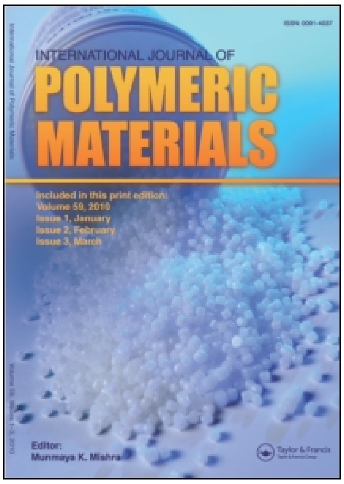

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N. A. Mukmeneva[a]; E. N. Cherezova[a]; I. F. Rusinac[b]; E. L. Shanina[c]; G. E. Zaikov[c]
[a] Kazan State Technological University, Kazan, Tatarstan Russia [b] Institute of Chemical Physics, Russian Academy of Sciences, Moscow, Russia [c] Institute of Biochemical Physics, Russian Academy of Sciences, Moscow, Russia

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Substituted Arylamines with 3,5-di-*tert*-butyl-4-hydroxybenzyl Fragment: Synthesis and Inhibiting Properties

N. A. MUKMENEVA[b], E. N. CHEREZOVA[b], I. F. RUSINA[c],
E. L. SHANINA[a] and G. E. ZAIKOV[a, *]

[a] Institute of Biochemical Physics, Russian Academy of Sciences, 4 Kosygin Str., Moscow 117977, Russia; [b] Kazan State Technological University, 68, Karl Marx Str., Kazan 420015 Tatarstan Russia; [c] Institute of Chemical Physics, Russian Academy of Sciences, 4 Kosygin Str., Moscow 117977, Russia

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Synthesis of some substituted arylamines is described. These substances were tested as antioxidants both in the liquid hydrocarbon and in the polymers. Their effectiveness was compared with common additives and as a result some conclusions about possibility of their usage is made.

Keywords: Arylamines; substitution; antioxidants; synthesis

AIMS AND BACKGROUND

Significant efforts recently are undertaken with the purpose of finding unclassical inhibiting systems. To such systems it is possible to attribute substances, which molecules contain not one, but two or several different functional groups having antioxidizing properties and able to exhibit synergy effects. In the present paper synthesis of some of such new effective antioxidants, formed as a result of interaction

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*Corresponding author.

between *N,N*-dimethyl(3,5-di-*tert*-butyl-4-hydroxybenzyl)amine (I) and a number of primary *p*-substituted arylamines is described and some data about their inhibition activity are given.

EXPERIMENTAL

Synthesis and Characterization of Substances III – VII

0,05 – 0,1 mole of *N,N*-dimethyl(3,5-di-*tert*-butyl-4-hydroxybenzyl)amine and 0,05 mole of arylamine in 10 ml of toluene or butanol were stirring at the temperature 120 – 130°C under nitrogen flow during 6 – 9 hours up to exhaustion of the initial arylamine. After termination of reaction the mix was cooled up to room temperature. Precipitated crystals were filtered off and recrystallized from hexane.

The NMR ^{1}H and ^{13}C spectra were registered by using spectrometer Gemini-200 with operating frequency 200 MGz. Stabilization of magnetic field was accomplished according to resonance of the deuterium nuclei (external standart). Spectra of substance IIIa were registered in solution ($CCl_4 + CD_3OD$), IIIb–d – in CCl_4, VIIe – in ($CCl_4 +$ $CHCl_3$), VIIf – in DMFA.

The IR-spectra of the samples in the Vaseline oil were obtained by using Fourier-spectrometer Perkin-Elmer 16CFT-IR.

Mass-spectra were recorded by using spectrometer Incos-50B under conditions of "thermal atomization". Temperature of ionic source 210°C, atomizator temperature 95°C, eluent – methanol : 0,05 M aqueos solution of ammonium acetate (96:4 by volume), eluent consumption 2.5 ml/min.

Analytical separation was carried out using liquid-phase chromatograph Spectra-Physics with a Nukleosil-C18 column 250 × 4 mm with granulation 10 microns. Eluent: methanol-water (96:4 by volume). Flow speed 1 – 2 ml/min. Detection was carried out in the UV region, wave length 254 nm.

Preparative separation was achieved using liquid-phase chromatographe Waers Delta Prep 40000 with a column Parasil Silica 300 × 19 mm. Eluent: methanol-water (92 – 98: 8 – 2 by volume).

