Tetrahedron, 1966, Vol. 22, pp. 209 to 215. Pergamon Press Ltd. Printed in Northern Ireland

ELECTRONIC SPECTRA OF DIAZOACETOPHENONES

L. L. LEVESON AND C. W. THOMAS
Chemistry Department, Bristol College of Science and Technology
Science Department, Bristol Technical College

(*Received* 15 *June* 1965; *in revised form* 30 *July* 1965)

Abstract—The electronic spectra of diazoacetophenone and thirteen nuclear-substituted diazoacetophenones are reported and discussed.

INTRODUCTION

ALTHOUGH the reactions of diazoketones have been extensively studied, the literature reveals a surprising scarcity of electronic spectral data for such compounds. We therefore report and discuss the results of our investigations into the UV and visible spectra of diazoacetophenone and a number of nuclear-substituted diazoacetophenones.

UV *spectra*

Table 1 lists the wavelengths of maximum absorption and molar extinction coefficients of diazoacetophenone in a number of different solvents. In most cases strong absorption bands are observed, at approximately 210, 250 and 290 mμ. The intensity of the absorption at 250 mμ decreases, compared with that at 290 mμ, as the proton-donating power of the solvent increases. No solvent was found in which either of these bands was completely eliminated and the absorption curves in aqueous solution were not significantly affected by changes in pH. In mixtures of butanol and hexane a well-defined isosbestic point was observed at 284 mμ.

The UV spectra of thirteen nuclear-substituted diazoacetophenones in n-butanol and n-hexane are summarized in Table 2 which lists the wavelengths of maximum absorption and the extinction coefficients of the compounds studied. All showed an absorption maximum at about 210 mμ. *p*-Methoxydiazoacetophenone and *p*-ethoxydiazoacetophenone displayed a single band only, whereas *p*-nitrodiazoacetophenone showed three absorption maxima, between 230 and 300 mμ. All the other compounds investigated showed two absorption bands similar to those of diazoacetophenone in this region. *m*-Nitrobenzene was anomalous in that the absorption in hexane was greatly suppressed.

With the exceptions of the four compounds already mentioned, and of *p*-chloro- and *m*-trifluoromethyldiazoacetophenones all the compounds gave a well-defined isosbestic point in hexane–butanol mixtures. The wavelengths of the isosbestic points are also recorded in Table 2 and a typical family of curves (that for *p*-methyldiazoacetophenone) is shown in Fig. 1.

As Bloor and Copley[2] have pointed out, there is no valid reason for expecting good correlations between spectroscopic data and reactivity substituent constants. Numerous attempted correlations of this type using the data of Tables 1 and 2

---

[1] A. J. Ultee Jr. and J. B. J. Soons, *Rec. Trav. Chim.* **71**, 565 (1952); from *Organic Electronic Spectral Data* Vol. 1. Interscience (1960).

[2] J. E. Bloor and D. B. Copley, *Chem. & Ind.* 526 (1960).

together with various reactivity substituent constants, were unsuccessful or only partially successful. A series of spectroscopic substituent constants $\sigma_s{}^+$, valid in hexane, can be calculated by Bloor and Copley's method using the data for substituted nitrobenzenes reported by Dearden and Forbes.[3]

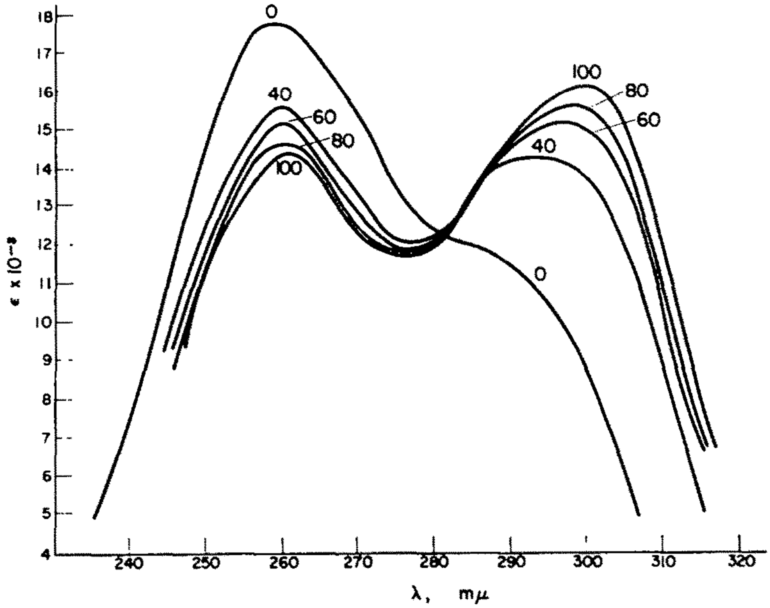

FIG. 1. UV spectra of *p*-methyldiazoacetophenone in mixtures of n-hexane and n-butanol. The numbers are the volume per cent of butanol in the mixture. ε is in l. mole^{-1} cm^{-1}.

