[Contribution from the Department of Chemistry, Fordham University, and the Memorial University of Newfoundland]

Steric Interactions in the Absorption Spectra of 2,2'-Diaroylbiphenyls. II.[1] 6,6'-Dinitro-2,2'-diaroylbiphenyls

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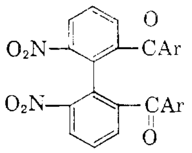
Received February 6, 1959

The ultraviolet absorption spectra of a number of 6,6'-dinitro-2,2'-diaroylbiphenyls in which the 2,2'-diaroyl substituents vary in bulk and electronic effects (aroyl = benzoyl, 4-methylbenzoyl, 2,4-dimethylbenzoyl, 2,4,6-trimethylbenzoyl, 2,5-dimethylbenzoyl, 2,3,5,6-tetramethylbenzoyl, 2,3,4,5,6-pentamethylbenzoyl and 4-methoxybenzoyl) are described in terms of the hypotheses postulated to account for the electronic spectra of 2,2'-diaroylbiphenyls. By comparison with a series of *m*-substituted nitrobenzenes, it is found, as predicted, that the 6,6'-dinitro-2,2'-diaroylbiphenyls absorb approximately as simple *m*-substituted nitrobenzenes.

Introduction

As intermediates in the synthesis of a series of *cis*-4,5-dinitro-9,10-diaryl-9,10-dihydrophenanthrenediols,[3] a number of 6,6'-dinitro-2,2'-diaroylbiphenyls have been prepared in which the 2,2'-diaroyl substituents vary in bulk and electronic effects.



I, Ar = phenyl
IV, Ar = 4-methylphenyl
V, Ar = 2,4-dimethylphenyl
VI, Ar = 2,4,6-trimethylphenyl
VII, Ar = 2,5-dimethylphenyl
VIII, Ar = 2,3,5,6-tetramethylphenyl
IX, Ar = 2,3,4,5,6-pentamethylphenyl
X, Ar = 4-methoxyphenyl

In Part I[1] of this series it was shown that the electronic absorption spectra of 2,2'-diaroylbiphenyls are consistent with the interpretation that the molecule does not absorb as *one* conjugated system; instead the absorptions of the partial chromophoric systems could be identified. The reason suggested for such absorption as so many chromophores was the operation of steric interactions which force the molecule into non-planar conformations. If this analysis is correct it follows that 6,6'-dinitro-2,2'-diaroylbiphenyls should also absorb as partial chromophoric systems.

Experimental[4]

Infrared Absorption Spectra.—Carbonyl absorption measurements were made by Dr. Lester P. Kuhn at the Ballistics Research Laboratory, Aberdeen Proving Ground, Md., with a Perkin-Elmer model 12B spectrometer equipped with LiF optics; concn., 10–15 mg./ml., cell thickness, 0.15 mm., $CHCl_3$ solvent.

Ultraviolet Absorption Spectra.—Ultraviolet absorption measurements were made in a Beckman quartz spectrophotometer model DU or in a Unicam spectrophotometer model SP 500 using 1-cm. quartz cells. Both λ_{max} and ϵ_{max} values, as determined by these two instruments, agreed to within ±1%. The recorded data are those obtained by the SP 500, in order to facilitate comparison with previous data.[5,6] Most of the compounds were only very slightly soluble in cyclohexane, hexane or ethanol and it was usually necessary to shake the solutions for periods of up to 24 hours in order to effect complete dissolution. For some of the compounds solvent mixtures had to be employed to effect dissolution. The spectral data are listed in Tables II, III and IV.

6,6'-Dinitro-2,2'-diaroylbiphenyls (I, IV–X).—The appropriate diketones (I, IV–X) were obtained directly by a Friedel–Crafts aroylation of benzene, *p*-toluene, *m*-xylene, mesitylene, *p*-xylene, durene, pentamethylbenzene and anisole, with 6,6'-dinitrodiphenoyl chloride (III) to afford, respectively, I, IV, V, VI, VII, VIII, IX and X. Reaction conditions, physical and analytical data are summarized in Table I. Compounds I, and IV–X are insoluble in boiling alcohol and easily recrystallized from acetone. Thus, the crude 6,6'-dinitro-2,2'-diaroylbiphenyls were digested with 20–50 ml. of ethanol which on boiling dissolved most of the undesired by-products of the Friedel–Crafts reaction. After suction filtration the residue was dissolved in the minimum of acetone, charcoaled, gravity filtered and allowed to crystallize. Several such recrystallizations invariably gave analytically pure diketone.

