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Synthesis and Stereochemistry of *exo*-4-Aminomethyltetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-9-ene

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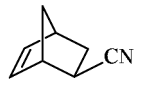
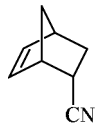
Abstract—Tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-9-ene-4-carbonitrile was synthesized by reaction of cyclopentadiene with stereochemically pure bicyclo[2.2.1]hept-2-ene-*exo*-4-carbonitrile. The preferential configuration of the adduct was proposed on the basis of the results of MMX calculations of four possible stereoisomers. Tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-9-ene-4-carbonitrile was reduced with lithium aluminum hydride to the corresponding aminomethyl derivative, and the latter was brought into reactions with *p*-toluene-, *p*-chlorobenzene-, and *p*-nitrobenzenesulfonyl chlorides, phenyl-, mesityl-, and *p*-tolylsulfonyl isocyanates, *o*-tolyl, *p*-tolylsulfonyl, and benzoyl isothiocyanates, and *p*-nitrophenyloxirane. The reaction with *p*-nitrophenyloxirane occurred in a regioselective fashion, in keeping with the Krasusky rule. *N*-Mesityl- and *N*-(*p*-tolylsulfonyl)-*N*′-(tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-9-en-4-*exo*-ylmethyl)ureas were oxidized with peroxyphthalic acid to obtain the corresponding epoxy derivatives. The structure of the products was confirmed by their IR and ^{1}H, ^{13}C, and two-dimensional NMR spectra. The structure of *N*-benzoyl-*N*′-(tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-9-en-4-*exo*-ylmethyl)thiourea was proved by the X-ray diffraction data.

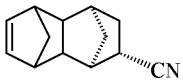
Bi- and tetracyclic Diels–Alder adducts based on cyclopentadiene are fairly promising compounds. Cyclopentadiene is a 1,3-diene with fixed cisoid conformation of the unsaturated fragment, which strongly favors its reactions with dienophiles. Cyclopentadiene was reported to react with acrylonitrile [1–3], as well as with bicyclic products of this reaction (compounds **Ia** and **Ib**) and their analogs, which were obtained as mixtures of stereoisomers [1, 4]. In these cases, stereoisomeric mixtures of tetracyclic nitriles **II** and **III** were formed.



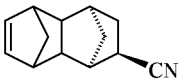
Ia



Ib



II



III

Stereoisomeric tetracyclic compounds **II** and **III** have found application in pulp and paper inductry [5] and as emulsifiers in manufacture of latexes [6], and their reduction products, the corresponding amines, are used in the preparation of detergents, selective herbicides, and medicines [7]. Therefore, simplified procedures for the synthesis of nitriles **II** and **III** have been developed [8], and some catalysts have been proposed [9].

Compounds **II** and **III** were synthesized from stereochemically pure *exo*- and *endo*-nitriles **Ia** and **Ib** by Vereshchagin and Arbuzov [10]. The authors made an attempt to determine the steric structure of adducts **II** and **III** by comparing their experimental dipole moments with those calculated by the vector scheme for four possible isomers **IIA**–**IID** differing by the mode of junction of the bicyclic fragments and orientation of the methylene bridges. Unfortunately, considerable differences between the theoretical and experimental values did not allow the authors to draw an unambiguous conclusion.

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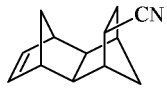
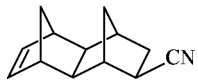
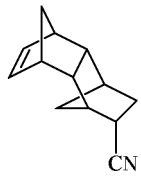


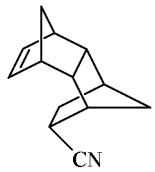
IIA



IIB



IIC



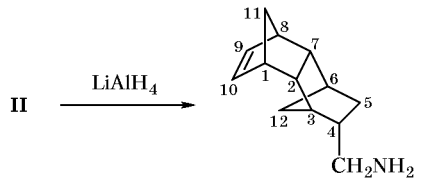
IID

The goal of our present study was to synthesize new derivatives of *exo*-4-aminomethyltetracyclo-[6.2.1.1^{3,6}.0^{2,7}]dodec-9-ene (**IV**) and examine their steric structure. As a preliminary step, we performed molecular-mechanics calculations (MMX) [11] of possible stereoisomers **IIA**–**IID**. In terms of the molecular-mechanics approach, particular components of the energy of a molecule cannot be considered separately from each other and none of the components (even predominating) can be regarded as a factor responsible for the observed difference in some molecular parameters (e.g., heats of formation). Taking the above into account, we are nevertheless prone to believe that comparison of calculated parameters for related compounds (provided that the same parametrization was used) should reveal essential trends in their variation for the series of isomers under study [13].

The results of calculation (Table 1) indicate that structure **IIC** with *endo*,*exo*-junction of the bicyclic fragments is the most energetically favorable. The strain energy increases in the series **IIA** < **IIB** < **IIC** < **IID**; the same order was found previously [12] for analogous stereoisomers of nitrile **III**. As follows from the data in Table 1, structure **IID** is characterized by increased angular strain, while the highest energy of van der Waals interactions is typical of **IIB**.

