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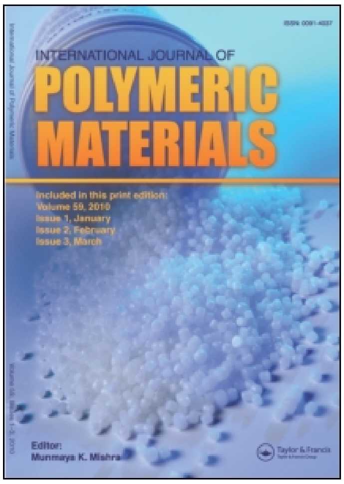

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Creation of Effective Stabilizer Structures

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Creation of Effective Stabilizer Structures

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Various antioxidants are used to protect polymers against oxidation. The development of new stabilizers requires a knowledge of the role which individual structural factors play in the mechanism of antioxidative stability. Experimental data on the structure of such molecules are compared with the results of their antioxidative action in different polymers.

KEY WORDS Polymer stabilization, antioxidants, structure.

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INTRODUCTION

Phenolic derivatives play an important role in stabilization for polymers. These compounds protect the polymers against thermooxidative destruction. Some of these are nontoxic and may be used for polymers that are in contact with food products, medical compounds, biological media (including human organism).

Phenolic derivatives are among the compounds permitted for protecting of food products, forage and cosmetics against oxidation.

Most of phenolic stabilizers do not influence the colour of the polymer and may be used for the production of white and light coloured goods.

The first patent on the application of phenolic stabilizer for the protection of polymer against oxidation was in USA in 1870.

During the last 120 years thousands of chemical compounds of different classes have been examined as stabilizers, still phenolic derivatives keep their importance as stabilizers.

During the last ten years the interest in them has increased because they do not form cancerogeneous nitrosoamines.

The constant increasing in number of publications in the field of phenolic compounds in the scientific and patent literature is indicative of their importance, Figure 1.

1. NEW ORTHO-PARA-BIS- AND TRISPHENOLS. REACTIVITY AND EFFICIENCY

Synthesis, properties and application of different phenolic stabilizers for the protection of polymers against oxidation, their structures, reactivity and efficiency,

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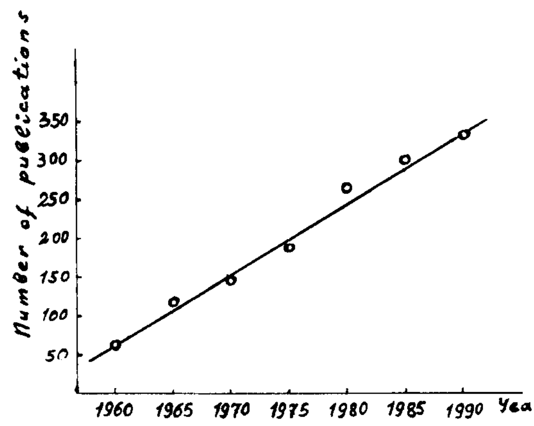
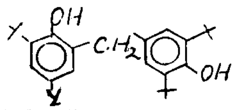


FIGURE 1 Dynamics of increasing of the publications about Ionol.

TABLE I

Reactivity and efficiency of ortho-para-bisphenols



NN	Y	* K, $M^{-1}sec^{-1}$	** E, mv	*** τ, min	**** AC
1.	CH_3	1.2	249	130	.69
2.	C_2H_5	.8	253	132	.51
3.	tert-C_4H_9	1.0	230	145	.60
4.	Cl	1.1	245	150	.91
5.	Br	1.2	242	144	.69
6.	Without stabilizer	–	–	20	.30

Notes:

* K - the rate constant of the model radical reaction;

** E - the potential of anodic oxidation;

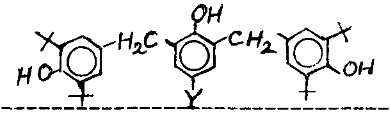
*** τ - the induction period of oxidation of polypropylene;

**** AC - aging coefficient for white model rubber (tensile strength, 48h.at 90°C);

+- - tert-butyl.

TABLE II

Reactivity and efficiency of ortho-para trisphenols



NN	Y	K, $M^{-1}sec^{-1}$	E, mv	τ, min	AC
1.	CH_3	2.2	158	150	.96
2.	C_2H_5	2.3	166	160	.67
3.	tert-C_4H_9	2.0	139	165	.91
4.	Cl	2.3	164	162	.63
5.	Br	1.9	160	142	.83
6.	Without stabilizer	-	-	20	.30

mechanism of action and transformations have been studied for a number of years.[1-25,30-41]

Creation of an industrial method for the production of 2,6-di-*tert*-butylphenol has opened up a route to the synthesis of a number of different phenolic stabilizers[11] such as *p*-derivatives: methyl (agidol 1 or ionol), di-methyl-amino-methyl (agidol 3 or "Mannich Base") and methoxy-methyl (agidol 42) from 2,6-di-*tert*-butylphenol.

The high reactivity of 2,6-di-*tert*-butyl-4-methoxymethylphenol in the alkylation reaction of aromatic compounds allows the synthesis of compounds containing fragments of the screened phenolic hydroxyl.[20]

Results on the reactivity and antioxidative activity of bisphenols obtained by the alkylation of 2,4-derivatives with 2,6-di-*tert*-butyl-4-methoxymethylphenol are presented in Table I. Substitution of alkyl by halogen in the *p*-position to hydroxyl does not influence the properties of these compounds. Data for trisphenols, the products of alkylation of *p*-substituted phenols with 2,6-di-*tert*-butyl-4-methoxymethylphenol, Table II, indicate that derivatives with alkyl radicals in the *p*-position to the hydroxyl are the best antioxidants.

Tris- and tetraphenol, Table III, containing two and three fragments of 2,6-di-*tert*-butylphenol are very active in polypropylene and vulcanites of polyisoprene.

