

m μ . The reaction mixture was worked up as previously described,²¹ the crude product being recrystallized from hexane. The pure 2-ethyl-*cis*-2,3-epoxy-1,3-diphenyl-1-propanol separated as white needles, m.p. 98.8–99.8°, yield 4.56 g. (71.2%). The infrared spectrum¹⁶ of the epoxy alcohol contains absorption bands at 3630 and 3520 cm.⁻¹. The ultraviolet spectrum had a maximum at 260 m μ (ϵ 46).

Anal. Calcd. for C₁₇H₁₈O₂: C, 80.28; H, 7.13. Found: C, 80.10; H, 7.12.

α -Ethyl-*cis*-benzalacetophenone Oxide (Iib).—A solution of 4.0 g. (0.0158 mole) of 2-ethyl-*cis*-2,3-epoxy-1,3-diphenyl-1-propanol in 30 ml. of pyridine was oxidized with the chromium trioxide–pyridine complex,²² prepared from 100 ml. of pyridine and 10 g. (0.10 mole) of chromium trioxide, as described by Wasserman and Aubrey.¹⁰ The pure α -ethyl-*cis*-benzalacetophenone oxide crystallized from hexane as white needles melting at 81.5–82.5°, yield 2.90 g. (73%). The infrared spectrum¹⁶ contains an absorption band at 1688 cm.⁻¹ and has no band in the 3 μ region attributable to a hydroxyl group. The ultraviolet spectrum has an absorption peak at 250 m μ (ϵ 12,300).

Anal. Calcd. for C₁₇H₁₆O₂: C, 80.92; H, 6.39. Found: C, 80.95; H, 6.66.

Rearrangement of α -Ethyl-*cis*-benzalacetophenone Oxide (Iib).—A solution of 254 mg. (0.001 mole) of the oxide in 12 ml. of benzene was saturated with boron trifluoride gas and allowed to stand at room temperature for 2 hr. After the mixture had been diluted with ether and washed with water, the solvents were removed and the crude solid which remained was recrystallized from alcohol. An additional recrystallization from methanol followed by two recrystallizations from petroleum ether afforded the pure keto form of 1,2-diphenyl-1,3-pentanedione, m.p. 93.0–95.0°, as white needles, yield 150 mg. (59%). A mixed melting point determination with the diketone obtained from the *trans*-oxide showed no depression.

In another experiment 254 mg. (0.001 mole) of the oxide was isomerized as previously described. A solution of the crude rearrangement product in alcohol was treated with 166 mg. (0.0015 mole) of phenylhydrazine and 0.4 ml. (0.007 mole) of acetic acid as previously described. The yield of 3-ethyl-1,4,5-triphenylpyrazole, m.p. 138.0–139.0°, was 282 mg. (87%). A mixed melting point determination with the pyrazole sample previously described showed no depression. When the reaction time for the rearrangement was 30 min. the yield of the pyrazole was 282 mg. (87%).

As a control experiment the α -ethyl-*cis*-benzalacetophenone oxide (254 mg., 0.001 mole) was treated with phenyl-

(22) G. I. Poos, G. E. Arth, R. E. Beyler and L. H. Sarett, *THIS JOURNAL*, **75**, 422 (1953).

hydrazine under the conditions used to prepare the derivative. The only material which could be isolated was the starting oxide, m.p. 81.0–82.0°, recovery 93%.

The infrared spectra¹⁶ of the crude reaction products obtained from the isomerizations of α -ethyl-*cis*-benzalacetophenone oxide and α -ethyl-*trans*-benzalacetophenone oxide were compared. The main constituent of each reaction mixture appeared to be the borofluoride complex of an enolized β -dicarbonyl compound (strong, relatively sharp band at 1555 cm.⁻¹).²³ Since neither of the spectra exhibit absorption in the 2700–2800 cm.⁻¹ region we regard the presence of any significant quantity of α -formyl- α -phenylbutyrophenone (XI), a possible rearrangement product, as very improbable.²⁴ The spectra of the two crude products differ only in the intensities of three weak bands found at 1675, 1710 and 1742 cm.⁻¹, these bands being more intense in the spectrum of the crude rearrangement product obtained from α -ethyl-*trans*-benzalacetophenone oxide. The bands of approximately equal intensity at 1675 and 1710 cm.⁻¹ are judged to represent a small amount of 1,2-diphenyl-1,3-pentanedione, the product isolated from each rearrangement after complete hydrolysis of the borofluoride complex. To verify this hypothesis the crude rearrangement product from the *trans*-oxide was recrystallized from methanol; the resultant solid after successive recrystallizations from methanol and hexane afforded pure 1,2-diphenyl-1,3-pentanedione, m.p. 92.5–94.5°, yield 47%. The infrared spectrum¹⁶ of the residue from the combined mother liquors exhibits the bands at 1675 and 1710 cm.⁻¹ as well as a broad band with its center at 1600 cm.⁻¹ (enolized β -dicarbonyl compound). The relative intensity of the band at 1742 cm.⁻¹ increased indicating that the component represented by this band has been concentrated by the partial removal of the 1,2-diphenyl-1,3-pentanedione. However, we were unable to isolate the small amount of this second component present in the reaction mixture. The location of band 1742 cm.⁻¹ attributed to this second component suggests that the material is not either of the two expected rearrangement products, α -formyl- α -phenylbutyrophenone (XI) or 1,3-diphenyl-3-ethyl-1,2-propanedione (XII).²⁵

(23) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 126.

