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SYMMETRICALLY BIFURCATE HYDROGEN BONDING–IV

STERIC REQUIREMENTS IN SYMMETRICALLY HYDROGEN-BONDED BIS(β-ACYLVINYL)AMINES AND THEIR ISOMERS

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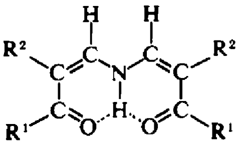
Abstract—The effect of the size and branching of alkyl substituents R^1 and R^2 on the formation of all possible stereoisomers of bis(β-acylvinyl)amines, $[R^1{-}CO{-}CR^2{=}CH]_2NH$, has been investigated. IR and NMR data show that steric requirements of these substituents and resonance stabilization of the *s-trans* system are the main factors determining the position of the dynamic equilibrium.

In the first paper of this series,[1] symmetrically bifurcate hydrogen bonding of the type (I) was found in a number of bis(β-acylvinyl)amines; at the same time, these compounds formed also unsymmetrical structures of type **2a** and **2b**.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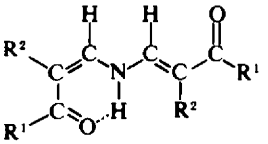
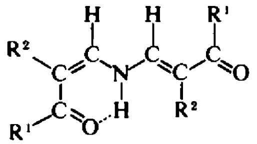
R^1 = alkyl; R^2 = H or alkyl


2a


2b

In order to determine the factors influencing the formation of the particular isomers we synthesized new suitably substituted bis(β-acylvinyl)amines **1**, **7** and **8**, and compared their IR and NMR spectra with those of the previously investigated[1] compounds **2** to **6** and **9**. The data obtained for equilibrated equimolar solutions clearly show that steric requirements of the alkyl substituents R and the resonance stabilization of the s-*trans* system are the main factors determining the dynamic equilibrium.

RESULTS

It has been noted[1] that the equilibrium between the isomeric forms depends on solvent and concentration. A detailed investigation reveals now, however, that in the absence of a catalyst the isomerization is extremely slow, particularly for solutions in non-polar solvents. Hydrochloric acid, which was shown[3] to catalyse the *cis-trans* isomerization of enamino ketones, was practically ineffective here but triethylamine has been found to enhance markedly the isomerization rate of bis(β-acylvinyl) amines. In a methanol solution the isomerization is noticeable without the use of catalysts but still takes several weeks to reach equilibrium at room temperature.

Details of the preparation of equilibrated mixtures of isomers are given in the Experimental section and the spectral data obtained presented in Tables 1 and 2, and Figs 1–3. Substance **1**, the mixture of isomers which was insoluble in tetrachloroethylene, was investigated in methanol (NMR) and methyl cyanide (IR) only and is discussed separately.

IR spectral assignments. As previously,[1] structural assignments derived from IR data are based on the "amide vinylogue band I" (AV-I),[4,5] i.e. the band due to a skeletal stretching vibration involving chiefly the C—O coordinate. For the three isomers occurring in non-polar solvents, i.e. **1**, **2a** and **2b**, five AV-I bands can normally be expected. Bands AV-I-*trans-s-cis* and AV-I-*trans-s-trans* differ strongly (see Table 1); the three different AV-I-*cis* bands were found[1] to overlap, however. While the AV-I-*cis* bands of **2a** and **2b** are obviously very close, that of **1** might in general be discernable, since the structural change affects directly the C=O fragment. Indeed, a prominent shoulder at ca 1666 cm^{-1} is visible on the high-frequency side of the band centred at 1660 cm^{-1} in the spectrum of a mixture of I (ca 30 per cent*), IIa and IIb (total ca 70 per cent*) of **2**. For the mixture containing 43%* of

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*Estimated by integration of signals in the NMR spectra.

