Instrumental Achievements

— X-Ray Analysis —

Characterization of Three Polymorphs of Tetrakis[3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionyloxymethyl]methane

Nobuhiro MARUBAYASHI, Yasuhiko ISHIDA and Mamoru HARATAKE

Research Laboratories, Yoshitomi Pharmaceutical Industries, Ltd., Yoshitomi-cho, Fukuoka 871, Japan

It is presently known that tetrakis[3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionyloxymethyl]methane (BHPM) exists in three polymorphs.^{1,2} They have been employed widely as useful antioxidants for plastics (Tominox-TT®, Irganox 1010® *etc.*). However, no detailed characterization of the polymorphs has yet been carried out. In the present study, the three polymorphs were characterized by infrared absorption spectrometry, differential scanning calorimetry (DSC) and X-ray crystallography.

Experimental

Three polymorphs were obtained according to procedures of the Official Patent Gazette.^{1,2} Infrared absorption spectra were recorded on a JASCO IR-810 spectrometer. The thermal analyses were carried out on a SEIKO I&E DSC 20. Single-crystal X-ray analyses were performed on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Cu K α radiation. Intensity data collection was accomplished by the ω -2 θ scan method. The obtained data were corrected for both Lorentz and polarization effects, but not for absorption. The structures were solved by a direct method with MULTAN 82 and refined by methods involving block-diagonal least-squares and a subsequent difference Fourier process.

Results and Discussion

The infrared absorption spectra of the three polymorphs (forms I, II and III) are shown in Fig. 1. The absorption bands assigned to the hydroxyl and carbonyl stretching vibrations were observed in the

Fig. 1 Infrared absorption spectra of BHPM polymorphs in KBr pellets. (A) form I; (B) form II; (C) form III.

Table 1 Thermal behavior of the three polymorphs

Form	Melting point/°C	Enthalpy changes/kJmol ⁻¹
I	122.2	86.7
II	111.9	71.4
III	117.5	84.7

Heating rate: 5.0°Cmin.⁻¹

Fig. 2 Chemical structure of BHPM and its atomic labeling.

respective regions. A slight splitting or broadening of these bands appeared in the spectra of forms I and II. The three forms show only endothermic peaks accompanying melting on the DSC curves. Table 1 lists the melting points and enthalpy changes on melting of the three polymorphs. Both values of form II were smaller than those of the other forms.

Table 2-a Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors of form I with the estimated standard deviation