(24) Absorption in this region, attributable to the C–H stretching vibration of an aldehyde function, is clearly discernible in the spectra of analogous compounds (see ref. 12).

(25) The absorption peaks attributable to the carbonyl functions in the homologous compounds, α -formyl- α -phenylpropiofenone and 1,3-diphenyl-1,2-propanedione, are found at 1670 and 1730 cm.⁻¹ and 1630 and 1705 cm.⁻¹, respectively.

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[CONTRIBUTION FROM THE MEMORIAL UNIVERSITY OF NEWFOUNDLAND]

Electronic Spectra and Molecular Dimensions. II.^{1,2} The "Buttrussing Effect" and Other Secondary Steric Interactions in Electronic Spectra

By W. F. FORBES AND W. A. MUELLER

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Steric interactions are known to directly affect the main band (B-band) in ultraviolet absorption spectra. Developing the concept of steric hindrance, the so-called buttrussing effect is examined, and it is shown that some other changes affecting both wave length shifts and absorption intensities can be rationalized by assuming the operation of more extended or indirect steric interactions.

Introduction

Steric effects in the B-band of ultraviolet absorption spectra have been shown³ to give rise to various changes. If the steric inhibition of reso-

nance is large and the coplanarity of the molecule is almost completely destroyed, bands occur which may be regarded as partial chromophore bands, that is, the molecule absorbs as two or more distinct entities.⁴ If the steric interaction is less pronounced in comparison with a planar reference molecule, a wave length shift (usually to shorter wave length) accompanied by decreased absorption

(1) Presented before the Division of Organic Chemistry at the Miami Meeting of the American Chemical Society, April, 1957.

(2) Part I, *Can. J. Chem.*, **34**, 1542 (1956).

(3) E. A. Braude and F. Sondheimer, *J. Chem. Soc.*, 3754 (1955); W. F. Forbes and W. A. Mueller, *Can. J. Chem.*, **34**, 1340, 1347 (1956); **35**, 488 (1957).

(4) Cf. L. W. Pickett, *et al.*, *THIS JOURNAL*, **72**, 44 (1950); **58**, 2296 (1936); E. Mueller and H. Neuhoß, *Ber.*, **72**, 2063 (1939).

intensity is observed. Lastly, a type of steric interaction can be detected in which the wave length of maximal absorption remains approximately constant, while the absorption intensity at maximal absorption is appreciably reduced.

Examples of this last type of steric hindrance have been discussed previously,³ and it has been shown that the hypothesis of steric inhibition of resonance accounts satisfactorily for the observed changes. More precisely, the hypothesis is that the individual non-hindered compounds exist in two conformations, *s-cis* and *s-trans*, both of which contribute to the observed absorption. "Hindered" compounds listed in the papers referred to still exist in both these conformations, but only one of these (the less hindered conformation) contributes appreciably to the observed maximal absorption.³ Using this hypothesis it is possible to obtain interference values of non-bonded atoms in solution and this approach has been outlined in Part I of this series. Since the values thus obtained are larger than those previously used,² it also suggests a rediscussion of a number of topics which previously have received only scant attention. In the following sections, therefore, some secondary steric interactions will be discussed with special reference to their possible detection in ultraviolet light absorption data.

The Buttressing Effect.—The buttressing effect for substituted benzene derivatives is defined as the interaction occurring due to a *m*-substituent exerting an indirect steric effect by "buttressing" the *o*-substituent; in this way a *m*-substituent may alter the steric interactions of the two other vicinal substituents. Convincing evidence for the operation of the buttressing effect is provided by the rates of racemization of certain optically active biphenyls,⁵ and the proposed interference values of carbon, hydrogen and oxygen as deduced in Part I² also suggest that a buttressing effect may sometimes be discerned in the B-band of ultraviolet absorption spectra. This latter suggestion is in fact confirmed by the spectra of a number of compounds.