Table 1. IR bands (cm^{-1}) of bis(β-acylvinyl)amines, [R^1—CO—CR^2=CH]$_2$NH in the 1700–1500 cm^{-1} region

			IR bands				
Comp.	R^1	R^2	AV-I[a] *trans-s-cis*	AV-I *cis* isomer I	AV-I *cis* isomer II	AV-I *trans-s-trans*	AV-II[b]
$1^{c,d,e}$	CH_3	H		1671			1598
$1^{d,e,f}$	CH_3	H		1663			1593
$1^{d,f}$	CH_3	H	1690	1661		1633	1598
$2^{c,d,e}$	iC_3H_7	H		1666			1595
2^c	iC_3H_7	H	1691	1666	1660 sh	1637 sh	1596
3^c	tC_4H_9	H	1688	1658	1650 sh		1594
4^c	C_2H_5	CH_3	1688	1665 sh	1660	1632	1591
5^c	nC_3H_7	C_2H_5	1680	1662 sh	1655	1631	1587
6^c	nC_4H_9	nC_3H_7	1678	1658 sh	1651	1629	1584
7^c	iC_3H_7	CH_3	1681	1665 sh	1659	1631	1585
8^c	iC_3H_7	iC_3H_7		1655 sh	1648	1621	1577
9^c	iC_4H_9	iC_3H_7		1657 sh	1650	1623	1581

[a] "Amide vinylogue band I" due to skeletal stretching vibration involving chiefly the CO co-ordinate; this nomenclature has been described.[4,5]

[b] Absorption band due to a complex vibration involving both skeletal stretch and N-H bending motion.

[c] 0·01 M solution in tetrachloroethylene.

[d] Non-equilibrated solution.

[e] Pure isomer I.

[f] 0·1 M solution in methyl cyanide.

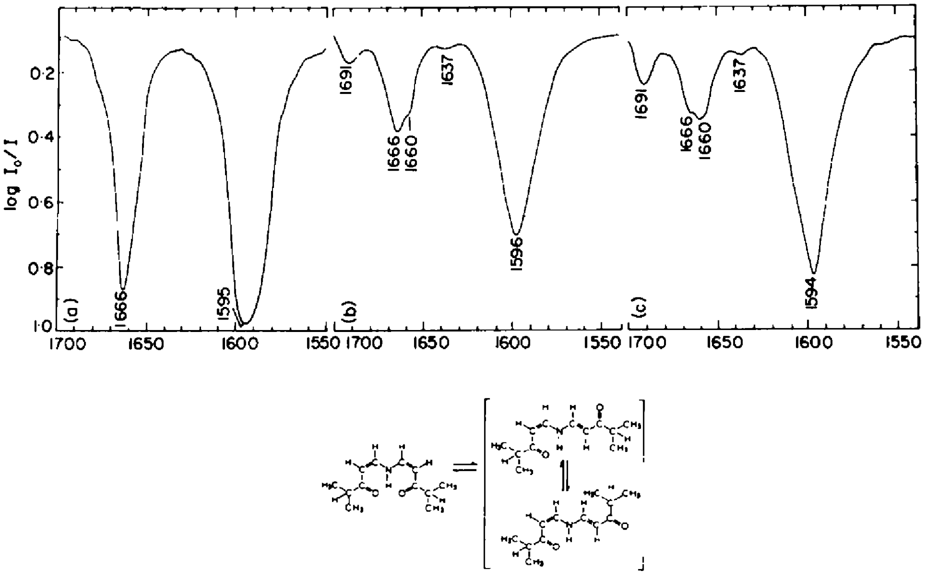

Fig 1. IR spectra of 0·01 M solutions of compound 2 in CCl$_4$: a, pure isomer I; b, equilibrium mixture of 43% I and 57% (IIa + IIb); c, a mixture of 30% I and 70% (IIa + IIb).

1 and 57%* of **2a** + **2b** the intensities of these two absorptions are reversed. These spectacular intensity changes accompanying the relatively small changes in the isomer population are easily explainable, since two *cis* fragments of the isomer I are created on isomerization in place of one such fragment of isomer **2** (**a** and/or **b**). Based on the assignments concerning (*sym-o,o'*-diacyldiphenyl)-amines[2] which exhibited the carbonyl bands of the mono- and bis-chelate distinctly separated (by 11-20 cm^{-1}) we ascribe here the lower frequency to the singly hydrogen-bonded carbonyl in **2a** and **2b** and the higher one to the carbonyl engaged in a weaker hydrogen bonding in the bifurcated system. This assignment is confirmed by

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*Estimated by integration of signals in the NMR spectra.