Results and Discussion

The main maxima of the ultraviolet absorption spectra in ethanolic solution are listed in Table II, together with the infrared carbonyl stretching frequencies in chloroform solution. Similar maxima of both monosubstituted (acetophenones, benzophenone and nitrobenzene) and disubstituted (*m*-nitrobenzaldehyde, *m*-nitroacetophenone, *m*-nitrobenzophenone and *m*-dinitrobenzene) benzenoid reference compounds are listed in Table III. It should be noted that in all the *m*-disubstituted compounds listed in Table III, both substituents (one of which is a nitro group) are electron-withdrawing.

Before assigning the bands of compounds I to X, we may consider the general factors which determine the electronic spectrum (B-bands) of an *m*-disubstituted benzene derivative. These are: (i) The occurrence of two main absorption bands in the spectra of a number of *m*-disubstituted benzene derivatives, such as *m*-nitrobenzaldehyde, *m*-nitroacetophenone and *m*-nitrobenzophenone (see Table III and *cf.* refs. 5,6,8), is explained by assuming that in the absence of direct mesomeric interaction two distinct B-bands[7] may be obtained

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(1) Part I, W. F. Forbes, F. T. Wallenberger, W. F. O'Connor and E. J. Moriconi, *J. Org. Chem.*, **23**, 224 (1958).

(2) Memorial University of Newfoundland, St. John's, Newfoundland, Can.

(3) These can be considered as 2,2'-two-carbon-atom bridged biphenyls whose non-planarity is ensured by the 6,6'-nitro groups. See D. C. Iffland and H. Siegel [This Journal, **80**, 1947 (1958)] and L. V. Dvorken, R. B. Smyth and K. Mislow [*ibid.*, **80**, 486 (1958)] for the asymmetry and its optical consequences of, respectively, three- and four-carbon-atom bridged biphenyls, devoid of 6,6'-substituents.

(4) All melting points are uncorrected. Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

(5) W. F. Forbes, *Can. J. Chem.*, **36**, 1350 (1958).

(6) J. C. Dearden and W. F. Forbes, *ibid.*, **36**, 1362 (1958).

(7) Band assignments correspond to those previously used in this series[1] and elsewhere.[5,6] The B-band thus described corresponds to

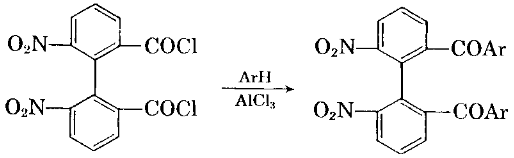
corresponding to the two monosubstituted benzene derivatives. This explanation implies that the electrons undergoing transitions are, in the initial state, highly localized in the substituents. The explanation accounts for the occurence of only *one* such band in compounds like *m*-dinitrobenzene, where the two substituents are identical, and for the occurrence of only one such band in *p*-disubstituted benzene derivatives where direct resonance interaction is possible between the two substituents.

(ii) An indirect electronic effect of one substituent on the other is expected. In the absence of direct resonance interaction, an electron-withdrawing substituent, apart from affecting the wave length of maximal absorption (*cf.* refs. 5, 9), will normally decrease the electron availability in the molecule and in this way apparently reduce the force constant of twist about the bond linking the other substituent to the benzene nucleus. This phenomenon has been discussed and illustrated by examples in a previous paper,[10] where it was shown that the effect can explain the observed *increased* absorption intensity in compounds of that type. In the same way, the greatly increased absorption intensity of *m*-dinitrobenzene compared with that of nitrobenzene (see Table III) may be explained.

