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ULTRAVIOLET SPECTRA OF HYDRAZONES—I

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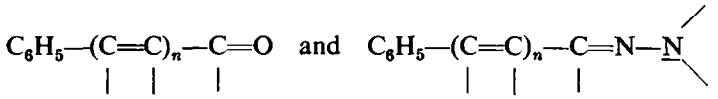
Abstract—The UV spectra of some hydrazones and alkylhydrazones were analysed in order to ascertain the contribution of the nitrogen lone pair to the conjugated system. In addition, the effect of steric hindrance on conjugation in dimethylhydrazones was investigated. It was found that the steric hindrance of the hydrazine methyl groups to the carbonilic methyl group decreases the intensity of the conjugation band.

IN spite of considerable studies of the UV absorption of hydrazones, the behaviour of these compounds is not completely understood. This is probably due to the absence of a systematic investigation and to the difficulty in their preparation and purification. In addition a direct comparison of the spectra available in literature is very difficult owing to the use of different apparatus and experimental conditions.

We commenced investigation of the different behaviour of two systems,



where $n = 0,1$. The data pertaining to the carbonyl compounds studied are reported in Table 1. It was observed that all the compounds studied exhibited two bands in the region of 220 mμ, whereas the literature reports only one.[1]

Since oximes[2] and methylimines[3] exhibit the same ultraviolet behaviour, it may be assumed that the —OH group of the former does not contribute to the conjugation of the complete system and its contribution, in terms of UV absorption, is comparable with a methylimino group. Bohlmann[4] showed that the substitution of an —OH

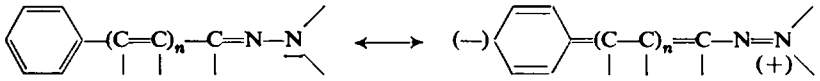
TABLE 1

Cinnamic aldehyde	λ_{max}	206	220	224	285
	log ε	4·04	4·08	4·08	4·38
α-Bromocinnamic aldehyde	λ_{max}	204	222	225	294
	log ε	3·90	3·70	3·69	4·31
α-Methylcinnamic aldehyde	λ_{max}	208	218	222 sh.	282
	log ε	3·95	3·98	3·93	4·36
Acetophenone	λ_{max}	207		242	280
	log ε	3·91		3·11	3·03
Benzalacetone	λ_{max}	208	220	224	285
	log ε	3·93	4·06	4·05	4·34

All the spectra listed were obtained using MeOH as solvent.

[1] *Organic Electronic Spectral Data*, Vol. I and II. Interscience, N.Y.
[2] L. K. Evans and A. Gillam, *J. Chem. Soc.* 565 (1943).
[3] G. Speroni in *The Chemistry of Heterocyclic Compounds*. Interscience, p. 193 (1962).
[4] F. Bohlmann, *Chem. Ber.* **84**, 400 (1951).

group for an $-NH_2$ (i.e., considering hydrazones instead of oximes) gives a red shift of 25 mμ. This bathochromic effect can be related to the contribution of a structure of the type[5]



The difference between oximes and hydrazones is mainly due to the fact that with the latter, the lone pair of electrons on the nitrogen atom participates in the conjugation of the system. Further evidence of this behaviour is indicated by the spectrum of the dimethylhydrazone of benzaldehyde which has three maxima, 208, 222 and 295 mμ, using methanol as solvent (Fig. 1). However, using methanol acidified with perchloric acid, only two bands are obtained, at 208 and 254 mμ (Fig. 1) (i.e. when the lone pair of nitrogen is not available for conjugation because of protonation, the spectrum is similar to that of benzaldoxime or methylbenzaldimine).

The replacement of one hydrogen of a hydrazone group by a methyl group gives rise to a red-shift of the conjugation band.[6] The hydrazone of benzaldehyde has a λ_{max} at 271 mμ, and the corresponding methyl- and dimethylhydrazones have λ_{max} at 285 and 295 mμ respectively. For methyl- and dimethylhydrazone, there are two more bands at 208 and 218 mμ sh. (Fig. 2) and at 208 and 222 mμ (Fig. 1) whereas for hydrazone there is only one broad band at 212 mμ (Fig. 2).

