[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO]

The Effects of Steric Inhibition of Resonance on Ultraviolet Absorption Spectra[1]

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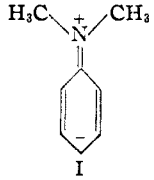
The effects of steric inhibition of resonance on absorption spectra, particularly in the ultraviolet, have been the subject of several investigations in recent years.[3] Frequently, however, the steric variations have been produced through such modifications of the compounds involved that the observed differences in absorption spectra could not be said unequivocably to require steric inhibition of resonance as an explanation. The present investigation probably presents (particularly in the case of the bicyclic amines) the closest approach yet made to the ideal case in which the only variable would be steric. The ortho substituted derivatives of dimethylaniline were chosen because here the spectroscopic effects of steric hindrance may be correlated with the results of previously published chemical investigation.[4] Only highly qualitative descriptions of the spectra of most of these compounds have appeared previously. The spectra of some nitrodimethylanilines also were measured and have been correlated with variations in the chemical properties of the compounds.

An explanation of the effects of steric variables on the absorption spectrum of dimethylaniline requires an assumption as to the nature of at least the first excited electronic state of the molecule. This state is probably a resonance hybrid to which structures I and II make a much greater contribution than they make to the unexcited state. For



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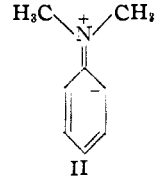

II

this reason the nitrogen-to-ring-carbon bond will probably have much more double bond character in the first excited state than in the unexcited state, where its double bond character is very slight. A double bond in this position requires that the entire molecule (with the exception of methyl hydrogen atoms) be planar. If steric factors oppose the assumption of a planar configuration thermal motions will less frequently bring the molecule to such a configuration; and whenever planarity is attained strain must be present. Presumably, non-planarity or strain will increase the energy of the excited state more than that of the unexcited state: the corresponding absorption will occur at higher frequencies. Also, since the unexcited molecule will less frequently possess the near-planar configuration demanded by the excited state the probability of excitation will be decreased: the absorption will be of lowered intensity. Hindrance to planarity should decrease the ionic character of the excited state, and this too may be responsible for a decreased intensity of absorption.[5]

In the spectra which follow it is apparent that the intensity effects associated with the steric inhibition of resonance are more reliably predicted from this simple theory than are the corresponding frequency shifts, although the latter frequently do conform to its predictions.

Discussion

I.—A very clear picture of the effect of steric hindrance on the absorption spectra of dimethylaniline derivatives is presented by Figs. 1 and 2. In the spectrum of the parent compound, dimethylaniline, the band nearest the visible corresponds to the first electronic excitation, and it is this band which we predict to be highly subject to modification by hindrance to planarity. This prediction is well borne out by the spectra. The curves in Fig. 1 show that both the damping and the displacement of the first absorption band increase with the number and bulk of the ortho alkyl groups, while meta and para alkyl groups have comparatively little effect. The spectrum of *o*-xylene[6] has been included for comparison with that of *o*-*t*-butyldimethylaniline.

The very close similarity among the spectra of aniline and the toluidines[7] gives support to the above steric interpretations, but the bicyclic amines whose spectra are presented in Fig. 2 offer a still more critical test of these interpretations. Each of these compounds is an analog of dimethyl-*o*-toluidine, in that it may be considered to have an alkyl group adjacent to a dialkylamino group. However, the five-membered ring should constrain N-methylindoline to lie in a plane without introducing much strain. As expected, the absorption is completely unhindered; in fact, the quinoidal structures seem to be even more favored than in dimethylaniline. The observed absence of hindrance in N-methyltetrahydroquinoline could not be predicted with quite so great cer-

(1) Presented before the Organic Division of the American Chemical Society, New York, September 12, 1944.

