

III. A Beckman DK spectrophotometer was used in this work. Kinetic data were taken at $35.35 \pm 0.1^\circ$ and at different temperatures held to $\pm 0.1^\circ$ in the range 25.5 – 26.2° . Activation energy plots permitted the adjustment of the rate constants to a common temperature $26.05 \pm 0.1^\circ$ given in Table I; in no case was the correction greater than 4%. The DDM concentration at *ca.* $0.0022 M$ was normally in the range $1/10$ to $1/80$ of the

acid so that pseudo-first-order kinetics applied; two runs at a ratio of $1/6$ are still acceptable for the pseudo-first-order treatment since only *ca.* 60% of the DDM reacts to give the ester (see eq. 3). All of the kinetic data are given in Table I.

Acknowledgment.—We wish to thank J. Belluzzi for preparing several of the acids.

[CONTRIBUTION FROM THE ORGANIC CHEMISTRY DIVISION, U. S. NAVAL ORDNANCE LABORATORY, WHITE OAK, SILVER SPRING, MD.]

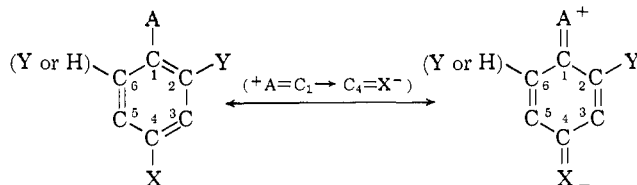
Steric Enhancement of Resonance. II. Absorption Spectra of N-Alkyl- and N,N-Dialkyl-2,4-dinitroanilines^{1,2}

BY MORTIMER J. KAMLET, HORST G. ADOLPH, AND JOHN C. HOFFSOMMER

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Close comparison of the ultraviolet spectra of 2,4-dinitroaniline (I) and its N-alkyl and N,N-dialkyl derivatives allows one to discern the spectral effects of *steric enhancement of* ($+R_2N=C_1 \rightarrow C_4=NO_2^-$) resonance as well as steric inhibition of ($+R_2N=C_1 \rightarrow C_2=NO_2^-$) resonance. The existence of another hitherto undescribed phenomenon, *the electronic buttressing effect*, is suggested to explain some of the spectral variations.

Steric diminution of electronic suppression of resonance interaction or, more succinctly, *steric enhancement of resonance* may occur in a system such as the following where, in Ingold's notation,³ A is a +M or +I substituent and X and Y are -M substituents. A measure



of resonance interaction between A and X (or between C₁ and X where A is a +I substituent) is the electronic transition energy of the ($+A=C_1 \rightarrow C_4=X^-$) band in the ultraviolet. This transition energy depends strongly on the ground-state electron density at A, λ_{\max} shifting to the red with increasing electron density at A, to the blue with decreasing electron density.

The ground-state electron density at A is, in turn, a strong function of the nature of Y and its degree of coplanarity with the ring. Coplanar Y effects both mesomeric and inductive electron withdrawal from A, thereby suppressing resonance interaction between A and X; noncoplanar Y exerts only its inductive effect,⁴ also suppressing A→X resonance interaction, but to a lesser extent.

It follows that as progressively increasing steric requirements of A force Y from coplanarity, ground-state electron withdrawal from A by Y will decrease and resonance interaction between A and X will increase. As concerns A→Y resonance interaction, this is the classical situation of steric inhibition of resonance. In the case of A→X resonance interaction, however, the newly reported phenomenon,¹ *steric*

enhancement of resonance, is being brought into play. It is an important corollary of the above that *steric enhancement of resonance in one molecular axis is always accompanied by steric inhibition of resonance in another molecular axis*.

