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(+)-5-*p*-Hydroxyphenyl-5-phenylhydantoin Camphor-10-sulphonate Ethyl Acetate

By M. H. J. Koch, G. Germain and J. P. Declercq
Institut Lavoisier, Université de Louvain, B-1348 Louvain la Neuve, Belgium
and Y. Dusausoy
Laboratoire de Minéralogie et de Cristallographie, équipe de Recherche associée au CNRS n° 162, Faculté des Sciences, Centre de 2e cycle, Case officielle n° 140, Nancy Cedex, France

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Abstract. Monoclinic; $P2_1$; $a = 16{\cdot}409$ (5), $b = 7{\cdot}422(3)$, $c = 13{\cdot}339(5)$ Å, $\beta = 114{\cdot}82°(2)$; 25°C; $C_{25}H_{26}N_2O_6S.C_4H_8O_2$; F.W. 520·3; Z = 2.

Introduction. The major metabolite of the anticonvulsant 5,5-diphenylhydantoin (DPH) in human liver is the levorotatory enantiomer of 5-*p*-hydroxyphenyl-5-phenylhydantoin (HPPH) (Butler, 1957).

This structure was determined in order to establish the absolute configuration of HPPH. The implications

Table 1. *Experimental data*

Source Cu $K\bar{\alpha}$; $\lambda = 1{\cdot}5418$ Å; $\theta_{\max} = 57°$
Confidence level: 2·5
Total number of independent reflexions: 2175
Total observed: 2004

Table 2. *Final positional and thermal parameters* (× 10^4) (*with standard deviations in parentheses*)

$$B = \exp\left[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)\right].$$

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
C(1)	−4735 (8)	−5210 (19)	−2615 (9)	31	89	24	−16	27	−6
O(2)	−5018 (9)	−4768 (20)	−3789 (9)	42	52	25	0	31	22
C(3)	−5015 (9)	−6229 (19)	−4367 (10)	34	49	39	−18	38	−6
N(4)	−4809 (8)	−7739 (16)	−3711 (8)	54	57	23	21	40	18
C(5)	−4636 (9)	−7271 (18)	−2642 (10)	28	68	36	32	22	10
O(6)	−4426 (7)	−8287 (14)	−1862 (7)	48	101	41	54	47	28
O(7)	−5150 (7)	−6264 (14)	−5374 (6)	62	94	22	−11	47	3
C(8)	−5479 (8)	−4859 (21)	−2221 (9)	34	71	45	−4	27	7
C(9)	−6380 (9)	−4706 (26)	−2957 (11)	33	160	45	8	29	16
C(10)	−7046 (10)	−4562 (32)	−2609 (14)	35	240	83	−41	55	10
C(11)	−6826 (15)	−4456 (36)	−1454 (22)	57	345	77	36	85	37
C(12)	−5923 (11)	−4552 (33)	−713 (12)	55	276	55	−16	61	2
C(13)	−5275 (9)	−4760 (27)	−1098 (10)	46	207	34	−6	54	−27
C(14)	−3846 (8)	−4259 (19)	−1917 (10)	23	79	36	−9	30	29
C(15)	−3846 (9)	−2455 (20)	−1682 (12)	35	54	73	−42	55	24
C(16)	−3044 (9)	−1505 (21)	−1161 (11)	25	116	65	−12	26	5
C(17)	−2260 (9)	−2418 (22)	−849 (11)	27	128	31	13	16	12
C(18)	−2217 (8)	−4191 (20)	−1039 (11)	20	95	53	4	7	17
C(19)	−3028 (16)	−5162 (32)	−1582 (19)	19	65	47	55	−7	120
O(20)	−1431 (6)	−1527 (16)	−241 (8)	25	143	57	−31	31	−38
S(21)	−1064 (2)	0 (0)	−812 (3)	34	114	62	−34	43	M9
C(22)	−909 (11)	−1290 (24)	−1831 (13)	54	150	80	−34	74	−31
C(23)	−605 (10)	−294 (23)	−2613 (12)	40	119	48	−15	31	−14
C(24)	−1307 (12)	−289 (36)	−3818 (14)	40	311	67	81	17	−3
C(25)	−809 (14)	32 (46)	−4549 (16)	82	485	60	24	61	−30
C(26)	160 (13)	267 (31)	−3674 (13)	48	208	86	23	60	11
C(27)	198 (15)	2085 (29)	−3129 (17)	81	196	93	68	89	−21
C(28)	−340 (13)	1764 (25)	−2422 (17)	67	157	82	−16	68	−43
C(29)	217 (11)	−1095 (25)	−2746 (12)	46	147	72	−11	64	25
C(30)	55 (17)	−3080 (34)	−3165 (22)	106	196	121	−89	158	2
C(31)	1094 (13)	−921 (43)	−1688 (18)	31	378	94	135	25	26
O(32)	−2102 (9)	−554 (35)	−4120 (12)	50	594	100	105	24	−47
O(33)	−1723 (9)	1316 (17)	−1287 (12)	55	101	155	38	113	76
O(34)	−207 (7)	436 (22)	47 (10)	39	325	90	−146	34	−169
C(35)	−2858 (17)	−5315 (74)	5641 (26)	61	1207	176	41	95	−10
C(36)	−2497 (16)	−5072 (52)	4790 (22)	65	462	166	−57	71	−34
O(37)	−3146 (11)	−4702 (31)	3806 (12)	92	417	102	−80	0	65
C(38)	−2767 (19)	−4590 (44)	3011 (23)	107	435	139	57	52	150
C(39)	−3548 (17)	−4510 (39)	1915 (22)	78	284	145	−28	85	61
O(40)	−1690 (12)	−5371 (44)	5000 (15)	82	783	184	220	113	6

