References and Notes

(1) For part III in this series see P. Kroneck, *J Am. Chem. Soc.*, **97**, 3839 (1975).
(2) Abstract from Ph.D. Thesis, V. Vortisch, Universität Konstanz, 1975.
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Electronic Spectra of α,β-Unsaturated Carbonyl Compounds. I. An Evaluation of Increments Characteristic of Changes in Configuration (cis/trans) and Conformation (s-cis/s-trans) Based on Direct Observation of the Isomerization of Enamino Aldehydes and Ketones

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Received June 25, 1975

Abstract: The trans,s-trans → cis,s-cis and trans,s-cis → cis,s-cis isomerization of enamino aldehydes and ketones has been followed directly by uv measurements. This enabled us to assign unambiguously the absorption maxima of those three configuration–conformation combinations and, consequently, to evaluate the spectral increments characteristic of the cis ⇌ trans and of the s-cis ⇌ s-trans isomerization. Three such calculation paths leading to identical results are described. The increments thus obtained are: 18 nm $\leq \Delta\lambda^{\text{s-cis}}_{\text{s-trans}} \leq$ 27 nm and -7 nm $\leq \Delta\lambda^{\text{cis}}_{\text{trans}} \leq 0$ nm. A set of spectral increments complementing the basic system of Woodward and the Fiesers has been proposed.

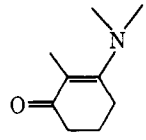
The relationship between the configuration and conformation of α,β-unsaturated carbonyl compounds and the frequency and intensity of their uv absorption has been the subject of numerous investigations during the last three decades. Although many valuable data were obtained, one serious difficulty remained until now: in order to obtain a given conformation, the parent reference compound had to be modified by a ring closure or by introducing bulky substituents. As a consequence, the contributions of (1) the conformational transformation and (2) the electronic properties of the new substituents or ring fragments to the frequency and intensity changes could not be separated. This point has often been ignored or inadequately treated.

For example, Ostercamp,[1] who investigated 78 enamino carbonyl compounds, attempted to circumvent this difficulty by making use of the averaged substituent increments known from other classes of α,β-unsaturated ketones, a procedure obviously suffering from some uncertainty. As a matter of fact, the differences between the calculated and experimental λ_{max} values cited by Ostercamp oscillate within the limits of 23 to -28 nm. Applied to the compounds studied in the present work, Ostercamp's system gives deviations of -15 to 19 nm. Apart from the ambiguities arising from the use of the averaged increments, some inadequacies of Ostercamp's scheme result from neglecting, in the case of conformationally labile compounds, the actual populations of rotamers. Ostercamp relied on earlier papers in which suppositions as to conformational uniformity of such compounds were expressed. However, in some newer papers, a simultaneous occurrence of two rotamers has been experimentally detected.[2] It appears that in a few cases the cis configuration was ascribed by Ostercamp to compounds which in solutions in methanol can be shown (by NMR) to exist predominantly in the trans form.

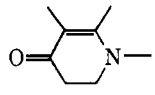
In a recent paper by Bienvenue,[3] the populations of the s-cis and s-trans rotamers of several enones were calculated assuming constant intensities of the infrared carbonyl stretching bands in a homologous series. The values thus obtained were then used for calculations based on additivities of the ultraviolet absorption curves in order to evaluate the shift of the absorption maximum characteristic of the s-trans → s-cis isomerization. The $\Delta\nu$ = 2400 cm^{-1} (11 nm) value thus obtained, though seemingly correct, was evaluated by using several assumptions whose validities are not obvious, e.g., constancy of ir $\nu_{C=O}$ intensities, independence of the rotamer populations on the concentration of solutions, etc.

Another problem often encountered concerns the application of Braude's[4] equation describing the dependence of the molar absorption coefficient on the dihedral angle between the plane of the carbonyl group and that of the double bond in a given conformation. Many attempts to calculate this angle in molecules bearing substituents of different steric requirements disregarded the fact that not only the angle in a given rotamer but also the equilibrium between the rotamers changes upon changing the bulkiness of the substituent. Since the closely positioned uv maxima due to the s-cis and s-trans rotamers are practically always unresolved, the data thus obtained have rarely any real meaning.[5,6]

Kashima, Yamamoto, and Sugiyama[7] evaluated the differential shift λ_{max} for the cis-trans configurational change by comparing spectra of compounds having similar substituents, e.g.



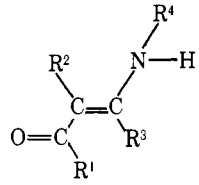
trans-s-trans



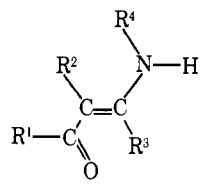
cis-s-trans

The analogy was purely formal, however. In fact, the geometry of the two types of molecules must be rather different since the heterocyclic ring contains the sp^2 (or nearly so) hybridized nitrogen atom in place of the sp^3 carbon in the carbocyclic ring. For that reason the $\Delta\lambda^{cis}_{trans}$ values of 16–28 nm observed can hardly be ascribed to the cis-trans izomerization alone. Some other questions related to this paper will be dealt with in the Discussion.

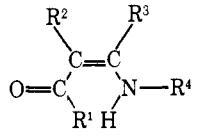
The results put forward in the present paper are more straightforward, particularly in the part concerning β-monoalkylamino-substituted α,β-unsaturated aldehydes and ketones **1–19,** which are capable, in principle, of existing in all the forms resulting from both the cis (i.e., *Z*) ⇌ trans (*E*) and s-cis (*Z*) ⇌ s-trans (*E*) isomerization.



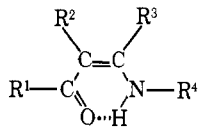
I, trans, s-trans (*EE*)



II, trans, s-cis (*EZ*)



III, cis, s-trans (*ZE*)



IV, cis, s-cis (*ZZ*)

R^1, R^2, R^3 = H or alkyl; R^4 = alkyl

While III has never been observed, the interconversion I → IV and II → IV could be monitored spectroscopically in a number of cases, thus enabling us to ascribe unequivocally the spectral characteristics to these conformations and configurations. On this basis, the Δλ values corresponding to the s-trans → s-cis and trans → cis isomerization could be calculated.

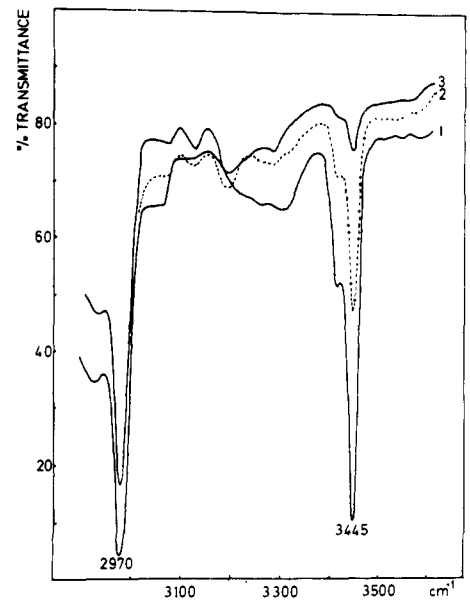


Figure 1. The time-dependent changes in the ir spectrum of 3-isopropylamino-2-propen-1-one (**2**) recorded in CCl_4 in the 3000–3500-cm^{-1} region. (1) Spectrum taken immediately after dissolving of the compound; (2) after 5 min; (3) after 24 h.