We have reported that steric enhancement of resonance is evidenced by progressive bathochromic spectral displacements in the series [2,4,6-trinitrotoluene, 1-ethyl-2,4,6-trinitrobenzene, 1-isopropyl-2,4,6-trinitrobenzene, 1-*t*-butyl-2,4,6-trinitrobenzene]¹ and [2,4-dinitrotoluene, 1-ethyl-2,4-dinitrobenzene, 1-isopropyl-2,4-dinitrobenzene, 1-*t*-butyl-2,4-dinitrobenzene].⁵ We wish now to demonstrate that this phenomenon also obtains with the N,N-dialkyl-2,4-dinitroanilines and may be discerned on detailed examination of the ultraviolet spectra of these and related compounds.

Band Assignments.—The spectrum of 2,4-dinitroaniline (I) above 280 m μ comprises a high intensity N → V band, λ_{\max} 336 m μ , upon whose longer wave length edge is superimposed a pronounced shoulder, $\lambda \sim 390$ m μ (Table I, Fig. 1). The spectral envelope appears to result from the fusion of two bands: (1) λ_{\max} 333–336 m μ (ϵ 13,500–14,000); (2) λ_{\max} 380–390 m μ (ϵ 4000–5000). Since higher absorption intensities are generally associated with longer transition moments, it is reasonable to couple band 1 with the ($+H_2N=C_1 \rightarrow C_4=NO_2^-$) electronic transition, band 2 with the ($+H_2N=C_1 \rightarrow C_2=NO_2^-$) transition.

Comparison of the spectrum of I with those of other mono- and polynitroanilines lends strength to these band assignments. An ($+H_2N=C_1 \rightarrow C_2=NO_2^-$) electronic transition in 2-nitroaniline leads to λ_{\max} 404 m μ (ϵ 5200); 2,6-dinitroaniline, with electronic transitions of this type in two mutually equivalent molecular axes, shows λ_{\max} 412 m μ (ϵ 9200). 4-Nitroaniline, on the other hand, shows higher intensity absorption characteristic of an ($+H_2N=C_1 \rightarrow C_4=NO_2^-$) electronic transition, λ_{\max} 371 m μ (ϵ 15,900). 2,4,6-Trinitroaniline, with one *para* electronic transition and two mutually equivalent *ortho* transitions, shows two distinct bands, λ_{\max} 318 m μ (ϵ 12,000), and λ_{\max} 408 m μ (ϵ 7800).

(5) Part III: M. J. Kamlet, H. G. Adolph, and B. Johnson, manuscript in preparation.

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

(2) V. Baliah and M. Uma [*Tetrahedron Letters*, No. 25, 21 (1960)] had used the term, *steric enhancement of resonance*, to describe the effect of a 2-alkyl group in increasing the probability of alkoxy or alkythio groups approaching coplanarity in such compounds as 2-methyl-4-nitroanisole or methyl 2-methyl-4-nitrophenyl sulfide. Although the same term adequately describes both sets of phenomena, the phenomena themselves are somewhat different. We regret that Baliah and Uma's paper had not come to our attention prior to the publication of Part I.

(3) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Section 7.

(4) R. W. Taft and I. C. Lewis, *J. Am. Chem. Soc.*, **80**, 2436 (1958)

TABLE I
 ULTRAVIOLET SPECTRA^a

Aniline	—(+R ₂ N=C ₁ →C ₄ =NO ₂ ⁻) transition—			—(+R ₂ N=C ₁ →C ₂ =NO ₂ ⁻) transition—		
	λ _{max} , mμ	ν _{max} , cm. ⁻¹	log ε	λ _{max} , mμ	ν _{max} , cm. ⁻¹	log ε
2-Nitro-				404	24,750	3.72
N-Methyl-2-nitro- ^b				~429 ^c	~23,300	~3.7
N-Ethyl-2-nitro- ^b				425 ^d	23,530	3.79
N,N-Dimethyl-2-nitro- ^b				416 ^e	24,040	3.47
4-Nitro-	371	26,950	4.20			
N-Methyl-4-nitro- ^b	386 ^f	25,900	4.27			
N-Ethyl-4-nitro- ^b	386 ^d	25,900	4.28			
N,N-Dimethyl-4-nitro-	390	25,640	4.28			
N,N-Diethyl-4-nitro- ^b	393.5 ^d	25,410	4.34			
2,4-Dinitro- (I)	336	29,760	4.16	390 (sh)	25,640	3.81
N-Methyl-2,4-dinitro- (II)	348	28,740	4.21	415 (sh)	24,100	3.80
N-Ethyl-2,4-dinitro- (III)	348	28,740	4.21	415 (sh)	24,100	3.81
N,N-Dimethyl-2,4-dinitro- (IV)	368	27,170	4.23
N,N-Diethyl-2,4-dinitro- (V)	375	26,670	4.23
2,6-Dinitro-				411	24,310	3.96
2,4,6-Trinitro-	318	31,450	4.08	407	24,570	3.90

