[CONTRIBUTION FROM THE CANCER RESEARCH LABORATORY, UNIVERSITY OF FLORIDA]

Physical Properties of the Aminoazobenzene Dyes. VIII. Absorption Spectra in Acid Solution[1]

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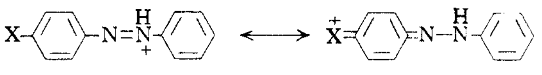
The absorption spectra in acid solution of approximately eighty azo dyes and, in particular, the long wave-length band of the monocationic salts has been investigated. In 4-substituted azobenzene derivatives the λ_{max} of the band associated with the cationic resonance structure, $C_6H_5—N^+H═N—C_6H_4—X \longleftrightarrow C_6H_5—NH—N═C_6H_4═X^+$, shifts to the red in the order: $H < OH < NH_2 < NHMe < NHEt < NMe_2 < SMe < NHC_6H_5$.

In 4-dimethylaminoazobenzene, DAB, there is a gradual shift toward the red with the substitution in the 4′-position of the following electron-donor groups: $H < Me < C_6H_5 = NHAc = OMe = N═N—C_6H_5 < SMe < NH_2 < NMe_2$. This red shift is believed to be due to the greater importance of structures involving electronic oscillation from one end of the molecule to the other. As there is a definite red shift for the monocationic salts of 2′- and 4′-alkoxy and amino derivatives of DAB and none for 3′-derivatives, as compared to DAB, the red shift must be due to an extraconjugative effect. The spectral red shift in a homologous series of monocationic salts of dyes such as 4-hydroxyazobenzene, 4-phenylazo-1-naphthol and 9-phenylazo-10-anthrol is postulated to be due to the increase in stability of the *p*-quinonic excited state structures and a consequent decrease in the change of energy involved in the transition of the molecule from the ground to the excited state on the absorption of light energy. The C_ϵ/A_ϵ ratios of some of the dyes were also discussed.

The presence and the relative proportion of the monocationic tautomers of the 4-aminoazobenzene dyes in acid solution has been investigated.[3–6] Many of these azo dyes have been shown to cause cancer in the rat.[7] In this paper a study is presented of the effect of various substituents on the long-wave-length band stemming from the cationic resonance structure of the C tautomer, I. In an organic compound which is capable of zwitterionic resonance, addition of a proton to the positive resonance terminal will usually cause a violet shift (toward the ultraviolet) of the long wave length band; addition of the proton to the negative resonance terminal will usually cause a red shift (toward the infrared). For example, in the aminoazobenzene dyes where an amino group is the positive resonance terminal, addition of a proton to this group shortens the chain of conjugation and causes a strong violet shift in the long-wave-length band. This new band is called an ammonium, or A, band.[5] Addition of a proton to the negative resonance terminal, *e.g.*, the β-azo nitrogen, causes a red shift. The new long-wave-length band has been called the cationic resonance, or C, band.[5] In a previous paper[8] it was shown that the fairly intense long-wave-length band of the azo dyes in neutral solution stems from a zwitterionic resonance structure. Increasing the electron-donor strength at the positive end of the molecule and/or increasing the electron-acceptor strength at the negative end of the molecule was found to cause a red shift in the spectrum. As this type of structure involves the expenditure of energy in the separation of charge, the addition of a proton to the negative resonance terminal would form a lower energy cationic resonance structure which would absorb at longer wave length.



I

The C band of 2′-, 3′- and 4′- nitro and acetyl derivatives of 4-dialkylaminoazobenzenes absorb at approximately 509 mμ. As 4-dimethylaminoazobenzene has its comparable band at 516 mμ, the effect of the electronegative groups on the C band is practically nil. In the simple 4-substituted azobenzene derivatives the wave-length maximum of the C band shifts to the red in the order: $H < OH < NH_2 < NHMe < NHEt < NMe_2 < SMe < NHC_6H_5$, Table I. Usually the bathochromic effect of a methylthio group is stronger than that of the hydroxyl group and weaker than that of the amino group, although it must be emphasized that in the present case, the spectra of azobenzene and its 4-hydroxy and 4-methylthio derivatives were determined in strongly acid solution while the amino compounds were determined in weakly acid solution. The absorption at a longer wave length of the 4-phenylaminoazobenzenes as compared to the analogous dimethylamino dyes is probably due to the following type of extraconjugation:

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[3] A. Hantzsch and A. Burawoy, *Ber.*, **63**, 1760 (1930).

