Part X.¹ Ultraviolet Absorption Spectra of Enamine Chemistry. Dienamines

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The u.v. absorption data for a series of cyclic and acyclic linear conjugated dienamines are reported. The morpholine and pyrrolidine groups in conjugation with the double bond system are shown to exert an auxochromic shift of +50 and +63 nm, respectively, and the effect of alkyl substituents is shown to vary with their position in the carbon chain (*i.e.* α , β , γ , or δ to the amino-group).

THE use of Woodward's rules ² for predicting the position of the π - π band of conjugated systems has been shown to hold remarkably well for alkylated dienes and less well for $\alpha\beta$ -unsaturated ketones. However, no satisfactory correlation of substituent effects in dienamine systems has yet been made. In an attempt to extend the scope of these rules to include dienamines various values for the auxochromic effect of the dialkylamino-group have been suggested, ranging from 46 (ref. 3) to 60-65 nm

TABLE 1

Observed and calculated λ_{max} values for cyclic dienamines (in hexane)

					$\lambda_{\rm max.}/{\rm nm}~(\Sigma \times 10^{-3})$				
	Dienamine				Calc.		Obs.		
	$R_{2}^{1}N$	\mathbb{R}^2	R³	\mathbb{R}^4	(a) *	(b) †	(c)		
(I)	Morpholino	\mathbf{H}	н	н	284	267	266 (13·0)		
(I)	- ,,	H	H	Me	284	267	$271 \ddagger (14.4)$		
(I)	,,	H	Me	н	284	267	266 (18·0)		
(1)	,,	Me	H	н	289	271	272(20.0)		
	**	н u	H		279	207	$275 \downarrow (13.0)$		
	"	п Ме	Me		289	207	208(17.9) 271(21.9)		
朌	,,	Ĥ	Ph		200	211	318(24.3)		
()	,,						238 (8.4)		
(III)	••				284	267	265 (23·9)		
(I)	Pyrrolidin-1-yl	н	\mathbf{H}	н	297	280	280 (16·2)		
(I)		\mathbf{H}	н	Me	297	280	$288 \ddagger (14.5)$		
(I)	,,	н	Me	H	297	280	279 (19.2)		
(1)		Me	H	н	302	284	283(22.0)		
	,,	H	H Ma		292	280	287 <u>†</u> (7·2)		
	**	л Мо	Mo		297	280	282()		
	**	H	Ph		302	204	338(22.7)		
(11)	,,	*1	111				242(10.3)		
(III)					297	280	279 (28·8)		

* With a base value of 214 nm for heteroannular dienes and 217 nm for acyclic dienes, +50 nm for morpholine, +63 nm for pyrrolidine, and +5 nm for alkyl substituents, ring residues, and exocyclic double bonds. † As before, but with values in Table 3 for alkyl substituents and ring residues.
‡ Previously shown to exist largely in the homoannular form.

(ref. 4). Since, in the ground state, the orbital interaction of the nitrogen lone pair with the π -electrons of the double bond is known to be greater for pyrrolidine than for morpholine enamines,⁵ it follows that a single value for the auxochromic effect of all dialkylaminogroups is not justified. We have prepared a number of morpholine and pyrrolidine dienamines in connection

with other work,⁶ and their u.v. absorption characteristics are summarised in Table 1 [column (c)]. These results show that there is a bathochromic shift of 13 nm (average) for pyrrolidine compared to morpholine dienamines. Comparison of the λ_{max} values [Table 2, column (c)] of 1-morpholinobutadiene (λ_{max} 267 nm) and 1-pyrrolidin-1-ylbutadiene (λ_{max} 280 nm), with the base value for acyclic dienes used in Woodward's rules (217 nm) indicates that there is an auxochromic shift of +50 and +63 nm for the morpholine and pyrrolidine substituents, respectively. However, we have consistently observed that the use of these values, in conjunction with the substituent corrections normally used in Woodward's rules to predict the λ_{max} values of dienamines, gives values [Tables 1 and 2, column (a)] some 15–20 nm greater than that observed. In a number of cases the observed λ_{max} values do not in fact differ greatly from those of the unsubstituted 1-morpholino- or 1-pyrrolidin-1-yl-butadienes (267 and 280 nm respectively). This indicates either that alkyl substituents do not have any effect on the λ_{max} values of dienamines or that their effect varies according to their position in the chain, a negative effect for one position cancelling a positive effect for another. The results of our investigations show conclusively that the latter is true, although the increments are small.

It has been suggested 7 that Woodward's rules are successful in predicting $\lambda_{max.}$ values for alkylated dienes since the excited state of butadiene is a mixture of ethylene exciton and charge-resonance states which is equivalent to a transition between two molecular orbitals which have coefficients equal in magnitude on each of the four carbon atoms. The effect of a substituent at C(1) would therefore be expected to be the same as that of a substituent at C(2). This situation would not be expected to appertain to dienamines, where the effective length of the conjugated system has been increased by the orbital interaction of the nitrogen lone pair.

