Journal of Organometallic Chemistry, 336 (1987) 49–57
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Intramolecular interactions in compounds bearing Si–O–C–C–N or C–O–C–C–N fragments

E.I. Brodskaya*, **M.G. Voronkov, D.D. Toryashinova, V.P. Baryshok,**
Institute of Organic Chemistry, Siberian Division of the U.S.S.R. Academy of Sciences, 664033 Irkutsk (U.S.S.R.)

G.V. Ratovski, D.D. Chuvashev and V.G. Efremov
Institute of Petroleum and Coal Chemical Synthesis, State University, Irkutsk (U.S.S.R.)

(Received May 8th, 1987)

Abstract

Two main types of intramolecualr interaction are possible in molecules of 2,2,6-trimethyl-1,3-dioxa-6-aza-2-silacyclooctane (VII), (2-trimethylsiloxyalkyl)amines (III–VI) and tris(2-R-ethyl)amines I–II, each of which bears a O–C–C–N fragment. These are: (i) through-bond coupling of nitrogen and oxygen lone pairs and (ii) interaction of the nitrogen or oxygen lone pair with $\sigma^\star$ MOs of the O–C–C–N skeleton arranged in the same plane (anomeric effect).

A CNDO/S calculation of the photoelectron spectrum of dimethyl(2-methoxyethyl)amine, $MeOCH_2CH_2NMe_2$ with differing spatial orientations of methoxy and dimethylamine moieties has shown that depending on the orientation of nitrogen or oxygen lone pairs these two types of interaction narrow the gap between nitrogen and oxygen orbitals (ca. 0.5–0.6 eV) or drive them apart ca. 1.8 eV. The former is indicative of the presence of only one intense band in the photoelectron spectra of I–II and two bands (ca. 10 and 11 eV) in the spectra of methylsilatranes (VIII, IX) and higher equilibrium constants in the hydrogen bonding of phenol with the above compounds.

Introduction

Our previous studies have shown that the increased electron donor properties of oxygen as well as the lower basicity of nitrogen in the silatranes, $RSi(OCHR'CH_2)_3N$, 1,3-dioxa-6-aza-2-silacyclooctanes, $R_2Si(OCHR'CH_2)_2NMe$ and (2-trimethylsiloxyalkyl)amines, $(Me_3SiOCHRCH_2)_nNMe_{3-n}$ ($n = 1$–3) all bearing a Si–O–C–C–N fragment could be explained in terms of through-bond interaction of

0022-328X/87/$03.50

O and N lone pairs which is independent of the presence and strength of transannular Si←N coupling * [1].

Nevertheless, the anomeric effect, i.e. interaction of the nitrogen or oxygen lone pairs with $\sigma^{\star}$ MOs of the N–C–C–O segment [5], which was not discussed in the previous article [1], may also take place in the compounds studied.

To ascertain which type of interaction is responsible for the observed anomaly in both hydrogen bonding and in the photoelectron spectra of the compounds with Si–O–C–C–N or C–O–C–C–N fragments, the CNDO/S semiempirical SCF MO method has been applied to dimethyl(2-methoxyethyl)amine, $MeOCH_2CH_2NMe_2$, which may have different orientations of OMe and NMe_2 groups. In addition, photoelectron spectra of tris(2-alkoxyethyl)amines, $(ROCH_2CH_2)_3N$ (R = Me, Et), 2,2,6-trimethyl-1,3-dioxa-6-aza-2-silacyclooctane, $Me_2Si(OCH_2CH_2)_2NMe$ and a number of methylsilatrane molecules, $MeSi(OCHRCH_2)_3N$ with R = H, Me and $MeSi(OCH_2CH_2)_2(CH_2CH_2CH_2)N$ have been obtained. The frequency shift between phenol or deuteromethanol as well as the equilibrium association constants and thermodynamic parameters for the hydrogen bonding of phenol and the compounds studied have been determined.