Fig. 2 shows a plot of this function against the frequency shifts (of the 250 mμ band) produced by substituting the electron-releasing groups in the *p*-position of diazoacetophenone. The result for *p*-methoxydiazoacetophenone appears to be discrepant. This may be due to the uncertain assignment of the absorption at 285 mμ in the spectrum of this compound, or perhaps to an inherent weakness in this type of correlation (in a different type of frequency correlation, described later, the result for the *p*-methoxydiazoacetophenone gives a good fit).

For comparison purposes, data for *p*-substituted benzaldehydes and acetophenones (also taken from Ref. 2) are included in Fig. 2, which confirms the expected electron-attracting nature of the —COCHN$_2$ group. Another interesting comparison is of the wavelength displacements observed on both m- and p-substitution of diazoacetophenone with those obtained on substitution of benzaldehyde. The results are shown in Fig. 3 from which it can be seen that the slope of the line relating the wavelength displacements is almost exactly unity (calculated by the least squares method). It may be concluded that the electron-withdrawing ability of the —COCHN$_2$ group is approximately the same as that of the —CHO group and, therefore,[3] intermediate between that of the —NO$_2$ and —COCH$_3$ groups.

The occurrence of an isosbestic point in the UV spectra of most of the diazoacetophenones studied in mixed solvents parallels the previously reported behaviour of

---

[3] J. C. Dearden and W. F. Forbes, *Canad. J. Chem.* **36**, 1362 (1958).

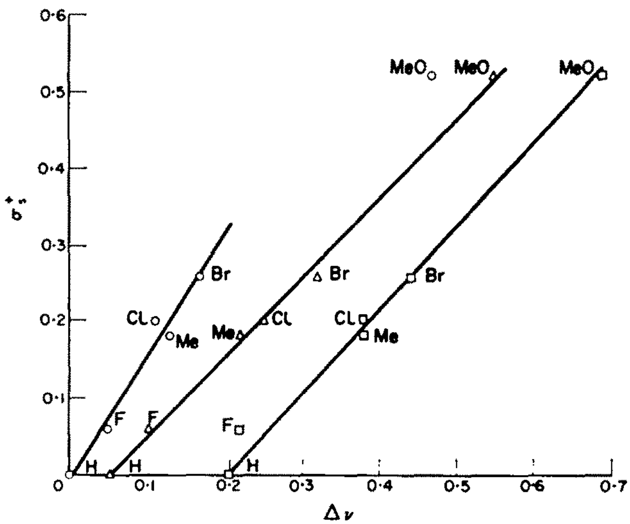

FIG. 2. Correlations between the spectroscopic substituent constant σ_r^+ and frequency shifts Δν (in hexane) observed on introducing *p*-substituents into 1. diazoacetophenone ○; 2. benzaldehyde △ and 3. acetophenone □. The spectroscopic substituent constants were evaluated from the data for nitrobenzenes given in Ref. 3 and the data for benzaldehydes and acetophenones were taken from the same source. For convenience 0·05 and 0·2 have been added to the frequency shifts of benzaldehydes and acetophenones, respectively.

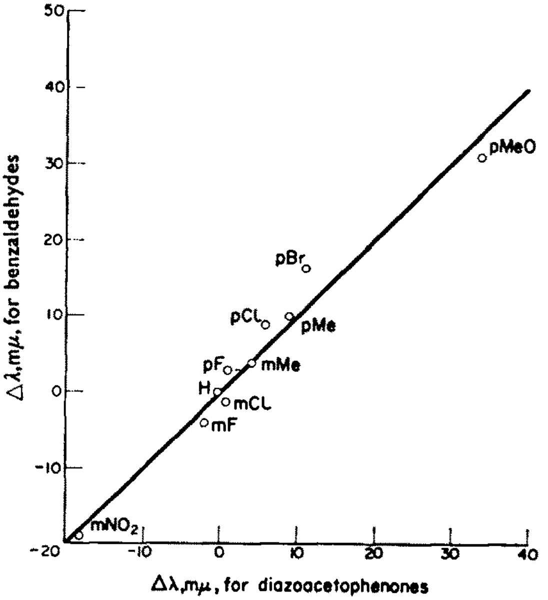

FIG. 3. Wavelength displacements observed on nuclear substitution of benzaldehyde and diazoacetophenone. All the values are for hexane as solvent; those for benzaldehydes were taken from Reference 3, those for diazoacetophenones from Tables 1 and 2.

