In order to ascertain the effect of alkali under more vigorous conditions, I was heated under reflux with 0.05 *N* alcoholic potassium hydroxide for thirty minutes. The solution was cooled to room temperature and the absorption spectrum determined. The curve is not shown since it was almost identical to that given for I after treatment with alkali at room temperature (Curve 6). The values found were: $\lambda_{\max.}$ 241 mμ (log ϵ = 4.01), 285 mμ (log ϵ = 3.89) and 377 mμ (log ϵ = 3.76); $\lambda_{\min.}$, 260 mμ (log ϵ = 3.36) and 309 mμ (log ϵ = 2.75).

Inspection of the absorption curve of compound II in alkali reveals the absence of a peak in the 220–250 mμ region. This would indicate a failure to open the γ-chromanone ring.

Summary

Studies on the ultraviolet absorption of some substituted β-benzoylacrylic acids, 2-carboxy-γ-chromones, and 2-carboxy-γ-chromanones have shown the significance of the maximum in the 220–250 mμ range which is present in the first two classes of compounds and missing in the third. The effect of alkali on the absorption curve and the use of such data for detecting the opening of the γ-chromanone ring has been pointed out.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE DEPARTMENT OF PHYSICS OF THE UNIVERSITY OF CHICAGO]

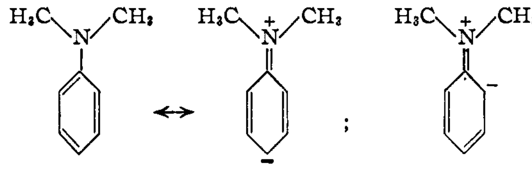
Geometry and Spectra of Substituted Anilines[1]

BY H. B. KLEVENS[2] AND J. R. PLATT

Steric inhibition of resonance effects on near ultraviolet absorption spectra have been investigated by numerous groups.[3] Steric inhibition to planarity in dye molecules and its effect on their spectra in the visible region has been reviewed recently.[4] The compounds reported here were studied by Remington[3] in the 2200–3000 Å. region and a correlation of spectral characteristics and parallel chemical effects of steric inhibition of resonance was included. He indicated that the absorption band nearest the red was the one most affected by steric hindrance. The absorption curves for N,N-dimethylaniline and six of its derivatives have been extended to 1700 Å.

The observed chemical and spectroscopic effects of steric hindrance in conjugated systems may be interpreted as follows. As indicated by Pauling,[5] resonance in conjugated systems implies approximate planarity of all the conjugated atoms, with the unsaturation electron orbitals oriented normal to the plane. Destruction of planarity by a "crowding" substituent causes one or more double-bond linkages to twist, losing part of their double bond character and partly destroying the conjugation. With 90° twist, a twisted link takes on some of the properties of a single bond, insulating from each other the sections (which may still be locally planar and conjugated) on each side of it. In this case, the spectral absorptions of these two sections become approximately independent and additive, usually making a great change from the spectrum of the initial completely planar conjugated system. It is shown here that for intermediate angles of twist, the changes in the spectrum are quantitatively related to the angle of twist.

The N,N-dimethylaniline is supposed to be a resonance hybrid of structures I, II and III with the $-N(CH_3)_2$ group oriented so that the two methyl C-atoms are in or nearly in the plane of the ring. This orientation is favored because



I II III

it allows the formation of structures like II and III in which the N electrons can be partially conjugated with the unsaturation electrons of the ring. The ultraviolet spectrum is therefore not like that of toluene or of isopropyl or *s*-butylbenzene,[6] where the alkyl substituent has no unsaturation electrons, but rather resembles that of styrene and diphenyl[7] where there is full conjugation with the ring.

In the N,N-dimethylanilines it is the $-N(CH_3)_2$ group which twists with relation to the ring as groups of progressively larger radii are added in the ortho position. The twist causes progressive

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[3] For example see: 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); **67**, 2127 (1945); Remington, *ibid.*, **67**, 1838 (1945).

[4] Brooker, White, Sprague, Dent and Van Zandt, *Chem. Rev.*, **41**, 325 (1947).

[5] Pauling, "The Nature of the Chemical Bond," Chap. VI, Cornell University Press, Ithaca, New York, 2nd edition, 1944.

[6] J. R. Platt and H. B. Klevens, *Chem. Rev.*, **41**, 301 (1947); *J. Chem. Phys.*, **16**, 832 (1948).

