CRYSTAL STRUCTURES OF SOME 3-(HYDROXYMETHYLENE)DIHYDRO-2(3*H*)-FURANONE DERIVATIVES

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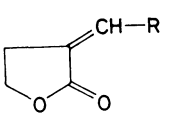
The crystal structures of (*Z*)-3-(*p*-toluenesulfonyloxymethylene)dihydro-2(3*H*)-furanone (*I*), (*E*)-3-(methanesulfonyloxymethylene)dihydro-2(3*H*)-furanone (*II*), and (*E*)-3-(benzoyloxymethylene)dihydro-2(3*H*)-furanone (*III*) were solved by direct methods. The intensities of the diffractions were recorded using MoK_α graphite monochromatized radiation, $\lambda = 0{\cdot}07107$ nm. The compound *I* is monoclinic, space group $P2_1/n$, with $a = 0{\cdot}8615(2)$, $b = 0{\cdot}5955(2)$, $c = 2{\cdot}3883(5)$ nm, $\beta = 93{\cdot}27(2)°$, $V = 1{\cdot}223(1)$ nm^3, $Z = 4$, $F(000) = 560$, $D_m = 1{\cdot}43$, $D_x = 1{\cdot}46$ Mg m^{-3}, $\mu = 0{\cdot}27$ mm^{-1}. The structure was refined to $R = 0{\cdot}042$ for 1 341 independent diffractions. Compound *II* is triclinic, space group $P\bar{1}$, with $a = 0{\cdot}5840(2)$, $b = 0{\cdot}8232(2)$, $c = 0{\cdot}9827(3)$ nm, $\alpha = 97{\cdot}68(3)$, $\beta = 110{\cdot}82(3)$, $\gamma = 108{\cdot}62(3)°$, $V = 0{\cdot}402(1)$ nm^3, $Z = 2$, $F(000) = 200$, $D_m = 1{\cdot}55$, $D_x = 1{\cdot}59$ Mg m^{-3}, $\mu = 0{\cdot}38$ mm^{-1}. The structure was refined to $R = 0{\cdot}041$ for 952 independent diffractions. Compound *III* is monoclinic, space group $P2/m$, with $a = 0{\cdot}9665(3)$, $b = 1{\cdot}1861(3)$, $c = 0{\cdot}9906(3)$ nm, $\beta = 112{\cdot}85(3)°$, $V = 1{\cdot}046(2)$ nm^3, $Z = 4$, $F(000) = 456$, $D_m = 1{\cdot}35$, $D_x = 1{\cdot}38$ Mg m^{-3}, $\mu = 0{\cdot}11$ mm^{-1}. The structure was refined to $R = 0{\cdot}048$ for 1 115 independent diffractions. The configurations of the compounds *I*, *II*, and *III* are in agreement with the assignments made on the basis of the NMR spectra.

The assignments of the (*E*)- or (*Z*)-configuration in the series of carboxylates and sulfonates of 3-(hydroxymethylene)dihydro-2(3*H*)-furanone seem to be well established[1-4] on the basis of the ^1H and ^{13}C NMR spectra. The same criteria



I, R = (*Z*)-*p*-$CH_3C_6H_4SO_3$
II, R = (*E*)-CH_3SO_3
III, R = (*E*)-$C_6H_5CO_2$

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TABLE I

Final atomic parameters of *I* and their e.s.d.'s in parentheses[a]

Atom	*x*	*y*	*z*	B_{eq}
S	4 648(1)	2 473(2)	1 131(04)	3·2(1)
O(1)	−0 879(3)	−0 926(4)	2 105(1)	4·8(2)
O(2)	1 188(3)	−2 350(4)	1 726(1)	5·5(3)
O(3)	3 303(3)	1 179(4)	1 454(1)	3·4(2)
O(4)	5 538(3)	0 661(4)	0 929(1)	4·4(2)
O(5)	5 335(3)	4 080(5)	1 506(1)	4·3(2)
C(1)	0 028(4)	2 708(7)	2 370(7)	4·0(3)
C(2)	−1 401(4)	1 227(7)	2 304(2)	4·3(4)
C(3)	0 577(4)	−0 780(6)	1 915(2)	3·6(3)
C(4)	1 136(4)	1 519(6)	2 011(1)	2·8(3)
C(5)	2 369(4)	2 427(6)	1 795(1)	3·2(3)
C(6)	3 609(4)	3 818(6)	0 582(1)	2·8(3)
C(7)	3 370(4)	2 763(6)	0 068(1)	3·4(3)
C(8)	2 505(4)	3 812(7)	−0 354(2)	4·1(3)
C(9)	1 853(4)	5 890(7)	−0 276(2)	4·0(3)
C(10)	2 107(4)	6 918(6)	0 238(2)	4·2(4)
C(11)	2 992(4)	5 929(6)	0 666(2)	3·5(3)
C(12)	0 868(5)	6 990(9)	−0 738(2)	6·2(5)