Nitrile **II** was synthesized according to the procedure reported in [10], by heating of a mixture of equimolar amounts of cyclopentadiene and bicyclo-[2.2.1]hept-2-ene-*exo*-5-carbonitrile (**Ia**) for 10 h at 170–175°C in a steel high-pressure reactor. Treatment of **II** with lithium aluminum hydride in boiling diethyl ether gave tetracyclic amine **IV** (Scheme 1).

Scheme 1.



IV

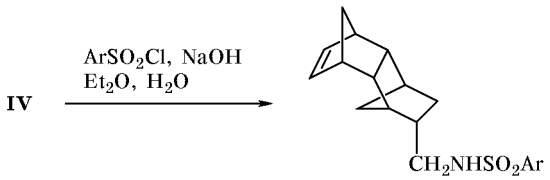
The IR spectrum of **IV** contained absorption bands at 3341 and 3264 cm^{-1} typical of stretching vibrations of the amino group and bands at 3022 and 713 cm^{-1} due to vibrations of the strained unsaturated fragment [14]. Amine **IV** was brought into reactions with various electrophilic reagents, such as arenesulfonyl chlorides, aryl and arylsulfonyl isocyanates and isothiocyanates, and *p*-nitrophenyloxirane. Arenesulfonamides **Va**–**Vc** were obtained by stirring a mixture of equimolar amounts of amine **IV**, arenesulfonyl chloride, and sodium hydroxide in a two-phase system [15] (Scheme 2). Urea derivatives **VIa**–**VIc** were synthesized by reaction of amine **IV** with phenyl, mesityl, and *p*-tolylsulfonyl isocyanates, respectively, in benzene at room temperature [16]. Similar reactions of **IV** with *o*-tolyl, *p*-tolylsulfonyl, and benzoyl isothiocyanates afforded substituted thioureas **VIIa**–**VIIc**. The reaction of amine **IV** with *p*-nitrophenyloxirane was performed in isopropyl alcohol, and the

Table 1. Calculated strain energies and heats of formation of stereoisomeric nitriles **IIA**–**IID**, kJ/mol

Parameter	**IIA**	**IIB**	**IIC**	**IID**
Total steric energy	227.02	221.96	213.55	231.33
Bond stretching	8.16	8.91	8.70	8.66
Angular strain	135.18	127.11	122.59	141.08
Torsion strain	61.50	61.88	61.79	16.16
Van der Waals interactions	31.46	33.30	29.92	31.04
Heat of formation, H_f (MMX)	248.74	243.68	235.27	253.05
Strain energy, E_s	197.57	192.51	184.09	201.88
Heat of formation, H_f (PM3)	279.92	266.96	278.04	298.04
Heat of formation, H_f (AM1)	299.88	280.36	287.24	307.81

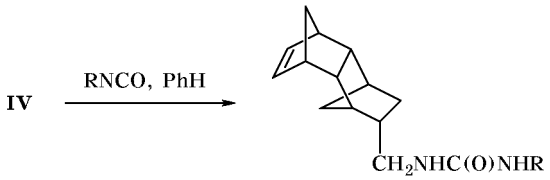
progress of the reaction was monitored by TLC [17] (Scheme 3).

Scheme 2.



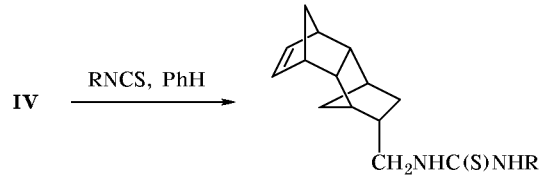
Va–Vc

V, Ar = 4-MeC_6H_4 (**a**), 4-ClC_6H_4 (**b**), 4-$O_2NC_6H_4$ (**c**).



VIa–VIc

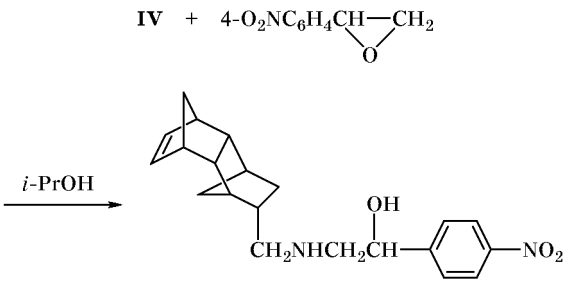
VI, R = Ph (**a**), 2,4,6-$Me_3C_6H_2$ (**b**), 4-$MeC_6H_4SO_2$ (**c**).



VIIa–VIIc

VII, R = 2-MeC_6H_4 (**a**), 4-$MeC_6H_4SO_2$ (**b**), PhCO (**c**).

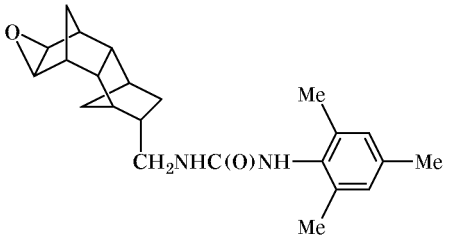
Scheme 3.



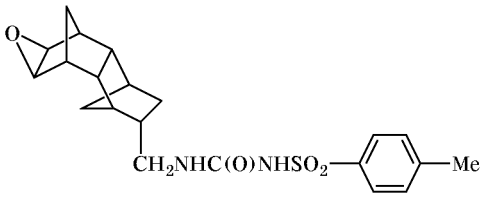
VIII

Molecules **V**–**VIII** contain a strained double bond. Cyclic olefins **VIb** and **VIc** were oxidized with monoperoxyphthalic acid which was prepared *in situ* from phthalic anhydride and 30% hydrogen peroxide. As a result, the corresponding epoxy derivatives **IX** and **X** were obtained.

