuK α)	0.7107 (MoK α)	0.7107 (MoK α)	1.5418 (CuK α)
μ (mm^{-1})	0.76	0.68	0.06	0.06	0.76
$2\theta_{max}$ (degrees)	110	110	45	40	120
Data collection	$+h+k+l$	$\pm h \pm k + l$	$\pm h \pm k \pm l$	$\pm h \pm k - l$	$\pm h + k + l$
Reflections measured	1374	3323	3948	2402	1565
Symmetry independent reflections	1082	2852	3518	2374	1068
<i>n</i> out of $ F \geq n\sigma_F$	1	2	2	2	2
Number of refined parameters	270	299	508	477	241
Final refinement values <i>R</i>	0.121	0.047	0.046	0.027	0.116
R_w	0.069	0.053	0.041	0.033	0.088
Final shift/ σ_{max}	0.33	0.04	0.50	0.20	0.10
Residual electron density ($e/\text{\AA}^3$)	$+0.42/-0.53$	$+0.28/-0.35$	$+0.42/-0.23$	$+0.12/-0.12$	$+0.41/-0.43$

TABLE VIII

Fractional atomic coordinates for C and O atoms ($\times 10^4$)^a and equivalent isotropic thermal parameters for (2*S*,6*S*)-4-benzoyloxy-6-benzoyloxymethyl-2-ethoxy-2*H*-pyran-3(6*H*)-one (**1**)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
O-1	-0.653(3)	-9168(5)	2338(16)	47(5)
C-2	-6510(5)	-9110(9)	3787(21)	39(8)
C-3	-6628(5)	-8041(12)	4529(29)	51(10)
C-4	-6439(5)	-7275(12)	2849(28)	52(10)
C-5	-6193(5)	-7485(10)	960(27)	51(9)
C-6	-6095(5)	-8580(9)	358(23)	49(9)
C-7	-5566(5)	-8691(8)	-944(21)	49(8)
O-31	-6884(3)	-7835(6)	6161(18)	63(6)
O-21	-6990(3)	-9412(6)	2696(17)	67(6)
C-21	-7080(6)	-10493(13)	2818(30)	107(15)
C-22	-6798(6)	-10933(11)	1068(33)	104(14)
O-41	-6582(3)	-6284(6)	3326(16)	54(6)
C-42	-6375(6)	-5849(11)	5189(24)	48(10)
O-42	-6029(3)	-6255(6)	6329(15)	62(6)
C-43	-6664(6)	-4894(10)	5678(25)	43(9)
C-44	-7036(5)	-4506(11)	4278(25)	59(10)
C-45	-7282(5)	-3615(11)	4958(29)	70(11)
C-46	-7111(6)	-3167(9)	6772(33)	71(11)
C-47	-6742(6)	-3578(11)	8348(25)	65(11)
C-48	-6499(5)	-4467(10)	7673(31)	65(10)
O-71	-5596(3)	-9640(6)	-2101(15)	52(5)
C-71	-5216(5)	-9860(10)	-3573(24)	42(8)
O-72	-4843(3)	-9271(6)	-3959(17)	75(6)
C-73	-5319(5)	-10792(11)	-4828(23)	47(9)
C-74	-5683(5)	-11501(10)	-4115(24)	56(10)
C-75	-5746(6)	-12327(10)	-5472(33)	77(11)
C-76	-5458(6)	-12448(12)	-7455(30)	75(12)
C-77	-5096(6)	-11726(13)	-8172(26)	71(12)
C-78	-5016(5)	-10911(10)	-6775(28)	50(9)

^a Standard deviations in parentheses.

Recrystallization of **2** from 2:1 EtOAc–cyclohexane afforded thin, colorless platelets, of which a suitable one was measured with a rotating anode. The cell data were determined from the positions of 8 reflexes with $72^\circ < 2\theta < 79^\circ$. Positional parameters are listed in Table IX.

(6*S*)-4-Benzoyloxy-6-benzoyloxymethyl-2*H*-pyran-3(6*H*)-one (**3**).—The cell data are based on 64 reflexes with $17^\circ < 2\theta < 20^\circ$. On refinement, high residual electron densities were observed, which indicate the existence of 10 and 7% of a disordered second conformation of the symmetry-independent molecules **3A** and **3B**. Through occupying O-5, O-71, and O-27, this disorder could be treated. Positional parameters are listed in Table X.