Atom	X	Y	Z	B _{eq}
O1A	8758(2)	2474(1)	11242(2)	3.34(6)
O2A	8990(2)	1917(1)	12956(3)	4.48(8)
O3A	4277(2)	1235(1)	13089(3)	5.94(9)
O1B	9814(2)	1866(1)	8307(2)	3.06(5)
O2B	11306(2)	1542(1)	8093(3)	3.84(7)
O3B	10991(2)	-900(1)	8586(3)	4.98(8)
O1C	11242(2)	2527(1)	12484(2)	3.32(6)
O2C	11012(2)	3083(1)	13968(2)	4.48(7)
O3C	15726(2)	3764(1)	18813(3)	6.04(9)
O1D	10084(2)	3132(1)	8393(2)	3.07(5)
O2D	8694(2)	3459(1)	6788(3)	3.81(6)
O3D	9007(2)	5900(1)	7596(3)	5.03(8)
C0	10000(2)	2501(1)	10032(3)	2.53(7)
C1A	9238(3)	2165(1)	10512(3)	3.10(9)
C2A	8713(2)	2313(1)	12481(3)	2.84(8)
C3A	8330(3)	2699(1)	13196(4)	3.28(9)
C4A	8015(3)	2504(1)	14411(3)	3.28(9)
C5A	7043(2)	2143(1)	13994(3)	2.58(7)
C6A	6874(2)	1856(1)	15046(3)	2.98(8)
C7A	5959(3)	1551(1)	14783(4)	3.32(9)
C8A	5210(3)	1535(1)	13391(4)	3.50(9)
C9A	5349(2)	1809(1)	12289(3)	2.98(8)
C10A	6283(2)	2108(1)	12643(3)	2.76(8)
C11A	5790(4)	1238(2)	15982(5)	4.88(13)
C12A	6719(5)	1350(2)	17432(5)	7.24(18)
C13A	4779(4)	1379(2)	16213(6)	6.91(19)
C14A	5709(6)	677(2)	15592(8)	8.59(26)
C15A	4496(3)	1806(1)	10769(4)	4.05(10)
C16A	3524(3)	2056(2)	10844(6)	6.35(15)
C17A	4186(4)	1274(2)	10087(5)	6.29(15)
C18A	4895(4)	2116(2)	9747(4)	5.50(13)
C1B	10637(2)	2167(1)	9497(3)	2.86(8)
C2B	10370(2)	1564(1)	7676(3)	2.58(8)
C3B	9567(3)	1289(1)	6411(3)	3.27(9)
C4B	10044(3)	914(1)	5737(3)	3.37(9)
C5B	10314(2)	442(1)	6552(3)	2.70(8)
C6B	11319(2)	286(1)	6973(3)	2.92(8)
C7B	11580(2)	-159(1)	7647(3)	3.02(8)
C8B	10777(3)	-448(1)	7914(3)	3.22(9)
C9B	9757(3)	-299(1)	7549(3)	2.90(8)
C10B	9548(2)	147(1)	6846(3)	2.91(8)
C11B	12720(3)	-316(1)	8102(4)	3.84(10)
C12B	13429(3)	59(2)	7626(6)	5.93(15)
C13B	13220(4)	-322(2)	9752(5)	6.97(17)
C14B	12746(4)	-820(2)	7376(7)	7.42(20)
C15B	8885(3)	-609(1)	7878(4)	3.64(10)
C16B	8603(4)	-1106(1)	7009(5)	4.98(13)
C17B	7857(3)	-332(2)	7451(6)	5.70(15)
C18B	9235(4)	-710(2)	9491(4)	5.57(14)
C1C	10757(3)	2831(1)	11272(3)	3.09(8)
C2C	11287(2)	2688(1)	13767(3)	2.78(8)
C3C	11673(3)	2300(1)	14868(3)	3.29(8)
C4C	11983(3)	2497(1)	16396(3)	3.21(8)
C5C	12959(2)	2857(1)	16955(3)	2.55(7)
C6C	13127(2)	3145(1)	18172(3)	3.03(8)
C7C	14041(3)	3452(1)	18821(3)	3.31(9)
C8C	14789(3)	3465(1)	18181(4)	3.54(9)
C9C	14651(2)	3190(1)	16940(3)	2.93(8)
C10C	13717(2)	2889(1)	16357(3)	2.80(8)
C11C	14213(4)	3759(2)	20190(4)	4.97(12)
C12C	13283(4)	3646(2)	20717(5)	7.11(18)
C13C	15227(4)	3620(2)	21428(5)	6.97(17)
C14C	14300(6)	4324(2)	19884(7)	8.41(23)
C15C	15507(3)	3193(1)	16278(4)	4.06(10)
C16C	15820(4)	3725(2)	15911(6)	6.35(17)
C17C	15112(4)	2883(2)	14854(5)	5.55(14)
C18C	16484(3)	2944(2)	17327(6)	6.32(16)
C1D	9359(2)	2833(1)	8858(3)	2.83(8)
C2D	9628(2)	3436(1)	7305(3)	2.61(7)
C3D	10436(3)	3710(1)	6844(4)	3.30(9)
C4D	9962(3)	4088(1)	5697(3)	3.32(9)
C5D	9689(3)	4558(1)	6243(3)	2.76(8)
C6D	8684(2)	4714(1)	5656(3)	2.90(8)
C7D	8416(2)	5159(1)	6065(3)	3.03(8)
C8D	9220(3)	5447(1)	7134(3)	3.22(9)
C9D	10241(3)	5298(1)	7790(3)	2.90(8)
C10D	10451(2)	4852(1)	7299(3)	2.91(8)
C11D	7281(3)	5317(1)	5383(4)	3.93(10)
C12D	6573(3)	4938(2)	4202(5)	5.94(14)
C13D	7255(4)	5822(2)	4629(7)	7.52(18)
C14D	6783(4)	5328(2)	6533(6)	6.92(18)
C15D	11119(3)	5609(1)	8896(3)	3.63(9)
C16D	11389(4)	6107(1)	8403(4)	4.98(12)
C17D	12146(3)	5334(2)	9590(5)	5.72(13)
C18D	10761(4)	5711(2)	10256(4)	5.60(14)