^a Solvent methanol unless otherwise noted; (sh) = shoulder or inflection. ^b Solvent ethanol. ^c P. Grammaticakis, *Bull. soc. chim. France*, [5] 17, 158 (1950). ^d W. A. Schroeder, P. E. Wilcox, K. N. Trueblood, and A. O. Dekker, *Anal. Chem.*, 23, 1740 (1951). ^e R. A. Morton and A. J. McGookin, *J. Chem. Soc.*, 901 (1934). ^f W. D. Kumler, *J. Am. Chem. Soc.*, 68, 1184 (1946).

For the reasons mentioned above, introduction of an electron-withdrawing group at C-2 of 4-nitroaniline should lower the ground-state electron density on the amine function, increase the (+H₂N=C₁→C₄=NO₂⁻)

pounds. Thus, the blue shifts for the corresponding bands are 4900 and 2600 cm.⁻¹ in the series [4-nitrotoluene, 2,4-dinitrotoluene, 2,4,6-trinitrotoluene] and 4200 and 1800 cm.⁻¹ in the series [nitrobenzene, 1,3-dinitrobenzene, 1,3,5-trinitrobenzene].^{1,5,6}

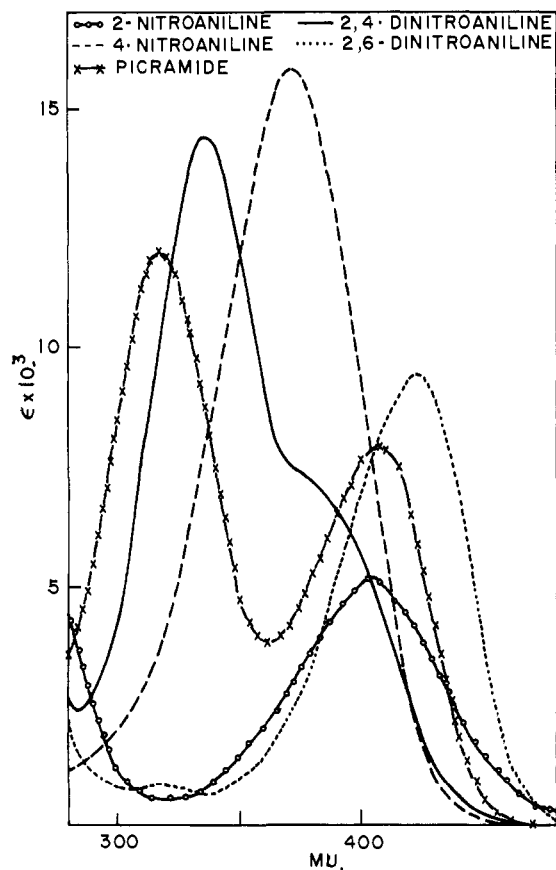


Fig. 1.—Absorption spectra of some mono- and polynitroanilines.

electronic transition energy, and shift this band to shorter wave lengths. Thus may readily be rationalized the 2810 cm.⁻¹ hypsochromic shift from 4-nitroaniline to the 336 mμ band of I and the further 1690 cm.⁻¹ shift to the 318 mμ band of picramide. Hypsochromic shifts of comparable magnitudes are observed for analogous reasons in other sets of com-