In biphenyls, where a buttressing effect is known to occur from rates of racemization data, evidence for this effect in ultraviolet absorption properties may be adduced from compounds like 3,3'-dimethoxybiphenyl which shows considerably lower absorption (ϵ_{\max} 12,000 at 250 $m\mu$) than that of biphenyl (ϵ_{\max} 17,000 at 249 $m\mu$).⁶ This type of effect is quite generally observed with *large m*-substituents (see below and particularly Table I). It is consistent with the explanation that the *m*-methoxy substituent, by buttressing the *o*-hydrogen atoms, decreases the planarity of the biphenyl system. A similar progressive lowering of absorption in the biphenyl series also has been noted for the spectra of biphenyl (ϵ_{\max} 20,300 at 246 $m\mu$), 3,3'-bis-(trifluoromethyl)-biphenyl (ϵ_{\max} 17,780 at 245 $m\mu$) and 3,3',5,5'-tetrakis-(trifluoromethyl)-biphenyl (ϵ_{\max} 15,850 at 242 $m\mu$),^{7a} where first two

and then four *m*-substituents contribute to a possible buttressing interaction.

It should be noted that the value of biphenyl as reported by Ross, *et al.*,^{7a} who themselves quote an earlier value for this compound, is probably high and consequently the correct extinction coefficient under identical circumstances is likely to be lower (*cf.* our own value of ϵ_{\max} 15,600–16,200²). This raises an important point, since it would appear to preclude the operation of a buttressing effect in the spectral data. However, as will be shown more fully elsewhere, the buttressing effect is of course not the only interaction operating in *m*-disubstituted benzene derivatives, and frequently it will be opposed by an interaction which causes a positive wave length displacement and intensity increases. Hence in considering the effect of *m*-substituents, it would be an oversimplification to consider exclusively the buttressing effect in causing the observed changes. In fact, a number of examples can be found, especially if the *m*-substituent is small, where an intensity increase is observed (*cf.*, for example, ref. 7b). However, the general decrease in extinction coefficients, whenever the substituents are large, is taken to point to the operation of the buttressing effect.

Further examples showing possible buttressing interactions are available in other benzene derivatives, and some of these are listed in Table I.

Table I illustrates how the introduction of large *m*-substituents frequently appears to inhibit at least some of the conjugation as shown by the decreased absorption intensity or disappearance of the B-band. For example, B-bands for spectra of *m*-iodo compounds have consistently lower absorption intensities and frequently occur only as inflections. Although other effects may also account for these changes the data correlate well with a steric interpretation. In already hindered compounds, on *m*-substitution, steric inhibition of resonance is enhanced (see the first two examples in Table I) and the effect is generally more pronounced for larger substituents. Thus it appears to be more pronounced for *m*-nitroacetophenone than for *m*-nitrobenzaldehyde as shown by a more pronounced intensity decrease for *m*-nitroacetophenone. The intensity decreases for the corresponding *m*-chloro compounds are similar, and this suggests that there the buttressing effect, if present, is similar. However, it is more probable that in *m*-chloro compounds the buttressing effect is of little importance. Not unexpectedly, with the larger bromo-substituent the buttressing effect is again more evident. Therefore, apparently the buttressing effect is more pronounced for bromine than for chlorine and is more pronounced for iodine than for bromine. This is entirely as anticipated.

We may note that the case for the buttressing effect is inherently not as definite as the evidence which indicates that the *ortho*-effect is primarily due to steric interactions. This follows because the intensity changes involved in *m*-isomers are much smaller and may partly be caused, for example, by

7b, 4967 (1953); (b) *cf.* A. J. Bilbe and G. M. Wyman, *ibid.*, **75**, 5312 (1953), for the spectra of 3,5-difluoroaniline and *m*-fluoroaniline; we are most grateful to a referee of this paper for drawing our attention to this.

(5) R. Adams and H. R. Snyder, *THIS JOURNAL*, **60**, 1411 (1938); M. Rieger and F. H. Westheimer, *ibid.*, **72**, 19 (1950); S. L. Chien and R. Adams, *ibid.*, **56**, 1787 (1934).

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

(7) (a) S. D. Ross, M. Markarian and M. Schwarz, *THIS JOURNAL*,

TABLE I

ABSORPTION MAXIMA (B-BANDS) OF *m*-SUBSTITUTED BENZENE DERIVATIVES EXHIBITING A DISTINCT BUTTRRESSING EFFECT AND REFERENCE COMPOUNDS (VALUES IN ITALICS REPRESENT INFLECTIONS)