Table 2 contains the yields, melting points, R_f values, IR spectral parameters, and analytical data of



IX



X

the prepared compounds. Their structure is confirmed by the IR spectra. The absorption at 1575–1550 cm^{-1}, which is typical of $\nu C{=}C$ in the norbornene series [18], and at 3065–3040 cm^{-1} ($\nu C{-}H$ of the olefinic fragment) is obscured by absorption bands of the aromatic fragments and N–H bonds [14]. Epoxy derivatives **IX** and **X** characteristically show in the IR spectra absorption bands at 855–850 cm^{-1} ($\nu C{-}O$) [19]. The spectra of all the products contain bands in the region 3400–3300 cm^{-1} ($\nu N{-}H$). In the spectra of sulfonamides **Va**–**Vc** and sulfonylureas **VIc** and **VIIb** we observed absorption bands in the regions 1350–1310 and 1180–1160 cm^{-1}, which belong to stretching vibrations of the SO_2 group. The IR spectra of urea derivatives are characterized by the presence of bands at 1670–1630 ($\nu C{=}O$), 1565–1555 ($\delta N{-}H$), and 1245–1255 cm^{-1} ($\nu C{-}N$). The spectra of thiourea derivatives lack amide I band, but absorption at 1350–1310 cm^{-1} is present due to vibrations of the thiocarbonyl group [14].

The ^1H NMR spectral parameters of tetracyclic compounds **Va**, **Vb**, **VIIb**, **VIIc**, and **VIII** are collected in Table 3. These data confirm the structure of the carbon skeleton proposed on the basis of theoretical calculations (Table 1). The signals were assigned using two-dimensional ^1H–{H} techniques for compounds **VIIb** and **VIIc**. Figure 1 shows the ^1H NMR spectrum of *N*-(tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-9-en-4-*exo*-ylmethyl)-*N'*-(4-tolylsulfonyl)urea (**VIIb**). It is seen that the olefinic protons, 9-H and 10-H, as well as protons in the bridgehead positions neighboring to the double bond (1-H and 8-H), are equivalent. This is explained by their remoteness from the substituent. By contrast, the "twin" protons 2-H/7-H and 3-H/6-H are characterized by different chemical shifts which provide a useful information. The difference in the

Table 2. Yields, melting points, R_f values, IR spectral parameters, and analytical data of *exo*-4-aminomethyltetracyclo-[6.2.1.1^{3,6}.0^{2,7}]dodec-9-ene derivatives **V–X**

Comp. no.	Yield, %	mp, °C	R_f (ether)	IR spectrum, ν, cm^{-1}	Found N, %	Formula	Calcd. N, %
Va	87.5	150–151	0.58	3320, 3030, 1580, 1550, 1310, 1180, 1150, 800, 700	4.12	$C_{20}H_{25}NO_2S$	4.08
Vb	72.4	124–125	0.58	3350, 3065, 1570, 1320, 1160, 725	3.92	$C_{19}H_{22}ClNO_2S$	3.85
Vc	88.9	133–134	0.49	3341, 3044, 1553, 1320, 1143, 715	3.76	$C_{19}H_{22}N_2O_4S$	3.70
VIa	63.4	170–173	0.56	3295, 3020, 1630, 1600, 1240, 730	4.61	$C_{20}H_{21}N_2O$	4.54
VIb	95.8	175–175.5	0.30	3315, 3056, 1632, 1560, 1243, 712	7.83	$C_{23}H_{30}N_2O$	7.99
VIc	92.5	81–82.5	0.89	3251, 3050, 1669, 1519, 1450, 1314, 1266, 1175, 718	7.30	$C_{21}H_{26}N_2O_3S$	7.25
VIIa	75.9	137–138	0.39	3298, 3040, 1560, 1550, 1320, 740	8.28	$C_{21}H_{26}N_2S$	8.28
VIIb	82.3	152–153	0.77	3266, 3067, 3034, 1537, 1478, 1380, 1362, 1330, 1262, 1116, 1085, 686	6.97	$C_{21}H_{26}N_2O_2S_2$	6.94
VIIc	92.5	178–179	0.89	3337, 3055, 3019, 1655, 1545, 1453, 1342, 1216, 1162, 726	7.61	$C_{21}H_{21}N_2OS$	7.63
VIII	89.8	58–60	0.42	3440, 3055, 1622, 1512, 1340, 1110, 1080, 750	7.96	$C_{21}H_{26}N_2O_3$	7.91
IX	90.3	185.5–187	0.77	3297, 3034, 1629, 1571, 1238, 851	7.60	$C_{23}H_{30}N_2O_3$	7.65
X	82.8	152–153	0.80	3305, 3042, 1671, 1524, 1462, 1310, 1250, 1170, 855	7.06	$C_{21}H_{26}N_2O_4S$	6.96