[7] Unpublished results of the authors.

loss of double bond character of the N–C_6H_5 bond; and, with 90° angle of twist, the spectrum becomes almost identical with that of a simple alkylbenzene, since the dimethylamine absorption as well as the alkyl absorption in this spectral region is negligible.

Spectra

The spectra of dimethylaniline and of its *o*-methyl, *o,o'*-dimethyl and *p*-methyl derivatives are shown in Fig. 1 and those of the *o*-halogen derivatives in Fig. 2. The curves are extended to the red of 2300 Å., where the dispersion of the fluorite spectrograph becomes small, by including the data on these compounds as reported by Remington.[3]

TABLE I

MAIN FEATURES OF SPECTRA OF DIMETHYLANILINES

Band	A	B	C	D	Total *f*
		Dimethylaniline			
Maxima (cm.$^{-1}$)	56800	50100	40000	33800	
ϵ_{max} (mole^{-1} cm.$^{-1}$)	36600	22200	13750	2300	
f calcd. from	(61700)	53300	44700	36250	
to: (cm.$^{-1}$)	53300	44700	36250	31200	
f	0.79	0.54	0.28	0.04	1.65
		o-Methyldimethylaniline			
Maxima (cm.$^{-1}$)	54000	48300	40400	Stepout	
ϵ_{max}	30800	11400	6300	1200	
f calcd. from:	(59100)	50500	43500	37000	
to:	50500	43500	37000	33000	
f	0.69	0.23	0.12	0.02	1.06
		o,o'-Dimethyldimethylaniline			
Maxima (cm.$^{-1}$)	51600	47400	38600	...	
ϵ_{max}	36100	8600	2200	...	
f calcd. from:	56900	48500	41000	...	
to:	48500	41000	33700	...	
f	0.66	0.15	0.05	...	0.86
		p-Methyldimethylaniline			
Maxima (cm.$^{-1}$)	54550	49200	39400	32900	
ϵ_{max}	20800	22800	15100	2100	
f calcd. from:	(58200)	51900	44400	35500	
to:	51900	44400	35500	30700	
f	0.40	0.46	0.32	0.03	1.21
		o-Fluorodimethylaniline			
Maxima (cm.$^{-1}$)	56900	49700	40000	35300	
ϵ_{max}	40100	17500	11600	2100	
f calcd. from:	(61400)	53000	44000	37000	
to:	53000	44000	37000	32000	
f	0.80	0.43	0.21	0.03	1.47
		o-Chlorodimethylaniline			
Maxima (cm.$^{-1}$)	53900	47100	39100	Stepout	
ϵ_{max}	36100	18500	7600	1800	
f calcd. from:	(58200)	50500	42000	36000	
to:	50500	42000	36000	31500	
f	0.72	0.39	0.14	0.03	1.28
		o-Bromodimethylaniline			
Maxima (cm,$^{-1}$)	53200	46300	39300	Stepout	
ϵ_{max}	36200	14600	5900	1700	
f calcd. from:	57300	49000	42000	36000	
to:	49000	42000	36000	31500	
f	0.74	0.30	0.12	0.03	1.19

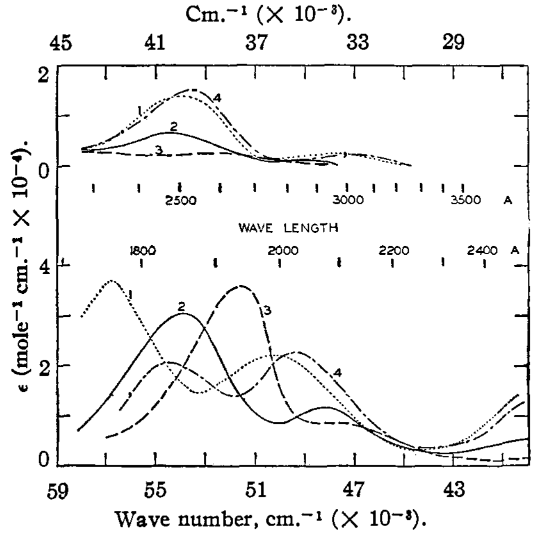

Fig. 1.—Spectra of alkyl substituted dimethylanilines: 1, N,N-dimethylaniline; 2, *o*-methyl-; 3, *o,o'*-dimethyl-; 4, *p*-methyl-.

