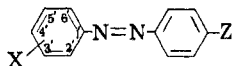


TABLE IV
 BANDS DUE TO ISO-PI-ELECTRONIC STRUCTURES


X ^b	λ_{\max} ($\epsilon \times 10^{-3}$)		X	λ_{\max} ($\epsilon \times 10^{-3}$)	
	95% EtOH Z = H	50% EtOH ^a Z = N ⁺ HMe ₂		95% EtOH Z = H	50% EtOH ^a Z = N ⁺ HMe ₂
4'-NO ₂	332 (24.0) ¹⁰	332 (7.1)	4'-OEt	349 (26.1) ¹⁷	354 (18.8)
4'-F	323 (20.3) ¹⁷	320 (14.4)	4'-N=N-C ₆ H ₅	359 (44.0)	355 (17.1)
H	318 (21.3)	320 (9.8)	2'-OMe	311 (12.5) ²¹	320 (8.9)
3',4'-(CH) ₄ ^c	328 (19.0) ¹⁸	325 (14.1)		360 (8.4)	360 (7.2)
2,2'-diMe	332 (17.4) ¹⁸	332 (13.8)	4'-SMe	362 (23.7) ^e	375 (13.8)
4'-Me	333 (23.5) ¹⁷	332 (12.3)	2',3'-(CH) ₄	372 (12.6) ¹⁸	380 (11.9)
4'-OMe	343 (36.0) ^{d,20}	352 (18.3)	4'-NH ₂	408 (27.5)	414 (14.5)
4'-NHAc	348 (31.6) ¹⁹	352 (15.2)		~440s (19.0)	~447s (12.2)

^a 1.2N hydrochloric acid. The acid solutions of these compounds also contain the C tautomer (see Tables I and II) which absorbs at a much longer wave length. ^b X refers to substituents in the prime ring except for X = 2,2'-diMe which, in the case of Z = H, refers to 2,2'-dimethylazobenzene and in the case of Z = N⁺HMe₂ refers to the A tautomer of the monocationic salt of 2,2'-dimethyl-4-dimethylaminoazobenzene. ^c The compound, X = 3',4'-(CH)₄, Z = H, is 2-phenylazonaphthalene. ^d In 50% alcoholic 1.2N HCl, λ_{\max} 348 m μ . ^e In 50% alcoholic 1.2N HCl, λ_{\max} 367 m μ .

nitrogen) of all types of 4-aminoazobenzene mono-cations with the spectra of the deaminated analogues in alcohol solution has shown that in all cases

the λ_{\max} are in the same region. A few examples of this phenomenon are given in Table IV.

EXPERIMENTAL

(17) P. Birnbaum, J. Linford, and D. Style, *Trans. Faraday Soc.*, **49**, 735 (1953).

(18) G. Badger and R. Buttery, *J. Chem. Soc.*, **1953**, 2156.

(19) A. Pongratz, G. Markgraf, and E. Mayer-Pitsch, *Ber.*, **71**, 1287 (1938).

(20) R. Zelinski and W. Bonner, *J. Am. Chem. Soc.*, **71**, 1791 (1949).

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Preparation of compounds. Most of the azo dyes were prepared by coupling the appropriate diazotized aromatic amine with the appropriate aromatic amine or phenol. Physical constants, procedures, and references have been given for many of the dyes in previous papers of the series.

Ultraviolet-visible absorption spectra. The absorption spectral data were determined with a Beckman Model DU Quartz spectrophotometer.

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[CONTRIBUTION FROM THE LOS ALAMOS SCIENTIFIC LABORATORY]

Ultraviolet Absorption Spectra of Dinitro Compounds

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Ultraviolet absorption spectra have been determined in polar and nonpolar solvents for several representative dinitro compounds. The solvent effects are compared with those in nitromethane.

Few ultraviolet absorption spectra of dinitro and polynitro compounds are recorded in the literature and most of these deal with the anions rather than with the unionized molecules.¹⁻³ The present study is concerned with solvent effects on dinitro compounds with terminal and nonterminal *gem*-dinitro groups and a comparable 1,2-dinitro compound.

