SYNTHESIS AND VIBRATIONAL SPECTRA OF N-exo-ARYLCARBAMOYLSYDNONEIMINES AND THEIR SALTS

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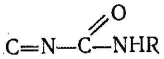
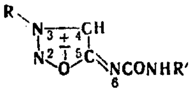
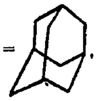
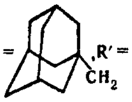
A number of arylcarbamoyl derivatives of sydnoneimines were synthesized, and their IR spectra and Raman spectra in the region of the characteristic vibrations of the exocyclic  $C{=}N{-}\overset{\overset{O}{/\!/}}{C}{-}NHR$ bond were studied. The integral intensities (A) of the C = O and C = N bands of those compounds constitute evidence for effective electronic interaction of the atoms in the exocyclic group. The structures of salts of the carbamoylsydnoneimines were investigated by means of their IR spectra, and it was proved that the protonation of these compounds takes place at the exocyclic nitrogen atom. It is shown that carbamoylsydnoneimines do not form dications even in solutions of strong acids.

In a continuation of our research on N-exo-carbamoylsydnoneimines [1] we accomplished the synthesis of a number of analogs of the medicinal preparation sidnokarb (I) — arylcarbamoyl derivatives of sydnoneimines containing phenylisopropyl (II, III), cyclohexyl (IV, V), and adamantyl (A) (VI, VII) substituents in the 3 position:



I-VII

I-III $R=C_6H_5CH_2CH(CH_3)$; IV, V $R=C_6H_{11}$; VI R= , $R'=C_6H_5$; VII R= , $R'=C_6H_5$;
I, IV $R'=C_6H_5$; II $R'=4'-CH_3OC_6H_4$;
III $R'=4'-C_2H_5OC_6H_4$; V $R'=3',4'-Cl_2C_6H_3$

These compounds, the structures of which were confirmed by the results of elementary analysis and the IR and PMR spectral data, were obtained by the action of various aryl isocyanates on the hydrochlorides of the corresponding sydnoneimines in pyridine. The previously unknown hydrochloride of 3-(1'-adamantyl)- and 3-(1'-methyladamantyl)sydnoneimines VIII and IX were synthesized via the usual scheme from N-cyanomethyl derivatives of 1-adamantylamine (X) and 1-methyladamantylamine (XI).

The literature contains individual data on the IR spectra of N_6-carbamoylsydnoneimines [2, 3], but no systematic examination of the characteristic frequencies of the exocyclic grouping has been reported. These data are of interest not only for the establishment of the peculiarities of the structures of compounds of this series but also may be of more general value for an understanding of the electronic properties of the carbamide grouping, particularly the character of the conjugation of the carbonyl group with the C=N bond and the unshared pair of electrons of the amide nitrogen atom.

In addition to the compounds synthesized in the present research, we also used the previously described [1] N_6-methylcarbamoyl-3-methylsydnoneimine (XII), N_6-methylcarbamoyl-3-phenylisopropylsydnoneimine (XIII) and its hydrochloride (XIIIa), N_6-2',4'-dinitrophenylcarbamoyl-3-methylsydnoneimine (XIV), and N_6-acetyl-3-methylsydnoneimine (XV) [2] and its hydrochloride (XVa) in the examination of the vibrational spectra.

Three intense absorption bands are observed in the IR spectra of carbamoyl derivatives of sydnoneimines at 1500-1700 cm^{-1} both in solution and in the crystalline state. To assign

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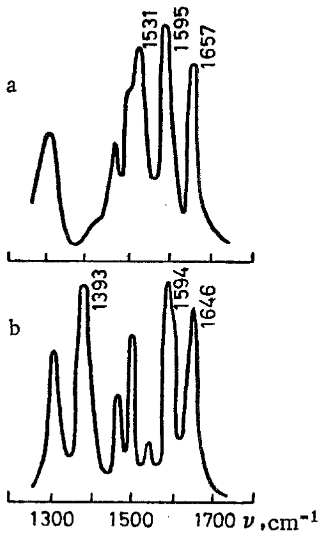


Fig. 1

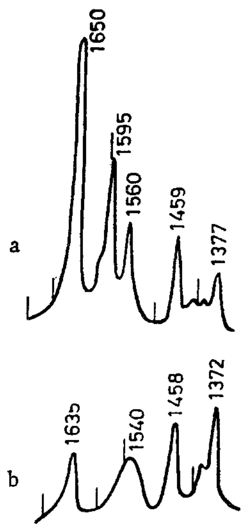


Fig. 2

Fig. 1. Fragments of the IR spectra of undeuterated (a) and deuterated (b) N_6-phenylcarbamoyl-3-phenylisopropylsydnoneimine dissolved in d_6-DMSO.

