Relations between Electronic Absorption Spectra and Spatial Configurations of Conjugated Systems. X. Benzaldehyde, Acetophenone and Related Compounds

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Benzaldehyde and Acetophenone

In the near ultraviolet absorption spectrum of benzaldehyde as well as that of acetophenone four band systems appear. The weakest band, which appears at about 320 mμ with the molecular extinction coefficient of the order of ten, is regarded as an $n \rightarrow \pi^*$ transition in the carbonyl group (R-band). The weak band with fine structure, which appears in the range between 270 and 290 mμ with the molecular extinction coefficient of about 1000~2000, is considered to correspond to the $A_{1g} \rightarrow B_{2u}$ transition in benzene, and therefore, to the "hidden transition" at about 275 mμ in biphenyl[1] (B-band, or Benzenoid band). The band at about 200 mμ is considered to correspond to the $A_{1g} \rightarrow B_{1u}$ transition in benzene. The strongest band at near 240 mμ, whose molecular extinction coefficient is about 15000, has been interpreted by Tanaka, Nagakura, and Kobayashi[2] as the "intramolecular charge-transfer absorption", which may be considered as the conjugation band (K-band). (The notation of the bands shown in parentheses is according to Gillam and Stern[3]). The present study is mainly concerned with the last "conjugation band".

O'Shaughnessy and Rodebush[4] found formerly that the introduction of two methyl groups into the ortho positions of acetophenone exerts a marked influence on the absorption spectrum, a fact which was explained in terms of the steric effect. Braude and his coworkers[5-8] have stated, on the basis of their classification of steric effects in ultraviolet absorption spectra, that *o*-methylated acetophenones and benzaldehydes show the steric effects of type 1, i. e. the steric effects which give rise to decreases in absorption intensity alone without causing any wavelength displacement of the bands. According to them, the steric effect of this type occurs when steric interaction is relatively weak, i. e. when the steric repulsion energy for the planar conformation is less than 3 kcal./mol., and is produced by "transitions between nonplanar ground states and uniplanar (or near-planar) excited states".

On the basis of the above mentioned view, they have applied their postulated relation between the intensity of the conjugation band and the angle of twist of the "single" bond to

1) H. Suzuki, This Bulletin, 32, 1340 (1959).
2) J. Tanaka, S. Nagakura and M. Kobayashi, *J. Chm. Phys.*, 24, 311 (1956).
3) A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry", 2nd. Ed., Edward Arnold Publishers, Ltd., London (1957), p. 141 and p. 262.
4) M. T.O'Shaughnessy and W. H. Rodebush, *J. Am. Chem. Soc.*, 62, 2906 (1940).
5) E. A. Braude, F. Sondheimer and W. F. Forbes, *Nature*, 173, 117 (1954).
6) E. A. Braude and F. Sondheimer, *J. Chem. Soc.*, 1955, 3754.
7) E. A. Braude and E. S. Waight, "Progress in Stereochemistry", 1, (edited by W. Klyne), Butterworths Scientific Publications, London (1954), p. 144 ff.
8) E. A. Braude, "Determination of Organic Structures by Physical Methods", (edited by E. A. Braude and F. C. Nachod), Academic Press, Inc., Publishers, New York (1955), p. 172 ff.

o-substituted benzaldehydes and acetophenones, and found that in the aldehydes the calculated angle of twist θ (i.e. the interplanar angle between the benzene ring and the carbonyl group) is about 20° in the presence of either the one or the two *o*-methyl groups, and that in the ketones the calculated interplanar angle is about 35° in the presence of the one, and about 60° in the presence of the two, *o*-methyl groups. In the calculations, they have taken the parent compounds, benzaldehyde and acetophenone, as the planar reference compounds for the corresponding derivatives. That is, they have assumed that there is no significant steric hindrance to the coplanarity of the molecular configuration with acetophenone as well as benzaldehyde. This assumption would be considered to be supported by the fact that, according to Braude and others, both the compounds exhibit their conjugation bands at almost the same wavelength (242 mμ, in hexane).

