room temperature, a small quantity of brown solid separated. This was collected (0.01 g.) and found to decompose above 250°. It was not further investigated. After standing for one day, crystals appeared in the filtrate. These were collected, dried at 50°, and found to weigh 0.92 g. Recrystallization from a mixture of chloroform with a small amount of added hexane yielded a product which melted at 140.5–141°.

Anal. Calcd. for $C_{14}H_{11}O_3NS$: C, 61.54; H, 4.03. Found: C, 61.41; H, 4.33.

2,4-Dinitrophenyl Acetonyl Sulfide.—This was prepared by refluxing 2 g. of 2,4-dinitrobenzenesulfenyl chloride with 20 ml. of acetone for several hours. Evaporation of the excess acetone and two crystallizations from absolute alcohol gave a good yield of lustrous brown crystals; m. p., 140–140.5°.

Anal. Calcd. for $C_9H_8O_5N_2S$: C, 42.18; H, 3.16. Found: C, 42.52; H, 3.42.

2,4-Dinitrophenyl acetonyl sulfide was also obtained by carrying out a similar reaction between 2,4-dinitrobenzenesulfenyl thiocyanate and acetone.

2,4-Dinitrophenyl Phenacyl Sulfide.—One gram of 2,4-dinitrobenzenesulfenyl chloride was dissolved in 10 ml. of ethylene chloride, 3.0 g. of acetophenone was added and the mixture was refluxed for two hours. An excellent yellow solid precipitated on cooling. This was collected, dried at 50° and found to weigh 1.3 g., (95% yield). After recrystallization from absolute alcohol, the product melted at 168–170°. The identical substance was also obtained by reacting, in a similar manner, 2,4-dinitrobenzenesulfenyl thiocyanate with acetophenone.

Anal. Calcd. for $C_{14}H_{10}O_5N_2S$: C, 52.82; H, 3.17. Found: C, 53.26; H, 3.31.

Summary

2-Nitrobenzenesulfenyl chloride and 2,4-dinitrobenzenesulfenyl chloride add to cyclohexene to yield the corresponding 2-chlorocyclohexyl aryl sulfides.

The reactions of 2-nitrobenzenesulfenyl thiocyanate and 2,4-dinitrobenzenesulfenyl thiocyanate with cyclohexene proceed in a manner similar to those of the corresponding sulfenyl chlorides, yielding 2-(arylthio)-cyclohexyl thiocyanates. The addition of 2-nitrobenzenesulfenyl thiocyanate to styrene has also been effected. In the attempted addition of benzenesulfenyl thiocyanate to cyclohexene, however, only phenyl disulfide was isolated.

The reactions of the 2-nitro- and the 2,4-dinitrobenzenesulfenyl chlorides and thiocyanates with acetone and with acetophenone, yielding β-keto sulfides, are also described.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

The Spectra of the p-Dimethylaminochalcones and of their Ions

BY ESTELLA R. KATZENELLENBOGEN AND GERALD E. K. BRANCH

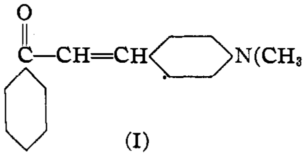
Lewis and Calvin[1] were able to interpret the spectra of a considerable number of organic molecules on the basis of the assumption that the electrons in these molecules act as quantized oscillators. They also postulated that the absorption spectrum of a molecule of appreciable polarizability in two dimensions should show two bands: the band at longer wave length being due to absorption of light vibrating along the direction of maximum polarizability (x-axis), and the second band being due to absorption of light vibrating along the direction of minimum polarizability (y-axis) which we shall assume to be perpendicular to the x-axis. These bands have been called x- and y-bands, respectively.

It should be noted that this theory accepts the basic concept of light absorption being due to the transition of the molecule from one quantum state to another. Further, the theory does not deny the possibility of calculating the energy difference of these states. It merely attempts to avoid the difficulties of such a calculation and yet to predict the spectrum of a molecule with some accuracy by making use of a classical picture and of some empirical facts, such as the magnitudes of the bathochromic or hypsochromic effects of certain groups.