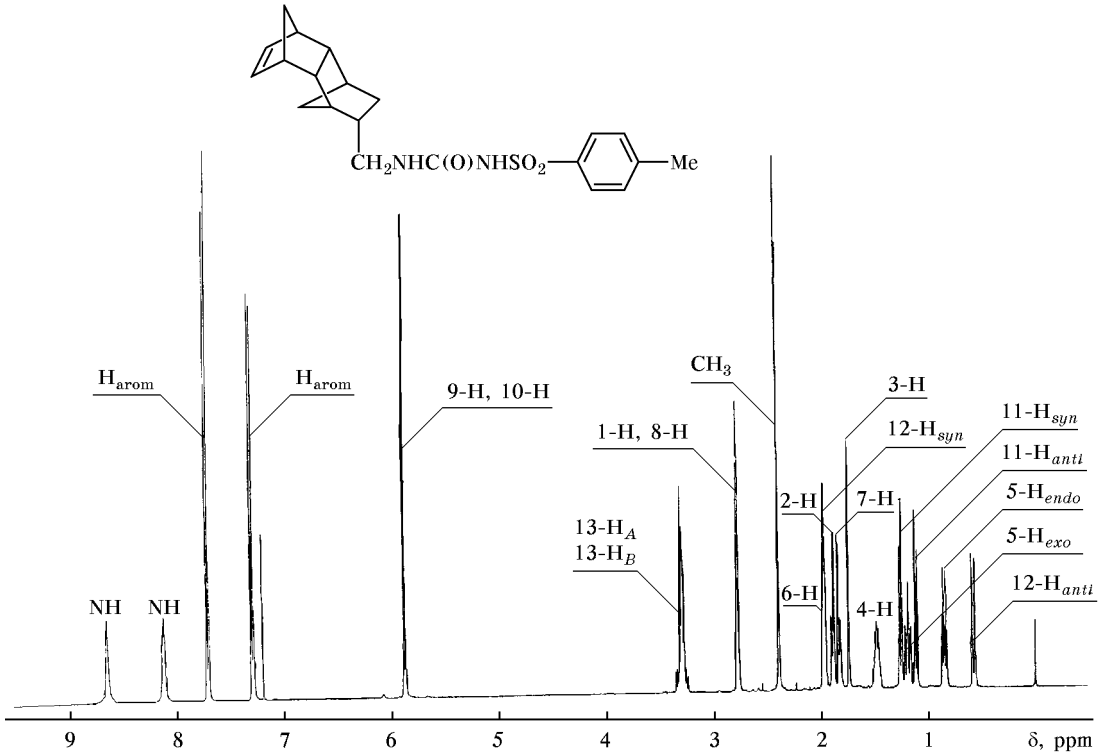


Fig. 1. ^{1}H NMR spectrum of *N*-(tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-9-en-*exo*-4-ylmethyl)-*N'*-(*p*-tolylsulfonyl)urea (**VIIb**).

Table 3. ^{1}H NMR spectral parameters of compounds **Va**, **VIb**, **VIIb**, **VIIc**, and **VIII**

Parameter	**Va**	**VIb**	**VIIb**	**VIIc**	**VIII**[a]
			Chemical shifts δ, ppm		
1-H, 8-H	2.80	2.79	2.77	2.78	2.76
2-H, 7-H	1.89, 1.85	1.90, 1,89	1.89, 1.82	1.91	1.88, 1.86
3-H	1.59	1.77	1.74	1.90	1.84
4-H	1.37	1.65	1.48	1.65	1.35
6-H	1.98	1.97	1.96	2.02	1.95
exo-5-H	1.25	1.38	1.19	1.28	1.19
endo-5-H	0.84	0.87	0.85	0.96	0.84
9-H, 10-H	5.91	5.92	5.88	5.88	5.87
syn-11-H, *anti*-11-H	1.26, 1.17	1.28, 1.19	1.25, 1.11	1.23, 1.10	1.23, 1.09
syn-12-H, *anti*-12-H	1.99, 0.49	1.92, 0.60	1.97, 0.58	1.99, 0.66	1.93, 0.53
13-H_A, 13-H_B	2.74, 2.69	2.96, 2.91	3.31, 3.28	3.42, 3.40	2.36, 2.25
NH	4.38, 7.26	5.61, 4.26	8.12, 8.64	10.69, 8.93	–
H_{arom}	7.29, 7.73	–	7.71, 7.29	7.77–7.44	7.16, 7.76
CH_3	2.43	2.79, 2.25	2.39	–	2.86, 2.52[b]
			Coupling constants *J*, Hz		
$^{3}J_{2,7}$	8.5	8.2	8.5	–	7.9
$^{3}J_{2,1}$	4.2	3.9	4.2	–	4.4
$^{3}J_{7,8}$	4.2	4.2	3.7	–	3.3
$^{2}J_{exo\text{-}5,endo\text{-}5}$	10.7	11.7	11.8	11.9	11.8
$^{3}J_{exo\text{-}5,4}$	–	8.2	8.5	8.5	8.2
$^{3}J_{exo\text{-}5,6}$	–	2.2	2.5	2.5	2.5
$^{3}J_{endo\text{-}5,4}$	4.0	4.5	4.4	4.4	4.4
$^{4}J_{endo\text{-}5,syn\text{-}12}$	4.0	4.5	4.4	4.4	4.4
$^{2}J_{syn\text{-}11,anti\text{-}11}$	7.8	7.8	8.0	8.0	8.2
$^{2}J_{syn\text{-}12,anti\text{-}12}$	10.0	10.3	11.0	10.7	10.7
$^{2}J_{13A,13B}$	12.4	13.5	12.6	13.2	11.7
$^{3}J_{13B,4}$	7.2	7.4	7.6	7.5	7.2
$^{3}J_{13A,4}$	5.7	5.7	5.6	5.5	5.9

[a] δ, ppm: 4.69 (1H, C**H**OH).
[b] CH_2.

