ЗАВИСИМОСТЬ АНТИОКСИДАНТНЫХ СВОЙСТВ НЕКОТОРЫХ ПРОСТРАНСТВЕННО-ЗАМЕЩЕННЫХ ФЕНОЛОВ ОТ РАСЧЕТНЫХ ПАРАМЕТРОВ СТРОЕНИЯ МОЛЕКУЛ АНТИОКСИДАНТОВ

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Выбор и оптимизация антиоксидантов и их количества зависят от многих факторов, включая состав топлива, технические характеристики топлива и условия хранения. Во время работы двигателей и механизмов они соприкасаются с воздухом, часто при повышенных температурах. В этих условиях и под каталитическим действием металлов окисляются смазочные масла и топливо. Традиционно актуальным является поиск соединений с высокой антиоксидантной активностью. В данной работе были изучены возможности программных пакетов для квантово-химических расчетов пространственно замещенных фенолов (SSP). Был синтезирован структурный ряд SSP, изучена их антиоксидантная активность, а затем были проведены квантово-химические расчеты структур с целью выявления зависимости их активности от определенных параметров. На этапе анализа литературы было выявлено лишь несколько расчетных параметров, от которых зависит антирадикальная активность соединения. Однако при изучении зависимостей было обнаружено, что активность фенолов в качестве антиоксидантов зависит от несколько большего числа параметров, таких как потенциал ионизации, энергия LUMO, энтальпия, полная энергия молекулы и валентный угол С-О-Н. Структура фенолов препятствует их растворимости в масле, что затрудняет тестирование таких соединений, как антиоксиданты. Было решено сначала растворить соединение в углеводородном растворителе, а затем добавить концентрат в масло. Антиоксидантную активность соединений измеряли по кислотному числу окисленного масла, содержащего исследуемое соединение. Результаты этой работы позволили нам определить зависимость антиоксидантной активности от различных параметров структуры фенола. В дальнейшем планируется расширить вышеупомянутую серию, аналогичную по структуре, а также провести испытания на антиоксидантную активность в маслах и топливах различных марок.

Ключевые слова: присадки к маслам, пространственно-замещенные фенолы, квантово-химические расчеты, антиоксидантные свойства

DEPENDENCE OF THE ANTIOXIDANT PROPERTIES
OF SOME SPATIALLY SUBSTITUTED PHENOLS ON THE CALCULATED PARAMETERS
OF THE STRUCTURE OF ANTIOXIDANT MOLECULES

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The choice and optimization of antioxidants and their amount depends on many factors, including the composition of the fuel, the technical characteristics of the fuel and the storage conditions. During the operation of engines and mechanisms, they come into contact with air, often at elevated temperatures. Under these conditions and under the catalytic action of metals, lubricating oils and fuels are oxidized. Traditionally, the search for compounds with high antioxidant activity is relevant. In this paper, the possibilities of software packages for quantum-chemical calculations of spatially substituted phenols (SSP) were studied. A structural series of SSPs were synthesized, their antioxidant activity was studied, and then quantum chemical calculations of the structures were carried out in order to identify the dependence of their activity on certain parameters. At the stage of literature analysis, only a few calculated parameters were identified, on which the antiradical activity of the compound depends. However, when studying the dependencies, it was found that the activity of phenols as antioxidants depends on a slightly larger number of parameters, such as the ionization potential, LUMO energy, enthalpy, total energy of the molecule and the C-O-H valence angle. The structure of phenols prevents their solubility in oil, which makes it difficult to test compounds such as antioxidants. It was decided to first dissolve the compound in a hydrocarbon solvent, and then add the concentrate to the oil. The antioxidant activity of the compounds was measured by the acid number of the oxidized oil containing the studied compound. The results of this work allowed us to determine the dependence of antioxidant activity on various parameters of the phenol structure. In the future, it is planned to expand the above-mentioned series, similar to the structure, as well as to conduct tests for antioxidant activity in oils and fuels of various brands. Antioxidants or inhibitors of oxidation processes play a major role in various spheres of human life: oil refining, food and cosmetics industry, drug manufacturing and many others.