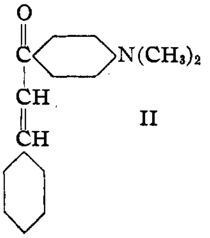
The temptation to avoid the calculation of the spectrum of an organic molecule becomes obvious if one considers that even such a relatively simple substance as a p-aminochalcone is a hybrid of more than fifty resonating forms, without invoking Dewar structures or structures with more than one separation of charge.

In this paper we shall show that the spectra of the p-dimethylaminochalcones and of their three positive ions can be predicted and interpreted by the theory of Lewis and Calvin.

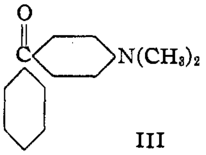
4-Dimethylaminochalcone (I) and 4′-dimethylaminochalcone (II) were chosen for this study since they are both vinylogs of p-dimethylaminobenzophenone (III) and differ only in the position of the vinyl group.



(I)



II



III

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[1] Lewis and Calvin, *Chem. Rev.*, **25**, 273 (1939).

Since a line joining the oxygen atom to the nitrogen atom in (I) and in (II) roughly corresponds to the direction of maximum polarizability in these molecules, one can say as a first approximation that in (I) the vinyl group chiefly increases the polarizability along the x-axis, but in (II) it chiefly increases the polarizability along the y-axis. Hence, if the theory of Lewis and Calvin is correct, λ_x of I should be greater than λ_x of II, and λ_y of II should be greater than λ_y of I.

Experimental

In the preparation of 4-dimethylaminochalcone the method of McLean and Widdows[2] was followed except for slight modifications; m. p. of product 113.4–113.5°, reported 113–114°. 4′-Dimethylaminochalcone was prepared by the method of Fecht[3]; m. p. of product 167–168°, reported 165°.

As solids these compounds are pure substances, not mixtures of isomers. We shall naïvely assume that the observed spectra are those of the *trans* isomers, or at least that the geometric configurations are the same as in chalcone.

The spectra were measured with a Beckman quartz spectrophotometer, readings being taken every 10 mμ., except in the high frequency region of the spectra of the third ions where readings were taken every 5 mμ. A gradually increasing width of slit from 0.02 mm. in the visible to 2 mm. at the lowest wave length was used. This corresponds to band widths of less than 3 mμ above 240 mμ, except where acetic anhydride was used as the solvent.

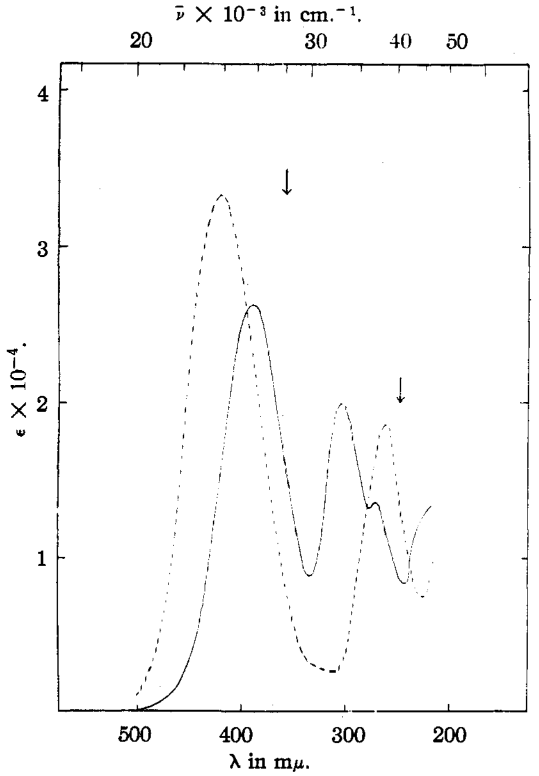

Fig. 1.—Spectra of the free bases in methanol: I, ----; II, —; arrows mark the positions of the maxima of the x- and y-bands of III.

The spectra of (I) and (II) were measured in methyl alcohol. The ketones form yellow solutions in this solvent. The spectra of the first ions were measured in methyl alcohol containing 0.100 mole per liter of anhydrous hydrochloric acid. These solutions appear colorless to the eye, but spectral analysis shows that only (I) is practically completely neutralized under these conditions (about 98%), while (II) is neutralized only to an extent of about 85% (see discussion of base strength below). The spectra of the second ions were measured in acetic anhydride containing 0.4% of concentrated sulfuric acid (d. 1.84 g./ml.). The acidified acetic anhydride solutions showed the pink color characteristic for the second ions, but they contained large amounts of unneutralized first ions. The spectra of the third ions were measured in concentrated sulfuric acid (d. 1.84 g./ml.). These solutions were yellow. No rapid sulfonation takes place at room temperature. This was shown by recovering the unchanged ketone from such a mixture after allowing it to stand for thirty minutes in the concentrated acid.