Table 4. ^{13}C NMR spectra of compounds **VIIb**, **VIIc**, and **VIII**

Compound no.	Chemical shifts δ_C, ppm
VIIb	46.9 (C^1); 48.3 (C^2); 49.5 (C^3); 44.1 (C^4); 37.8 (C^5); 38.3 (C^6); 41.1 (C^7); 46.8 (C^8); 135.7 (C^9); 135.6 (C^{10}); 53.4 (C^{11}); 31.3 (C^{12}); 50.2 (C^{13}); – 177.9 (C=S); 22.1 (CH_3); 145.6, 135.8, 130.4, 127.2 (C_{arom})
VIIc	46.9 (C^1); 48.3 (C^2); 49.5 (C^3); 43.9 (C^4); 37.9 (C^5); 38.4 (C^6); 41.2 (C^7); 46.8 (C^8); 135.8 (C^9); 135.5 (C^{10}); 53.4 (C^{11}); 31.3 (C^{11}); 50.2 (C^{13}); 167.0 (C=O); 179.7 (C=S); 133.7, 132.0, 129.3, 127.6 (C_{arom})
VIII	46.8 (C^1); 48.3 (C^2); 49.7 (C^3); 45.4 (C^4); 38.4 (C^5); 38.1 (C^6); 41.2 (C^7); 46.7 (C^8); 135.7 (C^9); 135.5 (C^{10}); 54.1 (C^{11}); 31.1 (C^{11}); 53.3 (C^{13}); 150.5, 126.7, 123.8 (C_{arom})

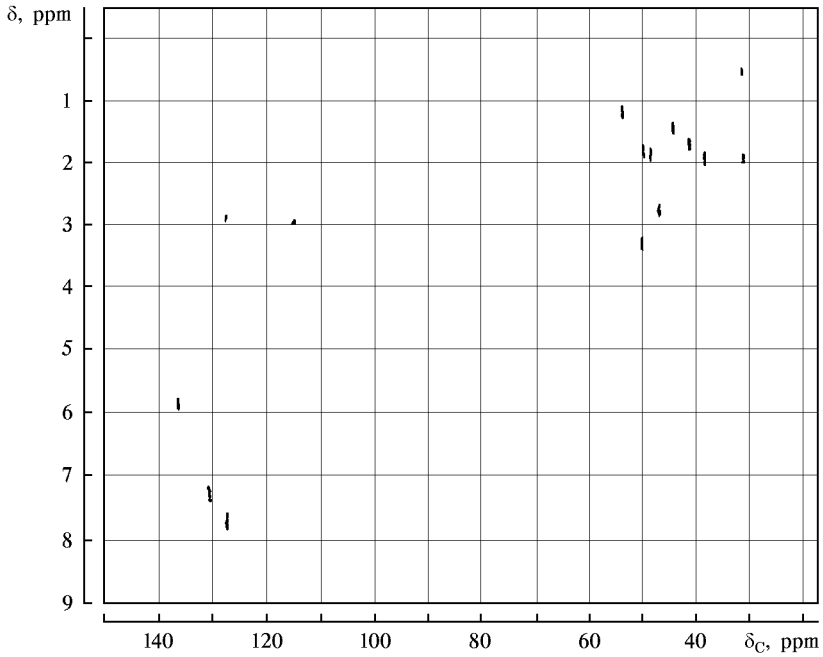


Fig. 2. $^{13}C-\{^1H\}$ NOESY spectrum of *N*-(tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-9-en-*exo*-4-ylmethyl)-*N'*-(*p*-tolylsulfonyl)urea (**VIIb**).

chemical shifts of 3-H and 6-H ($\Delta\delta$ = 0.1–0.3 ppm) indicates magnetic anisotropic effect of the C^4-C^{13} bond, which suggests *exo* orientation of the 4-substituent. Nonequivalence of 2-H and 7-H makes it possible to estimate the corresponding vicinal spin–spin coupling constant ($^3J_{2,7}$ = 8.2–9.0 Hz), which is typical of the *exo* orientation of these protons; this means *endo* orientation of the second bicyclic fragment with respect to the norbornene moiety. In the case of the *exo* orientation of the substituted bicyclic fragment relative to the unsaturated one (see structures **IIA** and **IIB**), the *endo*-oriented 2-H and 7-H protons would be coupled through a constant of no larger than 4–5 Hz. Structure like **IID** is ruled out by comparing the signals from protons on the bridging C^{11} and C^{12} methylene carbon atoms. These protons are characterized by strongly different chemical shifts and geminal coupling constants. In fact, protons on C^{11} in the unsaturated fragment have fairly similar chemical shifts, and the corresponding geminal coupling constant is equal to 7.7 Hz. The difference in the chemical shifts of protons of the second methylene bridge (C^{12}) is as large as 1.5 ppm (one of the signals is displaced strongly upfield, $\Delta\delta$ 0.49–0.66 ppm), and the geminal coupling constant is 9.8–11.0 Hz. Such differences in the resonance parameters of the two bridging groups are inconsistent with structure **IID**. A probable reason is that protons at C^{12} appear in the vicinity of the olefinic fragment which differently affects their chemical shifts due to its magnetic anisotropy. This is typical of structure **IIC**.