This may be explained if it is assumed that the replacement of a methyl group gives rise to a red-shift sufficient to show the two bands. Examination of the spectra of compounds reported in Tables 1 and 2 shows that the introduction of a $-\ddot{N}<$ group in a conjugated system has the same effect as a $>C=C<$ group. The band in question is located at high λ, as was pointed out for the case of phenylhydrazone of benzaldehyde and 1,4-diphenylbutadiene.[4] Because of the similar contribution of the two systems $>C=O$ and $>C=N-$, it would be expected that $C_6H_5-C=N-N<$ and C_6H_5-
$C=CH-C=O$ have the same conjugated band. This hypothesis is confirmed by
comparison of the spectra of cinnamic aldehyde (λ_{max} 285 mμ) (Fig. 2) and the methylhydrazone of benzaldehyde (λ_{max} 285 mμ) also of 5-phenyl-2,4-pentadienaldehyde (λ_{max} 324 mμ)[7] and the dimethylhydrazone of cinnamic aldehyde (λ_{max} 324mμ) (Fig. 3). The UV spectra of the hydrazone of acetophenone (Fig. 4) shows two bands; one at 208 and the other at 264 mμ). The blue-shift of this compound with respect to the hydrazone of benzaldehyde could be related to an effect of the methyl group. By studying the spectra of the dimethylhydrazone of cinnamic aldehyde and of the dimethylhydrazone of α-methylcynnamic aldehyde further evidence of the effect of the methyl group is obtained (Fig. 3). The spectrum of methylhydrazone of acetophenone (Fig. 4) has two maxima, at 206 mμ and 278 mμ and a shoulder at 218 mμ whereas the dimethylhydrazone (Fig. 4) has three maxima; at 206, 234 and 308 mμ. In this case as with the benzaldehyde derivatives the introduction of $-CH_3$ group (i.e. considering $-N<$ substituted hydrazones) gives rise to a red-shift of the second and third band. Nevertheless the behaviour of the dimethylhydrazone of acetophenone (I) is particularly

[5] N. H. Szmant and C. McGinnis, *J. Amer. Chem. Soc.* **74**, 240 (1952).
[6] D. Todd, *J. Amer. Chem. Soc.* **71**, 1353 (1949).
[7] W. Krauss and H. Grund, *Z. für Electrochem.* **58**, 767 (1954).

