TABLE 1. PMR Spectra of IIIa, b-VIa, b

Compound	Chemical shifts, δ, ppm
IIIa	0,90 (3H, t, J=5,5 Hz, γ-CH_3); 1,17...1,37 (4H, m, α- and β-CH_2); 1,46 (3H, s, CH_3); 3,39...3,63 (1H, m, 4-H); 3,87...4,23 (2H, m, 5-H); 5,40 (1H, s, $CHCl_2$)
IVa	1,51 (3H, s, CH_3); 5,47 (1H, s, $CHCl_2$)
IIIb	0,99 (6H, t, J=7,5 Hz, CH_3); 1,06...1,81 (10H, m, CH_2); 3,15...3,68 (1H, m, 4-H); 3,84...4,22 (2H, m, 5-H); 5,44 (1H, s, $CHCl_2$)
IVb	5,48 (1H, s, $CHCl_2$)
Va	0,48 (3H, t, J=6,0 Hz, γ-CH_3); 0,71...1,13 (4H, m, α- and β-CH_2); 1,15 (3H, s, CH_3); 3,02...3,32 (1H, m, 4-H); 3,59...4,16 (2H, m, 5-H); 5,29 (1H, s, $CHBr_2$)
VIa	1,19 (3H, s, CH_3); 5,36 (1H, s, $CHBr_2$)
Vb	0,52 (6H, t, J=80 Hz, CH_3); 0,72...1,35 (10H, m, CH_2); 2,87...3,16 (1H, m, 4-H); 3,34...3,80 (2H, m, 5-H); 5,30 (1H, s, $CHBr_2$)
VIb	5,36 (1H, s, $CHBr_2$)

(see Table 1): 2-dichloromethyl-2-methyl-4-propyl-1,3-dioxanes IIIa and IVa ($C_8H_{14}Cl_2O_2$) with bp 68-70°C (10 mm) and M^+ 212; 2-butyl-2-dichloromethyl-4-propyl-1,3-dioxolanes IIIb and IVb ($C_{11}H_{20}Cl_2O_2$) with bp 73-75°C (10 mm) and M^+ 254; 2-dibromomethyl-2-methyl-4-propyl-1,3-dioxolanes Va and VIa ($C_8H_{14}Br_2O_2$) with bp 96-98°C (10 mm) and M^+ 300; 2-butyl-2-dibromomethyl-4-propyl-1,3-dioxolanes Vb and VIb ($C_{11}H_{20}Br_2O_2$) with bp 102-104°C (10 mm) and M^+ 342.

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HETEROCYCLIC BIOANTIOXIDANTS

1.* REACTION OF 3-NITRO-4-CHLOROCOUMARIN WITH THIOLATING AGENTS

É. A. Parfenov and L. D. Smirnov

UDC 547.587.51:542.945.22

The reaction of 3-nitro-4-chlorocoumarin with thiolating agents in the presence of water leads to the formation of a mixture of 3-nitro-4-hydroxycoumarin, bis(3-nitro-4-coumarinyl) sulfide, and colored labile products of undetermined structure. The reaction path can be controlled by the choice of solvent, reagent ratio, and temperature regime and by the use of weakly basic additives.

Antioxidants (AO) are multipurpose products. The most fully studied are phenolic antioxidants, among which the sterically hindered phenols have the highest activity [2]. Natural heterocyclic compounds, including 3-hydroxypyridines, pyrones, coumarins, and related bicyclic systems, are a readily available raw materials. This makes it possible to conduct a synthetic investigation over a wide range of antioxidants (analogs of vitamins E and C, iron chelating agents, models of protective metalloenzymes) with retention of the biotic indications of the biological activity to a greater or lesser degree. This is particularly valuable in the development of pharmacologically active products [3], food additives, and medicinal stabilizers. Here it is necessary to take account of the special features of the natural antioxidants in the protective system of the organism, which are determined specifically in

*For the preliminary communication, see [1].