This rationalization now also supports the band assignments for some of the compounds listed in Tables III and IV. Thus the high intensity B-band in compounds like *m*-nitrobenzaldehyde, *m*-nitroacetophenone and *m*-nitrobenzoic acid is ascribed to benzoyl absorption because this explains satisfactorily the observed spectral changes. For example, the characteristic hypsochromic wave length displacement is observed on substituting a carboxyl for an acetyl group, and only the band associated with nitrobenzene absorption is appreciably displaced on changing the solvent from cyclohexane to ethanol. Further, since the electron-withdrawing ability of the nitro group is greater than that of the acetyl or carboxyl group, one would expect the less intense bands in *m*-nitroacetophenone, *m*-nitrobenzaldehyde and *m*-nitrobenzoic acid to correspond to nitrobenzene absorption. This empirical guide, however, proves inadequate for assigning the bands in *m*-nitrobenzophenone where the intensities of the two bands are similar and where, in fact, the slightly *more* intense B-band is tentatively assigned to nitrobenzene absorption (see Table III). This conclusion is based on the following reasoning: Benzophenone, compared with acetophenone affords a bathochromic wave length displacement accompanied by a marked intensity increase. Hence replacement of the $-CH_3$ group by the –Ph group apparently facilitates the benzoyl absorption, probably in a similar way in which the nitro group facilitates this same benzoyl absorption, and in this manner the replacement probably also causes the

Table I

6,6′-Dinitro-2,2′-diaroylbiphenyls



III

6,6′-Dinitro-2,2′-diaroylbiphenyls, Ar =	Mole ratio III/AlCl₃/ArH	Solvent	Reaction Color of complex	Time, hr.[a]	Yield, %	M.p., °C.	Empirical formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
C_6H_5 (I)	0.006/0.018/0.282	Benzene[b]	Light brown	12	81	235–237	$C_{26}H_{16}N_2O_6$	69.02	69.15	3.56	3.61
4-$(CH_3)C_6H_4$ (IV)	0.025/0.075/0.708	Toluene[b]	Light brown	8	84	255–257	$C_{28}H_{20}N_2O_6$	69.99	69.87	4.20	4.09
2,4-$(CH_3)_2C_6H_3$ (V)	0.006/0.018/0.203	*m*-Xylene[b]	Brown	12	72	216–218	$C_{30}H_{24}N_2O_6$	70.85	70.90	4.75	4.75
2,4,6-$(CH_3)_3C_6H_2$ (VI)	0.006/0.018/0.179	Mesitylene[b]	Dark brown	8	72	278–280	$C_{32}H_{28}N_2O_6$	71.63	71.75	5.26	5.49
2,5-$(CH_3)_2C_6H_3$ (VII)	0.006/0.018/0.203	*p*-Xylene[b]	Brown	12	75	189–191	$C_{30}H_{24}N_2O_6$	70.85	71.06	4.75	4.97
2,3,5,6-$(CH_3)_4C_6H$ (VIII)	0.003/0.009/0.013	Carbon disulfide	Red-brown	12	59	>325[c]	$C_{34}H_{32}N_2O_6$	72.32	72.43	5.71	5.94
2,3,4,5,6-$(CH_3)_5C_6$ (IX)	0.006/0.018/0.026	Carbon disulfide	Red	48	20	>325[c]	$C_{36}H_{36}N_2O_6$	72.95	73.00	6.12	6.26
4-$(OCH_3)C_6H_4$ (X)	0.006/0.018/0.229	Anisole[b]	Yellow	8	78	230–233	$C_{28}H_{20}N_2O_8$	65.62	65.89	3.92	4.11

[a] All reactions were mechanically stirred. [b] Both solvent and reactant. [c] With decomposition.

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the "first primary band" as described by Doub and Vandenbelt, to the "C-band" of Klevens and Platt, and to the "K-band" as described by Braude and Burawoy. It is planned to discuss this problem of band nomenclature at the forthcoming spectroscopy symposium sponsored by the ASTM at San Francisco in October, 1959.

(8) W. F. Forbes and I. R. Leckie, *Can. J. Chem.*, **36**, 1371 (1958).

(9) W. F. Forbes and A. S. Ralph, *ibid.*, **36**, 869 (1958).

(10) W. F. Forbes and J. F. Templeton, *ibid.*, **36**, 180 (1958).