Comparison of the data on the products of alkylation of 2,4-di-*tert*-butylphenol, 2-*tert*-butylphenol and phenol, Table III, with studies of the reactivity and efficiency of mesitylene derivatives,[26] indicates an increase in efficiency with increase in the number of 2,6-di-*tert*-butylphenol fragments in the stabilizer molecule in an additivity manner.[22]

These results are in good agreement with spectroscopic data, Table IV. The nature of the *p*-substituent has only a slight influence on the frequency of IR-absorbance for the OH-group.

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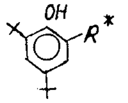
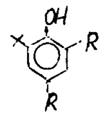
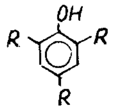
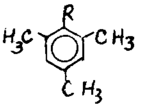
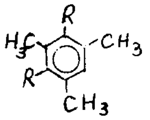
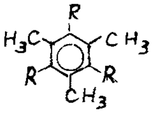
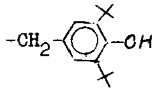
TABLE III

Reactivity and efficiency of phenol and mesitylene derivatives

NN	Compound	K, $M^{-1}sec^{-1}$	τ, min	AC
1.		.9	145	.60
2.		1.8	170	.69
3.		3.0	190	.95
4.		.3	90	.61
5.		.5	140	.69
6.		.7	150	.71

*R - 

The introduction of Cl or Br in the molecule produces a slight shift of band maximum in the range of 3530–3515 cm^{-1} (10–15 cm^{-1}).

UV- and IR-spectroscopy indicate an additivity of the 2,6-di-*tert*-butylphenol fragments in the mesitylene derivatives due to changes in the degree of conjugation owing to the existence of CH_2-group between the nuclei.[27]

In the case of ortho-ortho-bisphenols the introduction of halogen atoms into *p*-positions appreciably decreases the reactivity.[28] These results show that in the above series of compounds the reduction of reactivity and efficiency was not observed. Not only para-alkyl, but also para-halogen-derivatives are effective antioxidants.

Ortho-ortho-methylene- and thiobisphenols, are antioxidants and antiozonants and have wide practical application.

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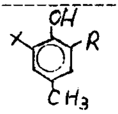
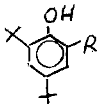
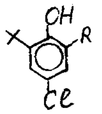
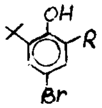
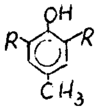
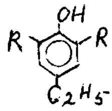
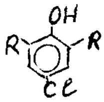
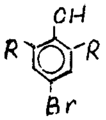
TABLE IV

IR-spectra of ortho-para-bisphenols and trisphenols

NN	Compound	ν,* cm^{-1}	$\gamma_{1/2}$,* cm^{-1}	ε,** M^{-1}cm^{-1}	A·10^4,*** M^{-1}cm^{-2}
1.		3530	76	289	3.5
		3647	15	671	1.6
2.		3531	96	229	3.5
		3648	16	657	1.7
3.		3516	82	280	3.6
		3647	15	618	1.5
4.		3516	76	282	3.4
		3647	16	653	1.6
5.		3532	78	273	3.4
		3642	17	1018	2.7
6.		3532	78	247	3.0
		3648	17	940	2.5
7.		3518	79	271	3.4
		3646	16	949	2.4
8.		3515	77	269	3.3
		3648	16	940	2.3

*ν and $\gamma_{1/2}$ – band frequency and half-width;

**$\varepsilon = (cl)^{-1}\lg I_0/I$ – molar coefficient of absorbance in max;

***$A = (cl)^{-1}\int(I_0/I)d\nu$ – integral molar coefficient of absorbance. Concentration of the compound 0.025 M, thickness of the solution 1 mm.

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2. ORTHO-ORTHO-METHYLENE- AND THIOBISPHENOLS. STRUCTURE AND PROPERTIES

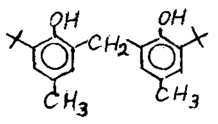
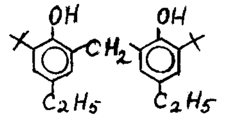
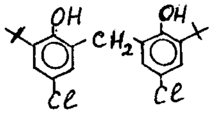
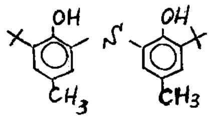
The processes of oxidations of ortho-ortho-bisphenols, their structure and the reasons for their different antioxidative activity have been studied.[45–74]

2,2′-methylene-bis-(4-methyl-6-*tert*-butylphenol)-agidol 2, antioxidant 2246 has optimum antioxidative activity,[67] Table V.

The introduction of a C_2H_5-group or halogen atom instead of the CH_3-group in *p*-position to the OH-group (compounds 2 and 3) or displace of the methylene

TABLE V

IR-spectra and antioxidative activity of ortho-ortho-bisphenols

NN	Compound	ν,* cm^{-1}	E, mv	τ, min	AC**
1.	 Agidol 2	3400 3600	180	220	.96
2.	 Agidol 7	3530	220	160	.87
3.	 AO-30	3562	230	130	.82
4.	 Agidol 32	3486	245	140	.76
5.	Without stabilizer	-	-	20	.30

Notes: *ν – band frequency (in max) in IR-spectra of crystals in the range of valent vibrations of OH-group; **AC-aging coefficient , based on tensile strength of model white rubber (24h. at 90°C).