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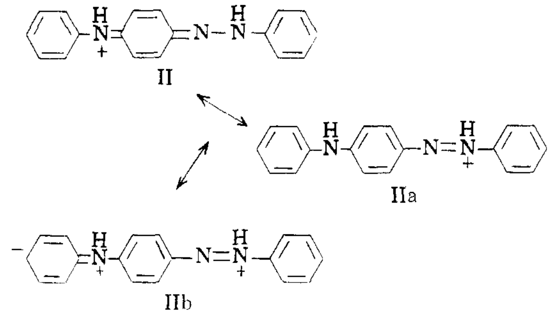

II

IIa

IIb

TABLE I

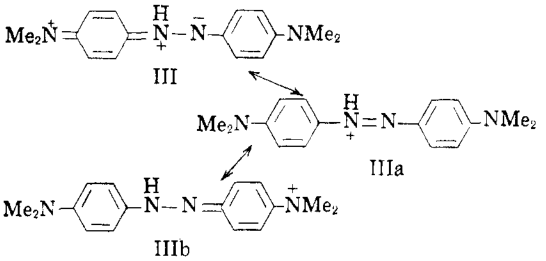
LONG WAVE-LENGTH BAND OF THE MONOCATIONIC SALTS OF 4-SUBSTITUTED AND 4,4'-DISUBSTITUTED AZOBENZENE DYES[a]

4-	4'-	λ_{max}	4-	4'-	λ_{max}
H	H	430[b]	NHC_6H_5	SCN	540
OH	H	476	NMe_2	C_6H_5	544
NH_2	H	500	NMe_2	NHAc	545
NHMe	H	505	NMe_2	OMe	548
NHEt	H	514	NMe_2	$N{=}NC_6H_5$	548
NMe_2	H	516	NMe_2	SMe	559
NMe_2	SCN	516	SMe	SMe	588[c]
NMe_2	Me	531	NHC_6H_5	SMe	590
SMe	H	532[c]	NMe_2	NH_2	610[d]
NHC_6H_5	H	540[e]	NMe_2	NMe_2	664[d]

[a] In 50% alcoholic 1*N* HCl. [b] In concentrated sulfuric acid.[10] [c] In a solution containing 25 ml. of 95% ethanol diluted to 100 ml. with concentrated sulfuric acid. [d] In glacial acetic acid. [e] In 50% alcoholic 6.8*N* sulfuric acid.[4]

This same type of extraconjugative effect is found in many types of compounds, *e.g.* $R\text{-}N^+H{=}CH\text{-}(CH{=}CH)_2\text{-}NHR$,[9] where R = Et, λ_{max} 400 and R = C_6H_5, λ_{max} 480 mμ. In any cationic resonance structure there are two positive resonance terminals separated by a chain of conjugated atoms. In the monocationic salts of the 4-aminoazobenzenes the two limiting resonance structures involve a positive charge on the amino nitrogen, *e.g.* II, and a positive charge on the β-azonium nitrogen, *e.g.* IIa. By extraconjugation is meant any additional conjugation which essentially lengthens the chain of conjugated atoms, *e.g.* IIb.