On the other hand, as will be shown in the succeeding part of this series, α-methylstyrene exhibits the conjugation band at an appreciably shorter wavelength than its parent compound, styrene. That is, it may be said that the α-methyl group in this system exerts the "steric effect of type 2" defined by Braude and others, i.e. the steric effect which causes not only a decrease in the intensity of the conjugation band but also a hypsochromic wavelength displacement of the band. Thus, the most probable configuration of α-methylstyrene is inferred to be nonplanar. While the geometry of the relevant part of benzaldehyde is considered to be similar to that of styrene, that of acetophenone is considered to be similar to that of α-methylstyrene. Accordingly, it is expected that the steric effects in acetophenone and in α-methylstyrene are likely to be very similar. That is, it is presumed, contrary to the opinion of Braude and others, that there should be appreciable steric interaction between the methyl group and the phenyl group in the planar conformation of acetophenone, and that, consequently, the most probable configuration of the molecule is not planar. According to Auwers and Eisenlohr[9], the value of the exaltation of molecular refraction, EM_D, for acetophenone (+0.52) is considerably smaller than the value for benzaldehyde (+0.80). This fact may be considered to indicate that acetophenone is less conjugated than benzaldehyde, and therefore, to support the above mentioned view.

It may be somewhat doubtful whether a deviation from the coplanar configuration results in a hypsochromic displacement of the "conjugation band" also in the present conjugated system, because the system containing a hetero-atom O is not quite analogous to the hydrocarbon conjugated systems (termed "normal") treated in the preceding parts of this series. Therefore, it seems to be necessary to make some comment on this point.

According to Nagakura and Tanaka[10], in the conjugated system C_6H_5–C=O the interaction between the lowest vacant orbtial of the carbonyl group (V_S) and the highest occupied orbital of benzene (H_B) is predominant, and to a first approximation the intense absorption bands in the wavelength region 230~260 mμ are regarded as due to the transition between the two new orbitals W_n and W_e which occur by the interaction between V_S and H_B. The new highest occupied orbital W_n is lower than H_B, and the new lowest vacant orbital W_e is higher than V_S. The energy separation between W_e and W_n will become greater when the interaction between V_S and H_B becomes greater. Accordingly, from this theory, it might be expected that a twist of the "single" bond between the phenyl group and the carbonyl group from the coplanar position would cause a bathochromic shift of the absorption band rather than a hypsochromic shift.

This surmise seems, however, to be denied by the fact that the absorption band maxima of 2-methylbenzaldehyde and of 2-methylacetophenone are at considerably shorter wavelengths than the corresponding 4-isomers. Especially, it is notable that the absorption maximum of 2-methylbenzaldehyde is at a shorter wavelength even than that of the 3-isomer. Thus, according to Braude and Sondheimer[6], the wavelengths (in mμ) of the absorption maxima of these compounds are as follows (figures in parentheses represent the molecular extinction coefficients): 4-methylbenzaldehyde, 251(15000) and 257 (12500); 3-methylbenzaldehyde, 245(13500) and 251(12000); 2-methylbenzaldehyde, 243(12500) and 251(13000); 4-methylacetophenone, 252 (15100); 2-methylacetophenone, 242(8700) and 245(8300). Since the electronic effect of an ortho-methyl group may be said to be approximately equivalent to that of a para-methyl group, it may be quite reasonable to consider the hypsochromic displacements observed above as mainly due to the steric effect of the ortho-methyl groups. Accordingly, it may be said that a deviation of the most probable conffiguration from the coplanarity causes a hypsochromic displacement of the "conjugation band" in the case of the conjugated system C_6H_5–C=O, just as in the cases of the normal conjugated systems. Therefore, from the foregoing consideration it may be expected that the conjugation band of acetophenone will be at a

9) K. v. Auwers and F. Eisenlohr, *Ber.*, **43**, 806 (1910).

10) S. Nagakura and J. Tanaka, *J. Chem. Phys.*, **22**, 236 (1954).