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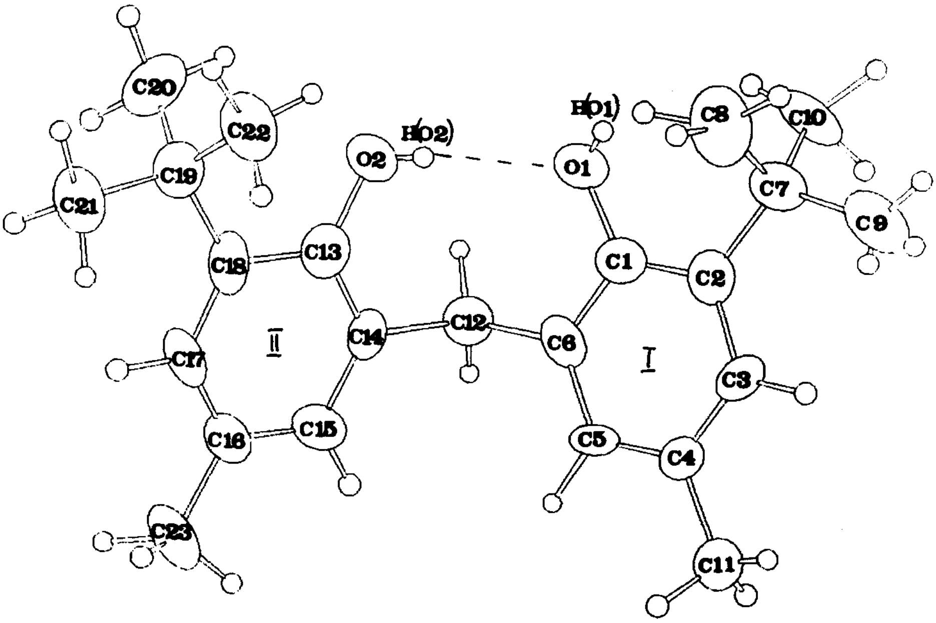

FIGURE 2 Molecular structure of 2,2′-methylene-bis-(4-methyl-6-*tert*-butylphenol) with thermal ellipsoids of the non-hydrogen atoms (X-ray diffraction analysis).

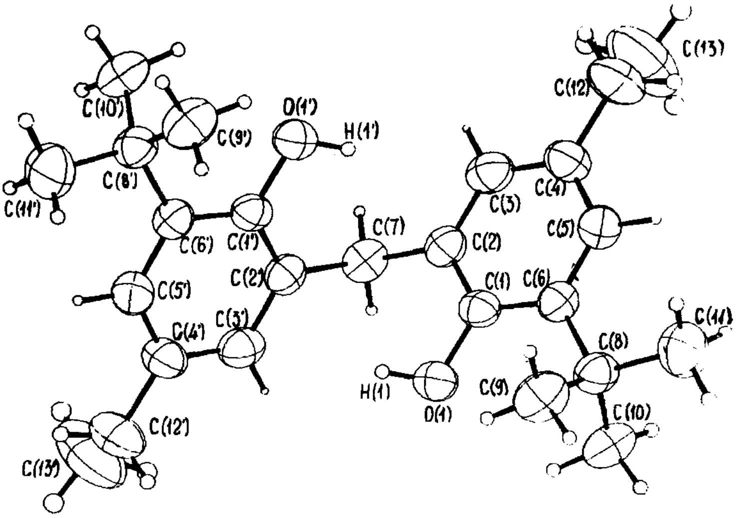

FIGURE 3 Molecular structure of 2,2′-methylene-bis-(4-ethyl-6-*tert*-butylphenol) with thermal ellipsoids of non-hydrogen atoms (X-ray diffraction analysis).

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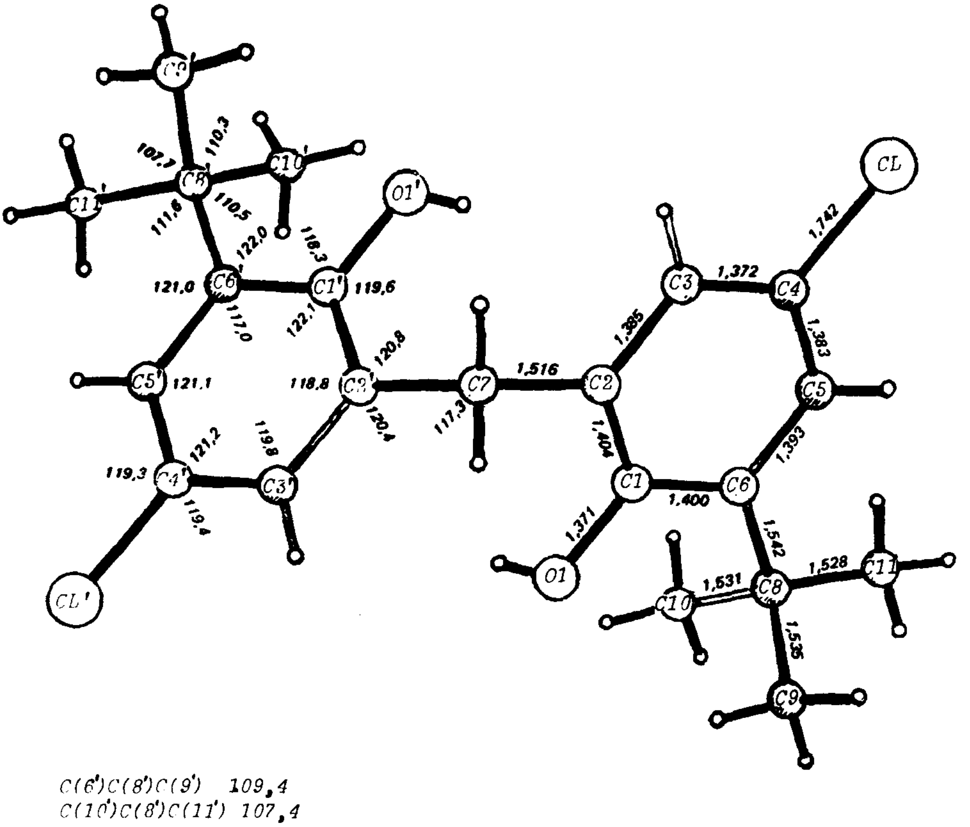

FIGURE 4 Molecular structure of 2,2'-methylene-bis-(4-chlor-6-*tert*-butylphenol) (X-ray diffraction analysis).

bridge between aromatic nuclei by a sulfur atom (compound 4) are accompanied by a reduction of antioxidative activity.

IR-spectroscopic study of crystals of these compounds[61,62] indicate the existence of a cis-conformation in agidol 2 and a trans- in crystals of the other bisphenols.