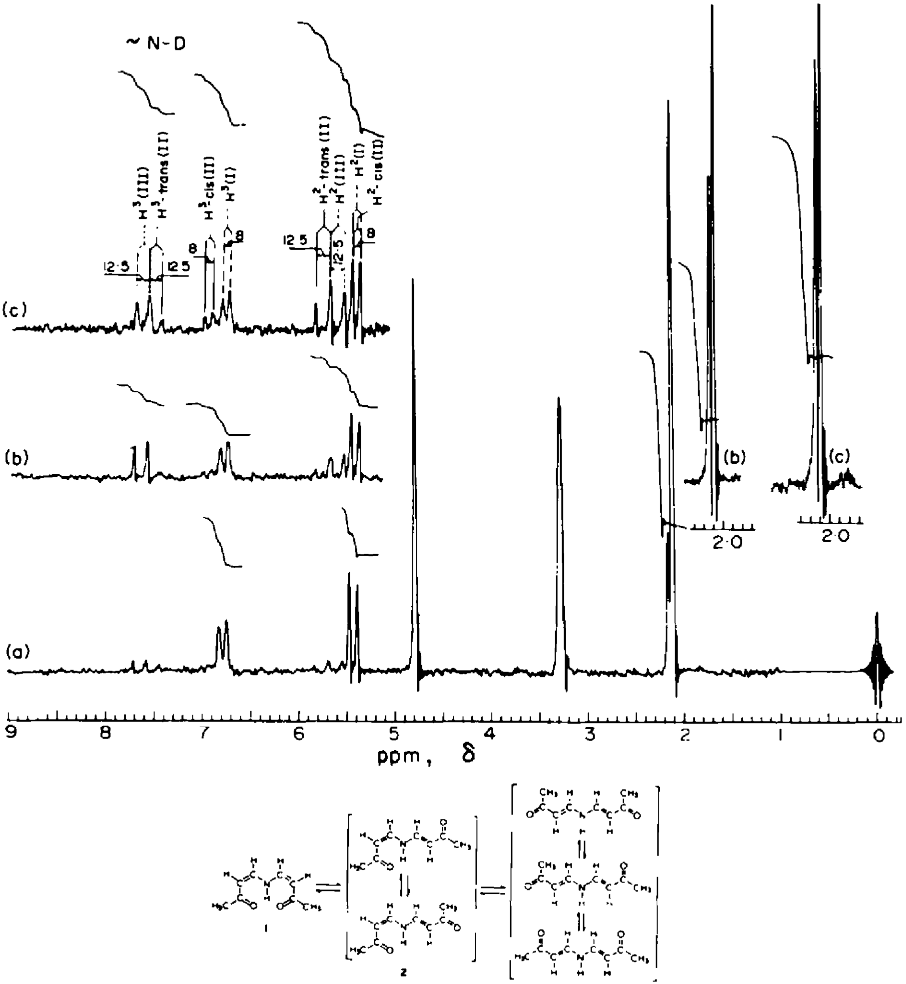

Fig 2. NMR spectra of ca. 0·1 M solutions of compound 1 in CD_3OD: a, freshly prepared solution of pure isomer I; b, the same solution after 24 hr; c, equilibrium mixture of isomers I, II and III in the same solution after 6 weeks.

the spectrum of the pure form I of 2 which exhibits a sharp, symmetric AV-I-*cis* band at 1666 cm^{-1}, i.e. exactly at the frequency of the above-mentioned shoulder (see Table 1 and Fig 1). A similar band pattern was found for 4 to 9 but the high-frequency shoulders were less pronounced owing to the lower molar fraction of the isomer I. For 3 consisting of a mixture of 41%* of 1 and 59%* of 2a + 2b the situation was similar to that concerning 2, shown in Fig 1b.