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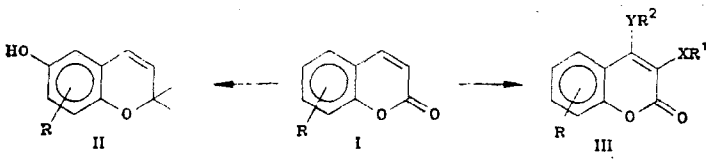
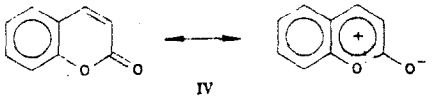
relation to the individual metabolites of molecular oxygen (organic and inorganic) and selectively with respect to the individual organs, tissues, and distribution inside and outside the cell.

No systematic searches have so far been made for various types of antioxidants based on coumarin. In [4,5], however, a possible path was indicated for the production of an antioxidant in the transition from coumarins (I) to chromenes (analogs of tocopherols). Some of these compounds have been detected in nature and have antimutagenic and antitumor activity [6] and also exhibit the characteristics of antijuvenile hormones [7].

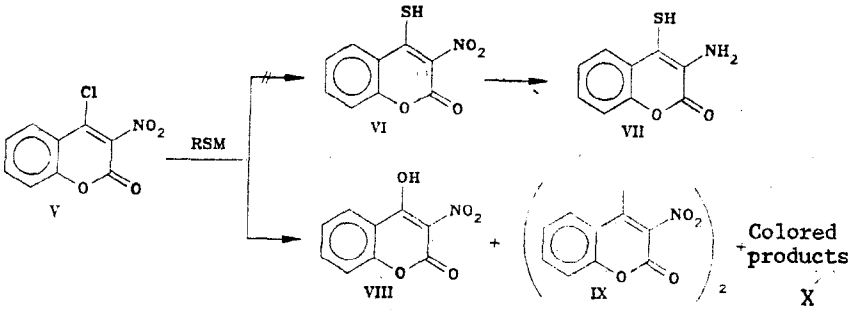


The other possible path is the transition to reductones, which are the analogs of ascorbic acid. With the inclusion of the N- and S-containing analogs there are nine possible main types of coumarin reductones (III) (X, Y = O, N, S). Of these two types have been found in nature, i.e., 3,4-dihydroxycoumarins (III) ($XR^1 = XR^2 = OH$) in the form of partially or completely methylated derivatives and 3-amino-4-hydroxycoumarins (III) ($XR^1 = NH_2$, $YR^2 = OH$), which are structural fragments of some antibiotics (novobiocin and others) [8]. The results from biological tests (in tests on the inhibition of the aggregation of thrombocytes [9] and antitumor activity [10]) have confirmed the prospects of synthetic research in this direction.

3-Amino-4-mercapto-substituted coumarins (III) ($XR^1 = NH_2$, $YR^2 = SH$) were previously unknown. We decided to synthesize the simplest representative of this type of reductone, i.e., compound (VII), from the readily obtainable 3-nitro-4-chlorocoumarin (V) [11] by the method developed for the pyrimidine analog [12]. In so far as evaluation of the effect of aromaticity on the reactivity has so far remained one of the central problems in the chemistry of coumarin (IV) [13], it is useful to examine our experimental results from this standpoint.



Experiment showed that the reaction between the coumarin (V), containing an activated chlorovinyl structural fragment, and sodium hydrosulfide takes place very readily and in DMFA or DMSO is complete after a few minutes at 18-20°C.



