from the filtrate. The filter cake, 60 g. of a light brown solid, was treated with ethanol and filtered. An additional 16.3 g. (22%) of gray crystals, m.p. 136–139°, separated from the filtrate. Recrystallization of the combined crops from ethanol gave long colorless prisms, m.p. 138–140°.

The literature procedure[5] employs an aqueous medium for this reaction. It was found that **5**, which is unstable in water, could not be dried quickly enough when prepared on a large scale in aqueous solution to permit isolation in reasonably pure quality. The infrared spectrum of a sample, m.p. 129–131°, prepared by the literature method was identical with that of the compound prepared above.

3,5-Diaminoisoxazole Hydrochloride (**6**).—A solution of 10 g. (0.1 mole) of 2-cyanoacetamidoxime and 1.0 g. (0.01 mole) of triethylamine in 300 ml. of methanol was stored at room temperature overnight and then concentrated under reduced pressure to 10 g. of a brown liquid. The liquid was dissolved in isopropyl alcohol and acidified with ethanolic hydrogen chloride. Addition of ether to the solution effected the separation of 9 g. (67%) of a light brown crystalline solid, m.p. 125–126° dec.

Anal. Calcd. for $C_3H_6ClN_3O$: C, 26.57; H, 4.43; Cl, 26.20; N, 31.00. Found: C, 26.74; H, 4.56; Cl, 26.02; N, 30.99.

The ultraviolet spectrum exhibits λ_{max}^{MeOH} 244 mμ (ε 25,000), which shifts to 228 mμ (ε 13,000) upon the addition of base.

One attempt to distill the crude base resulted in a violent explosion.

5-Acetamido-3-aminoisoxazole (**9**).—A solution of 10 ml. (0.1 mole) of acetic anhydride and 10 ml. of pyridine was added dropwise with stirring during 30 min. to a cold solution of 10 g. (0.1 mole) of crude 3,5-diaminoisoxazole and 10 ml. of pyridine. The off-white solid, 6.1 g., m.p. 184–192°, which separated was collected. Four recrystallizations from methanol provided the analytical sample, m.p. 195–197° dec.

Anal. Calcd. for $C_5H_7N_3O_2$: C, 42.55; H, 5.00; N, 29.78. Found: C, 42.88; H, 5.05; N, 29.57.

The ultraviolet spectrum exhibits λ_{max}^{MeOH} 239 mμ (ε 17,000), which shifts to λ_{max}^{MeOH} 248 mμ (ε 19,000) upon addition of ethanolic hydrogen chloride. The n.m.r. spectrum exhibits singlets at τ −1.15 (1H, NH—C=O), 4.18 (1H, 4-isoxazolyl H), 4.52 (2H, NH_2), and 7.88 (3H, $NC(=O)CH_3$).

3,5-Bisacetamidoisoxazole (**7**). **A.**—A solution of 1.0 g. (0.01 mole) of crude 3,5-diaminoisoxazole, 2.0 g. (0.02 mole) of acetic anhydride, and 10 ml. of pyridine was allowed to stand at room temperature for 15 hr. The colorless solid, 0.73 g., m.p. 185–205°, which separated was collected. Three recrystallizations from methanol provided colorless prisms, m.p. 203–205°.

Anal. Calcd. for $C_7H_9N_3O_3$: C, 45.90; H, 4.95; N, 22.94. Found: C, 46.15; H, 4.87; N, 22.90.

The ultraviolet spectrum exhibits λ_{max}^{MeOH} 227 mμ (ε 11,500) and 246 mμ (ε 11,600). The n.m.r. spectrum exhibits singlets at τ −1.45 (1H, NH—C=O), −0.74 (1H, NH—C=O), 3.25 (1H, 4-isoxazolyl H), 7.85 (3H, $NC(=O)CH_3$), and 7.88 (3H, $NC(=O)CH_3$).

B.—A mixture of 0.12 g. of 5-acetamido-3-aminoisoxazole, 0.11 g. of acetic anhydride, and 2 ml. of pyridine was stirred at room temperature for 3 days and concentrated under reduced pressure to a colorless solid. Recrystallization from methanol provided 0.05 g. of colorless prisms, m.p. 203–205°. The infrared spectrum was identical with that of material prepared in method A, above.