Fig. 2. Portions of the Raman spectra of N_6-methylcarbamoyl-3-methylsydnoneimine (a) and N_6-acetyl-3-methylsydnoneimine (b) (crystalline samples).

TABLE 1. Properties of N_6-exo-Carbamoyl Derivatives of Sydnoneimines

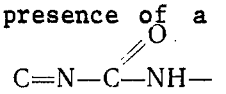
Compound	mp, °C*	Found, %			Empirical formula	Calc., %			IR spectrum, cm⁻¹				Yield, %
		C	H	N		C	H	N	$\nu_{C=O}$	$\nu_{C=N}$	δ_{NH}	$\nu_{4\text{-}H}$	
II	139—140	64,9	5,6	16,0	$C_{19}H_{20}N_4O_3$	64,8	5,7	15,9	1638	1600	1520 1535	†	59,0
III	117—118	65,5	5,9	15,8	$C_{20}H_{22}N_4O_3$	65,6	6,0	15,3	1640	1602	1520	†	55,0
IV	127—128 (dec.)	63,0	6,2	19,5	$C_{15}H_{18}N_4O_2$	63,0	6,1	19,3	1645	1598	1538	†	46,0
V	175—176	50,4	4,4	15,7	$C_{15}H_{16}Cl_2N_4O_2$	50,8	4,2	15,8	1646	1581	1515	†	61,5
VI	194—195 (dec.)	67,2	6,5	16,1	$C_{19}H_{22}N_4O_2$	67,6	6,6	16,6	1654	1598	1530	3198	68,5
VII	205—206 (dec.)	67,6	6,7	16,1	$C_{20}H_{24}N_4O_2$	68,2	6,8	15,9	1654	1600	1532	3200	57,5

*The compounds were recrystallized: II and III from isopropyl alcohol, IV from 50% alcohol, and V-VII from alcohol.

†The $\nu_{4\text{-}H}$ bands were masked by the ν_{NH} bands of the associated forms.

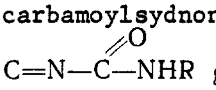
these bands we carried out the deuteration (with C_2H_5OD at room temperature) of N_6-phenylcarbamoyl-3-phenylisopropylsydnoneimine [sidnokarb (I)]. The spectrum of an undeuterated sample (Fig. 1) contains three bands at 1531, 1595, and 1658 cm^{-1}. After deuteration, the band at 1531 cm^{-1} is shifted to 1393 cm^{-1}, the band at 1595 cm^{-1} remains virtually unchanged, and the band at 1658 cm^{-1} is lowered ∿10 cm^{-1}. Thus the first band should be assigned to the deformation vibrations of the NH bond, the second should be assigned to the stretching vibrations of the C═N bond, and the highest-frequency band, which is shifted by approximately the same amount as in the case of deuteration of amides [4, 5], should be assigned preferably to $\nu_{C=O}$.

It follows from Table 1 and the data obtained in [3] that these three bands show up in the following ranges for carbamoyl derivatives with different substituents in the 3 position and in the exocyclic group: $\nu_{C=O}$ 1640-1660, $\nu_{C=N}$ 1580-1600, and δ_{NH} 1510-1540 cm^{-1}.