Another type of extraconjugative effect is shown by 4-aminoazobenzenes substituted in the 2'- and 4'-positions by electron donor groups. For example, in 4-dimethylaminoazobenzene there is a gradual shift toward the red with the substitution in the 4'-position of the following electron donor groups: H < Me < C_6H_5 = NHAc = OMe = $N{=}NC_6H_5$ < SMe < NH_2 < NMe_2, Table I. In 4,4'-bis-dimethylaminoazobenzene the extraconjugative resonance shown in III wherein the positive charge resonates from one amino group to the other apparently causes the strong red shift in the spectrum of the monocation of the compound. A similar type of bathochromic effect is postulated for 4-aminoazobenzene dyes containing 2'- and 4'-electron donor substituents.


III

IIIa

IIIb

There is a definite red shift for the 2'- and 4'-alkoxy and amino derivatives of DAB and none for the 3'- derivatives as compared to DAB, Table II. This indicates that the red shift must be due to an extraconjugative effect. The fused benzene ring in both 4'-dimethylaminophenylazonaphthalenes shows an extraconjugative effect equivalent to that of a 2'- or 4'- methoxy group.

2-Methoxy-, 2-methylthio-, 4-methoxy- and 4-methylthio-azobenzene exhibit a very strong red shift in acid solution, Table II. On the other hand the 3-methoxy and 3-methylthio derivatives, like azobenzene, give only a yellow color in strong acid solution. In all cases the proton has added to an azo nitrogen causing the formation of a cationic resonance system. In the 2- and 4- substituted derivatives the positive charge can resonate between the β-azonium nitrogen and the methoxy or methylthio hetero atoms. In the 3-substituted derivatives no such resonance can take place. Consequently the color and the spectra of these latter compounds closely resemble the color and spectra of azobenzene in the same solvent. The spectra of the much more basic 2- and 3-aminoazobenzenes in acid solution resemble that of azobenzene showing that the proton has gone to the amino nitrogen, Table II.

Points of resemblance have been found between the tautomerism of 4-hydroxyazobenzene derivatives and higher homologues and the tautomerism of the monocationic salts of the 4-aminoazobenzenes.[14] In this respect in alcohol solution 4-hydroxyazobenzene exists only as the azo dye, 4-phenylazo-1-naphthol exists as a mixture of azo and phenylhydrazone tautomers while '9-phenylazo-10-anthrol' exists wholly as the phenylhydrazone. These results parallel the reduction potentials[15,16] in alcohol of *p*-benzoquinone, 0.71 v.; α-naphthoquinone, 0.49 v.; 1,4-anthraquinone, 0.40 v.; and 9,10-anthraquinone, 0.15 v. These results mean that

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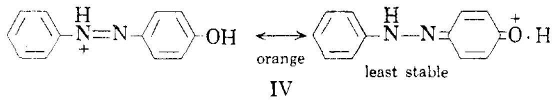
TABLE II

Visible Absorption Spectral Data of Miscellaneous Azo Dyes

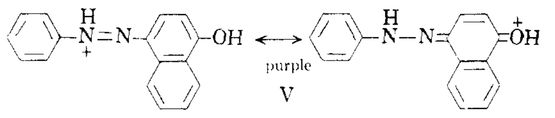
Compound	Color[a]	λ_{max}, mμ	Solvent	Compound	Color	λ_{max}, mμ	Solvent
2-Methoxy AB[b]	O	474	S[c]	4′-Methoxy DAB	V	548	[g]
3-Methoxy AB	Y	—	S	2′-Amino DAB	B	643	[h]
4-Methoxy AB	O	470	S	3′-Amino DAB	O	520s[i]	[h]
2-Methylthio AB[11]	G	—	S	4′-Amino DAB	B	610	[h]
3-Methylthio AB[11]	Y	—	S	4-Hydroxy AB	O	476	S
4-Methylthio AB	V	532	S	4-Phenylazo-1-naphthol	P	578	S
2-Amino AB	Pale P	570[d]	[e]	9-Phenylazo-10-anthrol	B[j]	—	S
3-Amino AB	Light Y	[d]	[e]	4-Phenylazo-1-naphthylamine[12]	V	545	[k]
4-Amino AB	R	502	[e]	4-Phenylazo-1-anthrylamine[13]	B	—	[l]
2′-Methoxy DAB	V	540	[g]	1,4′-Dimethylaminophenylazonaphthalene	V	540	[g]
3′-Ethoxy DAB	R	521	[g]	2,4′-Dimethylaminophenylazonaphthalene	V	545	[g]