TABLE II

ABSORPTION SPECTRA OF 6,6'-DINITRO-2,2'-DIAROYLBIPHENYLS

Values in italics represent inflections in this and subsequent tables

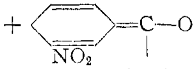
6,6'-Dinitro-2,2'-diaroylbiphenyls, Ar =	Ultraviolet bands[7] (ethanol)				Infrared carbonyl band	
	Nitrobenzene B-band		Second B-band		ν_{max}, CHCl$_3$, cm.$^{-1}$	
	λ_{max}, mμ	ϵ_{max}	λ_{max}, mμ	ϵ_{max}		
C_6H_5 (I)			248	48,000		1675
[OH (II)	*ca. 260*	*10,500*	223	32,500	Too insoluble	]
[Cl (III)	*ca. 255*	*9,500*[a]	235	23,000[a]	1768	1728]
4-$(CH_3)C_6H_4$ (IV)	*ca. 240*	*34,500*	261	37,000[b]	1713[c]	1669
2,4-$(CH_3)_2C_6H_3$ (V)	*ca. 260*	*30,000*	*ca.* 231	37,000		1671
2,4,6-$(CH_3)_3C_6H_2$ (VI)			244	35,000	1709	
2,5-$(CH_3)_2C_6H_3$ (VII)	*ca. 260–265*	Very faint infl.	235	38,000	1704	
2,3,5,6-$(CH_3)_4C_6H$ (VIII)			245	30,000[d]	1716	1681
2,3,4,5,6-$(CH_3)_5C_6$ (IX)			*ca.* 245	42,000[d]	1715[c]	1680
4-$(OCH_3)C_6H_4$ (X)	229	32,000[d]	290	32,500[d]		1664

[a] In cyclohexane solution. [b] In 10% chloroform solution or in ethanol solution. [c] Very weak. [d] In 10% chloroform solution.

TABLE III

ULTRAVIOLET ABSORPTION SPECTRA (MAIN MAXIMA) OF META-SUBSTITUTED NITROBENZENES AND REFERENCE COMPOUNDS

Compound	Solvent	Nitrobenzene B-band[7]		Second B-band[7]	
		λ_{max}, mμ	ϵ_{max}	λ_{max}, mμ	ϵ_{max}
Acetophenone[a]	Cyclohexane	...	....	237–238	12,500
Acetophenone[a]	Ethanol	...	....	240	12,500
Nitrobenzene[a]	Cyclohexane	252	9,000	...	....
Nitrobenzene[a]	Ethanol	257–258	8,000	...	....
m-Nitroacetophenone[a]	Cyclohexane	*254*	*7,000*	224	23,000
m-Nitroacetophenone[a]	Ethanol	*ca. 260*	*6,500*	226	22,500
m-Nitrobenzaldehyde[a]	Cyclohexane	*ca. 245*	*8,000*	225	26,000
m-Nitrobenzaldehyde	Ethanol	*ca.* 256	7,700	225–226	13,000[b]
m-Dinitrobenzene	Cyclohexane	228	21,000	...	....
Benzophenone	Cyclohexane	...	....	248	20,000
Benzophenone	Ethanol	...	....	249	18,500
m-Nitrobenzophenone	Cyclohexane	229	24,000[c]	*ca.* 246	19,500
m-Nitrobenzophenone	Ethanol	232	*21,000*[c]	*ca.* 248	19,000
6,6'-Dinitro-2,2'-dibenzoylbiphenyl (I)	Cyclohexane	...	....	245	40,000
6,6'-Dinitro-2,2'-dibenzoylbiphenyl (I)	Ethanol	...	....	248	48,000

[a] Data from ref. 8 and previous parts of that series. [b] Intensity values were determined as quickly as possible; no evidence for hemiacetal formation could be observed under those conditions. [c] This band is not too well defined. It is possible that transitions which may be associated with excited states of type +  contribute to this absorption (*cf.* 15). However, this seems improbable because *o*-nitrobenzophenone absorbs maximally near 260 mμ (H. H. Szmant and C. M. Harmuth, THIS JOURNAL, **81**, 962 (1959)), and if the absorption band were caused by this absorption the two benzoyl bands in the *ortho* and *meta* isomers would be expected to absorb either at similar wave length or the *ortho* isomer would be expected to absorb at shorter wave length. We intend to return to this discussion in a separate communication.

increased intensity of the nitrobenzene B-band and its location close to the B-band of *m*-dinitrobenzene (see Table III and *cf.* also discussion of compound X). As expected, the second B-band, which is assigned to the benzoyl chromophore, occurs at a similar maximal wave length in benzophenone and in a number of other benzophenones, such as *p*-methoxybenzophenone, where one ring remains unsubstituted.[11]

(iii) In more fully substituted *m*-substituted benzene derivatives various steric effects may operate such as direct steric interactions, steric interactions inhibiting resonance and buttressing effects.[12] These steric effects may account for the considerably reduced nitrobenzene absorption intensity in compound I, where it can no longer be detected, compared with the nitrobenzene absorption in *m*-nitrobenzophenone (see Table III and discussion of compound I).