The frequencies and integral intensities of the characteristic C═O, C═N, and NH bands in the spectra of solutions of the carbamoylsydnoneimines are presented in Table 2; for comparison, data for N_6-acetyl-3-methylsydnoneimine (XV), in which the carbonyl group can interact only with the exocyclic C═N bond, are also presented in Table 2. It follows from the data in Table 2 that in the case of N_6-exo-methylcarbamoylsydnoneimines (XII, XIII), as compared with the acetyl derivative (XV), there is a considerable increase (∿45 cm^{-1}) in the frequency of the C═N bond and redistribution of the intensities of the C═N* and C═O bands; however, the frequency of the carbonyl group changes only slightly in this case. Thus the the presence of a second donor group weakens the donor properties of the C═N bond in the  $C{=}N{-}\overset{O}{\overset{/\!/}{C}}{-}NH{-}$ chain appreciably. The C═O group in this system effectively interacts with the unshared pair of electrons of the NH group, as evidenced by: 1) the small change in the C═O frequency as compared with the acetyl derivative; 2) the closeness of the δ_{NH} frequency (Table 2, XII and XIII) to the frequencies of the second amide band [4] and its high intensity. The effect of the C═N bond is manifested in this case in the very high $A_{C=O}$ values, which reach 5.5 units and exceed the corresponding intensities in the spectra of amides [7, 8], and in the lowered (20-30 cm^{-1}) C═O frequencies as compared with amides.

The C═O band of carbamoylsydnoneimines has an anomalously high intensity not only in the IR spectra but also in the Raman spectra. Portions of the Raman spectra of crystalline N_6-methylcarbamoyl- (a) and N_6-acetyl-3-methylsydnoneimine (b) are shown in Fig. 2. One may form a judgment regarding the intensities of the C═O and C═N bands by comparing them with the band of the methyl groups at 1459 cm^{-1}, the number of which is the same in both molecules. Whereas the $\nu_{C=O}$ band at 1635 cm^{-1} in the spectrum of the acetyl derivative is of low intensity, the $\nu_{C=O}$ band in the Raman spectrum of the carbamoyl derivative is the most intense band, and its intensity far exceeds the intensity of the C═O group in the Raman spectra of amides [9, 10].

The simultaneous sharp increase in the intensity of the $\nu_{C=O}$ band in both the IR spectra of carbamoylsydnoneimines and the Raman spectra indicates similar trends for polarization and polarizability of the bonds that participate in the stretching vibration of the C═O group. The exocyclic chain of the compounds under consideration should consequently have good conducting properties, i.e., they should efficiently transmit the mutual electronic effect of atomic groups that are far away from one another. The fact that this is actually observed follows from a comparison of the data for methylcarbamoylsydnoneimines (Table 2, XII and XIII) and sidnokarb (I). Replacement of the methyl substituent attached to the nitrogen atom of the exocyclic group by a phenyl substituent (Table 2, I) leads to an almost twofold decrease in the intensity of the carbonyl band and to an increase† in the $\nu_{C=N}$ intensity, i.e., to "restoration" of the distribution of intensities that is characteristic for acetyl derivative XV. This effect is reinforced when acceptor groups are introduced into the benzene ring (for example, in XIV). Thus the mutual effect of atomic groups that are separated by more than five bonds is manifested in this case.

It has been shown [11] that the exocyclic nitrogen atom in N_6-acetyl derivatives of sydnoneimines has a rather high basicity — these compounds are capable of forming stable salts. It has been noted [2, 12] that salt formation is also characteristic for N_6-exo-carbamoylsydnoneimines. However, in contrast to acetyl derivatives, the exocyclic  $C{=}N{-}\overset{O}{\overset{/\!/}{C}}{-}NHR$ grouping in the latter contains three possible protonation centers — the two nitrogen atoms and the carbonyl oxygen atom.‡

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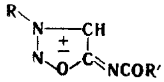
*We note that $A_{C=N}$ for acetylsydnoneimines has approximately the same value as $A_{C=O}$ for sydnones [6]

†In this case only the $A_{C=O}$ values are completely reliable. The band of vibrations of the benzene ring, the intensity of which may increase markedly when there are polar substituents in the ring, is superimposed on the C=N band.

‡It is known that amides are protonated in solutions of strong acids [13] and in trifluoroacetic acid [14]. However, up until now there has been no single point of view regarding the site of addition of the proton to the amide group. The IR spectral data are usually interpreted as evidence for protonation of the nitrogen atom [15]. Earlier NMR [16] and IR spectral data obtained for modal compounds [17] were interpreted in favor of protonation of the oxygen. Later NMR data for ureas [18], in agreement with the interpretation of the IR spectra [15], indicate that the proton evidently adds to the nitrogen atom of the amide group.

