Synthesis, Structure and Antioxidant Activity of Sulfur-Containing Tetrakisphenol

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Abstract—3-[2-(3,5-Di-*tert*-butyl-4-hydroxyphenylsulfanyl)acetoxy]2,2-bis[2-(3,5-di-*tert*-butyl-4-hydroxyphenylsulfanyl)acetoxymethyl]propyl 3,5-di-*tert*-butyl-4-hydroxyphenylsulfanylacetate was synthesized. Its structure was determined by means of ¹H and ¹³C NMR spectroscopy and X-ray-diffraction analysis. This compound was found to possess high antioxidant activity in the conditions of auto-oxidation of low-pressure polyethylene.

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Nowadays among the existing stabilizers the polyfunctional sulfur-containing sterically hindered phenols are of significant interest. The high antioxidant effect of compounds of this type is due to the presence in their structure of phenol and sulfide groups, which can act both independently of each other or inhibit synergistically the oxidation processes of polymers: to terminate the kinetic oxidation chain in the reaction with peroxide radicals and decompose the hydroper-oxides along a nonradical process [1, 2].

In this work synthesis of the new sterically hindered sulfur-containing tetrakisphenol, 3-[2-(3,5-di*tert*-butyl-4-hydroxyphenylsulfanyl)acetoxy]2,2-bis-[2-(3,5-di-*tert*-butyl-4-hydroxyphenylsulfanyl)acetoxymethyl]propyl 3,5-di-*tert*-butyl-4-hydroxyphenylsulfanylacetate **I**, was performed, and its structure and antioxidant activity was established. This compound is of significant interest since it is sulfur-containing analog of widely known industrial phenol antioxidant pentaerythritol-tetrakis-[3-(3,5-di-*tert*-butyl-4-oxyphe-nyl)propionate] (Irganox 1010), in whose structure the carbon atoms bonded with aromatic ring are substituted by the sulfur atom.

Synthesis of compound I was carried out by reaction of 2,6-di-*tert*-butyl-4-mercaptophenol II with chloroacetic tetraester of pentaerythritol III under argon in the presence of anhydrous triethylamine.

The structure and composition of compound **I** was confirmed by ¹H and ¹³C NMR spectroscopy, X-ray diffraction analysis, and elemental analysis.

Compound I molecule in the crystal takes a particular position. The carbon atom C^1 is located on a 2 axis and have a tetrahedral configuration (Fig. 1). Conformations of ester fragments are transoid and gauche, torsion angles $C^1C^{2a}O^{2a}C^{3a}$ and $C^1C^{2b}O^{2b}C^{3b}$





Fig. 1. Geometry of molecule I in crystal.

equal 175.5(1)° and 156.4(1)° respectively. Fragments OCCS in both substituents are in a gauche conformation [torsion angles $O^{2a}C^{3a}C^{4a}S^{4a}$ and $O^{2b}C^{3b}C^{4b}S^{4b}$, 72.1(2)° and 69.4(2)°]. Bond lengths and valence angles are given in Tables 1, 2.

In addition, in the crystal intermolecular hydrogen bonds O–H···O were observed between OH groups of aryl substituents and ester groups oxygen resulting in the three-dimensional networks (Fig. 2). The parameters of the hydrogen bonds are as follows: O^{8a} –

Bond	<i>d</i> , Å	Bond	<i>d</i> , Å
S ^{4b} -C ^{5b}	1.7745(17)	O ^{8a} –C ^{8a}	1.387(2)
$S^{4b} - C^{4b}$	1.823(2)	C^{3a} – O^{3a}	1.201(2)
$S^{4a} - C^{5a}$	1.7785(17)	C^{8b} – O^{8b}	1.380(2)
S^{4a} – C^{4a}	1.813(2)	O^{2a} – C^{2a}	1.441(2)
O^{2b} – C^{3b}	1.3343(19)	O^{2a} – C^{3a}	1.332(2)
O^{2b} – C^{2b}	1.4404(19)	C^{3b} – O^{3b}	1.196(2)
$C^1 - C^{2a}$	1.5234(19)	C^1-C^{2b}	1.5272(19)