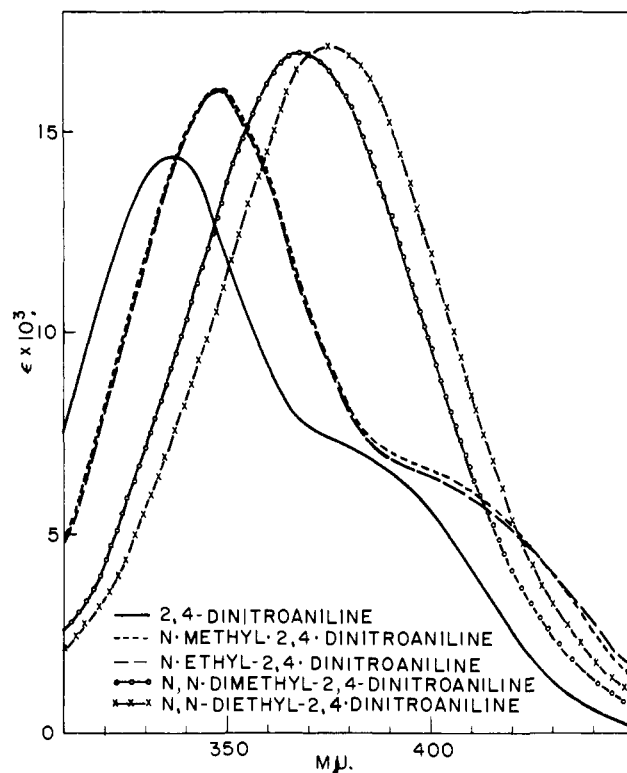
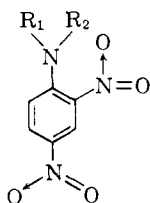


Fig. 2.—Absorption spectra of the N-alkyl- and N,N-dialkyl-2,4-dinitroanilines.

Spectra of the Alkyldinitroanilines.—We may now examine how the two longer wave length bands in 2,4-dinitroaniline are displaced on N-alkylation and N,N-dialkylation (Fig. 2). N-Methyl-2,4-dinitroaniline (II) shows a spectrum quite similar in shape to

(6) Maxima for the di- and trinitrobenzenes and toluenes are hypsochromically displaced relative to their "true" positions by strong overlap with intense shorter wave length bands. This increases the apparent effects of the second and third nitro groups in these series.



- I, $R_1 = R_2 = H$
 IIa, $R_1 = CH_3, R_2 = H$
 IIb, $R_1 = H, R_2 = CH_3$
 IIIa, $R_1 = C_2H_5, R_2 = H$
 IIIb, $R_1 = H, R_2 = C_2H_5$
 IV, $R_1 = R_2 = CH_3$
 V, $R_1 = R_2 = C_2H_5$

that of I in which both the maximum and the shoulder are bathochromically displaced relative to I by about 1000 cm^{-1} and the absorption intensity is increased by $\sim 10\%$. The spectrum of N-ethyl-2,4-dinitroaniline (III) is remarkably close in its resemblance to that of II as concerns both the positions and intensities of the dominant features. In going to N,N-dimethyl-2,4-dinitroaniline (IV) and N,N-diethyl-2,4-dinitroaniline (V) there are further pronounced bathochromic-hyperchromic displacements of the maximum by 1570 and 2070 cm^{-1} , respectively, relative to II and III. With the two dialkyl derivatives, however, it is particularly noteworthy that not even an inflection remains on the longer wave length band edge to mark the position of the shoulder which had been so pronounced in the cases of I, II, and III.

Spectral Effects of N-Alkylation.—With other sets of compounds where steric enhancement of resonance had been demonstrated^{1,5} it had been possible to vary the bulk of the C_1 -substituent without appreciably changing its electronic effects. Alkylation of the amine function, however, also modifies its electronic requirements, *viz.*,⁷ $\sigma_{NH_2} = -0.60$, $\sigma_{N(CH_3)_2} = -0.66$. In addition, hydrogen bonding to the solvent has pronounced bathochromic effects on the spectra of nitroanilines⁸ and such hydrogen bonding is diminished on N-alkylation and completely eliminated on N,N-dialkylation.