Of the remaining compounds **20–52,** the spectra of which will be discussed in the light of the results obtained for the former group **1–19,** a part are rigid both in the configurational and conformational aspect (**22, 24–28,** and **47–49**), **23** has a rigid s-cis conformation but undergoes a cis-trans isomerization, **29–46** have the trans configuration, **29–42** being at the same time conformationally labile while **43–46** retain the s-cis conformation because of the steric requirement of the C-alkyl substituents, and **20–21** retain both the cis configuration and the s-cis conformation for the same reason. Compounds **50–52,** the isomerization of which has not been followed by uv spectra, have been included in order to obtain the increment for the chelated primary amino group.

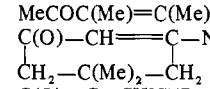
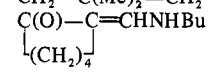
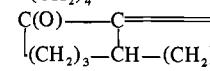
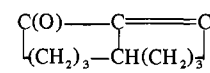
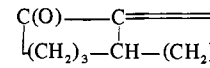
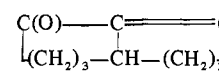
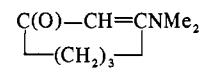
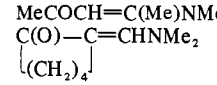
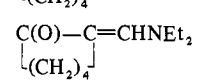
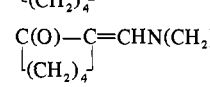
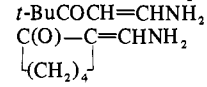
Results and Discussion

Uv spectral data are presented in Table I, and spectra particularly important for the discussion are reproduced in Figures 1-6.

Solid 3-isopropylamino-2-propen-1-one (**2**) has the trans (*E*) configuration and, when dissolved in nonpolar solvents, mainly the s-trans (*E*) conformation. The ir spectrum of **2** recorded immediately after the dissolution in carbon tetrachloride (Figure 1, curve 1) clearly indicates that, at the first moment the trans,s-trans system predominates. It was shown[2e] that for crystalline trans (*E*) compounds a spontaneous trans,s-trans (*EE*) ⇄ cis,s-cis (*ZZ*) isomerization takes place in nonpolar solutions. The ir spectrum (Figure 1, curve 3) shows that, at very low concentrations, the final equilibrium is shifted almost completely toward the cis,s-cis (*ZZ*) form. The monitoring of this process with the aid of uv spectra in a still more dilute solution (Figure 2) makes it possible to assign the disappearing band at 264 nm to the trans,s-trans (*EE*) isomer and the increasing one at 306 nm to the cis,s-cis (*ZZ*) isomer.

Consistent results were obtained for the other acroleins **1**,[8,9] **3,** and **4.** A similarly distinct trans,s-trans (*EE*) to

Table I. Ultraviolet Absorption Experimental Data for Enamino Aldehydes and Enamino Ketones in Cyclohexane, Methanol, and Water and Calculated Positions

		cis,s-cis (in C_6H_{12})				trans (in C_6H_{12})							
		λ_{max}, nm		Δ,		λ_{max}, nm		Δ,		λ_{max}, nm (ε)			
No.	Compd	Obsd	Calcd[a]	nm	ε	Obsd	Calcd[a]	nm	ε	In CH_3OH		In H_2O	
1	HCOCH=CHNHEt	306	306	0	14 200	265	266	−1	28 000	280	(31 000)	282	(36 400)
2	HCOCH=CHNH-*i*-Pr	306	306	0	14 100	264	266	−2	28 000	281	(35 600)	285	(39 300)
3	HCOCH=CHNH-*t*-Bu	305	306	−1	15 100	269	266	+3	30 000	285	(35 000)	286	(40 200)
4	HCOCH=CHNH-*c*-C_6H_{11}	308	306	+2	14 500	265	266	−1	29 000	284	(33 700)	285	(36 800)
5	EtCOC(Me)=CHNHMe	316	317	−1	11 300	282	282	0	21 000	300	(23 200)	304	(25 000)
6	PrCOC(Et)=CHNHMe	316	317	−1	12 300	282	282	0	23 300	300	(23 900)	306	(24 400)
7	MeCOCH=CHNHMe	300	301	−1	15 100					292	(21 100)	294	(26 100)
8	MeCOCH=CHNHEt	299	301	−2	15 200	278	281	−3		296	(22 400)	296	(27 200)
9	MeCOCH=CHNH-*i*-Pr	300	301	−1	17 100					299	(23 000)	298	(28 000)
10	MeCOCH=CHNH-*t*-Bu	302	301	+1	16 300					309	(24 500)	305	(29 700)
11	MeCOCH=CHNH-*c*-C_6H_{11}	303	301	+2	16 100	282	282	0		303	(21 500)	302	(25 900)
12	*i*-PrCOCH=CHNHMe	299	301	−2	17 200					299	(21 100)	300	(22 100)
13	*i*-PrCOCH=CHNHEt	300	301	−1	16 800	280	281	−1		304	(20 100)	304	(22 300)
14	*i*-PrCOCH=CHNH-*i*-Pr	300	301	−1	16 300	282	282	0		304	(20 100)	304	*b*
15	*i*-PrCOCH=CHNH-*t*-Bu	300	301	−1	17 400					312	(23 100)	312	(23 100)
16	*i*-PrCOCH=CHNH-*c*-C_6H_{11}	304	301	+3	17 300					311	(21 300)	310	*b*
17	*t*-BuCOCH=CHNHMe	300	301	−1	16 400					303	(19 400)	308	(21 300)
18	*t*-BuCOCH=CHNHEt	300	301	−1	17 200					306	(21 200)	310	(22 800)
19	*t*-BuCOCH=CHNH-*c*-C_6H_{11}	303	301	−1	15 900	287	282	+5		312	(20 800)	315	(24 100)
20	MeCOCH=C(Me)NHPr	306	306	0	15 500					312	(17 800)	312	(22 100)
21	MeCOC(Me)=C(Me)NHMe	322	322	0	13 000					330	(14 500)	328	(10 100)
22						271	267	+4	*b*	291	(32 800)	294	*b*
23		325	322	+3	13 000					330	(18 900)	329	(25 000)
24		306	308	−2	9 500					322	(13 600)		
25		325	327	−2	11 200					334	(15 000)	333	(11 400)
26		327	327	0	10 200					335	(16 300)	335	(12 800)
27		328	327	+1	11 700					337	(14 700)	337	(15 100)
28						280	279	+1	27 500	298	(33 000)		
29	HCOCH=CHNMe$_2$					272	274	−2	29 600	285	(35 500)	289	(36 600)
30	HCOCH=CHNPr$_2$					276	278	−2	32 400	288	(40 700)	292	(44 400)
31	HCOCH=CHN-*i*-Pr$_2$					276	278	−2	31 300	289	(38 400)	291	(43 100)
32	EtCOC(Me)=CHNEt$_2$					294	295	−1	23 200	306	(26 900)	314	(28 900)
33	HCOCH=C(Me)NMe$_2$					290			21 600	301	(35 300)		
34	MeCOCH=CHNMe$_2$					288			21 800	300	(28 000)	304	(29 200)
35	MeCOCH=CHNEt$_2$					292			21 200	305	(27 300)	306	(30 500)
36	MeCOCH=CHN-*i*-Pr$_2$					296			22 100	309	(28 300)	312	(30 200)
37	EtCOCH=CHNMe$_2$					288			21 300	303	(25 300)	306	(29 400)
38	EtCOCH=CHNEt$_2$					292			22 700	307	(26 000)		
39	PrCOCH=CHNMe$_2$					289			24 500	305	(27 000)	307	(28 600)
40	*i*-PrCOCH=CHNMe$_2$					290	292	−2	21 800	306	(26 100)	310	(29 200)
41	*i*-PrCOCH=CHNEt$_2$					294	295	−1	23 200	307	(26 000)	313	(27 200)
42	*i*-PrCOCH=CHN-*i*-Pr$_2$					296	295	+1	22 300	313	(28 200)	316	(27 600)
43	*t*-BuCOCH=CHNMe$_2$					292	292	0	23 600	311	(26 400)	317	(29 100)
44	*t*-BuCOCH=CHNEt$_2$					297	295	+2	21 900	316	(26 000)	320	(27 900)
45	*t*-BuCOCH=CHN-*i*-Pr$_2$					297	295	+2	22 600	316	(28 300)	320	(29 600)
46	MeCOCH=C(Me)NMe$_2$					293	293	0	24 000	310	(28 700)		
47						309	309	0	14 800	334	(19 200)	336	*b*
48						311	312	−1	17 200	334	(21 500)	336	*b*
49						312	312	0	17 200	334	(21 500)		
50	MeCOCH=CHNH$_2$	282	282	0	12 100					291	(18 600)		
51	*t*-BuCOCH=CHNH$_2$	282	282	0	10 400					294	(13 600)		
52		302	303	−1	10 000					316	(16 800)		