X-ray diffraction analysis,[63,65,67,70–74] Figures 2–5, have been carried out. Agidol 2, Figure 2, exists in a cis-conformation with both OH-groups arranged on one side of the plane passing through the bridge and the two carbon atoms of the aromatic nuclei linked with it.

Intramolecular hydrogen bonding OH ··· O takes place in the molecule; the geometry of this bond is given in Table VI. In contrast compounds 2–4 have trans-conformation, Figures 3–5, with intramolecular OH ··· π (compounds 2 and 3) and OH ··· S (compound 4) hydrogen bonds.[64,65,68]

If the bridge between nuclei of the bisphenol is branched, as in the —$C(CH_3)_2$— structure, the molecules have a trans-conformation with intramolecular OH ··· π hydrogen bonds.[71]

The presence of cis-conformation allows bisphenol to act more efficiently as an antioxidant because the hydroxyl groups are arranged sufficiently close to each other for simultaneous in "cell" deactivation of two radicals formed on destruction

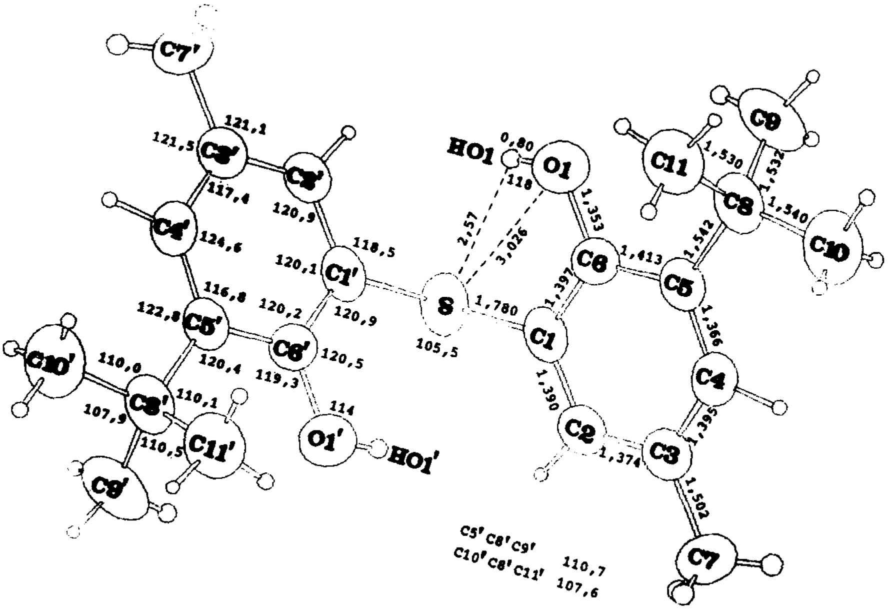

FIGURE 5 Molecular structure of 2,2'-thio-bis-(4-methyl-6-*tert*-butylphenol) with thermal ellipsoids of non-hydrogen atoms (X-ray diffraction analysis).

TABLE. VI

Geometric parameters of intramolecular hydrogen bonds in ortho-ortho-bisphenols

NN	Compound	Bond length, A^0	Angle, degree	Sum of Van-der-Vaals radii,A^0
1.	Agidol 2	H...O 2.10	O-H...O 149	H+O 2.45
2.	Agidol 7	H...C 2.33 2.51	-	H+C 2.87
3.	AO-30	H...C 2.60 2.65 C H···│ 2.58 C	-	H+C 2.87
4.	Agidol 32	H...S 2.57	O-H...S 118	H+S 3.0

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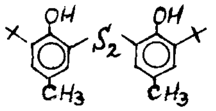
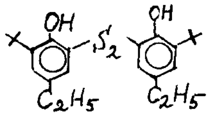
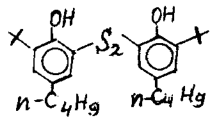
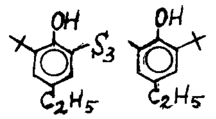
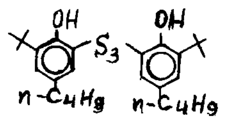
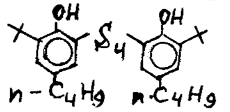
TABLE VII

Reactivity and antioxidative activity of ortho-ortho-bisphenols

NN	Compound	K, $M^{-1}sec^{-1}$	E, mv	τ, min
1.		.4	295	160
2.		.5	303	160
3.		.2	305	165
4.		1.8	245	163
5.		1.9	260	175
6.		9.5	-	185
7.	Without stabilizer	-	-	20

of hydroperoxide to be more favorable than in the case of the trans-conformation. This idea bases on a "cell" mechanism of antioxidant action.[15]

Thiobisphenols—compounds with the sulfur bridge between nuclei—are effective inhibitors against oxidation due to intramolecular synergism.

The problem about the influence of quantity of sulfur atoms in the bridge group on the properties of these compounds is of interest. Data on thiobisphenols are presented in Table VII and spectroscopic data in Table VIII and the results of X-ray diffraction analysis, Figures 6, and 7[66,69] and Table IX.

IR-spectra of solutions of thiobisphenols, Table VIII, shows the existence of intramolecular hydrogen bond OH ··· S.[62]

Non-valent distances S ··· H and S ··· O are much shorter than the sum of Van-der-Vaals radii and this shortening is greater in di-, than in mono-, and still more in trithiobisphenols, Table IX.

It is possible that bifurcation exists in the OH ··· S ··· HO[66] bond formed for monothiobisphenols.

