Ultraviolet Spectral Study of β-Amino-enones

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The u.v. spectra of β -amino-enones with *trans-s-trans, cis-s-trans,* and *cis-s-cis* structures are discussed. In the case of the *s-trans*-enone chromophore, the bathochromic shifts of β -amino-groups in the *cis*-position are 80—90 nm., and those of β -amino-groups in the *trans*-position are 60—70 nm. β -Monoalkylamino-enones show solvent effects which suggest the existence of tautomerism.

In the β -amino-enone system four geometric isomers, *trans-s-trans, trans-s-cis, cis-s-trans,* and *cis-s-cis,* are possible (Scheme 1). In the case of β -amino-enone



derived from acetylacetone and a primary amine, the cis-s-cis structure is fixed by intramolecular hydrogen bonding between the carbonyl and the amino-group. Azeotropic distillation of dimedone with primary or secondary amines gives 3-amino-5,5-dimethylcyclohex-2-enone derivatives which have the *trans-s-trans* structure. However, the compounds of cis-s-trans and trans-s-cis structures have never been described, except in the case of benzoquinolizines.¹ Recently we reported the synthesis of 2,3-dihydro-4-pyridones by the condensation of β -diketones with Schiff bases.^{2,3} These compounds possess the cis-s-trans structure.

Although the i.r. and n.m.r. spectra of β -aminoenones have been studied,^{4,5} little is known about their u.v. spectra. Cromwell⁶ has reported the u.v. spectra of compounds derived from acetylacetone and benzoylacetone, but no u.v. study that distinguishes the four different geometrical structures has been reported. We discuss here the bathochromic effect of the amino-group and solvent effects for twenty-two β -amino-enones *ciss-cis, trans-s-trans,* and *cis-s-trans* types. The spectra of acetylacetone, **3**-ethoxy-5,5-dimethylcyclohex-2enone, and **2**,**3**-dihydro-2,6-dimethylpyrone were used for comparisons.

RESULTS AND DISCUSSION

It has been reported that 4-aminopent-3-en-2-ones exist in both *trans-s-cis* and *cis-s-cis* structures in solution, and that *trans-s-cis* compounds are slowly converted into *cis-s-cis* compounds.⁷ The *cis-s-cis* structures are stabilised and held in a plane by intramolecular hydrogen bonding between carbonyl and NH groups, as demonstrated by NH proton n.m.r. signals at δ 9.0—15.0 p.p.m. The n.m.r. spectra of the 4-aminopent-3-en-2-ones (3), (4), and (5) show NH proton signals at δ 9.6, 11.2, and 12.5 p.p.m., respectively, thus confirming their *cis-s-cis* structures.

However, the NH proton signals of 3-benzylamino-5,5-dimethylcyclohex-2-enone (10) and 2,3-dihydro-6-methyl-2-phenyl-4(1H)-pyridone (12) appeared at δ 6.8 and 5.9 p.p.m., respectively, suggesting that neither *trans-s-trans* nor *cis-s-trans* β -amino-enones show intramolecular hydrogen bonding.

In the n.m.r. spectrum of 2,3-dihydro-6-methyl-1,2-diphenyl-4-pyridone (25), the ABX-type signals at δ 2.91 and 4.92 p.p.m. are assigned to the C-3 methylene protons and the C-2 methine proton. Since the coupling constants, J_{AB} , J_{AX} , and J_{BX} are 16.5, 6.4, and 6.4 Hz, respectively, the dihedral angles of N-C(2)-C(3)-C(4)can be calculated to be 60°. If these dihedral angles are fixed at 60° in a Dreiding model, the C=O and C=C double bonds and the amino-group are coplanar. The olefinic proton signal of (25) appeared at § 5.19 p.p.m., and that of 3-N-benzylanilino-5,5-dimethylcyclohex-2-enone (24) at 8 5.34 p.p.m. In view of this small difference and the conformations of Dreiding models we suggest that the *β*-amino-enone groups of 3-amino-5,5-dimethylcyclohex-2-enones and 2,3-dihydro-4-pyridones are fixed in planar trans-s-trans and cis-s-trans conformations, respectively.