[a] Results obtained from the additivity scheme by using the set of the spectral parameters of Table III. [b] Solubility too low to obtain quantitative data.

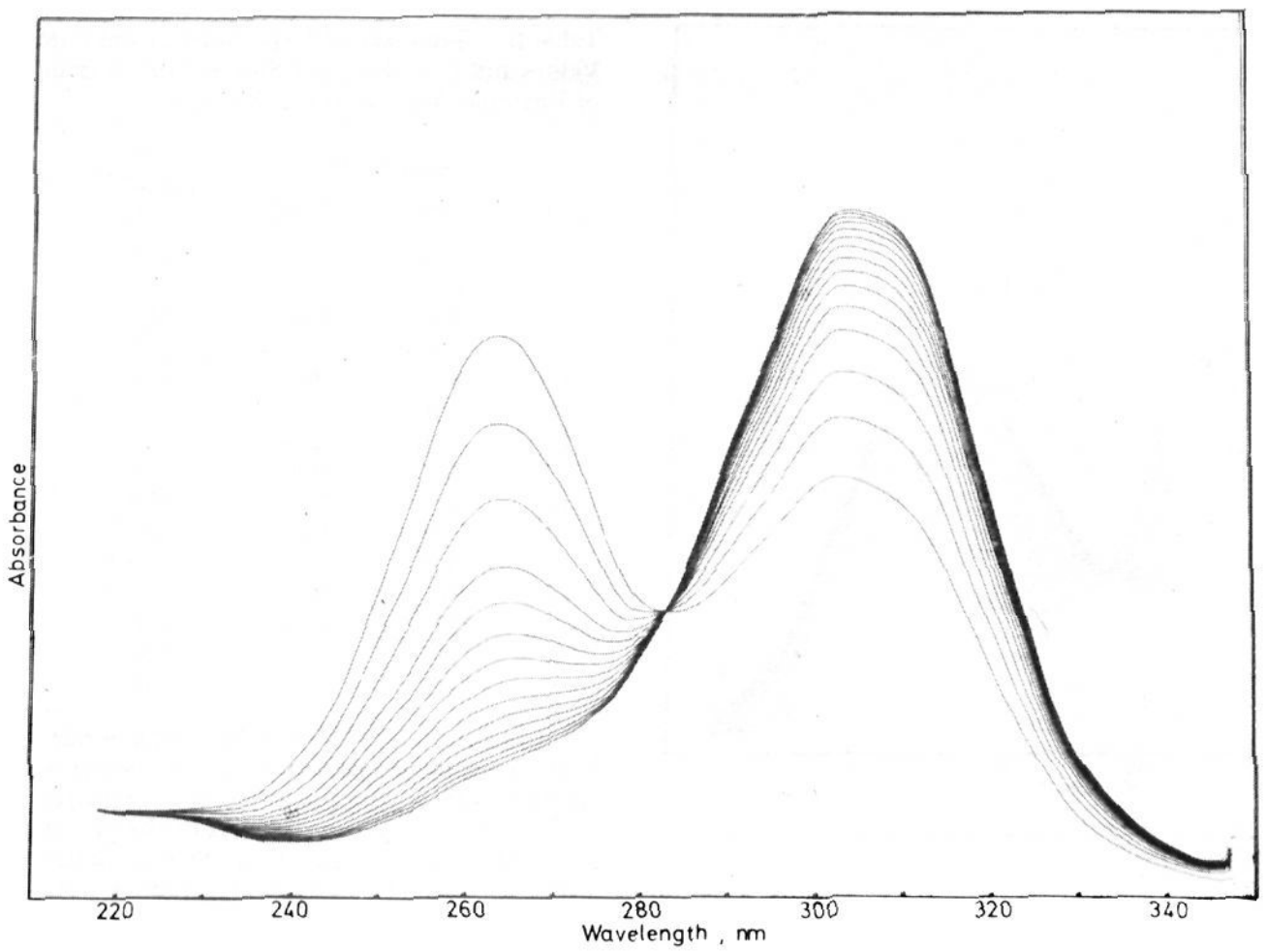


Figure 2. The time-dependent changes in the uv spectrum of 3-isopropylamino-2-propen-1-one (**2**) in cyclohexane.