XI RSM=$NaHS \cdot H_2O$, XII RSM=$Na_2S \cdot 9H_2O$, XIII RSM=K_2S, XIV RSM=KSCN, XV RSM=$Na_2S_2O_3 \cdot 5H_2O$, XVI RSM=$Na_2S_2 \cdot nH_2O$, XVII RSM=PhCOSNa

The reaction products were 3-nitro-4-hydroxycoumarin (VIII) (identified with a sample of the coumarin (VIII) obtained by nitration of 4-hydroxycoumarin [11] by a mixed melting test, the chromatographic mobility, the data from IR spectroscopy, and elemental analysis) and another nitrocoumarin [IR spectrum, 1747 and 1730 (C=O), 1604 and 1593 (C=C), 1552 and 1544 (antisymmetric NO_2), 1308 cm^{-1} (symmetric NO_2)]. The data from elemental analysis [the sulfur content was 50% of the calculated content for the expected mercaptocoumarin (VII)] and the negative qualitative reactions for the mercapto group (iodine—azide and the formation of copper and cadmium thiolates) made it possible to assign the structure of bis(3-nitro-4-coumarinyl) sulfide (IX). The expected 3-nitro-4-mercaptocoumarin (VI) could not be detected.

These facts prompted us to study the effect of the nature of the thiolating agent and the reaction conditions on the result. Tests on seven thiolating agents (XI-XVII) showed that the result of the reaction did not depend on the nature of the thiolating agent and the reaction in DMFA or DMSO always led to the formation of a mixture of the coumarins (VIII) and (IX). It was found that it is possible to change the reaction toward the exclusive formation of only one product by varying the reaction conditions. Thus, realization of the reaction in acetone, alcohol, dioxane,

or DMSO with the addition of 9% of water completely suppresses the formation of 3-nitro-4-hydroxycoumarin (VIII). In this case, however, the reaction mixture always contained an appreciable amount of the initial chlorocoumarin (V) as impurity. The addition of weakly basic additives to the reaction mixture (sodium acetate, pyridine, alcohol) completely suppressed the formation of the sulfide (IX) and gave a high yield of the coumarin (VIII).

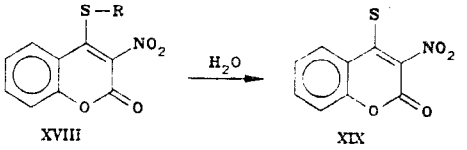
It should be noted that the formation of another unidentified minor product (X) was observed in all the variations of the reaction. This colored product behaved as a complex mixture under the conditions of TLC. Attempts to separate the mixture on a chromatographic column of silica gel proved unsuccessful, and the mixture eluted from the column was not identical with the initial mixture in its principal components (monitored by TLC). The addition of sodium hydrosulfide to the reaction mixture above the stoichiometric amount led to an increase in the yield of this product (X), and realization of the reaction at 90°C fully suppressed the formation of the other two products (VII) and (IX).

The formation of the product (X) and its properties indicate that partial reduction of the nitro group in 3-nitro-4-chlorocoumarin (V) takes place concurrently with substitution of the chlorine. Participation in a reaction with the transfer of electrons cannot be excluded for any of the thiolating agents (XI-XVII); methods for the preparative reduction of aromatic nitro compounds by sodium sulfide usually with heat are known (e.g., see [14]).

The formation of the 3-nitro-4-hydroxycoumarin (VIII) cannot be explained by reaction of the coumarin (V) with the hydroxide ion concurrent with thiolation. At the same time the formation of the two products, i.e., the ketone (enol) and the symmetric sulfide, is characteristic of the hydrolytic dissociation of thioketones (enethiols), which as a rule takes place in acidic (e.g., [15]) but not in alkaline media. In the latter, as known, the thiols form thiolates as stable products, although they are susceptible to oxidation in air.

In all the above-mentioned experiments the reaction mixtures contained water, introduced together with the thiolating agents (crystal hydrates) and/or solvent [up to 20-25 mole to 1 mole of the coumarin (V)]. In control tests [the reaction of chlorocoumarin (V) with potassium sulfide in DMSO or with potassium thiocyanate in DMFA or alcohol and also with ammonium thiocyanate in acetone or alcohol], conducted under strictly anhydrous conditions, it was not possible to detect the mercaptocoumarin (VI), the enol (VIII), or the sulfide (IX), but a compound of undetermined structure was isolated (see the experimental section). Consequently, water is a constant participant of the reaction in the discovered transformation of the chlorocoumarin (V) into the enol (VIII) and/or sulfide (IX).