The following twenty-two β -amino-enones may be grouped into three types: *cis-s-cis* (3, 4, and 5), *trans-s-trans* (10, 11, 17, 18, 23, and 24), and *cis-s-trans* (12, 13, 14, 15, 16, 19, 20, 21, 22, 25, 26, 27, and 28). Furthermore, the compounds of *trans-s-trans* and *cis-s-trans* structure may also be grouped, according to the nature of the amino-group, into three types: β -monoalkylamino-enones (10, 12, 13, 14, 15, and 16), β -dialkylamino-enones (17, 18, 19, 20, 21, and 22), and β -(phenylalkylamino)-enones (23, 24, 25, 26, 27, and 28).

The u.v. spectral data for these compounds in ethanol are listed in Table 1. The β -monoalkylamino-enones having the *cis-s-cis* structure (12, 13, and 14) show maxima at 315-318 nm. whereas the *trans-s-trans* compound (10) shows a maximum at 292 nm. The

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¹ M. von Strandtmann, M. P. Cohen, and J. Shavel, jun., J. Org. Chem., 1966, **31**, 797. ² N. Sugiyama, M. Yamamoto, and C. Kashima, Bull. Chem.

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shift (Δ_1) from *trans-s-trans* compounds to *cis-s-trans* is thus 23-26 nm.

The u.v. maxima of (17) and (18) appear at 303 nm. and those of (19), (20), and (21) at 319 nm. The shift



 (Δ_1) for β -dialkylamino-enones is thus 16 nm. Among the β -(phenylalkylamino)-enones, the maxima of (23) and (24) are at 303—305 nm. and those of (25), (26), and (27) at 327—333 nm.; the shift (Δ_1) is thus 22—28 nm.

For all the *trans-s-trans* structures, the extinction coefficients are 30,000—35,000 l. mole.⁻¹ cm.⁻¹, but those of *cis-s-trans* compounds are 14,000—18,000 l. mole⁻¹ cm.⁻¹.

The absorption maximum of 3-ethoxy-5,5-dimethylcyclohexenone (8), a *trans-s-trans* β -alkoxy-enone, appears at 251 nm. (ϵ 16,300). That of 2,3-dihydro-2,6-dimethylpyrone (9), a *cis-s-trans* β -alkoxy-enone, is at

⁸ P. Yates and D. J. MacGregor, *Tetrahedron Letters*, 1969, 453.

263 nm. (ϵ 14,000).⁸ The shift (Δ_1) for β -alkoxy-enones is thus 12 nm.

The results in Table 2 show that the absorption maxima of β -amino- and β -alkoxy-enones with *cis-s-trans* structures occur at longer wavelength than those of the *trans-s-trans* compounds, and that the extinction coefficients of the *cis-s-trans* compounds are *ca.* 10,000 l. mole⁻¹ cm.⁻¹ smaller than those of the *trans-s-trans* compounds.

TABLE 1

officient data for p anning onotice	U.v.	spectral	data	\mathbf{for}	β-amino-enones
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Com-	λ _{max.} (EtOH)		Δ.	Δ.	λ _{max.} (CHCL)		Δ.
pound	(nm.)	ε	$(nm.)^{\alpha}$	4 (nm.)b	(nm.)	ε	(nm.) •
(1)	221	11.500	· · ·	· /	· · ·		` '
$(\overline{2})$	273	10.500 d		52			
(3)	300	16,200		79			
(4)	312	16,700		91			
(5)	324	18,700		103			
(6)	235	12,930					
(7)	260	$12,600$ e		25			
(8)	251	16,300		16			
(9)	263	14,000	12	28			
(10)	292	31,200		57	284	25,700	8
(11)	310	20,300		75	305	19,800	5
(12)	315	14,500	23	80	303	13,400	12
(13)	318	14,100	26	83	307	12,000	11
(14)	318	14,400	26	83	306	14,000	12
(15)	339	12,200	47	104	329	12,200	10
(16)	345	9500	53	110			
(17)	303	35,000 f		68			
(18)	303	32,000 f		68			
(19)	319	17,200 9	16	84			
(20)	319	16,000 g	16	84			
(21)	319	16,600 g	16	84			
(22)	331	13,500 🛛	28	96			
(23)	303	30,000		68	301	28,500	2
(24)	305	29,000		70	303	28,900	2
(25)	327	18,000	22	92	324	16,600	3
(26)	333	16,900	28	98	330	20,900	3
(27)	329	17,600	24	94	327	17,300	2
(28)	353	21,500	48	118	356	14,300	3