[a] The values of the positional parameters have been multiplied by 10^4. The average temperature factor B_{eq} is defined as $B_{eq} = 1/3 \sum_i \sum_j B_{ij} a_i^* a_j^* \boldsymbol{a}_i \boldsymbol{a}_j$ (ref.[11]).

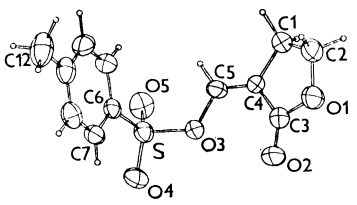

FIG. 1

A perspective view of the molecule of (*Z*)-3-(*p*-toluenesulfonyloxymethylene)dihydro-2-(3*H*)-furanone (*I*). The heavy atoms are represented as 50% ellipses, and the H atoms appear as 0·1 Å radius circles

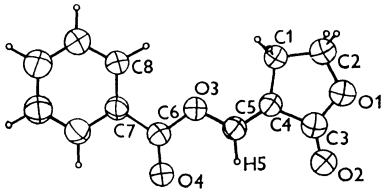

FIG. 2

A perspective view of the molecule of (*E*)-3-(methanesulfonyloxymethylene)dihydro-2-(3*H*)-furanone (*II*). The heavy atoms are represented as 50% ellipses, and the H atoms appear as 0·1 Å radius circles

TABLE II

Final atomic parameters of *II* and their e.s.d.'s in parentheses[a]

Atom	*x*	*y*	*z*	B_{eq}
S	3 475(2)	1 811(1)	3 219(1)	2·2(1)
O(1)	2 371(5)	3 348(3)	−2 818(3)	3·6(2)
O(2)	0 563(6)	4 573(4)	−1 562(3)	4·5(2)
O(3)	3 211(5)	1 582(3)	1 512(2)	3·6(2)
O(4)	1 871(5)	2 724(4)	3 428(3)	4'7(2)
O(5)	2 911(5)	0 045(3)	3 387(3)	3·6(2)
C(1)	4 050(7)	1 643(5)	−1 220(4)	3·2(3)
C(2)	3 681(8)	2 098(6)	−2 722(4)	4·6(3)
C(3)	1 724(6)	3 623(4)	−1 640(4)	2·4(2)
C(4)	2 717(6)	2 631(4)	−0 599(3)	2·0(2)
C(5)	2 330(6)	2 647(4)	0 641(3)	2·2(2)
C(6)	6 860(7)	3 142(5)	4 284(4)	3·0(3)

[a] See Table I.

TABLE III

Final atomic parameters of *III* and their e.s.d.'s in parentheses[a]

Atom	*x*	*y*	*z*	B_{eq}
O(1)	−4 708(3)	1 613(2)	3 899(2)	5·7(2)
O(2)	−4 352(3)	3 452(2)	3 718(3)	6·5(2)
O(3)	−1 309(2)	2 337(2)	1 791(2)	4·5(2)
O(4)	−0 663(3)	4 090(2)	1 402(3)	6·5(2)
C(1)	−3 256(4)	0 829(3)	2 638(4)	5·6(3)
C(2)	−4 152(4)	0 559(3)	3 568(4)	6·3(4)
C(3)	−4 091(4)	2 505(3)	3 487(3)	4·5(3)
C(4)	−3 110(4)	2 080(3)	2 766(3)	4·0(3)
C(5)	−2 270(4)	2 762(3)	2 381(3)	4·3(3)
C(6)	−0 484(4)	3 092(3)	1 374(4)	4·2(3)
C(7)	0 593(3)	2 524(3)	0 874(3)	3·7(3)
C(8)	0 870(4)	1 372(3)	1 046(4)	4·9(3)
C(9)	1 916(4)	0 905(3)	0 576(4)	5·9(4)
C(10)	2 685(4)	1 573(3)	−0 045(4)	5·6(3)
C(11)	2 391(4)	2 705(3)	−0 226(4)	5·4(3)
C(12)	1 349(4)	3 185(3)	0 224(4)	4·7(3)