Materials. Isotactic PP in the form of powder (ProFax 6501 produced by Himont Co (USA) with the molecular mass $M_w = 164400$, $M_w/M_n = 38$) was used. Traces of inhibitor were washed out with benzene in the Soxhlet apparatus. Butyl rubber was industrial product BK-1675.

Chlorobenzene and cumene were purified in accordance to the method, described earlier [1].

Samples Preparation and Oxidation of Organic Substrates

The initiated oxidation of cumene at the presence of the synthesized inhibitors was investigated with a chemiluminescence (CL) method using original equipment. As initiator azo-bis-isobutyronitrile, was used, for CL intensity amplification activator -europium chelate (europium tris-tenoiltrifluoroacetonate was with 1,1-phenanthroline) with concentration $1 \cdot 10^{-4}$mol/l was added to the system. As a solvent chlorobenzene was used. Ratio of hydrocarbon and solvent was 1:1 by volume. In details technique of measurement of the rate constants of inhibitor reaction with peroxy radicals of substrate (k_7) and of stoichiometrics inhibition coefficient (f), was described earlier [2]. Calculated quantities of inhibitors were added to the 10% solution of BR in hexane. Polymer was isolated from solution using method of degasification with live steam, than dried in the vacuum desiccator up to constant weigt.

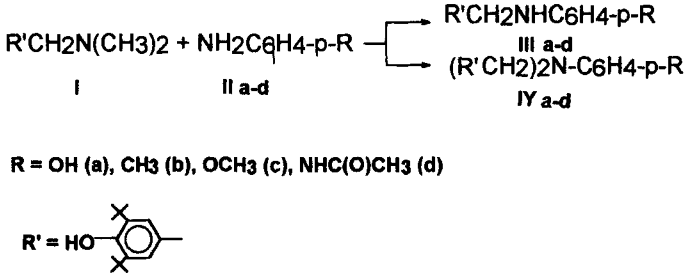
Autooxidation of butylrubber (BR) was carried out using manometric equipment at 170°C. The technique was described in [3].

Samples of PP with added inhibitors were prepared by addition of calculated quantity of inhibitors solutions in benzene to the weighed portion of polymer. After 3 hours solvent was evaporated under constant stirring of the mixture. For substances VIf and IIIa mix of benzene and acetone was used, because of low solubility of these substances in benzene.

Autoxidation of PP was carried out at 130°C. The techniques of oxidation and analysis of concentration of inhibitors in polymer are described in [4, 5].

RESULTS AND DISCUSSION

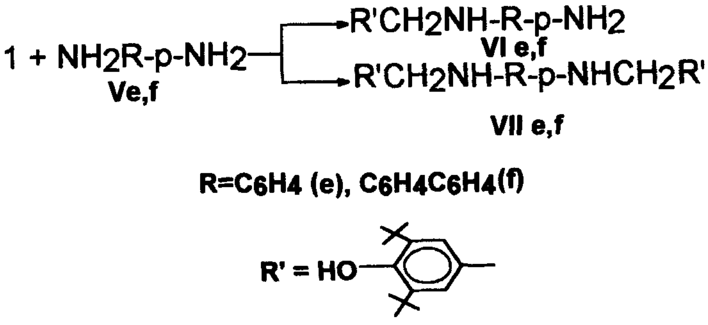
It is known that dimethylaminophenols have a tendency to the transamination reactions with primary and secondary alkyl- and arylamines. Transamination reaction with aliphatic primary amines leads to formation mono- and disubstituted substances [6]. The same reaction with primary arylamines according to authors of [7] proceeds with participation of only one of two hydrogen atoms bonded to nitrogen.



SCHEME 1

On the basis of liquid chromatography and chromato-mass-spectrometry data it was shown that both hydrogen atoms of arylamine molecule can be involved in the process (Scheme 1). During reaction two new maximums appeared in the chromatograms and chromatomass-spectra. Molecular masses of the obtained maximums corresponded to the ones of substances with one and two oxybenzyl substituents in the arylamine molecule. (Tab. I)

The reaction of substances (1) and (V) also results in formation of products containing in the structure one or two oxybenzyl groups (Scheme 2). Addition of the two oxybenzyl groups to the aryldiamines proceeds apparently with participation of both primary aminogroups, because in the NMR spectra peaks typical for NH_2-group are absent (Tab. II)



SCHEME 2

TABLE I Data of the chromato-mass-spectrometry investigation (m/z) of the products of the reaction between *N*,*N*-dimethyl(3,5-di-*tert*-butyl-4-hydroxybenzyl)amine (I) and arylamines (II, a – e) and (V, e, f)