The ^{13}C chemical shifts of compounds **VIIb**, **VIIc**, and **VIII** are listed in Table 4. The signals were assigned on the basis of the two-dimensional $^{13}C-\{^1H\}$ NMR spectra of **VIIb** (Fig. 2) and **VIIc**. Signals from carbon atoms of the olefinic fragment (C^9, C^{10}) and bridgehead carbon atoms (C^1, C^8) are located at δ_C 135.5–135.8 and 46.8–46.9 ppm, respectively. By analogy with the ^1H NMR spectra, considerable differences are observed between the chemical shifts of C^2, C^7 and C^3, C^6. Among the four methylene groups, the most downfield signal is that from C^{11} (δ_C 53.4–54.1 ppm), while the signal from C^{12} appears most upfield (δ_C 31.1–31.3 ppm). As in the spectra of substituted norbornenes, C^5 resonates in a strong field (δ_C 37.8–38.4 ppm). The ^{13}C NMR spectra also contain signals belonging to the substituents at the tetracyclic skeleton, specifically those of carbonyl and thiocarbonyl carbon atoms and methyl and phenyl groups. Amino alcohol **VIII** shows in the spectrum signals from carbon atoms neighboring to the hydroxy (δ_C 70.6 ppm) and amino groups (δ_C 57.0 ppm). The corresponding protons appear in the ^1H NMR spectrum as doublets of doublets at δ 4.69, 2.86, and 2.52 ppm, respectively. The presence of a CH group at the hydroxy group and of a methylene group at the amino group indicates that opening of the oxirane

Table 5. Coordinates of non-hydrogen atoms ($\times 10^4$) and their equivalent isotropic thermal parameters ($Å^2 \times 10^3$) in the structure of *N*-benzoyl-*N'*-(tetracyclo[6.2.1.1^{3,6}.0^{2,7}]-dodec-9-en-*exo*-4-ylmethyl)thiourea (**VIIc**)

Atom	*x*	*y*	*z*	U_{eq}
S^1	4432 (2)	590 (2)	1729 (1)	57 (1)
O^1	–2646 (5)	–1892 (4)	525 (2)	57 (1)
N^1	–37 (5)	15 (4)	1699 (1)	33 (1)
N^2	1206 (5)	–1136 (4)	705 (2)	38 (1)
C^1	–2538 (9)	–3611 (6)	4468 (2)	55 (1)
C^2	–3845 (7)	–3845 (7)	4208 (3)	66 (1)
C^3	–5400 (9)	–4669 (7)	3553 (3)	70 (2)
C^4	–3217 (9)	–4988 (6)	3369 (2)	57 (1)
C^5	–1467 (8)	–3198 (5)	3325 (2)	45 (1)
C^6	–1991 (7)	–1784 (5)	2913 (2)	41 (1)
C^7	243 (7)	–365 (5)	2935 (2)	37 (1)
C^8	656 (7)	604 (6)	3702 (2)	47 (1)
C^9	–1409 (7)	–422 (5)	4015 (2)	43 (1)
C^{10}	–993 (7)	–2237 (5)	4087 (2)	44 (1)
C^{11}	–2198 (1)	–5300 (6)	4072 (2)	64 (1)
C^{12}	–3259 (7)	–765 (6)	3397 (2)	45 (1)
C^{13}	179 (7)	906 (5)	2413 (2)	40 (1)
C^{14}	1698 (6)	–177 (5)	1384 (2)	34 (1)
C^{15}	–842 (7)	–1981 (5)	329 (2)	37 (1)
C^{16}	–794 (7)	–3102 (5)	–346 (2)	35 (1)
C^{17}	–2797 (8)	–4244 (6)	–673 (2)	51 (1)
C^{18}	–2875 (9)	–5351 (6)	–1289 (3)	66 (1)
C^{19}	–947 (1)	–5273 (6)	–1584 (2)	60 (1)
C^{20}	1073 (9)	–4156 (6)	–1276 (2)	58 (1)
C^{21}	1161 (8)	–3061 (6)	–657 (2)	49 (1)

ring occurs in a regioselective fashion according to the Krasusky rule.

The structure of epoxy derivative **IX** obtained from compound **VIb** is confirmed by the ^{1}H and ^{13}C NMR spectra. The ^{1}H NMR spectrum of **IX** lacks signals in the δ region of 6 ppm, but two closely located doublets are present at δ 3.03 and 3.02 ppm. Also, signals from protons of the benzene ring (δ 7.20 ppm), methyl groups (δ 2.22 and 2.17 ppm), and NH groups (δ 5.87 and 6.86 ppm) are observed. In going from **VIb** to epoxy derivative **IX**, the chemical shifts of protons of both methylene bridging groups change most strongly due to anisotropic effect of the oxirane fragment. The ^{13}C NMR spectrum of **IX** contains signals from carbon atoms of the oxirane ring (δ_C 51.61 and 51.75 ppm), carbonyl group (δ_C 157.4 ppm), methyl groups (δ_C 18.5 and 21.3 ppm), and substituted benzene ring.