Results and discussion

CNDO/S calculation of dimethyl(2-methoxyethyl)amine, $MeOCH_2CH_2NMe_2$

To investigate the contribution of nitrogen and oxygen lone pairs to the highest occupied molecular orbitals (HOMO) the CNDO/S calculation was carried out on some of the conformations of a simpler compound, $MeOCH_2CH_2NMe_2$ in which the N and O lone pairs are located either in the planes perpendicular to the O–C–C–N or in the same plane (Table 1). The dipole moment of this compound calculated for free rotation from the group moments is consistent with the experimental value (1.4 and 1.5 D, respectively [6]). For convenience only flat N–C–C–O conformations were chosen since rotation about the C–C bond does not influence the through-bond interaction [2]. Neither the through-bond nor the n, $\sigma^{\star}$ interaction are possible in conformation A; HOMOs differ by 2 eV. HOMO 1 is made up of the nitrogen lone pair and partly of the neighbouring CH_2 group, whereas HOMO 2 comprises the oxygen lone pair and the σ bond of the neighbouring CH_2 group.

When the nitrogen lone pair lies in the N–C–C–O plane (B, C) the energy of MO 1 is lowered (ca. 0.9–1.2 eV) while MO 2 increases slightly (ca. 0.2–0.5 eV). The decreased energy of MO 1 is consistent with n, $\sigma^{\star}$ coupling. Nevertheless, MO 1 includes most of the nitrogen and the neighbouring CH_2 moiety and MO 2 comprises the oxygen lone pair and the CH_2 group. MO 1 and MO 2 change considerably when the axes of the lone pairs are located in the N–C–C–O plane (D, E). In this case two HOMOs contain both nitrogen and oxygen lone pairs as well as the CH_2–CH_2 moiety. But the contribution from the nonbonding nitrogen AO is greater in MO 1 while the oxygen AO takes a more active part in MO 2 (E). The HOMOs are either brought together by ca. 0.5 eV (D) or moved apart ca. 1.8 eV (E) depending on the orientation of N and O lone pairs. It is the n, $\sigma^{\star}$ coupling that is dominating in conformation D. In conformation E the change in HOMOs is caused

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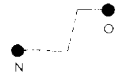
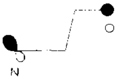
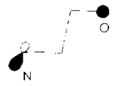
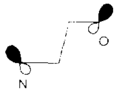
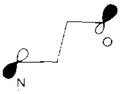
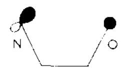
* This effect has been described in a number of reviews [2–4].

Table 1

CNDO/S calculation of contributions (%) by atoms and groups to the two highest occupied MOs of dimethyl(2-methoxyethyl)amine, $MeOCH_2CH_2NMe_2$ with different orientations of the nitrogen and oxygen lone pairs

Conformation	No.	ϵ [a] (eV)	Atoms or groups (%)			
			N	CH_2	CH_2	O
A 	1	−10.258	71.78	10.80	1.01	0.08
	2	−12.271	1.38	2.49	25.38	54.45
B 	1	−11.475	63.40	12.46	5.83	0.38
	2	−12.062	0.55	17.00	28.75	38.40
C 	1	−11.172	55.93	9.67	10.69	2.29
	2	−11.798	3.87	4.74	29.52	35.61
D 	1	−11.392	45.27	15.03	11.47	13.54
	2	−11.932	25.80	10.88	7.37	23.44
E 	1	−10.959	44.31	11.14	12.65	14.47
	2	−12.694	20.17	3.89	3.89	42.68
F 	1	−11.362	65.65	10.50	4.40	0.56
	2	−11.859	1.37	19.62	28.07	36.48

[a] Ionization energies of amines and ethers calculated by CNDO/S with parametrization are higher, usually by ca. 1–2 eV.

by two types of interaction: (i) nitrogen and oxygen lone pair coupling through intervening σ bonds and (ii) n, σ^* interaction of N and O lone pairs with suitably oriented σ^* MO of the adjacent N–C–C–O segment. HOMOs change slightly on going from B to D. A considerably greater increase in the energy of MO 1 and a significant lowering of MO 2 takes place when conformations C or D convert into E which seems to be provided with the lone pairs through bond interaction. This effect is maximal in conformation E [2].

In some conformations (B, C, D, F) HOMOs are drawn close together both upon mixing of lone pairs ($\Delta E_{1,2}$ 0.5 eV) and in the absence of mixed MOs ($\Delta E_{1,2}$ 0.6 eV). In these cases only one peak due to ionization of both HOMOs and single stretching mode frequency corresponding to hydrogen bonding with deuteromethanol is observed. At the same time, there are conformations such as A and E in which MO 1 and MO 2 differ considerably, but they are either mixed ($\Delta E_{1,2}$ 1.7 eV) or mainly localized on the nitrogen or oxygen atoms ($\Delta E_{1,2}$ 2.0 eV), the energy of MO 1 being maximal. Two or more bands may appear in the photoelectron spectra with $\Delta E_{1,2}$ ca. 1.5–2.0 eV for conformers A, E.