TABLE 2. Frequencies and Integral Intensities of the Bands of the Vibrations of the Side Chain of Carbamoyl Derivatives of Sydnoneimines



Compound	R	R′	Solvent	$\nu_{C=N}$, cm^{-1}	$A_{C=N}\cdot 10^{-4}$ $mole^{-1}/liter^{-1}\cdot cm^2$	$\nu_{C=O}$, cm^{-1}	$A_{C=O}\cdot 10^{-4}$ $mole^{-1}/liter^{-1}\cdot cm^2$	δ_{NH}, cm^{-1}	$A_{NH}\cdot 10^{-4}$ $mole^{-1}/liter^{-1}\cdot cm^2$	ν_{NH}, cm^{-1}
XV	CH_3	CH_3	$CHCl_3$	1558	5,5	1631	3,0	—	—	—
XII	CH_3	$NHCH_3$	d_6-DMSO	1600	2,8	1645	5,5	1520	2,7	—
XIII	$C_6H_5CH_2CH(CH_3)$	$NHCH_3$	$CHCl_3$	1598	2,4	1644	5,1	1515	3,1	3468
			d_6-DMSO	1601	3,1	1645	5,2	—	—	—
I	$C_6H_5CH_2CH(CH_3)$	NHC_6H_5	$CHCl_3$	1596	(5,5)	1655	3,1	1516	—	—
XIV	CH_3	$NHC_6H_4(NO_2)_2$	d_6-DMSO	1585	*	1665	2,1	1520	—	—
XIIIa	$C_6H_5CH_2CH(CH_3)$	$NHCH_3\cdot HCl$	$CHCl_3$	1635	2,4	1740	4,8	1555†	4,8	3300 3460 sh
XVa	CH_3	$CH_3\cdot HCl$	d_6-DMSO	1610	4,4	1731	2,5	1552‡	3,5	—

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*Superimposition of the ν_{as} NO_2 bands.

†This is the overall $\delta_{NH} + \delta_{N_6H^+}$ band.

‡$\delta_{N_6H^+}$.

We established the site of protonation of N_6-carbamoyl derivatives of sydnoneimine by means of the IR spectra in the case of N_6-methylcarbamoyl-3-phenylisopropylsydnoneimine XIII in solutions in weakly acidic and strongly acidic media. Fragments of the IR spectra of XIII in $CH_3OD + DCl$ (a) and in concentrated D_2SO_4 solutions (b, c) and of solutions of hydrochloride XIIIa in $CHCl_3$ are shown in Fig. 3.

Salt formation occurs in the case of an equimolar ratio of free base XIII and DCl (Fig. 3a), and as in the case of N_6-acetylsydnoneimines [11] the frequency of the C=N group is increased 30-40 cm^{-1}, and the frequency of the carbonyl group is increased ~100 cm^{-1} (Table 2, XIIIa and XVa). However, measurements of the integral intensities showed that in the case of close frequencies of the double bonds of the acetyl and carbamoyl salts the distribution of the intensities that is characteristic for carbamoyl derivatives is retained in the spectra of the latter. In addition, bands characteristic for the unprotonated CH_3—NH group are observed in the IR spectrum of the hydrochloride dissolved in $CHCl_3$ (Fig. 3, spectra e and f) at 3300-3400 cm^{-1}. The difference from the base molecule (Fig. 3, spectrum d) consists only in the stronger hydrogen bonds formed by this NH group in the hydrochloride. This explains the pattern observed in the IR spectrum of salt XIIIa in the region of NH deformation vibrations: During the formation of a hydrogen bond the band at 1520 cm^{-1} is shifted to higher frequencies [5] and is masked by the salt band at ~1550 cm^{-1}.

All of these data constitute unambiguous evidence that the carbamoylsydnoneimines are protonated at N_6. Only broadening and a small shift of the C=O and C=N bands, which can be explained by intermolecular interaction, are observed when the acid concentration is increased to 18 N (Fig. 3, spectra b and c). Thus the N_6 atom in carbamoylsydnoneimines retains its high basicity, and the NH group is found to be even less basic than in amides [19].