Solvent	<i>m</i> -Substituted compound		Reference compound		Ref.		
	Compound	λ_{\max} , m μ	ϵ_{\max}	Compound		λ_{\max} , m μ	ϵ_{\max}
Ethanol	2,3,4,5,6-Pentamethylacetophenone	(216	12,000) ^a	2,4,6-Trimethylacetophenone	242	3,600	3, 8
Ethanol	2,3,5,6-Tetramethylacetophenone	(212	11,500) ^a	2,6-Dimethylacetophenone	251	5,600	3, 8
Ethanol	<i>m</i> -Nitrobenzaldehyde	265	11,700	<i>p</i> -Nitrobenzaldehyde	265	11,400	9
Ethanol	<i>m</i> -Nitroacetophenone	ca. 261	6,600	<i>p</i> -Nitroacetophenone	263	13,800	9
Cyclohexane	<i>m</i> -Iodoacetophenone	{ 246 250 244	{ 6,800 6,000 8,000	Acetophenone	238-239	12,500	10
Cyclohexane	<i>m</i> -Iodobenzaldehyde	{ 249 253	{ 7,500 7,000	Benzaldehyde	241	14,000	10
Cyclohexane	<i>m</i> -Iodobenzoic acid	233	9,800	Benzoic acid	230	10,000	10
95% ethanol	<i>m</i> -Iodonitrobenzene	ca. 262	6,400	Nitrobenzene	260	8,000	11, 12
Cyclohexane	<i>m</i> -Iodoaniline	{ ca. 232 239	{ 10,400 8,700	Aniline	233	9,000	10
Ethanol	<i>m</i> -Iodoacetanilide	246	13,500	Acetanilide	242	14,500	13
Cyclohexane	<i>m</i> -Bromotoacetophenone	{ 240 245-246	{ 10,000 8,000	Acetophenone	238-239	12,500	10
Hexane	<i>m</i> -Bromobenzaldehyde	242	11,500	Benzaldehyde	241	14,000	10
95% ethanol	<i>m</i> -Bromobenzoic acid	225	8,500	Benzoic acid	228	10,000	14
95% ethanol	<i>m</i> -Bromonitrobenzene	ca. 259	6,200	Nitrobenzene	260	8,000	11, 12
Cyclohexane	<i>m</i> -Bromoaniline	235	7,800	Aniline	233	9,000	10
Ethanol	<i>m</i> -Bromoacetanilide	246	14,000	Acetanilide	242	14,500	13
Cyclohexane	<i>m</i> -Chloroacetophenone	239	10,000	Acetophenone	239	12,500	10
Hexane	<i>m</i> -Chlorobenzaldehyde	241-242	11,500	Benzaldehyde	241	14,000	10
95% ethanol	<i>m</i> -Chlorobenzoic acid	230	8,500	Benzoic acid	228	10,000	14
95% ethanol	<i>m</i> -Chloronitrobenzene	ca. 258	7,200	Nitrobenzene	260	8,000	11, 12
Cyclohexane	<i>m</i> -Chloroaniline	235	8,500	Aniline	233	9,000	10
Ethanol	<i>m</i> -Chloroacetanilide	245	14,900	Acetanilide	242	14,500	13

^a Absorption band represents absorption mainly due to 2,3,5,6-tetramethylbenzene (ϵ_{211} 8500 at 214 m μ).

association effects. Further, and partly because of this, the buttressing effect is frequently not detected in the spectra of *m*-substituted benzene derivatives. For reasons which will be explained elsewhere, acetophenones and nitrobenzenes provide favorable examples in the study of this effect.

At this point, the choice of interference radii for halogen atoms can be discussed. If we assume that the chlorine atom does not exert an appreciable buttressing effect, a simple scale diagram shows that the effective interference radius of the chlorine atom is less than 2.0 Å., assuming an effective interference radius of 0.95 Å. for hydrogen (using a value of 1.2 Å. for hydrogen, a corresponding value of 1.8 Å. is obtained for the chlorine atom). The maximum error for the value of the chlorine atom, however, is probably as high as 0.4 Å., because among other uncertainties the value depends on the hydrogen-radius, which has been estimated to be accurate only to within 0.1 Å. Further, apart from the other variables mentioned in Part I,² the possible buttressing effect of the other substituent on the *o*-hydrogen atom has been neglected (see also below). As it is, an interference radius for the chlorine atom of less than 2.0 Å. receives support from the value

of 1.73 Å. obtained for the chlorine atom by Bastiansen¹⁵ and from the accepted van der Waals radius for chlorine of 1.8 Å.¹⁶

For bromine, the buttressing effect is more pronounced. It is detectable in most *m*-isomers, occasionally causing the B-band to appear as an inflection only (*cf.* 14). Consequently, an effective interference radius of about 2.0 ± 0.4 Å. is indicated, which may be compared with the van der Waals radius of 1.95 Å.¹⁶ and with the value of 1.81 Å. obtained by Bastiansen¹⁵ from electron diffraction data. Whatever the exact value may be, the data even at this stage suggest that careful spectral analysis, given favorable circumstances, may detect the interactions involving the fringe of the van der Waals interference radii.

For iodine, as expected, the buttressing effect is yet more pronounced and the B-band of *m*-isomers occurs more frequently only as an inflection (and hence incidentally is less reliable for the accurate determination of absorption intensities). This suggests that the maximum effective interference radius of iodine is slightly greater than 2.0 Å. and the value of 2.1 ± 0.4 Å. may be suggested for iodine (*cf.* the van der Waals radius of 2.15 Å.¹⁶ and Bastiansen's value of 1.91 Å.¹⁵ for iodine).