TABLE I. ABSORPTION MAXIMA OF BENZALDEHYDE, ACETOPHENONE AND BENZOPHENONE

Compound	Solvent	"Benzenoid band"		"Conjugation band"		Ref.
		λ, mμ	ε	λ, mμ	ε	
Benzaldehyde	Hp	288.9	890	248.1	8600	*a*
		280.6	1410	(240.5)	13400	
		273.8	1520	236.9	14100	
			[C-band :	(204.8)	18900]	
	Hx	289	1200	248	12500	5-8
		280	1400	242	14000	
	E	280	1500	244	15000	3
Acetophenone	Hp	286.2	1180	(245.5)	9690	*a*
		278.3	1480	238.5	13130	
		275.2	1460			
		271.4	1440			
	Hp	279	890	238	12600	2
	Hx			242	13000	5,7,8
	E	278	1000	242	11750	2
	E	279	1200	243	13200	6
	E	278	1100	240	13000	3
Benzophenone	Hp	[(286)]	1550	248.5	19550	*a*
		[(277)]	2540			

Solvent: Hp, *n*-heptane; Hx, hexane; E, ethanol. Wavelengths in parentheses denote inflections, and those in double parentheses denote very indistinct inflections. Ref. *a*, the present work.

shorter wavelength than that of benzaldehyde. In this connection, it may be of some interest that in the case of the conjugated system C_6H_5–C=N the "conjugation band" maximum of the acetophenone analogue is at a considerably shorter wavelength than the corresponding one of the benzaldehyde analogue. Thus, according to Braude and Sondheimer[6], the wavelengths of the absorption maxima of the semicarbazones of benzaldehyde and of acetophenone are 281 mμ (22000) and 270 mμ (20400), respectively.

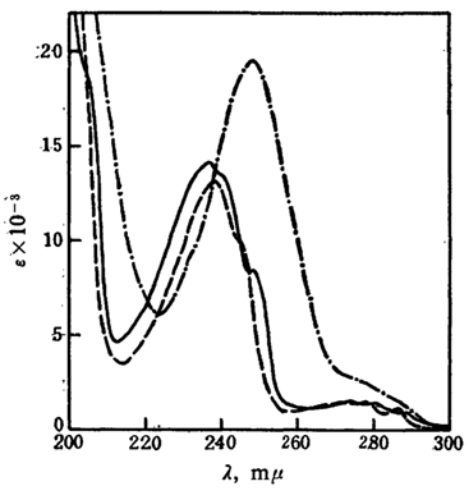

Fig. 1. Ultraviolet absorption spectra (in *n*-heptane): ——, benzaldehyde; ----, acetophenone; -·-·, benzophenone.

From this point of view, to re-examine the steric effect in acetophenone itself, the ultraviolet absorption spectra of acetophenone and of benzaldehyde in solutions in *n*-heptane have newly been measured. The results are shown in Fig. 1. In Table I, the data of the absorption maxima are summarized together with those found in the literature.

The conjugation bands of these compounds are not structureless, but have, though considerably diffuse, fine structures. The inflection at 245.5 mμ in the spectrum of acetophenone is at a shorter wavelength than the probably corresponding maximum at 248.1 mμ in the spectrum of benzaldehyde, in accordance with the expectation. On the other hand, the maximum at 238.5 mμ in the spectrum of acetophenone appears to correspond to the two bands at 240.5 and 236.9 mμ in the spectrum of benzaldehyde. Therefore, it seems somewhat doubtful which of the two bands of benzaldehyde is to be compared with the band of acetophenone.

p-Biphenylyl and 2-Fluorenyl Carbonyl Compounds

The author prepared *p*-phenylbenzaldehyde and *p*-phenylacetophenone as intermediates in the syntheses of *p*,*p*'-diphenylstilbene and its α,α'-dimethyl derivative, as described in the preceding part[11] of this series. In addition,

11) H. Suzuki, This Bulletin, 33, 410 (1960).

