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ELECTRONIC SPECTRA OF α,β-UNSATURATED CARBONYL COMPOUNDS—III

β-ALKYLAMINO AND β-DIALKYLAMINO ACRYLAMIDES

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Abstract—Several β-alkylamino, β-dialkylamino and β-aziridino acrylamides have been synthesized and their configuration and conformation established by means of NMR and IR. Cis and trans isomers have been isolated in some cases, and their respective $\pi \rightarrow \pi^*$ absorption maxima assigned. Configuration does not appreciably affect the frequency of this transition.

In previous papers of this series[1,2] a system of spectral constants accounting for the contribution of various structural elements, viz configuration, conformation, intramolecular hydrogen bond and alkyl substituents, to the observed position of the absorption maximum of the $\pi \rightarrow \pi^*$ band in enamino aldehydes and ketones, and in enols and their ethers has been proposed. This system involves comparison of spectra of stereo-isomers of the same molecule which eliminates the problem of the electronic contribution of alkyl substituents or ring fragments to the energy of the $\pi \rightarrow \pi^*$ transition, encountered in the additive systems put forward by other authors.[3,4] However, it was not possible to separate the spectral change for enamino derivatives due to trans→cis isomerization from that resulting from a simultaneous formation of an intramolecular hydrogen bond. In consequence, indirect data based on the assumption of equality of the spectral effect of intra- and inter-molecular hydrogen bonds had to be introduced into the system of additive increments.

This difficulty was overcome in the case of enol ethers since cis isomers could be isolated which were sufficiently stable for UV measurements to be made and, of course, did not contain intramolecular hydrogen bonds.

The present work combines the above two approaches, i.e. for β-monoalkylamino-acryl amides the evaluation of increments is based on spectral changes accompanying the trans→cis isomerization and formation of an intramolecular hydrogen bond while for some β-dialkylamino derivatives (viz aziridino) a direct comparison of the comparatively stable cis isomer (lacking the intramolecular hydrogen bond) with the trans isomer served as a basis for calculations. The results thus obtained are consistent with those previously described.[1,2]

RESULTS AND DISCUSSION

Configuration and conformation assignment

It is convenient to divide the compounds studied in this paper into two groups according to the stability of their configuration. The first group of molecules **1–7** undergo the trans⇌cis isomerization in solution. The second group includes all the *N,N,N,N*-tetra-substituted molecules **8–10** which have a fixed configuration.

Compounds **1–4** and **7** have been obtained in a crystalline form as pure trans *E*-isomers, while **5** and **6** are liquid mixtures of trans *E* and cis *Z* isomers. The configuration assignment is evidenced by both the NMR and IR spectra. The detailed analysis of the corresponding spectra will be given for 3-methylaminopropenoic di-isopropylamide **3** and 3-methylaminopropenoic dimethylamide **1** (Figs. 1–5).

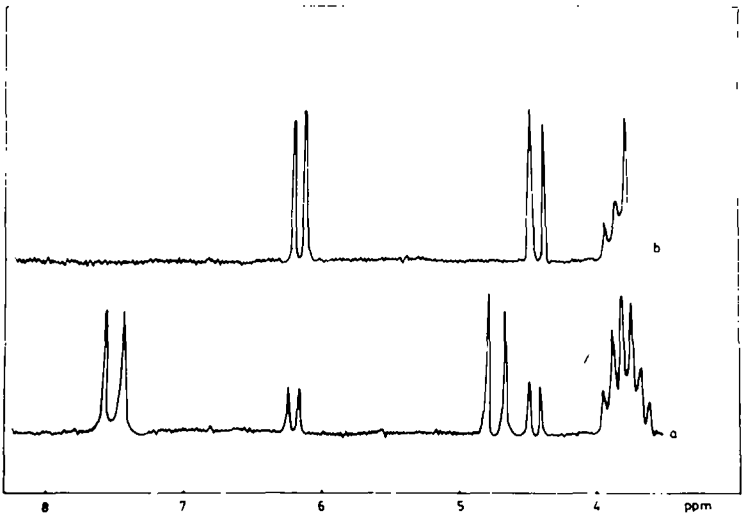

Fig. 1. The partial NMR spectrum of **3** in the vinylic proton region recorded in carbon tetrachloride. (a) immediately after dissolution of the compound; (b) after 24 hr.