(iv) The symmetry of the absorption bands may be affected by the second substituent either because of different electronic interactions in the *s-cis* or *s-trans* isomers, or because of steric interactions in one or both of these isomers.

I.—Compound I shows one, almost structureless, band in the 220–290 mμ region. This single B-band may *either* be ascribed to nitrobenzene absorption *or* to acetophenone, or rather benzophenone absorption. It is found that assigning the band to benzophenone absorption proves to be more satisfactory. Compound I, in fact, absorbs

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(11) Alternatively, it may be assumed that in the benzophenone system the second phenyl group *decreases* the resonance interaction in the benzoyl chromophore and that benzophenone and *m*-nitrobenzophenone absorb as one cross-conjugated system which has its own characteristic absorption band near 248 mμ. However, this hypothesis is not favored because of the known non-planarity of the benzophenone molecule (R. N. Jones, THIS JOURNAL, **67**, 2127 (1945)) which is assumed to prevent effective cross-conjugation, because an *m*-nitro group would be expected to cause an appreciable wave length displacement which is not observed, and because of the occurrence of *two* B-bands in a number of other unsymmetrically substituted benzophenones such as *p*-methoxybenzophenone (see discussion of compound X).

(12) W. F. Forbes and W. A. Mueller, THIS JOURNAL, **79**, 6495 (1957).

closely to the B-bands of benzophenone or of *m*-nitrobenzophenone (–COPh absorption, see Table III), and the B-band of compound I compared with the benzophenone B-band shows a distinct intensity increase, appreciable band widening, but only a slight hypsochromic wave length displacement. This displacement, which is ascribed to the nitro group, is paralleled in the infrared spectrum; *i.e.*, the infrared carbonyl stretching frequency of compound I is 1675 cm.$^{-1}$ and lies just outside the usual limits for a diaryl ketone (1670–1660 cm.$^{-1}$).[13] This displacement in the infrared in turn relates with the known effect of a nitro group, since the latter group frequently causes a displacement to higher frequency (*cf.* refs. 13a and 5).

Consideration of the previously discussed general point (iii) can explain the reduced intensity of the nitrobenzene absorption for compound I, where the nitrobenzene band can no longer be discerned. Steric interactions may, however, not be the only factor since the nitrobenzene B-band is evident only as an inflection in *m*-nitrobenzaldehyde and in *m*-nitroacetophenone, and since therefore the nitrobenzene B-band may merely be obscured for compound I where both B-bands would be expected to occur at similar wave length (*cf.* also discussion of compound IV).

II and III.—Table IV shows that the spectra of II and III are similar to the spectra of *m*-nitrobenzoic acid and *m*-nitrobenzoyl chloride, respectively. The less intense band near 255 mμ is again ascribed to nitrobenzene absorption, whereas the considerably more intense band near 230 mμ is ascribed to benzoic acid or benzoyl chloride absorption, respectively. For compounds II and III the nitrobenzene B-band can now be recognized, probably partly because the two B-bands occur at appreciably different wave lengths in these compounds.

TABLE IV

ULTRAVIOLET ABSORPTION SPECTRA (MAIN MAXIMA IN ETHANOL) OF *m*-SUBSTITUTED NITROBENZOIC ACIDS AND ACID CHLORIDES

Compound	Nitrobenzene B-band λ_{max}, mμ	ϵ_{max}	Second B-band λ_{max}, mμ	ϵ_{max}
m-Nitrobenzoic acid[a]	255	7,000	215	22,500
6,6′-Dinitro-2,2′-diphenic acid (II)	*ca. 260*	*10,500*	223	32,500
m-Nitrobenzoyl chloride[b,c]	*245*	*9,000*	228	25,000
6,6′-Dinitro-2,2′-diphenoyl chloride (III)[c]	*ca. 255*	*9,500*	235	23,000

[a] Data from ref. 5. [b] Ref. 16. [c] In cyclohexane solution.