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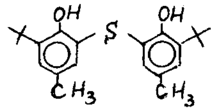
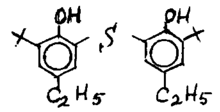
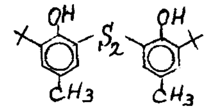
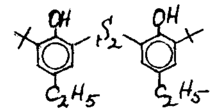
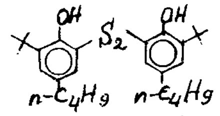
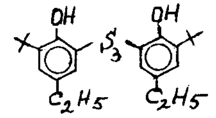
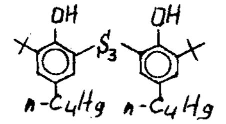
TABLE VIII

IR-spectra of the solutions* of ortho-ortho-thiobisphenols in CCl_4

NN	Compound	ν, cm^{-1}	$\gamma_{1/2}$, cm^{-1}	ε, $M^{-1}cm^{-1}$	$A \cdot 10^4$, $M^{-1}cm^{-2}$
1.		3427 3510	37 50	109 63	1.4 1.1
2.		3424 3508	36 51	97 50	1.3 .9
3.		3449	40	187	2.9
4.		3448	40	188	3.1
5.		3450	40	174	3.0
6.		3462	80	259	3.7
7.		3461	60	227	3.3

*Concentration of the compound .025 M, thickness of the solution 1 mm.

Spectroscopic and structural data indicate that intramolecular hydrogen bonds in polythiobisphenols are much stronger, than in monothiobisphenols.

The elongation of the sulfide bridge between aromatic nuclei is accompanied by an increase in reactivity and antioxidative activity of these compounds, Table VII.

The existence of a third sulfur atom, free of the intramolecular hydrogen bond in trithiobisphenols leads to the high activity of these compounds in model systems as well as polymers.

Tetrathiobisphenol has still greater reactivity, compound 6, Table VII.

The technical mixture of mono-, di- and trithiobisphenols, obtained from sulfur chlorides, shows a higher efficiency than the individual compounds, Table X.

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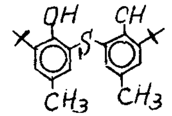
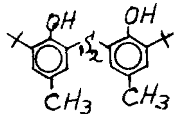
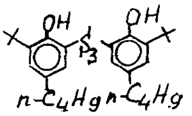
TABLE IX

Geometrical parameters of intramolecular hydrogen bonds in ortho-ortho-thiobisphenols

NN Compound	Bond Length, A^0	Angle, degree	Sum of Van-der-Vaas radii, A^0
1. 	S...H 2.57 S...O 3.026	O-H...S 118	S+H 3.0 S+O 3.13
2. 	S...H 2.49 S...O 2.990	O-H...S 116	S+H 3.0 S+O 3.13
3. 	S...H 2.41 S...O 2.985	O-H...S 125	S+H 3.0 S+O 3.13

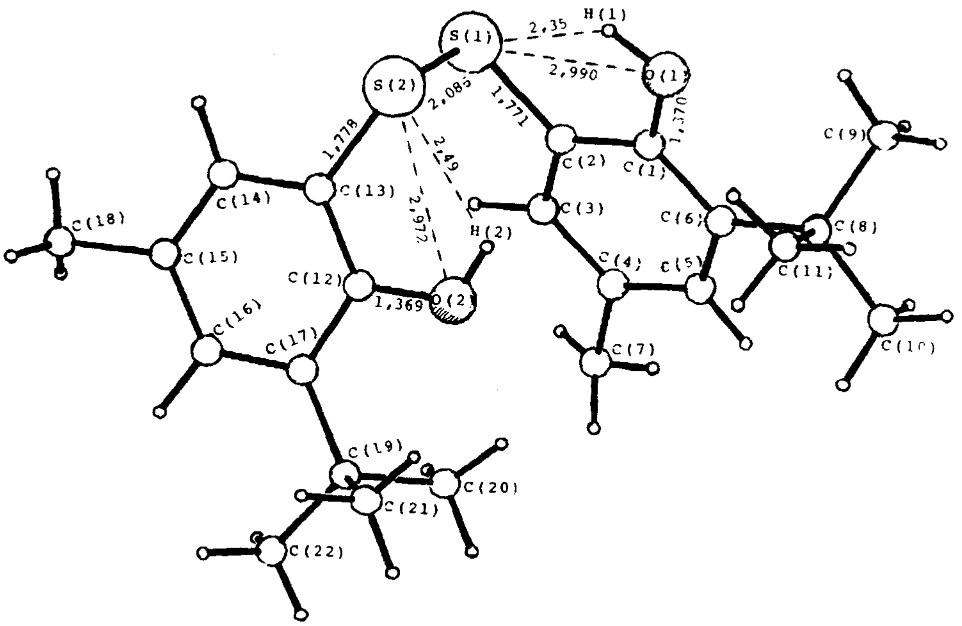


FIGURE 6 Molecular structure of 2,2′-di-thio-bis-(4-methyl-6-*tert*-butylphenol) (X-ray diffraction analysis).

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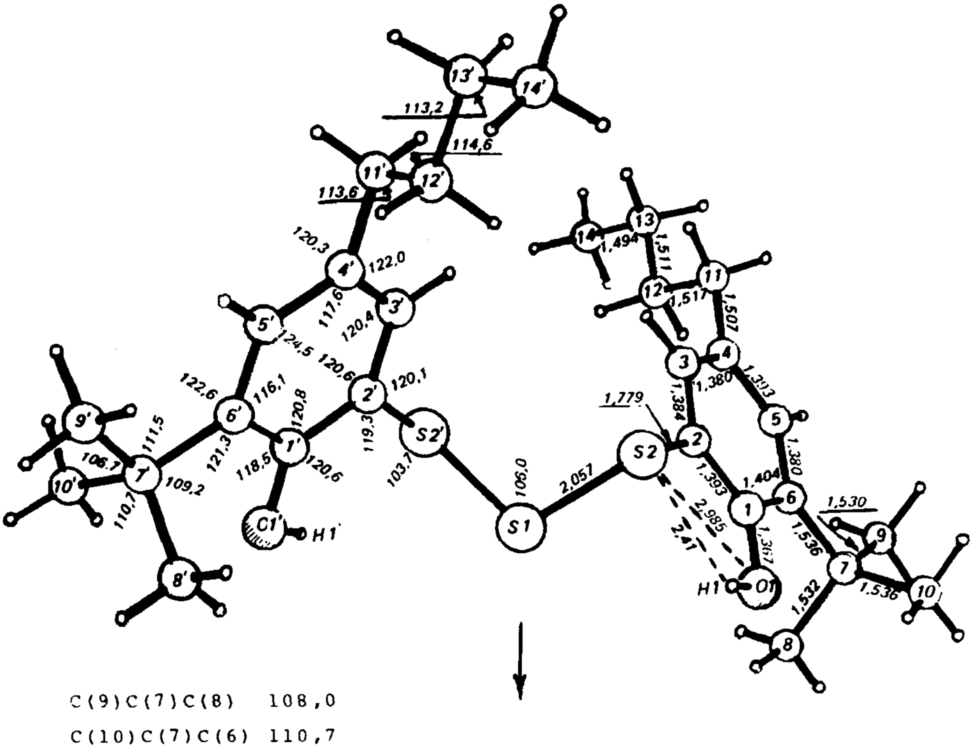

FIGURE 7 Molecular structure of 2,2'-tri-thio-bis-(4-methyl-6-*tert*-butylphenol) (X-ray diffraction analysis).