Key words: additives to oils, space-substituted phenols, quantum-chemical calculations, antioxidant properties

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Алексанян К.Г., Кошелев В.Н., Чебан Э.Г., Стоколос О.А., Килякова А.Ю., Сорокина А.С., Шамсутдинова Л.П., Газизов М.Б., Писцова А.Л., Алексанян Д.Р., Агаджанян С.А. Зависимость антиоксидантных свойств некоторых пространственно-замещенных фенолов от расчетных параметров строения молекул антиоксидантов. *Изв. вузов. Химия и хим. технология.* 2021. Т. 64. Вып. 11. С. 35–43

Antioxidants or inhibitors of oxidation processes play a major role in various spheres of human life: oil refining, food and cosmetics industry, drug manufacturing and many others [1].

Phenolic antioxidants take the lead among modern free-radical inhibitors of oxidation of organic and bioorganic substrates. In recent years they accounted for over 50% of the world market of plastic stabilizers and ~30% for rubbers and resins, while most food and medical antioxidants are also phenolic compounds [2].

Until recently, it was difficult to predict what effect the introduction of certain substituents might have on the change in chemical properties of various substances. Initially, the only ways of assessment were semi-empirical methods that could describe molecular-quantum structure, explain the properties of already obtained substances, and explain the relationship between geometric and electronic structures of molecules and their reactivity. Subsequently, with the development and improvement of non-empirical methods, a whole range of new opportunities opened up for researchers to study the most diverse and complex structures of organic molecules, such as the full and convergent prediction of substances' properties, detailed study of complex multistage reaction mechanisms, including catalytic ones, and much more. Nowadays, it can be stated with confidence that the development of computer technologies and quantum-chemical research became so effective that it is difficult to find any article devoted to theoretical or applied chemical research that would ignore the results of quantum-chemical calculations [3].

Today, we can confidently say that quantum-chemical methods have become one of the most important tools of chemical research. It is also important to emphasize that the role of such methods in various studies is growing each and every year. Computer technologies and quantum-chemical research made such a massive progressthat they can now be placed on the same footing as experimental research.

The aim of this work is to reveal the dependence of antioxidant activity on the calculated parameters: bond lengths, valence angles, ionization potentials, total energy of compounds, dissociation energy, HOMO energy, LUMO energy, heat of formation, dipole moments, enthalpy, entropy, Gibbs energy. The compounds obtained were tested for their antioxidant activities [4].

The mechanism of hydrocarbon oxidation is of a radical-chain nature and develops as follows:
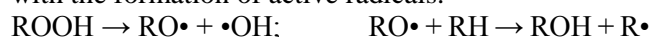
1) Formation of free radicals R• and hydroperoxide radicals $RO•_2$:

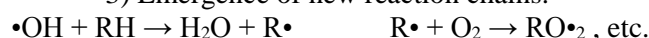Initiation $RH + O_2 \rightarrow R• + HO•_2$

Development of chain reaction $R• + O_2 \rightarrow RO•_2$

$RO•_2 + RH \rightarrow ROOH + R•$
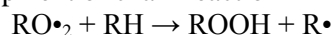
2) Decomposition of hydroperoxide molecule with the formation of active radicals:

$ROOH \rightarrow RO• + •OH;$ $RO• + RH \rightarrow ROH + R•$

3) Emergence of new reaction chains:

$•OH + RH \rightarrow H_2O + R•$ $R• + O_2 \rightarrow RO•_2$, etc.