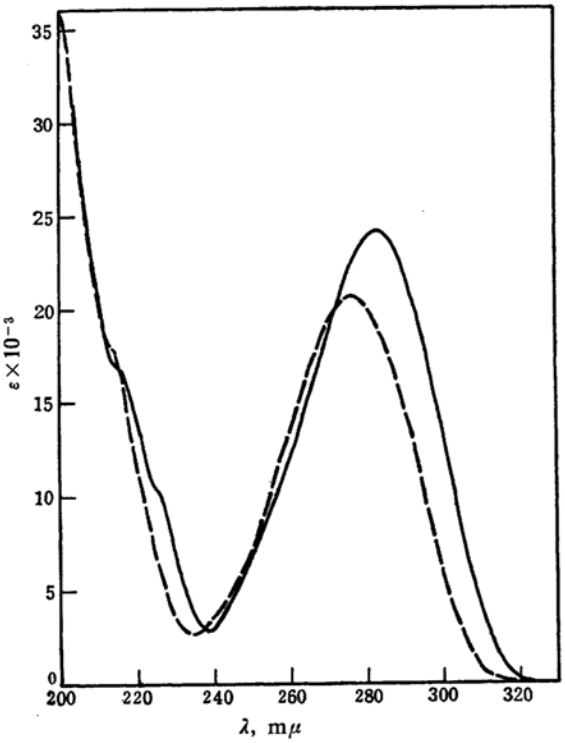

Fig. 2. Ultraviolet absorption spectra (in *n*-heptane): ——, *p*-phenylbenzaldehyde; ----, *p*-phenylacetophenone.

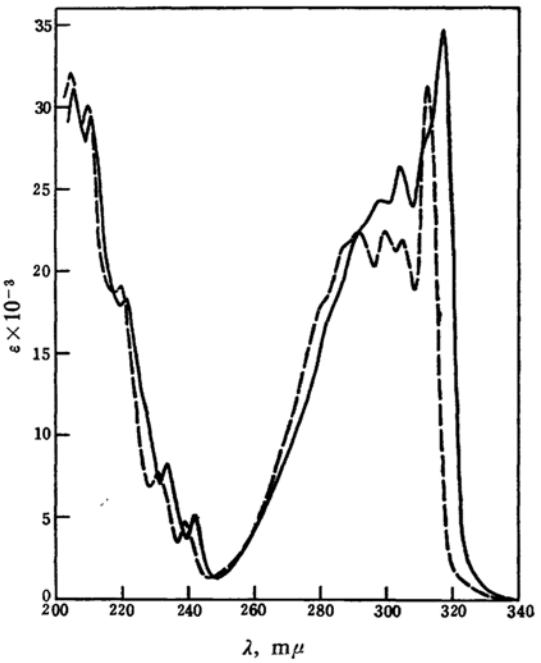

Fig. 3. Ultraviolet absorption spectra (in *n*-heptane): ——, 2-formylfluorene; ----, 2-acetylfluorene.

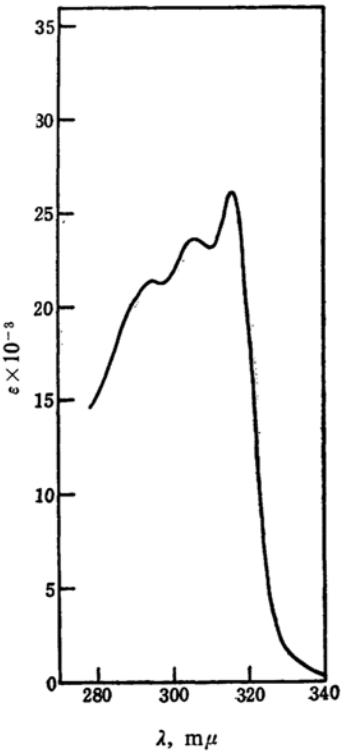

Fig. 4. Ultraviolet absorption spectrum of 2-acetylfluorene in benzene.

2-acetylfluorene and a compound which is considered to be probably 2-formylfluorene were prepared in attempts to prepare 1, 2-di-(2-fluorenyl)-ethylene and its 1, 2-dimethyl derivative. The absorption spectra of these analogues of benzaldehyde and of acetophenone seem to be of interest in connection with the above considerations. The spectra are shown in Figs. 2—4. In Table II, the data of the absorption maxima are summarized.