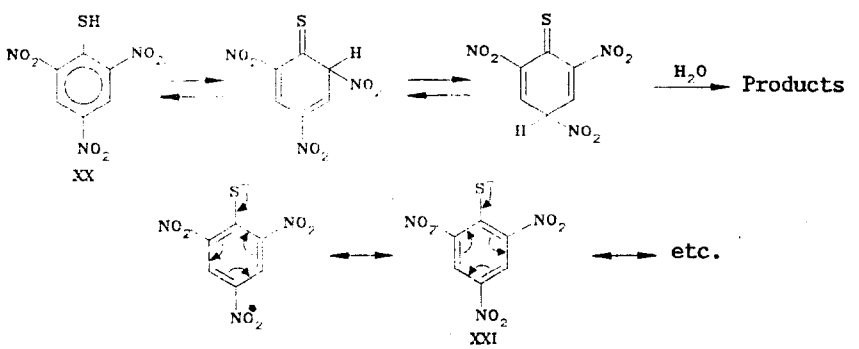
The unambiguous behavior of the three thiolating agents makes it possible to consider the water to be a participant of the process at two of its stages. The first is the saponification of the initially formed thioethers (XVIII).



XVIII XIX

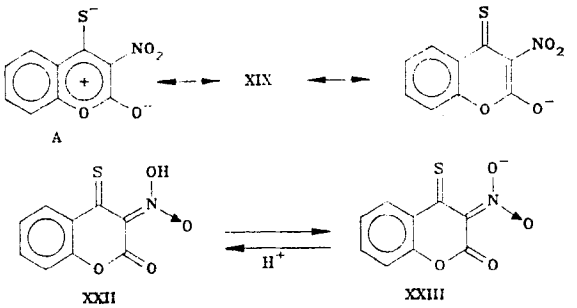
The sensitivity of the S—R bond (R = SO_3Na, $SC_9H_4NO_4$, CN, COPh) to hydrolysis is a result of the joint activating effect of the two electron acceptors (the carbonyl and nitro groups). This conclusion is supported by the reaction of the chlorocoumarin (V) with sodium acetate, which leads to the formation of a high yield of the hydroxycoumarin (VIII) as the only product. The 3-nitro-4-acetoxycoumarin formed at the first stage of the reaction could not be detected. For the same reason the enethiol (VI) formed during thiolation with sodium hydrosulfide should exhibit the characteristics of a fairly strong acid [pK_a value of hydroxycoumarin (VIII) in water 3.22 [16]] and should dissociate to an appreciable degree in solution.

What is the reason for the instability of the thiolate (XIX)? Comparison of compound (XIX) with the analogous activated system of the aromatic series shows that the strong thiopicric acid (XX) (pK_a of picric acid in water 0.38), formed in the reaction of picryl chloride with potassium sulfide with a yield of 100%, is quite stable in alkaline media, and its hydrolysis to picric acid and picryl chloride, which takes place according to the acid hydrolysis scheme [17,18], includes the stage of prototropic rearrangement thiophenol ⇄ cyclohexadienethione:

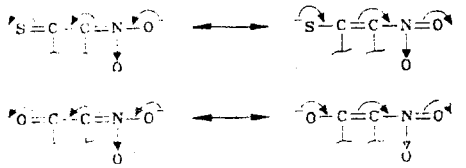


XX XXI

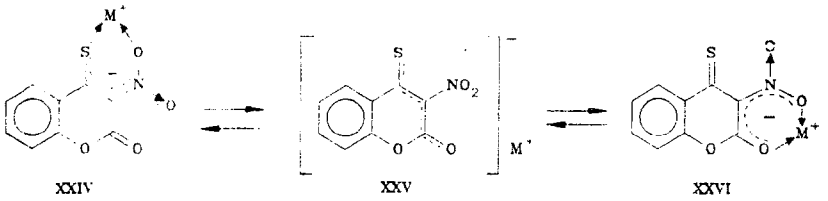
The stability of the picryl thiolate (XXI) is determined by the stabilizing mesomeric effect with the participation of the aromatic conjugation system. Such a method of stabilization is impossible for the coumarin thiolate (XIX). The interaction of the negative charge, localized at the sulfur or oxygen atom in the boundary structure (XIXA), with the electropositive aromatic system destroys the latter:



The aromatic boundary structure is impossible for the conjugate base (XXIII) of the nitronic acid (XXII), but the negative charge can be distributed in diene conjugation systems containing a sulfur or oxygen atom at the other end of the chain:



From this it can be concluded that the initially formed ion pair (XXIV) or (XXV) must have the ability to undergo metallotropy:



Since Na^+ or K^+ figures as counterion, according to the theory of hard and soft acids and bases the equilibrium must be shifted toward the form (XXVI) (hard acids react preferentially with hard coordination centers, oxygen). Here the sulfur is withdrawn from the system of delocalization of the negative charge, and the coumarin acquires the characteristics of a thioketone. The rate of establishment of the postulated equilibrium must depend on the ionic strength of the solution and the dielectric constant of the solvent. This may explain the discovered regulating effect of the addition of sodium acetate and change of solvent on the thiolation process.

Thus, the observations set out here emphasize the nonaromatic character of the behavior of the chlorocoumarin (V) in thiolation.

EXPERIMENTAL

Thin-layer chromatography was conducted on standard Silufol UV-254 plates. The substances were detected with UV light. The IR spectra were recorded on a Perkin-Elmer 580 instrument for tablets with potassium bromide. The mass spectra were obtained on a Varian MAT chromato-mass spectrometer (Germany) (ionization chamber 200°C, 70 eV, cathode emission current 1 mA, accelerating potential 3 kV). The elemental analyses of the obtained compounds for C, H, N, and S agreed with the calculated data.

3-Nitro-4-hydroxycoumarin (VIII) and Bis(3-nitro-4-coumarinyl) Sulfide (IX). To a suspension of 1.32 g (5.5 mmole) of $Na_2S \cdot 9H_2O$ in 5 ml of DMSO, while stirring at 18-20°C, we added 1.13 g (5.0 mmole) of the chlorocoumarin (V) in several portions over 1.5 min. The sodium sulfide dissolved, and the products was precipitated. The orange mixture was stirred for a further 13.5 min and was then diluted with 20 ml of water. The greenish-yellow precipitate of the sulfide (IX) was filtered off and washed with water. The yield was 0.45 g (44%); mp 252°C (from DMFA, decomp.). Mass spectrum, m/z (I, %): 412 (0.2) $[M^+]$, 366 (100) $[M - NO_2]^+$.

The filtrate was acidified to pH 2 with concentrated hydrochloric acid. The precipitate, consisting of the hydroxycoumarin (VIII) with an appreciable amount of the colored product (X) as impurity, was separated by filtration and washed with dilute hydrochloric acid. After recrystallization from alcohol the yield of the product (VIII) was 0.42 g (49%); mp 175-176°C. A sample of the coumarin (VIII) obtained by an independent method had the same melting point and chromatographic mobility in the 5:1:5 benzene—acetone—isopropanol and 9:1 chloroform—ethanol systems.