4) Breakdown of chain reaction:

$R• + R• \rightarrow R - R$ $R• + ROO• \rightarrow ROOR$
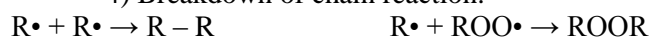
Since the process of hydrocarbons oxidation is radical-chain and proceeds with increasing rate, antioxidants must be able to "slake" the active hydrocarbon radicals, thus slowing down or completely stopping the chain reaction of oxidation.
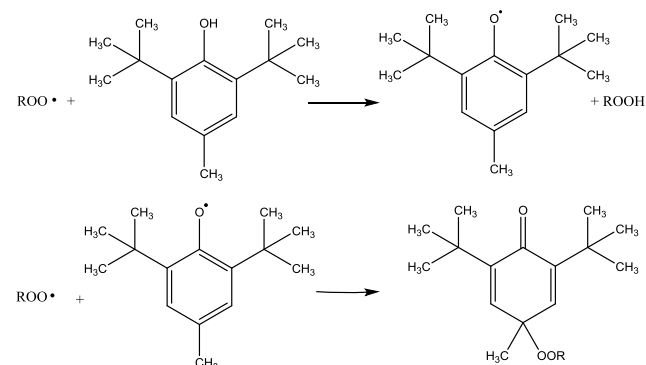

Fig. 1. The reaction mechanism of antioxidant additive using the example of Ionol
Рис. 1. Механизм реакции антиокислетильной присадки на примере ионола

The radical formed at the first stage is stabilized by bulky tert-butyl substituents. It does not participate in the continuation and development of hydrocarbon oxidation chain, but is able to interact with another radical, which leads to the formation of quinoid structure and helps to slow down the oxidation process [5-6]. The rate of this reaction is significantly influenced by the nature of para-substituents in phenol.

Compounds under study were synthesized in three stages [7-8]. At the first stage we have obtained 4-hydroxy-3,5-di-*tert*-butylbenzaldehyde in Duff reaction by interaction of 2,6-di-*tert*-butylphenol with urotropin in boiling acetic acid solution.
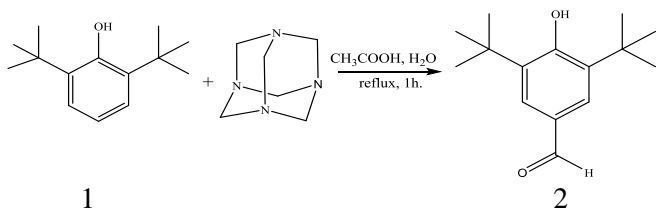
Fig. 2. The process of obtaining 4-hydroxy-3,5-di-*tert*-butylben-zaldehyde

Рис. 2. Процесс получения 4-гидрокси-3,5-ди-*трет*-бу-тилбензальдегида

At the second stage, the interaction of 4-hy-droxy-3,5-di-*tert*-butylbenzaldehyde with thionyl chloride at room temperature led to the formation of 4-hydroxy-3,5-di-*tert*-butylbenzylidene chloride [9].
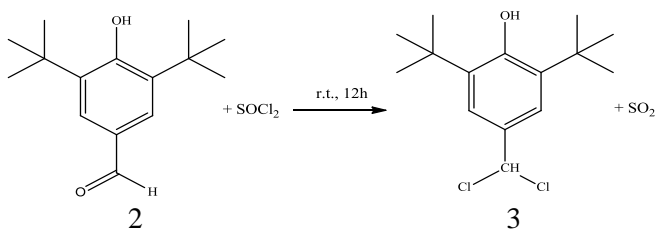

Fig. 3. The process of obtaining 4-hydroxy-3,5-di-*tert*-butylben-zylidene chloride

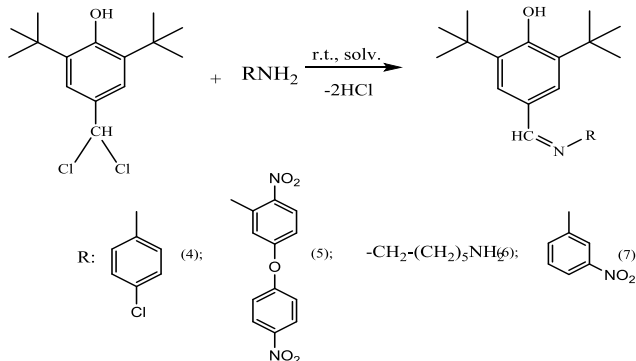Рис. 3. Процесс получения 4-гидрокси-3,5-ди-*трет*-бу-тилбензилиденхлорида