These calculations for dimethyl(2-methoxyethyl)amine are in good agreement with our set of experimental data below.

Photoelectron spectroscopy

Some photoelectron spectra obtained in the region below 20 eV are shown in Fig. 1. Vertical ionization potentials (*IP*) calculated from the maxima of the photoelectron spectra are listed in Table 2. In dimethyl ether (XI) and trimethylethoxysilane (XII) the band at lower *IP* accounts for ionization of the oxygen lone pair. The band below 8.5 eV is related to the nitrogen lone pair ionization of trialkylamines [10]. In the spectrum of dimethyl(2-oxyethyl)amine, HOCH$_2$CH$_2$NMe$_2$ two bands of almost equal intensity at 8.8 and 10.3 eV may be assigned to ionization from *n* orbitals of the nitrogen and oxygen lone pairs, respectively [6]. The *gauche* O–H · · · N conformation appears to be most stable. Two similar bands (8.9 and 10.6 eV) occur in the spectrum of methylbis(2-oxyethyl)amine, (HOCH$_2$CH$_2$)$_2$NMe and, therefore, the same conformations must exist. The intensity of the second band is almost twice as high so that it can be assigned to oxygen ionization.

The spectra of III–VI are more complex. Four bands in the spectra of III–V appear. According to the above consideration the band at ca. 8.3 eV in IV–VI and 7.95 eV in III is related to ionization from the N lone pair orbital. All bands in

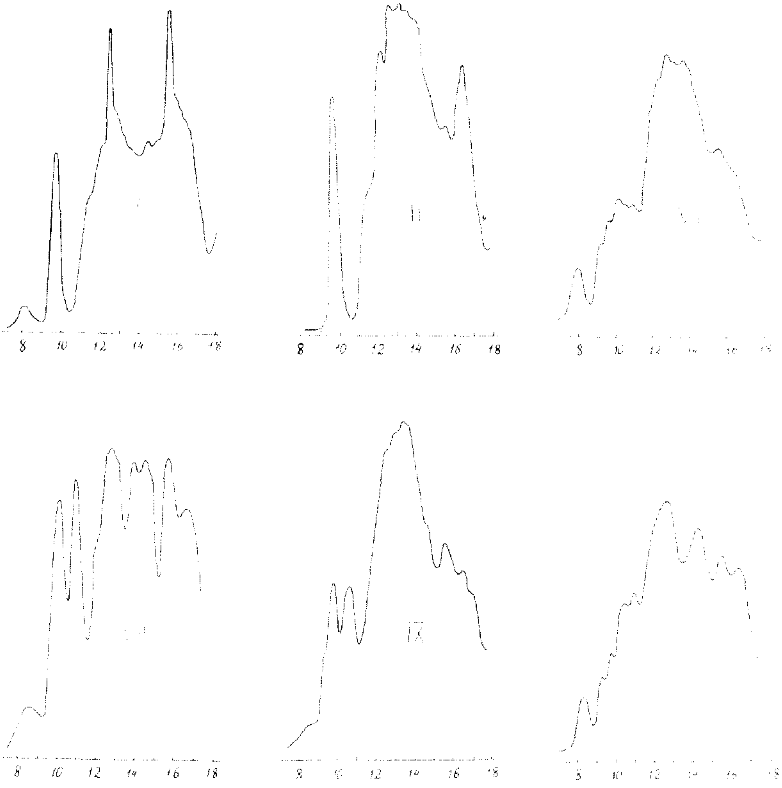


Fig. 1. Photoelectron spectra of compounds I, II and VII–X in counts/s vs. *IP* (eV).