Further evidence for a buttressing effect is provided by the observation that the combined ap-

(8) W. F. Forbes and W. A. Mueller, *Can. J. Chem.*, **33**, 1145 (1955).

(9) E. A. Walker and J. R. Young, *J. Chem. Soc.*, 2041 (1957).

(10) Data obtained in these laboratories.

(11) H. E. Ungnade, *This Journal*, **76**, 1601 (1954).

(12) M. J. Kamlet and D. J. Glover, *ibid.*, **77**, 5696 (1955).

(13) H. E. Ungnade, *ibid.*, **76**, 5133 (1954).

(14) C. M. Moser and A. I. Kohlenberg, *J. Chem. Soc.*, 804 (1951).

(15) O. Bastiansen, *Acta Chem. Scand.*, **4**, 926 (1950).

(16) L. Pauling, "The Nature of the Chemical Bond," 2nd. ed., Cornell University Press, Ithaca, N. Y., 1948, p. 189.

TABLE II
 ABSORPTION BANDS OF 2,5-DINITRO-1,4-DICHLOROBENZENE AND REFERENCE COMPOUNDS

Compound	Solvent	λ_{\max} , $m\mu$		ϵ_{\max}		λ_{\max} , $m\mu$		ϵ_{\max}		Ref.
		λ_{\max} , $m\mu$	ϵ_{\max}	λ_{\max} , $m\mu$	ϵ_{\max}	λ_{\max} , $m\mu$	ϵ_{\max}	λ_{\max} , $m\mu$	ϵ_{\max}	
2,5-Dinitro-1,4-dichlorobenzene	Water	221	23,900	236	..	252.5	6250	322.5	2720	18
<i>m</i> -Chloronitrobenzene	Water	208.5	17,300	224	6800	264	7100	313	1300	19
<i>o</i> -Chloronitrobenzene	Water	209	13,700	228	4400	260	4000	310	1400	19

parent effect of two *o*-substituents is sometimes very much greater than that of one. This previously has been ascribed by Hedden and Brown to the buttressing effect,¹⁷ and we accept this interpretation with only a slight modification. Thus, the fact that two *o*-groups sometimes have more than twice the effect of one *o*-group does not necessarily imply a buttressing effect. It may be explained by the existence of *s-cis* and *s-trans* configurational isomers.

It may also be shown that identification of the buttressing effect is not by any means limited to simple molecules and actually becomes frequently more important in spectral analyses of more complex molecules. This is illustrated by the following examples.

2-Carboxy-4,5-dimethoxy-2'-nitrobiphenyl absorbs as follows (see Fig. 1): λ_{\max} 223 $m\mu$, ϵ 38,000; λ_{\max} 256 $m\mu$, ϵ 16,000; λ_{inf} 296 $m\mu$, ϵ 6000.

The band at 256 $m\mu$ is ascribed to nitrobenzene absorption (nitrobenzene in ethanolic solution absorbs with ϵ_{\max} 8000 at 257 $m\mu$). The increased absorption in the biphenyl derivative is presumably due to additional absorption because of the other benzene ring, as well as due to interactions involving both rings. The inflection at 296 $m\mu$ presumably represents C-band absorption and is associated with the second benzene ring. It may be compared to a similar absorption band for *m*-anisic acid in ethanol (ϵ_{\max} 2450 at 293 $m\mu$ ¹⁴). The increased absorption intensity is again ascribed to the other benzene ring and biphenyl conjugation.

On introducing an *m*-methyl group the spectrum obtained (see Fig. 1) is λ_{\max} 218 $m\mu$, ϵ 33,000; λ_{inf} 256 $m\mu$, ϵ 10,700; λ_{inf} 294 $m\mu$, ϵ 4500. Both bands are evidently affected and the simplest explanation to account for the changes is that the methyl group dislodges the nitro group by means of the buttressing effect. This in turn increases the interplanar angle of the biphenyl system and consequently the decreased absorption intensity is observed.

In concluding this section, it should be emphasized that in a relatively complex spectral analysis, great care must be taken in the assignment of absorption bands. For example, it has been suggested that an inflection at 236 $m\mu$ in the spectrum of 2,5-dinitro-1,4-dichlorobenzene may be due to the buttressing effect.¹⁸ However, the spectrum of this tetrasubstituted compound, largely for steric reasons, will be comprised of the spectra of the disubstituted parent compounds.^{2,3} In this way, since *o*- and *m*-chloronitrobenzenes absorb maximally at four positions, it seems unnecessary to associate the inflection at 236 $m\mu$ with a buttressing effect

(see Table II). More probably, the inflection corresponds to the 228 $m\mu$ band in *o*-chloronitrobenzene slightly moved to longer wave length on account of the additional substituents.