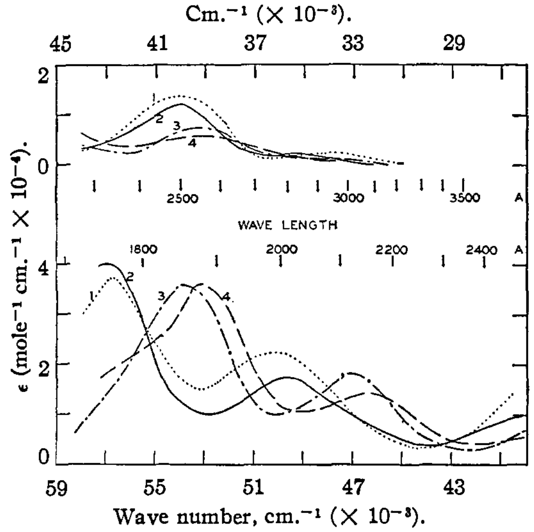

Fig. 2.—Spectra of ortho halogen dimethylanilines: 1, N,N-dimethylaniline; 2, *o*-fluoro-; 3, *o*-chloro-; 4, *o*-bromo-.

The spectra show four characteristic regions of absorption, near 1800, 2100, 2500 and 3000 Å., which are designated A, B, C and D, respectively. The values of the oscillator strengths, *f*, of these individual bands and of the total oscillator strength for each compound are given in Table I. They were computed from the integrated areas under the curves by use of the equation

$$= 4.32 \times 10^{-9} \int \epsilon \, d\nu$$

where ν is the frequency in cm.$^{-1}$ and ϵ is the molar extinction coefficient. For a given band, the areas were measured between the two minima on each side of the band. Since the short-wave length side of band A was incomplete in most cases, the curve was continued into the axis as a straight line of slope about 55° (on the scale of Figs. 1 and 2) in order to obtain approximate areas under this band. This slope seemed to represent the general trend of the curves in this region correctly.

Changes in the spectra with substitution may be due to two causes. First, the usual red shifts and changes in intensity will occur with alkylation or other substitution as already observed in alkylbenzenes[6]; and second, there will be the effects of steric hindrance and twist of the amine group in which we are more interested. In order to estimate the contribution from the first source, the spectrum was taken of the *p*-methyl derivative, in which no steric hindrance occurs. Its B, C and D bands as seen in Fig. 1 and Table I indeed show red shifts, but little change of intensity from the bands of the parent compound. The A band shows a strong red shift and also a reduction of *f*-value by one-half. It may be concluded that, when similar changes of *location* of the bands are observed in the other derivatives, they may be partly or wholly due to induction and similar effects of the substituent on the ring; but that the changes of *intensity* observed in the B, C and D bands of the other compounds must be accounted for almost entirely by the steric inhibition of the aniline resonance. The other compounds do not show such a loss of intensity in the A band as does the *p*-methyl derivative. Conceivably this is a special para effect, such as the special effects observed in greater or less degree in other para benzene derivatives, due here to some electronic oscillation along the long axis of the molecule with a partial electron shift from the electron-donating amino group.

The *o*-methyl spectrum shows the typical combined steric and substitution effects which are found in all the ortho derivatives. The A and B bands have strong red shifts, the C and D bands actual blue shifts. This tendency of the bands to come together was not observed in the *p*-methyl compound and so is probably due to steric effects. The total spread in the bands approaches the much smaller spread in the three ultraviolet benzene bands[6] as the $-N(CH_3)_2$ group is twisted. In addition there are some finer wave length changes due to the electronic character of the substituent, since the A bands have a greater red shift in the *o*-chloro and *o*-bromo derivatives than in *o*-methyl even though the latter has a larger van der Waals radius[8] and so presumably a larger angle of twist.

More striking than the red shifts is the weakening of the B, C and D bands in the ortho derivatives and the actual disappearance of any separate D band in the *o,o'*-dimethyl compound and in the *o*-*t*-butyl compound studied by Remington.[3] The spectra of the latter compounds become almost indistinguishable from those of alkylbenzenes. Bands B and C are theoretically forbidden and actually rather weak in benzene. Band D has no counterpart in benzene. It may retreat and weaken into the faint trimethylamine absorption near 2600 A.[9] as the $-N(CH_3)_2$ group twists, showing its effect only in increased intensity of the C band in this region.