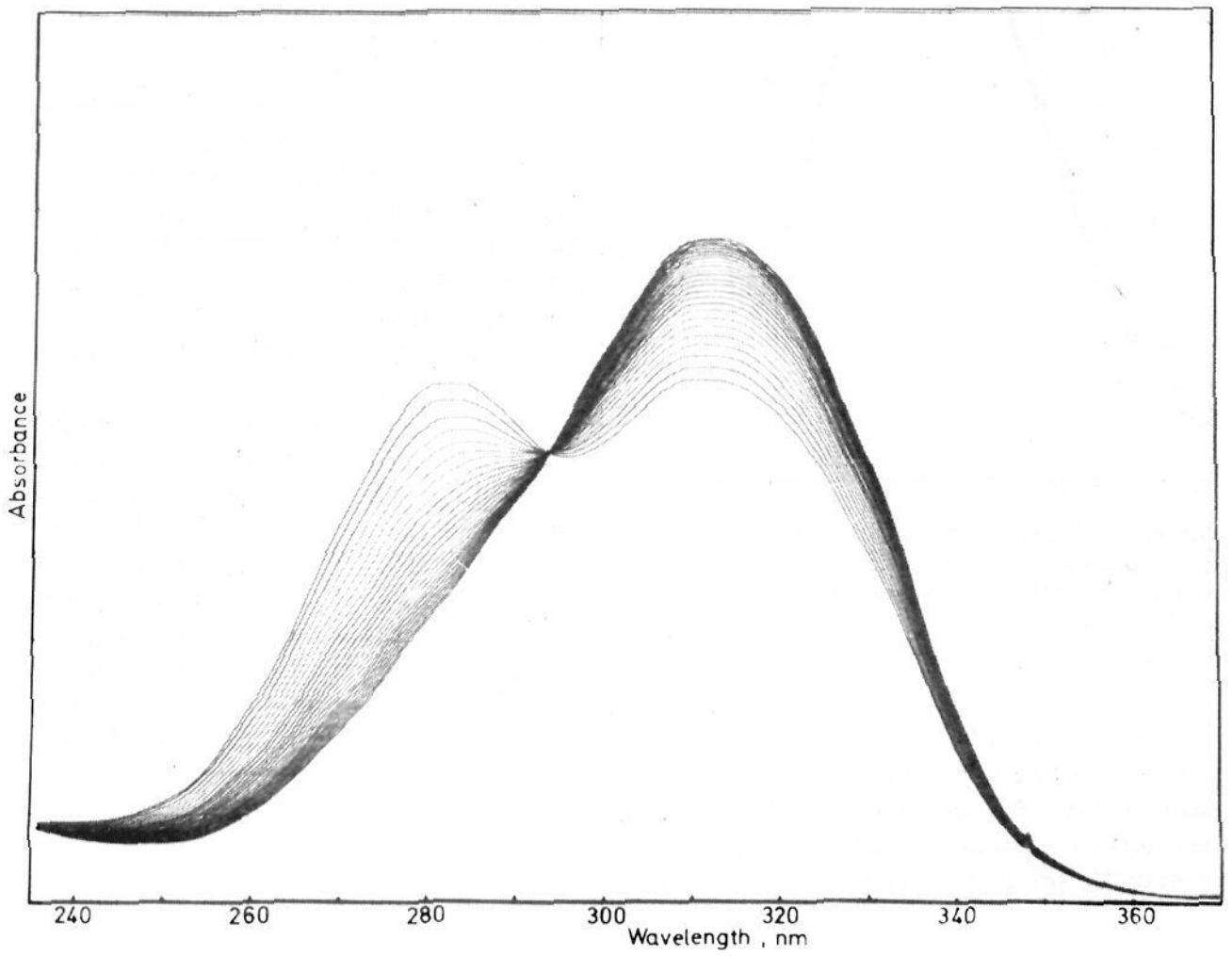


Figure 3. The time-dependent changes in the uv spectrum of 2-ethyl-1-methylamino-2-hexen-3-one (**6**) in cyclohexane.

cis,s-cis (ZZ) interconversion is also observed in ketones **5** and **6** (Figure 3), the differential values $\Delta\lambda_{cis,s\text{-}cis}^{trans,s\text{-}trans}$ being but slightly lower than those for **1–4.**

The shift of the absorption maximum of **2,** $\Delta\lambda_{cis,s\text{-}cis}^{trans,s\text{-}trans}$ = 42 nm, is composed of the contributions originating from a simultaneous change in configuration from trans (E) to cis (Z) and in conformation from s-trans (E) to s-cis (Z); automatically, the contribution of the intramolecular hydrogen bond is also included. Since the main object of this study is the determination of characteristic uv absorption maxima for structures I–IV, attempts will be made to reveal these partial contributions in order to make it possible to calculate those values which for any reason cannot be determined directly.

Spectral changes due to the trans ⇌ cis isomerization not accompanied by alteration of the conformation could best be observed in the case of 4,4-dimethyl-1-cyclohexylamino-1-penten-3-one (**19**). Since the *trans-tert*-butyl enamino ke-

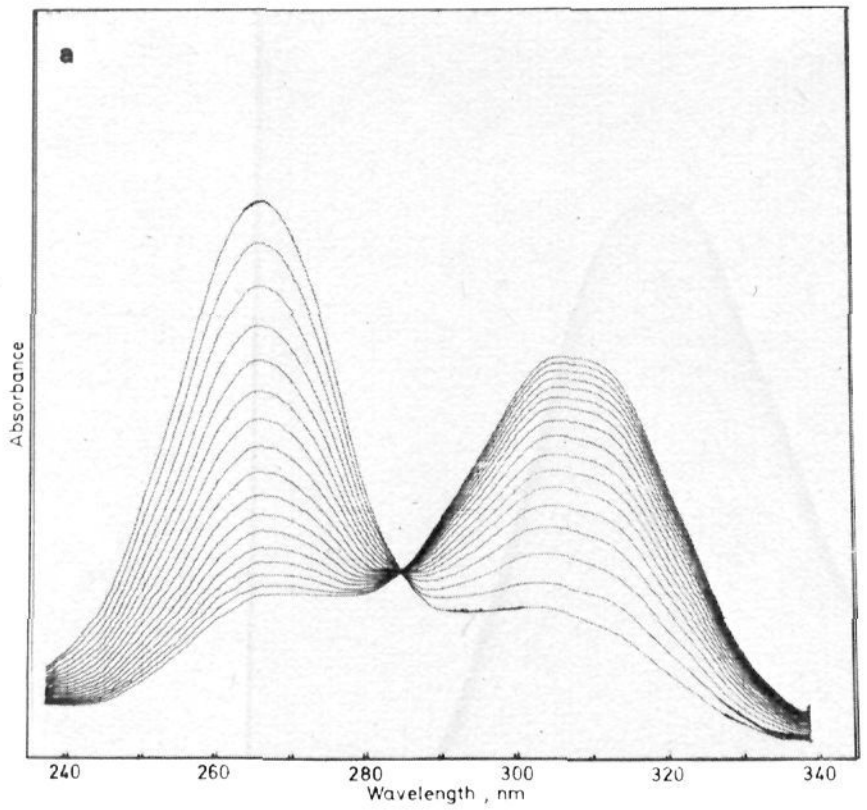


Figure 4. The time-dependent changes in the uv spectrum of (a) 3-cyclohexylamino-2-propen-1-one (**4**) in cyclohexane; (b) 4,4-dimethyl-1-cyclohexylamino-1-penten-3-one (**19**) in cyclohexane. The last spectrum in (b) was taken after 24 h.

tones have been shown to have the s-cis conformation,[2b,d] the maximum at 287 nm on the initial uv curve of the solution of the trans isomer[10] of **19** in cyclohexane (Figure 4b) corresponds to the trans,s-cis isomer II. The isomerization into the cis,s-cis isomer IV produces a spectral shift to 303 nm; i.e., the differential shift $\Delta\lambda^{cis,s\text{-}cis}_{trans,s\text{-}cis}$, which includes automatically the contribution of the intramolecular hydrogen bond now formed, amounts to 16 nm. By subtracting this value from $\Delta\lambda^{cis,s\text{-}cis}_{trans,s\text{-}trans} = 43$ nm obtained for the structurally most closely related aldehyde **4** (Figure 4a), a $\Delta\lambda$ value for the pure s-trans → s-cis isomerization can be estimated as $\Delta\lambda^{s\text{-}cis}_{s\text{-}trans} = 27$ nm.

Similar calculations can be carried out for 4-methyl-1-ethylamino-1-penten-3-one (**13**) and 4-methyl-1-isopropylamino-1-penten-3-one (**14**). The pure solid trans isomer of **13** was isolated and, after dissolution in methanol-d_4 at −50 °C, was shown by low-temperature NMR measurements to contain ca. 80% of the s-cis rotamer. Since the population of this rotamer is known to increase strongly in solutions in

Table II. Summary of Experimental and Calculated λ_{max} (C_6H_{12}) Values and Calculated $\Delta\lambda$ Shifts Characterizing Structural Changes of Enamino Aldehydes and Ketones

Compd	λ_{max} (C_6H_{12}), nm		$\Delta\text{-}\lambda_{total}$,[a] or [b] nm	$\Delta\text{-}\lambda^{cis}_{trans}$,[c] nm	$\Delta\lambda^{s\text{-}cis}_{s\text{-}trans}$,[d] nm
	cis	trans			
1	306	265	41[a]		21, 18, 21, 19, 24
8	299	279	20[b,e]	−3	
12	299	276[f,g]	23[b]	0	
13	300	280	20[b]	−3	
17	300	278[g]	22[b]	−1	
18	300	283[g]	17[b]	−6	
2	306	264	42[a]		25
14	299	282	17[b]	−6	
4	308	265	43[a]		22, 27
11	303	282	21[b,e]	−2	
19	303	287	16[b]	−7	
23	325	303[g]	22[b]	−1	
5	316	282	34[a]		
6	316	282	34[a]		

[a] λ(cis,s-cis, intramolecular hydrogen bond) − λ(trans,s-trans). [b] λ(cis,s-cis, intramolecular hydrogen bond) − λ(trans,s-cis). [c] Obtained by subtracting the differential hydrogen bond shift $\Delta\lambda^{H_2O}_{C_6H_{12}} = 23$ nm (see text) from the data of the preceding column. [d] $\Delta\lambda^{s\text{-}cis}_{s\text{-}trans} = \Delta\lambda^{a} - \Delta\lambda^{b}$. [e] Ca. 20% admixture of the s-trans conformation (see ref 17 on the effect of admixture on λ_{max}). [f] Calculated according to the first indirect scheme. [g] Calculated according to the second indirect scheme.

nonpolar solvents, the initial uv curve of the solution of **13** or **14** in cyclohexane corresponds practically to the trans,s-cis isomer II.[11,12] By comparing **13** and **14** with the related acrolein derivatives **1** and **2**, respectively, the relevant differential shifts have been obtained (see Table II).