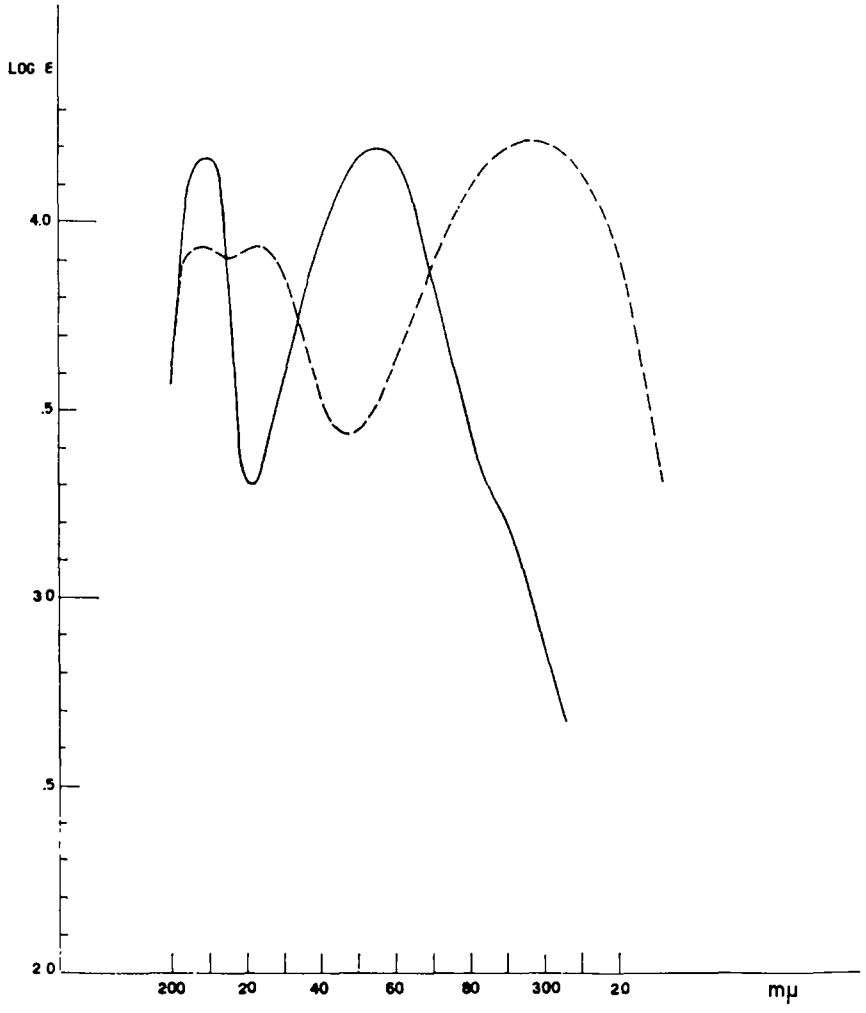


FIG. 1. ——— dimethylhydrazone of benzaldehyde (solvent: methanol acidified with perchloric acid; – – – – dimethyl hydrazone of benzaldehyde.

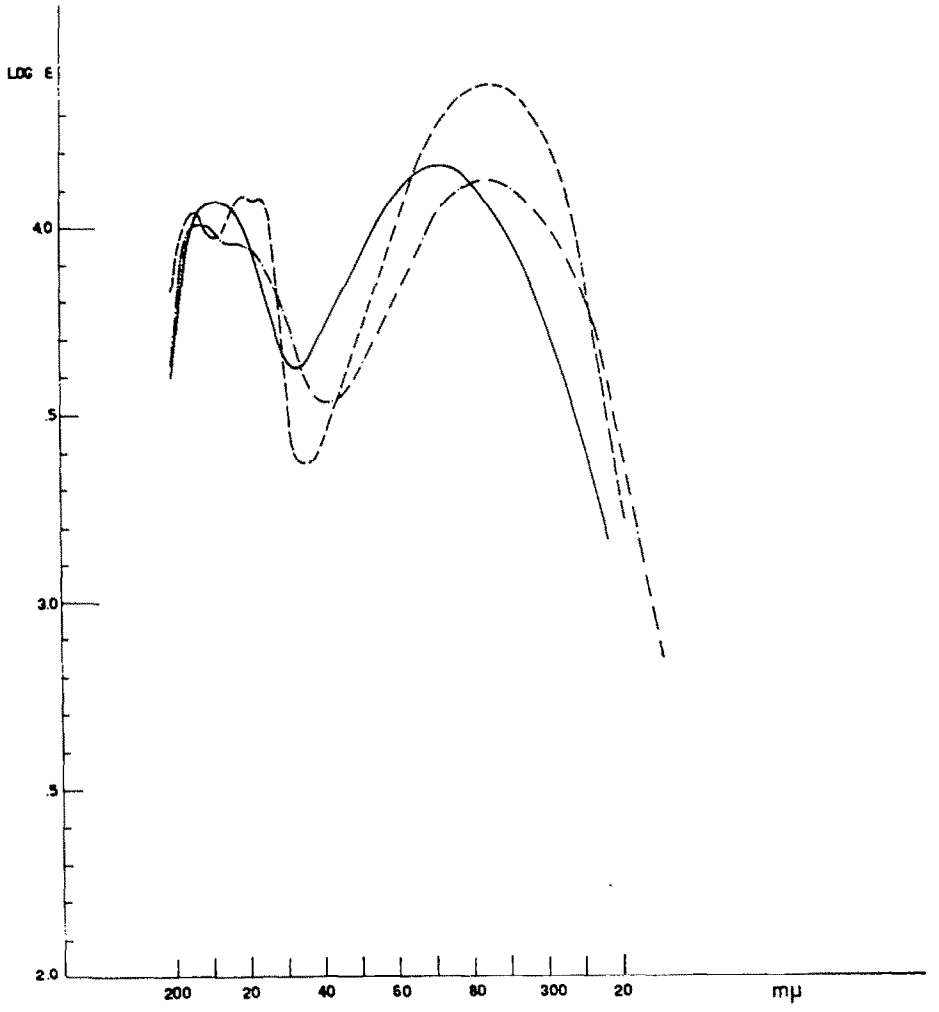


FIG. 2. ——— hydrazone of benzaldehyde; – – – – cinnamic aldehyde; · – · – · – · methylhydrazone of benzaldehyde.