3-Nitro-4-hydroxycoumarin (VIII). A. To a suspension of 0.74 g (10 mmole) of sodium hydrosulfide monohydrate in a mixture of 20 ml of DMSO and 1 ml of 95% ethyl alcohol was stirred at 18-20°C, and 2.26 g (10 mmole) of the chlorocoumarin (V) was added over 10 min. The mixture was stirred for a further 25 min, diluted with 40 ml of water, and separated from the small amount of precipitate by filtration. The filtrate was acidified to pH 2 with concentrated hydrochloric acid. The precipitated hydroxycoumarin (VIII) was separated, washed with dilute hydrochloric acid, and recrystallized from alcohol. The yield was 1.22 g (59%); mp 175-176°C.

B. The product was obtained from 2.40 g (10 mmole) of $Na_2S \cdot 9H_2O$, 4.10 g (30 mmole) of $AcONa \cdot 3H_2O$, and 2.26 g (10 mmole) of the coumarin (V) in 10 ml of DMSO by analogy with method A. The yield was 1.83 g (88%); mp 175-176°C.

C. The product was obtained from 2.26 g (10 mmole) of the coumarin (V) and 1.47 g (10 mmole) of sodium acetate trihydrate in 10 ml of DMSO under the same conditions. The yield was 1.81 g (87%); mp 175-176°C; after recrystallization from alcohol, mp 176-177°C.

From 1.17 g (10.5 mmole) of potassium sulfide, 2.46 g (30 mmole) of anhydrous sodium acetate, and 2.26 g (10 mmole) of the coumarin (V) in 10 ml of DMSO not containing moisture (with the other conditions the same) we isolated 1.99 g of a substance of undetermined structure (containing C, H, N, and S), insoluble in organic solvents, water, acids, and 5% sodium bicarbonate solution; mp 328-335°C (decomp.). IR spectrum: 1708 (C=O), 1645 (C=C), 1605 (Ar), 1535 (antisymmetric NO_2), 1321 cm^{-1} (symmetric NO_2).

Bis(3-nitro-4-coumarinyl) Sulfide (IX). To a suspension of sodium disulfide, prepared from 1.20 g of $Na_2S \cdot 9H_2O$ and 0.16 g of elemental sulfur followed by the addition of 10 ml of dioxane, we added with stirring at 18-20°C 2.26 g (10 mmole) of the chlorocoumarin (V) in small portions over 1.5 min. The mixture was stirred for a further 30 min. According to TLC, the sample contained the initial chlorocoumarin (V), the sulfide (IX), and a small amount of the colored product (X) as impurity. The chromatographic pattern did not change after further stirring for 3 h 30 min. The yellowish precipitate was filtered off, washed with water, dried in air, and treated with 25 ml of warm chloroform (40-50°C). The sulfide (IX) was separated by filtration and washed with chloroform. The yield was 0.99 g (48%). The melting points and IR spectra agreed with the corresponding characteristics of the sulfide (IX) from the first experiment.

The chloroform filtrate was evaporated under a low vacuum. We obtained 1.14 g (50%) of the initial coumarin (V); mp 162-163°C (from benzene). The product was identical with a sample of the initial coumarin (V) in its melting point and chromatographic mobility in the 19:1 benzene—acetone and 19:1 benzene—ethyl acetate systems. It gave a positive Beilstein test.

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INDOLE DERIVATIVES

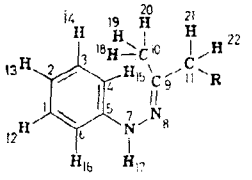
137.* QUANTUM-CHEMICAL STUDY OF THE CONFORMATION OF SOME PHENYLHYDRAZONES AND THEIR ENEHYDRAZINE TAUTOMERS

Dzh. A. Kereselidze, M. I. Raevskii, Sh. A. Samsoniya, I. Sh. Chikvaidze, and N. N. Suvorov

UDC 547.02.54:530.145

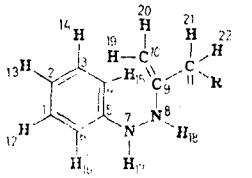
It was shown by the data from quantum-chemical calculations that the phenylhydrazones of certain unsymmetrical carbonyl compounds (methyl ethyl ketone, acetoacetic and levulinic acids) have the transoid conformation in relation to the N—N bond. The relation between the regioselectivity of the Fischer reaction and the structure of the calculated compounds is discussed.