The spectra of 1 are not directly comparable because, due to its insolubility in non-polar solvents, they were measured in solutions in methyl cyanide; besides, the possibility of the polar forms 3a–c to occur in this polar solvent renders the possible assignments uncertain at this stage.

The IR data are presented in Table 1. Representative spectra are shown in Figs 1, 3.

NMR spectral assignments have been discussed in detail in Part I of this series.[1] New aspects are concerned with isomer 3 first observed in this work. Rotation in the *trans* part of the molecule was too rapid for the *s-cis* and *s-trans* conformers a–c to be observable; hence, all spectral changes discussed refer to geometrical isomerism, i.e. to *cis-trans* isomerization. The interpretation is simplified here owing to the exchange of the amine proton for deuterium occurring in methanol-d_4 used as a solvent.

Spectrum (a) (Fig 2) is that of almost pure isomer I of 1, the small admixture of 2 and/or 3 being manifested both by the new vinylic protons signals and by the splitting of the methyl signal. In the spectrum of the equilibrated mixture of the isomers of 1 (Fig 2c) the H^2 signal of isomer 2

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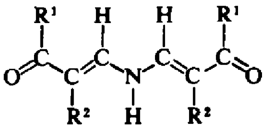
*Estimated by integration of signals in the NMR spectra.

Table 2. Main ^1H chemical shifts, coupling constants and isomer population of bis(β-acylvinyl)amines, $[R^1CO-CR^2=CH^3]_2NH^4$

						Chemical shifts δ[ppm]										Coupling constants [Hz]						
			Isomer			R^2				H^3				H^4		$^3J_{H^2H^3}$				$^3J_{H^3H^4}$		
		Concentration (M)	population [%]				II				II						II				II	
Substance	Solvent		I	II	III	I	*cis*	*trans*	III	I	*cis*	*trans*	III	I	II	I	*cis*	*trans*	III	I	*cis*	*trans*
1	CD_3OD	ca. 0·1	43	26	31	5·48	5·48	5·80	5·67	6·80	6·98	7·55	7·65	a	a	8·0	8·0	12·5	12·5	a	a	a
2	C_2Cl_4[b]	0·2	43	57	—	5·32	5·37	5·82	—	6·66	7·01	7·50	—	13·2	11·3	8·3	8·0	13·0	—	11·2	11·0	13·0
	CD_3OD[c]	ca. 0·1	70	20	10	5·45	5·45	5·90	5·22	6·82	7·05	7·50	7·65	a	a	8·3	8·3	13·0	12·5	a	a	a
3	C_2Cl_4[b]	0·1	41	59	—	5·50	5·50	6·02	—	6·60	6·92	7·42	—	13·4	11·6	8·3	8·3	12·5	—	11·6	11·2	12·5
4	C_2Cl_4[b]	0·2	6	94	—	1·95	1·95	1·89	—	6·35	6·69	7·22	—	d	11·3	—	—	—	—	11·2	10·7	12·3
	CD_3OD[c]	ca. 0·1	—	80	20	2·0	2·0	1·80	1·84	—	6·98	7·60	7·75	a	a	—	—	—	—	a	a	a
5	C_2Cl_4[b]	0·2	6	94	—	e	e	e	—	6·41	6·72	7·22	—	d	11·7	—	—	—	—	12·0	10·5	12·7
6	C_2Cl_4[b]	0·2	12	88	—	e	e	e	—	6·38	6·70	7·22	—	d	11·7	—	—	—	—	11·0	11·0	12·5
7	C_2Cl_4[b]	0·2	5	95	—	1·98	1·98	1·88	—	6·45	6·80	7·28	—	d	11·6	—	—	—	—	11·0	11·0	12·0
8	C_2Cl_4[b]	0·04	14	86	—	e	e	e	—	6·45	6·72	7·50	—	d	12·0	—	—	—	—	11·0	11·0	12·5
9	C_2Cl_4[b]	0·2	16	84	—	e	e	e	—	6·48	6·75	7·30	—	d	12·0	—	—	—	—	11·0	11·0	12·5

[a] Not measurable owing to exchange of H^4 for deuterium.
[b] 0·6% triethylamine added.
[c] Non-equilibrated mixture of isomers I, II and III.
[d] Not measurable owing to low concentration of this isomer.
[e] Not listed because of overlapping of signals due to different isomers.