To separate primary electronic and hydrogen-bonding effects from steric effects, it is therefore profitable to compare spectral shifts for the alkylated dinitroanilines with those for comparable derivatives in the 4-nitroaniline series where steric effects should be nil and in the 2-nitroaniline series where steric effects should be strong. A reasonable first approximation is that electronic and hydrogen-bonding effects in the three series should be comparable.

N-Methylation of 2,4-dinitroaniline causes λ_{max} to shift 1020 cm^{-1} to the red ($\Delta \log \epsilon = +0.05$; Table II). The effect is substantially the same on N-ethylation of I. For comparison, both N-methyl- and N-ethyl-4-nitroaniline are displaced relative to 4-nitroaniline by a similar amount, -1050 cm^{-1} ($\Delta \log \epsilon = +0.07$).⁹ It would appear from this that the effect of N-monoalkylation on band 1 results from primary

(7) R. W. Taft in M. S. Newman, Ed., "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 571.

(8) (a) J. H. P. Utley, *J. Chem. Soc.*, 3252 (1963); (b) M. J. Kamlet, *Israel J. Chem.*, 1, 428 (1963).

(9) The -1050 cm^{-1} shift is a summation of $+670\text{ cm}^{-1}$ caused by decreased hydrogen bonding to the solvent and -1720 cm^{-1} caused by the pure electronic effect of the alkyl group in increasing ground-state electron density on the amine function (ref. 8b). In isooctane solvent the shift from 4-nitroaniline to N-methyl-4-nitroaniline is -1700 cm^{-1} (ref. 8a).

electronic and hydrogen-bonding factors only and that steric enhancement of resonance has not yet come into play. This would seem reasonable if II and III took the preferred *s-trans* conformations (IIa and IIIa rather than IIb and IIIb).

TABLE II
SPECTRAL DISPLACEMENTS ON N-ALKYLATION

X	($+R_2N=C_1 \rightarrow C_4=NO_2^-$) band $-\Delta\nu_{max}[\nu_{max} - \nu_{max}^{X-NH_2}]$, cm^{-1}		$\Delta\Delta\nu_{max}$, cm^{-1}
	4-N O_2 C $_6$ H $_4$ -X	2,4-(NO $_2$) $_2$ C $_6$ H $_3$ -X	
CH $_3$ NH-	-1050	-1020	+30
C $_2$ H $_5$ NH-	-1050	-1020	+30
(CH $_3$) $_2$ N-	-1310	-2590	-1280
(C $_2$ H $_5$) $_2$ N-	-1540	-3090	-1550

Bearing this out, the shoulder (band 2) shows no decreased intensity in II or III relative to I such as would be expected if there were steric inhibition of ($+RHN=C_1 \rightarrow C_2=NO_2^-$) resonance. Further, $\Delta\nu$ of the shoulder from I to II or III is about the same¹⁰ as the shift for the corresponding band in going from 2-nitroaniline to N-methyl- or N-ethyl-2-nitroaniline which similarly show no decreased absorption intensity characteristic of steric inhibition of resonance.

N,N-Dialkylation. Steric Enhancement of Resonance.—In going from 2-nitroaniline to N,N-dimethyl-2-nitroaniline, on the other hand, there is pronounced steric inhibition of ($+R_2N=C_1 \rightarrow C_2=NO_2^-$) resonance as evidenced by $\Delta \log \epsilon = -0.25$. The same appears to apply to an even greater extent with N,N-dimethyl- and N,N-diethyl-2,4-dinitroaniline, where not even an inflection marks the position of an ($+R_2N=C_1 \rightarrow C_2=NO_2^-$) electronic transition. The latter compounds thus satisfy the requirements mentioned above, *i.e.*, the mesomeric electron-withdrawing substituent at C-2 has been forced from coplanarity and we may anticipate steric enhancement of ($+R_2N=C_1 \rightarrow C_4=NO_2^-$) resonance in going from II and III to IV and V.