The structure of the tetracyclic skeleton was also proved by X-ray analysis of a single crystal of **VIIc** (Fig. 3, Table 5). The N^1, C^{14}, S^1, N^2, C^{15}, and O^1 atoms lie in one plane (deviations from the mean-square plane do not exceed 0.016 Å). The fragment $C^{13}N^1C^{14}(=S^1)N^2C^{15}(=O^1)C^{16}$ has a *cis*,*cis* configuration: the torsion angles $C^{13}N^1C^{14}N^2$ and $C^{14}N^2C^{15}C^{16}$ are 177.3 (3)° and –177.8 (3)°, respectively. The configuration is fixed via intramolecular hydrogen bonding $O^1\cdots HN^1$ with the following parameters: $O^1\cdots H$ 2.03 Å, $\angle O^1HN^1$ 134°, and attractive interaction $S^1\cdots H^{13B}$, 2.73 Å (the sum of the corresponding van der Waals radii is 3.00 Å [20, 21]). This fragment is turned through an angle of 14° with respect to the benzene ring plane due to steric hyndrances, namely shortened intramolecular contact $H^{21}\cdots HN^2$ [1.97 Å (2.23 Å)]. The planar fragment is oriented *trans* with respect to the C^7-C^8 bond [the torsion angle $C^8C^7C^{13}N^1$ is 175.7 (3)°] and is almost orthogonal to the C^7-C^{13} bond [$C^7C^{13}N^1C^{14}$ –87.0 (4)°].

The oxo and thioxo groups are arranged in the transoid mode with respect to ech other. The substituent on C^7 is equatorial relative to the bicyclic fragment: the torsion angle $C^9C^8C^7C^{13}$ is 123.9 (4)°. The bicycloheptene and bicycloheptane fragments are fused *cis*: the torsion angle $H^{10}C^{10}C^5H^5$ is 1°. Both bicyclic moieties have a transoid configuration, i.e., the bridging C^{11} and C^{12} atoms appear at the opposite sides of the mean-square plane passing through the C^1 and C^{10} atoms. As a result, the following shortened intramolecular contacts are observed $C^2\cdots H^{12B}$ 2.45 Å (2.87 Å), $C^3\cdots H^{12B}$ 2.44 Å (2.87 Å), $H^5\cdots H^7$ 2.17 Å (2.32 Å), and $H^{10}\cdots H^{8A}$ 2.21 Å (2.32 Å).

Thus, the spectral and X-ray diffraction data, as well as the results of theoretical calculations, provide convincing proofs for the proposed structure of tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-9-en-*exo*-4-carbonitrile derivatives.

EXPERIMENTAL

The IR spectra were recorded on a Specord 75IR spectrophotometer in the range from 4000 to 400 cm^{-1} from samples prepared as KBr pellets. The ^{1}H NMR spectra were measured on a Varian VXR spectrometer at 300 or 400 MHz using chloroform-*d* as solvent and TMS as internal reference. The ^{13}C NMR spectra were obtained on a Varian Gemini BB instrument at 100.57 MHz using COSY and NOESY techniques. The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates; diethyl ether–hexane (2 : 1) or pure diethyl ether was used as eluent; spots were visualized by treatment

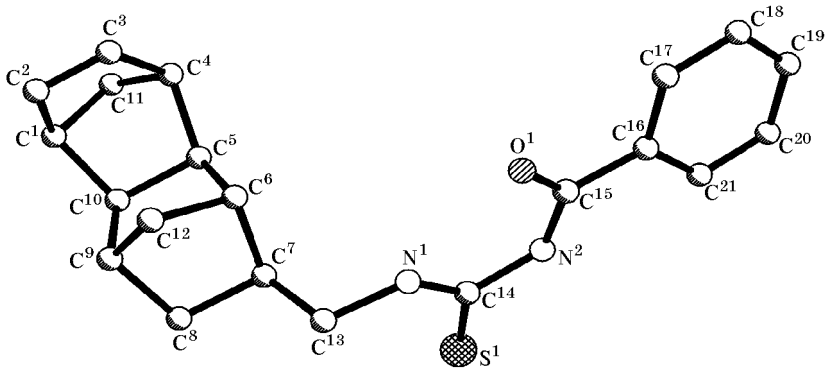


Fig. 3. Structure of the molecule of *N*-benzoyl-*N*′-(tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-9-en-*exo*-4-ylmethyl)thiourea (**VIIc**) according to the X-ray diffraction data.

with iodine vapor. Elemental analyses were obtained on a Carlo Erba analyzer.

Tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-9-ene-*exo*-4-carbonitrile (II) was synthesized as described in [10]. A mixture of 9.52 g (0.08 mol) of nitrile **Ia**, 5.28 g (0.08 mol) of cyclopentadiene, and a catalytic amount of hydroquinone was heated for 10 h at 170–175°C in a steel high-pressure reactor. The product was isolated by distillation. Yield 4.98 g (33.5%), bp 148–153°C (9 mm), n_D^{20} 1.5278; published data: bp 165–170°C (16 mm), n_D^{20} 1.5353 [10]. IR spectrum, ν, cm^{-1}: 3022, 2239, 713.