Table 1. Bond lengths in the molecule of compound I

 $\begin{array}{l} \mathrm{H}^{8a}\cdots\mathrm{O}^{3a'}\left(1/2-x,-1/2+y,1/2-z\right), d(\mathrm{O}^{8a}-\mathrm{H}^{8a})\ 0.84(4)\\ \mathrm{\mathring{A}},\ d(\mathrm{H}^{8a}\cdots\mathrm{O}^{3a'})\ 2.22(4)\ \mathrm{\mathring{A}},\ d(\mathrm{O}^{8a}\cdots\mathrm{O}^{3a'})\ 2.959(2)\ \mathrm{\mathring{A}},\\ \mathrm{angle}\ \mathrm{O}^{8a}\mathrm{H}^{8a}\mathrm{O}^{3a'}\ 147(3)^{\mathrm{o}};\ \mathrm{O}^{8b}-\mathrm{H}^{8b}\cdots\mathrm{O}^{3b''}\ (-x,\ 1-y,\ -z)\\ d(\mathrm{O}^{8b}-\mathrm{H}^{8b})\ 0.71(4)\ \mathrm{\mathring{A}},\ d(\mathrm{H}^{8b}\cdots\mathrm{O}^{3b''})\ 2.16(4)\ \mathrm{\mathring{A}},\ d\\ (\mathrm{O}^{8b}\cdots\mathrm{O}^{3b''}\ 2.818(2)\ \mathrm{\mathring{A}},\ \mathrm{angle}\ \mathrm{O}^{8b}\mathrm{H}^{8b}\mathrm{O}^{3b''}\ 155(4)^{\mathrm{o}}. \end{array}$

The study of antioxidant activity of compound I in the conditions of auto-oxidation of low-pressure polyethylene (LPPE) shows that it provides essentially longer induction period of oxidation (τ) for polymer in comparison with high-effective industrial antioxidants Irganox 1010 and TB-3 [bis-(3,5-di-*tert*-butyl-4hydroxybenzyl)sulfide]. The induction periods of LPPE oxidation (200°C, 250 mm Hg) are given below:

Antioxidant (0.1 wt %)	τ, min
None	8
Irganox 1010	60
ТБ-3	35
Compound I	85



Fig. 2. Hydrogen bonds in crystal of compound I.

EXPERIMENTAL

The ¹H and ¹³C NMR spectra were recorded on a Bruker AVANCE-600 spectrometer (600 and 150 MHz) relative to signals of the residual protons of deuterated solvents.

X-Ray diffraction analysis of compound I was performed on a Bruker Smart APEX2 automatic diffractometer (Mo K_{α} irradiation, graphite monochromator, ω -scanning) at 20°C. Structure was solved by the direct method using SIR program [3]. The extinction was not accounted for owing to its negligible value. The hydrogen atoms were placed into the calculated position and refined in a *rider* model. Coordinates for the hydrogen atoms at the oxygen atoms were revealed from the differential Fourier charts and refined in the isotropic approximation. All calculations were performed using WinGX program package [4]. The figure was made by means of PLATON program [5]. Bond lengths and bond angles are given in Tables 1, 2.

Table 2. Bond angles in the molecule of compound I

Angle	ω, deg	Angle	ω, deg
$C^{2a}C^1C^{2a}$	111.36(18)	$\mathrm{C}^{6a}\mathrm{C}^{5a}\mathrm{S}^{4a}$	118.45(13)
$C^{2a}C^1C^{2b} \\$	108.33(9)	$\mathrm{C}^{10a}\mathrm{C}^{5a}\mathrm{S}^{4a}$	121.57(13)
$\mathrm{C}^{5b}\mathrm{S}^{4b}\mathrm{C}^{4b}$	100.55(8)	$C^{3b}C^{4b}S^{4b}$	110.78(12)
$\mathrm{C}^{5a}\mathrm{S}^{4a}\mathrm{C}^{4a}$	102.28(8)	$\mathrm{C}^{6a}\mathrm{C}^{5a}\mathrm{S}^{4a}$	118.45(13)
$C^{3b}O^{2b}C^{2b}$	117.08(13)	$\mathrm{C}^{10a}\mathrm{C}^{5a}\mathrm{S}^{4a}$	121.57(13)
$O^{3b}C^{3b}O^{2b}$	122.85(16)	$O^{3b}C^{3b}O^{2b}$	122.85(16)
$C^{3a}O^{2a}C^{2a}$	116.95(13)	$O^{2b}C^{3b}C^{4b}$	111.29(15)
$O^{2b}C^{3b}C^{4b}$	125.83(16)	$O^{3a}C^{3a}O^{2a}$	122.77(17)
$O^{2b}C^{2b}C^1$	106.98(11)	$O^{2a}C^{3a}C^{4a}$	110.92(16)
$O^{3a}C^{3a}C^{4a}$	126.29(16)		