The spectral displacements of band 1 fulfill this expectation. The second methyl group in going from II to IV causes ν_{max} to shift 1570 cm^{-1} to the red ($\Delta \log \epsilon = +0.02$); the second ethyl group in going from III to V causes a displacement of -2070 cm^{-1} ($\Delta \log \epsilon = +0.02$). These compare with shifts of -260 cm^{-1} ($\Delta \log \epsilon = +0.01$) from N-methyl- to N,N-dimethyl-4-nitroaniline¹¹ and -490 cm^{-1} ($\Delta \log \epsilon = +0.06$) from N-ethyl- to N,N-diethyl-4-nitroaniline. We attribute the differences in the effects of the second alkyl groups in comparing these two series of compounds ($\Delta\Delta\nu_{max}$ in Table II) to steric enhancement of ($+R_2N=C_1 \rightarrow C_4=NO_2^-$) resonance. These differences are $-(1280-1310)\text{ cm}^{-1}$ for N,N-dimethyl-2,4-dinitroaniline and $-(1550-1580)\text{ cm}^{-1}$ for the N,N-diethyl derivative. These values correspond to 17 and 21 $m\mu$, respectively, at the wave lengths in question.

Relative magnitudes of electron withdrawal by coplanar and noncoplanar conjugating substituents may be evaluated by comparing σ_{para} with σ_I , the former being a measure of combined inductive and mesomeric effects and the latter measuring the pure inductive

(10) This is best measured by comparing band edges.

(11) Again this may be broken down as follows: $+830\text{ cm}^{-1}$ due to elimination of hydrogen bonding to solvent and -1090 cm^{-1} due to the pure electronic effect of the second methyl group (ref. 8b). In isooctane solvent the shift from N-methyl-4-nitroaniline to N,N-dimethyl-4-nitroaniline is -1100 cm^{-1} (ref. 8a).

contribution to the substituent constant.⁴ For the nitro group these values are +1.27 and +0.63,⁴ so that a noncoplanar nitro group at C-2 should reduce ground-state electron density on the amine function by about half the extent of a coplanar nitro group.

It is a constructive exercise to assume that the 2-nitro group is completely coplanar in 2,4-dinitroaniline and completely noncoplanar in N,N-diethyl-2,4-dinitroaniline. The blue shifts caused by this substituent in the maxima of the former compound relative to 4-nitroaniline and the latter compound relative to N,N-diethyl-4-nitroaniline should then be proportional to σ_{para}/σ_I . As an independent check of our reasoning, we may compare the observed position of the maximum for V with λ_{max} predicted as follows.

For 4-nitroaniline, $\nu_{max} = 26,950 \text{ cm.}^{-1}$; for 2,4-dinitroaniline, $\nu_{max} = 29,760 \text{ cm.}^{-1}$; effect of coplanar 2-nitro group = +2810 cm.^{-1} . For N,N-diethyl-4-nitroaniline, $\nu_{max} = 25,410 \text{ cm.}^{-1}$; predicted effect of noncoplanar 2-nitro group = $(0.63/1.27)(2810) = +1390 \text{ cm.}^{-1}$. This leads to a prediction of $\nu_{max} = 26,800 \text{ cm.}^{-1}$ for N,N-diethyl-2,4-dinitroaniline, corresponding to $\lambda_{max} 373.5 \text{ m}\mu$. The observed position for V is 375 $\text{m}\mu$.

The Electronic Buttressing Effect.—A further difference between several of the spectra discussed above deserves additional comment. It has been mentioned that, on dimethylation of 2-nitroaniline, reduction by somewhat less than half in the ($+R_2N=C_1 \rightarrow C_2=NO_2^-$) absorption intensity was observed, but that on dimethylation of I the corresponding band appeared to vanish completely. To confirm that band 1 in compound IV was not disturbed on its longer wave length side by any absorption attributable to band 2, the band half-widths at half-height on both sides of the maximum were compared. The values were: from ν_{max} to the blue, 2700 cm.^{-1} ; from ν_{max} to the red, 2400 cm.^{-1} ; *i.e.*, disturbance of the symmetry of the band, if any, was on the shorter wave length side and was probably due to slight overlap with the tail of a shorter wave length band. A putative explanation for this difference in behavior in N,N-dimethylation is as follows.

