either from a 1:1 complex formation with the solvent or from a direct physical perturbation.

In this investigation the ultraviolet spectra of the series of dinitroparaffins prepared were observed in both 95% ethanol (Fig. 1) and in dioxane (Fig. 2). The molar absorbtivities of these compounds were approximately twice as great as those reported for similar mononitroparaffins, indicating that the nitro groups absorb independently with little or no interaction in the molecule. Both bathochromic and hyperchromic shifts were observed with increasing chain length in the series. Less solvent perturbation occurs with secondary nitroparaffins than with similar primary compounds. No absorption band was observed near 380 mμ when ethanol was used as solvent and therefore it appears that no ionization of these compounds in the solvents studied occurs.[8] Thus the α,ω-dinitroalkanes are considerably weaker acids than either nitromethane or the *gem*-dinitro compounds.

In the case of *gem*-dinitroparaffins, the molar absorptivity is increased by the active solvents to the extent that the 280 mμ band was completely submerged.[7] With this series of α,ω-dinitroparaffins, the molar absorptivities were increased only slightly (9–10 absorptivity units) when dioxane was employed as solvent. Of those compounds examined, 1,3-dinitropropane appears to be the strongest acid in the series. This would indicate that solvent perturbation in the case of *gem*-dinitro compounds (stronger acids) involves a considerable amount of 1:1 complex formation. However, the small amount of solvent perturbation of α,ω-dinitroparaffins is probably the result of active solvent molecules forming a cage in close proximity to and surrounding the solute (a physical perturbation).

Electrolyses of aqueous solutions of the *aci*-salt of 1,6-dinitrohexane using a procedure described by Bahner were unsuccessful in an attempt to prepare 1,2-dinitrocyclohexane via oxidative ring closure.[9]

EXPERIMENTAL

The dinitroalkanes (Table I) were prepared essentially by the modified Victor Meyer procedure.[10] A representative procedure is described for the preparation of 1,6-dinitrohexane.

1,6-Dinitrohexane. To 1.5 l. of freshly distilled dimethylformamide at 0° were added, with stirring, 180 g. (3.0 mol.) of dry urea, 180 g. (2.61 mol.) of dry sodium nitrite, and 146.4 g. (0.6 mol.) of redistilled 1,6-dibromohexane. The mixture was allowed to stir at 0° for 90 min. after which time 160 g. (1.27 mol.) of anhydrous phloroglucinol was added to scavenge the nitrite esters formed. The reaction mixture was allowed to warm to room temperature over a period of 24 hrs. The mixture was then poured into 1 l. of crushed ice and extracted with methylene chloride. The extracts were washed with water and a saturated salt solution, and then dried. The solvent was removed under reduced pressure and the residual liquid was fractionally distilled, b.p. 100–103°/0.3 mm. The distillate recrystallized from absolute methanol at −78°.

1,6-Diiodo-1,6-dinitrohexane. To a cold solution of 8.4 g. (0.38 mol.) of the disodium salt of 1,6-dinitrohexane, (prepared from the reaction of 1,6-dinitrohexane with sodium methoxide in methanol) in 75 ml. distilled water was added a cold solution of 11.4 g. (0.07 mol.) sodium iodide and 19.2 g. (0.07 mol.) iodine in 100 ml. water.[11] Decolorization of the iodine solution was instantaneous and was accompanied by the formation of a light yellow finely divided precipitate. The precipitate was removed by filtration and washed with a cold solution of sodium iodide and several portions of water to yield 10.4 g. (64%) of impure 1,6-diiodo-1,6-dinitrohexane. The product was recrystallized from petroleum ether (30–60°), from ethanol-water and from carbon tetrachloride to yield pure product, m.p. 68.5–69.5°. The compound gave a positive qualitative test for iodine.

Anal. Calcd. for $C_6H_{10}N_2O_4I_2$: C, 16.83; H, 2.36. Found: C, 16.70; H, 2.21.

Ultraviolet absorption spectra. The ultraviolet absorption spectra were determined for freshly prepared 2–3 × 10^{-2} molar solutions in purified solvents with a Cary Model 11 recording spectrophotometer. Cell corrections, determined with pure solvent, were subtracted from the absorbancy values.

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(9) C. Bahner, U. S. patent 2,485,803, Oct. 25, 1949; *Chem. Abstr.*, **44**, 2876 (1950).

(10) N. Kornblum, H. Larson, R. Blackwood, D. Mooberry, E. Eliveto, and G. Graham, *J. Am. Chem. Soc.*, **78**, 1497 (1956).

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(12) J. Kispersky, H. Hass, and D. Holcomb, *J. Am. Chem. Soc.*, **71**, 516 (1949).

Structure and Spectra. I. Ultraviolet Absorption Spectra of 2,4-Dinitrophenylhydrazones of Aliphatic Dienones and Styryl Ketones

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The ultraviolet absorption spectrum of 2,4-dinitrophenylhydrazones of saturated and α,β-unsaturated carbonyl compounds is characterized by two distinct bands at 250–260 mμ and 350–400 mμ. The absorption of the 2,4-dinitrophenylhydrazones of styryl ketones, where the α,β-olefinic bond is conjugated to an aryl moiety, has now been examined. In every case a third maximum was observed at 300–310 mμ, not as a shoulder on the two other bands, but as a separate band, usually having an absorption intensity lower than the other two.

The spectra of some 2,4-dinitrophenylhydrazones of styryl ketones are reported in Table I, and some examples are described in Fig. 1. It is seen that the K-bands fall in the region 390–400 mμ, which is beyond that found by Braude and Jones[1] for

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(1) E. A. Braude and E. R. H. Jones, *J. Chem. Soc.*, 498 (1945).