Since the A band changes little in intensity in these ortho compounds, the loss of intensity in the other bands produces a loss of total oscillator strength as may be seen in Table I. The high total *f*-value of dimethylaniline decreases with substitution to values comparable with alkylbenzenes.[6] The *o*-methyl *f*-value actually becomes less than that for *o*-xylene, which is an approximate hydrocarbon analog, but this may be due either to the effect of branching (the true analog is *o*-methylisopropylbenzene whose spectrum has not been measured below 2200 Å.) or to the electronegativity of the nitrogen atom.

Thus there are three features of the spectra which show a change toward an alkylbenzene character with increasing bulkiness of the ortho substituents: (1) the red shifts, especially of the A and B bands, causing reduction of the total spread of the bands; (2) the decreasing total oscillator strengths; and (3) the strongly decreasing relative and absolute intensities in bands B, C and D.

Oscillator Strengths, van der Waals Radii and Angles of Twist.—The above discussion of the spectra has advanced the idea that the application of strain through a crowding substituent in the ortho position should decrease the conjugation effect of the $N-C_6H_5$ bond and thus decrease the total *f*-value. On plotting the *f*-values against the van der Waals radii of ortho substituents[8] as shown in Fig. 3, it is seen that the total *f* actually decreases linearly with the size of the crowding group within the accuracy of the spectroscopic determinations.

This relation suggests making estimates of the angle of twist from the van der Waals radii; and determining not just the variation of the total *f*-value, but the variation of the *f*-values for the individual A, B and C bands as functions of this angle of twist. Of course at room temperature the $-N(CH_3)_2$ group will undergo thermal motions of various kinds including thermal twisting about the $N-C_6H_5$ axis. It is the effective angle of twist, suitably averaged over these motions, which is desired; but it is the minimum angle of twist required by the crowding which is easiest to estimate. How these two angles are related will be discussed qualitatively below. To estimate the minimum angle, certain simplify-

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(8) Reference 5, p. 189.

(9) H. B. Klevens and J. R. Platt, This Journal, 69, 3055 (1947).

ing assumptions about the geometry are helpful. They are: (1) The ring and immediately adjacent atoms lie in a plane. (2) All ring carbon angles are held at 120°. (3) The covalent bond distances are as given by Pauling.[10] (4) The nitrogen methyls and the ortho substituent touch at the minimum angle of twist as static rigid spheres with (a) Pauling's van der Waals radii for the ortho substituent.[8] (b) An effective radius of 1.2 Å. for the nitrogen methyls. (5) (a) The N–C_6H_5 bond distance is 1.35 Å. (b) I. The nitrogen valences are planar at 120° to each other. II. Alternative: The nitrogen valences become increasingly pyramidal as the group is twisted, assuming the ammonia configuration when the C–C line is perpendicular to the ring.

Assumption 5a is plausible for dimethylaniline itself, allowing the N–C_6H_5 bond to have some double-bond character. In this case 5bI and 4a lead to the absurdly small value of 4b if the dimethyl carbons are to be in the plane of the ring. This amounts to letting 4b bear the burden for various van der Waals compressions and bond-bendings which will occur both in the twisted and untwisted cases in violation of assumptions 2, 4a and 5bI. This seems to be as convenient a way as any to handle these uncertain variations.

Assumption 5bI is convenient for calculation, but it seems unlikely that it can remain valid as the dimethyl group is twisted, since the twist destroys the conjugation which probably encourages planarity in the untwisted state. The next most convenient assumption is 5bII. The angle of twist to be considered is then that of the C–C line in the dimethyl group, since the orientation of the nitrogen *p*-orbitals must be skew-perpendicular to this line. The angle of twist computed on assumption 5bI would have to reach about 123° before the angle of the C–C line on assumption 5bII would reach 90°. So for these estimates it will be sufficient to take all of the angles of twist on the pyramidal assumption as $^3/_4$ of the corresponding angles on the planar assumption. There is some added uncertainty in the numerical value of this factor because deviations from assumption 1 will alter the angles in the same direction as the alterations caused by assumption 5bII. Any small variation in the N–C_6H_5 distance and of the C–N–C angle with the angle of twist may be neglected since the motions involved are almost perpendicular to the line of centers of the touching groups.