Results

The spectra of the p-dimethylaminochalcones and of their ions are shown in Figs. 1–3.

The spectra of the chalcones (Fig. 1) show two well-defined fairly symmetrical bands, the x- and the y-bands of the substances. The arrows in Fig. 1 indicate the position of the x- and y-bands of (III). Figure 2 shows the spectra of the first ions. The weak bands in the 400 mμ region are due to unneutralized base, so that the spectrum of the first ion of (II) again has two bands, but the absorption curve of the first ion of (I) does not reach a second maximum at wave lengths longer than 230 mμ, the limit of measurements in this particular solvent. The spectra of the second ions (Fig. 3) show x-bands close to 500 mμ, but no estimate of the position of the y-bands can be made since the spectra of the residual first ions predominate at higher frequencies. The spectra of the

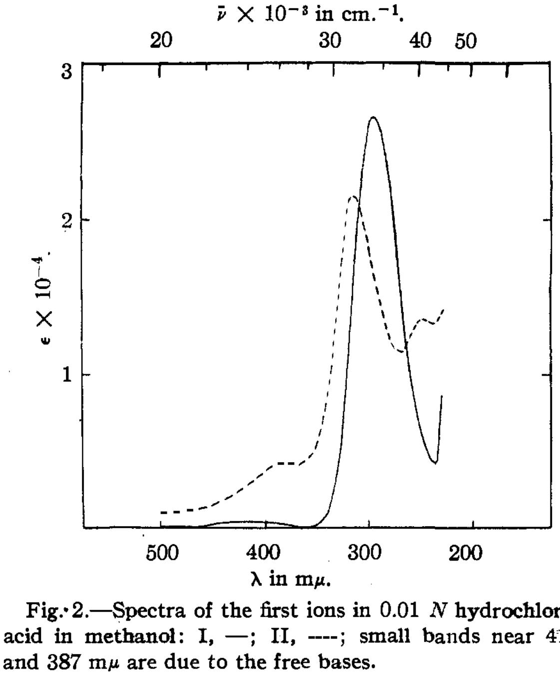

Fig. 2.—Spectra of the first ions in 0.01 N hydrochloric acid in methanol: I, —; II, ----; small bands near 419 and 387 mμ are due to the free bases.

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[2] McLean and Widdows, *J. Chem. Soc.*, **105**, 2173 (1914).

[3] Fecht, *Ber.*, **40**, 3893 (1907).

third ions are also shown in Fig. 3. The first two absorption bands are probably not x- and y-bands, but are partials. In addition both spectra show bands of a complicated structure in the 260-220 mμ region.

The data are summarized in Table I. The positions of the maxima of the two main bands of each substance are listed under the headings λ_1 and λ_2 in the order of decreasing wave length. The corresponding molecular extinction coefficients are shown in the columns headed ϵ_1 and ϵ_2, respectively. Blank spaces in the column headed λ_2 indicate that the position of the second band is indefinite owing to the interference of the spectra of other substances. Extinction coefficients are not given where the extent of neutralization is not known. In the case of the first ion of (II) the data are corrected for incomplete neutralization. This correction was negligible for the first ion of (I). Data for (III), chalcone, and benzophenone are included in the table for comparison.

Table I

Compound	Solvent	λ_1, mμ	$\epsilon_1 \times 10^{-4}$ cm.$^{-1}$	λ_2, mμ	$\epsilon_2 \times 10^{-4}$ cm.$^{-1}$
I[a]	CH_3OH	419	3.3	264	1.8
II[a]	CH_3OH	387	2.6	303	2.0
III[b]	CH_3OH	356	2.7	248	1.6
First ion of I	0.1 N HCl in CH_3OH	294	2.7	<230	...
First ion of II	0.1 N HCl in CH_3OH	315	2.2	248	1.4
Benzophenone[c]	C_2H_5OH	253	1.9	<220	...
Chalcone[d]	C_2H_5OH	313	?	288	?
Second ion of I	$(CH_3CO)_2O$ $+0.4\%$ H_2SO_4	483	...	...	...
Second ion of II	$(CH_3CO)_2O$ $+0.4\%$ H_2SO_4	490	...	...	...
IV	Concd. H_2SO_4	425	3.7	290	0.6
V	Concd. H_2SO_4	396	4.0	319	1.1