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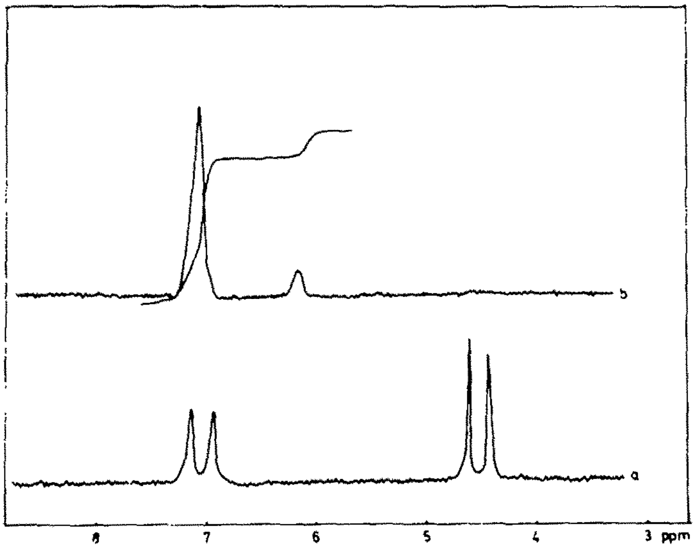


Fig. 2. The partial NMR spectrum of **1** in the vinylic proton region recorded in CD_3OD: (a) immediately after dissolution of the compound; (b) after 24 hr. Due to exchange of the α-protons into deuterium, the β protons corresponding to cis and trans protons become singlets.

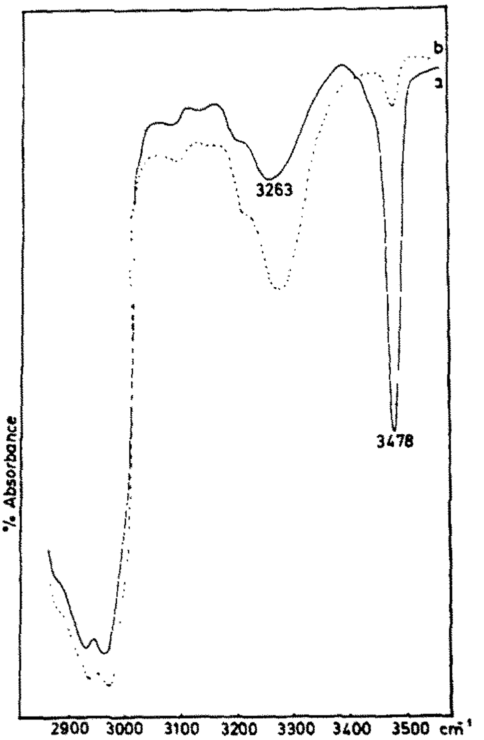


Fig. 3. IR spectrum of **3** in 2850–3500 cm^{-1} region measured in carbon tetrachloride: (a) immediately after dissolving the compound; (b) after equilibrium was reached.

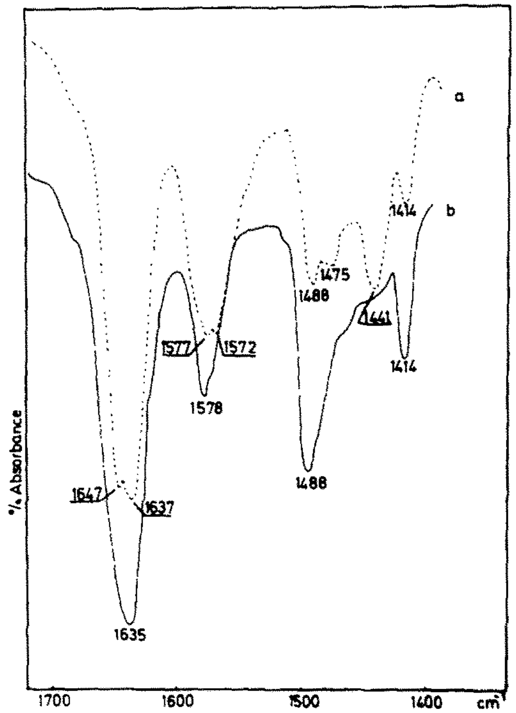


Fig. 4. IR spectrum of **3** in the double bond stretching region measured in tetrachloroethylene: (a) recorded immediately after dissolving the compound; (b) after equilibrium was reached.