[a] See Table I.

have been applied for assignment of the (*E*)- or (*Z*)-configuration in other derivatives of 3-(hydroxymethylene)dihydro-2(3*H*)-furanone[3,5] and in derivatives of other α-hydroxymethylene lactones[1,6,7]. We considered it useful to check the NMR assignment criteria against the X-ray structure of model compounds of the 3-(hydroxymethylene)dihydro-2-(3*H*)-furanone series. (*Z*)-3-(*p*-Toluenesulfonyloxymethylene)dihydro-2(3*H*)-furanone (*I*), (*E*)-3-(methanesulfonyloxymethylene)dihydro-2(3*H*)-furanone (*II*), and (*E*)-3-(benzoyloxymethylene)dihydro-2(3*H*)-furanone (*III*) were chosen for the structure determinations.

TABLE IV

Interatomic distance (.10^1 nm) in *I*, *II*, and *III* with e.s.d.'s in parentheses

Bond	*I*	*II*	Bond	*III*
C(1)–C(2)	1·516(5)	1·529(5)		1·524(6)
C(2)–O(1)	1·449(5)	1·459(6)		1·448(4)
O(1)–C(3)	1·360(4)	1·352(4)		1·353(4)
C(3)–O(2)	1·186(5)	1·199(5)		1·193(4)
C(3)–C(4)	1·465(5)	1·468(5)		1·479(5)
C(4)–C(1)	1·498(5)	1·500(5)		1·491(5)
C(4)–C(5)	1·322(5)	1·315(4)		1·304(5)
C(5)–O(3)	1·393(4)	1·393(4)		1·371(4)
O(3)–S	1·623(2)	1·609(2)	O(3)–C(6)	1·366(4)
S–O(4)	1·423(3)	1·425(3)		
S–O(5)	1·417(3)	1·430(3)		
S–C(6)	1·740(3)	1·744(4)	C(6)–C(7)	1·477(5)
C(6)–C(7)	1·383(5)		C(7)–C(8)	1·390(4)
C(7)–C(8)	1·370(5)		C(8)–C(9)	1·383(6)
C(8)–C(9)	1·376(6)		C(9)–C(10)	1·384(6)
C(9)–C(10)	1·380(6)		C(10)–C(11)	1·370(5)
C(10)–C(11)	1·372(5)		C(11)–C(12)	1·372(5)
C(11)–C(6)	1·384(5)		C(12)–C(7)	1·390(5)
C(9)–C(12)	1·503(6)			

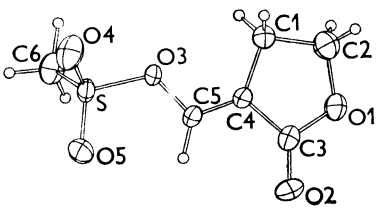

FIG. 3

A perspective view of the molecule of (*E*)-3-(benzoyloxymethylene)dihydro-2(3*H*)-furanone (*III*). The heavy atoms are represented as 50% ellipses, and the H atoms appear as 0·1 Å radius circles

EXPERIMENTAL

The compounds were prepared according to ref.[1]. Crystals suitable for X-ray analysis were obtained by recrystallization from alcohol solutions in the form of well-developed colourless needles. Their experimental densities were determined by the flotation method in a H_2O–K_2HgI_4 mixture. The space groups and preliminary lattice parameters were obtained from Weissenberg photographs. Final values of the lattice parameters were refined on 15 diffractions in the range $10 < 2\Theta < 25°$ recorded on a Syntex $P2_1$ diffractometer and are given in the abstract. The intensities of the diffractions of all three compounds were measured with $\Theta - 2\Theta$ scan technique. They were corrected for the L_p-factor but no absorption correction was applied. The structures were solved by direct methods in a straightforward manner and all the atoms, except the H's, were refined anisotropically by the block-diagonal matrix least-squares method with weights