⁽²⁵⁾ λ (EtOH) (cis-s-trans) – λ (EtOH) (trans-s-trans). ^b λ (EtOH) (β-amino-enones) – λ (EtOH) (enones). ^c λ (EtOH) – λ (CHCl₃). ^d P. Grossman, Z. phys. Chem., 1924, **109**, 305. ^e E. R. Bloat, V. W. Eager, and D. C. Silverman, J. Amer. Chem. Soc., 1946, **68**, 566. ^f G. H. Alt and A. J. Speziale, J. Org. Chem., 1965, **30**, 1407. ^g Ref. 1.

TABLE 2

Bathochromic shifts due to auxochromes at the βpositions of enones

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cis-s-cis	trans-s-trans	cis-s - trans				
52 nm.	16-20 nm.	28 nm.				
79	57	80 - 83				
91	68	84				
103	68 - 70	92 - 98				
	<i>cis-s-cis</i> 52 nm. 79 91 103	<i>cis-s-cis trans-s-trans</i> 52 nm. 16—20 nm. 79 57 91 68 103 68—70				

3-Amino-5,5-dimethylcyclohex-2-enones and 2,3-dihydro-4-pyridones contain an enone chromophore with an amino-group auxochrome; thus bathochromic and hyperchromic effects of β -amino-groups may be measured by comparison with the spectrum of 3-methylcyclohex-2-enone (6) $[\lambda_{max}, 235 \text{ nm}, (\varepsilon 12,930)^9]$. In the *transs*-*trans* structure, in which the auxochrome is attached

⁹ L. K. Evans and A. E. Gillam, J. Chem. Soc., 1941, 815; J. Meinwald and R. F. Grossman, J. Amer. Chem. Soc., 1956, 78, 992.

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to the trans- β -position of the s-trans enone chromophore, the bathochromic shifts (Δ_2) of the monoalkylaminogroup is 57 nm., that of the dialkylamino-group is 68 nm., and those of the phenylalkylamino-group and the alkoxy-group are 68-70 and 16 nm., respectively. The hyperchromic effect of the amino-group is ca. 20,000 l. mole⁻¹ cm.⁻¹, whereas that of the alkoxy-group is 3000 l. mole⁻¹ cm.⁻¹. In the case of the cis-s-trans structure, with the auxochrome at the cis- β -position of the s-trans enone chromophore, the bathochromic shifts (Δ_{0}) of monoalkylamino-, dialkylamino-, phenylalkylamino-, and alkoxy-groups are 80-83, 84, 92-94, and 28 nm., respectively, and the hyperchromic effects are 1000, 3500, 5000, and 1000 l. mole⁻¹ cm.⁻¹, respectively.

Comparison with the absorption maximum of pent-3-en-2-one (1) [221 nm. (ϵ 11,500)¹⁰] shows that for the cis-s-cis compounds the bathochromic shifts due to amino-groups are 80-100 nm. and that the hyperchromic shifts are 5000-7000 l. mole⁻¹ cm.⁻¹, whereas the bathochromic effect of the hydroxy-group is 52 nm.

For the compounds (15), (16), (22), and (28), which contain the phenyl group at the β -position of *cis-s-trans* β -amino-enones, the bathochromic effect of the β phenyl group is *ca*. 20 nm.