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(3) For example: Ley and Pfeiffer, *Ber.*, **54**, 363 (1921); Pickett, Walter and France, THIS JOURNAL, **58**, 2296 (1936); Thielacker and Ozegowski, *Ber.*, **73**, 898 (1940); O'Shaughnessy and Rodebush, THIS JOURNAL, **62**, 2906 (1940); Williamson and Rodebush, *ibid.*, **63**, 3018 (1941); Sherwood and Calvin, *ibid.*, **64**, 1350 (1942); Jones, *ibid.*, **65**, 1815, 1818 (1943).

(4) Brown, Widiger and Letang, *ibid.*, **61**, 2597 (1939).

(5) *Cf.* Mulliken, *J. Chem. Phys.*, **7**, 121 (1939).

(6) "International Critical Tables," Vol. V, McGraw-Hill Book Co., New York, N. Y., 1929, p. 361.

(7) Wolf and Herold, *Z. physik. Chem.*, **B13**, 201 (1931).

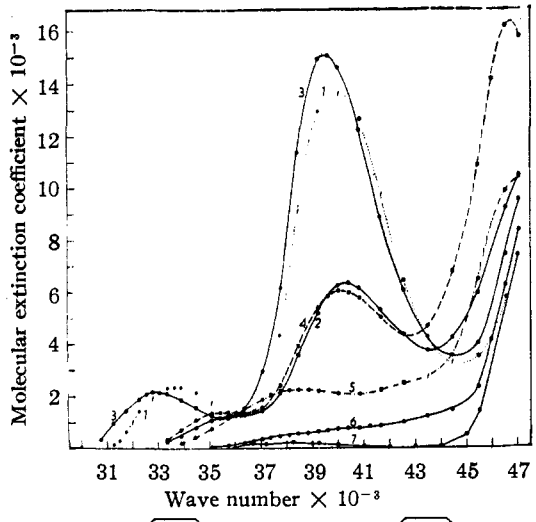
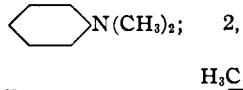
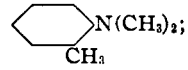
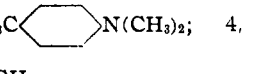
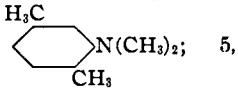
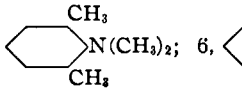
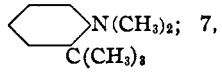
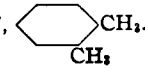


Fig. 1.—1,  ; 2,  ;

3,  ; 4,  ; 5,  ; 6,  ; 7,  .

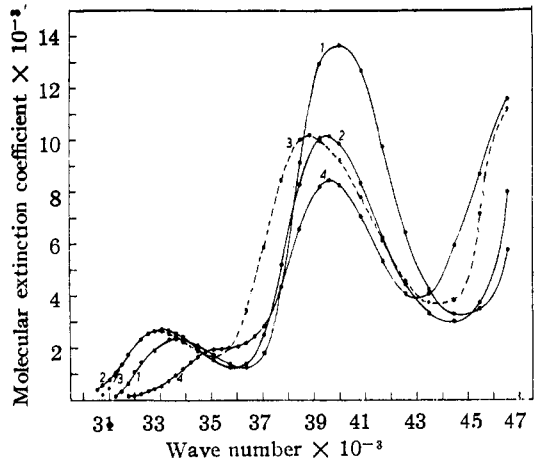
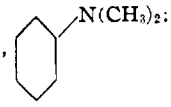
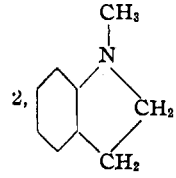
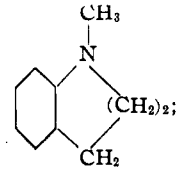
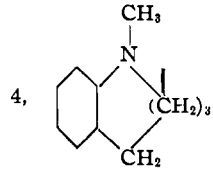


Fig. 2.—1,  ; 2,  ;

3,  ; 4,  .

tainty, but here again the quinoidal structures seem to be highly favored. The low intensity and high frequency of the first absorption band of N-methyl-*homo*-tetrahydroquinoline would be predicted in view of the highly probable non-planarity of the seven-membered ring.