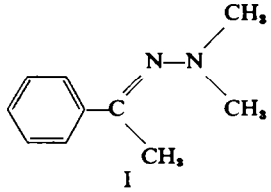
TABLE 2

C_6H_5—CH=NNH_2	λ_{max}	212		271	
	log ε	4·07		4·16	
C_6H_5—CH=NNHCH_3	λ_{max}	208	218 sh.	285	
	log ε	4·01	3·95	4·12	
C_6H_5—CH=$NN(CH_3)_2$	λ_{max}	208	222	295	
	log ε	3·94	3·93	4·22	
C_6H_5—C(CH_3)=NNH_2	λ_{max}	208		264	
	log ε	4·08		4·04	
C_6H_5—C(CH_3)=NNHCH_3	λ_{max}	206	218 sh.	278	
	log ε	4·08	3·90	3·98	
C_6H_5—C(CH_3)=$NN(CH_3)_2$	λ_{max}	206	234	308	
	log ε	4·05	4·05	3·35	
C_6H_5—CH=CH—CH=$NN(CH_3)_2$	λ_{max}	206	237	324	
	log ε	4·04	3·86	4·51	
C_6H_5—CH=CH—C(CH_3)=$NN(CH_3)_2$	λ_{max}	210	218	278	330
	log ε	4·14	4·11	4·34	3·69
C_6H_5—CH=C(CH_3)—CH=$NN(CH_3)_2$	λ_{max}	206	238 sh.	310	
	log ε	4·02	3·80	4·50	

All the spectra listed were obtained using MeOH as solvent.

interesting for it shows a different pattern from the dimethylhydrazones of aldehydes, i.e. benzaldehyde and cinnamic aldehyde.

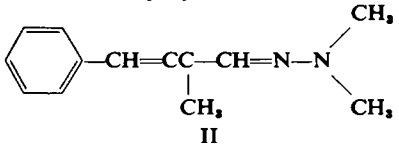
In fact, with the former compound a third band of low intensity is obtained, which can be explained by correlation of this effect with the steric hindrance between the $-CH_3$ group of acetophenone and dimethyl group of the hydrazinic part as shown below.



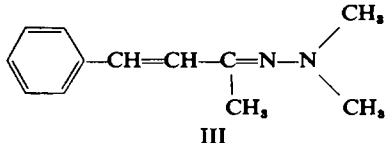
I

Braude *et al.*[8] has found a similar effect with hindered carbonyl compounds. He has shown that in the *o,o'* derivatives of acetophenone the intensity of the band is lower than would be expected. This was related to the steric hindrance between the 2,6-dimethyl groups of the ketone.

If this effect is of the same nature for compound I, one must find an analogous behaviour for the dimethylhydrazones of conjugated ketones, whereas the dimethylhydrazones of conjugated methylaldehydes must have the same pattern as α-non-substituted dimethylhydrazones.



II



III

[8] E. A. Brande, F. Sondheimer and W. F. Forbes, *Nature* **173**, 117 (1954).