The absorption bands of *m*-nitrobenzoic acid and *m*-nitrobenzoyl chloride resemble the spectra of II and III, respectively, except that the extinction coefficients of the latter compounds are higher. This then suggests that the two halves of the molecule absorb independently, presumably because of steric interactions. Steric interactions may also be responsible for the relatively decreased nitrobenzene absorptions in compounds II and III (*cf.* general point (iii)). A secondary effect is that the B-bands in compounds II and III are displaced slightly to longer wave length, compared with the B-bands in *m*-nitrobenzoic acid and *m*-nitrobenzoyl chloride (*cf.* also the discussion of compound X), and this effect is ascribed to the other phenyl groups. A parallel effect is again observed in the infrared since the infrared carbonyl doublet, which is also observed for benzoyl chloride, occurs for compound III at 1768 and 1728 cm.$^{-1}$, that is, at *lower* frequency than for benzoyl chloride. For benzoyl chloride the peaks occur at 1773 and 1736 cm.$^{-1}$,[13b] and the nitro group alone would be expected to *raise* the carbonyl frequency in benzoyl chloride (see discussion of compound I).

IV.—In compound IV, the steric interactions are evidently similar, as a first approximation, to those of compound I. As expected, the second B-band is displaced bathochromically, and the band which in compound I occurs at 248 mμ in ethanolic solution, occurs for compound IV at 261 mμ (see Table II). This is qualitatively the bathochromic displacement that would be anticipated on introducing a *p*-methyl substituent. It is *not* the displacement that would be anticipated for the nitrobenzene B-band.

An ill-defined inflection, which may be ascribed to nitrobenzene absorption, occurs near 240 mμ for compound IV. This again suggests that the failure to identify the nitrobenzene B-band in compound I is caused by this band being hidden in compound I by the benzoyl B-band since both B-bands probably occur at similar wave length. In compound IV, on the other hand, the two B-bands are sufficiently apart to permit the tentative identification of the nitrobenzene B-band. The nitrobenzene B-band in compound IV is hypsochromically displaced, compared with the B-band of nitrobenzene, toward the position where the nitrobenzene B-band occurs in compounds like *m*-dinitrobenzene or *m*-nitrobenzophenone (see Table III for the spectrum of *m*-nitrobenzophenone and *cf.* also ref. 15).

The infrared carbonyl band of compound IV is of interest, since again two peaks occur. Following Jones, Forbes and Mueller,[14] it is tempting to associate these doublets with an equilibrium between conformational isomers, but no conclusion seems warranted at this stage. It may be noted, however, that whenever the carbonyl frequency of the non-nitrosubstituted diaroylbiphenyl is known, a consistent displacement of 7 ± 1 cm.$^{-1}$ is observed compared with one of the peaks of the corresponding 6,6′-dinitro-2,2′-diaroylbiphenyl (see ref. 1 and Table II).

V, VI, VII, VIII and IX.—For all these compounds the steric interactions in the benzophenone chromophore of the molecule are increased, and as expected the intensity of the benzoyl B-band is somewhat reduced compared with the absorption of compound I. As a result the absorption corresponding to the alkyl-substituted benzene ring becomes less important and the spectra may be compared with

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(13) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen and Co. Ltd., London, 1954; (a) pp. 114–119, (b) p. 110.

(14) R. N. Jones, W. F. Forbes and W. A. Mueller, *Can. J. Chem.*, **35**, 504 (1957); but *cf.* also P. Yates and L. L. Williams, THIS JOURNAL, **80**, 5896 (1958).

those of *m*-nitrobenzaldehyde or *m*-nitroacetophenone (see Table III).[15]

X.—Compound X shows a well-defined maximum at 290 mμ, which we associate with the *p*-methoxybenzophenone or *p*-methoxyacetophenone chromophore. This B-band is displaced bathochromically as would be anticipated on introducing a *p*-methoxy substituent. Further, the band at 290 mμ (ϵ 32,500) has its analog in the spectrum of *p*-methoxybenzophenone which in ethanol shows a doublet band at 283 and 288 mμ (ϵ 16,000),[16] with about half the above extinction coefficient. (*p*-Methoxybenzophenone in ethanol also shows a second B-band at 249 mμ, ϵ 9000,[16] which has previously been referred to in this paper.) This again confirms the hypothesis of the molecule absorbing as two or more chromophoric entities and, as expected, the infrared carbonyl band of X (1664 cm.$^{-1}$) occurs at a lower frequency than that in compounds I (1675 cm.$^{-1}$) and IV (1669 cm.$^{-1}$).