The λ_{max} values for acyclic dienamines [Table 2, column (c)] clearly demonstrate the bathochromic effect of alkyl substituents at the β - and γ -positions. However,

293; J. Chem. Soc. (C), 1970, 716.
 ⁷ J. N. Murrell, 'The Theory of the Electronic Spectra of Organic Molecules,' Methuen, London, 1963.

¹ Part IX, P. W. Hickmott, B. J. Hopkins, and C. T. Yoxall,

J. Chem. Soc. (B), 1971, 205.
 ² R. B. Woodward, J. Amer. Chem. Soc., 1941, 63, 1123;
 1942, 64, 72; L. Fieser and M. Fieser, 'Steroids,' Reinhold, New York, 1959. ⁸ F. W. Heyl and M. E. Herr, J. Amer. Chem. Soc., 1953, 75,

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⁴ C. N. R. Rao, 'Ultraviolet and Visible Spectroscopy,' Butterworths, London, 1967; N. S. Isaacs, 'Experiments in Physical Organic Chemistry,' MacMillan, London, 1969. ⁵ W. D. Gurowitz and M. A. Joseph, *Tetrahedron Letters*, 1965,

^{4433.} ⁶ N. F. Firrell and P. W. Hickmott, J. Chem. Soc. (B), 1969,

	Dienamine (IV)						$\lambda_{\rm max}/{\rm nm}~(\Sigma~ imes~10^{-3})$		
	\mathbf{D}_{2} \mathbf{D}_{3} \mathbf{D}_{4} \mathbf{D}_{5} \mathbf{D}_{6}					Calc.		Obs	
R ¹ .N	α	B	κ. γ	δ	δ	Ref.	(a) * (b) †		(c)
Morpholino	н	н	'n	н	\mathbf{H}		ζ,	• • •	267 (22.5)
	Et	H	н	\mathbf{Me}	Me	1	282	267	267·5 (14·5)
"	H	Me	н	H	\mathbf{H}	а	272	272	272 (2Ì·5)
	\mathbf{H}	Me	н	Me	\mathbf{H}	а	277	272	267 (16·4)
<i>"</i>	н	Et	н	Et	н	b	277	272	272(12.4)
,,	н	н	Me	н	н		272	269	270 (20·9)
.,	\mathbf{H}	н	н	Me	н		272	267	267 (15·0)
	H	\mathbf{H}	н	Me	Me	а	277	271	271 (22·6)
Pvrrolidin-1-vl	H	\mathbf{H}	н	н	\mathbf{H}				280 (22·0)
.,	H	\mathbf{Et}	н	\mathbf{Et}	н	Ь	290	285	289(14.5)
	\mathbf{H}	н	н	Me	н		285	280	280 (20.7)
,,	н	н	н	Me	Me	a	290	284	281.5 (24.8)

TABLE 2 Observed and calculated λ_{max} values for acyclic dienamines (in hexane)

* † See Table 1 for footnotes.

^a H. Leatte, Rev. Port. Quim., 1965, 7, 214. ^b G. Opitz and W. Merz. Annalen, 1962, 652, 139.

a single alkyl substituent at the δ -position has no apparent effect, although the combined effect of two substituents in this position again causes a shift to longer wavelengths. Although crotonaldehyde is readily converted into the 1,3-bis(dialkylamino)alk-1-ene (VIII), which decomposes when heated to the 1-dialkylaminobutadiene (IX), all attempts to prepare linear conjugated dienamines containing a substituent at the α -position only [*i.e.* (VI)] have been unsuccessful¹ since the carbonyl group [in (VII)] is too unreactive for further condensation with the secondary amine to occur. However, we have prepared a morpholine dienamine containing an α - and two δ -substituents¹ (IV; $R^2 = Et$, $R^3 = R^4 = H$, $R^5 = R^6 = Me$) and the λ_{max} value (267.5 nm) (Table 2) clearly demonstrates that the bathochromic effect associated with the two 8-substituents has now been nullified by the α -substituent.

Consideration of these results has led us to propose the increments summarised in Table 3 to account for the

TABLE 3

Influence of alkyl substituents (or ring residues) on $\lambda_{max.}$ values of dienamines (in nm) $C(\alpha) \qquad C(\beta) \qquad C(\gamma) \qquad C(\delta)$ (One) $C(\delta)$ (Two)

influence of alkyl substituents or ring residues on the λ_{max} values of linear conjugated dienamines. The calculated values thus obtained for cyclic and acyclic dienamines [Tables 1 and 2, column (b)] are in generally good agreement with observed values except for those dienamines which have previously been shown ⁶ to contain considerable quantities of homoannular forms [as (V)]. The latter would be expected to absorb at longer wavelengths and overlap of the bands due to the hetero- and homo-annular forms present could then lead to an apparent single absorption band at intermediate wavelengths and of lower intensity, as observed.