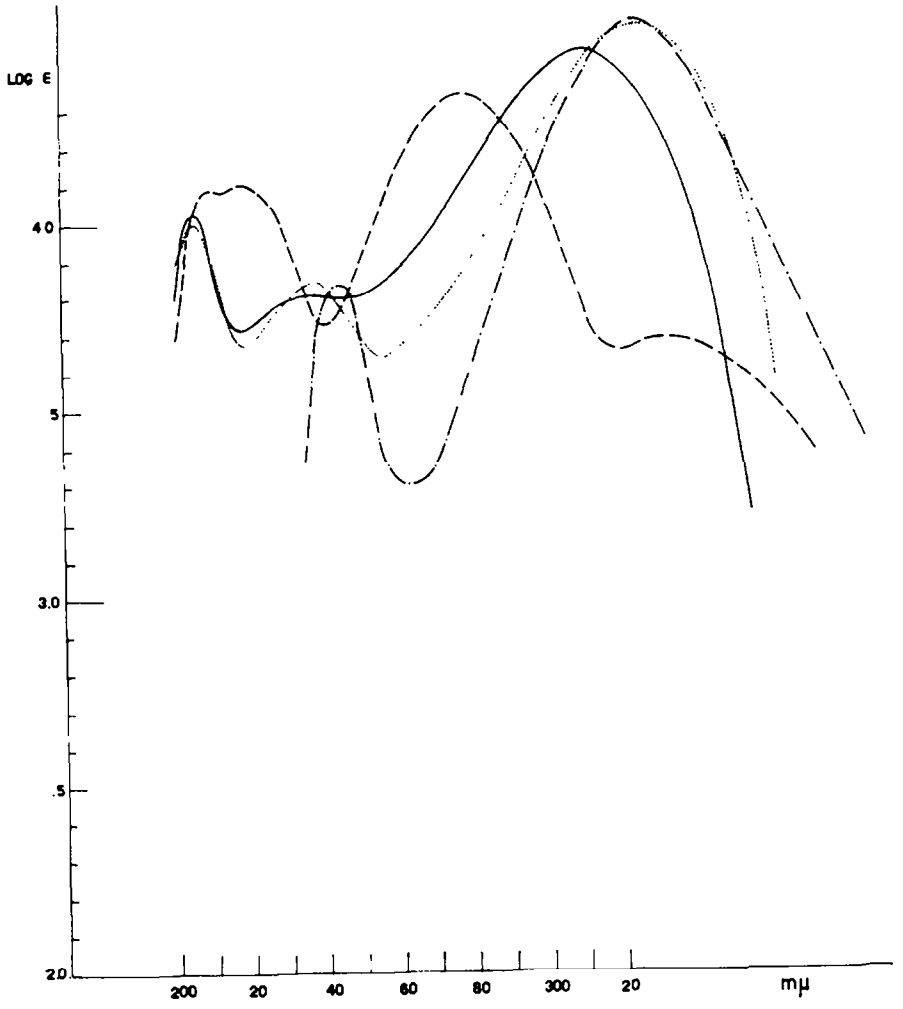


FIG. 3. ——— dimethylhydrazone of α-methylcinnamic aldehyde; – – – – dimethylhydrazone of benzalacetone; . – . – . – . 5-phenyl-2,4-pentadienaldehyde; . . . . . dimethylhydrazone of cinnamic aldehyde.