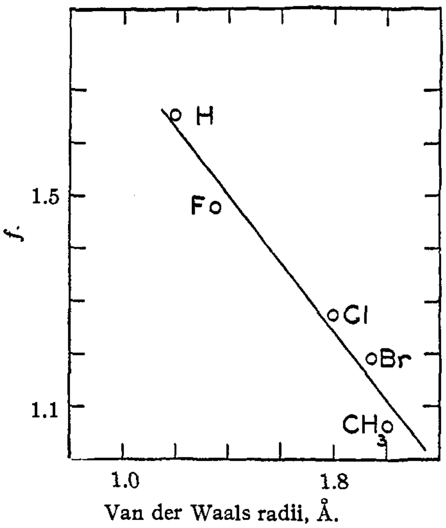

Fig. 3.—Change in total oscillator strength, *f*, of substituted dimethylanilines with increase in size of ortho substituent.

Assumption 5bII is one way of explaining the much closer spectroscopic resemblance of the *o,o'*-dimethyl derivative to a xylene than the *o*-methyl derivative; provided we accept the evidence that, when the C–C line is perpendicular to the ring, the nitrogen unsaturation electrons are decoupled from the ring and the electronic behavior becomes that of an alkylbenzene. For on assumption 5bII, the C–C line is still far from perpendicular with one *o*-methyl, the nitrogen valence pyramid bending away from the substituent and remaining fairly free to twist. With two *o*-methyls, the second one fits in between the two nitrogen methyls, and the C–C line is forced to be nearly perpendicular. These relations may be seen easily with a model.

The improved resemblance of the *o,o'*-dimethyl spectrum to that of a xylene might also be explained with planar nitrogen valences by assuming a larger nitrogen methyl radius than is given in 4b, so that the C–C line is almost perpendicular to the ring when no bond-bending occurs. Then, with thermal motion, plus bond-bending induced by the twisting force, one *o*-methyl might allow considerable deviation of the C–C line from 90°, while two *o*-methyls would hold it at the angle more exactly. But the twisting force is surely much weaker than the bond-bending force, especially near 90°, where the twisting energy should have a maximum and the force should vanish. These planar assumptions seem less plausible for explaining the *o,o'*-behavior than do the pyramidal assumptions of the preceding paragraph.

The minimum angles of twist computed in this way for the two cases are given in the columns marked "Planar" and "Pyramidal" in Table II.

TABLE II

ANGLES OF TWIST

o-Substituent	Computed minimum angle Planar	Computed minimum angle Pyramidal	Effective spectroscopic angle
Fluoro	29°	22°	33°
Chloro	58°	44°	44°
Bromo	65°	49°	54°
Methyl	75°	56°	60°
Dimethyl (*o,o'*)	75°	90°	(90° assumed)

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(10) Reference 5, p. 164–167.

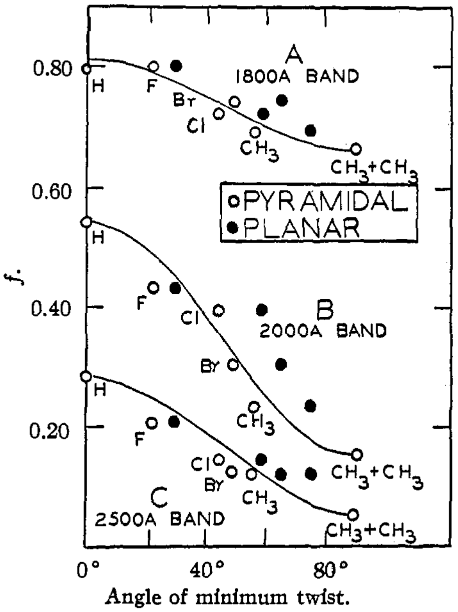

Fig. 4.—Variation in value of oscillator strength, *f*, of each band, A, B and C with minimum angle of twist for different ortho substituents. Planar and pyramidal nitrogen valence directions are assumed.