EXPERIMENTAL⁴

The required compounds were prepared essentially by literature methods as indicated, and purified by fractional distillation or crystallization. 1,1-Dinitroethane, 1,1-dinitropropane, and 1,1-dinitropentane were obtained from the corresponding 1-halo-1-nitroparaffins by the ter Meer reaction.⁵ The experimental details are given only for 1,1-dinitropropane.

1,1-Dinitroethane boiled at 45° (2 mm.); yield 30%, n_D^{25} 1.4320, $\lambda(\text{NO}_2)$ 6.34, 7.50 μ .

1,1-Dinitropropane. To a flask containing 50 ml. of methanol were added simultaneously, while stirring a solution of

(1) G. Kortüm, *Z. physik. Chem.*, **B43**, 271 (1939); *Z. Elektrochem.*, **47**, 55 (1941).

(2) W. R. Edwards and C. W. Tate, *Anal. Chem.*, **23**, 826 (1951).

(3) J. Reinhart, J. G. Meitner, and R. W. Van Dolah, *J. Am. Chem. Soc.*, **77**, 496 (1955).

(4) Analyses by M. J. Naranjo.

(5) E. ter Meer, *Ann.*, **181**, 1 (1876).

1-chloro-1-nitropropane (123 g., 1 mole) in 200 ml. of methanol and a solution of potassium nitrite (85 g., 1 mole) and potassium hydroxide (56 g., 1 mole) in 300 ml. of 66% aqueous methanol. The rate of addition was regulated so as to maintain gentle refluxing of the alcohol. The mixture was stirred for 1 hr. and allowed to stand overnight. The yellow potassium salt was filtered with suction, washed with methanol and ether, suspended in ether, and treated with hydrogen chloride gas while cooled with ice. The formed potassium chloride was filtered. The blue filtrate gave 68 g. (50%) of green oil which was fractionated from a 1×50 cm. packed column, b.p. 45° (1 mm.), yield 55.7 g., n_D^{25} 1.4320, $\lambda(\text{NO}_2)$ 6.35, 7.50 μ .

1-Bromo-1-nitropentane. 1-Nitropentane was prepared from 1-bromopentane by the Victor Meyer reaction⁵ in 62% yield. The pure compound, b.p. 57° (9 mm.), n_D^{25} 1.4161, $\lambda(\text{NO}_2)$ 6.42, 7.25 μ , 0.2 mole, was added to a solution of sodium hydroxide in 100 ml. of water at 0° and treated with bromine (0.2 mole) at 0° . The mixture was stirred 0.5 hr. and extracted with chloroform. The extract was washed with sodium bicarbonate, sodium bisulfite, and water, dried over calcium chloride, and fractionated. 1-Bromo-1-nitropentane boiled at 37° (0.5 mm.), n_D^{25} 1.4627, yield 21.1 g. (54%), $\lambda(\text{NO}_2)$ 6.38, 7.41 μ .

Anal. Calcd. for $\text{C}_5\text{H}_{10}\text{BrNO}_2$: C, 30.64; H, 5.14; N, 7.14. Found: C, 30.57; H, 4.88; N, 7.69.

1,1-Dinitropentane was obtained from 1-bromo-1-nitropentane (19.6 g., 0.1 mole) as described for the propane derivative. The pale yellow oil (8.0 g., 49%) boiled at $43-44^\circ$ (0.1 mm.), n_D^{25} 1.4370, $\lambda(\text{NO}_2)$ 6.34, 7.52 μ .

Anal. Calcd. for $\text{C}_5\text{H}_{10}\text{N}_2\text{O}_4$: C, 37.04; H, 6.21; N, 17.29. Found: C, 36.76; H, 6.14; N, 16.73.

Ultraviolet absorption spectra. Ultraviolet absorption spectra were determined for freshly prepared 1×10^{-3} to 1×10^{-5} molar solutions in purified solvents with a Beckman Model DR spectrophotometer. Cell corrections, determined with pure solvents, were deducted from the absorbance readings. Duplicate determinations showed the

molar absorptivities to be correct to within $\pm 0.5\%$. The experimental results are given in Table I.