[a] O = orange; Y = yellow; G = green; V = violet; P = purple; R = red; B = blue. [b] AB is azobenzene. [c] S is concentrated sulfuric acid. [d] The band for 2-amino AB at 570 mμ may be due to a slight amount of impurity or a very small amount of the C tautomer.[5] Otherwise the spectra in acid of 2- and 3-aminoazobenzene closely resemble the spectrum of azobenzene. [e] In 50% alcoholic 6*N* hydrochloric acid. [f] DAB is 4-dimethylaminoazobenzene. [g] In 50% alcoholic 1.2*N* hydrochloric acid. [h] In 95% acetic acid. [i] s = shoulder. [j] Unstable color. [k] In alcoholic 0.1*N* hydrochloric acid. [l] In "acid solution."[13]

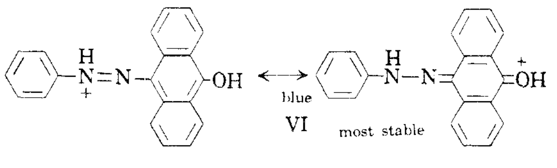
p-quinone structures increase in stability in the following order: *p*-benzoquinone < α-naphthoquinone < 1,4-anthraquinone < 9,10-anthraquinone. A somewhat similar explanation can be given for the spectral red shift in the two series; 4-hydroxyazobenzene, IV < 4-phenylazo-1-naphthol, V < 9-phenylazo-10-anthrol, VI and 4-aminoazobenzene < 4-phenylazo-1-naphthylamine < 4-phenylazo-1-anthrylamine, Table II. In these compounds an increase in the stability of the *p*-quinonic excited state structure parallels the increasing red shift, *e.g.*



IV



V

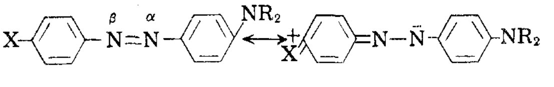


VI

A shift toward longer wave length would naturally result from any decrease in the change in energy involved in the transition of a molecule from the ground to the excited state on the absorption of light energy.

An investigation of the absorption spectra of azobenzene dyes containing a 4-alkylthio or a 4-phenylamino substituent in acid solution indicates the probably complete predominance of the C tautomer, Table III. The weak band at approximately 350–370 mμ in the acid spectra of 4-alkylthioazobenzenes has, as yet, not been satisfactorily diagnosed.

As the electron-donor strength of a group in the 4′-position of a 4-dialkylaminoazobenzene increases from hydrogen to methoxy, the C_ϵ/A_ϵ ratio decreases and the C band shifts toward the visible.[5] DAB has a C_ϵ/A_ϵ ratio of 3.6 while 4′-methoxyDAB has a C_ϵ/A_ϵ ratio of 1.0 in 50% alcoholic 1.2 N hydrochloric acid. The decrease in the C_ϵ/A_ϵ ratio is believed to be due to a decrease in the electron density at the β-nitrogen because of the following type of competitive resonance

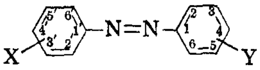


In 4′-methylthioDAB, C_ϵ/A_ϵ 2.0, an additional factor is probably present. This is the presence of the B tautomer involving proton addition to the α-azo nitrogen. The C and B tautomers would both be expected to absorb near 560 mμ. In the 4′-amino-DAB derivatives and possibly 2′-aminoDAB four monocationic tautomers, involving proton addition to the amino and azo nitrogens, should be present. The base-strengthening effect of the 2-methyl group on the β-nitrogen is shown by the increased C_ϵ/A_ϵ ratios on addition of a 2-methyl group to 4′-methylthioDAB and 4′-amino-DAB. This is in line with previous work.[5]