Steric Interactions in Molecules Possessing a High Degree of Rigidity.—Examples where at least in theory ultraviolet spectra may provide an unusually sensitive index of steric inhibition of resonance (orbital delocalization) are rigid molecules which cannot readily take up alternate configurations. This is illustrated in Fig. 2.

In Fig. 2A solid lines indicate the potential energy curves of a hypothetical non-hindered molecule A-B, where electronic interaction across the central bond is possible and planarity represents the energetically most favorable configuration. The dotted lines indicate potential energy curves if steric interactions are present, but are small. These steric interactions may raise the energy levels of both ground and electronic excited states. As shown in Fig. 2A, the transition energy of the absorption will hardly be affected because the steric interaction is largely hidden on account of the permitted free rotation as indicated by shallow energy curves. Figure 2B indicates a similar system A-B in which the molecule is approximately coplanar because of molecular environment. Free rotation is now considerably more difficult, and consequently the slightly sterically hindered coplanar conformation will exert a greater effect on the absorption band. This follows because even a small interplanar angle appreciably raises the energy level of the ground state and hence more transitions will be confined to the coplanar conformation where the steric effect will be apparent. In this way, it is conceivable that a steric interaction of say 3 kcal./mole or less (*i.e.*, steric hindrance which will not normally be detectable if there is free rotation) may cause a wave length shift in a molecule when the atomic environment does not permit free rotation. Further, on altering the interplanar angle θ , a considerable energy increase will occur in both ground and electronic excited states, and therefore the over-all transition energy in a more rigid system may be considerably altered. This variation may cause either a positive or a negative wave length shift, depending on the relative positions of ground and excited states energy levels.

This increased steric interference, presumed to be due to greater rigidity, has been noted previously for polycyclic systems by Braude and Sondheimer²⁰ (and references cited there), and in all probability this type of steric interference accounts also for many of the "anomalous" spectra of other cyclic systems.^{21,22} To illustrate the importance of rigid-

(17) G. D. Hedden and W. G. Brown, *THIS JOURNAL*, **75**, 3744 (1953).

(18) G. S. Hammond and F. J. Modic, *ibid.*, **75**, 1385 (1953).

(19) L. Doub and J. M. Vandenbelt, *ibid.*, **71**, 2414 (1949).

(20) E. A. Braude and F. Sondheimer, *J. Chem. Soc.*, 3773 (1955).

(21) R. N. Moore and G. S. Fisher, *THIS JOURNAL*, **78**, 4362 (1956); R. C. Cookson, *J. Chem. Soc.*, 282 (1954); O. H. Wheeler, *THIS JOURNAL*, **78**, 3216 (1956); W. M. Schubert and W. A. Sweeney,

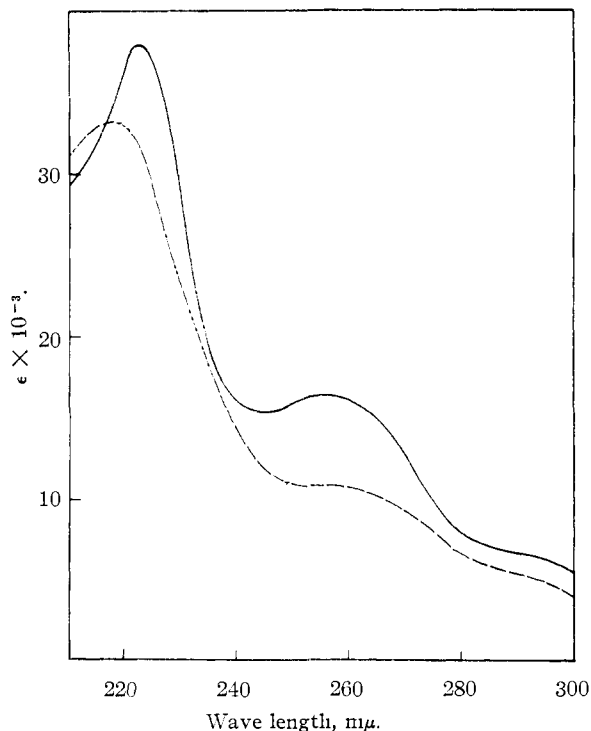


Fig. 1.—Ultraviolet absorption spectra in ethanol: —, 2-carboxy-4,5-dimethoxy-2'-nitrobiphenyl; ·····, 2-carboxy-4,5-dimethoxy-2'-nitro-3'-methylbiphenyl.

ity in a system we may consider the recently reported data for some azulenes, which are listed in Table III. The effect observed for 5,6-benzazu-

TABLE III

MAIN ULTRAVIOLET ABSORPTION MAXIMA (LONG WAVE LENGTHS) OF AZULENES IN CYCLOHEXANE ²³		
Compound	λ_{\max} , m μ	ϵ_{\max} , m μ
1,2-Benzazulene	383	4600
5,6-Benzazulene	355.5	3550
Azulene	338.5	4000

lene, which appears to be steric in origin but cannot be explained in terms of conventional interference radii,^{3,23} may now tentatively be ascribed to this type of steric interaction. It may be noted that in this example molecular models indicate an interference radius for hydrogen of *ca.* 1.0 Å., approaching the value usually accepted for the van der Waals radius and slightly in excess of the value of 0.95 ± 0.1 Å.², *i.e.*, the value which normally can be detected in ultraviolet spectra.