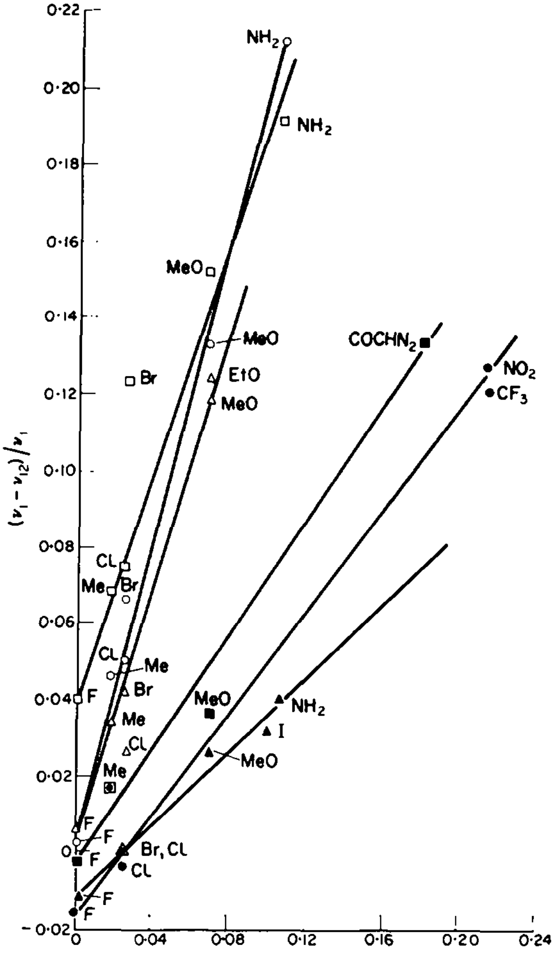

Fig. 4. Frequency correlations according to the method of Gowenlock and Morgan[10]. 1. *p*-substituted benzaldehydes □; 2. *p*-substituted nitrobenzenes ○; 3. *p*-substituted diazoacetophenones △; 4. *m*-substituted nitrobenzenes ■; 5. *m*-substituted diazoacetophenones ●; 6. *m*-substituted benzaldehydes ▲.
All the values are for hexane solution except that for *m*-methoxy nitrobenzene, which is for alcohol, and all are taken from reference 3 or Table 2. For convenience 0·028 has been added to the y-axis of line 1.

certain aliphatic diazoketones. In the latter cases the behaviour has been attributed to tautomerism between azo and iso-diazo forms[4] and to an equilibrium involving interaction between the diazoketone and the solvent.[5] However, it seems most likely that the isosbestic points observed with both aliphatic and aromatic diazoketones can reasonably explained on the basis of conformational isomerism.[6]

---

[4] F. A. Miller and W. B. White, *J. Amer. Chem. Soc.* **79**, 597 (1957).

[5] E. Fahr, *Chem. Ber.* **92**, 398 (1959).

[6] C. Pecile, A. Föffani and S. Ghersetti, *Tetrahedron* **20**, 823 (1964); F. Kaplan and G. K. Meloy, *Tetrahedron Letters* No. 35, 2427 (1964).

It was impossible to calculate reasonably consistent values for the spectroscopic moment of the —$COCHN_2$ group, using Platt's values[7] for the moments of the other substituent group. This is not surprising in the light of the large extinction coefficients of these absorption bands, and the apparent strong interaction of the —$COCHN_2$ group with the benzene ring.

The strong absorption bands at approximately 250 and 290 mμ may be due to intramolecular charge transfer in accordance with the ideas of Tanaka *et al.*,[8] who consider it unlikely that the high intensity band of benzene ($\lambda_{max} \sim 204$ mμ) would be shifted to such a large extent by substitution. If this is correct the absorption at approximately 210 mμ in the spectra of diazoketones may be attributed to an $A_{1g} \rightarrow B_{1u}$ transition. Alternatively, the bands at 250 and/or 290 mμ may be considered as the shifted 204 mμ ($A_{1g} \rightarrow B_{1u}$) band of benzene and the band at 210 mμ would have some other origin, as was suggested by Doub and Vandenbelt[9] in their spectral studies on substituted benzene derivatives.