The nitrobenzene B-band would be expected to be hypsochromically displaced and intensified since the $-COC_6H_4OCH_3$-*p* group may be regarded as a better electron-withdrawing substituent than the –COPh group (see general point (ii)). This is borne out by the data, since no nitrobenzene B-band is observed for compound X in the region 230 to 260 mμ, but a band now occurs at 229 mμ which may be associated with nitrobenzene absorption (*cf.* Table III for the nitrobenzene B-band of *m*-nitrobenzophenone).

Acknowledgments.—The authors are indebted to Miss Florence Jackman, Miss V. M. Walsh and to Rev. Bro. D. C. Clancy for the careful determination of the ultraviolet absorption data, and to Dr. Lester P. Kuhn for the infrared data. Thanks are also due to Dr. M. J. Kamlet for valuable discussions.

Financial assistance from the Research Corporation, the U. S. Public Health Service, National Cancer Institute (C-3325 C1), and the National Research Council of Canada is gratefully acknowledged.

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(15) If only one *o*-methyl substituent is present it is possible that the "normal" benzophenone absorption still contributes to the observed absorption band. For example, the inflection near 260 mμ for compound V may partly be associated with such benzophenone absorption. More precisely, in a substituted benzophenone up to four B-bands may contribute to the observed absorption spectrum.[16] Whenever two such B-bands are likely to occur at similar wave length, as for compound V where both the nitrobenzene B-band and the *p*-methylbenzoyl B-band would be expected to absorb near 260 mμ, any band *assignment is clearly tentative. In this connection it should* be noted that our previous assignment[1] which ascribed this band to the 2,4-dimethylbenzoyl moiety was perhaps too definite if only because it is extremely difficult to obtain the precise location of the maximal absorption for compound V. In fact, compound V affords only very indistinct maxima and numerous determinations were necessary before the present data were accepted. These data, incidentally, should now replace the earlier values.[1]

(16) Unpublished information.

[Contribution from the Faculty of Engineering, Kyoto University]

Reaction of 4-Dimethylaminoazobenzene and Related Compounds with 4,4'-Bis-(dimethylamino)-benzhydrol[1]

By Kenichi Fukui, Yoshiaki Inamoto, Hisao Kitano and Chikayoshi Nagata

Received April 13, 1959

Reaction of 4,4'-bis-(dimethylamino)-benzhydrol (Michler's hydrol) with 4-dimethylaminoazobenzene, 2'-methyl-4-dimethylaminoazobenzene, 3'-methyl-4-dimethylaminoazobenzene and 4-methylaminoazobenzene catalyzed by sulfuric acid affords 4'-alkylated products in each case, *e.g.*, 4'-[4,4'-bis-(dimethylamino)-benzhydryl]-4-dimethylaminoazobenzene. Neither azobenzene nor 4'-methyl-4-dimethylaminoazobenzene is alkylated under similar conditions.

Investigation of chemical reactivities of carcinogenic compounds may contribute to the elucidation of mechanism of carcinogenesis by these compounds, since the first step in carcinogenesis is believed to be a chemical combination of these compounds with proteins.[2] It seems very interesting to study the Friedel–Crafts alkylation[3] of 4-dimethylaminoazobenzene (DAB) and related compounds, some of which are powerful carcinogens,[2] because electrophilic substitution of DAB other than nitration[4] and sulfonation[5] has not been reported.

Sulfuric acid was chosen as catalyst for these alkylation studies because it seemed a milder reagent than aluminum chloride which causes rearrangements[3] and fission of the azo linkage.[6] In addition, sulfuric acid serves as a solvent for the reaction. 4,4'-Bis-(dimethylamino)-benzhydrol (Michler's hydrol) was adopted as the alkylating agent for DAB because it was considered one of the highly reactive alcohols owing to the fact that nuclear alkylation of *p*-nitrosodimethylaniline can be effected by Michler's hydrol, while not by benzyl alcohol and benzhydrol[7] which are relatively active alkylating agents.[3]

Although Michler's hydrol has been utilized for the alkylation of various aromatic compounds, *e.g.*, amines,[8-10] phenols,[11] *m*-xylene,[12] aryl hal-

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[1] This work is supported financially by a grant-in-aid from the Ministry of Education, Japan.

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