The spectra of 2′-, 3′- and 4′-aminoDAB derivatives in acetic acid show the presence of a long-wave-length C band and a shorter-wave-length band which may be due to the A tautomer (involving proton addition to the primary amino group)

TABLE III

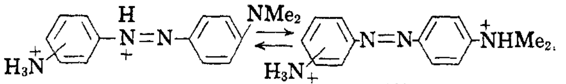
THE C_ϵ/A_ϵ RATIO OF 4-AMINO- AND 4-ALKYLTHIO- AZOBENZENE DYES



X^a	Y^a	λ_{max} ($\epsilon \times 10^{-3}$) C Band	λ_{max} ($\epsilon \times 10^{-3}$) A Band	Solvent^b	$\frac{C_\epsilon}{A_\epsilon}$
H	4-SMe	532 (57.3)^c	—	75% H_2SO_4	∞
H	2-Me-4-SEt	540 (42.6)^c	—	75% H_2SO_4	∞
4′-SMe	4-SMe	588 (55.9)^d	—	50% H_2SO_4	∞
4′-SCN	4-NHC_6H_5	540 (50.8)	—	1.2*N* HCl	∞
4′-SMe	4-NHC_6H_5	590 (54.3)^e	—	1.2*N* HCl	∞
4′-SMe	4-NMe_2	559 (22.2)	380 (14.2)	0.06*N* HCl	1.6
		559 (27.5)	375 (13.8)	1.2*N* HCl	2.0
4′-N^+HMe_2	4-SMe	554 (57.0)^f	—	95% H_2SO_4	—
4′-SMe	2-Me-4-NMe_2	553 (44.1)	374 (8.48)	1.2*N* HCl	5.2
2′-NH_2	4-NMe_2	643 (18.7)	472 (8.72)^g	95% AcOH	—
2′-N^+H_3	4-NMe_2	488 (2.38)^h	322 (28.2)	1.2*N* HCl	0.11
		503 (4.15)^i	320 (19.8)	6*N* HCl	0.21
3′-NH_2	4-NMe_2	520s (9.40)	430 (20.0)^g	95% AcOH	—
3′-NH_2	4-NMe_2	504 (38.1)	316 (9.28)	1.2*N* HCl	4.1
4′-NH_2	4-NMe_2	610 (21.5)	414 (14.5)^g	95% AcOH	—
4′-N^+H_3	4-NMe_2	504 (40.4)	315 (9.20)	1.2*N* HCl	4.4
4′-NH_2	2-Me-4-NMe_2	595 (28.3)	415 (8.48)^g	95% AcOH	—
4′-N^+H_3	2-Me-4-NMe_2	505 (50.9)	323 (4.60)	1.2*N* HCl	11.1
4′-NMe_2	4-NMe_2	664 (35.2)	430 (13.1)^g	95% AcOH	2.7
4′-N^+HMe_2	4-NMe_2	505 (50.5)	309 (6.9)	1.2*N* HCl	7.3
4′-N^+HMe_2	4-N^+HMe_2	405 (33.2)^j		95% H_2SO_4	

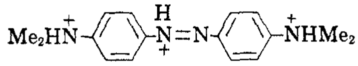
[a] X represents a 2′-, 3′-, or 4′-substituent in the prime ring, while Y represents the 4- or 2,4- substituent(s) in the other ring. [b] All solutions were 50% alcoholic except 75% sulfuric acid (75 ml. of concentrated sulfuric acid diluted to 100 ml. with 95% ethanol) and 95% sulfuric acid and acetic acids (5 ml. of 95% ethanol diluted to 100 ml. with the appropriate commercial acid). [c] Also a shoulder at 360–370 mμ. [d] Also λ_{max} 355, ε 1680. [e] Also λ_{max} 425, ε 5840 which may be due to the presence of some base. [f] Also λ_{max} 370, ε 3400. [g] This band could be due to the presence of base in solution. [h] A shoulder at about 440, ε 1630 stems from the R band of the A tautomer. [i] A shoulder present at 440, ε 1250 stems from the R band of the A tautomer. [j] Shoulders present at 485, ε 6250 and 319, ε 10900 stem from the two dicationic tautomers also present.