In Figs. 3, 4 and 5 are presented the spectra of another series of similar compounds with varying degrees of hindrance. In each case, the hindered compound absorbs in the first band with less intensity than does dimethylaniline or its unhindered isomer, the effectiveness of the hindrance varying as would be predicted from the scale representation (Fig. 6). In the cases of the ortho

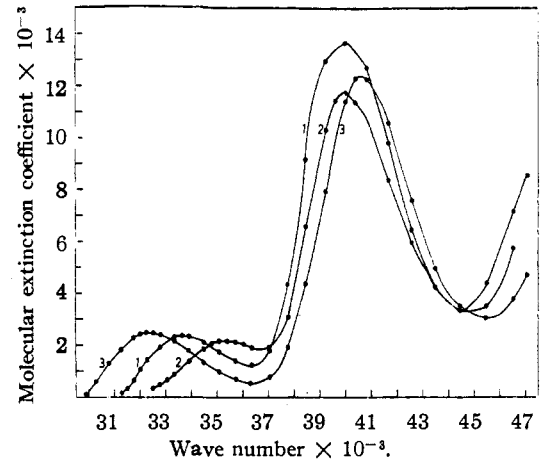
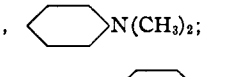
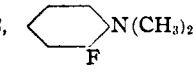
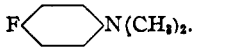


Fig. 3.—1,  ; 2,  ;

3,  .

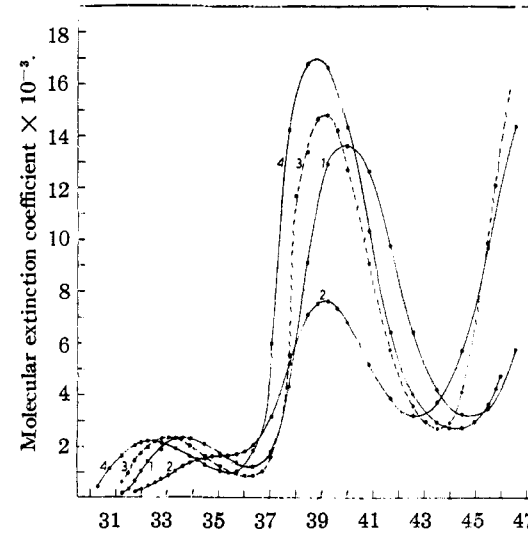
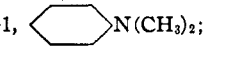
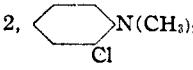
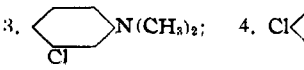
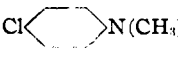


Fig. 4.—1,  ; 2,  ;

3,  ; 4, 

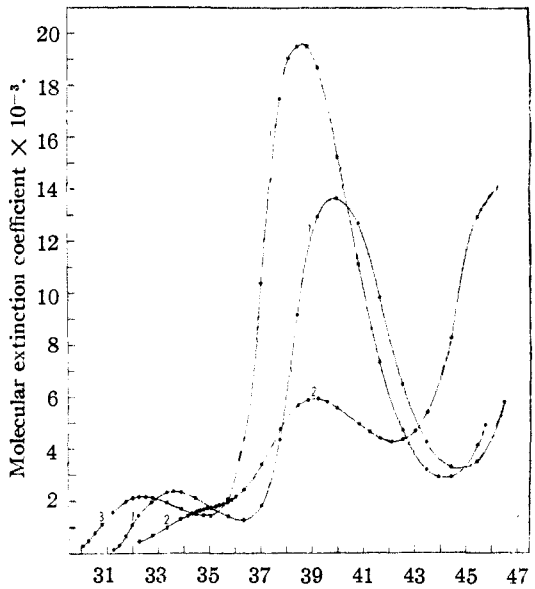
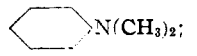
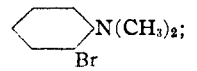
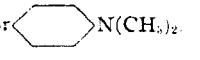
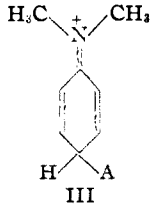