(2*S*,6*S*)-4,6-Dibenzoyloxy-2-methyl-2*H*-pyran-3(6*H*)-one (**4**) and its (2*S*,6*R*)-epimer (**5**).—The data collections were done on a colorless crystal needle as described for **1** and **3**. In the case of **4**, the anisotropic refinement was done for all carbon and hydrogen atoms of the two independent molecules **4A** and **4b** with

TABLE IX

Fractional atomic coordinates for C and O atoms ($\times 10^4$)^a and equivalent isotropic thermal parameters for (2*R*,6*S*)-4-benzoyloxy-6-benzoyloxymethyl-2-cyclohexyloxy-2*H*-pyran-3(6*H*)-one (2)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
O-1	7976(1)	3210	-1582(1)	65(1)
C-2	8601(1)	4170(6)	-0830(2)	63(1)
C-3	8413(1)	4800(6)	0352(2)	65(1)
C-4	7894(1)	3111(6)	0704(2)	63(1)
C-5	7597(1)	1284(6)	0045(2)	66(1)
C-6	7715(1)	1009(6)	-1170(2)	65(1)
C-7	7029(1)	0316(7)	-2009(2)	81(1)
O-21	8812(1)	6288(5)	-1285(1)	79(1)
C-21	9176(1)	6019(6)	-2258(2)	65(1)
C-22	9019(2)	8321(7)	-2957(3)	83(1)
C-23	9421(2)	8352(8)	-3966(3)	92(1)
C-24	10229(2)	7944(7)	-3537(3)	93(1)
C-25	10374(2)	5610(8)	-2848(3)	90(1)
C-26	9981(1)	5629(7)	-1831(2)	79(1)
O-31	8694(1)	6470(6)	0939(2)	98(1)
O-41	7798(1)	3345(5)	1855(1)	73(1)
O-42	7036(1)	6473(5)	1308(1)	78(1)
C-41	7365(1)	5216(5)	2061(2)	60(1)
C-42	7342(1)	5377(6)	3316(2)	61(1)
C-43	7689(1)	3638(7)	4112(2)	69(1)
C-44	7625(2)	3827(7)	5266(2)	83(1)
C-45	7217(2)	5659(7)	5607(2)	85(1)
C-46	6877(2)	7373(7)	4828(2)	86(1)
C-47	6942(2)	7224(6)	3663(2)	75(1)
O-71	6488(1)	2118(6)	-1876(2)	86(1)
O-72	5925(1)	1684(6)	-3718(2)	103(1)
C-71	5974(1)	2690(7)	-2801(2)	72(1)
C-72	5503(1)	4689(7)	-2536(2)	74(1)
C-73	5589(2)	5663(7)	-1424(2)	84(1)
C-74	5151(2)	7589(8)	-1230(3)	101(2)
C-75	4627(2)	8525(9)	-2133(4)	106(2)
C-76	4538(2)	7499(10)	-3220(3)	106(2)
C-77	4980(2)	5622(9)	-3440(3)	91(2)

^a Standard deviations in parentheses.

fixed hydrogen atoms and an isotropic temperature factor⁴⁹. Positional parameters are listed in Tables XI and XII.