TABLE 1. UV ABSORPTION CHARACTERISTICS OF DIAZOACETOPHENONE

Solvent	λ_{max} (mμ)	ϵ_{max} (l. mole^{-1} cm^{-1})	λ_{max} (mμ)	ϵ_{max} (l. mole^{-1} cm^{-1})	λ_{max} (mμ)	ϵ_{max} (l. mole^{-1} cm^{-1})	λ_{max} (mμ)	ϵ_{max} (l. mole^{-1} cm^{-1})
Hexane	211	13,400	251	12,900	280 (*sh*)	10,200	290 (*sh*)	9,300
Cyclohexane	210	11,300	251	12,700	280 (*sh*)	9,900	290 (*sh*)	9,150
Acetonitrile			255	11,300	285 (*sh*)	10,800	295	11,300
Dioxan			253	10,650	285 (*sh*)	9,500	297	9,460
Chloroform			253	10,900	293	11,100		
Butanol	210	6,200	252	12,000	297	12,900		
Ethanol*	210	13,800	252	12,000	297	12,600		
Water	200 (*sh*)	11,600	250	9,520	297	15,000		

(*sh*) indicates a shoulder on the absorption curve.

* λ_{max} values of 251 mμ (ϵ_{max} 135 l. mole^{-1} cm^{-1}) and 296 mμ (ϵ_{max} 195 l. mole^{-1} cm^{-1}) have been reported previously[1] for ethanol as solvent.

Gowenlock and Morgan[10] consider that the frequency correlations obtained with Doub and Vandenbelt's results support the latters' explanation of the origins of the UV absorption bands of disubstituted benzene derivatives. They obtained a linear relationship between the relative frequency shifts, $(\nu_1 - \nu_{12})/\nu_1$, of a series of disubstituted derivatives (substituent '1' being common) and the relative frequency shifts of monosubstituted benzene derivatives, $(\nu_H - \nu_2)/\nu_H$, where ν_H is the value for benzene.

Frequency correlations with our results are poor for the absorption at approximately 210 mμ, but reasonably good for the absorption at approximately 250 mμ in hexane as can be seen from Fig. 4. The result for *p*-nitrodiazoacetophenone is anomalous and is not shown; Gowenlock and Morgan also report discrepancies with *p*-nitro substituted compounds. The result for *m*-trifluoromethyldiazoacetophenone fits the line if $\lambda_{max} = 294$ mμ is chosen. This is not an unreasonable choice, since the absence of an isosbestic point in the spectrum of this compound suggests that the

---

[7] J. R. Platt, *J. Chem. Phys.* **19**, 265 (1951).

[8] J. Tanaka, S. Nagakura and M. Kobayashi, *J. Chem. Phys.* **24**, 311 (1956).

[9] L. Doub and J. M. Vandenbelt, *J. Amer. Chem. Soc.* **69**, 2714 (1947); **71**, 2414 (1949).

[10] B. G. Gowenlock and K. J. Morgan, *Spectrochim. Acta* **17**, 310 (1961).