[a] These spectra were measured by V. Alexa, *C. A.*, **37**, 3668[4] (1943), but the data were not available for comparison. [b] Unpublished measurements by Dr. B. M. Tolbert. [c] Jones, This Journal, **67**, 2127 (1945). [d] Russel, Todd and Wilson, *J. Chem. Soc.*, 1940 (1934).

Discussion

The Chalcones.—The theory of color advanced by Lewis and Calvin predicts that the absorption maximum of a band will be shifted to the red whenever the conjugate system responsible for the band is extended by a vinyl group. It is apparent that the spectra of (I) and of (II) agree with this theory. The x-band of (I) reaches a maximum at markedly longer wave length than that of (II), but the y-band of (II) is found at longer wave length than that of (I).

A comparison of the spectra of (I) and of (II) with the spectrum of (III) shows that the interpolation of a vinyl group has the expected effect. It greatly increases the wave length of the x-band or the y-band according to whether the vinyl group is interpolated between the carbonyl and the dimethylaniline radicals ((I)) or between the carbonyl radical and the phenyl group ((II)). The value of $\lambda_{xI} - \lambda_{xIII} = 63$ mμ, and $\lambda_{yII} - \lambda_{yIII} = 55$ mμ.

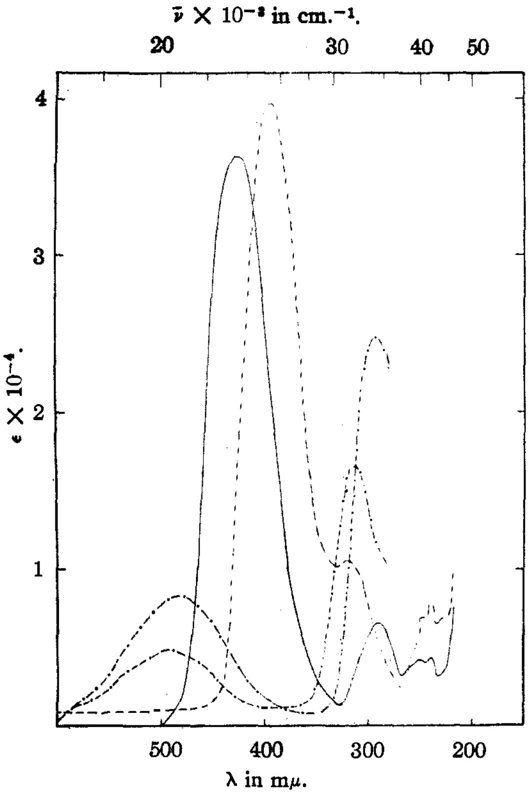


Fig. 3.—Spectra of second and third ions: -·-·-, second ion of I; --·--, second ion of II; ———, third ion of I; ----, third ion of II. The spectra of the second ions were measured in acetic anhydride with 0.4% of sulfuric acid. The bands at 294 and 315 mμ are due to the first ions. The spectra of the third ions were measured in sulfuric acid (d. 1.84 g./ml.).

However λ_{yI} is also greater than λ_{yIII} and λ_{xII} is greater than λ_{xIII}. It is an oversimplification to assume that vibrations along one of the two radicals attached to the carbonyl group contributes only to the x-band and vibrations along the other group contribute only to the y-band. In reality the vibrations along either of these groups have components along both the x- and the y-axes. Hence the interpolation of the vinyl group increases the wave lengths of both x- and y-bands whether it is interpolated as in (I) or as in (II).

The First Ions.—The first ions are formed by the addition of a proton to the amino groups. This destroys the auxochromic power of these groups and the main interaction occurs between the carbonyl group and the more polarizable of the other two radicals. In the case of the ion of (II) this group is indubitably the styryl radical, so that the vinyl group extends the main chain of the ion. In consequence this substance should absorb at much longer wave length than benzophenone. The first strong absorption band of the latter compound is found at 253 mμ as compared to the band at 315 mμ of the ion. It should be noted that the *x*-band of the ion is quite close to the *y*-band of the free base ($\Delta\lambda = 12$ mμ), indicating that the bands are due to essentially the same system.