EXPERIMENTAL

The PMR spectra of d_6-DMSO solutions of the compounds were recorded with a Varian HA-100D spectrometer with hexamethyldisiloxane as the internal standard. The IR spectra were obtained with a UR-10 spectrometer; the spectra of all of the crystalline compounds were recorded from KBr pellets. Solutions of the N-exo- derivatives of sydnoneimines and their salts in $CHCl_3$ and d_6-DMSO were investigated in KBr and CaF_2 cuvettes. The integral intensities of the bands (A) were determined by measurements of the areas [20]; the spectral slit width was 2.3 cm^{-1}. The accuracy in the determination of the A values for the well-resolved bands was ±8%. The Raman spectra were obtained with a DFS-24 spectrometer with excitation by a helium-cadmium laser (λ 441.6 mm); the samples were compressed into pellets with KBr. Envelopes (25 × 40 mm) made from polyethylene film (by moderate heating of the edges without an adhesive) were pre-

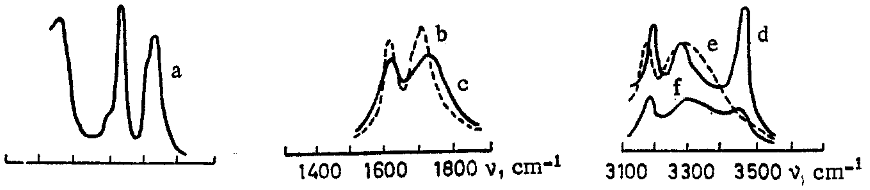

Fig. 3. Fragments of the IR spectra of N_6-methylcarbamoyl-3-phenylisopropylsydnoneimine XIII: a) in $CH_3OD + DCl$ (equimolar ratio of the free base and DCl), $c = 9.2 \cdot 10^{-2}$ mole/liter, $l = 0.06$ mm; b) in 40% D_2SO_4, $c = 5.5 \cdot 10^{-1}$ mole/liter; c) in 60% D_2SO_4, $c = 5.5 \cdot 10^{-1}$ mole/liter; d) in $CHCl_3$, $c = 2.2 \cdot 10^{-1}$ mole/liter, $l = 0.15$ mm; e) hydrochloride XIIIa in $CHCl_3$, $c = 3.77 \cdot 10^{-2}$ mole/liter, $l = 1.0$ mm; f) hydrochloride XIIIa in $CHCl_3$, $c = 1.2 \cdot 10^{-2}$ mole/liter, $l = 2.0$ mm.

pared for investigation of the IR spectra of solutions of the compounds in concentrated acids. A few drops of the solution were introduced into the envelope, after which it was placed in the standard clamp.

3-(1'-Adamantyl)sydnoneimine Hydrochloride (VIII). Concentrated HCl was added to 2.0 g (0.013 mole) of 1-adamantylamine X in 25 ml of water up to pH 2-3, after which 0.89 g (0.013 mole) of KCN and 1.24 g (0.013 mole) of formalin were added at 5°C. The mixture was stirred for 3 h, after which it was extracted with ether. The ether extract was dried, and ether solution of HCl was added, and the mixture was worked up to give 1.5 g of 1-adamantylaminoacetonitrile hydrochloride with mp 249-250°C. Found: Cl 16.2%. $C_{12}H_{18}N_2 \cdot HCl$. Calculated: Cl 15.7%. A solution of 0.45 g (0.0065 mole) of $NaNO_2$ in 15 ml of water was added at 2-3°C to a solution of a hydrochloride in 100 ml of aqueous HCl. After 3 h, the mixture was worked up to give 0.8 g of N-nitroso-3-(1'-adamantyl)acetonitrile with mp 115-116°C. A 0.5-g sample of the latter was treated with 20 ml of an alcohol solution of HCl, and the mixture was worked up to give 0.58 g of hydrochloride VIII with mp 130-132°C (dec., from methanol by the addition of ether). Found: Cl 13.3%. $C_{12}H_{17}N_3O \cdot HCl$. Calculated: Cl 13.9%.

3-(1'-Methyladamantyl)sydnoneimine Hydrochloride (IX). A solution of 3.5 g (0.017 mole) of 1-methyladamantylamine hydrochloride XI in 50 ml of water was treated with 1.25 g (0.019 mole) of KCN and 1.75 g (0.058 mole) of formalin at 3°C and pH 3. After 3 h, the oil was extracted with ether, dried, and treated with an ether solution of HCl to give 2.7 g of 1-methyladamantylaminoacetonitrile hydrochloride with mp 222-224°C (from alcohol). Found: C 65.1; H 9.1; Cl 14.5%. $C_{13}H_{20}N_2 \cdot HCl$. Calculated: C 65.0; H 8.8; Cl 14.8%. A solution of 0.8 g (0.015 mole) of $NaNO_2$ in 10 ml of water was added at 3-5°C to a solution of the hydrochloride in 150 ml of methanol, and the mixture was stirred for 3 h. The alcohol was then removed by evaporation, 20 ml of concentrated HCl was added to the residue, and the mixture was heated on a boiling-water bath for 30 min. It was then evaporated and worked up to give 2 g of hydrochloride IX with mp 210-212°C (dec., from alcohol by the addition of ether). Found: C 57.5; H 7.4; Cl 13.5; N 15.6%. $C_{13}H_{19}N_3O \cdot HCl$. Calculated: C 57.9; H 7.4; Cl 13.1; N 15.6%.