TABLE 2. UV ABSORPTION CHARACTERISTICS OF SUBSTITUTED DIAZOACETOPHENONES

Substituent	Solvent	λ_{max} (mμ)	ε_{max} (l. mole^{-1} cm^{-1})	λ_{max} (mμ)	ε_{max} (l. mole^{-1} cm^{-1})	λ_{max} (mμ)	ε_{max} (l. mole^{-1} cm^{-1})	λ_{max} (mμ)	ε_{max} (l. mole^{-1} cm^{-1})	Wavelength of isosbestic point (mμ)
m-F	hexane	211	12,700	247	10,600	285	10,000			285
	butanol	216	8,500	248	9,700	298	10,900			
m-Cl	hexane	212	25,500	250	11,100	289	10,600			288
	butanol	210	14,900	250	10,800	295	12,500			
m-Br	hexane	218	24,300	251	11,700	289	11,200			286
	butanol	224	17,100	251	10,200	296	12,300			
m-CH_3	hexane	213	18,500	255	14,000	286	11,400			282
	butanol	218	13,300	255	12,300	293	14,900			
m-NO_2	hexane	224	5,600	275 (*sh*)	3,400	295	2,600			*
	butanol	233	18,100	300	11,400					
m-CF_3	hexane	213	13,200	228 (*sh*)	12,800	243	12,500	294	11,500	*
	butanol	220	8,000	245	9,600	301	11,200			
p-F	hexane	210	15,300	252	11,700	290	8,900			283
	butanol	216	9,200	253	11,100	297	12,300			
p-Cl	hexane	215	14,100	258	17,400	294 (*sh*)	10,900			*
	butanol	216	11,400	258	13,400	301	12,600			
p-Br	hexane	214	14,700	262	19,300	293 (*sh*)	11,400			285
	butanol	219	11,100	262	15,200	301	14,100			
p-CH_3	hexane	214	16,400	260	17,800	290 (*sh*)	11,400			283
	butanol	218	12,300	261	14,200	300	16,200			
p-NO_2	hexane	204	12,200	237	12,200	263	14,700	300	10,200	*
	butanol	214	7,500	244 (*sh*)	12,300	266	13,200	310	11,400	
p-CH_3O	hexane	218	16,400	285	20,800					*
	butanol	219	14,100	305	27,000					
p-C_2H_5O	hexane	210	17,000	218 (*sh*)	14,700	287	20,600			*
	butanol	224	11,700	306	25,200					

(*sh*) indicates a shoulder on the absorption curve.

* no isosbestic point observed.

bands at 250 and 290 mμ in this case are not comparable with the bands at these wavelengths in the spectra of other substituted diazoacetophenones.

For comparison, Fig. 4 also shows the frequency correlations obtained with the corresponding bands of substituted nitrobenzenes and benzaldehydes in hexane. In all cases the correlations are quite good for *meta* and *para* derivatives.

Visible spectra

In carbon tetrachloride and chloroform solutions all the diazoacetophenones studied exhibited a low intensity absorption band (λ_{max} ca. 400 mμ, ϵ_{max} ca. 25 l. mole^{-1} cm^{-1}). The electronic transition involved is probably of the $n \rightarrow \pi^*$ type due to the diazo group, in view of the fact that the band shows the characteristic blue (hypsochromic) shift on changing to the more polar solvent. The λ_{max} and ε_{max} values varied with concentration and in relatively dilute solutions (ca. 0·05M) the band developed fine structure.

A more detailed study of the visible spectra of these substances is being undertaken.

EXPERIMENTAL

The diazoacetophenones used in this study were all prepared by the method of Newman and Beal[11] and the m.ps have been recorded by other workers.[12–18] A dry ethereal solution of the appropriate acyl chloride (0·25 mole) in ether (1 l.) was added with stirring to a solution containing diazomethane (0·3 mole) and triethylamine (0·3 mole) in dry ether (1·5 l.) at 0°. The mixture was then allowed to stand at room temp for 2 hr, filtered to remove the precipitated triethylamine hydrochloride and the diazoketone was isolated by evaporation of the ethereal filtrate at about 40°. The crude diazoketones were purified by recrystallization to constant m.p. from pet. ether or, in the cases of the *m*- and *p*-nitrodiazoacetophenones, from abs EtOH. Diazomethane was prepared by the method of de Boer.[19]

The UV and visible spectra were obtained using a Perkin–Elmer model 137 recording spectrophotometer. The solvents used were analytical reagent or spectroscopic grade, with dilutions as necessary.

[11] M. S. Newman and P. Beal, *J. Amer. Chem. Soc.* **71**, 1506 (1949); **72**, 5163 (1950).
[12] W. Bradley and G. Schwartzenburg, *J. Chem. Soc.* 2904 (1928).
[13] P. Karrer and W. Graff, *Helv. Chim. Acta* **28**, 824 (1945).
[14] W. M. Morgans, R. Robinson and W. Baker, *J. Chem. Soc.* 374 (1933).
[15] E. R. Marshall, J. A. Kuck and R. C. Elderfield, *J. Org. Chem.* **7**, 444 (1942).
[16] A. L. Wilds and A. L. Meader, *J. Org. Chem.* **13**, 763 (1948).
[17] F. Arndt, B. Eistert and W. Partale, *Ber. Dtsch. Chem. Ges.* **60**, 1364 (1927).
[18] M. Berenbom and W. S. Fones, *J. Amer. Chem. Soc.* **71**, 1629 (1949).
[19] T. J. de Boer, *Rec. Trav. Chim.* **73**, 229 (1954).