of these results are discussed by Poupaert, Cavalier, Claesen & Dumont (1975). The crystals were obtained by slow evaporation of a solution in ethyl acetate. The space group was determined from preliminary Weissenberg photographs. The intensities were measured with a Nonius automatic three-circle diffractometer. The experimental conditions are given in Table 1.

The structure was solved by direct methods with *MULTAN* (Germain, Main & Woolfson, 1971) and refined by block-diagonal least-squares calculations with the programs written by Ahmed, Hall, Pippy & Huber (1966). The final value of $R=\sum||F_o|-|F_c||/\sum|F_o|=0{\cdot}09$ for all observed reflexions.* The scattering factors were those given in *International Tables for X-ray Crystallography* (1962). The final parameters are given in Table 2.

Table 3. *Intramolecular bond distances and angles (with standard deviations in parentheses)*

C(1)—O(2)	1·472 (16)	O(20)-S(21)	1·617 (12)
C(1)—C(5)	1·540 (19)	S(21)-C(22)	1·766 (17)
C(1)—C(8)	1·541 (19)	S(21)-O(33)	1·397 (14)
C(1)—C(14)	1·533 (19)	S(21)-O(34)	1·429 (14)
O(2)—C(3)	1·332 (19)	C(22)-C(23)	1·522 (24)
C(3)—N(4)	1·375 (18)	C(23)-C(24)	1·535 (23)
C(3)—O(7)	1·266 (14)	C(23)-C(28)	1·579 (25)
N(4)—C(5)	1·376 (17)	C(23)-C(29)	1·551 (26)
C(5)—O(6)	1·212 (16)	C(24)-C(25)	1·533 (30)
C(8)—C(9)	1·394 (20)	C(24)-O(32)	1·208 (26)
C(8)—C(13)	1·393 (17)	C(25)-C(26)	1·537 (30)
C(9)—C(10)	1·359 (24)	C(26)-C(27)	1·521 (31)
C(10)-C(11)	1·430 (32)	C(26)-C(29)	1·570 (26)
C(11)-C(12)	1·396 (33)	C(27)-C(28)	1·558 (34)
C(12)-C(13)	1·369 (25)	C(29)-C(30)	1·558 (31)
C(14)-C(15)	1·375 (21)	C(29)-C(31)	1·541 (28)
C(14)-C(19)	1·396 (30)	C(35)-C(36)	1·496 (42)
C(15)-C(16)	1·395 (22)	C(36)-O(37)	1·327 (31)
C(16)-C(17)	1·355 (22)	C(36)-O(40)	1·253 (36)
C(17)-C(18)	1·347 (22)	O(37)-C(38)	1·439 (36)
C(17)-O(20)	1·421 (19)	C(38)-C(39)	1·486 (40)
C(18)-C(19)	1·416 (29)		