When recorded within the shortest possible time, an NMR spectrum of crystalline *N*-deuterated **3** dissolved in tetrachloride exhibits an AB system for vinyl protons. The coupling constant $^3J_{HH} = 12.5$ Hz is characteristic of the trans configuration. The amount of cis isomer rapidly increases and after several hours an equilibrium is reached. In non-polar solvents like cyclohexane, tetrachloroethylene and carbon tetrachloride the trans$\rightleftharpoons$cis equilibrium is almost completely shifted towards the cis isomer (Fig. 1). However, in methanol the trans isomer strongly prevails. In the cases of **1**, **2** and **3**, the equilibrated mixture contained only 18% of cis isomer (Fig. 2). The population of that isomer increases with increasing size of the alkyl group at the vinylic nitrogen and in the case of **7** the equilibrium refers to 60% of cis and 40% of trans isomer.

A further confirmation of the configuration assignment follows from the IR spectra. The IR spectrum (Fig. 3)

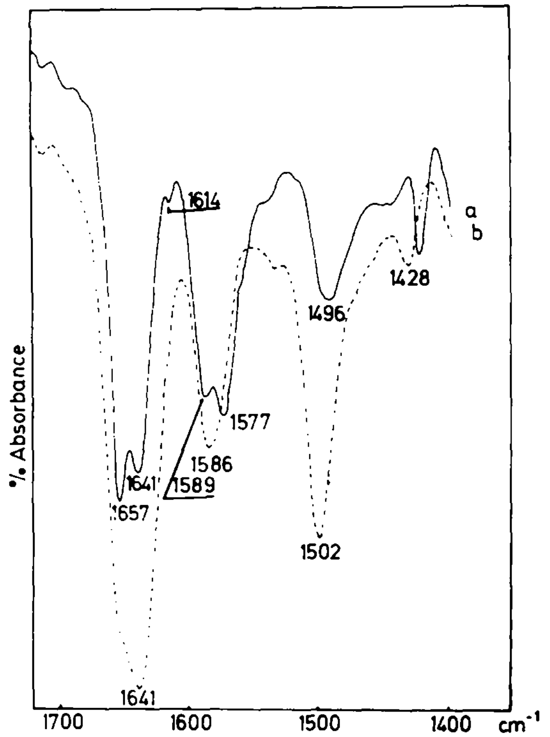
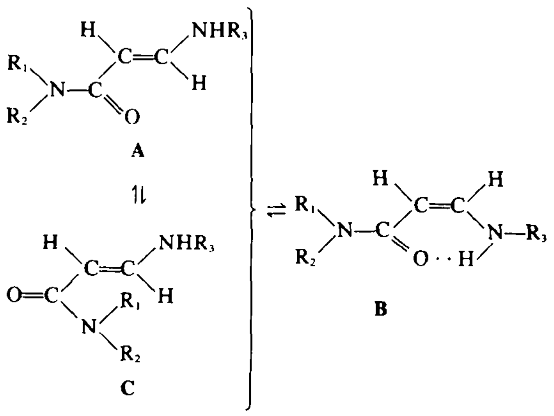


Fig. 5. IR spectrum of **1** in the double bond stretching region measured in tetrachloroethylene: (a) recorded immediately after dissolving the compound; (b) after equilibrium was reached.

recorded immediately after the preparation of a dilute carbon tetrachloride solution of **3** exhibits in the 3000–3500 cm^{-1} region a characteristic band of a free N-H group. In addition to this band observed at 3478 cm^{-1} a broad weaker one at 3263 cm^{-1} is observed and can be attributed to the H-bonded N-H group. The intensity of the 3263 cm^{-1} band increases on the expense of the 3478 cm^{-1} band, unambigously indicating the intramolecular character of the H-bond. This proves that the cis-*s*-cis isomer is formed in the isomerization process.

The assignment of conformation in the first group of molecules is not so straightforward.



