aqueous silver nitrate. It had $n^{25}\mathrm{D}$ 1.4639. The n.m.r. spectrum showed two different olefinic proton multiplets centering at 3.85 and 4.11 τ.

Anal. Calcd. for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found: C, 70.89; H, 7.90.

Acetolysis of *exo*-Dehydronorbornyl *p*-Bromobenzenesulfonate.—*exo*-Dehydronorbornyl *p*-bromobenzenesulfonate, m.p. 79–81°[26] (prepared from alcohol, with analysis as 99% pure, 500 mg., 1.8 mmoles), was added to 50 ml. of glacial acetic acid and allowed to stand in the dark at room temperature for 24 hr. The solvolysis mixture then was poured into ice-water and extracted five times with 50-ml. portions of pentane. The combined pentane solution was then extracted once with water and once with 5% sodium carbonate, and dried over anhydrous magnesium sulfate. The pentane was removed by distilling through a fractionating column to minimize loss of product. The products then were analyzed by gas chromatography as 92.0% nortricyclyl acetate (XII) and 8.0% dehydronorbornyl acetate (XI). Results were essentially identical (92.2% XII and 7.8% XI) when potassium acetate was present in the solvolysis mixture.

Acetolysis of Nortricyclyl *p*-Bromobenzenesulfonate.—The procedure was as above except that the reaction time was 3 days.

The *p*-bromobenzenesulfonate, m.p. 80–82°,[26] was prepared from nortricyclyl alcohol of 99% purity by analysis (vapor-phase chromatography). The solvolysis products contained 95.4% of nortricyclyl acetate (XII) and 4.6% of dehydronorbornyl acetate (XI). With potassium acetate present, the product was 95.0% nortricyclyl acetate and 5.0% dehydronorbornyl acetate.

Methanolysis of Nortricyclyl *p*-Bromobenzenesulfonate.—The methanolysis reactions were run in the same fashion as the acetolyses except that the reaction time was 10 hr. at room temperature. Analysis showed 93.0% of nortricyclyl methyl ether (XII) and 7.0% of dehydronorbornyl methyl ether (XI). In the presence of pyridine, the product analysis was 93.5% XII and 6.5% XI.

Methanolysis of *exo*-Dehydronorbornyl *p*-Bromobenzenesulfonate.—The reaction time was 3.2 hr. at room temperature. The methyl ether product was 92.0% of XII and 8.0% of XI in the presence or absence of pyridine.

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[26] S. Winstein, H. M. Walborsky and K. Schreiber, *J. Am. Chem. Soc.*, **72**, 5795 (1950).

[CONTRIBUTION FROM THE ORGANIC CHEMISTRY DIVISION, U. S. NAVAL ORDNANCE LABORATORY, WHITE OAK, SILVER SPRING, MD.]

Steric Enhancement of Resonance. I. Absorption Spectra of the Alkyltrinitrobenzenes

BY MORTIMER J. KAMLET, JOHN C. HOFFSOMMER AND HORST G. ADOLPH

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The absorption spectra of the alkyltrinitrobenzenes between 214 and 400 mμ are considered as comprising bands deriving from two non-equivalent N → V transitions and over-all substituent effects are regarded as summations of the effects on the individual bands. The influence of alkyl group bulk on one band is consistent with steric inhibition of resonance in the classical sense, but to explain effects on the second transition the existence of a hitherto undescribed phenomenon, termed "steric enhancement of resonance," is suggested.

Progressive hypsochromic–hypochromic spectral displacements in the series [nitrobenzene, *o*-nitrotoluene, *o*-nitrocumene, *o*-nitro-*t*-butylbenzene (Table I)][1] and [trinitrobenzene, trinitromesitylene, trinitro-*t*-butylxylene][2] have been ascribed to steric inhibition of resonance, *i.e.*, progressively decreasing ring-nitro interaction with increasing bulk of *o*-alkyl substituents. We wish now to report that in the related series [*sym*-trinitrobenzene (I), 2,4,6-trinitrotoluene (II), 1-ethyl-2,4,6-trinitrobenzene (III), 2,4,6-trinitrocumene (IV), 1-*t*-butyl-2,4,6-trinitrobenzene (V) (Table I, Fig. 1)] steric inhibition of resonance will not alone account for spectra–structure variations and to suggest the operation of a further phenomenon which may properly be termed "steric diminution of electronic suppression of resonance interaction" or, more succinctly, "steric enhancement of resonance."

In comparing the spectrum of II in methanol with that of I, it is observed that the decrease in band-height is accompanied by a *bathochromic* displacement of $\lambda_{\max}$. More readily noted is the broadening of the spectral envelope toward longer wave lengths with the consequence that the half-band integrated intensity[3] decreases only 17% as compared with a 29% decrease in $\epsilon_{\max}$ (Table I). With III a further decrease in $\epsilon_{\max}$ is accompanied by a further small bathochromic shift, a slight broadening of the band toward longer wave lengths and no significant change in half-band integrated intensity. Of interest is the appearance of an inflection at ~255 mμ. In the spectrum of IV the original band-maximum persists only as an inflection at ~230 mμ and the inflection at ~255 mμ has grown more pronounced. The spectral envelope in the case of V has broadened further still, the 255 mμ inflection has become a maximum and not even a change in slope remains to mark the original position of $\lambda_{\max}$. It is noteworthy that the half-band integrated intensity of the newly emerged band of V is of the order observed for *p*-nitrotoluene (Table I) and expected for *p*-nitro-*t*-butylbenzene.[4]

These unusual substituent effects may more readily be rationalized if consideration is first devoted to spectra–structure variations in the series nitrobenzene, *m*-dinitrobenzene, *sym*-tri-

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[1] W. G. Brown and H. Reagan, *J. Am. Chem. Soc.*, **69**, 1032 (1947).