O(2)—C(1)—C(5)	100·7 (11)
O(2)—C(1)—C(8)	112·6 (11)
O(2)—C(1)—C(14)	109·7 (11)
C(5)—C(1)—C(8)	106·4 (11)
C(5)—C(1)—C(14)	112·9 (11)
C(8)—C(1)—C(14)	113·8 (11)
C(1)—O(2)—C(3)	111·0 (12)
O(2)—C(3)—N(4)	110·7 (12)
O(2)—C(3)—O(7)	126·1 (13)
N(4)—C(3)—O(7)	123·1 (13)
C(3)—N(4)—C(5)	110·1 (12)
C(1)—C(5)—N(4)	107·3 (11)
C(1)—C(5)—O(6)	126·3 (13)
N(4)—C(5)—O(6)	126·3 (13)
C(1)—C(8)—C(9)	122·1 (12)
C(1)—C(8)—C(13)	120·6 (12)
C(9)—C(8)—C(13)	117·3 (14)
C(8)—C(9)—C(10)	122·1 (16)
C(9)—C(10)-C(11)	119·9 (19)
C(10)-C(11)-C(12)	118·1 (22)
C(11)-C(12)-C(13)	120·1 (20)
C(8)—C(13)-C(12)	122·3 (16)
C(1)—C(14)-C(15)	119·7 (12)
C(1)—C(14)-C(19)	121·0 (15)
C(15)-C(14)-C(19)	119·1 (16)
C(14)-C(15)-C(16)	121·0 (14)
C(15)-C(16)-C(17)	118·4 (14)
C(16)-C(17)-C(18)	123·2 (14)
C(16)-C(17)-O(20)	120·0 (13)
C(18)-C(17)-O(20)	116·7 (13)
C(17)-C(18)-C(19)	118·8 (16)
C(14)-C(19)-C(18)	119·4 (19)
C(17)-O(20)-S(21)	121·0 (9)
O(20)-S(21)-C(22)	100·7 (7)
O(20)-S(21)-O(33)	109·4 (7)
O(20)-S(21)-O(34)	102·5 (7)
C(22)-S(21)-O(33)	111·3 (8)
C(22)-S(21)-O(34)	109·3 (8)
O(33)-S(21)-O(34)	121·3 (9)
S(21)-C(22)-C(23)	117·3 (12)
C(22)-C(23)-C(24)	113·6 (15)
C(22)-C(23)-C(28)	120·4 (15)
C(22)-C(23)-C(29)	116·3 (14)
C(24)-C(23)-C(28)	101·6 (15)
C(24)-C(23)-C(29)	100·8 (14)
C(28)-C(23)-C(29)	101·3 (14)
C(23)-C(24)-C(25)	107·5 (18)
C(23)-C(24)-O(32)	125·4 (20)
C(25)-C(24)-O(32)	127·0 (22)
C(24)-C(25)-C(26)	101·1 (19)
C(25)-C(26)-C(27)	106·6 (18)
C(25)-C(26)-C(29)	103·1 (17)
C(27)-C(26)-C(29)	102·6 (16)
C(26)-C(27)-C(28)	103·5 (18)
C(23)-C(28)-C(27)	103·8 (16)
C(23)-C(29)-C(26)	94·4 (14)
C(23)-C(29)-C(30)	112·2 (16)
C(23)-C(29)-C(31)	112·6 (16)
C(26)-C(29)-C(30)	112·4 (17)
C(26)-C(29)-C(31)	113·1 (16)
C(30)-C(29)-C(31)	111·2 (18)
C(35)-C(36)-O(37)	111·5 (28)
C(35)-C(36)-O(40)	121·8 (30)
O(37)-C(36)-O(40)	126·3 (29)
C(36)-O(37)-C(38)	109·0 (23)
O(37)-C(38)-C(39)	105·4 (24)

Discussion. The conformation of the molecule and the numbering scheme are shown in Fig. 1 and the bond distances and angles in Table 3.

The absolute configuration of (+) HPPH is *R* according to the convention of Cahn, Ingold & Prelog

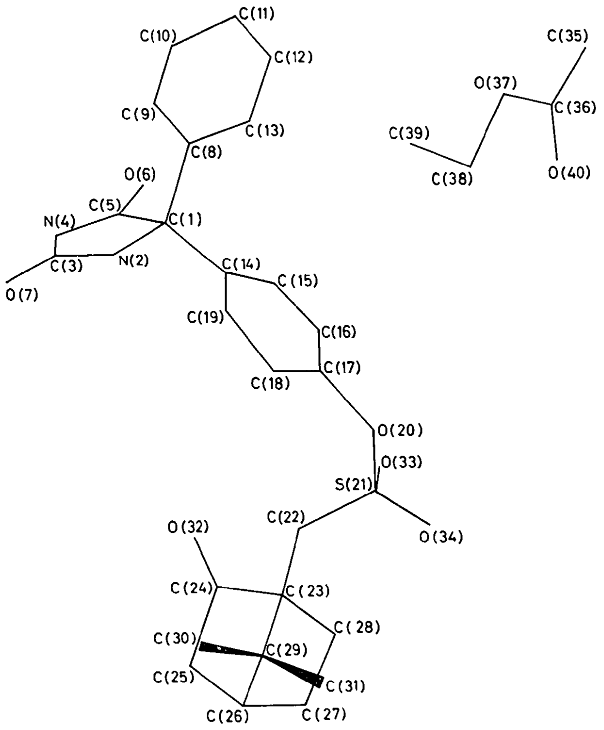

Fig. 1. Conformation and atomic numbering of $C_{25}H_{26}N_2O_6S.C_4H_8O_2$.