***exo*-4-Aminomethyltetracyclo[6.2.1.1^{3,6}.0^{2,7}]-dodec-9-ene (IV)** was synthesized by reduction of 15.00 g (0.08 mol) of nitrile **II** with 3.80 g (0.10 mol) of lithium aluminum hydride in dry diethyl ether. Yield 9.82 g (65.3%), bp 132°C (4 mm), n_D^{20} 1.4608. IR spectrum, ν, cm^{-1}: 3341, 3264, 3022, 713.

***N*-(Tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-9-en-*exo*-4-ylmethyl)-*p*-toluenesulfonamide (Va).** A solution of 0.19 g (0.001 mol) of *p*-toluenesulfonyl chloride in 10 ml of diethyl ether was added dropwise under stirring to a dispersion of 0.19 g (0.001 mol) of amine **IV** in 10 ml of ether and 2 ml of 20% aqeuous sodium hydroxide. When the reaction was complete (TLC), the product (contaminated with NaCl) was dissolved by shaking with 20 ml of a 1 : 1 chloroform–water mixture, the organic layer was separated and dried over calcined magnesium sulfate, and the solvent was removed. The residue was purified by recrystallization from a 2 : 1 isopropyl alcohol–water mixture. Compounds **Vb** and **Vc** were synthesized in a similar way.

***N*-Phenyl-*N*′-(tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-9-en-*exo*-4-ylmethyl)urea (VIa).** A solution of 0.19 g (0.001 mol) of amine **IV** in 5 ml of benzene was added to a solution of 0.12 g (0.001 mol) of phenyl isocyanate in 5 ml of benzene. When the reaction was complete (TLC), the precipitate was filtered off, washed with benzene on a filter, and dried. The product was purified by recrystallization from benzene at room temperature. Compounds **VIb** and **VIc** were synthesized in a similar way.

***N*-(Tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-9-en-*exo*-4-ylmethyl)-*N*′-(*o*-tolyl)thiourea (VIIa).** A solution of 0.19 g (0.001 mol) of amine **IV** in 5 ml of dry benzene was added with cooling to a solution of 0.16 g (0.001 mol) of *o*-tolyl isothiocyanate in 5 ml of benzene. When the reaction was complete (TLC), the precipitate was filtered off, washed with benzene on a filter, and dried. The product was purified by recrystallization from benzene. Compounds **VIIb** and **VIIc** were synthesized in a similar way.

***N*-[2-Hydroxy-2-(*p*-nitrophenyl)ethyl]-*exo*-4-aminomethyltetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-9-ene (VIII).** A mixture of 0.16 g (0.001 mol) of *p*-nitrophenyloxirane and 0.19 g (0.001 mol) of amine **IV** was dissolved in 10 ml of isopropyl alcohol. When the reaction was complete (TLC), the precipitate was filtered off, washed with isopropyl alcohol on a filter, and dried. The product was purified by recrystallization from a 2 : 1 isopropyl alcohol–water mixture.

***N*-(*exo*-9,10-Epoxytetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-*exo*-4-ylmethyl)-*N*′-mesitylurea (IX).** To a mixture of 0.25 g (0.001 mol) of compound **VIb**, 0.30 g (0.002 mol) of phthalic anhydride, and 0.03 g (0.0005 mol) of urea in 10 ml of ethyl acetate we added dropwise under stirring at room temperature 0.14 g (0.11 ml, 0.002 mol) of 30% hydrogen peroxide, and the mixture was stirred until the reaction was complete (TLC). Phthalic acid was neutralized with a saturated solution of sodium carbonate, the organic layer was separated, and the aqueous layer

was extracted with three portions of ethyl acetate. The extracts were combined with the organic phase, dried over magnesium sulfate, and evaporated. The product was purified by recrystallization. Compound **X** was synthesized in a similar way.

X-Ray analysis of compound VIIc. Triclinic crystals. $C_{21}H_{34}N_2OS$. Unit cell parameters (20°C): a = 6.106(9), b = 7.85(1), c = 19.54(4) Å; α = 97.0(1)°, β = 95.8(1)°, γ = 104.5(1)°; V = 894(2) Å^3; M = 362.48; Z = 2; space group $P1$; d_{calc} = 103.9 g/cm^3; $\mu(MoK_\alpha)$ = 0.192 mm^{-1}, $F(000)$ = 376. The unit cell parameters and intensities of 3203 reflections (2915 independent reflections with R_{int} = 0.05) were measured on a Siemens P3/PC automatic four-circle diffractometer (MoK_α, graphite monochromator, $2\theta/\theta$ scanning, $2\theta_{max}$ = 50°). The structure was solved by the direct method using SHELX97 software package [22]. The positions of hydrogen atoms were determined by the difference synthesis of electron density and were refined by the "rider" model with $U_{iso} = 1.2U_{eq}$. The structure was refined with respect to F^2 by the full-matrix least-squares procedure in anisotropic approximation for non-hydrogen atoms to wR_2 = 0.1745 (from 2915 reflections), R_1 = 0.066 (from 1681 reflections with $F > 4\sigma(F)$, S = 1.016). The final coordinates of non-hydrogen atoms are listed in Table 5.

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