In the spectra of these compounds, the possible bands corresponding to the bands of benzaldehyde and of acetophenone in the range between 270 and 290 mμ are completely hidden by the intense conjugation bands. The bands appearing in the range between near 215 mμ and near 240 mμ are considered to be probably the ones due to transitions from the highest occupied orbital to the vacant orbitals localized in benzene rings whose energy is $-\beta$, or from the occupied orbitals localized in benzene rings whose energy is $+\beta$ to the lowest vacant orbital, analogously to the bands of stilbene and related compounds appearing in almost the same range[12,13]. It may be noteworthy that the bands at 200~210 mμ have about double the intensity of the corresponding band of benzaldehyde, in conformity

12) H. Suzuki, ibid., 33, 379 (1960).
13) H. Suzuki, ibid., 33, 389 (1960).

TABLE II. ABSORPTION MAXIMA OF *p*-BIPHENYLYL AND 2-FLUORENYL CARBONYL COMPOUNDS

Compound	Solvent	A-band		B-band		C-band	
		λ, mμ	ε	λ, mμ	ε	λ, mμ	ε
p-phenylbenzaldehyde	Hp	283.5	24150	[(226)]	10100		
				(215.5)	16900		
p-Phenylacetophenone	Hp	276.2	20650	(214.5)	17750	200.0	35700
2-Formylfluorene	Hp	317.2	34600	242.3	5050	210.5	29400
		(312.2)	28200	234.0	8220	205.2	31100
		304.4	26300	221.2	18320		
		297.7	24200				
		(293.5)	22900				
		[(285)]	18400				
2-Acetylfluorene	Hp	312.8	31200	239.3	4730	209.7	30500
		305.1	21850	231.1	7730	204.5	32000
		299.7	22400	219.8	19100		
		291.8	22450				
		(287.2)	21450				
		(280.9)	18050				
	B	315.8	26100				
		305.3	23650				
		294.8	21350				
		[(289.5)]	20200				

The notation of the bands is quite analogous to the one in the case of stilbenes in Part V of this series: A-band refers to the conjugation band. Solvent: Hp, *n*-heptane; B, benzene. Wavelengths in parentheses denote inflections, and those in double parentheses denote very indistinct inflections.

with the number of benzene rings in a molecule.

The conjugation band of *p*-phenylacetophenone is at an appreciably shorter wavelength than that of *p*-phenylbenzaldehyde, both the bands being structureless, (cf. Fig. 2). The conjugation bands of the two fluorenyl compounds have fine structures. Also with these compounds, the bands of the acetophenone analogue are at shorter wavelengths than the probably corresponding bands of the benzaldehyde analogue (cf. Fig. 3). These hypsochromic shifts of the conjugation bands observed in the comparison of the acetophenone analogues with the corresponding benzaldehyde analogues are considered to be mainly due to the steric effect of the methyl groups. This means that in these acetophenone analogues there exist steric interactions between the methyl groups and the benzene rings which cause the hypsochromic wavelength displacements of the conjugation bands relative to the conjugation bands of the corresponding benzaldehyde analogues, and that, consequently, the most probable configurations of these acetophenones are nonplanar.

By analogy with these facts, it may be inferred that the most probable configuration of acetophenone itself is nonplanar. Probably, the fact that the introduction of a methyl group at the carbonyl carbon atom of benzaldehyde to give acetophenone does not result in any appreciable hypsochromic wavelength displacement of the conjugation band is merely apparent. Further, this fact should not be considered to indicate the absence of the steric interference in acetophenone or the absence of the hypsochromic shift arising from the steric effect. It seems more reasonable to consider that the hypsochromic shift caused by the steric effect is so small that it is compensated by the electronic bathochromic effect of the methyl group. Accordingly, also the apparent absence of hypsochromic shift in *o*-methylated acetophenones, e. g. 2-methylacetophenone and 2, 4, 6-trimethylacetophenone, as compared with acetophenone should probably be interpreted similarly. From this point of view, not only the application of the hypothesis of Braude and others to the acetophenone derivatives but also their classification of steric effects in ultraviolet absorption spectra or their basic theory itself seems to be criticizable. This subject will be discussed more fully in the succeeding part of this series.

It remains to refer to the spectrum of 2-acetylfluorene in benzene shown in Fig. 4. It is of interest that this spectrum differs considerably from the spectrum in *n*-heptane. Thus, when

the solvent is changed from *n*-heptane to benzene, the first (from longer wavelengths side) maximum of fine structure of the conjugation band is reduced markedly in the intensity, and further, the second and the third maxima appear to merge into a maximum. Also with this compound, analogously to the cases of stilbene and related compounds discussed in earlier parts[11-13] of this series, considerably large red-shifts (about 3 mμ) associated with the change of solvent are observed.

