

in alkali to give a yellow solution. Two recrystallizations of this solid from ethanol gave XVI as pale yellow, short needles, m.p. 248–250° decomposing to a red liquid.

Anal. Calcd. for $C_{21}H_{15}N_3O_3$: N, 9.61. Found: N, 9.55.

The infrared spectrum of XVI (chloroform) showed peaks at 3049s cm^{-1} (aromatic C—H), 1730w cm^{-1} (saturated acid C=O), 1527s–1351s cm^{-1} (C—NO₂), 1215s cm^{-1} (broad) (C_s—C), 929m cm^{-1} (confirmatory —COOH).

The silver salt was prepared in the usual way and dried at 80° for two days.

Reaction of the silver salt of XVI with bromine. The silver salt of XVI (3.0 g., 5.5 millimoles) was suspended in dry carbon tetrachloride (30 ml.) and treated with dry bromine (1.0 g., 6 millimoles) in further solvent (10 ml.) under a nitrogen gas sweep as described previously for the silver salt of I. Carbon dioxide evolution commenced in about five minutes at room temperature and was completed at the reflux temperature (77°) in thirty minutes. The carbon dioxide evolved (measured as barium carbonate) was 1.47 millimole (26.8% yield). Treatment of the reaction mixture as described before gave recovered XVI (70%) and a yellow solid (about 25–30%), m.p. 70–85°. This solid gave a precipitate of silver bromide readily in alcoholic silver nitrate (5%) and developed acidity when refluxed in aqueous alcohol. Potassium permanganate in acetone (0.5%) was

quickly decolorized by the solid. While the alkaline conditions required for the hydroxamic acid test for esters appeared to affect the substance, a negative ester test was obtained.

The ready solvolytic loss of hydrogen bromide from the substance suggests that it contains XVII, while the unsaturation evident implies the presence of at least some olefin, probably XVIII.²⁸

Acknowledgment. The authors wish to thank Professor C. E. Moore for certain technical assistance and Miss E. Godar for some of the infrared spectra.

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(28) While the purpose of using XVI in this study was strictly the comparison of the carbon dioxide percentage (bromodecarboxylation percentage) with I, the reaction of XVI is of great interest in itself, perhaps being the first reported instance of appreciable rearrangement, not caused by side reactions, in the Hunsdiecker reaction series. A more detailed investigation of this point is under way in this laboratory and will be reported separately.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FORDHAM UNIVERSITY]

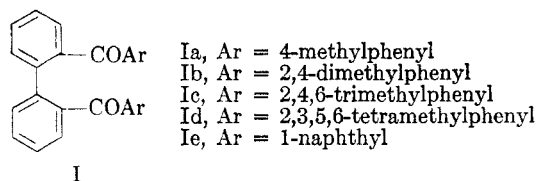
Steric Interactions in the Absorption Spectra of 2,2'-Diaroylbiphenyls

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The electronic absorption spectra of 2,2'-biphenylaldehyde, (+) 6,6'-dinitro-2,2'-di(2,4-dimethylbenzoyl)biphenyl, and a series of 2,2'-diaroylbiphenyls in which the 2,2'-diaroyl substituents increase in bulk (Aroyl = 4-methylbenzoyl, 2,4-dimethylbenzoyl, 1-naphthoyl, 2,4,6-trimethylbenzoyl, and 2,3,5,6-tetramethylbenzoyl) are discussed in terms of current theories.

As part of a configurational study of *cis*- and *trans*-9,10-diaryl-9,10-dihydro-9,10-phenanthrene-diols in which the 9,10-diaryl substituents increase in bulk, five 2,2'-diaroylbiphenyls (I) have been prepared as intermediates.² The structures of these diketones, synthesized by a Friedel-Crafts reaction



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(2) (a) E. J. Moriconi, F. T. Wallenberger, L. P. Kuhn, and W. F. O'Connor, *J. Org. Chem.*, **22**, 1651 (1957); (b) E. J. Moriconi, F. T. Wallenberger, and W. F. O'Connor, *J. Am. Chem. Soc.*, in press.