However, because of a strong steric repulsion between the sizable *N,N*-dialkylamid group and the β vinylic hydrogen the *s*-cis conformation **A** will be favoured in comparison with the conformation *s*-trans **C**. This effect should be expecially well marked for **3** ($R_1 = R_2 =$ i-Pr) and this expectation is confirmed by IR (Fig. 4). The 1647 and 1572 cm^{-1} bands of the immediately recorded spectrum gradually disappear and can be ascribed to the trans isomer. They are analogous to the so-called vinylogous amide bands I and II of enamino ketones and aldehydes,[5] i.e. they correspond to vibrations of mainly νC=O and (νC=C + δN-H)† character, respectively. While the latter is of little use for conformational assignments to enamino carbonyl compounds, the former unambigously indicates that the conformation of the trans isomer of **3** is *s*-cis **A**. The absorption of the alternative *s*-trans conformation **C**, expected[5a,c,d] to occur near 1610–1620 cm^{-1}, is not detectable. However, for compound **1** with much smaller $R^1 = R^2 =$ Me substituents, the IR spectrum recorded immediately after dissolution of a solid sample shows a discernible, though weak band at 1614 cm^{-1}; this absorption disappears completely in the course of isomerization (see Fig. 5).

Among the other compounds studied in the present paper **8** and **9** exist only as the trans isomers. The compound **10** was obtained in both configurations. In all these cases the configuration is unambigously proved by the NMR spectra ($^3J_{HH} = 12.5$ Hz for **8**, **9** and **10** trans and J = 8.5 Hz for **10** cis). The conformational uniformity of trans-**8**, **9** and **10** was confirmed by IR. Only two bands characteristic for the *s*-cis conformation were observed in the double bond region (see Table 1). In the case of cis-**10** the IR spectrum indicates that also this compound exists in one conformation only (one νC=C and one νC=O band). Due to a strong steric repulsion between the aziridine ring and *N,N*-diisopropylamide group this should be evidently the *s*-cis conformation.

Having assigned both the conformation and configuration of the compounds **1–10**, we have measured their UV spectra in the different solvents. The results are collected in Tables 2 and 3. When assigning the band maximum for a given configuration the previously observed feature[1] that the UV spectrum is relatively independent of the small admixture of the other isomers (up to ~30%), was used.

Determination of the cis-trans UV shift

Any set of the so-called spectral increments follows from the assumption of additivity of structural changes. In the case of the UV spectra of π-electron systems this idea can be given a firm theoretical justification,[6] provided that structural changes represent a small perturbation to some parent system. As shown in our previous papers[1,2] the same idea can be also extended to account for the change in the molecular conformation and/or configuration. The results obtained for enol ethers[2] directly confirm the validity of this approach.

The assumption of additivity of the corresponding spectral increments is not sufficient for the determination of all the necessary parameters for compounds **1–7**. The data of Table 2 indicate that for molecules **1–3** the total shift $\Delta\lambda^{\text{cis-s-cis}}_{\text{trans-s-cis}}$ ranges from 16 nm to 26 nm. This value, however, includes both the shift due to the change of the configuration and the shift due to the formation of the intramolecular hydrogen bond, i.e. according to the additivity assumption

$$\Delta\lambda^{\text{cis-s-cis}}_{\text{trans-s-cis}} = \Delta\lambda^{\text{cis}}_{\text{trans}} + \Delta\lambda_{\text{H-bond}}.$$

As already mentioned, in the case of enamino derivatives the separation of two presumably additive components of

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†The isotope shift of this band upon deuteration of **1** is from 1586 cm^{-1} to 1575 cm^{-1}, $\nu D/\nu H = 0.95$ for the trans isomer.

Table 1. Wave numbers (cm $^{-1}$) of absorption band or β-alkylaminoacrylamides

No.		Compound	νNH^b free	νC=O^a trans	νC=O^a cis	νC=C^a cis	νC=C^a trans
1		MeNHCH=CHCONMe$_2$	3480	1657 1614	1641	1586	1577
2		MeNHCH=CHCONEt$_2$	3480	1649	1635	1586	1572
3		MeNHCH=CHCONiPr$_2$	3478	1647	1637	1577	1572
4		EtNHCH=CHCONMe$_2$	3460	1651	1637	1586	1576
5		EtNHCH=CHCONiPr$_2$	3460	1645	1635	1574	1559
6		iPrNHCH=CHCONMe$_2$	3446	—	1633	1582	—
7		t-BuNHCH=CHCONMe$_2$	—	1655	1634	1595	1585
8		Me$_2$NCH=CHCONMe$_2$		1650			1587
9		Et$_2$NCH=CHCONMe$_2$		1657			1588
10	trans	NCH=CHCONiPr$_2$		1652			1605
	cis				1642	1620	

^{a}C$_2$Cl$_4$, Cell thickness 1 mm, concentration 0.018 M.
^{b}CCl$_4$, Cell thickness 5 cm, concentration 0.0022 M.