Fig. 4. The process of obtaining 2,6-di-*tert*-butyl-4-(R-N-iminomethyl)phenols

Рис. 4. Процесс получения 2,6-ди-*трет*-бутил-4-(R-N-амино-метил)фенолов

At the third stage, the studied products were produced by interaction of 4-hydroxy-3,5-di-*tert*-bu-tylbenzylidene chloride with primary amines at room temperature Conditions of the experiments and yield of reaction products are presented in Table 1.

Testing of the obtained compounds was carried out with the use of I-20 oil. The additive was first dissolved in heated oil, and the samples were oxidized inPetroTestinstrument according to ASTM D 4636 standard. Discs of various non-ferrous metals were used as catalysts. The test was conducted at 150 °C for 4 h with constant air blow [6, 7].

The tested compounds antioxidant activity was assessed using the acid indexvalue determined after oxidation of oil according to GOST-5985-79.

Table 2 presents the results of calculation of the studied molecules done with the help of Gaussian and MORAS software.

The aim of this work is to reveal the dependence of antioxidant activity on the calculated parameters: bond lengths, valence angles, ionization potentials, total energy of compounds, dissociation energy, HOMO energy, LUMO energy, heat of formation, dipole moments, enthalpy, entropy, Gibbs energy. The compounds obtained were tested for their antioxidant activities [4].

Below in green are my suggestions to change the wording.

Introduction of electron-deficient substituent in para-position of hydroxyl group leads to an increase in bond length in phenol hydroxyl group. Values vary from 1.0009 Å (compound 3) to 1.0061 Å (compound 7) and 1.0067 Å (compound 5). The higher values are shown by molecules containing nitro groups.

The greatest O-H bond length in phenol hydroxyl group is observed in compound 5 and equalsto 1.0069 Å. The opposite effect has also been observed: O-H bond length decreases with the introduction of electron-donating substituent in para-position.

The least bond length is observed atIonol molecule and equals to 1.0003 Å. Based on the obtained results, we can assume that the bond length decreases with the growth of electron density inhydroxyl group [9, 10].

Table 1

Conditions of experiments
Таблица 1. **Условия проведения экспериментов**

№ of compound	Amine	Solvent	Melting point, °C	Yield, %
4	4-chlorbenzeneamine	benzene	120-122	96
5	2-nitro-5-(4-nitrophenoxy)benzeneamine	Diethyl ether	170-172	88
6	1,6-hexanediamine	Acetone	165-167	83
7	3-nitrobenzeneamine	Diethyl ether	152-154	76

Results of quantum-chemical calculations of the synthesized compounds
Таблица 2. **Результаты квантово-химических расчетов синтезированных соединений**

№ of compound	Name of compound	CN	Bond length O-H, Å	Valence angle C-O-H, °	Ionization potential, eV	LUMO energy, eV	Dipole moments, D	Dissociation energy, O-H, eV
	2,6-di-*tert*-butyl-4-methylphenol (Ionol)	0.26316	1.0003	112.10	8.484	0.421	1.720	12.306
4	2,6-di-*tert*-butyl-4-[N-(4-chlorphenyl)iminome-thyl]phenol	0.87260	1.0029	112.50	8.844	0.077	5.723	10.430
5	2,6-di-*tert*-butyl-4-{N-[2-ni-tro-5-(4-nitrophenoxi)phe-nyl]iminomethyl}phenol	1.18421	1.0069	112.45	9.064	-0.583	2.545	7.351
6	bis(2,6-di-*tert*-butyl)-4,4'-[N,N'-1,6-hexandiil-1,6-diiminomethyl]diphenol	0.71053	1.0036	112.20	8.697	0.205	4.150	11.471
7	2,6-di-*tert*-butyl-4-[N-(3-ni-trophenyl)iminomethyl]phe-nol	1.05263	1.0061	112.52	9.011	-0.407	7.789	8.203
3	4-hydroxi-3,5-di-*tert*-butylbenzylidenechloride	0.68632	1.0009	112.40	9.096	0.400	3.175	9.405
1	2,6-di-*tert*-butylphenol	0.52632	1.0017	112.28	8.732	0.371	1.680	12.052