Similarly, compounds **8** and **11** which were also isolated as pure trans isomers have been compared with **1** and **4**, respectively, and yielded differential shifts but slightly deviating from those discussed above, in spite of a considerable admixture of the trans,s-trans isomer I in the initial solutions in cyclohexane (see Table II and the discussion on the role of admixtures).

The $\Delta\lambda^{s\text{-}cis}_{s\text{-}trans}$ value for 4-methyl-1-methylamino-1-penten-3-one (**12**) had to be obtained in a more indirect way as the pure trans isomer was not available. The time-dependent changes in the uv spectrum of the solution of **12** in cyclohexane (Figure 5) are much smaller than was the case with **13, 14,** and **19.** It follows from the parallel NMR and ir measurements that the initial curve exhibiting a broad maximum at 296 nm corresponds to a mixture of ca. 70% of the *cis,s-cis* (*ZZ*) *isomer IV and only 30% of the trans,s-cis* (*EZ*) isomer II. Hence, the λ_{max} of the latter cannot be determined directly. Fortunately, this isomer predominates at equilibrium in a dilute aqueous solution, thus enabling us to evaluate the position of its absorption maximum in cyclohexane by subtracting the solvent induced shift value $\Delta\lambda^{H_2O}_{C_6H_{12}}$ from the λ_{max} (H_2O) 300 nm obtained for that aqueous solution. A few remarks have to be added here. Although the equilibrium mixture in the aqueous solution contains ca. 20% of the cis,s-cis (*ZZ*) isomer IV[13] and more than 15% of the trans,s-trans (*EE*) isomer I,[14] the λ_{max} (H_2O) can be assumed to reflect rather closely the true maximum of the remaining ≤65% of the trans,s-cis (*EZ*) isomer II. Indeed, measurements on especially prepared mixtures[15,16] of compounds having similar relative spectral characteristics showed the maximum of the main component to be insensitive toward the addition of 20% of another component whose λ_{max} lay at wavelengths higher by 20 nm and whose ϵ_{max} was by ca. one-third smaller[17] (simulation of addition of isomer IV to isomer II). Since the contribu-

Table III. Constants for Calculation of Absorption Maxima of Enamino Aldehydes and Ketones, $O{=}C(R^1){-}C(R^2){=}C(R^3){-}NR^4R^5$

Substituents and structural features	cis,s-cis[a]	trans,s-cis	trans,s-trans
Aldehyde	220	*b*	220
Ketone	215	215	215
NH_2	67	*b*	*b*
NHMe	86	63	46
NMe_2	*b*	77	54
$NHCH_2Alk$	86	66	46
$N(CH_2Alk)_2$	*b*	80	58
$NHCHAlk_2$	86	67	46
$N(CHAlk_2)_2$	*b*	80	58
R^2, Alk	16	14	20
R^3, Alk	5	1	10
Exocyclic double bond	5	3	*b*

[a] Including intramolecular hydrogen bond. [b] No experimental data available for calculations.

tion of isomer I is of the same order of magnitude but in the opposite direction, both the contributions may confidently be assumed to cancel each other. Now, taking for the solvent-induced shift $\Delta\lambda^{H_2O}_{C_6H_{12}}$ the value obtained experimentally for the most closely related compound **13,** i.e., 24 nm (see Table I), one can estimate the position of the $\Delta\lambda^{trans,s\text{-}cis}_{max}$ (C_6H_{12}) of **12** at 276 nm. The maximum on the final curve of the solution in cyclohexane (Figure 5) corresponding to the practically pure cis,s-cis (*ZZ*) isomer IV is at 299 nm, which yields the differential shifts $\Delta\lambda^{cis,s\text{-}cis}_{trans,s\text{-}cis} = 299 - 276 = 23$ nm and $\Delta\lambda^{s\text{-}cis}_{s\text{-}trans} = 41 - 23 = 18$ nm.

The above indirect scheme of calculations cannot be applied to the higher substituted ketones **15** to **18** as, because of the increasing amount of the cis,s-cis isomer IV in solutions in water,[18] it is not possible to estimate reliably the position of the absorption maximum of the trans,s-cis isomer II. The same can be said with regard to the series **7** to **10,** within which the ratio I/II remains approximately constant, whereas the population of the isomer IV gradually increases at the expense of I and II. The bathochromic shift observed within both of these series, though readily explicable in qualitative terms, renders any calculation of the above type uncertain.

On the other hand, the conformationally rigid butylaminomethylenecyclohexanone (**23**), which undergoes a rapid trans → cis isomerization in nonpolar solvents, yields a value close to $\Delta\lambda^{cis,s\text{-}cis}_{trans,s\text{-}cis} = 22$ nm when treated according to the indirect scheme applied above for **12** ($\Delta\lambda^{H_2O}_{C_6H_{12}}$ was taken here as 26 nm, which is a mean value obtained for the related dialkylaminomethylene derivatives **47** and **48**).

The experimentally inaccessible value of the absorption maximum of the trans,s-cis isomer of **17** and **18** in nonpolar solvents can be evaluated using still another indirect scheme. A comparison of a number of open-chain monoalkylamino derivatives with corresponding dialkylamino analogues having the same (or nearly so) populations of configurational and conformational isomers reveals that the increment for the second N-alkyl group is approximately constant, amounting to $\Delta\lambda^{N\text{-}Alk_2}_{NH\text{-}Alk} = 14$ nm for the trans,s-cis isomer needed in these considerations (**41**[19] vs. **13, 42** vs. **14, 35**[20] vs. **8**). Subtracting this value from 292 nm obtained experimentally for **43,** we arrive at a "theoretical" value for the trans,s-cis isomer of **17,** $\lambda^{trans,s\text{-}cis}_{max}$ (C_6H_{12}) 278 nm which leads to $\Delta\lambda^{cis,s\text{-}cis}_{trans,s\text{-}cis} = 300 - 278 = 22$ nm and $\Delta\lambda^{s\text{-}cis}_{s\text{-}trans} = 41 - 22 = 19$ nm. In the same manner, **44** compared with **18** yields for the latter $\lambda^{trans,,s\text{-}cis}_{max}$ (C_6H_{12}) 283 nm, $\Delta\lambda^{cis,s\text{-}cis}_{trans,s\text{-}cis} = 300 - 283 = 17$ nm, and $\Delta\lambda^{s\text{-}cis}_{s\text{-}trans}$ 24 nm (cf. Table II). The validity of this calculation scheme is corroborated by the fact that **12** compared with **40** yields a value of $\lambda^{trans,s\text{-}cis}_{max}$

