Functional group and substituent effects, both steric and electronic, upon the ultraviolet absorption spectra of some *N*-alkyl- and *N*,*N*-dialkyl-derivatives of some cinnamamides and benzalcyanoacetamides

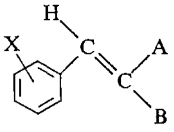
A. D. Delaney,[1] D. J. Currie, and H. L. Holmes
Chemistry Section, Defence Research Establishment Suffield, Ralston, Alberta

Received August 14, 1968

Conjugative and steric constants for *N*-substituted carboxyamide groups have been derived which allow the calculation of the long wavelength absorption maxima of *N*-alkyl- and *N*,*N*-dialkyl-derivatives of cinnamamide and benzalcyanoacetamide. Deviations between calculated and observed values indicate that there may be steric interference between bulky *N*,*N*-dialkylcarboxyamide groups and the benzylic hydrogen atom.

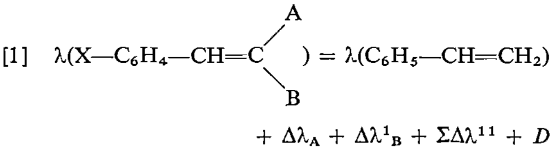
Canadian Journal of Chemistry, **47**, 3278 (1969)

Ultraviolet (u.v.) absorption spectra have been recorded for a number of *N*-alkyl- and *N*,*N*-dialkyl-derivatives of cinnamamide and benzalcyanoacetamide and their 4-chloro-, 4-methoxy-, and 3,4-methylenedioxy derivatives. The constancy of the long wavelength absorption maxima for the *N*-alkylcinnamamides, **1**(A = CONHR, B = H), and for the *N*-alkyl-benzalcyanoacetamides, **1**(A = CONHR, B = CN), and the close approximation of these (Tables I and II) to the respective values for the cinnamamides, **1**(A = $CONH_2$, B = H), and the benzalcyanoacetamides, **1**(A = $CONH_2$, B = CN), indicate that the *N*-alkyl group does not influence significantly the polarization of the conjugated system in these compounds. The effect of two alkyl groups on the carboxyamide nitrogen atom upon polarization of the conjugated system, on the other hand, is much more pronounced especially for bulky alkyl groups. For example, the absorption maximum of *N*,*N*-diisopropylcinnamamide is at a wavelength 5 mμ shorter than that of the *N*,*N*-di-*n*-propyl analogue. This probably results from interference between the isopropyl groups and the hydrogen atom on the β carbon atom rotating the *N*,*N*-diisopropylcarboxyamide group out of the plane of the styrene moiety, thus reducing overlap of the π orbitals. The assumption is made above that, in analogy with the configuration of benzalcyanoacetamide, the CONHR and $CONRR^1$ groups of these compounds are *trans* to the phenyl group.



1

Equation [1] was developed earlier in these laboratories (1) for calculating the long wavelength absorption maxima for conjugated heteroenoid compounds with the generalized structure **1**.



$$[1]\quad \lambda(\mathrm{X{-}C_6H_4{-}CH{=}C}\overset{\mathrm{A}}{\underset{\mathrm{B}}{}}) = \lambda(\mathrm{C_6H_5{-}CH{=}CH_2}) + \Delta\lambda_A + \Delta\lambda^1{}_B + \Sigma\Delta\lambda^{11} + D$$

The term $\Delta\lambda_A$ is the conjugative effect (mμ units) of the *trans* group, $\Delta\lambda^1{}_B$ is the inductive effect of the *cis* group in the same units, while $\sum\Delta\lambda^{11}$ is the sum of the steric effects of the A, B, and phenyl groups. *D* quantitates the effect (mμ units) of phenyl substituents, X, upon the absorption maximum (1, 3).

This equation has now been applied to these *N*-alkyl- and *N*,*N*-dialkyl-derivatives and for CONHR, $\Delta\lambda_A$ is +24 mμ and $\Delta\lambda^{11}$ is −10 mμ, while for $CONRR^1$, $\Delta\lambda_A$ is +31 mμ and $\Delta\lambda^{11}$ is −20 mμ.[2] Using these values, long wavelength absorption maxima have been calculated for the cinnamamides (Table I) and benzalcyanoacetamides (Table II) and compared with the observed

---

[1] Summer student; present address: McGill University, Montreal, Quebec.

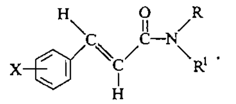
[2] The spectra of cinnamic acid, benzalcyanoacetic acid, and benzalmalonic acid (Table XI) provided values for the carboxyl group of $\Delta\lambda_A = +25.5$ mμ, $\Delta\lambda^1{}_B = +30.5$ mμ, and $\Delta\lambda^{11} = -9.0$ mμ. The conjugative effect ($\Delta\lambda_A \simeq +46.5$ mμ) and the steric effect ($\Delta\lambda^{11} \simeq -7.5$ mμ) for —C(O)Cl are obtained similarly from cinnamoyl chloride and benzalcyanoacetylchloride.