Hydrogenation of 5-Acetamido-3-aminoisoxazole. 4-Amino-6-hydroxy-2-methylpyrimidine (**12**).—A solution of 0.50 g. (3.5 mmoles) of 5-acetamido-3-aminoisoxazole in 20 ml. of ethanol was hydrogenated at room temperature and atmospheric pressure with platinum oxide catalyst. During 2.25 hr., 3.7 mmoles of hydrogen was taken up. A colorless solid separated during the hydrogenation. After warming to dissolve the solid, the mixture was filtered. Upon cooling, 0.19 g. of colorless microcrystals, m.p. 298–303°, separated from the filtrate. The infrared spectrum was identical with that of authentic 4-amino-6-hydroxy-2-methylpyrimidine (Aldrich Chemical Co.).

3,5-Diamino-α-(*p*-nitrophenyl)-4-isoxazolemethanol (**13**).—A solution of 1.1 g. (0.01 mole) of crude 3,5-diaminoisoxazole, 3.0 g. (0.02 mole) of *p*-nitrobenzaldehyde, and 110 ml. of ethanol was allowed to stand at room temperature overnight. A yellow solid, 1.7 g., m.p. 156–160°, separated and was collected. Two recrystallizations from acetone–carbon tetrachloride provided yellow microcrystals, m.p. 164–165°.

Anal. Calcd. for $C_{10}H_{10}N_4O_4$: C, 48.00; H, 4.02; N, 22.39. Found: C, 47.90; H, 4.14; N, 22.07.

The ultraviolet spectrum exhibits λ_{max}^{MeOH} 232 mμ (ε 10,800) and 269 mμ (ε 8400), which changes to λ_{max}^{MeOH} 249 mμ (ε 25,000)[10] upon addition of hydrogen chloride.

2-Cyano-2-*p*-nitrobenzylideneacetamidoxime (**14**).—A solution of 10 g. (0.1 mole) of 2-cyanoacetamidoxime, 30 g. (0.2 mole) of *p*-nitrobenzaldehyde, and 750 ml. of methanol was allowed to stand at room temperature for 2 days and was then concentrated under reduced pressure to a tacky orange solid. Recrystallization from acetonitrile provided 9.3 g. (40%) of yellow crystals, m.p. 189–191° dec. Two additional recrystallizations gave the analytical sample as orange prisms, m.p. 190–192° dec.

Anal. Calcd. for $C_{10}H_8N_4O_3$: C, 51.72; H, 3.47; N, 24.13. Found: C, 51.97; H, 3.02; N, 24.22.

The ultraviolet spectrum exhibits $\lambda_{max}^{CH_3CN}$ 294 mμ (ε 13,700) and 346 mμ (ε 11,900).

3,5-Diamino-4-*p*-nitrobenzylisoxazole Hydrochloride (**16**).—A solution of 0.76 g. (0.02 mole) of sodium borohydride in 10 ml. of methanol was added to a stirred suspension of 0.47 g. (0.002 mole) of 2-cyano-2-*p*-nitrobenzylideneacetamidoxime in 20 ml. of methanol. After 2 hr. at room temperature, the yellow solution was acidified with ethanolic hydrogen chloride. The mixture was filtered, and the filtrate was concentrated under reduced pressure to 0.75 g. of a yellow solid. The solid was treated with hot ethanol. The mixture was filtered, and the filtrate was concentrated to 0.51 g. of an off-white solid, m.p. 150–155°. This solid was dissolved in isopropyl alcohol and precipitated with hexane, to yield 0.33 g. of a cream-colored solid, m.p. 153–156° dec.

Anal. Calcd. for $C_{10}H_{11}ClN_4O_3$: C, 44.36; H, 4.07; Cl, 13.12; N, 20.70. Found: C, 44.47; H, 4.16; Cl, 13.02; N, 20.95.

The ultraviolet spectrum exhibits λ_{max}^{MeOH} 252 mμ (ε 16,900), which changes to λ_{max}^{MeOH} 234 mμ (ε 10,600) and 272 mμ (ε 8700) upon addition of sodium hydroxide.