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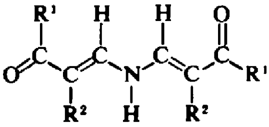

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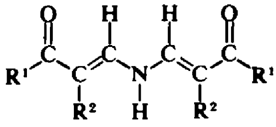


3c

overlaps with that of **1** but the H^3 signal of **2** is shifted downfield from that of **1** thus giving a key for the full interpretation of the spectrum. Indeed, since its integrated intensity must be equal to that of the signals of the *trans* part of **2** all signals can be assigned unambiguously by a simple arithmetical procedure to calculate the equilibrium $1 \rightleftharpoons 2 \rightleftharpoons 3$. Integration of the two methyl signals independently confirms the $1/2+3$ ratio calculated.

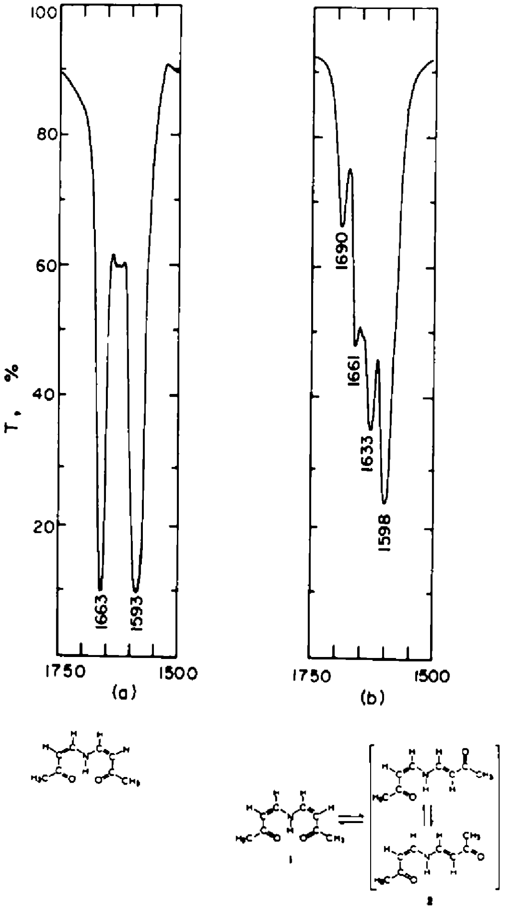


Fig 3. IR spectra of 0·1 M solutions of compound **1** in CH$_3$CN: a, pure isomer I; b, a mixture of isomers **1**, **2a** and **2b**.

NMR data are presented in Table 2. The representative spectra are shown in Fig 2.

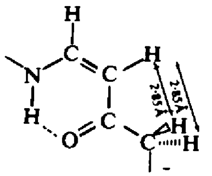
DISCUSSION

From simple model considerations, the strongest repulsive interactions in isomer I occur between substituents R^1 and R^2. For the reasons that follow from the subsequent discussion it will be practical to analyze the molecules with $R^2 = H$ (**1** to **3**) separately from those containing the R^2 alkyl substituent (**4** to **9**).

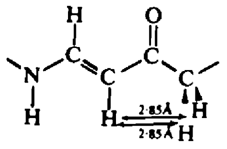
In order to estimate the steric interactions in bis(β-acylvinyl)amines a simplified model had to be used, since the molecules are far too complex to be liable to exact analysis. Equal bond lengths and angles were taken for both the *s-cis* and *s-trans* conformations and no allowance was made for their distortion (i.e. optimalization was not attempted). The following set of parameters was used: C—H 1·09 Å, C—N 1·38 Å, C=C 1·35 Å, =C—C= 1·47 Å, —C—C— 1·52 Å, C=O 1·22 Å.[6] The interatomic H—H distances were calculated for the most probable orientation of the methyl groups.