Conclusions

It has been shown in previous communications that the *ortho*-effect in the B-band of ultraviolet absorption spectra can best be explained by assuming the operation of steric interactions associated with repulsions between vicinal non-bonded atoms.

ibid., **77**, 2297 (1955); E. A. Braude, *Chemistry & Industry*, 1557 (1954); R. Huisgen, W. Rapp, I. Ugi, H. Walz and E. Mergenthaler, *Ann.*, **586**, 1 (1954).

(22) E. Heilbronner and R. Gerdil, *Helv. Chim. Acta*, **39**, 1996 (1956); W. F. Forbes, *ibid.*, **40**, in press.

(23) E. Kloster-Jensen, E. Kováts, A. Eschenmoser and E. Heilbronner, *ibid.*, **39**, 1051 (1956).

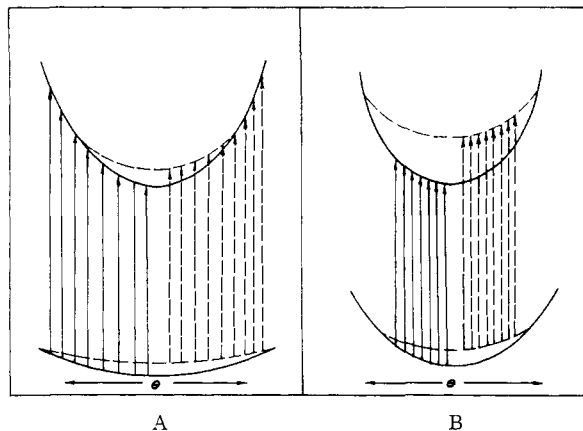


Fig. 2.—Schematic representation of electronic transitions between ground and excited states for non-rigid (A) and more-rigid (B) systems in the absence (solid lines) or presence (dotted lines) of small steric interactions.

Extending this hypothesis we can conclude that the buttressing effect must also be taken into account, particularly when analyzing the spectra of more complex molecules. However, care is required in the spectral analysis of complex molecules, because only infrequently can the buttressing effect be identified with certainty.

The limit of the interference radius, that is the smallest steric interaction which may be detected in the B-band of ultraviolet spectra, probably varies with the compound under investigation. An interference radius larger than the normal value can sometimes be detected in molecules where free rotation is restricted, since this can be shown to increase the sensitivity to steric interactions in certain examples. Unfortunately, in molecules of this type, other indirect interactions frequently so modify both energy curves that no simple generalizations are justified and each set of examples must be examined separately.

All the data discussed indicate that interactions involving interference radii tending toward van der Waals radii often play their part in determining ultraviolet spectra. Previous suggestions that much smaller interference radii generally should be used in estimating steric effects are ascribed to inadequate spectral analyses.

Experimental

2-Carboxy-4,5-dimethoxy-2'-nitrobiphenyl and 2-Carboxy-4,5-dimethoxy-2'-nitro-3'-methylbiphenyl.—We are grateful to Dr. Z. Valenta of the University of New Brunswick for generous samples of these compounds. The melting points of the substances were 207 and 216°, respectively.²⁴

The preparation of all the other compounds has previously been described,³ or is well known. All spectra were determined under the same conditions as described in the first paper of this series.² The spectral data are recorded in Table I and Fig. 1. It is seen from Fig. 1, that for this example the band shape for the nitrobenzene B-band remains reasonably similar, and this general similarity of band shape is also observed for most of the pairs of compounds listed in Table I. Consequently, since no quantitative comparisons are intended at present, the molecular extinction coefficients

(24) K. Wieser, Z. Valenta, A. J. Manson and F. W. Stonner, *This Journal*, **77**, 675 (1955).

(ϵ) are assumed to provide an adequate measure of the intensity changes. This statement is not intended to preclude minor changes in band shape on *m*-substitution. However, it may be noted that frequently ϵ_{\max} and oscillation strengths are directly related one to another (*cf.* ref. 25).