Introduction of donor substituents into para-position of hydroxyl group leads to a decrease in bond length. So the lowest value was for Ionol (1.0003 Å). The values obtained confirm this observation. Thus, we see that as electron density on hydroxyl group goes up, O-H bond length decreases.

The change in the value of C-O-H valence angle is not significant, probably due to the influence of bulky tert-butyl substituents. Compared to 2,6-di-*tert*-butylphenol (1) whose C-O-H valence angle was 112.28°. The introduction of donor groups leads to its decrease (112.20°, 112.10°). And introduction of electron-deficient groups – to increase (112.40-112.52°).

The highest ionization potential (Table 2) is observed for compound 3 (9.096 eV), the lowest – for Ionol (8.484 eV), which is also due to the difference in donor-acceptor properties of substituents in para-position and agrees with the general theory stating that the introduction of the acceptor increases electron density in hydroxyl group of phenol, as well as its reactivity.

The dissociation energy was calculated as the difference in the sums of energies of dissociation products and the non-dissociated molecule [11-14].

As a result, it was also observed that the highest dissociation energy was observed for Ionol - 12.306 eV, the lowest - for compound 5 - 7.351 eV.

LUMO energy characterizes the affinity of the molecule to electron. It is noteworthy that compound 5 h the lowest LUMO value - 0.583 eV, and Ionol has the highest - 0.421 eV [15, 16].

Below graphical dependences of acid index of the oxidized oil on some calculated parameters are presented.
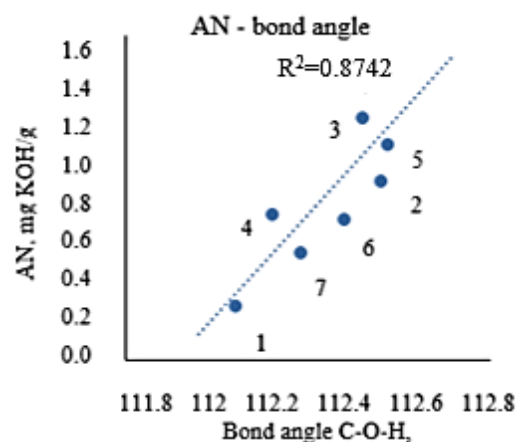

Fig. 5. Dependence of acid number on bond angle C-O-H
Рис. 5. Зависимость кислотного числа от угла связи С-О-Н

Thus, a number of new space-substituted phenols have been studied.

Based on quantum-chemical calculations in Gaussian and MORAS applications, we have determined physical constants of the synthesized substances, investigated. The dependence of antioxidant activity on calculated parameters, allowing to assess the compound's antioxidant activity in fuels and oils [17, 18].