Starting amine	*m/z (rel.int., %)*
IIa	326 (100.00), 327 (5.78), 328 (18.25); 546 (17.98)
IIb	326 (87.17), 327 (9.50); 544 (100.00), 545 (34.71), 546 (3.80)
IIc	342 (100.00), 343 (25.49); 560 (22.67), 561 (10.54)
IId[a]	369 (6.08), 370 (2.27), 737 (100.00); 519 (50.73), 520 (18.28), 587 (50.21)
Ve[a,b]	327 (100.00); 544 (17.54), 545 (45.00), 546 (19.70)
Vf[a,b]	403 (100.00), 404 (41.00); 521 (20.01), 622 (6.92)

[a] – reaction time 9 hrs.
[b] – ratio (I) : (V) = 2 : 1.

TABLE II Parameters of the NMR ^{1}Hspectra of the synthesized compounds III, VI, VII (δ, ppm)

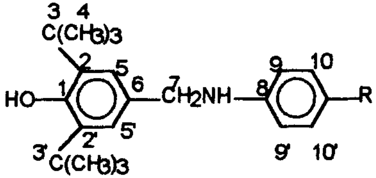
Substance	CH_3C	CH_2NH	NH_2, NH	OH	C_6H_4, C_6H_2
IIIa	1.41	4.07	4.90	4.9	7.12;6.62 – 6.69
IIIb[a]	1.52	3.34	3.34	5.15	7.18 – 6.60
IIIc[b]	1.59	4.23	3.39	5.16	7.18, 7.23;6.66 – 6.79
IIId[c]	1.40	3.73		4.80	6.60
VIe	1.46	4.08	3.22	5.15	7.13,6.44 – 6.48
VIIe	1.53	4.18	3.15	5.20	7.20 – 6.60
VIIf	1.64	4.46	3.90	6.03	7.50; 6.90

[a] $\delta C6H4\underline{CH3}$ = 2.21 ppm.
[b] $\delta C6H4O\underline{CH3}$ = 4.71 ppm.
[c] $\delta C(O)\underline{CH3}$ = 2.20 ppm.

Obtained mono- and di-substituted products were separated by repeated crystallization or using method of high-efficient liquid chromatography and were characterized (Tabs. II – IV).

In the IR-spectra of substances IIIa – d, VIe – f and VIIe – f can be distinctly seen valence oscillations of the secondary aminogroups υ_{NH}

TABLE III NMR ^{13}C spectra parameters (δ, ppm) of the synthesized compounds with common structure



Substance	C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8	C^9	C^{10}	C^{11}	C^{12}	CH_3N
I	154.02	138.23	126.45	131.36	35.45	31.15	65.54	–	–	–	–		45.53
IIIa	150.62	138.62	125.64	131.43	35.56	31.20	51.57		118.43	116.80			
IIIb	155.17	137.81	127.97	132.20	36.90	33.22	47.98		115.54			23.22	
IIIc	155.4	137.89	127.07	132.03	36.84	33.00	52.29	154.60	116.45	116.45	57.68		
									117.24	117.24			
VIe	151.04	139.68	122.86	134.01	32.58	28.75	48.24		112.63	114.81	–	–	
VIIe	155.43	138.32	127.26	133.00	36.93	33.93	33.07	52.75	143.58	117.16			
VIIf	153.45	139.36	126.55	131.59	34.96	30.84	48.35	148.17	113.38	124.00	129.66		

TABLE IV Melting points, molecular masses and results of element analysis of synthesized compounds

Substance	*Melting point, °C*[a]	*Detected, %*			*Formula*	*Calculated, %*			*M*[b]	
		C	*H*	*N*		*C*	*H*	*N*	*Detected*	*Calculated*
IIIa	200–203	76.41	9.34	5.00	$C_{21}H_{29}NO_2$	77.06	8.87	4.28	327	327
IVa	178–180	79.85	9.48	3.01	$C_{36}H_{51}NO_3$	79.27	9.36	2.57	545	545
IIIb	78–80	80.26	10.07	5.00	$C_{22}H_{31}NO$	81.23	9.54	4.31	325	325
IVb	203–206	81.95	9.89	3.02	$C_{37}H_{53}NO_2$	81.77	9.76	2.58	543	543
IIIc	95–96	76.93	9.89	4.46	$C_{22}H_{31}NO_2$	77.42	9.09	4.11	341	341
IVc	194–200	79.43	9.52	2.97	$C_{37}H_{53}NO_3$	79.43	9.48	2.50	559	559
IIId	162–164	75.28	8.75	7.83	$C_{23}H_{32}N_2O_2$	75.00	8.70	7.61	368	368
IVd	183–183.5	77.52	9.00	4.75	$C_{38}H_{54}N_2O_2$	77.82	9.22	4.78	586	586
VIe	131–132	77.43	9.76	8.58	$C_{21}H_{30}N_2O$	77.3	9.20	8.59	326	326
VIIe	193	79.67	9.52	5.34	$C_{36}H_{50}N_2O_2$	79.70	9.23	5.17	542	542
VIf	189–191	80.10	8.52	6.81	$C_{27}H_{34}N_2O$	80.60	8.46	6.97	402	402
VIIf	254–256	81.35	9.52	4.75	$C_{42}H_{56}N_2O_2$	81.29	9.03	4.52	620	620