Parameter	Value		
Color, habit	Transparent prismatic		
Empirical formula	$C_{69}H_{100}O_{12}S_4$		
Crystal system	Monoclinic		
Space group	C2/c		
Unit cells parameters	a = 18.3787(11),		
	b = 15.0469(9),		
	c = 27.4223(16) Å		
	$\alpha = 90.00$		
	$\beta = 105.092(1),$		
	$\gamma = 90.00^{\circ}$		
Volume, Å ³	7321.9(8)		
Ζ	4 (molecule is in particular position)		
Molecular weight	1249.73		
$d_{\rm calc}$, g cm ⁻³	1.134		
Extinction coefficient,	1.84		
μ Mo, cm ⁻¹			
<i>F</i> (000)	2696		
Interval θ	$2.05 \le \theta \le 26.00$		
$R_{ m int}$	0.02		
Index measurement	$-22 \le h \le 22,$		
interval	$-18 \le k \le 18,$		
	$-33 \le l \le 33$		
Reflections measured/	27377/7200		
independent			
Number of the observed	5519		
reflections with $I > 2\sigma(I)$			
Final values of diver-	R = 0.0417		
gence factors	$R_{\rm W} = 0.1331$		
	$R_{\rm all} = 0.0571$		
	$R_{ m Wall}=0.1485$		
Fit parameter	1.077		
Δ/σ	0.00		
Number of refined	404		
parameters			

Table 3. The main crystallographic parameters and structure refinement details for compound I

The main crystallographic data for structure I are given in Table 3.

3-[2-(3,5-Di-*tert*-**butyl-4-hydroxyphenylsulfanyl)**acetoxy]-2,2-bis-[2-(3,5-di-*tert*-butyl-4-hydroxyphenyl-sulfanyl)acetoxymethyl]propyl 3,5-di-*tert*-butyl-**4-hydroxyphenyl-sulfanylacetate (I).** To a solution of 1.4 g of thiol II and 0.65 g of ester III in 10 ml of anhydrous acetone at room temperature in the argon atmosphere was added 0.81 ml of triethylamine. The reaction mixture was stirred for 2 h, poured into water, and acidified with diluted HCl. The precipitate was filtered off and dried in air to constant mass. Yield 1.56 g (85%), mp 149–150°C (hexane). ¹H NMR spectrum (CDCl₃, δ , ppm): 1.44 s (72H, CMe₃), 3.54 s (8H, CH₂S), 4.09 s (8H, CH₂O), 5.26 s (4H, OH), 7.28 s (8H, ArH). ¹³C NMR spectrum (CDCl₃, δ , ppm): 30.247 q (CMe₃, ¹J 126.1 Hz), 34.502 (CMe₃), 38.474 t (CH₂O, ¹J 142.0 Hz), 42.396 (C), 63.189 t (SCH₂, ¹J 150.2 Hz), 123.811 (C¹), 129.298 d (C², ¹J 159.7 Hz), 137.097 s (C³), 154.078 d. t (C⁴, ²J 3.6 Hz, ³J 8.7 Hz), 169.398 (C=O). Found, %: C 66.51; H 8.51; S 9.98. C₆₉H₁₀₀O₁₂S₄. Calculated, %: C 66.35; H 8.01; S 10.26.

2,6-Di-*tert*-butyl-4-mercaptophenol (II) was synthesized by procedure [6].

3-(2-Chloroacetoxy)-2,2-bis-(2-chloroacetoxymethyl)propyl chloroacetate (III) was obtained by procedure [7].

The stabilized samples of LPPE of brand 80B produced by OAO Kazanorgsintez were prepared by mixing powdered polymer with acetone solution of calculated amount of antioxidant followed by samples drying in vacuum box to constant mass. Auto-oxidation of LPPE was carried out on a stationary manometer apparatus by procedure [8] at 200°C and oxygen pressure 250 mm Hg.

REFERENCES

- 1. Gorbunov, V.N., Maslova, N.N., and Gurvich, Ya.A., *Khimiya i tekhnologiya stabilizatorov polimernykh materialov* (Chemistry and Technology of Stabilizers of Polymer Materials), Moscow: Khimiya, 1981.
- Grassi, N. and Scott, J., Destruktsiya i stabilizatsiya polimerov Destruction and Stabilization of Polymers, Moscow: Mir, 1988.
- Altomare, A., Cascarano, G., Giacovazzo, C., and Viterbo, D., *Acta Crystallogr. Sect. A*, 1991, vol. 47, p. 744.
- 4. Farrugia, L.J., J. Appl. Crystal., 1999, vol. 32, p. 837.
- 5. Spek, A.L., Acta Crystallogr. Sect. A, 1990, vol. 46, p. 34.
- 6. RF Patent no. 2075471, 1997, Russ. Zh. Khim, 1998, 16H74P.
- 7. Andriyanov, K.A. and Emel'yanov, V.N., *Zh. Obshch. Khim.*, 1963, vol. 34, no. 11, p. 3817.
- Piotrovskii, K.B. and Tarasova, Z.N., *Starenie i* stabilizatsiya sinteticheskikh kauchukov i vulkanizatorov (Ageing and Stabilization of Synthetic Rubbers and Vulcanizers), Moscow: Khimiya, 1980.