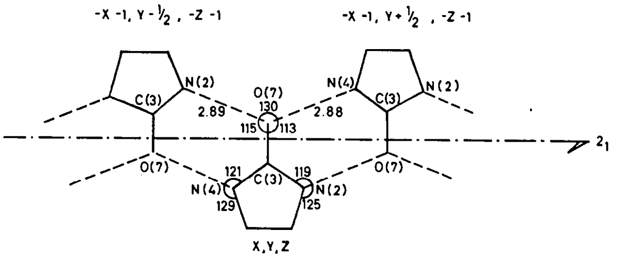

Fig. 2. Hydrogen-bonding pattern in $C_{25}H_{26}N_2O_6S.C_4H_8O_2$.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31114 (12 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

(1966) with the configuration of camphor as a reference (Fredga & Miettinen, 1947; Wunderlich, 1967).

The hydantoin ring is planar as in DPH (Camerman & Camerman, 1970). The angles between the phenyl groups and the hydantoin ring are given in Table 4 with the corresponding values in DPH.

Table 4. *Angles between the planes of the rings in HPPH and DPH*

HPPH		DPH	
phenyl–hydantoin:	104°	phenyl–hydantoin:	114°
phenol–hydantoin:	104	phenyl–hydantoin:	113
phenol–phenyl:	105	phenyl–phenyl:	90

The molecules are hydrogen bonded to two neighbouring molecules as shown in Fig. 2.

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SHORT COMMUNICATIONS

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Acta Cryst. (1975). B31, 2549

Some chlorides with the inverse spinel structure: Li_2TCl_4 (T=Mg,Mn,Fe,Cd).

By C. J. J. van Loon and J. de Jong, *Gorlaeus Laboratories, Section of Solid State Chemistry, University of Leiden, P.O. Box* 75, *Leiden, The Netherlands*

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X-ray diffraction patterns suggest that the compounds Li_2TCl_4 (T = Mg, Mn, Fe, Cd) have the inverse spinel structure. A structure refinement, based on neutron diffraction powder data, has been carried out for Li_2MnCl_4.

Introduction

An investigation of the systems NaCl–TCl_2 and LiCl–TCl_2 (T = Mg, Mn, Fe, Co, Ni, Cu, Zn, Cd, Ca, Sr, Ba, Pb) has been started in order to enlarge the number of structural data available for comparison with theoretically derived structure models. A systematic derivation of $^{VI}A^{VI}BX_3$ structures (van Loon, 1974) has been carried out, but the number of ABX_3 compounds found within the investigated range is only very small. Three compounds, *viz.* $NaMnCl_3$, $NaMgCl_3$ and $NaCdCl_3$, have been prepared. Single crystals of one of these isostructural compounds, $NaMnCl_3$, have been used in a structure refinement (van Loon & Verschoor, 1973). Several compounds with different stoichiometries (Na_2TCl_4, Na_6TCl_8, $Na_2T_3Cl_8$; T = Mg, Mn, Fe, Cd) have been established and their structures determined (van Loon & IJdo, 1975). The compounds Na_2CoCl_4, Na_2ZnCl_4 and Li_2ZnCl_4 apparently have the chrysoberyl (Wyckoff, 1964) structure; their structure refinement will be the subject of a subsequent paper.

Experimental

LiCl was dried *in vacuo* at 400°C. $MnCl_2$ was obtained by dehydrating $MnCl_2.4H_2O$ in HCl atmosphere in steps up to 350°C, followed by melting in dry nitrogen. Molten $MgCl_2$ was obtained by heating Mg metal at 900°C in a stream of dry HCl gas. $FeCl_2$ and $CdCl_2$ were obtained from the hydrates $FeCl_2.4H_2O$ and $CdCl_2.xH_2O$ by

Table 1. *Structural data of* Li_2TCl_4 *compounds*

Space group: $Fd3m$, $Z=8$ (origin at centre, $\bar{3}m$)

		x	y	z	n
Li(1)	16(*d*)	0·5	0·5	0·5	0·25
Li(2)	8(*a*)	0·125	0·125	0·125	0·25
Mn	16(*d*)	0·5	0·5	0·5	0·25
Cl	32(*e*)	0·2564 (1)	0·2564 (1)	0·2564 (1)	1·0

	a
Li_2MnCl_4	10·5031 (3) Å
Li_2MgCl_4	10·413 (1)
Li_2CdCl_4	10·637 (5)
Li_2FeCl_4	10·405 (3)

Refinement of site occupation number

n[Li(1) at 16(d)] = 0·284 (8)

n[Li(2) at 8(a)] = 0·216 (8)

n[Mn(1) at 8(a)] = 0·034 (8)

n[Mn(2) at 16(d)] = 0·216 (8)

$c = 0·0410$ (4) $B = -1·94$ (6)

$x_{Cl} = 0·2564$ (1)