The first ion of (II) is a *p*-aminium derivative of chalcone. The positive charge of the aminium group should have a hypsochromic effect but it is only of secondary importance in the *x*-band. Hence the *x*-bands of chalcone and of the first ion of (II) should be very similar. Their maxima are at 318 mμ and at 315 mμ, respectively. The hypsochromic action of the aminium group is a more important factor on the wave length of the *y*-band and λ_y of (II) (248 mμ) is markedly less than λ_y of chalcone (288 mμ). This difference is much greater than other examples mentioned later of the hypsochromic effect of the aminium group.

In the ion of (I) the extension of a positive charge into the styryl group is hindered by the positive charge of the aminium group. The two radicals attached to the carbonyl group are therefore more nearly optically equivalent than they are in chalcone. That the styryl radical is still the more polarizable of the two groups can be deduced from the fact that λ_x of (I) (294 mμ) is greater than λ_x of benzophenone (253 mμ). The maximum of the *x*-band should therefore fall between the maxima of the *x*-bands of benzophenone and chalcone.

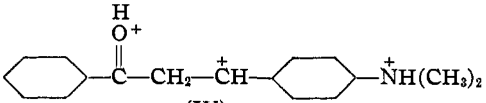
Equalization of the polarizability of the two radicals attached to the carbonyl group puts the *y*-axis perpendicular to the carbonyl group and eliminates this group as a factor in the *y*-band. Hence in benzophenone and to a lesser extent in the first ion of (I), the *y*-bands should be at much shorter wave lengths than those of less symmetrical aromatic ketones. Neither benzophenone nor the first ion of (I) showed the maxima of the *y*-bands in the range of wave lengths measured.

The Second Ions.—The second ion is formed by the addition of acid to the amino group and also to the carbonyl group. The absorption bands of the second ions of (I) and of (II) are very nearly equal. The difference (about 7 mμ) can be attributed to the hypsochromic effect of the aminium group. This is the smallest hypsochromic effect observed.

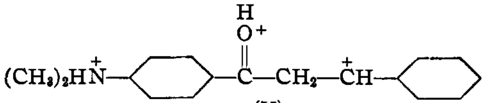
In an unsaturated ketone the derivation of other resonating structures from the classical structure involves a separation of electrical charges. This is generally associated with low λ_{max} values, unless some strong auxochrome in the molecule assists the separation of charge. If a proton is added to the oxygen atom of the ketonic group, the resonating structures are derivable without a separation of charge. Such ions in general have greater values of λ_{max} than the corresponding ketones. This rule is followed in the present case. The second ions have bands at much longer wave lengths than chalcone. The bathochromic effect of a proton on the oxygen atom of the carbonyl group is greater than that of a *p*-dimethylamino radical, as can be seen by a comparison of the spectra of the second ion of (II) and that of the free base (I).

The Third Ions.—An increase of the acidity of the solvent over that at which the second ions are formed, produces a further change in the spectra of (I) and of (II) (Fig. 3). These changes are reversed by decreasing the acidity and are presumably due to neutralization. It is not necessary to state specifically what the acids are that add to the molecule, for as long as the acids do not enter into the resonance, their specific effects on the spectra would be small. We shall use a proton to represent the acid and we shall call the products the third ions of (I) and of (II).

The most likely place for the proton to add is at the aliphatic double bond on the carbon atom next to the carbonyl group. In this way the proton adds without disturbing the benzene resonance and introduces a resonance between a carbonium ion and a phenyl radical. The structures are shown in the formulas below, (IV) being derived from (I) and (V) from (II).



(IV)



(V)

These structures have two chromophores, C_6H_5-$C{=}\overset{+}{O}H$ (often written as $C_6H_5\overset{+}{C}{-}OH$) and $\overset{+}{C}C_6H_5$, insulated from each other by a methylene group. Each of these chromophores should produce an absorption band. These bands are partials rather than *x*- and *y*-bands. In view of the large values of λ_x of the second ions the longer of the two bands has been assigned to the $C_6H_5C{=}\overset{+}{O}H$ chromophore in both cases.