and/or the base itself. The spectra of these derivatives in 50% alcoholic 1.2 *N* hydrochloric acid show the presence of a C Band with one proton added to the 2′-, 3′- or 4′-amino nitrogen and the other added to the β azo nitrogen, VII, and an A band with a proton attached to each amino group, VIII. The spectra of the 3′- and 4′-aminoDAB derivatives in 50% alcoholic 1.2 *N* hydrochloric acid are closely similar to the spectrum of DAB[5] in the same solvent. The spectrum of 2′-aminoDAB, C_ϵ/A_ϵ 0.11, in 50% alcoholic 1.2 *N* hydrochloric acid resembles that of 2′-methylDAB,[5] C_ϵ/A_ϵ 0.29, in the same solvent. Some of the factors which probably contribute to the very small proportion of C tautomer present in the acid solution are the steric hindrance and proton repulsion of the 2′-N^+H_3 group, and the decrease in the electron density of the β- azo nitrogen due to the inductive effect of the -N^+H_3 group.



VII VIII

The spectrum of 4,4′-bisdimethylaminoazobenzene in 95% sulfuric acid consists of the tricationic dye, IX, λ_{max} 405 mμ, iso-*pi*-electronic with the monocationic salt of azobenzene, λ_{max} 430 mμ. The bands at 485 and 319 mμ are due to the presence of the dicationic tautomers, Fig. 1.



IX

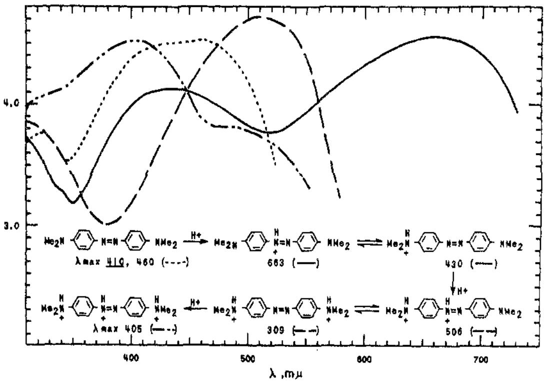
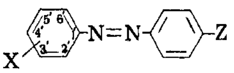


FIG. 1. VISIBLE ABSORPTION SPECTRA: 4,4′-Bisdimethylaminoazobenzene in 95% ethanol (......); in 95% acetic acid (———); in 50% alcoholic 1.2 *N* hydrochloric acid (- - - -); in 95% sulfuric acid (—··—··).

Comparison of the A bands (arising from the tautomer involving proton addition to the amino

TABLE IV

BANDS DUE TO ISO-PI-ELECTRONIC STRUCTURES



X[b]	λ$_{max}$ (ε × 10^{-3}) 95% EtOH Z = H	λ$_{max}$ (ε × 10^{-3}) 50% EtOH[a] Z = N$^+$HMe$_2$	X	λ$_{max}$ (ε × 10^{-3}) 95% EtOH Z = H	λ$_{max}$ (ε × 10^{-3}) 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] 1.2*N* 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$^+$HMe$_2$ 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 1.2*N* HCl, λ$_{max}$ 348 mμ. [e] In 50% alcoholic 1.2*N* HCl, λ$_{max}$ 367 mμ.

nitrogen) of all types of 4-aminoazobenzene monocations 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

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.

GAINESVILLE, FLA.

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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.

EXPERIMENTAL[4]

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, λ(NO_2) 6.34, 7.50μ.

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

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(4) Analyses by M. J. Naranjo.

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