Table 2

Ionization potentials of acyclic and cyclic derivatives of (2-oxyalkyl)amines and model compounds

Compound		IP_N (eV)	IP_{OCCN} (eV)
$(MeOCH_2CH_2)_3N$	(I)	7.94	9.71
$(EtOCH_2CH_2)_3N$	(II)		9.70
$(Me_3SiOCH_2CH_2)_3N$	(III)	7.94	9.67, 10.30, 11.10
$Me_3SiOCH_2CH_2NMe_2$	(IV)	8.31	9.73, 10.24, 11.14
$(Me_3SiOCH_2CH_2)_2NMe$	(V)	8.34	9.73, 10.31, 11.24
$(Me_3SiOCHMeCH_2)_2NMe$	(VI)	8.39	9.60, 9.85, 10.08, 10.80, 11.27
$Me_2Si(OCH_2CH_2)_2NMe$	(VII)	8.19	9.52, 10.04, 10.54, 11.32
$MeSi(OCH_2CH_2)_3N$	(VIII)	8.49	10.21, 11.0
$MeSi(OCHMeCH_2)_3N$	(IX)	8.77	9.95, 10.78
$MeSi(OCH_2CH_2)_2N$ $(CH_2CH_2CH_2)$	(X)	8.42	9.47, 9.96, 10.63, 11.04
EtOEt	(XI)		9.70 [a]
$EtOSiMe_3$ [b]	(XII)		9.28, 9.97
$MeSi(OEt)_3$	(XIV)		10.8 [c]
$EtNMe_2$	(XV)	8.39 [d]	

[a] Ref. 7. [b] Ref. 8. [c] Ref. 9. [d] Ref. 10.

9.6–11.3 eV region result from the ionization of an electron of the free pair of the oxygen and Si–C bonds [8]. The presence of two, and three, $Me_3SiOCH_2CH_2$ fragments in V, and III, by analogy proportionally increases the intensity of the latter bands with the same changes in the spectra of (2-oxyethyl)amines. Methyl groups introduced into the α-position to the oxygen atom (VI) split some of the bands but the spectrum does not change. The splitting may be caused by some conformational distortion owing to steric hindrance of methyl groups.

All this indicates that in the gas phase the conformations of compounds III–V may be of the type A or E ($\Delta E_{1,2} > 1.4$ eV).

The photoelectron spectra of I and II show an intense band at ca. 9.7 eV. Tris(2-methoxyethyl)amine I also has a weak band at 7.95 eV (about 10 times less intense). The absence of the band from this region in the spectrum of II may be due to its very low intensity. It means that compounds I and II exist in conformations similar to C and D with HOMOs as close as possible, i.e., the nitrogen lone pair lies in the plane of at least one N–C–C–O fragment or C–C bond and oxygen lone pair. Nevertheless the conformations of the A and E types are also possible.

The sp^3 nitrogen lone pair hybridization is sensitive to the degree of α-branching at nitrogen [11]. The decrease in nitrogen lone pair ionization for I and III (7.95 eV) may be caused by increasing the angle α, flattening the nitrogen.

The spectrum of 2,2,6-trimethyl-1,3-dioxa-6-aza-2-silacyclooctane(VII) consists of five bands. Evidently, a large number of conformations of the above types A–E can be achieved in this compound. Phenyl group attached to silicon does not change the number of conformations (8.24, 10.43, 10.87 and 11.43 eV) and two bands at 8.88 and 9.45 eV due to π MO ionization of phenyl group appear in the spectrum of 2,6-dimethyl-2-phenyl-1,3-dioxa-6-aza-2-silacyclooctane, $MePhSi(OCH_2CH_2)_2NMe$ (unfortunately, it appears that the spectrum of this compound as depicted in ref. 1 is not correct).

The silatrane cage geometry corresponds closely to conformations with two HOMOs (F). One thus expects either one or two peaks in 1/3 ratio in the photoelectronic spectra. However, a weak band below 9 eV and two peaks of approximately equal intensity ($IP_1/IP_{2,3}$ ratio is ca. 1/12 for VIII and 1/9 for IX), occur in the spectra of 1-methyl- and 1,3,7,10-tetramethylsilatrane (VIII and IX). From a previous calculation [1], the two peaks at 10.2 and 11 eV in the spectrum of 1-methylsilatrane (VIII) are attributed to MOs involving AOs of nitrogen, oxygen, silicon, carbon atoms of methyl groups as well as O–C–C fragments, respectively.

Two bands of about equal intensity in the spectra of silatranes VIII, IX cannot be accounted for by structures A–F thus implying some kind of coupling in one semicycle, Si–O–C–C–N. We had assumed the interaction of the oxygen lone pair of one semicycle with the σ^* MOs of the Si–O–C bonds of the other semicycles.