Steric strain in N,N-dimethyl-2-nitroaniline may be relieved by rotation from planarity of either the Me_2N-

or the NO_2- group or by increasing the $(Me_2)N-C_1-C_2$ angle or the $C_1-C_2-N(O_2)$ angle or by any combination of these possibilities. An energetically preferred conformation would probably find this compound with both the NO_2- group and the Me_2N- group partially noncoplanar, *i.e.*, partial $\pi-\pi$ overlap between nitro and ring, partial $p-\pi$ overlap between amino and ring. The ($+R_2N=C_1 \rightarrow C_2=NO_2^-$) band is still evident, but with decreased absorption intensity following the $[\cos^2 \theta = \epsilon/\epsilon_0]$ relationship.¹²

In the case of N,N-dimethyl-2,4-dinitroaniline, rotation from planarity of the amine function would strongly decrease ($+R_2N=C_1 \rightarrow C_4=NO_2^-$) resonance interaction, so that conformations involving rotation or bond distortion of the amine group would be energetically less favored than had been the case in the absence of the 4-nitro substituent. Relief of steric strain would then require greater rotation from planarity of the 2-nitro substituent, decreasing its $\pi-\pi$ overlap with the ring to a very much greater extent; $\cos^2 \theta$ would approach zero and the band would virtually disappear.

If this explanation for these spectral differences applied, the action of the 4-nitro substituent in decreasing coplanarity of the 2-nitro substituent by "stiffening" the 1-dimethylamino substituent might be termed an *electronic buttressing effect*.

Experimental

All materials were commercially available or prepared by literature methods. They were purified by standard means to meet conventional spectrophotometric criteria of purity. Absorption spectra were determined in methanolic solution using a Cary Model 14 recording spectrophotometer with matched 1-cm. silica cells. Concentrations were $3-5 \times 10^{-6} M$. Previously described precautions¹³ were taken to guard against photochemical transformations.

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(12) E. A. Braude in E. A. Braude and F. C. Nachod, Ed., "Determination of Organic Structures by Physical Methods," Academic Press, Inc., New York, N. Y., 1955, p. 174.

(13) M. J. Kamlet and L. A. Kaplan, *J. Org. Chem.*, **22**, 576 (1957).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MOUNT HOLYOKE COLLEGE, SOUTH HADLEY, MASS.]

Substituent Effects on Nuclear Magnetic Resonance Chemical Shifts in *para*-Substituted Phenylhexachlorobicyclo[2.2.1]heptenes and Ethylbenzenes¹

BY KENNETH L. WILLIAMSON, NANCY CRAVEN JACOBUS, AND KAREN TABOR SOUCY

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The internal chemical shifts in a series of *para*-substituted 5-phenylhexachlorobicyclo[2.2.1]heptenes have been found to be independent of dihedral angle, in contrast to 5-substituted hexachlorobicyclo[2.2.1]heptenes. The chemical shifts of the aliphatic protons in the bicyclic series as well as the chemical shifts of the methyl and methylene protons in *para*-substituted ethylbenzenes have been correlated with the Hammett σ -constant of the substituent.

The purpose of the work reported herein was to determine whether an angular dependence of the internal

chemical shifts of the aliphatic protons would be noted in the series of *para*-substituted 5-phenylhexachlorobicyclo[2.2.1]-2-heptenes (1a-e). It has previously been shown² that the internal chemical shifts, $\delta_X - \delta_A$

(1) This work was supported by grants from the Public Health Service, Division of General Medical Sciences (GM10224-01), and from the Petroleum Research Fund of the American Chemical Society.

(2) K. L. Williamson, *J. Am. Chem. Soc.*, **85**, 516 (1963).