Benzophenone

Lastly, the spectrum of benzophenone, which is shown in Fig. 1 and in Table I, is briefly discussed. It is evident that the two benzene rings in benzophenone can not be simultaneously coplanar with the plane of the carbonyl bond owing to the steric necessities. This situation is very similar to that in the case of 1, 1-diphenylethylene which will be treated in the succeeding part of this series. However, in contrast to the fact that 1, 1-diphenylethylene shows the conjugation band at almost the same position as the conjugation band of styrene, the conjugation band of benzophenone, which is structureless, has the maximum at an appreciably longer wavelength than that of benzaldehyde. This situation is rather similar to that observed in the comparison of the spectrum of tetraphenylethylene with that of *trans*-stilbene, the maximum of the former being at a longer wavelength than that of the latter[13]. Thus, it may be considered that the angle through which each benzene ring in benzophenone is rotated out of the plane of the carbonyl bond is not so large as the corresponding angle in 1, 1-diphenylethylene. However, it can not be asserted so, because the maximum of the conjugation band of benzophenone may be compared, alternatively, with the minor maximum of fine structure of the conjugation band of benzaldehyde at almost the same wavelength (i. e. at 248.1 mμ).

Experimental

All the spectra were measured with a Cary recording spectrophotometer Model 14 M-50.

The specimens of benzaldehyde and of acetophenone were obtained by distillation of commercial products under reduced pressure.

Benzophenone was prepared by the method described in Organic Syntheses[14]; colorless prisms melting at 48~48.5°C.

p-Phenylbenzaldehyde was prepared by the method described in Organic Reactions[15]. From 150 g. of biphenyl, 124 g. of the purified product was obtained after treatment with activated charcoal and repeated recrystallization from petroleum ether (b. p. 80~100°C); colorless thin plates melting at 60~61°C. About 5 g. of biphenyl was recovered.

p-Phenylacetophenone was prepared by the method described by Long and Henze[16]. From 77.1 g. of biphenyl, 87.4 g. of the purified product was obtained (89% of the theoretical amount); colorless crystals melting at 119~121.5°C.

2-Formylfluorene was prepared almost analogously to the preparation of *p*-phenylbenzaldehyde. Thus, a stream of dry carbon monoxide and hydrogen chloride was passed for about 4.5 hr. into a well-stirred solution of 42 g. of fluorene in 200 ml. of dry benzene containing 59 g. of anhydrous aluminum chloride and 11 g. of cuprous chloride at 35~40°C. The dark-colored reaction mixture was poured into a mixture of ice and small quantities of concentrated hydrochloric acid. The violet-colored mixture was extracted with benzene. The benzene solution was concentrated to about 300 ml. by evaporation, and the solution was shaken with an excess of a saturated solution of sodium bisulfite and small quantities of ethanol. The brown bisulfite compound was collected, washed repeatedly with ethanol and then with ether, and warmed with aqueous sodium carbonate. The aldehyde was then collected, dried on a porous plate, and crystallized twice from petroleum ether. The yield of faint yellow needles melting at 85.5~86.5°C was 6.3 g. It might be somewhat doubtful whether this product is the desired compound, 2-formylfluorene, because, according to Rodd[17], treatment of fluorene with ethyl formate and potassium ethoxide gives 9-formylfluorene which sinters at about 70°C and melts at about 90°C. However, the ultraviolet absorption spectrum of this product is considered to have revealed that this product is not 9-formylfluorene, but probably 2-formylfluorene.

2-Acetylfluorene was prepared by the method described in Organic Syntheses[18]. From 40 g. of fluorene, 24.4 g. of the product was obtained after purification by treatment with activated charcoal and by twofold recrystallization from ethanol (48.9% of the theoretical amount); colorless crystals melting at 127.5~128°C.

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15) R. Adams (Editor-in-Chief) "Organic Reactions", Vol. V, John Wiley & Sons, Inc., New York (1949), p. 298.
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