TABLE I

Ultraviolet Absorption Spectra of 2,4-Dinitrophenylhydrazones of Styryl Ketones mμ[a]

2,4-Dinitrophenylhydrazone of	Formula	First Band		K-Band		Third Band	
		λ_{max}	ϵ	λ_{max}	ϵ	λ_{max}	ϵ
Benzalacetone[b]	I	258	15,600	395	40,100	307	14,800
Benzalacetophenone[c]	II	257	28,000	397	40,000	307	22,300
5-Carbethoxy-3-phenyl-2-cyclopentenone-2-acetic acid[d]	III	263	30,000	390	32,500	301	15,300
Ethyl 3-phenyl-2-cyclopentenone-2-acetate[d]	IV	268	23,000	395	34,000	300	15,800
Ethyl 3-β-naphthyl-2-cyclopentenone-2-acetate[e]	V	263	25,000	400	36,000	314	12,500

[a] All measurements were made in chloroform, using a Beckman DU spectrophotometer. [b] N. L. Drake and P. Allen Jr., *Org. Syntheses*, Coll. Vol. I, 77 (1951). [c] E. P. Kohler and H. M. Chadwell, *Org. Syntheses*, Coll. Vol. I, 78 (1951). [d] E. D. Bergmann, S. Yaroslavsky, and H. Weiler-Feilchenfeld, *J. Am. Chem. Soc.*, **81**, 2775 (1959). [e] E. D. Bergmann and S. Yaroslavsky, unpublished results.

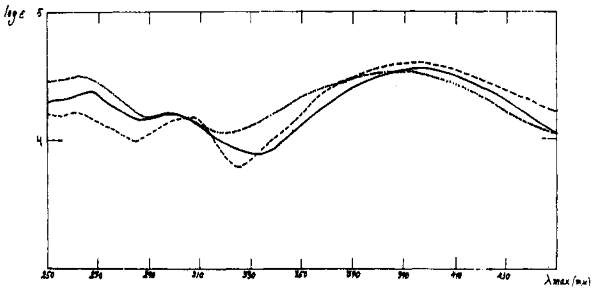

Fig. 1. Ultraviolet absorption spectra of 2,4-dinitrophenylhydrazones of styryl ketones: I ----. III ····. IV ——.

2,4-dinitrophenylhydrazones of α,β-unsaturated carbonyl compounds. The characteristic shift to longer wave lengths and the appearance of a third ultraviolet absorption band constitute two criteria which may help identify the 2,4-dinitrophenylhydrazones of styryl ketones.

The spectra of the 2,4-dinitrophenylhydrazones of the aliphatic dienone system have been examined by Braude and Jones.[1] The K-bands fall in the region 390–400 mμ, found by us characteristic for the 2,4-dinitrophenylhydrazones of styryl ketones. As for the appearance of a third band, the results are summarized in Table II. In some cases there appears a third ultraviolet band, while in others not. A careful examination of the latter cases will reveal the rule in the dienone system.

TABLE II

A Third Band in the Ultraviolet Spectra of the 2,4-Dinitrophenylhydrazones of Aliphatic Dienones (mμ)

2,4-Dinitrophenylhydrazone of	Formula	Third Band
$CH_3CH{=}C(CH_3)CH{=}CHCHO$	VI	308
Furfural	VII	302
ψ-Ionone	VIII	309
β-Ionone	IX	—
$C(CH_3)_2{=}CHCOCH{=}C(CH_3)_2$	X	—
Benzophenone	XI	—

Compound X is not a 2,4-dinitrophenylhydrazone of a normal (long-chained) dienone, but of a cross-conjugated one. According to Woodward[2] and Ruzicka[3] cross-conjugated dienones absorb approximately as α,β-unsaturated ketones, that is about 50 mμ lower than the normal dienones.[4] Therefore 2,4-dinitrophenylhydrazones of cross-conjugated dienones should show the same spectral properties as those of α,β-unsaturated ketones.

Benzophenone, carrying a phenyl group on each side of a carbonyl radical, has the properties of a cross-conjugated dienone. Indeed, its absorption maximum (252 mμ[5]) falls in the region of α,β-unsaturated ketones.

We may therefore conclude that every 2,4-dinitrophenylhydrazone of a normal dienone system (in contrast with 2,4-dinitrophenylhydrazones of a cross-conjugated one) shows a third band in the ultraviolet absorption spectrum. The only exception is the absorption of the 2,4-dinitrophenylhydrazone of β-ionone. But as this ketone shows many other abnormal properties (*e.g.*, the K-band of its 2,4-dinitrophenylhydrazone is about 20 mμ lower than that of ψ-ionone,[1] and the K-band of its semicarbazone is about 25 mμ lower than that of ψ-ionone[6]) it cannot upset the rule.

One would expect longer conjugated 2,4-dinitrophenylhydrazones to contain the third band, too. Indeed the 2,4-dinitrophenylhydrazones of the two trienones furfurylidene diethyl ketone and 2,4,6-octatrienal cited by Braude and Jones,[1] do show this band.

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(2) R. B. Woodward, *J. Am. Chem. Soc.*, **62**, 1208 (1940); **63**, 1123 (1941).

(3) L. Ruzicka *et al.*, *Helv. Chim. Acta*, **21**, 1735 (1937).

(4) *Cf.* E. A. Braude and F. C. Nachod, *Determination of Organic Structures by Physical Methods*, Academic Press, N. Y., 1955, p. 155, Table 10.

(5) H. Ley and H. Wingchen, *Ber.*, **67**, 501 (1934).

(6) A. Burawoy, *J. Chem. Soc.*, 20 (1941).