DISCUSSION

The ultraviolet absorption spectra of simple nitroparaffins are characterized by a low intensity transition without fine structure at around 280 $m\mu$ and a band of greater intensity below 200 $m\mu$.⁷

Solvent effects on these absorption spectra have been examined in detail to date only for a single compound, namely nitromethane.⁸ This compound gives "normal" spectra in solvents such as heptane, isoöctane, and petroleum ether; *i.e.*, "inactive" solvents; whereas the molar absorptivities are increased to nearly double in "active" solvents such as benzene. Active solvents, which include carbon tetrachloride, toluene, and dioxan, are believed to exert their specific effects either by complex formation with the solute molecules or by a physical solvent perturbation.⁸

Dinitroparaffins similarly possess a low-intensity absorption band near 280 $m\mu$. The molar absorptivities of these bands, compared with similarly constituted mononitroparaffins, are roughly doubled, regardless of whether the nitro groups are gem or vicinal. The nitro groups therefore absorb inde-

TABLE I
ULTRAVIOLET ABSORPTION SPECTRA OF DINITRO COMPOUNDS

1,1-Dinitro-Solvent	Ethane		Propane		Pentane	
	λ_{max}	ϵ	λ_{max}	ϵ	λ_{max}	ϵ
0.1 Hydrochloric acid	275	45.5	277	48.3	277	59.8
Acetonitrile	276	45.5	277	53.5	277	58.8
Methanol	276	47.2	277	52.0	277	59.2
Ethanol	276	52.6	277	54	278	61.5
Chloroform	280	52.7	280	57.9	280	63.5
Cyclohexane	280.5	54.6	281	61	281	63.7
Dioxan	(280) ^a	115	(280) ^a	117	(280) ^a	120
Benzene	(280) ^a	190	(280) ^a	198	(280) ^a	207
		2,2-Dinitropropane		2,3-Di-me-2,3-dinitrobutane		
		λ_{max}	ϵ	λ_{max}	ϵ	
Water		276	46.5	279	62.5	
0.1N Hydrochloric acid		276	47.5	279	61.1	
Acetonitrile		278	47.7	280	61.5	
Methanol		278	52	280	62.0	
Ethanol		278	52	281	61.9	
Chloroform		279	54	282	75.4	
Cyclohexane		280	55	284	75.7	
Dioxan		(280) ^a	105	282	77.8	
Benzene		(280) ^a	174	280	87.5	

^a No maximum.

(6) N. Kornblum, B. Taub, and H. E. Ungnade, *J. Am. Chem. Soc.*, **76**, 3209 (1954).

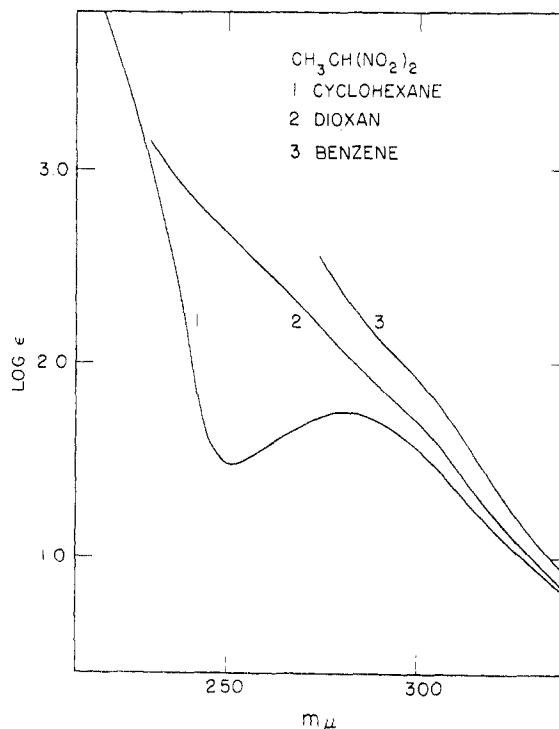


FIG. 1. ULTRAVIOLET ABSORPTION SPECTRUM OF 1,1-DINITROETHANE IN (1) CYCLOHEXANE, (2) DIOXAN, AND (3) BENZENE.