TABLE V

Valence angles (°) in *I*, *II*, and *III* and their e.s.d.'s in parentheses

Angle	*I*	*II*	Angle	*III*
C(4)–C(1)–C(2)	101·9(3)	102·9(3)		102·4(3)
C(1)–C(2)–O(1)	106·5(3)	107·0(3)		107·6(3)
C(2)–O(1)–C(3)	111·2(3)	112·0(3)		111·2(3)
O(1)–C(3)–C(4)	108·1(3)	108·6(3)		108·6(3)
O(1)–C(3)–O(2)	121·5(3)	120·9(3)		121·8(3)
C(4)–C(3)–O(2)	130·5(3)	130·5(3)		129·5(3)
C(3)–C(4)–C(1)	108·4(3)	109·4(3)		108·9(3)
C(3)–C(4)–C(5)	125·9(3)	121·4(3)		121·2(3)
C(1)–C(4)–C(5)	125·6(3)	129·1(3)		129·9(3)
C(4)–C(5)–O(3)	120·9(3)	117·2(3)		119·9(3)
C(5)–O(3)–S	118·5(2)	121·9(2)	C(5)–O(3)–C(6)	117·4(3)
O(3)–S–O(4)	102·4(1)	108·7(2)	O(3)–C(6)–O(4)	122·2(3)
O(3)–S–O(5)	107·7(1)	103·9(2)	O(3)–C(6)–C(7)	111·9(3)
O(3)–S–C(6)	103·0(2)	102·1(2)	O(4)–C(6)–C(7)	125·9(3)
O(4)–S–O(5)	120·8(2)	119·5(2)	C(6)–C(7)–C(8)	122·3(3)
O(4)–S–C(6)	111·0(2)	111·0(2)	C(6)–C(7)–C(12)	117·6(3)
O(5)–S–C(6)	110·1(2)	110·0(2)		
S–C(6)–C(7)	120·2(3)			
S–C(6)–C(11)	119·6(3)			
C(11)–C(6)–C(7)	120·2(3)		C(12)–C(7)–C(8)	120·0(3)
C(6)–C(7)–C(8)	119·5(3)		C(7)–C(8)–C(9)	119·0(3)
C(7)–C(8)–C(9)	121·3(4)		C(8)–C(9)–C(10)	120·6(4)
C(8)–C(9)–C(10)	118·3(5)		C(9)–C(10)–C(11)	120·0(4)
C(9)–C(10)–C(11)	121·7(4)		C(10)–C(11)–C(12)	120·3(3)
C(10)–C(11)–C(6)	118·9(3)		C(11)–C(12)–C(7)	120·0(3)
C(8)–C(9)–C(12)	120·7(4)			
C(10)–C(9)–C(12)	121·0(4)			

$w = 1/\sigma^2|F_o|$. The refinement was carried out on $|F_o|$ and was stopped when the average shifts of the refined parameters were less than $0{\cdot}3\sigma$. All the programs employed during the structure solution and refinement were part of the XTL program system supplied by the Syntex Corp.

(*Z*)-3-(*p*-Toluenesulfonyloxymethylene)dihydro-2(3*H*)-furanone (*I*)

Out of 2 132 diffractions, maximum $2\Theta = 50°$, $0 < h < 10$, $0 < k < 7$, $-27 < l < 27$, measured, only 1 341 with $I < 3{\cdot}0\sigma(I)$ were considered observed and were used in the structure solution and refinement. The structure was refined to $R = 0{\cdot}042$, $R_w = 0{\cdot}042$.* Hydrogen atoms were positioned theoretically and refined isotropically. The final atomic parameters including B_{eq} are given in Table I.**

TABLE VI

Relevant interatomic distances (.10^1 nm) and angles (°) in some natural furanone derivatives with e.s.d.'s in parentheses

Parameter	Strigol[8]	Miscandenin[9]	Ineupatorolide[10]
		Bonds	
C(1)–C(2)	1·553(7)	1·514(6)	1·543(7)
C(2)–O(1)	1·471(7)	1·459(5)	1·437(6)
O(1)–C(3)	1·341(7)	1·363(6)	1·352(8)
C(3)–O(2)	1·218(7)	1·193(6)	1·198(9)
C(3)–C(4)	1·454(8)	1·484(7)	1·499(10)
C(4)–C(1)	1·505(8)	1·491(6)	1·492(7)
C(4)–C(5)	1·328(8)	1·324(7)	1·304(9)
C(5)–O(3)	1·369(7)		
		Angles	
C(4)–C(1)–C(2)	101·5(4)	99·6(3)	103·1(4)
C(1)–C(2)–O(1)	107·2(4)	102·8(3)	106·3(4)
C(2)–O(1)–C(3)	111·0(4)	108·4(3)	111·4(4)
O(1)–C(3)–C(4)	110·1(4)	108·3(3)	109·4(6)
O(1)–C(3)–O(2)	121·2(5)	121·1(4)	121·2(6)
C(4)–C(3)–O(2)	128·7(5)	130·6(4)	129·5(7)
C(3)–C(4)–C(1)	110·0(4)	104·1(3)	106·6(5)
C(3)–C(4)–C(5)	120·7(5)	123·2(3)	122·8(6)
C(1)–C(4)–C(5)	129·3(5)	132·7(3)	130·6(6)
C(4)–C(5)–O(3)	120·6(5)		

* $R_w = [\sum w_i(|F_o| - |F_c|)^2/\sum w_i|F_o|^2]^{1/2}$.