Thus, the existence of dependences between the activity of space-substituted phenols and the calcu-

lated quantum-chemical parameters has been experimentally proved and clearly demonstrated. This is evidenced by high values of correlation coefficients (R = 0.7-0.9).
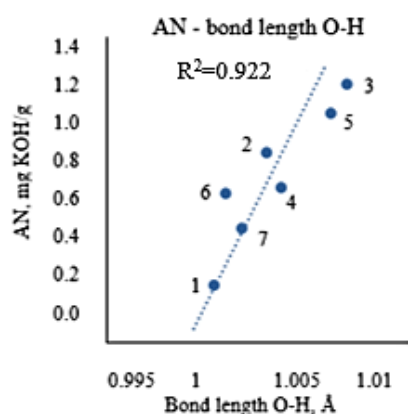

Fig. 6. Dependence of acid number on bond length O-H
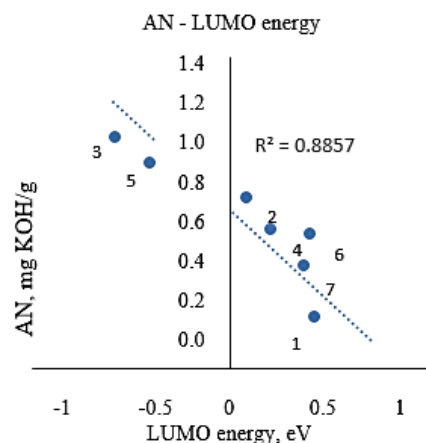Рис. 6. Зависимость кислотного числа от длины связи O-H

Fig. 7. Dependence of acid number on LUMO energy of the molecule
Рис. 7. Зависимость кислотного числа от энергии LUMO молекулы
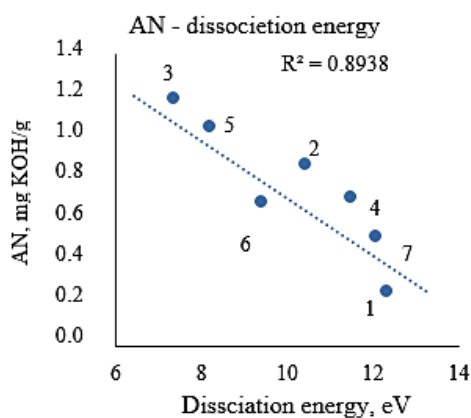

Fig. 8. Dependence of acid number on dissociation energy O-H
Рис. 8. Зависимость кислотного числа от энергии диссоциации O-H

The presence of these dependencies opens new horizons in the approach to development of new antioxidants based on space-substituted phenols. It will allow to considerably optimize and bring the search and development of new antioxidant compounds toawhole new level [19-24].

EXPERIMENTAL PART

^{1}H NMR spectra were recorded on Tesla BS-567A instruments with an operating frequency of 100 MHz, Bruker WP-250, operating frequency 250 MHz, and Bruker MSL-400, operating frequency 400 MHz, using deuterated solvent (CDCl₃) residual proton signals.

Alltheusedsolvents were purified and absolutized according to standard procedures.

(4-Hydroxy-3,5-di-tert-butylbenzaldehyde) (2)

A mixture of 20.6 g (0.1 mol) of 2,6-di-*tert*-butylphenol, 28.0 g (0.2 mol) of urotropine, 170 ml of glacial acetic acid and 30 ml of water were gently boiled while stirring for 1 h. From the reaction mass, about 80 ml of aqueous acetic acid were distilled for 1 h. After cooling down, a crystalline product was isolated from the reaction mass, filtered and washed twice with water. After filtration, drying and recrystallization from toluene, 21 g (90%) of light yellow lamellar crystals, melting point 187-189 °C, were obtained.

^{1}H NMR spectrum (DMSO-d6), δ, parts by weight: 1.38(s, 18H, C(CH₃)₃), 5.47(s,1H, OH), 7.95(s, 2H, CH), 9.54(s, 1H, COH).

Found (%): .C, 76,97; H, 9,57; O, 13,76. Calculated (%): C, 76,88; H, 9,46; O, 13,65.