Table 2-b Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors of form II with the estimated standard deviation

Atom	X	Y	Z	B _{eq}
O1A	9923(2)	932(2)	1367(2)	4.42(8)
O2A	8979(2)	-6(2)	56(2)	4.79(9)
O3A	9839(2)	-1995(2)	5196(3)	5.70(12)
O1B	8957(2)	2325(2)	1803(2)	4.90(10)
O2B	8658(3)	2389(3)	3302(3)	7.64(16)
O3B	2923(2)	676(2)	-58(3)	6.72(13)
O1C	10882(2)	2769(2)	43(2)	4.52(9)
O2C	9635(3)	2271(4)	-1236(3)	9.64(20)
O3C	11121(4)	6005(2)	-1183(4)	8.66(19)
O1D	11847(2)	3050(2)	2544(2)	5.11(9)
O2D	13209(3)	2823(3)	2670(5)	10.30(20)
O3D	14797(3)	6939(2)	7428(3)	7.91(14)
C0	10406(3)	2255(2)	1397(3)	3.29(10)
C1A	9920(3)	1453(2)	720(3)	3.78(11)
C2A	9423(3)	203(2)	917(3)	4.02(12)
C3A	9483(4)	-306(3)	1611(4)	5.61(17)
C4A	9393(3)	-8(3)	2660(3)	4.53(14)
C5A	9516(3)	-560(2)	3319(3)	4.02(12)
C6A	10359(3)	-725(2)	3562(3)	4.17(13)
C7A	10502(3)	-1221(2)	4165(3)	4.02(12)
C8A	9752(3)	-1529(2)	4548(3)	4.09(13)
C9A	8874(3)	-1403(2)	4292(3)	3.85(12)
C10A	8781(3)	-911(2)	3668(3)	3.97(12)
C11A	11443(3)	-1398(3)	4393(4)	5.10(16)
C12A	11970(4)	-1038(4)	5524(4)	6.46(19)
C13A	11300(4)	-2279(3)	4084(5)	6.52(20)
C14A	12098(4)	-1054(4)	3765(5)	7.68(26)
C15A	8031(3)	-1789(3)	4651(3)	4.53(14)
C16A	7156(4)	-1542(5)	4267(6)	8.22(27)
C17A	8249(4)	-1569(4)	5812(4)	6.60(20)
C18A	7788(5)	-2671(3)	4245(6)	7.87(23)
C1B	9929(3)	2431(3)	2263(3)	3.99(12)
C2B	8385(3)	2304(3)	2407(4)	5.25(16)
C3B	7381(3)	2177(4)	1842(5)	6.35(19)
C4B	6814(3)	1370(3)	1728(4)	5.05(15)
C5B	5767(3)	1211(3)	1275(4)	4.55(13)
C6B	5123(3)	840(3)	1719(4)	4.68(14)
C7B	4162(3)	653(3)	1309(4)	4.60(14)
C8B	3868(3)	861(3)	426(4)	4.82(14)
C9B	4484(3)	1253(3)	-39(4)	4.81(14)
C10B	5443(3)	1425(3)	408(4)	4.73(14)
C11B	3481(4)	219(3)	1825(4)	5.70(17)
C12B	2820(4)	698(4)	2142(5)	7.50(23)
C13B	2911(4)	-577(3)	1113(5)	6.68(20)
C14B	4024(5)	80(5)	2806(5)	8.04(26)
C15B	4144(4)	1474(3)	-1023(4)	5.64(17)
C16B	4974(4)	1939(4)	-1353(5)	8.03(25)
C17B	3620(4)	743(4)	-1885(4)	6.90(20)
C18B	3491(5)	1894(4)	-857(6)	8.23(27)
C1C	10324(3)	2826(3)	765(3)	4.21(13)
C2C	10469(4)	2518(3)	-938(4)	5.21(15)
C3C	11140(4)	2531(3)	-1598(4)	5.34(16)
C4C	12000(4)	3231(3)	-1218(4)	4.86(15)
C5C	11763(3)	3969(2)	-1202(3)	4.16(13)
C6C	11014(3)	4507(3)	-294(3)	4.46(13)
C7C	11716(3)	5197(3)	-251(4)	4.74(14)
C8C	11348(4)	5327(3)	-1182(4)	5.45(16)
C9C	11176(4)	4803(3)	-2118(4)	4.75(14)
C10C	11389(3)	4132(3)	-2092(3)	4.51(14)
C11C	11888(4)	5779(3)	766(4)	6.72(19)
C12C	12290(6)	5453(5)	1650(5)	9.89(32)
C13C	10851(6)	5911(4)	929(6)	8.72(28)
C14C	12608(8)	6541(5)	807(7)	12.42(38)
C15C	10769(5)	4984(4)	-3133(4)	6.34(20)
C16C	11441(7)	5680(4)	-3282(6)	9.46(32)
C17C	9780(6)	5054(6)	-3167(6)	9.98(35)
C18C	10705(6)	4298(4)	-4039(5)	8.89(29)
C1D	11421(3)	2304(2)	1840(3)	3.61(11)
C2D	12755(4)	3234(3)	2924(4)	6.25(17)
C3D	13183(6)	3996(5)	3630(7)	10.94(33)
C4D	12697(7)	4181(5)	4207(7)	10.89(34)
C5D	13533(13)	4944(4)	5194(7)	17.67(72)
C6D	13646(9)	5630(4)	4932(6)	13.02(47)
C7D	14089(9)	6313(3)	5886(5)	5.86(21)
C8D	14373(4)	6270(3)	6669(4)	6.10(17)
C9D	14228(5)	5586(4)	6964(5)	8.00(25)
C10D	13805(10)	4915(4)	8188(6)	13.16(50)
C11D	14187(5)	7068(3)	5370(5)	6.87(20)
C12D	13723(8)	6947(5)	4231(6)	11.14(38)
C13D	15213(6)	7526(5)	5588(8)	10.64(37)
C14D	13660(6)	7553(5)	5936(7)	10.04(33)
C15D	14504(6)	5549(5)	8071(6)	9.19(30)
C16D	13995(6)	6019(6)	8708(6)	10.65(37)
C17D	14190(9)	4692(6)	8150(8)	12.79(48)
C18D	15583(6)	5868(7)	8528(9)	12.25(47)