(10) The intensity of the maximum is dependent upon the amount of acid present.

Steric Enhancement of Resonance. III. Absorption Spectra of the 1-Alkyl-2,4-dinitrobenzenes[1]

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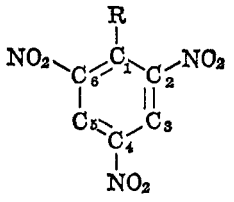
We have suggested that progressive bathochromic displacements of ultraviolet maxima and longer wave length band edges in the series, 1,3,5-trinitrobenzene, 2,4,6-trinitrotoluene, 1-ethyl-2,4,6-trinitrobenzene, 1-isopropyl-2,4,6-trinitrobenzene, 1-*t*-butyl-2,4,6-trinitrobenzene, might be ascribed to a phenomenon which we have characterized as steric diminution of electronic suppression of resonance interaction or, more succinctly, *steric enhancement of resonance.*[3] In the system I, as the bulk of R increased, the nitro groups in positions 2 and 6 were forced increasingly from coplanarity, and steric inhibition of ($R—C_1^+ \rightarrow C_2=NO_2^-$) and ($R—C_1^+ \rightarrow C_6=NO_2^-$) resonance resulted in successively lowered intensity of the band deriving from these electronic transitions. The same

(1) Part II: M. J. Kamlet, H. G. Adolph, and J. C. Hoffsommer, *J. Am. Chem. Soc.*, **86**, 4018 (1964).

(2) Work done in part while M. J. K. was attached to the Embassy of the United States, Office of Naval Research, London.

(3) M. J. Kamlet, J. C. Hoffsommer, and H. G. Adolph, *J. Am. Chem. Soc.*, **84**, 3925 (1962).

behavior had been observed earlier for simple *o*-nitroalkylbenzenes by Brown and Reagan.[4] A further consequence of the diminishing resonance contributions of the *o*-nitro groups, however, concerned the ($R—C_1^+ \rightarrow C_1{=}NO_2^-$) electronic transition in I. The increasing ground-state C_1 electron density led to *enhancement* of resonance in this molecular axis with progressively decreasing electronic transition energy; this band showed a consequent shift to higher wave lengths. The summation of effects on both bands as evidenced in the total spectral envelope was hypochromic and, as mentioned above, bathochromic.



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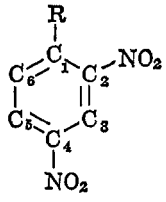

IIa, R = H
b, R = CH_3
c, R = C_2H_5
d, R = *i*-C_3H_7
e, R = *t*-C_4H_9

We now report that the same phenomenon is evident in the series, 1,3-dinitrobenzene, 2,4-dinitrotoluene, 1-ethyl-2,4-dinitrobenzene, 1-isopropyl-2,4-dinitrobenzene, 1-*t*-butyl-2,4-dinitrobenzene (IIa–e) (Figure 1 and Table I). Maxima and band edges shift to longer

TABLE I

ULTRAVIOLET SPECTRA[a]

Compound	λ_{max}, mμ	$\epsilon \times 10^{-3}$	Half-band integrated intensity[b] $\times 10^{-7}$
m-Dinitrobenzene (IIa)	234	17.1	7.73
2,4-Dinitrotoluene (IIb)	241.5	14.3	7.42
1-Ethyl-2,4-dinitrobenzene (IIc)	242	13.5	7.24
1-Isopropyl-2,4-dinitrobenzene (IId)	246	11.6	5.84
1-*t*-Butyl-2,4-dinitrobenzene (IIe)	261.5	10.6	3.69

[a] Solvent methanol. [b] L. cm.$^{-1}$/mole cm.

wave lengths with increasing bulk of R and half-band integrated intensities decrease until in the case of IIe there appears to evolve a new band whose half-band integrated intensity approximates those observed for *p*-nitrotoluene and expected for *p*-nitro-*t*-butylbenzene.[5]

Detailed explanations for the spectral shifts in the present series conform exactly with those proposed[3] for the corresponding shifts of the corresponding compounds in the trinitro series.