An analogous coupling of π-orbitals of unsaturated fragments (R) with group antibonding σ^* orbitals involving two P–Cl bonds in compounds $RPCl_2$ and $RP(O)Cl_2$ was found by UV absorption spectroscopy [12]. The interaction depends on the number (n) of P–Cl bonds at phosphorus and is constant when $n = 2, 3$ and disappears when $n = 1$.

The group orbitals involving the two Si–O–C groups are suggested to participate in analogous interaction with the oxygen lone pair in the third semicycle, Si–O–C–C–N. In the other compounds studied there were no conditions suitable for this interaction. In contrast to the spectra of 1-methyl- and 1,3,7,10-tetramethylsilatranes, the spectrum of 1-methyl-2-carbasilatrane (X) contains five bands at 8.42, 9.47, 9.96, 10.63 and 11.04 eV and is similar to that of 2,2,6-trimethyl-1,3-dioxa-6-aza-2-silacyclooctane (VII). This provides evidence for the absence of the above interactions in VII and X in which the oxygen lone pair cannot interact with σ^* of two Si–O bonds. Consequently, the structures with the greatest difference in HOMOs (8.42 and 11.04 eV) and the various other conformations (9.47, 9.96 and 10.63 eV) are most likely to exist in 1-methyl-2-carbasilatrane.

The band at 8.7 eV in the spectrum of 1-methylsilatrane has been assigned to tris(2-oxyethyl)aminen produced by hydrolysis [1]. In the spectrum of 1-methylsilatrane obtained by us the first band is at 8.49 eV (IP in the spectrum of tris(2-oxyethyl)amine corresponds to 8.7 eV [9]). The 8.49/10.2 eV band ratio does not change with time (the tris(2-oxyethyl)amine formed accelerates hydrolysis of silatranes [13] and, consequently the 8.7 eV band should appear in the spectrum). The band at 8.49 eV in the PE spectrum of 1-methylsilatrane thus corresponds to the molecule itself, rather than to the hydrolysis product. In light of this the weak bands about 8.8 and 8.42 eV in the spectra of IX and X are also attributable to these molecules. At the same time, the first IP in the PE spectra of the silatranes (8.49, 8.8 and 8.42 eV for VIII, IX and X, respectively) seem to be higher than those of trialkylamines [10] and compounds I, IV–VII. The expected value of the first IP in the spectra of VIII–X is ca. 7.94 eV, which is similar to that of I. In fact, in the spectra of N-methylazacyclooctane, $MeN(CH_2)_7$ and N-methylazacyclononane, $MeN(CH_2)_8$ the first ionization bands are at 8.08 and 7.93 eV, respectively [14], whereas in the 5-membered analog, $MeN(CH_2)_4$ the IP is higher (8.40 eV) owing to strained small rings. The higher first IP for silatranes VIII–X may then be interpreted in terms of transannular Si←N bond and silatrane cage strain caused by this bonding.

Thus, weak bands in the region 8.4–8.8 eV in the spectra of VIII–X are caused by other conformations of the silatrane cage with no interaction occurring between the nitrogen lone pair and the antibonding σ^* of C–C–O fragments.

Hydrogen bonding

Our previous studies have shown the $\Delta\nu$(OH) and $\Delta\nu$(OD) stretching in intermolecular hydrogen bonding between either phenol or deuteromethanol and tris(2-alkoxyethyl)amines (I, II) or (2-trimethylsiloxyalkyl)amines (III, VI, VII) (273–297 or 102–116 cm^{-1}) to be considerably lower than in those of the hydrogen-bonded complexes with triethylamine XV (556 or 233 cm^{-1}, respectively) (Table 3).

The energy of hydrogen bond (ΔH) linking the phenol and each of compounds I–III (29–31 kJ mol^{-1}) seems to be intermediate in comparison with those of oxygen XI, XII and XIV (25–28 kJ mol^{-1}) and nitrogen XV (33.5 kJ mol^{-1}) organic bases.