Table 2. UV absorption experimental data for β-alkylaminoacrylamides

No.	λ_{max} (nm) and ϵ in cyclohexane trans-*s*-cis (**A**)	cis-*s*-cis (**B**)		$\Delta\lambda^{\mathbf{B}}_{\mathbf{A}}$	λ_{max} (nm) and ϵ in dioxane trans-*s*-cis (**A**)	cis-*s*-cis (**B**)		$\Delta\lambda^{\mathbf{B}}_{\mathbf{A}}$	λ_{max} (nm) and ϵ in methanol	
1	266^b	282	15,500	16^d	266	283	14,250	17	277	23,000
2	261	282	20,400	21	266	280	13,700	14	279	20,600
3	256	282	18,000	26	266	281	15,900	15	279	18,550
4	—	283^a	22,200	—	275^b	283	17,900	8	279	26,200
5	—	284^c	20,800	—	—	283	17,200	—	281	25,600
6	—	284^c	20,450	—	—	284	19,500	—	283	25,200
7	—	284^a	21,000	—	279^b	286	20,400	7	289	28,100
8	273	—	22,100	—	278	—	25,000	—	285	26,900
9	277	—	21,200	—	281	—	31,000	—	288	32,100

^{a}Due to the very fast isomerization of the pure trans isomer, only the max of the cis isomer could be recorded.
^{b}The position of λ_{max} (trans) presumably too high due to the fast isomerization.
^{c}Due to the very fast isomerization of not separable cis and trans isomers, only the λ_{max} of the final cis isomer could be recorded.
^{d}Value presumably too small due to fast isomerization.

Table 3. UV absorption experimental data for β-aziridinoacrylamides

Compound		λ_{max} (nm) and ϵ in cyclohexane		$\Delta\lambda^{\text{cis}}_{\text{trans}}$ (nm)	λ_{max} (nm) and ϵ in dioxane		$\Delta\lambda^{\text{cis}}_{\text{trans}}$ (nm)	λ_{max} (nm) and ϵ in methanol		$\Delta\lambda^{\text{cis}}_{\text{trans}}$ (nm)
10	trans	247	16,800	3	252	17,350	0	257	14,200	−6
	cis	250	6000		252	6900		251	9500	
		222^a	8600		223^a	8510		219^a	6640	

^{a}Absorption, probably due to a partial chromophore.

$\Delta\lambda^{\text{cis-}s\text{-cis}}_{\text{trans-}s\text{-cis}}$ was achieved indirectly. It was assumed that the value of $\Delta\lambda$ corresponding to the intramolecular H-bond is comparable with the shift due to the intermolecular H-bond for an appropriate conformation (*s*-cis). For the compounds **1–3** the appropriate data for trans configuration, i.e. $\Delta\lambda_{\text{H-bond}}$ (intermol) = $\lambda_{max}(CH_3OH) - \lambda_{max}(C_6H_{12})$ are 11, 18 and 23 nm respectively. Thus, according to previous ideas $\Delta\lambda^{\text{cis}}_{\text{trans}} = \lambda_{max}(\text{cis}) - \lambda_{max}(\text{trans}) - \Delta\lambda_{\text{H-bond}}$ one obtains 5,3 and 3 nm for **1**, **2** and **3** respectively.

Although the value of $\Delta\lambda^{\text{cis}}_{\text{trans}}$ determined in this way appears to be quite consistent, it follows from the indirect data and still needs a separate justification. This in principle can be given by the UV data for compounds **8–10**.

Unfortunately, for all secondary amines but aziridine the syntheses yield always the trans isomer only. As for aziridine derivatives, the comparison of the cis and trans isomers in aprotic solvents confirms the conclusion inferred from the spectra of the β-monoalkyl derivatives **1–7** in that $\Delta\lambda^{\text{cis}}_{\text{trans}}$ amounts to 3 nm for **10** in cyclohexane, zero nm in dioxane, and −6 nm in methanol. Thus the present estimate of $\Delta\lambda^{\text{cis}}_{\text{trans}}$ for β-*N*-monoalkyl derivatives gives 3–5 nm and the direct data for β-aziridine substituted compound **10** lead to $\Delta\lambda^{\text{cis}}_{\text{trans}}$ values ranging from −6 to +3 nm. The numerical values of $\Delta\lambda^{\text{cis}}_{\text{trans}}$ from **10** confirm the validity of an assumption concerning the value due to the intramolecular H-bond.