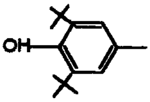
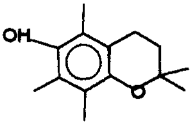
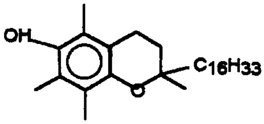
[a] from hexane.

[b] chromato-mass-spectrometry data.

3360 – 3390 cm^{-1} and peacs of deformation oscillation of the NH_2 group δ_{NH_2} 1600 – 1700 cm^{-1} disappear except for the reactions of dimethylaminomethylphenol (I) with aryldiamines (Ve, f) in which only one aminogroup is involved. In the last case the shift of the maximum to the low-frequency region takes place.

In the Table V results of measurement of constants k_7 and stoichiometrics inhibition coefficient f for eight synthesized inhibitors are given, and for comparison the data for reference substances 2,6-di-*tert*-butyl-4-methylphenol (ionol), chroman and α-tocopherol are given also.

TABLE V

Substance	$k_7 \times 10^{-4}$, l/*mole* · *sec*	f
IIIa	2,09	3,51
IIIb	0,84	2,54
IIIc	0,92	2,38
IIId	0,89	2,63
VIe	1,23	2,97
VIf		
VIIe		
VIIf		
Ionol	1,43	2,0
		
Chroman	17,5	2,0
		
α-tocopherol	36,0	2,0
		

As follows from the data, given in the table, the investigated inhibitors have rather high k_7 and f values, and the f values specify participation in the inhibiting process more, than one functional group.

For all investigated inhibitors f values were higher, than for model substances, but especially high f values were obtained for substances IIIa and VIe.

For check of inhibiting properties of the synthesized substances the experiments on inhibition of autoxidation of polypropylene and butylrubber were carried out. In a Figure 1 the dependence of the induction period of BR oxidation on concentration of the inhibiting additives is given. For comparison in the same figure the data for the stabilizer used in an industry for the given polymer – 2,2′-bis (4-methyl-6-*tert*-butylphenyl)methane (2246) are given. From these data follows, that the majority of the synthesized substances has higher antioxidizing efficiency, than 2246. It is apparently a result of the

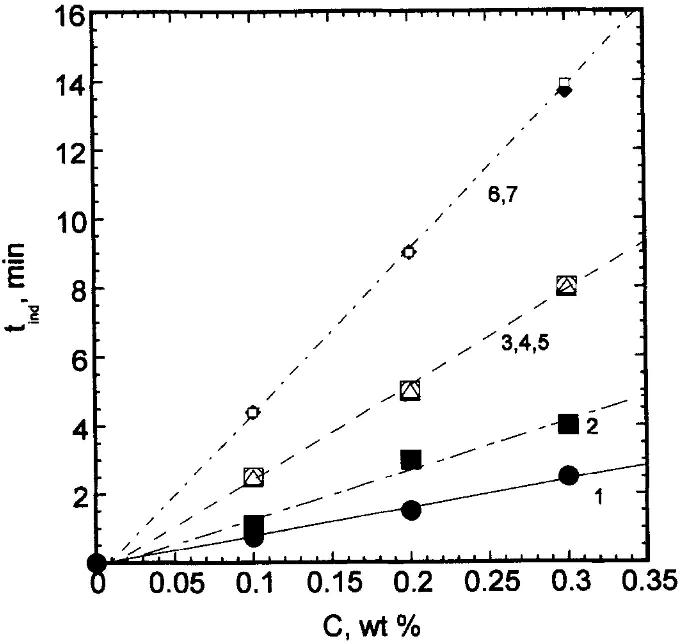


FIGURE 1 Dependence of the induction period of butyl rubber oxidation on the additives concentrations. Oxygen pressure 250 mm Hg, $T = 170°C$. 1 – IIId, 2 – antioxidant 2246, 3 – IIIb, 4 – IIIa, 5 – IIIc, 6 – VIe, 7 – VIIe.

presence in molecules of these inhibitors of the various on a nature active groups, ensuring effect of a synergy during substrate oxidation. The comparison of inhibiting action of substances IIIa and VIe with summary action of inhibitors representing as though their components, was carried out, for IIIa – with 2,6-di-*tert*-butyl-4-methylphenol (ionol) and initial aminophenol IIa, and for VIe – with ionol and aminophenol Ve. The received results are presented in Table VI.