N-exo-Carbamoyl Derivatives of Sydnoneimines (Table 1). A solution of 0.1 mole of sydnoneimine hydrochloride in 500 ml of dry pyridine was treated at 2-4°C with 0.1 mole of isocyanate. After stirring for 3 h, the reaction mixture was poured into water, and the product was recrystallized from an appropriate solvent.

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MASS SPECTROMETRIC STUDY OF MONOALKYL-SUBSTITUTED THIACYCLANES

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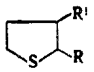
UDC 543.51:547.732'818

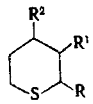
Monosubstituted α- and β-alkylthiophans and α-, β-, and γ-alkylthiacyclohexanes were subjected to a comparative mass spectrometric study. The stability of the M^+ ion increases on passing from α- to β-alkylthiophans and from α- to β- and γ-alkylthiacyclohexanes. In the case of α-alkylthiophans and α- and β-alkylthiacyclohexanes the principal process is associated with ejection of the substituent as a whole, whereas a portion of the alkyl substituent, with retention of one CH_2 group in the composition of the charged fragment, is eliminated from the molecular ions of β-alkylthiophans and γ-alkylthiacyclohexanes.

There have been several reports of the mass spectrometric study of cyclic sulfides. The mass spectra of ethylene sulfide [1], unsubstituted thiophan [2], α-alkylthiophans [3], α,α'-dialkylthiophans [4], α-alkylthiacyclohexanes [5], and some saturated two-ring and three-ring sulfides [6] have been analyzed in detail. However, in the case of alkylthiacyclanes only compounds that contain a substituent attached to the α-C atom with respect to the sulfur atom have been investigated. This orientation of the substituent determines the principal pathway of fragmentation under electron impact, which involves the ejection of an alkyl radical as a whole and the formation of an onium ion. The literature contains virtually no mass spectrometric data on β-alkylthiacyclopentanes or β- and γ-alkylthiacyclohexanes (some spectra of the lower homologs can be found in [7, 8]). However, data of this sort are necessary in the solution of structural analysis problems in the chemistry of sulfur-containing compounds of petroleum and in the chemistry of cyclic sulfides.

In the present research we made a comparative mass spectrometric study of monoalkyl-substituted thiacyclopentanes (I-X) and thiacyclohexanes (XI-XX) with substituents in different positions in the ring. The mass spectra of investigated compounds are presented in Table 1.



I-X



XI-XX

I $R=CH_3$, $R^1=H$; II $R=H$, $R^1=CH_3$; III $R=C_2H_5$, $R^1=H$; IV $R=H$, $R^1=C_2H_5$; V $R=n\text{-}C_4H_9$, $R^1=H$; VI $R=H$, $R^1=n\text{-}C_4H_9$; VII $R=n\text{-}C_6H_{13}$, $R^1=H$; VIII $R=H$, $R^1=n\text{-}C_6H_{13}$; IX $R=H$, $R^1=n\text{-}C_5H_{11}$; X $R=H$, $R^1=c\text{-}C_6H_{11}$; XI $R=CH_3$, $R^1=R^2=H$; XII $R=R^2=H$, $R^1=CH_3$; XIII $R=R^1=H$, $R^2=CH_3$; XIV $R=C_2H_5$, $R^1=R^2=H$; XV $R=R^2=H$, $R^1=C_2H_5$; XVI $R=R^1=H$, $R^2=C_2H_5$; XVII $R=R^2=H$, $R^1=C_4H_9$; XVIII $R=R^1=H$, $R^2=n\text{-}C_4H_9$; XIX $R=R^1=H$, $R^2=n\text{-}C_6H_{13}$; XX $R=R^1=H$, $R^2=c\text{-}C_6H_{11}$

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