Within the first group of compounds, the interaction between R^1 and H^2 is practically identical in the isomers **1** and **2a** while strong additional repulsion between R^1 and α-hydrogen (H^3) occurs in **2b**. This is shown for the simple molecule of **1** but the same conclusion can be drawn in the case of **2** and **3**.

In consequence, the isomer ratio **1**/**2a** was close to unity (see Table 2) in the equilibrium mixtures for either **2** or **3**. Isomer **2b** occurred in a very small concentration for **2** (see Fig 1) and was not detectable with **3** owing to a very strong repulsion between R^1 and H^3. With **1**, in which steric interactions are much weaker, this isomer is formed



1



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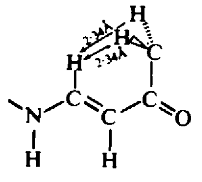


2b

readily (it exhibits the strongest IR carbonyl band at 1633 cm^{-1}; see Fig 3b) assisted by the greater resonance energy of the *s-trans* system. Although, the data for **1** obtained in a different solvent are not directly comparable, the above result seems to be convincing.

Substance **1** dissolved in a highly polar solvent (methanol) tends to form the polar *trans-trans* isomer **3**; at equilibrium, the concentration of this isomer amounts to 31% (see Table 2 and Fig 2). A similar result was obtained semiquantitatively for **2**.

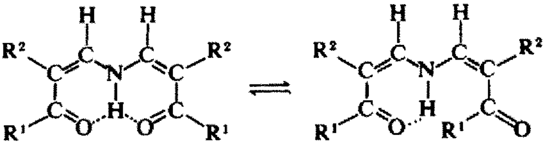
An entirely different situation comes about in compounds **4** to **9** bearing R^2 alkyl substituents. Repulsion between R^1 and R^2 in the isomer I increases drastically, as seen from the models of compounds containing at least two hydrogens at the first carbon atom in the substituents R^1 and R^2.

Again, isomer IIa offers no alternative in this respect (being even more strained due to the repulsion between R^2 and H-N) but, contrary to what was found for **1** to **3**, isomer IIb is less strained here, since the comparatively small decrease in the H-H distance is outweighed by the lesser number of non-bonded interactions, viz., only two between R^1 and H^3 as compared with four in IIa between R^1 and R^2. In addition, isomer IIb is stabilized by the greater resonance energy of the *s-trans* system. In consequence, **4** occurs almost exclusively as IIb, with a small admixture of IIa detectable by IR spectrum and a ca 6 per cent admixture of I (see Tables 1 and 2 and ref 1). This result parallels that for 2,3-dimethylbutadiene[7] which was found to exist entirely in the *s-trans* form. Also, in N,N-dialkyl enaminoketones containing similar structural elements the *trans-s-trans* isomer was found[8] predominant.

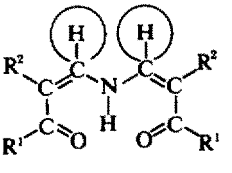
The results for the homologues of **4** are not much different, since the steric interactions in isomers **1**, **2a** and **2b**, though increased, remain in the same proportion as in the situation illustrated by the below model formula.

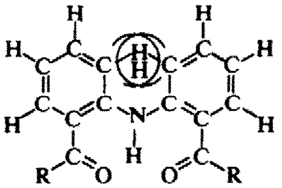
Conformational changes in the *trans* part of the molecule are of particular interest in view of the results on enamino ketones and aldehydes obtained previously.[4,5,9,10] According to those data, the amount of the *trans-s-trans* isomer (analogous to the *trans* part of IIb) decreased along with increasing steric requirement of R^1, provided R^2 = H; already with R^1 = i-Pr the strain was so strong as to render this isomer almost non-existent. Now it was shown in the case of **4** to **9** that despite strong steric hindrance not only is this rotamer able to exist but it even prevails if a still stronger hindrance occurs in the alternative conformation.