The *f*-values, even if they are functions of orientation of the dimethyl group alone, should not be related to the *minimum* angle of twist but rather to the *effective* angle of twist. This angle will be the angle at which the *f*-value will equal the mean *f*-value of the molecule averaged over its thermal twisting motion. This effective angle will be only slightly greater than the minimum angle, but may not be much greater, because the minimum angle will be a turning-point of the motion, which will increase the probability of angles near it. Consequently, the *f*-values of the A, B and C bands of these compounds are plotted in Fig. 4 as functions of the minimum angles given in Table II. A cosine-square curve is drawn on each diagram, as this is the simplest function which has maxima and minima 90° apart. At 0° the curve is passed approximately through the dimethylaniline *f*-value and at 90° through the value for the *o,o'*-dimethyl derivative. This assumes that the second *o*-methyl contributes nothing to the intensity except as it affects twist. Such reasoning may not be correct for the A band; but it is a good approximation for the B and C bands, for which the benzene, toluene and xylene *f*-values are all near 0.15 (B) and 0.00 (C), close to the *o,o'*-dimethyl values. The curves are entirely determined by these points at 0 and 90° and in each case fit the remaining four points for the pyramidal assumption to within the errors of angle estimate. In two cases in the A band, the order of the points is interchanged, but the deviations involved are much smaller than the experimental uncertainty in the *f*-values, which is about 10%. The fit is about as good for the *f*-values from Remington's data on the C band as it is for the *f*-values from our data on the A and B bands. The fluorine points lie as close to the curves as do the others. It is surprising that the electronegativity of this substituent has so little effect.

We could reverse the above argument and use the *f*-values and the cosine-square law curves of Fig. 4 to compute an "effective spectroscopic angle of twist" for each substituent. Curves B and C are the steepest and give the most reliable angles by this method. Averages of the two angles from these two curves for each compound are given in Table II in the last column.

Pauling[11] has shown the relationship which exists between bond distances and double bond character in C–C linkages, and indicates that a suitable translation of his curve and change in vertical scale can be used for bonds between other atoms. If we assume that the *f*-values in bands B and C are linear functions of the double-bond character of the N–C_6H_5 bond, we can estimate from such a curve how the N–C_6H_5 bond distance is affected by ortho substitution, as shown in Table III.

TABLE III

PREDICTED CHANGE IN N–C_6H_5 BOND DISTANCE WITH LOSS OF CONJUGATION DUE TO ORTHO SUBSTITUTION

o-Substituent	Bond distance (Å.)
H	1.37[a]
F	1.39
Cl	1.42
Br	1.44
CH_3	1,46
$C(CH_3)_3$	1.47[b]

[a] The double-bond character of dimethylaniline is taken to be equal to 0.25; distances determined from Pauling's curves, translated downward. [b] For *t*-butyl substitution, the distance is taken to be the equivalent to the single C–N bond distance of 1.47 Å. as in monoalkylamines.

We assume the double-bond character changes from zero for *t*-butyl substitution to 0.25 for dimethylaniline itself. The latter value corresponds to an extra resonance energy of 7 kcal./mole for this bond as found experimentally.[12]

The last columns of Tables III and II then amount to predictions, from spectroscopic evidence, of the N–C_6H_5 bond distance in *o*-substituted dimethylanilines and of the average angle of twist of the C–C line in the –$N(CH_3)_2$ group with respect to the plane of the ring in these compounds. It would be valuable to have these predictions tested by X-ray or electron diffraction methods.

Relation to Other Spectra

Empirically, the A, B and C bands of dimethylaniline seem to have a one-to-one correspondence to the 1800, 2100 and 2500 Å. bands of alkyl-

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(11) Reference 5, p. 174.

(12) L. Pauling and J. Sherman, *J. Chem. Phys.*, **1**, 606, 679 (1933).

benzenes, respectively, and transform smoothly and continuously into these bands as the nitrogen orbitals are rotated. The largest wave length shifts in this transformation are only 200 Å., and even these shifts may be partly accounted for by the alkyl substitution effect on the ring. This appears to give a partial answer to the old dispute whether the intense band near 2500 Å. in certain conjugated phenyl derivatives is really related to the very weak band in benzene near this position or whether the coincidence is only an accident. From the aniline spectra, we must say, it is no accident.