The chemical structure of BHPM and its atomic labeling are shown in Fig. 2. The atomic coordinates and equivalent isotropic temperature factors of non-hydrogen atoms are given in Table 2. The BHPM molecule spreads out the four flexible side chains (A, B, C and D), namely the four 3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionyloxymethyl groups. In order to

Table 2-c Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors of form III with the estimated standard deviation

Atom	X	Y	Z	Beq
O1	-878(1)	153(1)	1895(3)	3.56(5)
O2	-1283(2)	-676(1)	3292(5)	9.50(13)
O3	-3898(1)	1962(1)	7958(3)	4.37(6)
C0	0(0)	0(0)	0(0)	2.60(1)
C1	-534(1)	-348(1)	989(4)	2.96(1)
C2	-1254(2)	-84(2)	3028(4)	4.05(8)
C3	-1649(2)	452(2)	3838(4)	3.75(8)
C4	-2055(2)	161(2)	5145(5)	4.29(9)
C5	-2542(2)	660(2)	5864(4)	3.27(7)
C6	-3170(2)	783(2)	5230(4)	3.14(7)
C7	-3639(1)	1218(1)	5872(3)	2.72(6)
C8	-3456(1)	1528(1)	7251(3)	2.80(6)
C9	-2833(1)	1421(1)	7950(3)	2.76(6)
C10	-2365(1)	981(2)	7224(4)	3.16(7)
C11	-4339(2)	1336(2)	5153(4)	3.51(7)
C12	-4423(2)	906(3)	3709(5)	5.99(12)
C13	-4432(2)	2085(2)	4730(6)	5.64(12)
C14	-4898(2)	1089(2)	6225(5)	4.14(8)
C15	-2856(2)	1749(2)	9477(4)	3.50(7)
C16	-1948(2)	1543(2)	10020(5)	5.14(10)
C17	-2659(2)	2527(2)	9338(5)	5.18(11)
C18	-3159(2)	1530(2)	10705(4)	4.54(9)