 β -Amino-enones may be expected to exist also as β-imino-enols. The tautomeric equilibrium can be influenced by change in solvent,¹¹ and the changes can be followed by u.v. spectroscopy.¹² We have measured the u.v. spectra of compounds (10), (12), and (25) in nhexane, chloroform, and ethanol [dielectric constants 1.890, 4.806, and 24.30, respectively]. Table 3 shows

TABLE 3

Solvent effects in the u.v. spectra of β -amino-enones

Com- pound	$\lambda_{max.}$ (EtOH) (nm.)	$\lambda_{max.}$ (CHCl ₃) (nm.)	Δ ₃ (nm.) ^a	λ _{max.} (hexane) (nm.)	Δ_4 (nm.) ^b
(10)	292	284	8	271	21
(12)	315	303	12	290	25
(25)	327	324	3	311	16
	• λ(EtOH) -	$\lambda(CHCl_3).$	•λ(EtOH) -	$-\lambda$ (hexane).	

that the solvent shifts of (10) and (12) are larger than those of (25). The u.v. spectra of various β -monoalkylamino- and β -(phenylalkylamino)-enones in chloroform were also measured; the shifts (Δ_3) with respect to solutions in ethanol are presented in Table 1. For β -(phenylalkylamino)-enones the shifts are 0-3 nm., whereas the β -monoalkylamino-enones show shifts of 8-12 nm. The results indicate that the latter exist in the tautomeric state with β -imino-enols, whereas the phenylalkylamino-enones do not.

EXPERIMENTAL

U.v. spectra were measured with a Hitachi EPS-3T spectrometer for solutions in 95% ethanol or chloroform.

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N.m.r. spectra were measured with a Hitachi H-60 high resolution spectrometer for solutions in deuteriochloroform with tetramethylsilane as internal standard.

4-Aminopent-3-en-2-ones were prepared from acetylacetone and ammonia or amines: 4-aminopent-3-en-2-one (3), b.p. 203-210° (lit.,¹³ 209°), δ 1·90 (s, 3H), 1·99 (s, 3H), 4.97 (s, 1H), 6.4 (s, 1H), and 9.6 (s, 1H) p.p.m.; 4-benzylaminopent-3-en-2-one (4), b.p. 180-184°/17 mm. (lit.,14 183-183.5°/17 mm.), δ 1.80 (s, 3H), 1.97 (s, 3H), 4.29 (d, 2H), 4.97 (s, 1H), 7.18 (m, 5H), and 11.1 (s, 1H) p.p.m.; 4-anilinopent-3-en-2-one (5), b.p. 153-158°/18 mm., m.p. 51° (lit.,¹⁵ 51-53°), δ 1.98 (s, 3H), 2.08 (s, 3H), 5.14 (s, 1H), 6.9-7.5 (m, 5H), and 12.5 (s, 1H) p.p.m.

3-Ethoxy-5,5-dimethylcyclohex-2-enone (8) was prepared from dimedone and ethanol according to the procedure of Beringer;¹⁶ m.p. 62° (lit.,¹⁶ 60-61°).

3-Amino-5,5-dimethylcyclohex-2-enones were prepared from dimedone and amines in the presence of sulphuric acid by azeotropic distillation: 3-benzylamino-5,5-dimethylcyclohex-2-enone (10), m.p. 129° (lit.,¹⁷ 129-130°), δ 1.01 (s, 6H), 2.06 (s, 2H), 2.27 (s, 2H), 4.18 (d, 2H), 5.03 (s, 1H), 6.8 (s, 1H), and 7.21 (s, 5H) p.p.m.; 3-anilino-5,5-dimethylcyclohex-2-enone (11), m.p. 181° (lit.,¹⁷ 177°), δ 1.03 (s, 6H), 2·13 (s, 2H), 2·32 (s, 2H), 5·48 (s, 1H), 6·0-7·3 (m, 5H), and 7.8 (s, 1H) p.p.m.