Fig. 5.—1,  ; 2,  ; 3, 

and para isomers of chloro-,[8] bromo-[8] and iodoaniline,[8] the ortho isomer always absorbs with the greater intensity, the ratio of intensities varying from 1.3 (chloro) to 1.7 (iodo). No explanation is offered for the observed shifts in frequency of maximum absorption.

Essentially, we have taken the stability of such structures as I and II as the principal requirement for the characteristic low frequency absorption of dimethylaniline and its derivatives (alkyl and halogeno). Steric factors influencing the stability of those structures would be expected to influence in a like manner the stability of III and IV, where A represents an electrophilic reagent. (Here A is



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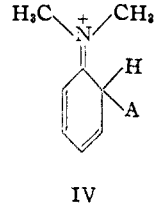


IV

taken as positively charged, but the same conclusions hold for any electrophilic reagent.) The rate of a substitution reaction in which III or IV is the active intermediate would be expected to be increased or decreased as the stability of these structures is increased or decreased (by the operation of steric factors). Thus, a parallelism between the low frequency absorption of dimethylaniline derivatives and their reactivity toward electrophilic reagents was to be expected.

(8) Purvis, *J. Chem. Soc.*, **103**, 1638 (1913).

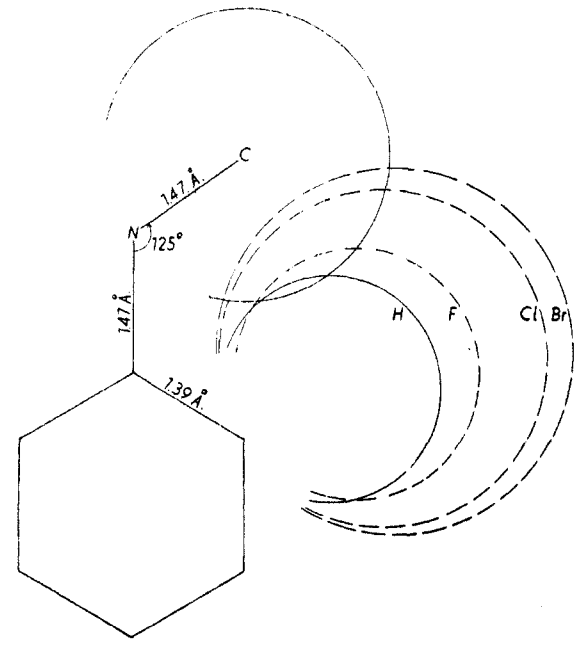


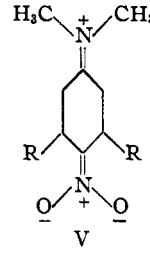
Fig. 6.—Scale representation of *o*-halogenodimethylanilines based upon dimensions given by Pauling.[9] The single-bond distances are used for the C—N bonds, although the C—N—C angle is given a value corresponding to a double bond between ring-carbon and nitrogen. Van der Waals radii are used except in the case of the methyl group. Here the hydrogen atoms are omitted, and the van der Waals radius calculated for carbon is used since rotation of the methyl group could conceivably allow the methyl hydrogen atoms to avoid the hindering group. The omission of the methyl hydrogen atoms and the selection of the bond angles and distances make the hindrances depicted minimal.