4-Hydroxy-3,5-di-tert-butylbenzylidene chloride (3)

The addition of 18.5 ml (0.26 mol) of thionyl chloride to 11.7 g (0.05 mol) of 4-hydroxy-3,5-di-*tert*-butylbenzaldehyde results in a red-orange solution. After ageing of the reaction mass at room temperature for 20 h and distillation of volatiles under vacuum, a crystalline product was obtained, which was recrystallized from isooctane. We have obtained 10.9 g (75.4%) of compound (3), melting point 102-104 °C. ^{1}H NMR spectrum (CCl₄ + acetone − d₆), δ, parts by weight:1.38 (s, 18H,C(CH₃)₃], 5.40 c (1H,OH), 6.61 s (1H,CH), 7.27 s (2H,CH₆H₂).

Found (%): C, 62,41; H, 7,82; Cl, 24,63; O, 5,68. Calculated (%): C, 62,29; H, 7,67; Cl, 24,51; O, 5,53.

2,6-Di-tert-butyl-4-[N-(4-chlorophenyl)iminomethyl]phenol (4)

To a solution of 0.185 g (1.45 mmol) of parachloraniline in 7 ml toluene with vigorous stirring, we have added a solution of 0.172 g (0.91 mmol) of 4-hydroxy-3,5-di-*tert*-butyl benzylidene chloride in 5 ml

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toluene. The resulting solution was aged at room temperature for 24 h. After distillation of volatiles under slight heating, a crystalline product was obtained, which was recrystallized from diethyl ether. We have obtained 0.30 g (95.8%) of compound (4), melting point 120-122 °C.

^{1}H NMR spectrum (DMSO-d$_6$, δ, parts by weight): 1.36(s, 18H, C(CH$_3$)$_3$), 5.23(s, 1H, OH), 7.02(dd, 2H, CH), 7.4(dd, 2H, CH), 7.5 (d, 2H, CH), 8.64 (s, 1H, CHN).

Found (%): C, 73,48; H, 7,74; Cl, 10,39; N, 4,15; O, 4,79. Calculated (%): C, 73,35; H, 7,62; Cl, 10,31; N, 4,07; O, 4,65.

2,6-du-tert-butyl -4-{N-[2-nitro-5-(4-nitrophenoxy)phenil]iminomethyl} phenol (5)

To a solution of 0.275 g (1 mmol) of 2-nitro-5-(4-nitrophenoxy)benzolamine in 80 ml of diethyl ether under vigorous stirring, we have added a solution of 0.18 g (0.95 mmol) of 4-hydroxy-3,5-di-*tert*-butyl benzylidene chloride in 15 ml of diethyl ether. The resulting solution was aged at room temperature for 48 h. After distillation of volatiles under slight heating, a crystalline product was obtained, which was recrystallized from diethyl ether. We have obtained 0.41 g (88%) of compound (5), melting point 170-172 °C (with decomposition).

^{1}H NMR spectrum (DMSO-d$_6$, δ, parts by weight): 1.35 (s, 18H, C(CH$_3$)$_3$), 5.38 (s, 1H, OH), 6.64 (s, 1H, CH), 6.94 (d, 1H, CH), 7.12 (dd, 2H, CH), 7.51 (s, 2H, CH), 8.14 (d, 1H, CH), 8.24 (dd, 2H, CH), 8.46 (s, 1H, CHN).

Found (%): C, 66,12; H, 6,08; N, 8,73; O, 19,64. Calculated (%): C, 65,98; H, 5,95; N, 8,55; O, 19,53.

Bis(2,6-di-tert-butyl)-4,4'-[N, N'-1,6-hexanediol-1,6-diiminomethyl]-diphenol (6)

To a solution of 0.116 g (1 mmol) of hexamethylenediamine in 15 ml acetone under vigorous stirring, we have added a solution of 0.378 g (2 mmol) of 4-hydroxy-3,5-di-*tert*-butyl benzylidene chloride in 25 ml acetone. The resulting solution was aged at room temperature for 24 h. After distillation of volatiles under slight heating, a crystalline product was obtained, which was recrystallized from diethyl ether. We have obtained 0.452 g (82.5%) of compound (6), melting point 163-167 °C (with decomposition) [references to be verified].