As in the trinitro series, it is again a constructive exercise to assume that blue shifts of the maxima of 1,3-dinitrobenzene relative to nitrobenzene and of 1-*t*-butyl-2,4-dinitrobenzene (IIe) relative to *p*-nitro-

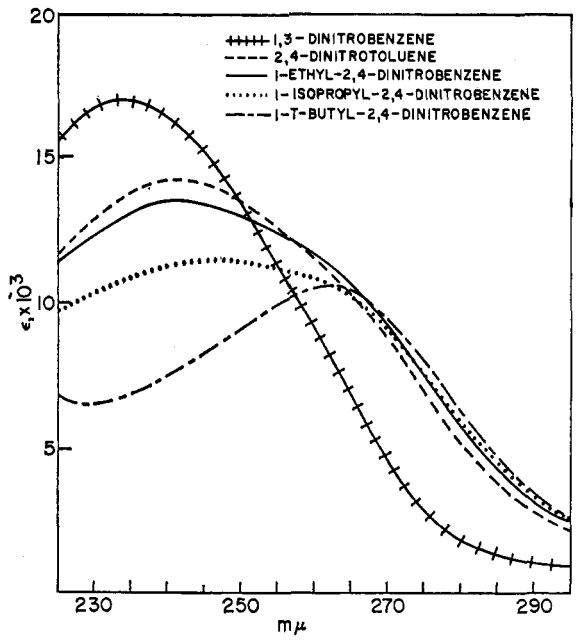

Figure 1.—Absorption spectra of the 1-alkyl-2,4-dinitrobenzenes in methanol.

t-butylbenzene should be in the ratio of electron withdrawal from C_1 by coplanar and noncoplanar nitro groups, *i.e.*,[6] the ratio of σ_p to σ_I. We may then compare the observed position of λ_{max} with a value predicted for IIe as follows.

For nitrobenzene, ν_{max}^{MeOH} 38,500 cm.$^{-1}$; for dinitrobenzene, ν_{max} 42,735 cm.$^{-1}$, $\Delta\nu_{max}$ = 4235 cm.$^{-1}$; for *p*-nitro-*t*-butylbenzene, ν_{max} 36,400 cm.$^{-1}$, $\Delta\nu_{max}$ (predicted for IIe) = (0.63/1.27)(4235) = 2100 cm.$^{-1}$. This leads to a predicted ν_{max} of 38,500 cm.$^{-1}$ for IIe, corresponding to λ_{max} = 260 mμ. The observed λ_{max} (Table I) is 261.5 mμ.

We take this opportunity also to correct numerical errors regarding half-band integrated intensities which appeared in part I of this series.[3] The following values (all $\times 10^7$) may be regarded as being more nearly correct: 1,3,5-trinitrobenzene, 12.89; 2,4,6-trinitrotoluene, 10.84; 1-ethyl-2,4,6-trinitrobenzene, 10.51; 1-*t*-butyl-2,4,6-trinitrobenzene, 3.33; nitrobenzene, 2.68; *m*-dinitrobenzene, see Table I; and *p*-nitrotoluene, 3.12. Since relative values are about the same, the conclusions drawn in part I remain unaltered.

Experimental

The 1-alkyl-2,4-dinitrobenzenes were prepared by published procedures. 1-*t*-Butyl-2,4-dinitrobenzene[7] was recrystallized from ethanol to a melting point of 62–62.5° (uncor.). 1-Ethyl- and 1-isopropyl-2,4-dinitrobenzene were purified by distillation through a spinning-band column as described by Hansch and Helmkamp.[8] The purity of the fractions used for determination of the spectra was estimated to be >97% from their vapor phase chromatograms, the main impurities being the corresponding 2,6 isomers.

Absorption spectra were determined between 215 and 400 mμ in methanol as described in part I of this series,[3] as were the half-band integrated intensities listed in Table I.

(4) W. G. Brown and H. Reagan, *J. Am. Chem. Soc.*, **69**, 1032 (1947).
(5) See below, Table I, and footnotes 3 and 4 of ref. 3.
(6) See footnotes 11 and 12 of ref. 3.
(7) D. F. du Toit Malherbe, *Ber.*, **52**, 321 (1919).
(8) C. Hansch and G. Helmkamp, *J. Am. Chem. Soc.*, **73**, 3080 (1951).