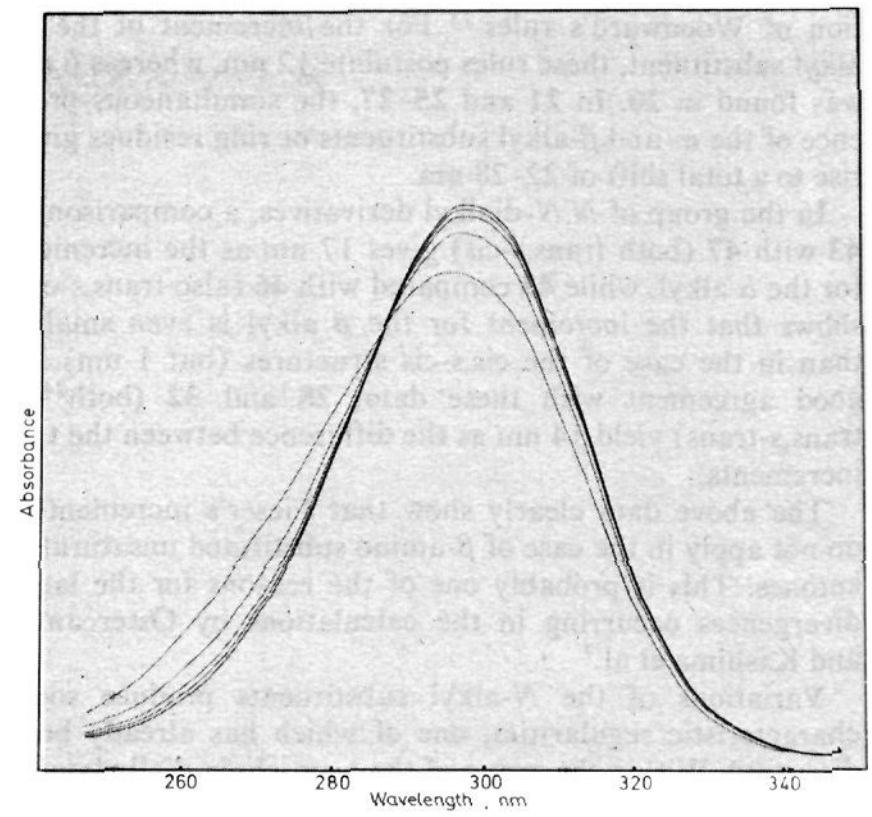


Figure 5. The time-dependent changes in the uv spectrum of 4-methyl-1-methylamino-1-penten-3-one (**12**) in cyclohexane.

(C_6H_{12}) 276 nm, which is identical with that calculated according to the first indirect scheme.

The shift of the absorption maximum due to the change in configuration from trans to cis ($\Delta\lambda^{cis}_{trans}$) is unavoidably coupled in all instances investigated here, with the shift caused by the intramolecular hydrogen bond. However, assuming the spectral effect of the intramolecular and intermolecular hydrogen bond to be approximately equal, the "pure" $\Delta\lambda^{cis}_{trans}$ value can be estimated by subtracting the water-induced shift $\Delta\lambda^{H_2O}_{C_6H_{12}} = 23$ nm[21] from the $\Delta\lambda^{cis,s\text{-}cis}_{trans,s\text{-}cis}$ values experimentally observed for **8** (20 nm), **11** (21 nm), **13** (20 nm), **14** (17 nm), and **19** (16 nm) or indirectly calculated for **12** (23 nm), **17** (22 nm), **18** (17 nm), and **23** (22 nm).

In this way we obtain slightly negative $\Delta\lambda^{cis}_{trans}$ values ranging from 0 to −7 nm. This result is close to what was found in this respect by Bienvenue[3] ($\Delta\lambda^{cis}_{trans} = 0$), but plainly contradicts the estimates by Ostercamp[1] ($\Delta\lambda^{cis}_{trans} = 10$ nm, regardless of conformation) and Kashima et al.[7] ($\Delta\lambda =$ 16 to 28 nm, for the fixed s-trans conformation), already criticized in the Introduction. It should be added that the bathochromic shift due to the intramolecular hydrogen bond is probably greater than that resulting from intermolecular hydrogen bond; i.e, $\Delta\lambda^{cis}_{trans}$ is most likely even more negative than indicated above.

In order to eliminate the problem of the intramolecular hydrogen bond, attempts were undertaken to obtain cis and trans N,N-disubstituted derivatives. Unfortunately, this proved impossible with regard to ketones and aldehydes, but cis and trans β-aziridineacrylamides, $i\text{-}Pr_2NCO\text{-}CH{=}CHN(CH_2)_2$ (both s-cis) have been synthesized and exhibited $\Delta\lambda^{cis}_{trans} = 3$ in hexane and −6 nm in methanol,[22] i.e., values close to the above estimates.

The increments for the α- and β-alkyl substituents can be best derived from the data on chelated cis,s-cis isomers investigated in nonpolar solvents, whereas in the majority of other cases, the nonsubstituted reference compounds and/or the substituted compounds under discussion are liable to conformational changes which render the calculations of the increments uncertain. Taking λ_{max} 300 nm as the reference value (the average for **7–19**), one obtains 16 nm for the increment of the α-alkyl substituent in **5** and **6** and 25 nm in **23,** compared with 10 nm given in Fieser's modifica-

tion of Woodward's rules.[23] For the increment of the β-alkyl substituent, these rules postulate 12 nm, whereas 6 nm was found in **20.** In **21** and **25–27,** the simultaneous presence of the α- and β-alkyl substituents or ring residues gives rise to a total shift of 22–28 nm.

In the group of *N,N*-dialkyl derivatives, a comparison of **43** with **47** (both trans,s-cis) gives 17 nm as the increment for the α alkyl, while **43** compared with **46** (also trans,s-cis) shows that the increment for the β alkyl is even smaller than in the case of the cis,s-cis structures (but 1 nm). In good agreement with these data, **28** and **32** (both[24,25] trans,s-trans) yield 14 nm as the difference between the two increments.

The above data clearly show that Fieser's increments[23] do not apply in the case of β-amino substituted unsaturated ketones. This is probably one of the reasons for the large divergences occurring in the calculations by Ostercamp[1] and Kashima et al.[7]

Variations of the *N*-alkyl substituents produce some characteristic regularities, one of which has already been discussed. Within the group of the open-chain dialkylamino derivatives, a further substitution of the *N*-methyl hydrogens produces a rather regular bathochromic shift of ca. 4 nm[26] (e.g., 288, 292, and 296 nm for **34, 35,** and **36,** respectively). Taking this regularity into account, the spectral data on compounds **34–45** can be interpreted from the point of view of a gradual shift of the conformational equilibrium towards the s-cis rotamer, along with increasing steric requirements of the alkyl substituent of the carbonyl group. In solution in cyclohexane, the s-cis rotamer prevails already in methyl ketones **34–36** (in comparison, 73% was found for **34** in $CH_2{=}CCl_2$[12]); hence, a further increase of the population of this rotamer up to 100% in **43–45** has little effect on the position of the absorption maximum. In solutions in methanol and water, the range of the spectral changes is wider because of increased population of the s-trans rotamer in the case of the lower homologues.[12]

Although the small number of compounds investigated does not permit a rigorous regression analysis, a preliminary set of spectral increments can be proposed on the basis of the data already collected. Since the system takes into account a variety of combinations of structural elements, it is only natural that the proposed set is more complicated than the parent Woodward–Fiesers system or the subsequent systems based on simplified considerations.

The consistency of the above system of spectral constants is illustrated in Table I by the rather small deviations of the experimental λ_{max} values from the calculated ones.