Ostercamp[3] and Kashima,[4] independently proposed a set of additive spectral increments for enaminoketones, suggesting that $\Delta\lambda^{\text{cis}}_{\text{trans}}$ = 10 nm and 16–26 nm respectively. Our data clearly indicate that these values are too high.

It can be concluded that the configuration changes of λ_{max} in the compounds studied in this series of papers are relatively small and do not affect appreciably the position of the $\pi \rightarrow \pi^*$ band maximum. On the other hand, as shown in a previous paper,[1] the change of conformation induces a substantial shift of λ_{max} i.e. $\Delta\lambda^{s\text{-cis}}_{s\text{-trans}} = 18$–$27$ nm. Thus $\Delta\lambda^{cis}_{trans}$ in comparison with $\Delta\lambda^{s\text{-cis}}_{s\text{-trans}}$ can be treated as almost negligible.

EXPERIMENTAL

Spectra

UV spectra were recorded using a Beckman Acta M-VI Spectrophotometer (spectrograde solvents) with cells of 1 cm path length. IR spectra were recorded on Beckman 4240 and Perkin-Elmer Model 325 instruments. In the range 3000–3600 cm^{-1} Unicam SP 700 apparatus, tungsten lamp, with 10 cm path length cells was used. NMR data were obtained on a JNM-4H-100 Jeol instrument with TMS as the internal reference when CCl_4, $CDCl_3$ or CD_3OD were used as solvents and with DSS in the case of aqueous solutions.

cis-3-Bromoacrylyl chloride

A mixture of stoichiometric amounts of cis-3-bromoacrylic acid[7] (15.1 g, 0.1 mole) and phosphorus trichloride (9.0 g, 0.067 mole) was heated at 65° for 30–45 min. The reaction was followed by means of NMR, but no traces of the trans isomer were detected. The distillation under vacuum (b.p. 56–58°/20 mm Hg) gave 10.1 g of cis-3-bromoacrylyl chloride (60%).

3-*Bromoacrylamides*

Ethereal solutions of cis-3-bromoacrylyl chloride (8.45 g, 0.05 mole) and the corresponding amine (0.1 mole) were mixed after cooling in an ice-water bath. Amine hydrochloride was immediately filtered off, the ether quickly evaporated and a small admixture of 3-*N*,*N*-disubstituted acrylic amides was removed on silica gel column. Usually a mixture of cis and trans isomers was obtained and it was used in further reaction without a separation and an additional purification.

3-N-*mono- and* 3-N,N-*Disubstituted acrylic amides*

The mixture of cis and trans isomers of 3-bromoacrylamides obtained in a previous step was mixed with 2-fold excess of anhydrous amine in an ethereal solution and left for 2 days at room temperature, amine hydrochloride was then removed and the ether evaporated. 7 was an exception; the reaction mixture had to be boiled for 4 hr and then it was worked up as for other compounds.

3-*Aziridinoacrylamide*

3-Aziridino-*N*,*N*-diisopropylacrylamide was obtained from the corresponding propiolic amide and aziridine (5-fold excess) in the methanolic solution. The reaction mixture was kept at room termperature for 24 hr, then methanol evaporated and the mixture of the cis and trans isomers separated on neutral alumina preparative plates, eluent ethyl acetate.

All crude compounds were purified by distillation or sublimation under high vacuum before measurements. Physical properties and analytical data for the obtained compounds are collected in Table 4.

Table 4. Physical properties and analytical data of the prepared compounds

No.		M.p. (°C) or b.p. (°C/mm Hg)		%N calcd.	%N found
1		66–67;	84/0.5	21.87	21.80
2		57–58;	108/0.4	17.94	17.84
3		68–69;	110/0.5	15.21	15.20
4		64–65		19.71	19.73
5			105/0.5	14.14	14.12
6			96/0.3	17.95	17.62
7		73–74		16.45	16.49
8		57–58		19.71	19.58
9		[a]		16.47	16.27
10	trans	—		14.28	14.35
	cis	—		14.28	14.20

[a] Molecular distillation under high vacuum.

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