Finally, the possibility of conformational changes in the *cis* parts of the molecule e.g. isomerization of I into the *cis-s-cis–cis-s-trans* isomer will briefly be discussed.



Isomerization similar to the above was found[2] in (*sym-o,o'*-diacyl)-diphenylamines and the instability of the double chelate was attributed to repulsion of the aromatic hydrogens. In bis(β-acylvinyl)amines there is virtually no repulsion between the hydrogens occupying a similar position;



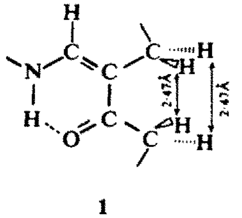


hence the stabilization of I by the bifurcate hydrogen bonding can be expected sufficient to oppose the tendency for rotational motion. As, in addition, no experimental data indicating the presence of the *cis-s-trans* structure were obtained, the conformational changes in the *cis* part can be excluded from further consideration.

EXPERIMENTAL

Most compounds (**2** to **6** and **9**) studied in the present work were described earlier.[1] The constants and analyses of new compounds, which were obtained in a similar manner, are given in Table 3.

Equilibrated mixtures of isomers were obtained by keeping at 90° 0·2 molar solutions in tetrachloroethylene



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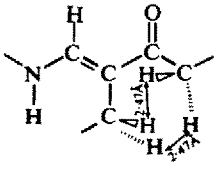
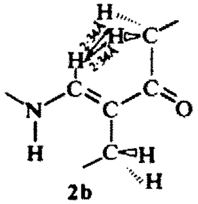


2a



2b

Table 3.

			Analyses					
		M.p.		calc. (%)			found (%)	
Compound	Formula	(°C)	C	H	N	C	H	N
1	$C_8H_{11}NO_2$	132–133	62·74	7·19	9·15	62·95	7·21	9·15
7	$C_{14}H_{23}NO_2$	92–95	70·89	9·70	5·91	70·82	9·79	5·98
8	$C_{18}H_{31}NO_2$	121–123	73·71	10·58	4·78	73·79	10·30	4·80

containing 0·6% of triethylamine until no further spectral changes occurred. For IR measurements these solutions were diluted to a 0·01 M concentration just before recording the spectra; under these conditions practically no changes of the population of isomers occur.

IR spectra were measured on a VEB Carl Zeiss-Jena UR-20 spectrometer equipped with sodium chloride optics and calibrated with polystyrene.

NMR spectra were recorded in tetrachloroethylene and in methanol on a Varian HA-60/IL and on a JEOL JNM-4H-100 spectrometers.

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REFERENCES

[1] J. Dąbrowski and Z. Świstun, *J. Chem. Soc.* (*B*), 818 (1971)

[2] Part III, J. Dąbrowski, Z. Świstun and U. Dabrowska, *Tetrahedron* **15**, 2257 (1973)

[3] K. Herbig, R. Huisgen and H. Huber, *Chem. Ber.* **99**, 2546 (1966).

[4] J. Dąbrowski, *J. Mol. Structure*, **3**, 227 (1969)

[5] J. Dąbrowski and U. Dąbrowska, *Chem. Ber.*, **101**, 3392 (1968)

[6] A. J. Sadlej and J. Dąbrowski, *J. Mol. Structure* **7**, 1 (1971), and references therein.

[7] C. F. Aten, L. Hedberg and K. Hedberg, *J. Amer. Chem. Soc.*, **90**, 2463 (1968).

[8] H. Dodziuk, K. Kamieńska-Trela and J. Dąbrowski, *Roczniki Chem.*, **44**, 393 (1970)

[9] J. Dąbrowski, K. Kamieńska-Trela, *Spectrochim. Acta*, **22**, 211 (1965); *Roczniki Chem.*, **38**, 1121 (1964)

[10] L. Kozerski and J. Dąbrowski, *Org. Magn. Resonance* (in press).