Table 3 Selected torsion angles of the side chains on BHPM

Form	Chain	τ_1	τ_2	τ_3	τ_4
I	A	-134.2	172.6	166.4	-68.1
	B	177.3	-176.9	-175.6	76.4
	C	-134.1	172.2	166.6	-68.7
	D	177.6	-176.9	-175.5	75.8
II	A	172.4	177.9	44.2	-177.1
	B	167.4	-179.1	105.7	173.4
	C	113.3	176.7	-38.7	-63.2
	D	-172.7	179.4	38.9	161.8
III	all	-166.5	-174.6	-178.6	-171.7

τ_1 : C0-C1-O1-C2, τ_2 : C1-O1-C2-C3, τ_3 : O1-C2-C3-C4, τ_4 : C2-C3-C4-C5.

compare the molecular structure of each form, selected torsion angles of the side chains are listed in Table 3. The two chains (A and C) in form I contain *gauche* conformations at the C1-O1 and C3-C4 bonds; the other chains (B and D) show such conformations at C3-C4. Thus, BHPM in form I possesses an approximate two-fold axis of rotation as an element of molecular symmetry. On the other hand, the torsion angles in form II have no such regularity. It has been found that the symmetry of the molecular structure in form II is lower than those in forms I and III. In form III, the BHPM molecule has a four-fold axis of rotatory inversion symmetry, which coincides with the symmetry of the unit cell at the origin.

Figure 3 illustrates the molecular packing of the three forms; their crystal parameters are summarized in Table 4. The space groups are triclinic $P\bar{1}$ for forms I and II, and tetragonal $\bar{4}$ for form III. The density of form II, containing a less regular molecular structure, is smaller than those of the other forms, indicating that the BHPM molecules are packed loosely. This is also seen in the larger temperature factors of the side chain atoms in form II. The BHPM molecule possesses alkoxy-carbonyl (ester) and hydroxyl groups that are capable of forming hydrogen bonding. As Table 5 shows, some oxygen atoms of BHPM in forms I and II

(A)

(B)

(C)

Fig. 3 Molecular packing views of the three polymorphs along the *c*-axis. (A) form I; (B) form II; (C) form III. The dotted lines express the intermolecular hydrogen bonding.

Table 4 Crystal parameters of the three polymorphs

	Form I	Form II	Form III
Chemical formula	$C_{73}H_{106}O_{12}$		
Molecular weight	1177.7		
Crystal system	triclinic	triclinic	tetragonal
Space group	$P\bar{1}$	$P\bar{1}$	$I\bar{4}$
a (Å)	13.649 (1)	15.199 (2)	19.791 (2)
b	27.060 (4)	18.730 (2)	19.791 (2)
c	10.068 (1)	13.951 (1)	8.842 (1)
α (°)	90.02 (1)	101.71 (1)	90.00
β	111.57 (1)	101.13 (1)	90.00
γ	94.29 (1)	103.69 (1)	90.00
Volume (Å ³)	3458.1 (7)	3655.3 (7)	3463.1 (6)
Z	2	2	2
Dx (gcm ⁻³)	1.130	1.069	1.129
F(000)	1284	1284	1284
μ (mm ⁻¹)	0.56	0.53	0.56
R	0.085	0.106	0.043

Table 5 Geometry of possible intermolecular hydrogen bonding

Form	Acceptor	Donor	Distance/Å
I	O2A	O3B	3.167
	O2C	O3D	3.168

II	O2A	O3B	2.867
	O2B	O3A	3.119
	O2D	O3D	2.991

are brought so close (*ca.* 3 Å) that intermolecular hydrogen bonding between the hydroxyl groups on the terminals of the BHPM and carbonyl groups on the side chains (dotted lines in Fig. 3 (A),(B)) is formed. The

modes of hydrogen bonding interaction in both forms depend heavily on the characteristic molecular structures. Not all hydroxyl and carbonyl groups of the BHPM molecule in both forms participate in hydrogen bonding. The existence of free and associated groups allows a reasonable interpretation of the splitting, or broadening, of the IR absorption bands mentioned above. In contrast to forms I and II, form III does not provide hydrogen bonding, in which the van der Waals interaction is a predominant packing force. Taking into account the differences in the enthalpy change upon melting among the three forms, the hydrogen bonding interaction does not seem to contribute significantly to the stabilization of the crystal structures. Consequently, the thermal behavior of the three forms may be ascribed to the degree of looseness of molecular packing.

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