Solvent-induced shifts of the λ_{max} caused by the change of configuration and conformation were already discussed several times in this paper, but there remains the important question of whether the magnitude of the shift does or does not depend on the particular configuration or conformation. The majority of the additive schemes known to date[27] do not differentiate the solvent-induced shifts, but Ostercamp[1] observed bathochromic shifts $\Delta\lambda_{C_6H_{12}}^{MeOH}$ = 7–13 nm for three cis,s-cis enamino ketones and $\Delta\lambda_{Et_2O}^{MeOH}$ = 17 nm for one trans,s-trans enamino ketone. Our results confirm this tendency and add more detailed data on this topic.

For cis,s-cis ketones **20, 21, 25, 26,** and **27,** both the $\Delta\lambda_{C_6H_{12}}^{MeOH}$ and $\Delta\lambda_{C_6H_{12}}^{H_2O}$ lie within the close limits of 6–9 nm.

For trans,s-cis compounds **43–46,** $\Delta\lambda_{C_6H_{12}}^{MeOH}$ = 18–19 nm and $\Delta\lambda_{C_6H_{12}}^{H_2O}$ = 23–25 nm. The cyclic trans,s-cis ketones **47–49** exhibit somewhat higher values, $\Delta\lambda_{C_6H_{12}}^{MeOH}$ = 22–25 nm and $\Delta\lambda_{C_6H_{12}}^{H_2O}$ = 25–27 nm; it can be assumed that solvation by the active proton-donating solvents causes some flattening of the nonplanar cyclic structures (vide infra), thus producing an additional bathochromic shift.

The alkyl N,N-disubstituted trans,s-trans aldehydes and ketones **29–32** exhibit $\Delta\lambda_{C_6H_{12}}^{MeOH}$ = 12–13 nm and $\Delta\lambda_{C_6H_{12}}^{H_2O}$ = 15–20 nm, whereas for the corresponding *N*-monoalkyl derivatives, the shifts are markedly higher: $\Delta\lambda_{C_6H_{12}}^{MeOH}$ = 15–19 nm and $\Delta\lambda_{C_6H_{12}}^{H_2O}$ = 17–24 nm. It seems that this additional bathochromic shift can be explained by the amphoteric character of methanol and water which solvate both ends of the chromophore —O—H··· O=C—C=C—N—H···O, thus enhancing its mesomeric character.

Table IV. Dihedral Angle φ between the Planes of the C=O and C=C Bonds

Compd[a]	φ, deg	Compd	φ, deg
7–19[a]	0	26[a]	38
5[a]	34	27[a]	33
6[a]	31	43–46	0
21[a]	28	47	37
23[a]	28	48	30
25[a]	35	49	30

[a] Isomers cis,s-cis.

It follows from the above that the averaged increments for the solvent effect known in the literature[27] should not be used when comparing results obtained in different solvents. Moreover, since the differentiated solvent-induced shifts are hardly explicable in rigorous terms, it seems expedient to avoid the polar solvents whenever possible.

The direct observation of separate absorption maxima of the particular isomers enables one to estimate angular distortions in crowded or otherwise strained molecules by comparing their absorptivities (ε) with those of sterically nonhindered planar molecules (ϵ_0). For example, the strain-free cis,s-cis isomers of the ketones **7–19,** which may be assumed planar, exhibit remarkably constant absorptivities, thus affording a reliable average reference value ϵ_0 16 500 for the cis,s-cis isomers of the crowded α-alkyl substituted ketones **5, 6,** and **21** and of the somewhat distorted cyclic ketones **23** and **25–27.** By applying Braude's equation,[4] $\epsilon/\epsilon_0 = \cos^2 \phi$, the values of the dihedral angle φ between the planes of the C=O and C=C bonds shown in Table IV were obtained.

Although the values of φ must be viewed as rough estimates, it is obvious that nonbonded interactions between R^1 and R^2 produce a considerable strain which, while not sufficient to overcome the stabilizing effect of the intramolecular hydrogen bond, results in a marked twist of the molecule. If no hydrogen bond is present, as with **32,** or its energy is low, as in the case of bifurcate hydrogen bonds,[25,28] the molecules tend to isomerize into the energetically favored trans,s-trans form (see Figure 6 for ir spectrum of **32**).

With the cyclic ketones **23** and **25–27,** the deviation from planarity is caused by the strain due to distortion of the valence angles at the C_{sp^3} carbons. A similar nonplanar deformation is noticeable for the N,N-disubstituted trans,s-cis cyclic ketones **47–49,** listed in the lower part of Table IV, if their absorptivities are compared with those of the not strained trans,s-cis open-chain ketones **43–46.** However, nonplanar deformation of the *N,N*-dialkylamino group produced by its interaction with the R^2 substituent present in **47–49** in the form of the ring residue[12] contributes most probably to the observed lowering of the absorptivities of the latter compounds. Hence, the calculated angles must be somewhat overestimated.

Although appreciable interaction of substituents occurs in neither isomer of the enamino aldehydes, they are of little use for calculations of nonplanar deformations in ketones, as the absorptivities of these two groups of compounds differ for reasons not related to planarity.

The absorption intensities measured for the solutions in methanol and in water are less informative, as they are de-

pendent on several factors simultaneously. First, by changing cyclohexane for methanol or water, an equilibrium shift toward the trans isomer takes place. Second, a similar shift occurs with respect to the s-trans rotamer in the case of the conformationally labile compounds. Third, the magnitude of these shifts varies within very broad limits depending on the alkyl substituents.[18] Nevertheless, there is no doubt that protic solvents produce a marked increase of the absorptivity independently of the structural changes, as seen from its ca. 30% enhancement in the case of the trans isomer of the aldehydes **1–4,** which consists of practically pure s-trans rotamer already in cyclohexane.

Finally, the discussion on the possible enolization of enamino ketones put forward by Kashima et al.[7] deserves mention. The authors have assumed that the solvent-induced shifts in ethanol are due to an appreciable admixture of the β-imino enol tautomer. However, as shown previously,[29] the isomerism of this type does not occur in enamino ketones to a discernible degree; this has also been confirmed by the work of Greenhill,[30] who showed that the equilibrium is shifted toward the keto form with a constant of 10^8.

Conclusion

The contribution of configuration and conformation to the observed frequency of the $\pi \rightarrow \pi$ electronic transition of enamino aldehydes and ketones is thought to have been obtained more directly and reliably than was done in other investigations. The advantage of the calculation scheme applied here consists in comparing spectra of different configurational-conformational combinations *of the same molecule;* where comparisons of different molecules were necessary, the structural variations were limited to alterations in the alkyl substituent linked to carbonyl, this substituent as such being known to exert no marked influence on the absorption maximum. After the spectral characteristics of the cis,s-cis, trans,s-cis, and trans,s-trans molecules had been established, the comparison with α- and β-alkyl substituted compounds of related stereochemistry yielded the increments for these substituents.

Experimental Section

Spectra. Ultraviolet spectra were recorded using Unicam SP 700, Carl-Zeiss Jena Specord, and Beckman Acta M-VI spectrophotometers (spectrograde solvents) with cells of 1-cm path length. Several spectra were repeated in 10-cm cells, but no changes in the positions of the maxima due to dilution were observed.

Infrared spectra were recorded on a Carl-Zeiss Jena UR-20 spectrophotometer and some of them repeated on a Perkin-Elmer Model 325. In the range 3000–3600 cm^{-1}, Unicam SP 700 apparatus, tungsten lamp, with 10-cm path length cells were used.

NMR data were obtained on a Jeol JNM-4H-100 instrument with Me_4Si 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. Low-temperature spectra were recorded using Jeol Jes-VT-3 temperature controller.

Preparation of Compounds. Preparation of a number of compounds investigated in the present work has been described previously by the authors and by others (see ref: **1**,[31] **2–3**,[2e] **7–8**,[32] **9**,[33] **10, 22–23**,[34] **18**,[2d] **28, 34–35, 37–41, 43–44, 46**,[2b] **29**,[2c] **32, 48**,[35] **33**,[36] **50–52**[37]).