The energy and structure of the possible conformers of the phenylhydrazones of methyl ethyl ketone (I, IV) (R = CH_3), acetoacetic acid (I, IV) (R = COOH), and levulinic acid (I, IV) (R = CH_2COOH) and their enehydrazine tautomers (II, IV, V, VI) were calculated by the AM1 quantum-chemical method [2] in order to determine the most likely conformation of the initial compounds in the Fischer indolization of arylhydrazones. The results are given in the diagram and in Table 1. All the structural and energy indices were obtained as a result of full optimization of the geometry of the investigated molecules.



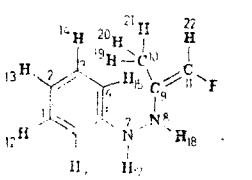
I

$r_{15,18}=2{,}30$; $r_{15,19}=2{,}98$; $r_{15,20}=3{,}93$; $r_{4,10}=3{,}02$; $r_{6,10}=4{,}00$; $\theta_{4,5,7,8}=56{,}6$; $\theta_{5,7,8,9}=8{,}3$; $\theta_{7,8,9,10}=3{,}2$; $\theta_{7,8,9,11}=-175{,}9$



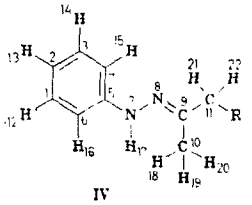
II

$r_{15,19}=4{,}38$; $r_{15,20}=4{,}71$; $r_{4,10}=5{,}44$; $r_{6,10}=6{,}30$; $\theta_{4,5,7,8}=37{,}5$; $\theta_{5,7,8,9}=-52{,}7$; $\theta_{7,8,9,10}=39{,}3$; $\theta_{7,8,9,11}=-146{,}5$



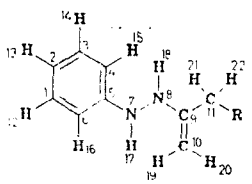
III

$r_{15,19}=5{,}11$; $r_{15,20}=4{,}68$; $r_{15,21}=4{,}21$; $r_{4,10}=5{,}19$; $r_{6,10}=6{,}00$; $\theta_{4,5,7,8}=39{,}0$; $\theta_{5,7,8,9}=48{,}0$; $\theta_{7,8,9,10}=55{,}9$; $\theta_{7,8,9,10}=-130{,}4$



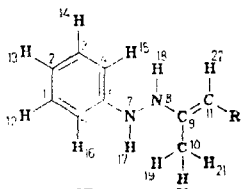
IV

$r_{15,18}=5{,}80$; $r_{17,18}=3{,}74$; $\theta_{4,5,7,8}=-0{,}93$; $\theta_{5,7,8,9}=177{,}5$; $\theta_{7,8,9,10}=0{,}68$; $\theta_{7,8,9,11}=-179{,}2$



V

$r_{15,18}=2{,}47$; $r_{17,19}=2{,}40$; $\theta_{4,5,7,8}=-5{,}88$; $\theta_{5,7,8,9}=-167{,}9$; $\theta_{7,8,9,10}=-24{,}2$; $\theta_{7,8,9,11}=160{,}9$



VI

$r_{15,18}=3{,}04$; $r_{17,19}=3{,}05$; $\theta_{4,5,7,8}=-27{,}9$; $\theta_{5,7,8,9}=153{,}4$; $\theta_{7,8,9,10}=-46{,}4$; $\theta_{7,8,9,11}=137{,}9$

R=CH_3, r — distance between atoms ., (A), θ — dihedral angles

*For Communication 136, see [1].

I. V. Dzhavakhishvili Tbilisi State University, Tbilisi. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1038-1040, August, 1991. Original article submitted July 7, 1988. Revision submitted October 13, 1990.

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