(3) W. E. Bachmann, *J. Am. Chem. Soc.*, **54**, 1969 (1932); W. E. Bachmann and E. J. Chu, *J. Am. Chem. Soc.*, **57**, 1095 (1935); D. Nightingale, H. E. Heiner, and H. E. French, *J. Am. Chem. Soc.*, **72**, 1875 (1950); R. C. Fuson and C. Hornberger, *J. Org. Chem.*, **16**, 637 (1951); R. C. Fuson and R. O. Kerr, *J. Org. Chem.*, **19**, 373 (1954).

between diphenoyl chloride and the appropriate arene, have been previously established by unequivocal methods.³

Compounds of this type should also be of special interest since they provide examples in which steric effects are known to cause changes in the light absorption properties. In particular, steric effects in electronic spectra of organic compounds have been classified into two types: Type I steric effects, which give rise to intensity changes only, and Type II steric effects, which normally also cause appreciable wavelength displacements.⁴ Acetophenones show steric effects of the former type, whereas biphenyls show steric effects of the latter type. Consequently, it would be a matter of interest to determine which type of steric effect occurs in the compounds under investigation. With this in mind, a spectral analysis of the compounds Ia to Ie and of a suitable reference compound, 2,2'-biphenylaldehyde (II), has been carried out.

(4) E. A. Braude, F. Sondheimer, and W. F. Forbes, *Nature*, **173**, 117 (1954); E. A. Braude and F. Sondheimer, *J. Chem. Soc.*, 3754 (1955).

Compound III, (+) 6,6'-dinitro-2,2'-di(2,4-dimethylbenzoyl)-biphenyl, is also included to compare the effect of molecular rigidity on absorption spectra. Results are summarized in Table I.

TABLE I
ABSORPTION SPECTRA OF 2,2'-DIAROYLBI-PHENYLS

Compound	Ultraviolet ^a				Infrared ^b Carbonyl Band ν_{\max} cm. ⁻¹
	B-band		C-band		
	λ_{\max} m μ	ϵ_{\max}	λ_{\max} m μ	ϵ_{\max}	
II	252	18,500	284	3,100 ^d	1699
			294	4,200	
Ia	262	31,600	287	13,400 ^e	1661
Ib	260	23,400	289	10,400 ^e	1664
Ic	252	16,800	287	5,800	1673
Id	250	16,900	300	5,700	1674
Ie	259	21,800 ^e	285	9,500	1660
			312	12,700	
III	257	13,700	288	8,100 ^e	1671
	243	16,000			

^a Values of ethanolic solution; the band designation is the same as the one used by Forbes *et al.* in *Can. J. Chem.*, **35**, 1049 (1957) and preceding papers of that series. ^b Values in chloroform solution; this band, due to the infrared carbonyl stretching frequency, will be referred to as the "carbonyl band" throughout this paper. ^c Values in italics in this and the subsequent table represent inflections.

The simplest 2,2'-diaroylbiphenyl is compound II, which may be regarded as a di-*ortho*-substituted biphenyl where both *o*-substituents are fairly small. It is also known that two *o*-substituents in a biphenyl system normally destroy most of the 1,1'-biphenylic conjugation.⁵ Therefore the spectrum of II may be anticipated to resemble the spectrum of benzaldehyde; or perhaps that of an orthosubstituted benzaldehyde, which also absorbs in a similar wave length range as biphenyl, that is near 250 m μ . Since the benzaldehyde and biphenyl spectra absorb closely to each other, no definite assignment can be made on the basis of location of maximal absorption alone. However, the following three factors enable us to ascribe the absorption band of II at 252 m μ , $\epsilon = 18,500$ primarily to benzaldehyde absorption:

(i) In ethanol, II shows an absorption band at 252 m μ ; in cyclohexane solution this splits into a maximum at 248 m μ and an inflection at 255 m μ . This, as well as the general shape of the B-band, is characteristic of benzaldehyde absorption. By contrast, the biphenyl band does not exhibit any such fine structure.⁵ Table II lists the B-band of II together with the B-bands of two *ortho*-substituted benzaldehydes.

(ii) If the absorption band of II at 252 m μ corresponds to benzaldehyde absorption, the absorption bands in Ia to Id should, by analogy, correspond to benzophenone absorption. It would be

(5) E. A. Braude and W. F. Forbes, *J. Chem. Soc.*, 3776 (1955).

TABLE II
ABSORPTION MAXIMA (B-BANDS) OF *Ortho*-SUBSTITUTED BENZALDEHYDES IN HEXANE SOLUTION⁶

Compound	λ_{\max} , m μ	ϵ_{\max}
2,2'-Biphenyldialdehyde (II)	248	19,300
	255	17,300
<i>o</i> -Chlorobenzaldehyde	246	10,800
	252	8,500
<i>o</i> -Methoxybenzaldehyde	246	10,600
	253	8,500

anticipated that steric effects in the series Ia to Id cause essentially type I steric effects, since the system then resembles an acetophenone system. This is found to be so (Table I). If biphenyl absorption were chiefly responsible for the observed absorption band, one would expect steric effects essentially of type II in Ia to Id similar to those observed in biphenyl.