TABLE I

Calculated and average observed absorption maxima for some *N*-alkyl- and *N*,*N*-dialkyl-cinnamamides* in ethanol

X	R†	R^1†	Number of compounds	λ_{max} (mμ) Average obs. value	λ_{max} (mμ) Calculated value
H	H	H	1	272.5	272
	Alkyl	H	10	274 ± 1	273.5
	Alkyl	Alkyl	7	279 ± 1‡	280
4-Cl	H	H	1	303	—
				~277	277
	Alkyl	H	9	304	—
				~294	—
				~284	—
				277 ± 0.5	278.5
	Alkyl	Alkyl	2	~305	—
				~295	—
				286	285
				~282	—
4-CH_3O	H	H	1	~305	306.5
				~297	—
				292	—
	Alkyl or cycloalkyl	H	10	~305	308
				291.5	—
	Alkyl	Alkyl	3	310 ± 0.5	315
				299	—
O-3 CH_2 O-4	H	H	1	322.5	320.5
				290	—
				~283	276.5
	Alkyl or cycloalkyl	H	6	321 ± 0.5	322
				290 ± 0.5	—
				~283	278
	Alkyl	Alkyl	4	326 ± 0.5	329.5
				292.5 ± 0.5	—
				~287	284.5

*General formula:



†The R and R^1 groups are those listed in Tables III–VI.
‡When $R = R^1 = i\text{–}C_3H_7$, λ_{max} = 275.5 mμ.

values (Tables III–VI and Tables VII–X respectively).[3] For all the compounds listed λ observed = 0.98 λ calculated + 6.3. The correlation coefficient, *r*, is 0.99 and the standard errors of *r* and the estimate are 0.01 and 2.7 respectively.

Substituent X wavelength increments or *D* values (1, 3) were useful in predicting the positions of the long wavelength absorption bands of phenyl-substituted derivatives of the *N*-alkyl- and *N*,*N*-dialkyl-derivatives of the benzalcyanoacetamides. These *D* values, however, only provided one or two of the multiple absorption bands of 4-chloro-, 4-methoxy-, and 3,4-methylenedioxy-cinnamamides and their *N*-alkyl- and *N*,*N*-dialkyl-derivatives (Table I). A similar inadequacy of *D* values has been noted for other unifunctional styrene derivatives, e.g. 4-chloro-derivatives of ethyl cinnamate, cinnamanilide and β-nitropropenylbenzene.

The preparation of these compounds is described by Delaney *et al.* (2). Their spectra were determined with a Cary model 15 spectrophotometer using 10^{-3} *M* ethanolic solutions of the

---

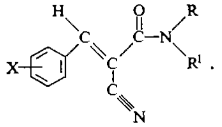
[3] Photocopies of Tables III–XI may be obtained free of charge, upon request, from The Depository of Unpublished Data, National Science Library, National Research Council of Canada, Ottawa, Canada.

TABLE II

Calculated and average observed absorption maxima for some *N*-alkyl- and *N*,*N*-dialkyl-benzalcyanoacetamides* in ethanol

				λ_{max} (mμ)	
X	R†	R¹†	Number of compounds	Average obs. value	Calculated value
H	H	H	1	299	302
	Alkyl or cycloalkyl	H	9	298±1.5	298.5
	Alkyl	Alkyl	3	295±6	295
4-Cl	H	H	1	307	307
	Alkyl or cycloalkyl	H	10	305±1.5	303.5
	CH_3	CH_3	1	301	300
4-CH_3O	H	H	1	336	340
	Alkyl or cycloalkyl	H	9	335±0.5	336.5
	Alkyl or cycloalkyl	Alkyl or cycloalkyl	4	328.5±0.5‡	332
O-3 CH_2 O-4	H	H	1	355.5 309	355.5 307
	Alkyl or cycloalkyl	H	5	355±2 308±1	351.5 303.5
	Alkyl	Alkyl	4	349±0.5 303	347.5 300

*General formula:



†The R and R¹ groups are those listed in Tables VII–X.
‡When R = R¹ = i–C_3H_7 or C_6H_{11}, λ_{max} = 326.5 mμ.

compounds.[4] Light isomerization of the *N*-alkyl and *N*,*N*-dialkyl derivatives of 4-methoxy- and 3,4-methylenedioxy-benzalcyanoacetamides required that the spectra of these compounds be determined as quickly as possible and in the absence of sunlight. The absorption maxima and the extinction coefficients of the cinnamamide- and benzalcyanoacetamide-derivatives are listed in Tables III to X.

Acknowledgment

The authors thank Mr. C. E. Lough for valuable discussions and for recording the ultraviolet spectra.

1. D. J. Currie, C. E. Lough, R. F. Silver, and H. L. Holmes. Can. J. Chem. **45**, 1567 (1967).
2. A. D. Delaney, D. J. Currie, and H. L. Holmes. Can. J. Chem. This issue.
3. D. J. Currie and H. L. Holmes. Can. J. Chem. **47**, 863 (1969).

---

[4] A hypsochromic shift of 3–3.5 mμ was observed for the maxima when cyclohexane was the solvent.