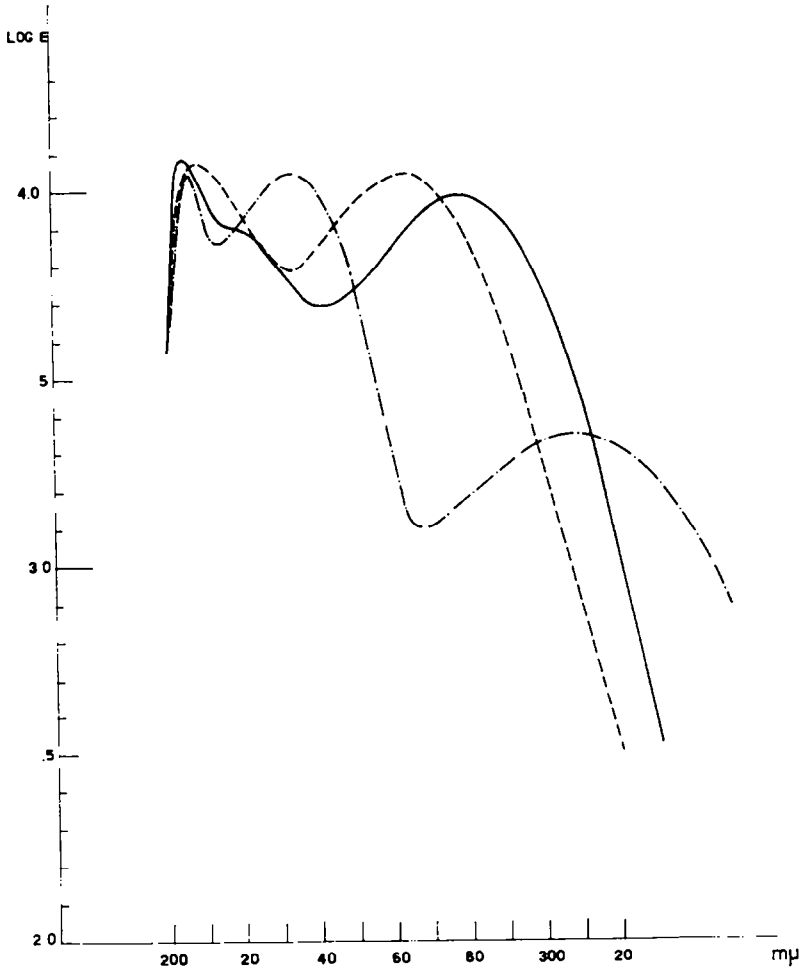


FIG. 4. ——— methylhydrazone of acetophenone; – – – – – hydrazone of acetophenone; . – . – . – . dimethylhydrazone of acetophenone.

Accordingly compounds (II) and (III) were prepared and their spectra studied (Fig. 3). For (II) there are three bands at 206, 238 and 310 mμ but (III) shows a different behaviour. In this case four bands were observed at 210, 218, 278 and 330 mμ. The significant feature is the low intensity of the last band, as expected, and the presence of a new band at 278 mμ.

EXPERIMENTAL

Methylhydrazone of acetophenone. Anhydrous methylhydrazine (5·5 g) and acetophenone (15 g) were heated with BaO and barium acetate in a sealed tube for 16 hr at 120°C. After filtering the liquid was fractionally distilled and the fraction boiling at 68°C at 0·04 mm Hg was retained and purified by gas chromatography; it melts at 20–21°C. (Found: C, 72·8; H, 8·4; N, 18·9. $C_9H_{12}N_2$ requires: C, 72·9; H, 8·2; N, 18·9%.)

Dimethylhydrazone of benzalacetone. Benzalacetone (16 g) dissolved in EtOH (15 cc) was added to N,N-dimethylhydrazine (6 g) and refluxed for 12 hr with BaO and barium acetate. After filtering the liquid was fractionally distilled and the fraction boiling at 92°C at 0·03 mm Hg was retained and purified by gas chromatography. (Found: C, 75·9; H, 8·7; N, 15·0. $C_{12}H_{16}N_2$: requires: C, 76·6; H, 8·6; N, 14·9%.)

Dimethylhydrazone of α-methylcinnamic aldehyde. α-Methylcinnamic aldehyde (1·33 g) dissolved in MeOH (5 cc) was added to N,N-dimethylhydrazine (0·6 g) and refluxed with BaO for 2 days. After filtration, the solvent was evaporated under vacuum and a colourless residue which was purified by vacuum sublimation at 25°C (0·01 mm Hg) was obtained. M.p. 44°C. (Found: C, 75·9; H, 8·6; N, 15·2. $C_{12}H_{16}N_2$ requires: 76·6; N, 8·6; N, 14·9%.)

Dimethylhydrazone of cinnamic aldehyde. Cinnamic aldehyde (17 g) and anhydrous N,N-dimethylhydrazine (9 g) were refluxed with BaO for 3 days in a system fitted with a $CaCl_2$ guard-tube. Further BaO and Et_2O (100 cc) were then added and refluxing continued for some hours. After fitration and removal of Et_2O, the product was distilled under red. press. (0·12 mm Hg; b.p. 108°C). An oily, yellowish liquid was obtained. (Found: C, 76·0; H, 7·9; N, 16·1. $C_{11}H_{14}N_2$: requires: C, 75·8; H, 8·1; N, 16·1%.)