From the data, given in the table, follows, that synthesized antioxidants are approximately double more effective than the appropriate mixes of ionol and arylamine. Use of a mix of two antioxidants also gives effect of synergy, but "the internal synergy" appears considerably larger.

It is necessary also to note, that introduction of the second aminogroup (VIe, VIIe) considerably strengthens antioxidizing action.

The following series of experiments were carried out for check of antioxidizing efficiency of the synthesized substances during oxidation of polypropylene.

In the Table VII results of measurement of induction periods of PP oxidation at the presence of five synthesized antioxidants and for ionol, taken for comparison, are given. Concentration of the additives – 5×10^{-4} mole/kg.

TABLE VI Induction periods of BR-1675 oxidation at the presence of various antioxidants

Experiment number	*Antioxidant*	*Conc., wt%*	*Induction period, min*
1	IIa	0,2	200
2	ionol	0,2	50
3	IIa	0,1	280
	ionol	0,1	
4	IIIa	0,2	500
5	Ve	0,2	250
6	Ve	0,1	350
	ionol	0,1	
7	VIe	0,2	900

TABLE VII

Antioxidant	III*a*	III*b*	III*c*	III*d*	VI*e*	*Ionol*
Induction period	96	46	43	27	160	90

As well as in the BR case, the best result shows antioxidant, which molecule contains 2 aminogroupes. Longer, than for ionol induction periods of PP oxidation at the presence of substances IIIa and VIe are not connected with ionol evaporation during experiment, all experiments were carried out in conditions excluding losses connected to additives evaporation. On the Figure 2 data are presented which show kinetics of VIe consumption during PP oxidation. Evidently after rather quick consumption in the beginning of the process concentration of VIe becomes practically constant. Such behavior is likely due to inhibitor regeneration in the oxidation process. For comparison data for ionol are given on the same figure. In the region where VIe concentration is almost constant, concentration of ionol decreases rapidly.

It is interesting to mention that phenol IIIa which consumption in PP at high initial concentration 2×10^{-2} mole/kg is a very quick process demonstrates rather good inhibiting properties (See Tab. VII). The most real interprertation of this fact is the difference of concentrations of additive in these two experiments. In the antioxidants consumption experiments initial concentration was more, than 10

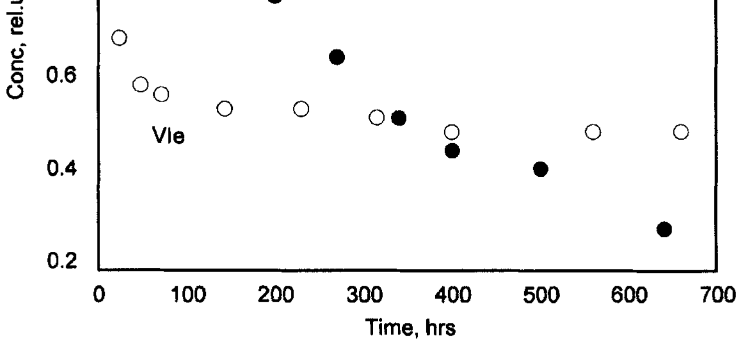


FIGURE 2 Kinetics of ionol and antioxidant VIe consumption during polypropylene autooxidation. $T = 130°C$, air. Initial concentration of additives 0.02 mole/kg.

times higher, than in the experiments in which induction periods were measured. Phenol IIIa has to oxidize rather easy because of formation of quinoid structure and at high concentrations this process controls the consumption rate. At lower concentrations contribution of oxidation to the summary process is much lower and IIIa behaves as good inhibitor.

From the above mentioned data follows, that synthesized antioxidants have the high antioxidizing characteristics (k_7 and f) in a liquid phase, and also can successfully be used as antioxidants for polymeric materials. Especially perspective is the antioxidant VIe, well recommending itself in cumene as well as in the both investigated polymer systems.

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