The aldehydes **4, 30,** and **31** were obtained from propynal and the corresponding amine in ethereal solutions. The reaction mixtures were left overnight at room temperature, the ether was evaporated, and the products were distilled or sublimed twice under reduced pressure. Compound **4** was additionally purified on neutral alumina preparative plates, eluent benzene:ethyl acetate 1:1.

During synthesis of **1,** care has to be taken to ensure that the ethereal solutions of aldehyde and ethylamine are mixed at room temperature. When the reaction was carried out at lower temperatures (for example, in a dry ice bath), a white, crystalline precipitate of a compound of unknown structure was obtained.

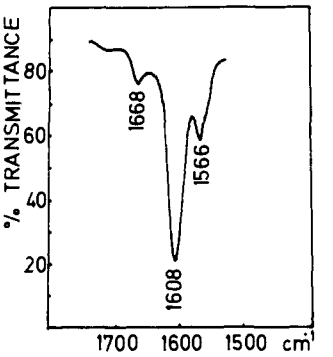


Figure 6. Ir spectrum of 2-methyl-1-diethylamino-2-penten-3-one (**32**) in C_2Cl_4 in the 1500–1700-cm^{-1} region.

Table V. Physical Properties and Analytical Data for the New Compounds

Compd	Mp or bp (mm Hg), °C	% N calcd	% N found
4	145 (2)	9.15	9.31
5		11.02	11.09
6		9.03	8.74
11	128 (1.3)	8.38	8.57
12	82 (3)	11.02	11.24
13	88–89 (3)	9.92	9.92
14	85–86 (2)	9.03	9.27
15	92 (4)	8.23	8.09
16	141 (3)	7.18	7.01
17	79 (2)	9.92	10.00
19	86–89	6.69	6.65
20	107 (3)	9.92	9.99
21	38	11.02	11.09
24	132–134	8.48	8.22
25	41–42	7.82	7.73
26		7.64	7.90
27		6.31	6.23
30	124–125 (0.5)	9.03	9.20
31	75–78	9.03	9.07
37	150 (0.8)	8.23	8.27
42	150 (2)	7.10	7.30
	49		
45	69	6.68	6.28

Compounds **5** and **6** were obtained from the sodium derivatives of 1-hydroxy-2-methyl-1-penten-3-one and 1-hydroxy-2-methyl-1-hexen-3-one, respectively, and methylamine hydrochloride in methanol solution. Sodium chloride was filtered off, the methanol evaporated, and the compound dissolved in ether; traces of sodium chloride were removed. The products were purified on neutral alumina preparative plates (eluent benzene–ethyl acetate 1:1) and then distilled in vacuo. Very pure trans isomer of **6** crystallized partly in the form of large crystals after being kept several days in a refrigerator. These crystals were separated, quickly washed with hexane, dried out under vacuum, and then used without further purification.

Compounds **11–16, 36,** and **42** were obtained from the corresponding β-chlorovinyl ketones and the appropriate amine according to a known procedure,[32] in the case of **17, 19,** and **45,** *tert*-butylhydroxymethylene ketone instead of chlorovinyl ketone was the starting material.

Compounds **20** and **21** were synthesized from acetylacetone and methylacetylacetone and the corresponding amine,[2b] respectively.

The derivatives of decalindione **24–27** were obtained in the following manner: 0.001 M of decalindione was heated with a tenfold excess of anhydrous amine in a sealed Carius tube for approximately 4 h at 80–90 °C. Compound **24,** an exception, was obtained by keeping decalindione with liquid, anhydrous ammonia in a sealed tube for 3 days at room temperature. After cooling, amine or ammonia was evaporated, and the oily residue was purified on a neutral alumina (grade II) column. The products were then sublimed under vacuum (~1 mmHg).

The substances investigated were freshly distilled or sublimed before the measurements. Compounds **1–4, 6, 8, 11, 13, 14,** and **19** crystallized in the trans form after being kept in a refrigerator.

Physical properties and analytical data for the new compounds are collected in Table V.

Acknowledgment. The authors thank Dr. Z. Swistun for measurements of several spectra. This work is a part of the Polish Academy of Sciences Program for Structural Research, No. PAN-3.

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(13) Ca. 22% in a 0.1 M solution, according to a NMR spectrum; undoubtedly, the percentage of this isomer was even smaller in the 0.0001 M solution used for uv measurements.
(14) Estimated by assuming some further shift toward I in water as compared with methanol for which a 15% value was obtained by low-temperature NMR measurements.
(15) In view of the possible influence of intermolecular interactions, we considered it advisable to compare experimental data on mixtures prepared for the purpose with the results of mathematical analysis of two mixed absorption bands carried out by Vandenbelt and Henrich.[16] The agreement is quite satisfactory.
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(17) The absorption curve of a mixture of 80% of **30** and 20% of **36** was somewhat broadened as compared with that of neat **30**, but the maximum lay at 292.5 nm; i.e., the difference was only 0.5 nm (cf. Table I). For a mixture containing 70% of **30** and 30% of **36**, the maximum was observed at 293.5 nm; i.e., the total difference amounted to only 1.5 nm.
(18) Because of low solubility of **14, 15, 16, 18,** and **19** in water, it was only possible to determine directly the percentage of the isomer IV for **12, 13,** and **17** (22, 30, and 20%, respectively, according to NMR spectra of 0.1 M solutions). On the other hand, the data on 0.1 M methanol solutions clearly demonstrate the dramatic increase in the population of IV along with increasing size of the *N*-alkyl substituents (33, 45, 62, 72, and 73% for the isopropyl ketones **12, 13, 14, 15,** and **16,** respectively, and 44, 61, and 73% for the *tert*-butyl ketones **17, 18,** and **19**).
(19) About 97% of the *s*-cis rotamer.[11]
(20) About 70% of the *s*-cis rotamer.[12]
(21) A mean value from the data on ketones which exist mainly (**13, 14, 40, 41, 42**) or entirely (**19, 43–45, 47, 48**) in the trans-*s*-cis form.
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Three Different Consecutive Orbital Symmetry-Controlled Reactions in the Novel Stereospecific Synthesis of 1-Phenyl-4-(1-phenylethenyl)naphthalene. The Reaction of 3,4-Diphenylthiophene 1,1-Dioxide with Ethynylbenzene

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Abstract: The major product of the reaction of 3,4-diphenylthiophene 1,1-dioxide (2) with ethynylbenzene (3) was not 1,2,4-triphenylbenzene (**1**) as expected, but an isomer, 1-phenyl-4-(1-phenylethenyl)naphthalene (**4**). Deuterium labeling studies involving 2,5-dideuterio-3,4-diphenylthiophene 1,1-dioxide (**11**) indicated that the 1-phenylethenyl moiety originated from the thiophene system in a highly stereospecific manner, giving (*E*)-3-deuterio-1-phenyl-4-(2-deuterio-1-phenylethenyl)-naphthalene (**13**-*E*) as the major isomer (9:1). A mechanism for the formation of **4** has been proposed which involves three different consecutive orbital symmetry-controlled reactions.

The synthesis of the lower melting (99.1–99.6 °C) crystalline form of 1,2,4-triphenylbenzene (**1**) in low yield by the 4 + 2 cycloaddition reaction of 3,4-diphenylthiophene 1,1-dioxide (**2**) with ethynylbenzene (**3**), followed by the loss of sulfur dioxide has been reported.[1] Our own efforts to synthesize **1** resulted in the isolation of the higher melting (121–122 °C)