Amongst the stabilizers for medical goods—trisphenol 1,3,5-tris-(3',5'-di-*tert*-butyl-4'-hydroxybenzyl)mesitylene—agidol 40 (ionox 330) is nontoxical and does not influence the colour.

The mechanism of antioxidative action and the high efficiency of agidol 40 (τ = 240 min.) can be explained on the base of the results of X-ray diffraction analysis. Agidol 40 molecule contains four aromatic nuclei. In space it represents a "basket," the "bottom" of which is formed by a mesitylene ring and the walls—by three rings containing space hindered hydroxyl groups, Figure 8. The "basket" has a "pocket"—for entrapment of hydroperoxide radicals and their quick deactivation by OH-groups arranged at the boundary of the "basket" walls.

The crystals of a new stabilizer-analog of agidol 40, tris-phenol using *m*-xylene instead of mesitylene 1,3,5-tris- (3',5'-di-*tert*-butyl-4'-hydroxybenzyl)*m*-xylene are isostructural to the crystals of agidol 40. The space conformation of molecule remains the same on substitution of a methyl group in the central ring by a hydrogen atom.

The existence of a "basket" conformation provides high antioxidative activity of the new stabilizer (τ = 230 min.), which can be synthesized from an accessible raw material—*m*-xylene.

TABLE X

Testing of technical mixture of thiobisphenols as a stabilizer for white rubber (mixture composition: mono—36%, di—42%, tri—22%)

NN	Property	Without stabilizer	Mixture of Thiobis-phenols, 1 ppm	Agidol 32, 1 ppm	Agidol 2, 1 ppm
1.	Tensile strength, MPa	17.3	20.3	17.6	17.9
2.	Elongation at break,%	800	700	760	790
3.	Aging coefficient based on tensile strength at 90°C, 24h.	.32	.82	.77	.94
4.	Fatigue strength up to destruction, thousands of cycles:				
	at bending	43.2	64.5	60.5	69.0
	at elongation 100%	24.9	36.5	34.0	43.3

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3. GRAFTING STABILIZERS ON THE BASE OF 2,6-DI-*TERT*-BUTYLPHENOL

During the last years the stabilizer grafting has been used to protect polymers against aging. These compounds react with the polymer and their period of effectiveness is lengthened. They do not evaporate from the polymers at high temperature and are not extracted from the polymer by organic solvents or migrate to the surface of the polymer.[75,76]

The problem of grafting stabilizers, methods of joining them to the polymers, mechanism of action, efficiency and use in different polymers has been extensively discussed.[76-83]

The protection of white and coloured rubbers for medical and materials in contact with food requires the use of nontoxic stabilizers which do not influence the colour of the polymer. So compounds with space hindered phenolic fragments are ideal.

Table XI, the structures of stabilizers based on 2,6-di-*tert*-butylphenol, which contain esters groups of acrylic or maleic acids are presented.

The reactivity of these compounds in model anodic oxidation reactions[84]—E = 200–230 mv—is close to the value for the active stabilizers: agidol 1 (220 mv) and agidol 2 (200 mv).

Antioxidative activity in model systems based on polypropylene[85] are too high. Induction periods for oxidation of polypropylene τ_{pp} are higher than τ_{pp} of agidol

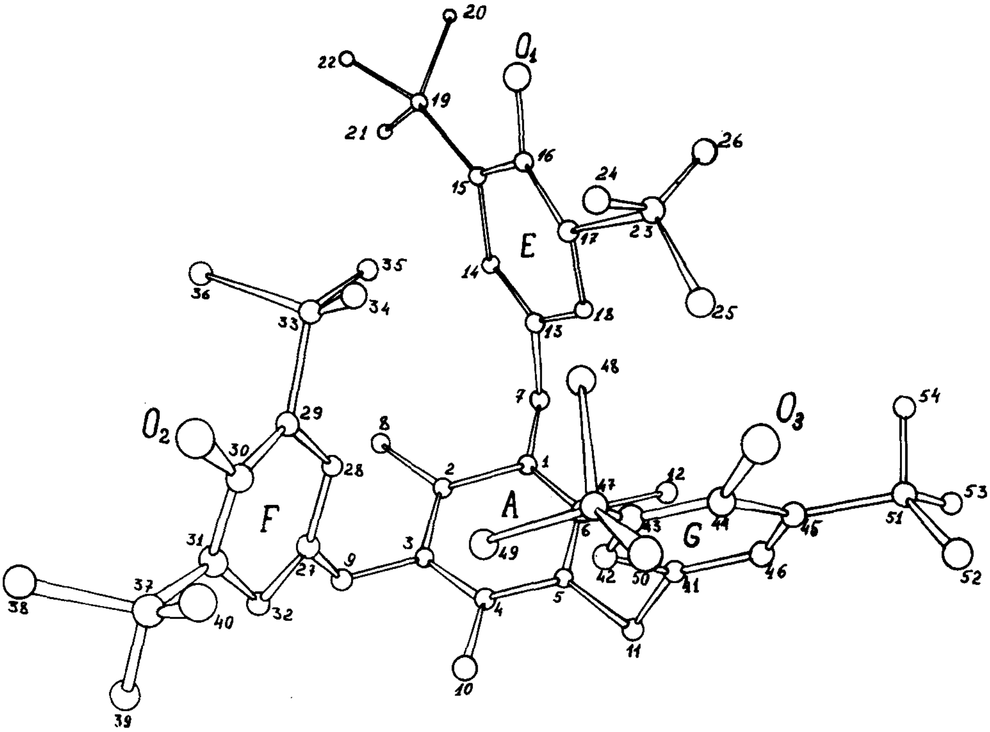

FIGURE 8 Molecular structure of 1,3,5-tris-(3′,5′-di-*tert*-butyl-4′-oxybenzil)mesitylene (X-ray diffraction analysis).