Another way of showing the same thing was devised in the course of a discussion between C. C. J. Roothaan and one of the authors (J. R. P.). It is based on the idea that the perturbation of the position or intensity of the benzene energy levels ought to become more severe as the ionization potential of a substituent approaches that of benzene itself. Since empirically the position seems not to change with many different substitutions, a relation is to be sought between the intensity of bands at a certain location and the ionization potential of the substituent. A plot of the log of the f-value of the 2500 Å. bands in compounds of the type Ph-X[13] *versus* the ionization potential of Me-X[14] is shown in Fig. 5. It is seen that for the five compounds plotted, in which the atom adjacent to the benzene is in the second row of the periodic table, and in which the double-bond character of the bond is not large, an excellent straight line is obtained. The f-value on this line reaches 1.0 near the ionization potential of benzene itself (or more properly, toluene), which is to say that just this amount of perturbation transforms the forbidden transition of benzene to a completely allowed one. Theoretically, the perturbation of the benzene states depends not only on the ionization potential of the substituent, but also on the "overlap integral" which determines the amount of coupling between the ring carbon and the adjacent atoms.[15] The latter may vary considerably in other rows of the periodic table, or with increased double-bond character, displacing the line of Fig. 5 for such substituents.

The fact that aniline lies on the line determined by the phenol and toluene confirms our other evidence that the three spectra are generically related, in spite of the unsaturation electrons introduced by the nitrogen in aniline. And the fact that the intensities in this 2500 Å. region in styrene and diphenyl also lie on the line shows that their bands too are derived in some sense from the benzene bands. In this connection, it has been found that styrene has A and B bands at almost the same positions as dimethylaniline.[7] Diphenyl has a B band at somewhat shorter wave lengths than the other compounds, and the absorption near 1700 Å. seems to be rising to an A band at wave lengths slightly shorter than can be reached in n-heptane solution.[7] It must be concluded that the pattern of three bands, A, B and C, of comparable intensity in this region is characteristic of conjugation of a ring with an adjacent atom and is only slightly affected by the structural details beyond this atom.

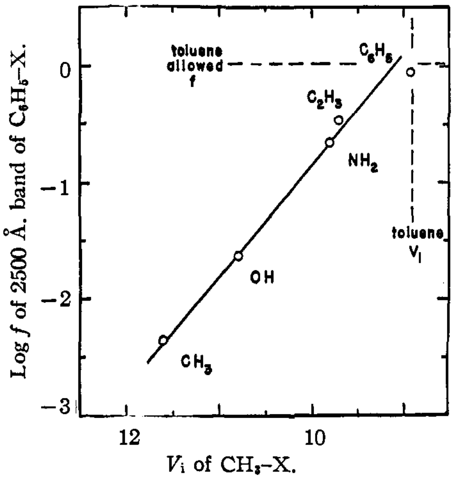

Fig. 5.—Perturbation of 2500 Å. benzene band by substituents.

If the line (or lines) of Fig, 5 is confirmed by data on other compounds or can be given a more rigorous theoretical justification, this might become a useful method of determining ionization potentials of unknown groups, since the measurement of spectral intensity in the quartz region to the required accuracy is simpler than the spectroscopic or electron impact determination of ionization potentials.

We conclude therefore: (A) That the benzene bands near 1800, 2100 and 2500 Å. retain their identity and are not shifted in position by more than about 200 Å. by any monosubstitution of complexity up to that of benzene itself, regardless of conjugation as long as the double bond character of the bond adjacent to the ring is not too large.

(B) That in the absence of steric hindrance the intensity in these bands is determined largely by the ionization potential of the substituent and perhaps in addition by a coupling constant between the substituent and the ring.

Experimental

The seven compounds reported here were obtained from Prof. Weldon G. Brown and were the same compounds used and described by Remington.[3] The spectrograph used was a Cario–Schmitt–Ott fluorite instrument kindly loaned to us by the University of Michigan. The experimental techniques and procedures were the same as those described previously.[6,9] Solutions were

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(13) Values determined from many curves in the American Petroleum Institute Catalog of Ultraviolet Spectrograms.

(14) W. C. Price, *Chem. Rev.*, **41**, 257 (1947).

(15) R. S. Mulliken, unpublished results.

made up by weight in *n*-heptane which had been cleaned so as to transmit in our 0.013-cm. cells to 1700 Å.[9]

Acknowledgment.—We are indebted to Prof. Weldon G. Brown for supplying the compounds and to Prof. R. S. Mulliken and to C. C. J. Roothaan for helpful discussions on the interpretation of the spectra. Mrs. Dorothy Iker Lossy assisted ably in photometering the plates and reducing the data.