This parallelism is well illustrated by consideration of the acid catalyzed deuterium exchange reaction of dimethylaniline, for which the active intermediate has been postulated to be the product of direct addition of a deuteron at the ortho or para position (III or IV, A = deuterium).[5] Brown, Widiger and Letang have investigated the effect of steric factors on the rate of this reaction, employing many of the compounds whose spectra are recorded above, and the agreement between the spectral and chemical approaches is excellent. Both absorption and exchange are hindered by ortho halogen atoms, and in both cases the hindrance increases with the weight of the halogen. In the case of the nucleo-alkyl and bicyclic amines the order of exchange reactivity was found to be N-methylindoline > N-methyltetrahydroquinoline > dimethylaniline > N-methyl-*homo*-tetrahydroquinoline > dimethyl-*p*-xylidine > dimethyl-*o*-toluidine. This is, with but one minor exception, identical with the order which would be predicted from either the fre-

(9) Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 1940.

quencies or the intensities of the first absorption bands.[10]

II.—*p*-Nitrodimethylaniline and its derivatives may be considered in much the same manner as the simpler derivatives of dimethylaniline. In this case, structure V (R = H or CH_3) would be expected to make a very large contribution to the first excited state. The introduction of any



V

group which tends to keep either the aminomethyl groups or the oxygen atoms out of the plane of the ring should therefore interfere with the first absorption band (A). Figure 7 shows how this prediction is borne out when the nitro group is hindered.[11] When one hindering methyl group is introduced the shift in frequency, though very small (80 cm.$^{-1}$), is in the expected direction; but the introduction of the second causes a shift of 400 cm.$^{-1}$ in the opposite direction. Qualitatively, the effect of hindering groups on the intensity of absorption is as predicted, and the only surprising feature is the very small reduction caused by the first methyl group as compared with the large effect of the second. This confirms other evidence[12] indicating that the hindrance offered a nitro group by one adjacent methyl group is very slight compared with the hindrance offered by two such groups.

It is interesting to note that bands B and C come more closely to resemble the nearby bands in the spectrum of dimethylaniline as the resonance of the nitro group with the ring is decreased by the hindering methyl groups.

The kinetics of the reaction with methyl iodide of each of the *p*-nitroamines has been investigated. Brown and Fried[13] found that the doubly hindered compound reacted slightly more than twice as rapidly as did the singly hindered compound; whereas Evans, Watson and Williams[14] had previously reported that under similar conditions *p*-nitrodimethylaniline did not react. These differences are in the expected direction since hindrance of the nitro group should decrease its deactivating influence in such a reaction. Brown

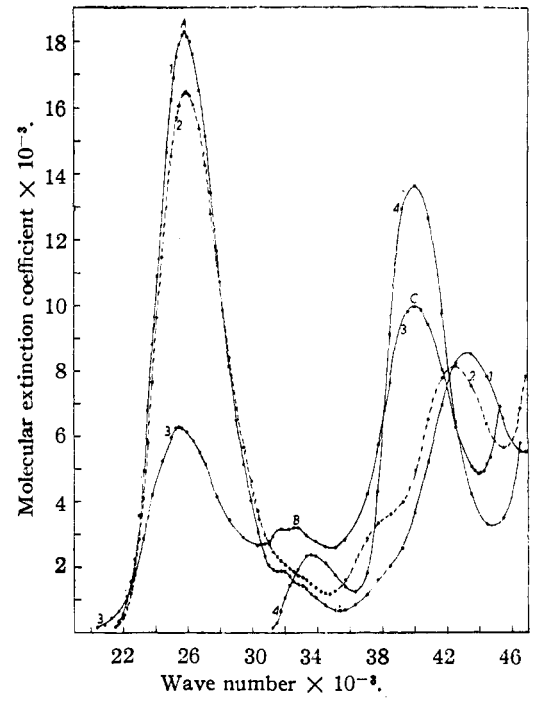


Fig. 7.—1, O_2N–C$_6$H$_4$–$N(CH_3)_2$; 2, O_2N–C$_6$H$_3$(CH_3)–$N(CH_3)_2$; 3, O_2N–C$_6$H$_3$(CH_3)$_2$–$N(CH_3)_2$; 4, C$_6$H$_5$–$N(CH_3)_2$.

and Fried suggest that the difference which they observed might be "hardly greater than could be ascribed to the methyl groups as such," but the spectral curves seem hardly to be amenable to such an explanation.