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1 (120 min). Some of these values, mainly for esters of maleic acid are close to τ_{pp} for agidol 2 (220 min).

The results of the study of antioxidative activity of some grafting stabilizers in polyisoprene rubber SKI-3 by IR-spectroscopy are shown in Figure 9. The stabilizers 2 and 4, Table XI, are close to agidol 2 in their inhibition activity of thermooxidation for rubber films in air for a period of 45 min at 130°C, with a concentration of stabilizer of 10^{-5} M/g of rubber.

The induction periods for oxidation of polyisoprene rubber in the presence of grafted stabilizers τ_{pi} (min) are given in Table XI.[88]

The rate of absorption of oxygen by the film of rubber containing stabilizer at the temperature close to the temperature of vulcanization was used as a measure of the rate of oxidation. The temperature of oxidation was 150°C, stabilizer concentration 10^{-5} M/g of rubber, the rate of oxygen feed was 8–11 cm^3/h, the thickness of rubber film—10–15 mcm.[86] The connection of the stabilizer to the rubber is monitored by study of the UV-spectra of alcohol extracts of films before and after heating at 150°C for 30 min. UV-spectra of the extracts, Figure 10, indicate that stabilizers 5 and 6 are connected to the polymer; the spectra of the extracts from the films are lacking the absorption bands in the range 260–280 nm typical for the phenols after heating. UV-spectra of the extracts of films containing nongrafting stabilizer agidol 2 are identical both before and after the heating.

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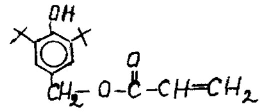
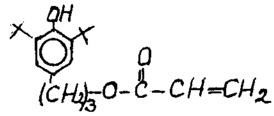
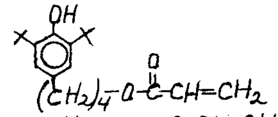
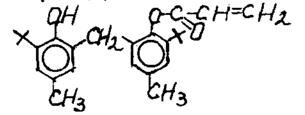
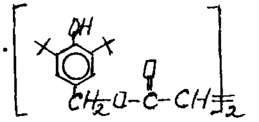
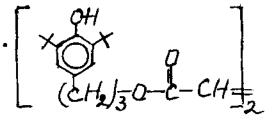
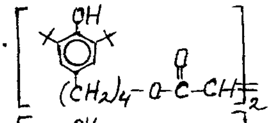
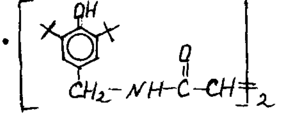
TABLE XI

Reactivity and antioxidative activity of grafting phenolic stabilizers

NN	Compound	E, mv	τ_{pp}, min	τ_{pi}, min
1.		224	160	-
2.		230	200	20
3.		239	150	-
4.		221	150	7
5.		-	200	22
6.		203	215	30
7.		212	240	18
8.		-	200	-

The values of τ_{pi}, Table XI, for compound 4 is close to agidol 1 (τ_{pi} = 10 min) but compounds 5 and 6 are close to agidol 2 (τ_{pi} = 25 min).

Compounds 2 and 7 are comparable to agidol 2.

The high antioxidative activity of grafted stabilizers can be explained with the help of structural data. Compound 4 has a cis-conformation, Figure 11,[87] similar to agidol 2 hence its high antioxidative activity.

Grafting of stabilizers to the rubber during the process of vulcanization is demonstrated by experiment. Stabilizers 2 and 6 were introduced into the unfilled polyisoprene mixture with the help of rolling cylinders and plates formed were

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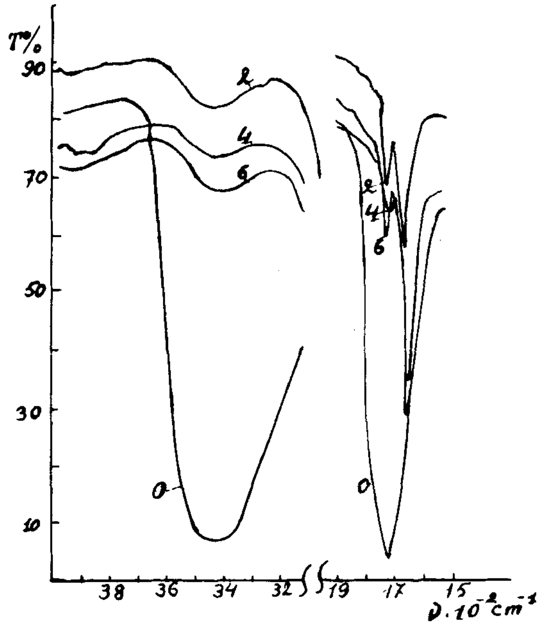

FIGURE 9 IR-spectra of films of rubber SKI-3 containing stabilizers NN 4,6 (numbers of compounds are the same as in Table XI) and Agidol 2 after oxidation in air at 130°C during 45 min.: 0—specimen without stabilizer, 2—specimen with Agidol 2, 4—specimen with stabilizer N 4, 6—specimen with stabilizer N 6.