The association equilibrium constants K_{ass} of phenol with oxygen bases (8–11 l mol^{-1}) are about five times less than those for complexes with triethylamine (50 l mol^{-1} at 301 K). It should be noted that for the hydrogen-bonded complexes of phenol with compounds I–III and VI, K_{ass} is 4–8 times higher than those for the analogous oxygen organic compounds. This may be due to the appearance of the conformatioins B, C and D in the solution. The equilibrium constants for cyclic molecules such as VII, IX and X are only 2–3 times higher than those in the intermolecular bond C_6H_5OH–C_2H_5OR (XI, XII, XIV). Thus, the increase of K_{ass} and $\Delta\nu$(OH) or $\Delta\nu$(OD) in hydrogen-bonded complexes of compounds I–III and VI–X as compared with XI–XIV is caused by the interaction of nitrogen and oxygen lone pairs either with a through-bond or with occupied σ^* orbitals of the N–C–C–O fragment. The above-mentioned lowering of MO 1 corresponds to a higher frequency shift corresponding to hydrogen bonding of the type OH(D) · · · N.

Table 3

Stretching shifts, $\Delta\nu$(OH), and $\Delta\nu$(OD) for the hydrogen-bonded complexes of C_6H_5OH and CH_3OD with acyclic or cyclic (2-oxyalkyl)amine derivatives, model compounds (solvent CCl_4), and thermodynamic parameters of the hydrogen bonding between phenol and the above compounds (solvent heptane)

No.	IR		UV				
	$\Delta\nu$(OH) (cm^{-1})	$\Delta\nu$(OD) (cm^{-1})	T (K)	K_{ass} (l mol^{-1})	$-\Delta H$ (kJ mol^{-1})	$\delta(\Delta H)$	$-\Delta S$ (J mol^{-1} K^{-1})
I	273	102	293	76.1	29.4	1.7	64.6
II	283	110	293	79.5	28.9	1.3	62.3
III	297	114 [a]	293	44.9	31.3	1.0	75.3
VI	295	116	293	48.3	28.0	2.5	62.7 [b]
VII	286	112	293	15.9	29.9	1.3	79.1 [b]
IX	275	98	293	18.1	32.4	2.6	72.0 [b]
X	301		293	31.3	23.0	2.0	50.7
XI	275 [c]	105	298	11.4	25.1	–	62.4 [d]
XII	266	99	293	8.0	28.0	1.05	78.3 [b]
XIII [e]	257	94	293	9.6	26.6	0.4	72.0 [b]
XIV	246	78	293	11.0	23.5	1.7	60.4 [b]
XV	556 [c]	233 [f]	301	52.4	33.5 [g]		

[a] Ref. 1. [b] Ref. 15. [c] Ref. 16. [d] Ref. 17. [e] $Me_2Si(OEt)_2$. [f] Ref. 18. [g] Ref. 19.

The associated bands due to the bonding of OH(D) · · · H and OH(D) · · · O may, however, superpose. Complex formation with compounds I–III, VI seems to proceed either with nitrogen or with oxygen atoms whereas that with compounds VIII–X involves only the oxygen atom. This is in agreement with the higher K_{ass} for phenol bonding with compounds I–III, VI. The association band corresponding to deuteromethanol–nitrogen bonding not involved in any interaction appears only in the IR spectra of IV and V [1].

Experimental

He(1) photoelectron spectra, infrared and ultraviolet absorption spectra of the compounds under consideration were recorded as described earlier [1,15].

The association equilibrium constants K_{ass} of the hydrogen–bonded complexes of phenol with compounds studied in heptane are determined by ultraviolet spectroscopy using the Benesi–Hildebrand equation for the 1/1 composition [20]. The phenol concentration was 5×10^{-4} mol l^{-1}, the concentration of the electron-donor was $5 \times 10^{-3} - 5 \times 10^{-2}$ mol l^{-1} for I–III and VI and $10^{-2} - 10^{-1}$ mol l^{-1} for VII–XIV.

Tris(2-alkoxyethyl)amines I and II were prepared by alkaline alcoholysis of tris(2-chloroethyl)amine hydrochloride [21], and were purified by double-distillation.

$(C_2H_5OCH_2CH_2)_3N$: b.p. 108°C/11 mmHg, n_D^{20} 1.4330; $(CH_3OCH_2CH_2)_3N$: b.p. 233°C/720 mmHg; ref. data: b.p. 134°C/12 mmHg, n_D^{20} 1.4515 [22].

The purity of the compounds investigated was verified by GC-MS on a Varian MAT-212 instrument.

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