The absorption curves of *o*- and *p*-nitrodimethylaniline are presented in Fig. 8, and data on the low frequency absorption maxima of *o*- and *p*-nitrodimethylaniline and the corresponding primary amines are given in Table I. In each case the

TABLE I

THE FIRST ABSORPTION MAXIMUM OF NITROANILINES AND NITRODIMETHYLANILINES

Compound	Frequency (cm.$^{-1}$)	Molecular extinction coefficient
o-Nitrodimethylaniline	24,100	2,460
p-Nitrodimethylaniline	25,800	18,290
o-Nitroaniline[a]	25,000	6,310
p-Nitroaniline[a]	27,010	16,200

[a] Glotz, *Bull. soc. chim.*, [5] **1**, 1148 (1934); solvent, alcohol.

absorption of the ortho compound is less intense than that of the para isomer, but this difference is far more pronounced in the case of the tertiary amines. Also, the increase in frequency accompanying the change from *o*-nitro to *p*-nitro is less in the case of the tertiary than in the case of the primary amines. These differences agree with

(10) The anomalous compound is N-methyltetrahydroquinoline whose first absorption maximum occurs at a slightly lower frequency than that of N-methylindoline.

(11) The author is indebted to Dr. B. A. Bluestein of this department for the data on the absorption of 1-dimethylamino-3,5-dimethyl-4-nitrobenzene. The conditions were identical with those under which the spectra of the other compounds of this group were measured.

(12) Borsche, *Ann.*, **386**, 351 (1911).

(13) Brown and Fried, THIS JOURNAL, **65**, 1841 (1943).

(14) Evans, Watson and Williams, *J. Chem. Soc.*, 1345 (1939).

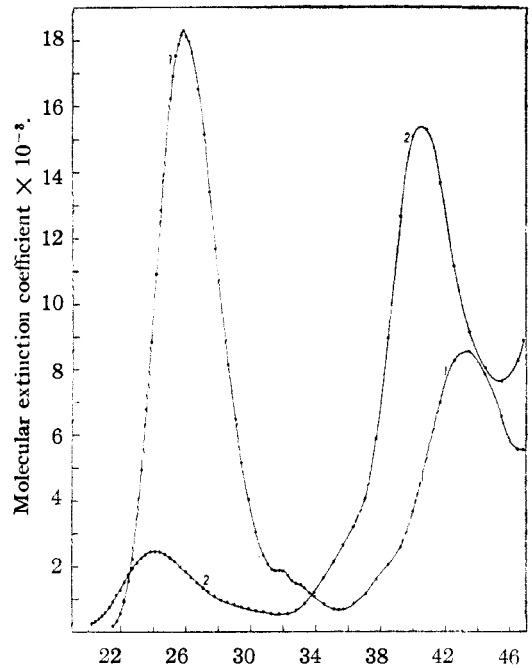


Fig. 8.—1, O_2N⟨⟩$N(CH_3)_2$; 2, ⟨⟩$N(CH_3)_2$ (NO_2).

predictions based on steric hindrance, but may be partially due to the impossibility of hydrogen bonding in *o*-nitrodimethylaniline.

Interestingly, the most strongly hindered of the nitroamines are also the most strongly colored. Both *o*-nitrodimethylaniline and 1-dimethylamino-3,5-dimethyl-4-nitrobenzene are reddish orange whereas the other two compounds of the group are yellow. Thus, visual observation might lead one to the erroneous conclusion that the intensity of absorption is increased rather than decreased by steric hindrance.