ACKNOWLEDGMENTS

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TABLE X

Fractional atomic coordinates for C and O atoms ($\times 10^4$)^a and equivalent isotropic thermal parameters for the two forms (**3A** and **3B**) of (6*S*)-4-benzoyloxy-6-benzoyloxymethyl-2*H*-pyran-3(6*H*)-one (**3**)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
O-1A	12 141(2)	5975(2)	2844(5)	54(1)
C-2A	11 390(4)	5504(4)	4604(8)	65(2)
C-3A	10 571(3)	6441(3)	5592(7)	57(2)
C-4A	10 401(3)	7453(3)	4028(7)	50(2)
C-5A	10 864(3)	7498(4)	1936(7)	57(2)
C-6A	11 687(3)	6543(4)	1088(7)	59(2)
C-7A	12 499(4)	7101(5)	− 636(10)	71(3)
O-31A	10 069(2)	6304(2)	7461(5)	75(2)
O-41A	9 607(2)	8309(2)	4819(4)	53(1)
C-41A	9 771(3)	9 001(3)	6 477(6)	41(2)
O-42A	10 591(2)	8 941(2)	7 143(4)	61(1)
C-42A	8 852(3)	9 777(3)	7 333(6)	48(2)
C-43A	7 993(3)	9 944(3)	6 250(7)	57(2)
C-44A	7 156(3)	10 674(3)	7 127(7)	64(2)
C-45A	7 171(3)	11 245(4)	9 076(7)	66(2)
C-46A	8 007(3)	11 118(4)	10 127(7)	66(2)
C-47A	8 873(3)	10 363(3)	9 280(6)	55(2)
O-71A	13 201(2)	6 175(2)	− 1 643(5)	65(2)
C-71A	13 803(3)	6 456(4)	− 3 637(7)	60(2)
O-72A	13 744(2)	7 414(3)	− 4 561(5)	67(2)
C-72A	14 528(3)	5 456(3)	− 4 393(7)	55(2)
C-73A	15 071(4)	5 531(4)	− 6 593(7)	73(2)
C-74A	15 792(4)	4 632(5)	− 7 385(9)	83(3)
C-75A	15 937(4)	3 663(5)	− 5 957(0)	87(3)
C-76A	15 405(4)	3 573(5)	− 3 840(9)	93(3)
C-77A	14 691(3)	4 458(4)	− 3 004(7)	69(2)
O-1B	2 680(2)	2 566(3)	6 019(6)	75(2)
C-2B	3 103(3)	2 833(4)	3 722(9)	66(2)
C-3B	3 937(3)	1 924(4)	2 755(8)	64(2)
C-4B	3 874(3)	739(3)	3 925(7)	62(2)
C-5B	3 099(3)	451(4)	5 503(7)	62(2)
C-6B	2 271(3)	1 390(3)	6 391(7)	57(2)
C-7B	2 000(4)	1 194(4)	8 911(8)	65(3)
O-31B	4 576(2)	2 172(3)	1 081(6)	82(2)
O-41B	4 719(2)	− 113(2)	3 179(5)	72(2)
C-41B	4 643(4)	− 621(4)	1 331(8)	56(2)
O-42B	3 941(2)	− 478(3)	373(6)	91(2)
C-42B	5 602(3)	− 1 425(3)	585(7)	51(2)
C-43B	5 641(3)	− 1 990(4)	− 1 393(7)	67(2)
C-44B	6 488(4)	− 2 737(4)	− 2 203(7)	69(2)
C-45B	7 299(3)	− 2 894(4)	− 1 022(8)	71(3)
C-46B	7 282(3)	− 2 331(4)	927(8)	71(2)
C-47B	6 415(3)	− 1 569(3)	1 756(7)	60(2)
O-71B	1 208(2)	2 110(3)	9 689(5)	63(2)
C-71B	651(3)	1 863(4)	11 654(8)	67(3)
O-72B	705(3)	922(3)	12 755(5)	72(2)
C-72B	− 96(3)	2 885(3)	12 457(7)	54(2)
C-73B	− 267(3)	3 880(4)	11 087(7)	62(2)
C-74B	− 975(3)	4 792(4)	11 903(8)	70(2)
C-75B	− 1 497(3)	4 699(4)	14 072(8)	77(3)
C-76B	− 1 301(4)	3 732(5)	15 447(8)	80(3)
C-77B	− 613(3)	2 808(4)	14 675(7)	62(2)

^a Standard deviations in parentheses.