(7) R. N. Haszeldine, *J. Chem. Soc.*, 2525 (1953); H. E. Ungnade and R. Smiley, *J. Org. Chem.*, **21**, 993 (1956); A. E. Gillam and E. S. Stern, *Electronic Absorption Spectroscopy*, Edward Arnold, London, 1954.

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pendently and there is little or no interaction between them.

Terminal *gem*-dinitro compounds are ionized in alkali, in water aqueous solvents, alcohols, and ordinary acetonitrile. The ions give rise to new, highly intense absorption bands near 380 $m\mu$.¹ In carefully dried acetonitrile the new bands disappear and in dried alcohols the ionization is sufficiently small so that it may be neglected in determining the molar absorptivities of the unionized molecules at 280 $m\mu$.

In inactive solvents the wave lengths as well as the molar absorptivities of the 280 $m\mu$ bands in dinitroparaffins decrease with an increase in polarity or dielectric constant; *e.g.*, the blue shift of the maxima (in each case) for cyclohexane \rightarrow hydrochloric acid is of the order of 4 $m\mu$ and the hypochromic shift about 10 units of molar absorptivity. The

transition therefore may be classified, as in the case of simple nitroparaffins, as a *blue-shift* band.⁹

Active solvents cause only a slight increase in the molar absorptivities of 2,3-dimethyl-2,3-dinitrobutane but have very pronounced effects in increasing the absorptivities of *gem*-dinitro compounds. In the latter cases the 280 $m\mu$ band is completely submerged, possibly because of a simultaneous blue shift of the band (Fig. 1). Regrettably, solvent absorption in the active solvents imposes considerable limitations on measurements in the short wave length region.

In all cases examined, the molar absorptivities of the maxima increase with molecular weight as was observed for the monofunctional compounds.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF SYNTEX, S.A.]

Steroids. LXXXVI.¹ Synthesis of Monofunctional 11-Ketones

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Syntheses of the four monofunctional 11-keto steroids, androstan-11-one (IVa), testan-11-one (IVb), allopregnan-11-one (VIa) and pregnan-11-one (VIb) are described.

In this paper the synthesis of the four monofunctional steroidal 11-ketones—androstan-11-one (IVa), testan-11-one (IVb), allopregnan-11-one (VIa) and pregnan-11-one (VIb)—are described. The first³ and the last⁴ of these have been prepared previously in milligram quantities, whereas the other two are new. This project was undertaken at the request of Dr. Samuel Hall of the U.S. Public Health Service, Bethesda, Md.

For the preparation of androstan-11-one (IVa), we employed allopregnane-17 α ,21-diol-3,11,20-trione 21-acetate (Ia) as starting material, a substance readily prepared by the hydrogenation of cortisone acetate.⁵ Saponification of the acetate Ia produced the diol IIa, which on side-chain degradation by the excellent Rigby-Norymberski sodium bismuthate method⁶ smoothly yielded androstane-3,11,17-trione (IIIa). This route to the triketone

compares very favorably as regards yield and availability of starting materials with those described previously.^{3,7} Finally, reduction of IIIa by the Huang-Minlon modification of the Wolff-Kishner procedure⁸ without employing specially dried hydrazine furnished a mixture of androstane and androstan-11-one (IVa), from which the latter was separated in *ca.* 30% yield by chromatography. Although it has been shown that under particular experimental conditions the Huang-Minlon reduction may result in the removal of the 11-keto group,⁹ it has generally been assumed that the usual conditions⁸ do not affect this function. The structure of the 11-ketone IVa was confirmed by the elemental analysis (one oxygen function) by the infrared spectrum (six-membered ketone) and by the close agreement in melting point with the sample prepared by Steiger and Reichstein³ from androstane-3,11,17-trione (IIIa) by reduction to androstane-3 β ,17 β -diol-11-one by means of hydro-

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