^{1}H NMR spectrum (DMSO-d$_6$, δ, parts by weight): 1.33 (s, 36H, C(CH$_3$)$_3$), 1.55 (dd, 4H, CH$_2$), 3.65 (dd, 4H, CH$_2$), 5.33 (s, 2H, OH), 7.42 (d, 4H, CH), 8.08 (s, 2H, CHN).

Found (%): C, 75,94; H, 10,99; N, 8,51; O, 4,95. Calculated (%): C, 75,85; H, 10,91; N, 8,42; O, 4,81.

2,6-di-tert-butyl-4-[N-(3-nitrophenyl)iminomethyl]phenol (7)

To a solution of 0.138 g (1 mmol) of ortho-nitroaniline in 40 ml of diethyl ether under vigorous stirring, we have added a solution of 0.189 g (1 mmol) of 4-hydroxy-3,5-di-*tert*-butyl benzylidene chloride in 20 ml of diethyl ether. The resulting solution was aged at room temperature for 24 h. After distillation of volatiles under slight heating, a crystalline product was obtained, which was recrystallized from diethyl ether. We have obtained 0.269 g (76%) of compound (7), melting point 152-154 °C.

^{1}H NMR spectrum (DMSO-d$_6$, δ, parts by weight): 1.35 (s, 18H, C(CH$_3$)$_3$), 5.38 (s, 1H, OH), 6.64 (s, 1H, CH), 6.94 (d, 1H, CH), 7.12 (dd, 2H, CH), 7.51 (s, 2H, CH), 8.14 (d, 1H, CH), 8.24 (dd, 2H, CH), 8.46 (s, 1H, CHN).

Found (%): C, 71,28; H, 7,52; N, 8,01; O, 13,73. Calculated (%): C, 71,16; H, 7,39; N, 7,90; O, 13,54.

Bis(2,6-di-tert-butyl)-4,4'-[N, N'-1,6-hexanediol-1,6-diiminomethyl]-diphenol (6)

To a solution of 0.116 g (1 mmol) of hexamethylenediamine in 15 ml acetone under vigorous stirring was added a solution of 0.378 g (2 mmol) of 4-hydroxy-3,5-di-*tert*-butyl benzylidene chloride in 25 ml acetone. The resulting solution was aged at room temperature for 24 h. After distillation of volatiles under slight heating a crystalline product was obtained, which was recrystallized from diethyl ether. We have obtained 0.452 g (82.5%) of compound (6), melting point 163-167 °C (with decomposition).

^{1}H NMR spectrum (DMSO-d$_6$, δ, parts by weight): 1.33 (s, 36H, C(CH$_3$)$_3$), 1.55 (dt, 4H, CH$_2$), 3.65 (dd, 4H, CH$_2$), 5.33 (s, 2H, OH), 7.42 (d, 4H, CH), 8.08 (s, 2H, CHN).

2,6-di-tert-butyl-4-[N-(3-nitrophenyl)iminomethyl]phenol (7)

To a solution of 0.138 g (1 mmol) of ortho-nitroaniline in 40 ml of diethyl ether under vigorous stirring was added a solution of 0.189 g (1 mmol) of 4-hydroxy-3,5-di-*tert*-butyl benzylidene chloride in 20 ml of diethyl ether. The resulting solution was aged at room temperature for 24 h. After distillation of volatiles under slight heating a crystalline product was obtained, which was recrystallized from diethyl ether.We have obtained 0.269 g (76%) of compound (7), melting point 152-154 °C.

1H NMR spectrum (DMSO-d$_6$, δ, parts by weight): 1.37 (s, 18H, C(CH3)3), 5.33 (s, 1H, OH), 7.32 (dt, 1H, CH), 7.52 (s, 2H, CH), 7.68 (t, 1H, CH), 7.81 (t, 1H, CH), 8.02 (dt, 1H, CH), 8.62 (s, 1H, CHN).

The authors declare the absence a conflict of interest warranting disclosure in this article.

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