(iii) Scale models indicate that the biphenyl system in compound II is nonplanar.⁷

Two additional points concerning the spectrum of II may also be noted. First, although the absorption intensity of II is almost exactly twice the intensity of the two *o*-substituted benzaldehydes listed in Table II, this does not imply that biphenyl absorption will not contribute to the observed absorption. In fact, biphenyl conjugation quite probably contributes to the observed absorption intensity, because *ortho*-substituted benzaldehydes normally absorb with a smaller extinction coefficient than the parent compound.⁸ Secondly, the carbonyl band of II at 1699 cm.⁻¹ lies within the expected absorption range for aryl aldehydes, that is between 1715 and 1695 cm.⁻¹⁸ It also absorbs closely to the reported absorption bands of 1- and 2-naphthaldehyde which in 0.02 molar carbon tetrachloride solution occur at 1700 and 1702 cm.⁻¹ respectively.⁹

In the next example, Ia, steric inhibition of 1,1'-biphenylic conjugation has presumably increased. Consequently, as mentioned above, we would expect this system to absorb essentially as two molecules of *p*-methylbenzophenone. This hypothesis is supported by the data. Benzophenone absorbs maximally in ethanol at 252 m μ ($\epsilon = 17,400$)¹⁰ and a *p*-methyl substituent would be expected to cause a bathochromic wave length displacement of about 9 m μ (benzaldehyde to *p*-methylbenzaldehyde and acetophenone to *p*-

(6) W. F. Forbes and J. C. Dearden, unpublished information.

(7) W. F. Forbes and W. A. Mueller, *Can. J. Chem.*, **34**, 1542 (1956).

(8) L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*, Methuen and Co. Ltd., London, 1954, p. 114-119.

(9) I. M. Hunsberger, *J. Am. Chem. Soc.*, **72**, 5626 (1950).

(10) L. J. Andrews and W. W. Kaeding, *J. Am. Chem. Soc.*, **73**, 1007 (1951).

methylacetophenone both afford shifts of $9 \text{ m}\mu^4$). In this way, an expected maximal absorption at $261 \text{ m}\mu$ is obtained, in excellent agreement with the experimentally obtained value of $262 \text{ m}\mu$. It may be noted that the absorption of benzophenone may be related to the spectrum of acetophenone by assuming the non-planarity of the two benzene rings (*cf.* ref. 11) and this tends to justify the assumed bathochromic shift of $9 \text{ m}\mu$ for the *p*-methyl substituent. Jones¹¹ also noted a "suggestion of an inflection" near $280 \text{ m}\mu$ for benzophenone and this may correspond to the inflection observed for compound Ia at $287 \text{ m}\mu$. The carbonyl band of Ia at 1661 cm.^{-1} corresponds with the expected infrared absorption for a diaryl ketone, which is reported to occur between 1670 and 1660 cm.^{-1} ⁸

In compound Ib a type I steric effect, namely a reduced absorption intensity without appreciable wave length displacement, is observed (Table I). It should be compared with the change from *p*-methylacetophenone ($\lambda_{\text{max}} 252 \text{ m}\mu$, $\epsilon = 15,100$) to 2,4-dimethylacetophenone ($\lambda_{\text{max}} 251 \text{ m}\mu$, $\epsilon = 14,000$).⁴ The greater intensity decreases in the series Ia, Ib may be ascribed either to further reduced biphenylic absorption, or more generally to secondary steric interactions caused by the introduction of two additional methyl groups into an already crowded system. The carbonyl band at 1664 cm.^{-1} again lies between the limits as stated for Ia; the shift of 3 cm.^{-1} relative to Ia may be compared with a similar shift occurring between *p*-methylacetophenone (1687 cm.^{-1}) and *o*-methylacetophenone (1690 cm.^{-1}),¹² and may be indicative of steric interaction.