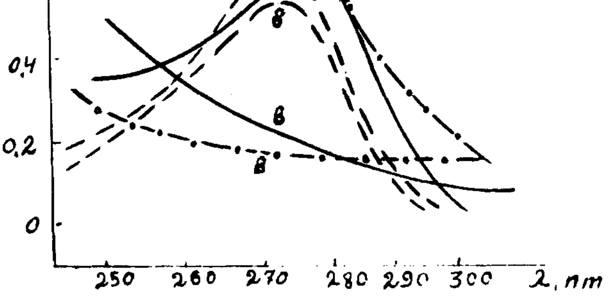

FIGURE 10 UV-spectra of extracts of polyisoprene films containing grafting stabilizers NN 5, 6 (numbers of compounds as in Table XI) and non-grafting stabilizer Agidol 2 before (a) and after (b) heating at 150° during 30 min.

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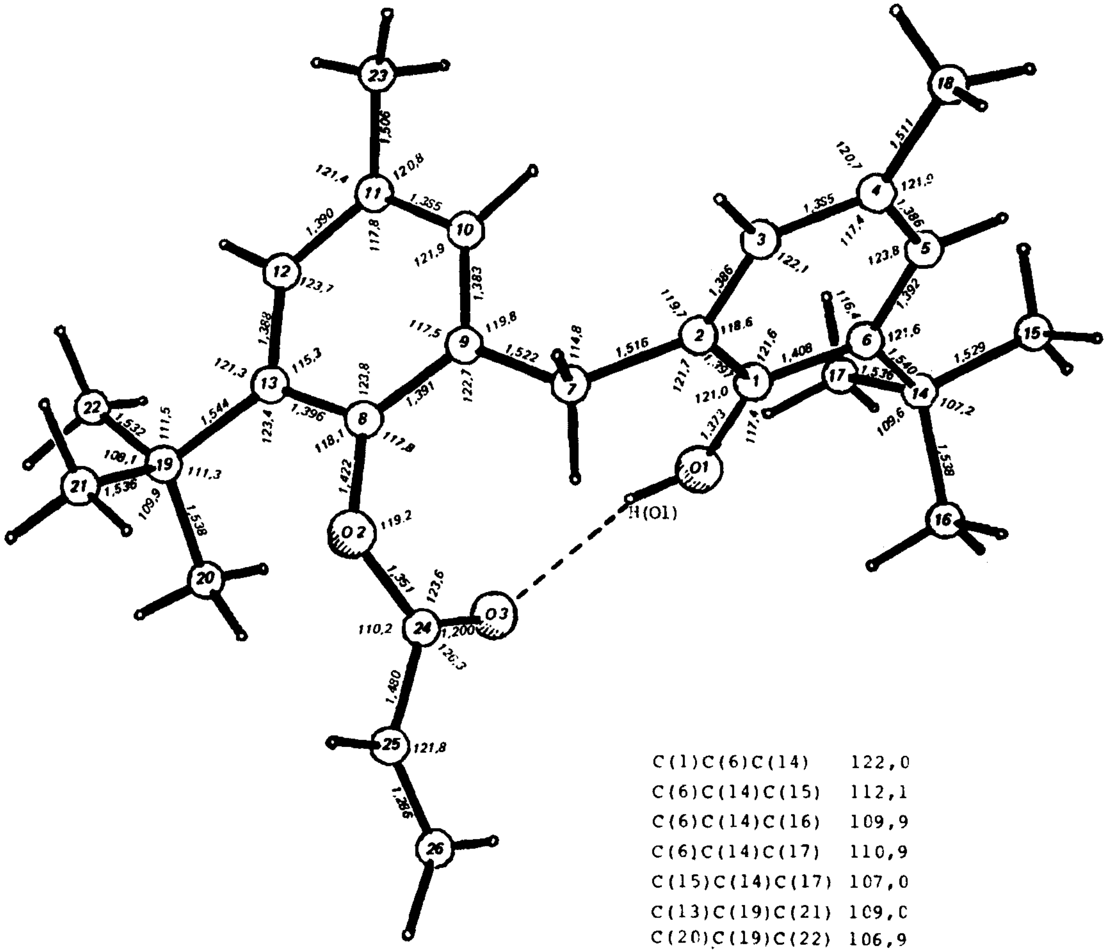

C(1)C(6)C(14)	122,0
C(6)C(14)C(15)	112,1
C(6)C(14)C(16)	109,9
C(6)C(14)C(17)	110,9
C(15)C(14)C(17)	107,0
C(13)C(19)C(21)	109,0
C(20)C(19)C(22)	106,9

FIGURE 11 Molecular structure of monoacrilic ester of 2,2′-methylene-bis-(4-methyl-6-*tert*-butylphenol) (X-ray diffraction analysis).

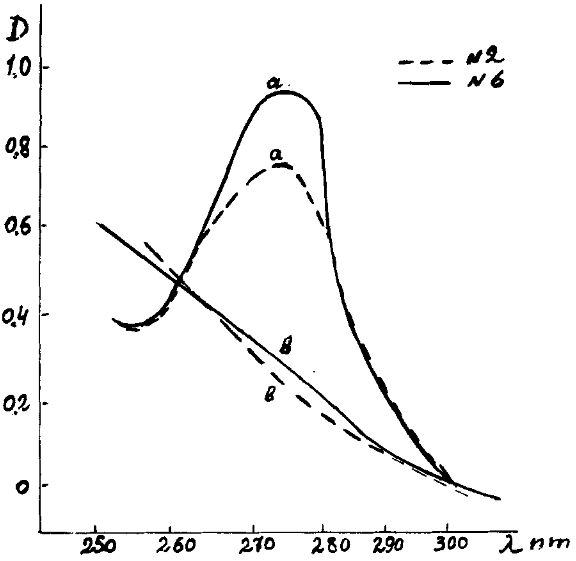

FIGURE 12 UV-spectra of the extracts of polyisoprene plates containing stabilizers NN 2 and 6 (numbers of compounds as in Table XI) before (a) and after (b) vulcanization.

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vulcanized at 130°C for 30 min. Before and after the vulcanization the plates were extracted with the boiling ethyl alcohol for 3 hours. Figure 12 indicates that extracts from plates before vulcanization (a) and after vulcanization (b) indicates grafting of the antioxidant.

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