** A list of the structural factors and B_{ij} values can be obtained upon request from the authors.

(*E*)-3-(Methanesulfonyloxymethylene)dihydro-2(3*H*)-furanone (*II*)

Only 952 diffractions of a total of 1 125 measured, maximum $2\Theta = 46°$, $0 < h < 6$, $-8 < k < 8$, $-10 < l < 8$, had $I > 3{\cdot}06\sigma(I)$ and were used for structure solution and refinement. The structure was refined to $R = 0{\cdot}041$ and $R_w = 0{\cdot}048$. Hydrogen atoms were positioned theoretically and were not refined. The final atomic parameters including B_{eq} are given in Table II.

(*E*)-3-(Benzoyloxymethylene)dihydro-2(3*H*)-furanone (*III*)

The structure was solved and refined for 1 115 diffractions with $I < 3{\cdot}0\sigma(I)$, which were considered observed from a total of 1 656 measured up to $2\Theta = 50°$, $0 < h < 10$, $0 < k < 13$, $-11 < l < 10$, to $R = 0{\cdot}048$ and $R_w = 0{\cdot}055$. Hydrogen atoms were positioned theoretically and were not refined. The final atomic parameters including B_{eq} are summarized in Table III.

RESULTS AND DISCUSSION

Compounds *I*, *II*, and *III* are depicted in Figs 1, 2 and 3, resp. The furanone cycles deviate slightly from planarity, the average displacement *D* of C(1), C(2), O(1), C(3) and C(4) atoms from the best plane being approximately $3{\cdot}7\sigma(D)$, where atom C(2) exhibits the largest displacement. The lengths of the corresponding bonds of the furanone fragment common to all three molecules are equivalent within the $1{\cdot}96\sigma$ limit. This is also true for the S—O and S—C bond lengths of the —O—S(O)$_2$—C— fragment of the compounds *I* and *II* (Tables IV and V). The bond lengths and angles of *I*, *II* and *III* are in good agreement with those found for some natural furanone derivatives, strigol[8,12], miscandenin[9], and ineupatorolide[10]. The relevant interatomic distances and angles for these compounds are summarized in Table VI.

For the (*E*)- or (*Z*)-configurations, Figs 1, 2, and 3 clearly reveal that the configuration of *I* is (*Z*)- and those of *II* and *III* are (*E*)-configurations. This fully confirms the results obtained from the NMR data and it seems safe to conclude that the NMR criteria can be successfully applied to other series of α-*exo*-methylenelactone derivatives.

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REFERENCES

1. Howie G. A., Stamos I. K., Cassady J. M.: J. Med. Chem. *19*, 409 (1976).
2. Treptow W. L.: *Thesis*. The University of Utah, Salt Lake City 1980.
3. Stang P. J., Treptow W. L.: J. Med. Chem. *24*, 468 (1981).
4. Jonas J.: Collect. Czech. Chem. Commun. *49*, 1907 (1984).
5. Mazal C., Jurka J., Jonas J.: Collect. Czech. Chem. Commun. *49*, 2509 (1984).
6. Mazal C., Rothová V., Jonas J.: Collect. Czech. Chem. Commun. *50*, 348 (1985).
7. Mazal C., Jonas J.: Collect. Czech. Chem. Commun. *52*, 199 (1987).
8. Coggon P., Luhan P. A., McPhail A. T.: J. Chem. Soc., Perkin Trans. 2, *1973*, 465.
9. Cox P. J., Sim G. A.: J. Chem. Soc., Perkin Trans. 2, *1974*, 1359.

10. Baruah N. C., Baruah R. N., Sharma R. P., Baruah J. N., Herz W., Watanabe K., Blojnt J. F.: J. Org. Chem. *47*, 137 (1982).
11. Fischer R. X., Tillmanns E.: Acta Crystallogr., C *44*, 775 (1988).
12. Brooks D. W., Bevinakatti H. S., Powell D. R.: J. Org. Chem. *50*, 3779 (1985).

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