With this assumption the principal band of (IV) should have a longer wave length than that of (V), for in (IV) there is no hypsochromic effect of an aminium group on this band. For exactly the same reason the second band of (V) should have a greater λ_{max} than the corresponding band of (IV). The principal bands of the third ions should reach their maxima at shorter wave lengths than the *x*-bands of the second ions, for the latter bands are chiefly due to similar chromophores extended by a vinyl group.

The Quantitative Effects of the Groups

The spectra discussed above are those of substances that can be derived from benzophenone or from each other by introducing the dimethylamino radical or the dimethylaminium group in the *para* position, by interpolating a vinyl group, or by adding a proton to the carbonyl group. The effects of these four structural changes on the position of the absorption bands have been collected in Table II. In this table $\Delta\lambda$ is the difference between λ_{max} of the band described in the third and fourth columns and λ_{max} of the band described in the first two columns.

TABLE II

Parent compd.	Band	Derived compd.	Band	$\Delta\lambda$ in mμ
Effect of —CH=CH—				
Benzophenone	*x*	Chalcone	*x*	60
p-Dimethylamino-benzophenone (III)	*x*	4-Dimethylamino chalcone (I)	*x*	63
p-Dimethylamino-benzophenone (III)	*y*	4′-Dimethylamino chalcone (II)	*y*	55
Third ion of I	First	Second ion of II	*x*	65
Third ion of II	First	Second ion of I	*x*	87
Effect of $—N(CH_3)_2$				
Chalcone	*x*	I (free base)	*x*	106
Benzophenone	*x*	III	*x*	103
Chalcone	*y*	II	*x*	99
Effect of $—\overset{+}{N}H(CH_3)_2$				
Second ion of II	*x*	Second ion of I	*x*	− 7
Chalcone	*x*	First ion of I	*x*	−19
Chalcone	*y*	First ion of II	*y*	−40
Third ion of I	First	Third ion of II	First	−29
Third ion of II	Second	Third ion of I	Second	−29
Effect of H^+ on $>C=O$				
First ion of II	*x*	Second ion of II	*x*	175
First ion of I	*x*	Second ion of I	*x*	189

Base Strength of the *p*-Dimethylamino-chalcones

The dissociation constants of (I) and of (II) were determined by measuring the spectra of the ketones in methyl alcohol solutions that contained enough hydrochloric acid to about half convert the bases to the first ions. Then, knowing the spectra of the bases and their salts, one can calculate the amount of free base present provided Beer's law is obeyed. Beer's law was shown to hold for both the ketones and their ions over a two fold change of concentration. Since the hydrogen ion concentration is also known one can calculate the equilibrium constant for the reaction

$$\text{ion} = \text{base} + H^+$$

i. e., the dissociation constants of the conjugate acids of (I) and of (II).

The constants were found to be 2×10^{-3} and 2×10^{-2} for the conjugate acids of (I) and of (II), respectively. No attempt was made to correct the constants for the deviation of the activity coefficients from unity. In comparison anilinium ion has a dissociation constant of 1×10^{-6} (corrected value).[4]

Acknowledgments.—We wish to thank Mr. Robert Kallo for his help in the preparation of the chalcones, and Dr. Bert M. Tolbert for the use of his measurement of the spectrum of *p*-dimethylaminobenzophenone.

Summary

The spectra of the free bases, the first ions, the second ions, and the third ions of the two isomeric *p*-dimethylaminochalcones have been measured.

The spectra have been compared with each other and with the spectra of chalcone, *p*-dimethylaminobenzophenone and benzophenone. The relationships between these spectra have been discussed on the basis of the Lewis–Calvin theory of *x*- and *y*-bands, and it is shown that the results confirm this theory.

Bathochromic effects were found for the interpolation of CH=CH, the *p*-dimethylamino group, and the addition of a proton to the oxygen atom of a ketone group. The *p*-dimethylaminium group was found to have a hypsochromic effect.

It was shown that the *p*-dimethylaminochalcones are weaker bases than aniline, and that 4′-dimethylaminochalcone is a weaker base than 4-dimethylaminochalcone.

BERKELEY, CALIFORNIA RECEIVED JANUARY 21, 1947

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[4] Goldschmidt and Aas, *Z. physik. Chem.*, **112**, 444 (1924).