5,5-Dimethyl-3-methylanilinocyclohex-2-enone (23) was prepared from N-methylaniline and dimedone as white needles, m.p. 84° (from n-hexane), & 1.01 (s, 6H), 2.07 (s, 2H), 2.16 (s, 2H), 3.24 (s, 3H), 5.29 (s, 1H), and 7.0-7.5 (m, 5H) p.p.m. (Found: C, 78.55; H, 8.5; N, 6.0. C₁₅H₁₉NO requires C, 78.55; H, 8.35; N, 6.1%).

3-Benzylanilino-5,5-dimethylcyclohex-2-enone (24) was prepared from N-benzylaniline and dimedone as colourless needles, m.p. 111-111.5°, 8 1.02 (s, 6H), 2.17 (s, 4H), 4.80 (s, 2H), 5.34 (s, 1H), and 6.9-7.4 (m, 10H) p.p.m. (Found: C, 82.4; H, 7.8; N, 4.5. C₂₁H₂₃NO requires C, 82.6; H, 7.6; N, 4.5%).

2,3-Dihydro-4-pyridones were prepared by procedures previously described: 2,3,18

2,3-Dihydro-6-methyl-2-phenyl-4(1H)-pyridone (12), m.p. $160-161^{\circ}$, δ 2.01 (s, 3H), 2.1-2.8 (m, 2H), 4.66 (q, 1H), 4.93 (s, 1H), 5.9 (m, 1H), and 7.37 (s, 5H) p.p.m.; 3benzyl-2,3-dihydro-6-methyl-4(1H)-pyridone (13), m.p. 159-160°, § 2.00 (s, 3H), 2.7-3.0 (m, 3H), 4.2-4.4 (m, 1H), 4.95 (s, 1H), 5.3 (s, 1H), and 6.9-7.3 (m, 10H) p.p.m.; 2,3-dihydro-6-phenethyl-2-phenyl-4(1H)-pyridone (14), m.p. $124-126^{\circ}$, $\delta 2\cdot 2-3\cdot 1$ (m, 6H), $5\cdot 48$ (q, 1H), $4\cdot 92$ (s, 1H), 5.6 (s, 1H), and 7.0-7.4 (m, 10H) p.p.m.; 2,3-dihydro-2,6-diphenyl-4(1H)-pyridone (15), m.p. 149-150°, 8 2.4-3.1 (m, 2H), 4.88 (q, 1H), 5.46 (s, 2H), and 7.2-7.7 (m, 10H) p.p.m.; 2,3-dihydro-5-methyl-2,3-diphenyl-4(1H)pyridone (16), 8 1.98 (s, 3H), 2.93 (m, 2H), 3.38 (s, 1H), 4.82 (t, 1H), and 6.8-7.4 (m, 10H) p.p.m.; 2,3-dihydro-6-methyl-1,2-diphenyl-4-pyridone (25), m.p. 84-85°, δ

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1.80 (s, 3H), 2.4—3.1 (ABXm, 2H), 4.90 (t, 1H), 5.04 (s, 1H), and 7.1—7.2 (m, 10H) p.p.m.; 3-benzyl-2,3-dihydro-6-methyl-1,2-diphenyl-4-pyridone (26), m.p. 179—180°, 8 2.02 (s, 3H), 2.8—3.4 (m, 4H), 4.55 (s, 1H), 5.22 (s, 1H), and 6.9—7.4 (m, 15H) p.p.m.; 2,3-dihydro-6-phenethyl-1,2-diphenyl-4-pyridone (27), m.p. 99—100°, 8 2.3—2.9 (m, 4H), 2.72 (ABXm, 2H), 4.90 (t, 1H), 5.34 (s, 1H), and 6·9—7·4 (m, 15H) p.p.m.; 2,3-dihydro-1,2,6-triphenyl-4-pyridone (28), m.p. 149—151°, δ 2·7—3·6 (ABXm, 2H), 5·30 (t, 1H), 5·58 (s, 1H), and 6·8—7·6 (m, 15H) p.p.m.

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