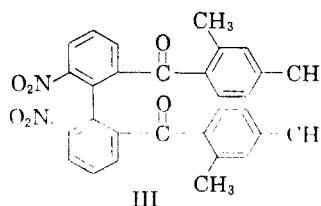
Compound Ic also exhibits a pronounced steric effect (a wave length displacement of $8 \text{ m}\mu$ relative to Ib and a definite decrease in absorption intensity) on introducing a second ortho-substituent in the benzophenone system. The change should be compared with a similar wave length displacement occurring between 2,4-dimethylacetophenone ($\lambda_{\text{max}} 251 \text{ m}\mu$, $\epsilon = 14,100$) and 2,4,6-trimethylacetophenone ($\lambda_{\text{max}} 242 \text{ m}\mu$, $\epsilon = 3600$).⁴ It may be noted that the spectral change from Ib to Ic can be regarded as a type II steric effect. Alternatively, the spectrum of Ic compared to that of compound II (Table I) does not show a wave length displacement of the B-band, and the change may consequently also be regarded as a type I steric effect. This illustrates a general principle: namely that a steric effect, apparently type II, may actually represent a type I steric effect. In the particular example of the 2,2'-diaroylbiphenyls a possible explanation comes readily to mind; that is, in compound Ic transitions involving the phenyl ring of the biphenyl system are preferred for steric

reasons to transitions involving the 2,2'-disubstituted phenyl ring. In this way, the spectrum of Ic reverts to the spectrum of compound II. In the acetophenone series also, acetophenone, *o*-methylacetophenone, and 2,4,6-trimethylacetophenone are reported to absorb at $242 \pm 1 \text{ m}\mu$.⁴ However, the explanation there is less readily obvious and the relevant discussion will be deferred for the present.

For the compound Id, the B-band is similar to that of Ic. This is in agreement with the hypothesis that for compounds Ic and Id transitions occur preferentially which involve the phenyl ring of the biphenyl system. Transitions involving the phenyl ring of the biphenyl system may also account for the somewhat greater residual absorption intensity of the B-band in the present series (Ic and Id), compared to the absorption intensities of 2,4,6-trimethyl-⁴ and 2,3,5,6-tetramethylacetophenones.¹² On the other hand, there is some evidence that transitions involving the other phenyl rings also contribute to the observed absorption. This is indicated by the C-band which shows the characteristic shift to longer wave length (Table I) and this relates with the known sensitivity of this band to *meta*-substituents. (*Cf.*, for example, the C-bands of 2,4-dimethyl- and 2,5-dimethylacetophenones which are reported to absorb maximally at 282 and $296 \text{ m}\mu$ respectively.)⁴ The carbonyl bands for compounds Ic and Id at 1673 and 1674 cm.^{-1} , not unexpectedly, now also occur outside the limits recorded for diaryl ketones (1670 - 1660 cm.^{-1}),⁸ and approach the values found for compound II (1699 cm.^{-1}).

The absorption of compound Ie, by analogy with the other compounds, would be anticipated to be similar to that of 1-naphthophenone or to that of a PhCOR entity as in Ic or Id. The infrared carbonyl band for Ie at 1660 cm.^{-1} indicates a resemblance with compound Ia (1661 cm.^{-1}) rather than with 1-acetonaphthone, which in 0.02 molar carbon tetrachloride solution is reported to occur at 1685 cm.^{-1} .⁹ Since, however, the B-band occurs only as an inflection, no definite assignment seems warranted.

Compound III is an *o,o'*-tetrasubstituted biphenyl in which the blocking 6,6'-nitro groups ensure optical stability. It would be expected therefore that in III, the two phenyl rings of the biphenyl system become electronically independent, and the absorption spectra of the system would revert to a 1,2-disubstituted nitrobenzene chromophore.



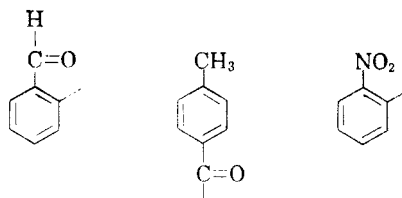
(11) R. N. Jones, *J. Am. Chem. Soc.*, **67**, 2127 (1945).

(12) W. F. Forbes and W. A. Mueller, *Can. J. Chem.*, **35**, 488 (1957).

It was observed that the band shape of compound III differs from that of compounds in the I series. A maximal absorption occurs in ethanol at 257 $m\mu$. Nitrobenzene and a number of ortho-substituted nitrobenzenes similarly absorb maximally in ethanolic solution. For example, 2-carboxy-4,5-dimethoxy-2'-nitrobiphenyl absorbs maximally at 256 $m\mu$ ($\epsilon = 16,000$), and 2-carboxy-4,5-dimethoxy-2'-nitro-3'-methylbiphenyl, which is slightly more sterically hindered because of the buttressing effect of the additional methyl group, still absorbs at 256 $m\mu$ ($\epsilon = 10,700$).¹³ Therefore this maximal absorption of compound III is ascribed to nitrobenzene absorption.