TABLE XI

Fractional atomic coordinates for C and O atoms ($\times 10^4$)^a and equivalent isotropic thermal parameters for the two forms (**4A** and **4B**) of (2*S*,6*S*)-4,6-dibenzoyloxy-2-methyl-2*H*-pyran-3(6*H*)-one (**4**)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
O-1A	-1198(2)	4084(2)	-16570(2)	54(1)
C-2A	-999(2)	5183(2)	-16423(3)	54(1)
C-3A	-2249(3)	6407(2)	-16401(3)	54(1)
C-4A	-3454(2)	6161(2)	-15441(3)	50(1)
C-5A	-3425(3)	4959(2)	-14870(3)	56(1)
C-6A	-2189(2)	3780(2)	-15236(3)	55(1)
C-7A	106(3)	5352(3)	-17951(5)	81(1)
O-31A	-2269(2)	7513(2)	-17032(3)	80(1)
O-41A	-4583(2)	7256(2)	-15012(2)	58(1)
C-41A	-5169(2)	8103(2)	-16391(3)	54(1)
O-42A	-4847(2)	7849(2)	-17860(3)	71(1)
C-42A	-6232(2)	9322(2)	-15830(4)	54(1)
C-43A	-6555(3)	9519(3)	-14087(3)	66(1)
C-44A	-7527(3)	10704(4)	-13646(5)	84(2)
C-45A	-8161(3)	11671(3)	-14938(6)	80(2)
C-46A	-7836(3)	11474(3)	-16666(6)	84(2)
C-47A	-6866(3)	10310(3)	-17144(5)	70(1)
O-61A	-1777(2)	3164(2)	-13537(2)	56(1)
C-61A	-1270(2)	1823(2)	-13098(3)	48(1)
O-62A	-1174(2)	1129(2)	-14014(2)	66(1)
C-62A	-868(2)	1345(2)	-11332(3)	48(1)
C-63A	-832(2)	2187(3)	-10474(3)	58(1)
C-64A	-410(3)	1693(3)	-8880(4)	74(1)
C-65A	-54(3)	369(3)	-8115(4)	75(1)
C-66A	-115(3)	-474(3)	-8935(4)	73(1)
C-67A	-516(3)	10(3)	-10563(4)	62(1)
O-1B	6365(2)	-849(2)	-3481(2)	60(1)
C-2B	6623(3)	288(2)	-4625(3)	55(1)
C-3B	6049(2)	1391(2)	-3598(3)	53(1)
C-4B	6055(2)	951(2)	-1651(3)	53(1)
C-5B	6506(2)	-330(3)	-882(3)	55(1)
C-6B	6848(2)	-1342(2)	-1911(3)	54(1)
C-7B	6094(4)	694(3)	-6300(4)	84(1)
O-31B	5691(2)	2549(2)	-4319(3)	64(1)
O-41B	5767(2)	1937(2)	-769(2)	62(1)
C-41B	4512(3)	2891(3)	-650(3)	54(1)
O-42B	3642(2)	2689(2)	-794(3)	73(1)
C-42B	4415(2)	4133(2)	-346(3)	54(1)
C-43B	5443(3)	4210(3)	47(4)	67(1)
C-44B	5326(4)	5415(3)	234(4)	85(2)
C-45B	4178(4)	6519(3)	8(4)	85(2)
C-46B	3176(4)	6451(3)	-405(5)	82(1)
C-47B	3284(3)	5254(3)	-576(4)	66(1)
O-61B	8272(2)	-1952(2)	-2374(2)	57(1)
C-61B	8829(3)	-3223(2)	-2553(3)	59(1)
O-62B	8245(2)	-3925(2)	-2106(4)	90(1)
C-62B	10243(2)	-3629(3)	-3405(3)	57(1)
C-63B	10811(3)	-2724(3)	-4268(4)	74(1)
C-64B	12116(4)	-3136(5)	-5157(6)	98(2)
C-65B	12856(3)	-4466(5)	-5156(5)	93(2)
C-66B	12309(3)	-5373(4)	-4276(5)	81(2)
C-67B	11003(3)	-4961(3)	-3406(4)	73(1)

^a Standard deviations in parentheses.

TABLE XII

Fractional atomic coordinates for C and O atoms ($\times 10^4$)^a and equivalent isotropic thermal parameters for (2*S*,6*R*)-4,6-dibenzoyloxy-2-methyl-2*H*-pyran-3(6*H*)-one (5)

Atom	x	y	z	U_{eq}
O-1	-564(7)	-178(27)	-2311(7)	53(6)
C-2	-394(10)	-1489(32)	-1396(10)	37(8)
C-3	847(11)	-2350(31)	-1301(10)	37(8)
C-4	1373(11)	-3122(35)	-2267(10)	46(9)
C-5	873(10)	-2543(34)	-3100(8)	37(8)
C-6	-208(10)	-1219(28)	-3192(9)	30(6)
C-7	-1263(11)	-3543(38)	-1272(11)	79(11)
O-31	1329(7)	-2785(29)	-508(6)	64(6)
O-41	2455(7)	-4324(29)	-2202(6)	46(5)
C-41	2537(12)	-6403(38)	-1724(10)	43(9)
O-42	1687(8)	-7567(31)	-1525(8)	76(7)
C-42	3781(13)	-7249(37)	-1613(9)	44(9)
C-43	4675(12)	-5662(37)	-19464(10)	54(10)
C-44	5829(17)	-6609(53)	-1836(13)	123(17)
C-45	6015(15)	-8508(47)	-1336(15)	84(14)
C-46	5173(17)	-10100(55)	-941(13)	118(17)
C-47	4005(16)	-9144(51)	-1097(10)	97(14)
O-61	-1144(6)	-2831	-3574(6)	52(5)
C-61	-1336(11)	-2860(36)	-4558(9)	34(8)
O-62	-820(7)	-1613(25)	-5129(6)	54(6)
C-62	-2289(10)	-4491(32)	-4833(10)	33(8)
C-63	-2567(11)	-6352(35)	-4240(11)	52(10)
C-64	-3415(11)	-8081(38)	-4540(10)	63(11)
C-65	-4034(12)	-7628(44)	-5438(10)	65(11)
C-66	-3766(11)	-5858(33)	-6021(10)	43(9)
C-67	-2895(10)	-4074(40)	-5746(9)	56(9)

^a Standard deviations in parentheses.

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