Experimental

Materials.—The spectra were measured with a Beckman Quartz Spectrophotometer, Model DU.[15] The width of the spectral band which the instrument passes at a given wave length setting may be varied within limits imposed by the sensitivity of the instrument and the transparency of the solvent, both of which vary with the wave length. Since several batches of solvent were used and the sensitivity of the instrument was improved during the course of the investigation, the band widths were not the same for all compounds. In those cases where the band width was greatest it lay between 20 and 30 ångströms (between 300 and 500 cm.$^{-1}$). The solutions whose spectra were being measured were contained in stoppered quartz cells, and the thickness of the liquid layer was one centimeter. The intensity of the light transmitted by the solution was compared with that transmitted by the pure solvent.

The solvent for the nitroamines was U. S. P. absolute alcohol, fractionated to remove most of the benzene. The rest of the compounds were dissolved in 2,2,4-trimethylpentane. Rohm and Haas pure isoöctane was stirred overnight with aqueous permanganate, and the manganese dioxide as well as excess permanganate was destroyed with bisulfite. The hydrocarbon was washed with water, dried over potassium hydroxide, and distilled.

p-Nitrodimethylaniline was prepared from dimethylaniline by nitrosation followed by oxidation with permanganate[16] and was recrystallized from 95% alcohol, whose transparency exceeded that of the solvent used in the spectral investigation. The product melted sharply at 165° (cor.). Various values for the melting point are to be found in the literature. Wurster reports 160°[16]; Baudisch, 162.5°[17]; Sprowls, 162°.[18]

o-Nitrodimethylaniline was prepared from *o*-nitrochlorobenzene and dimethylamine according to the method of LeFèvre.[19] Purification was accomplished by recrystallization of the picrate. The picrate was decomposed with aqueous sodium hydroxide and the resulting oil was dried and distilled before use.

All the other compounds had been prepared and purified by other members of this department. The sample of *o*-*t*-butyldimethylaniline had been prepared by Dr. M. Z. Fineman; the two derivatives of *p*-nitrodimethylaniline by Dr. S. Fried[13]; and the remaining compounds by Drs. A. Widiger and N. Letang.[4]

Procedure.—Each of the compounds except the *p*-nitroamines was distilled *in vacuo* immediately before use and a middle fraction was used. The solutions of these compounds were approximately 10^{-4} molar, except in the case of *o*-*t*-butyldimethylaniline, whose absorption was so weak that a 10^{-3} molar solution was required. Duplicate curves run on *o*-chlorodimethylaniline agreed within 0.4%. Five × 10^{-5} molar solutions of the nitroamino compounds were prepared by triple volumetric dilution. After a sample of the most dilute solution had been removed to the spectrophotometer cell the flask was emptied, drained briefly and weighed. A new aliquot of the next most dilute solution was then pipetted in and the solution was again diluted to volume. In each case the absorption of the second solution agreed with that of the first (after correction for the small amount of liquid retained by the flask) and showed that no appreciable errors were being introduced by adsorption.

Results.—The molecular extinction coefficient is plotted against the frequency (in cm.$^{-1}$) because in this scheme the area under the curve is an undistorted measure of the intensity of absorption.

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Summary

1. The effects on absorption spectra to be expected from steric inhibition of resonance have been briefly discussed.

2. The absorption spectra extending into the ultraviolet as far as 47,000 cm.$^{-1}$ of dimethylaniline and nineteen derivatives have been measured.

3. Systematic variations in the spectra of these compounds have been correlated with steric inhibition of resonance. Molecular planarity has been shown to be a requirement for the characteristic absorption of dimethylaniline and of *p*-nitrodimethylaniline.

4. Parallel chemical effects of steric inhibition of resonance in the compounds studied have been discussed.

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