Further, since compound III is also a meta-substituted nitrobenzene, it would be anticipated to afford an absorption spectrum of a meta-disubstituted benzene. That is, no appreciable resonance interaction occurs between the two substituents, and the molecule absorbs essentially as two mono-substituted benzenes. It follows that the electronic spectrum would include nitrobenzene absorption. It also follows that the maximal absorption due to the 2,4-dimethylbenzoyl moiety, which in Ib is located at 260 $m\mu$, should occur in the absorption spectrum of III. Now, it is known that a nitro group in the meta position gives rise to an interaction which often causes an appreciable hypsochromic shift.¹⁴ For example, in ethanolic solution the acetophenone band at 240 $m\mu$ occurs in *m*-nitroacetophenone at 226 $m\mu$ and a similar hypsochromic shift is observed in hexane solution. Therefore, we would anticipate in the spectrum of III a second maximal absorption near 260 $m\mu$ - 14 $m\mu$ = 246 $m\mu$, and the observed maximal absorption at 243 $m\mu$ presumably corresponds to this band.

The 2,2'-diarylbiiphenyls have in this way been shown to give rise to B-bands corresponding to the following chromophoric systems within the molecule:



Depending on the substituents, absorptions corresponding to any one of these chromophoric systems may predominate, and the steric effects arising in the electronic spectra are classified as mainly type I steric effects.

Nitrobenzene, as will be shown elsewhere,¹⁴ therefore provides a good illustration of type I steric effects, and may also, because of the large

effective interference radius of the nitro group, be used to illustrate secondary steric interactions such as the buttressing effect. The carbonyl band of III at 1671 cm^{-1} lies between that of compound Ib (1664 cm^{-1}) and that of compound Ic (1673 cm^{-1}). Since the change in the carbonyl bands from Ib to Ic has been tentatively ascribed to increased steric inhibition of resonance, the value of 1671 cm^{-1} for compound III may also correspond to increased steric interactions in the 2,4-dimethylbenzophenone chromophores because of the nitro groups. The hypothesis receives support since III is an optically stable biphenyl isomer. The hypothesis of increased steric interaction may also explain the slight discrepancy (3 $m\mu$) between the calculated and observed values for the second B-band at 243 $m\mu$ in compound III.

Finally, Braude, and Sondheimer⁴ have indicated that electronic absorption spectra are a less sensitive index of steric effects than reaction rates. It is perhaps significant, then, that the indicated order of increasing steric interference Ia, Ib, Ic, and Id (B-bands, Table I) based on ultraviolet measurements is inversely related to the rates of lead tetraacetate cleavage of the *cis*-9,10-diaryl-9,10-dihydro-9,10-phenanthrenediols,^{2b} obtained, respectively, from these diketones.^{2a}

EXPERIMENTAL¹⁵

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; Conc., 10 mg./ml., cell thickness, 0.1 mm., $CHCl_3$ solvent.

Ultraviolet absorption spectra. Ultraviolet absorption measurements were made in a Beckmann Quartz Spectrophotometer Model DU or in a Unicam Spectrophotometer Model SP 500 using 1-cm. quartz cells.

Preparation of compounds. Details of preparation and properties of compounds Ia, Ib, Ic, Id, Ie, and II, may be found in ref. 2.

(+)-6,6'-Dinitro-2,2'-di(2,4-dimethylbenzoyl)biphenyl (III), m.p. 222-224°, $[\alpha]_D^{25} +145.8$ ($c = 0.60$, acetone), was prepared in 85% yield from a Friedel-Crafts reaction between *m*-xylene and (+)-6,6'-dinitro-2,2'-diphenoyl chloride.

Anal. Calcd. for $C_{30}H_{24}O_6N_2$: C, 70.85; H, 4.75. Found: C, 70.74; H, 4.64.

(+)-6,6'-Dinitro-2,2'-diphenoyl chloride, m.p. 155-157°, $[\alpha]_D^{25} +55.0$ ($c = 1.10$, $CHCl_3$) was prepared in 96% yield from $SOCl_2$ and (+)-6,6'-dinitro-2,2'-diphenic acid,¹⁶ m.p. 230-231°, $[\alpha]_D^{25} +132.0$ ($c = 0.50$, methanol).

Acknowledgment: The authors wish to thank the Research Corp. for grants supporting this work, and Dr. Lester P. Kuhn for the infrared absorption data.

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(15) All melting points are uncorrected. The microanalyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

(16) This compound was generously supplied to us by Professor Kurt Mislow, New York University, University Heights, N. Y.

(13) W. F. Forbes and W. A. Mueller, *J. Am. Chem. Soc.*, **79**, 6495 (1957).

(14) W. F. Forbes, *et al.*, unpublished information.