The hypsochromic effect of an α -alkyl substituent can be explained in terms of electronic or steric effects. Molecular orbital calculations⁸ on the ground state and excited ⁸ state of simple enamines indicate that the electron density is greater at $C(\alpha)$ than at $C(\beta)$ in the excited state. Assuming this to be the case in dienamines, an electron-donating substituent at $C(\alpha)$ would be expected to destabilise the excited state relative to the ground state and thus exert a hypsochromic effect.



Alternatively, since the charge migration from the amino-group to the double-bond system in aniline is greater in the excited state than in the ground state,⁷ the hypsochromic effect of an α -substituent could be attributed to steric interactions in the dienamine impeding the contribution of the amine portion to the excited charge-transfer states, resulting in destabilisation of the excited state and a shift to shorter wavelengths. Although it is not possible to differentiate between this steric and electronic destabilisation of the excited state by an α -substituent, we consider the electronic effect to

⁸ E. M. Evleth, J. Amer. Chem. Soc., 1967, 89, 6445.

be the most likely since, in the examples we have examined, steric interactions between the α -substituent and the amine residue are either weak (as in the case of the cyclic dienamines) or can readily be relieved by rotation about a carbon-carbon single bond.

EXPERIMENTAL

U.v. spectra were determined on a Unicam SP 800 spectrophotometer for solutions in hexane. ¹H N.m.r. and i.r. spectra were determined on Varian A 60 and Perkin-Elmer 527 instruments, respectively, and the high resolution mass spectral determinations were carried out by the Physico-Chemical Measurements Unit, Harwell, by courtesy of the S.R.C.

Preparation of $\alpha\beta$ -Unsaturated Aldehydes.—(a) 3-Methylbut-2-enal was prepared by the reaction of 1-bromo-3-methylbut-2-ene with hexamethylenetetramine ⁹ (15%), b.p. 70—73° at 11.8 kN m⁻², ν_{max} (film) 1670 (C=O) and 1633 cm⁻¹ (C=C), τ (CDCl₃) 8.02 and 7.82 (each 3H, s) (Me₂C=), 4.06 (1H, dm, J 8 and 1.5 Hz, =CH), and -0.07 (1H, d, J 8 Hz, CHO).

(b) Pent-2-enal was obtained by acid hydrolysis ¹⁰ of 1,1-diethoxypent-2-ene ¹¹ (37%), b.p. 59—64° at 8.6 kN m⁻², ν_{max} (film) 1692 (C=O) and 1648 cm⁻¹ (C=C), τ (CCl₄) 8.85 (3H, t, J 7 Hz, Me), 7.62 (2H, m, J 7 and 6 Hz, CH₂), 3.92 (1H, dd, J 16 and 7.5 Hz, =CH), 3.12 (1H, dt, J 16 and 6 Hz, CH=), and 0.43 (1H, d, J 7.5 Hz, CHO).

Preparation of Dienamines.-The cyclic dienamines (Table 1) were already available.⁶ The u.v. data of some β -alkyl, β , δ - and δ , δ -dialkyl, and α , δ , δ -trialkyl substituted aminobutadienes are given in Table 2. The γ - and δ monoalkyl substituted aminobutadienes were prepared by addition of the $\alpha\beta$ -unsaturated aldehyde (0.05 mol. equiv.) to the secondary amine (morpholine or pyrrolidine) (0.1 mol. equiv.) and anhydrous potassium carbonate (6.9 g) with stirring at -10° . After 2 h at ambient temperature the mixture was filtered, the potassium carbonate was washed with ether, and the combined filtrates were evaporated to give the 1,3-dimorpholino-(or 1,3-dipyrrolidin-1-yl)-alk-1ene. This was heated to 100-130° at 105 mmHg and when elimination of the secondary amine had ceased the pressure was reduced and the residue was distilled rapidly. In this way the following were obtained:

(a) 1-Morpholinobuta-1,3-diene (38%), b.p. 102° at 1.6 kN m⁻², ν_{max} (film 1640 cm⁻¹ (C=C), m/e 139 (M^+), τ (CDCl₃) 7.08 and 6.30 (each 4H, m, morpholine ring), 5.37 (1H, dd, 4-H, *cis*- and *gem*-coupled), 5.18 (1H, dd, 4-H, *trans*- and *gem*-coupled), 4.84 (1H, dd, 2-H, *trans*- and *vic*-

⁹ W. G. Young and S. L. Linden, J. Amer. Chem. Soc., 1947, **69**, 2912.