Summary

1. The effects of steric inhibition of resonance on the absorption spectra of substituted dimethylanilines to 1700 Å. have been determined.

2. Total oscillator strengths have been shown to decrease almost linearly with the van der Waals radius of the group substituted in the ortho position.

3. The minimum angle of twist of the –N(CH$_3$)$_2$ group with respect to the ring was estimated from the van der Waals radius of each crowding group. Within the accuracy of the estimates, the oscillator strengths of the different bands vary with the cosine-square of the angle.

4. With certain simple assumptions, purely spectroscopic calculations were made of the angle of twist and of the variation of the N–C$_6$H$_5$ bond order and bond distance. These predictions could be tested by electron or X-ray diffraction.

5. The three strong aniline bands transform into the three alkylbenzene bands with respect to both intensity and position as the angle of twist approaches 90°.

6. A plot of log oscillator strength of the 2500 Å. bands in mono-substituted benzenes *versus* ionization potential of the substituents shows a straight line relationship when the connecting atoms are in the second row of the periodic table and have small double-bond character. Aniline lies on this curve, which goes from toluene at one extreme to diphenyl at the other.

7. The conclusion from (5) and (6) is that the bands of all these compounds are derived from the parent benzene bands with very little change of position and with regular changes of intensity according to rule (6).

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Preparation and Properties of Some Substituted Germanes[1]

BY O. H. JOHNSON AND W. H. NEBERGALL

I. Preparation of Substituted Germanes by Alkyl- or Aryllithium Compounds

In an earlier paper[2] it was reported that attempts to prepare isopropyltricyclohexylgermane, phenyltricyclohexylgermane and tetracyclohexylgermane by treatment of bromotricyclohexylgermane with the appropriate Grignard reagent were unsuccessful, although the reaction between bromotricyclohexylgermane and methyl-, ethyl-, *n*-propyl-, *n*-butyl-, *n*-amyl- and benzylmagnesium bromides proceeded readily. In the present investigation the organolithium compounds, isopropyllithium, phenyllithium and *o*-tolyllithium were employed in the reaction

$$(C_6H_{11})_3GeBr + RLi \longrightarrow (C_6H_{11})_3GeR + LiBr$$

to determine whether or not the use of these more vigorous alkylating and arylating agents would result in the formation of the substituted tricyclohexylgermanes which were not produced by the use of Grignard reagents.

The preparation of phenyltricyclohexylgermane was successful, but it was found that neither the isopropyl nor the *o*-tolyl groups could be substituted for the bromine by the action of isopropyllithium and *o*-tolyllithium, respectively, upon bromotricyclohexylgermane. In addition, the reaction of cyclohexyllithium in large excess with germanium tetrachloride resulted in the formation of chlorotricyclohexylgermane[3] as the sole product.

$$GeCl_4 + 3C_6H_{11}Li \longrightarrow (C_6H_{11})_3GeCl + 3LiCl$$

Likewise, an excess of cyclohexylmagnesium bromide reacted with tetraethoxygermane to form bromotricyclohexylgermane.

Application of the organolithium technique in the preparation of tetrasubstituted germanes gave decidedly better yields than the standard Grignard and Fittig procedures. For example, Simmons, Wagner and Muller[4] reported poor yields in the synthesis of tetraarylgermanes by the classical methods of Grignard and Fittig although Worrall[5] obtained an 80% yield of tetraphenylgermane by the usual Grignard technique by substituting toluene for ether as the solvent. The writers obtained a 90% yield of tetraphenylgermane by the reaction of an excess of phenyllithium with germanium tetrachloride in ether solution.

II. Action of Lithium Aluminum Hydride upon Some Substituted Germanes

The interaction of lithium aluminum hydride with the appropriate halides of silicon, of germa-

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[1] From a thesis submitted by William H. Nebergall to the Graduate School of the University of Minnesota in partial fulfillment of the requirements of the degree of Doctor of Philosophy.

[2] Johnson and Nebergall, THIS JOURNAL, 70, 1706 (1948).

[3] The description of the preparation of chlorotricyclohexylsilane by a similar procedure will appear in a later paper.

[4] Simmons, Wagner and Muller, *ibid.*, 55, 3705 (1933).

[5] Worrall, *ibid.*, 62, 3267 (1940).