(25) B. M. Wepster, *Rec. trav. chim.*, **76**, 335 (1957).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WEST VIRGINIA UNIVERSITY]

A Novel Ring Closure Involving a Nitro Group; Preparation of Phenanthridine-5-oxide¹

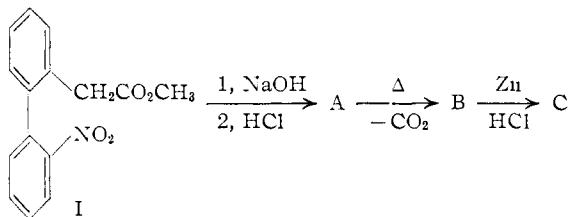
BY CHESTER W. MUTH, JOHN C. ELLERS AND O. FRED FOLMER

RECEIVED JULY 3, 1957

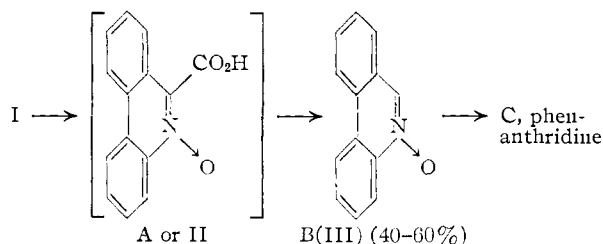
In the biphenyl series a nitro group in the 2-position will react with an activated methylene group in the 2'-position in the presence of sodium hydroxide or sodium methoxide to form substituted phenanthridine-5-oxides. Cyano, carbomethoxy and carbamyl groups are activating groups; hydrogen, hydroxyl, bromo and carboxyl do not serve as activators.

Discussion

An unexpected reaction was observed when methyl 2-(2'-nitrophenyl)-phenylacetate (I)² was warmed with methanolic sodium hydroxide in an effort to saponify it. The product obtained was not the parent acid of I, but was compound A, an acid, which had no nitro group and which decomposed with gas evolution to yield compound B. Compound B could be treated with zinc and hydrochloric acid to produce compound C.



Compound C was identified as phenanthridine by comparison of its picrate with that of an authentic sample. Compound B was identified as phenanthridine-5-oxide (III) by m.m.p., infrared spectrum and by its picrate. Since the gas given off in the decomposition of compound A was carbon dioxide, the structure postulated for compound A is 6-carboxyphenanthridine-5-oxide (II). With this information the foregoing reactions may be rewritten



Since the reaction was very rapid under mild conditions and since the literature did not disclose such a reaction, a further investigation appeared prof-

(1) Supported by the National Science Foundation, Research Grant G-1581, whose help we wish to gratefully acknowledge. From the Ph.D. dissertation of O. F. F., 1957, and M.S. thesis of J. C. E., 1958, both from West Virginia University. Presented in part at the 130th Meeting of the A.C.S., Atlantic City, N. J., September, 1956.

(2) C. W. Muth, W. L. Sung and Z. B. Papanastassiou, *THIS JOURNAL*, **77**, 3393 (1955).

able. The further study of this reaction was approached along two lines. First, the reaction of ester I was investigated under a variety of conditions to learn more about the yields, the structure of the acid material and the mechanism of the reaction. Secondly, the carbomethoxy group was replaced by other groups and the resulting compounds were tested for this cyclization.

The bases used which effected the cyclization of ester I were sodium hydroxide in methanol or water and sodium methoxide in methanol. The results are summarized in Table II.

With low base concentration ester I yielded 6-carbomethoxyphenanthridine-5-oxide (IV), whereas ester I with high base concentration and longer reaction time produced acid A and III or acid II and III. Acid A evolved a gas at 120-138° and melted at about 200°, whereas acid II melted at about 200° with no previous gas evolution. Both acids A and II reacted with diazomethane to give the same ester; both yielded phenanthridine-5-oxide when warmed with dimethylformamide and their infrared spectra were nearly identical.

The use of a nitrogen atmosphere³ or an equal molar quantity of hydroquinone had no effect on the reaction, hence it is assumed that the cyclization is not an oxidation-reduction process. Since the cyclization is not affected by acids (concentrated or dilute sulfuric acids) or by dehydrating agents (acetic anhydride or thionyl chloride) nor by ammonium hydroxide, but only by strong bases (sodium hydroxide and sodium methoxide) it seems likely that the cyclization is a base-catalyzed reaction similar to an aldol condensation.

That hydrolysis of the ester group is not a necessary condition for the cyclization is shown by the production of the cyclized ester, 6-carbomethoxyphenanthridine-5-oxide (IV). This is also shown by the fact that the parent acid, 2-(2'-nitrophenyl)-phenylacetic acid (V), of ester I does not cyclize.

Seven model compounds were subjected to basic conditions to determine whether cyclization would occur. These compounds were the same as methyl 2-(2'-nitrophenyl)-phenylacetate (I) except that the carbomethoxy group was replaced (see V-XI).

With R as carboxyl (V), hydrogen (VI), hydroxyl (VII) and bromine (VIII) no cyclization

(3) T. Tsuruta, T. Fueno and J. Furukawa, *ibid.*, **77**, 3265 (1955).