coupled), 3.87 (1H, d, 1-H, trans-coupled), and 3.75 (1H, dt, 3-H, cis-, trans-, and vic-coupled) $[J_{1,2}$ 13 Hz, $J_{2,3} = J_{3,4}$ (cis) = 10 Hz, $J_{3,4}$ (trans) 16 Hz, and $J_{4,4}$ (gem) 2.5 Hz]. The intermediate 1,3-dimorpholinobut-1-ene showed v_{max} (film) 1655 cm⁻¹ (C=C), τ (CDCl₃) 8.82 (3H, d, Me), 7.48 (4H, m, CH₂·N·CH₂), 7.18 (5H, m, CH₂·N·CH₂ and CH), 6.28 (8H, m, CH₂·O·CH₂), 5.65 (1H, dd, J 14 and 8.5 Hz, 2-H), and 4.01 (1H, d, J 14 Hz, 1-H).

(b) 1-Pyrrolidin-1-ylbuta-1,3-diene (17%), b.p. 95° at 1.6 kN m⁻², ν_{max} (film) 1630 cm⁻¹ (C=C), τ (CDCl₃), 8·2 and 6·88 (each 4H, m, pyrrolidine ring), 5·56 (1H, dd, 4-H, cis- and gem-coupled), 5·30 (1H, dd, 4-H, trans- and gem-coupled), 5·05 (1H, dd, 2-H, trans- and vic-coupled), 3·75 (1H, dt, 3-H, cis-, trans-, and vic-coupled), and 3·53 (1H, d, 1-H, trans-coupled) [$J_{1,2}$ 13 Hz, $J_{2,3} = J_{3,4}$ (cis) = 10 Hz, $J_{3,4}$ (trans) 16·5 Hz, $J_{4,4}$ (gem) 2·5 Hz]. The intermediate 1,3-dipyrrolidin-1-ylbut-1-ene showed τ (CDCl₃) 8·78 (3H, d, Me), 8·17 (8H, m, CH₂ β nitrogen), 7·45 (5H, m), and 7·0 (4H, m) (CH₂·N·CH₂ and CH), 5·58 (1H, dd, J 14 and 9 Hz, 2-H), and 3·73 (1H, d, J 14 Hz, 1-H).

(c) 3-Methyl-1-morpholinobuta-1,3-diene (47%), b.p. 110° at 1.6 kN m⁻², ν_{max} . (film) 1631 and 1601 cm⁻¹ (C=C), m/e153·1153 (M^+) (C₉H₁₅NO requires 153·1154), τ (CDCl₃) 8·17 (3H, s, Me), 7·07 and 6·29 (each 4H, m, morpholine ring), 5·36 and 5·29 (each 1H, m, 4-H), 4·63 (1H, d, J 14 Hz, 2-H), and 3·84 (1H, d, J 14 Hz, 1-H). Attempts to prepare the corresponding pyrrolidine dienamine were unsuccessful, presumably owing to polymerisation.

(d) 1-Morpholinopenta-1,3-diene (11%), b.p. 120° at 1.9 kN m⁻², v_{max} (film) 1652 and 1625 cm⁻¹ (C=C), m/e 153·1152 (M⁺) (C₉H₁₅NO requires M, 153·1154), τ (CDCl₃) 8·29 (d, J 6·5 Hz, Me), 7·13 and 6·29 (m, morpholine ring), 4·83 (dd, 2-H, trans- and vic-coupled), 4·62 (dq, 4-H, transand vic-coupled), 3·97 (dd, 3-H, trans- and vic-coupled), 3·94 (d, 1-H, trans-coupled) ($J_{1,2}$ 13·5 Hz, $J_{2,3}$ 10 Hz, $J_{3,4}$ 15 Hz, $J_{4,5}$ 6·5 Hz).

(e) 1-Pyrrolidin-1-ylpenta-1,3-diene (35%) as a mixture of isomers [cis-trans-isomerism about the C(3)-C(4) double bond], b.p. 104° at 1.9 kN m⁻² [Found: N, 10.5%; m/e 137.1198 (M⁺). C₉H₁₅N requires N, 10.2%; M⁺ 137.1204], v_{max} (film) 1642 and 1620 cm⁻¹ (C=C), τ (CDCl₃) 8.31 (d, J 6.5 Hz, Me), 8.13 and 6.9 (each 4H, m, pyrrolidine ring), 4.9 (2H, m, 2- and 4-H), 4.0 (1H, m, 3-H), and 3.48 and 3.6 (each 1H, d) (J 13.5 Hz, 1-H of stereoisomers).

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¹⁰ P. Grünanger and D. Grieco, *Gazzetta*, 1958, **88**, 296.

¹¹ R. Kuhn and C. Grundmann, Chem. Ber., 1937, 70, 1894.