[2] P. Fielding and R. J. W. Le Fèvre, *J. Chem. Soc.*, 2812 (1950).

[3] Since the total transition probability is measured by $\int \epsilon d\nu$ over the band, we feel this to be a better intensity measure for intercomparison purposes than $\epsilon_{\max}$. Most of the bands herein described, however, are strongly overlapped by high-intensity shorter-wave length bands. For this reason integrated intensities were taken only from the band maxima toward the red. These half-band integrated intensities undoubtedly still incorporate substantial but undetermined contributitions from the underlying tails of the shorter-wave length transitions, so that intercomparisons are meaningful only in a qualitative sense.

[4] The spectra of *p*-nitrotoluene and *p*-nitro-*t*-butylbenzene in methanol should show no greater differences than have been reported for these compounds in isoöctane (Table I).[1] From an inspection of Fig. 1 of ref. 1, they appear to show closely comparable half-band integrated intensities.

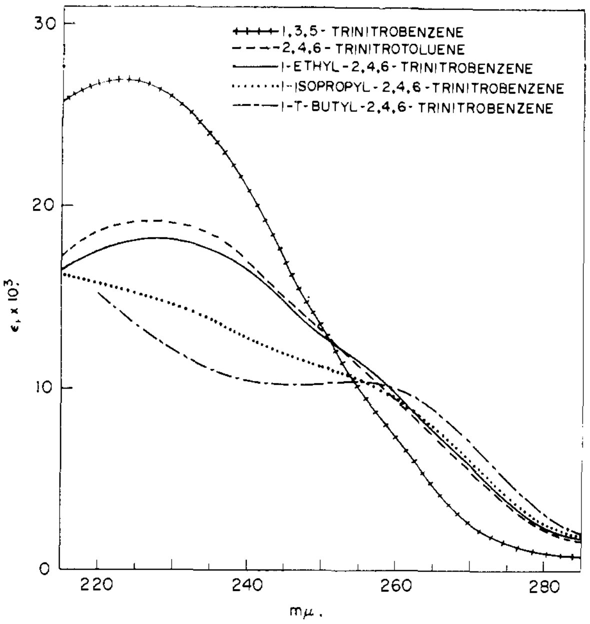
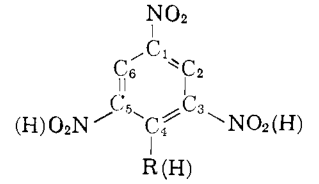
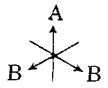


Fig. 1.—Absorption spectra of the alkyltrinitrobenzenes in methanol.

nitrobenzene. The 260 mμ band in the nitrobenzene spectrum is attributed[5] to an electronic transition in the direction $(C_4^+ \rightarrow C_1{=}NO_2^-)$. In *m*-dinitrobenzene two mutually equivalent electronic transitions, $(C_4^+ \rightarrow C_1{=}NO_2^-)$ and $(C_6^+ \rightarrow C_3{=}NO_2^-)$, and in *sym*-trinitrobenzene three mutually equivalent electronic transitions, $(C_4^+ \rightarrow C_1{=}NO_2^-)$, $(C_6^+ \rightarrow C_3{=}NO_2^-)$ and $(C_2^+ \rightarrow C_5{=}NO_2^-)$, contribute to progressively larger total transition probabilities as evidenced by increasing values of ϵ_{max} and half-band integrated intensities.[6]





The pronounced hypsochromic displacement of the maximum in going from mono- to di- to trinitrobenzene may be ascribed to an increase in the energy required for transitions to the individual electronic excited states as, in the electronic ground state, the added nitro groups effect successively greater electron withdrawal from C_2, C_4 and C_6, *i.e.*, transition energy to the excited state $(C_4^+ \rightarrow C_1{=}NO_2^-)$ increases with decreasing ground state electron density at C_4. To the extent that these hypsochromic shifts mark lessened interaction energies of the individual nitro groups with the ring in both ground and electronic excited states, this phenomenon may be termed "electronic suppression of resonance interaction."

Table I

Ultraviolet Spectra

Compound	λ_{max}, mμ[a]	$\epsilon \times 10^{-3}$	Half-band integrated intensity[d]
1,3,5-Trinitrobenzene	224 (M)	26.9	6.20
	225 (E)[c]	26.0	
2,4,6-Trinitrotoluene	227 (M)	19.2	5.16
1-Ethyl-2,4,6-trinitro-	227.5 (M)	18.3	
benzene	~255s	~11.5	5.05
2,4,6-Trinitrocumene	~230s (M)	~14.6	
	~255s	~10.5	
1-*t*-Butyl-2,4,6-trinitrobenzene	255 (M)	10.4	1.64
Nitrobenzene	259.5 (M)	8.1	1.29
	260 (E)[c]	8.1	
	252 (I)[b]	8.6	
m-Dinitrobenzene	234 (M)	17.0	3.66
	235 (E)[c]	17.3	
o-Nitrotoluene	250 (I)[b]	5.95	
o-Nitrocumene	247 (I)[b]	3.76	
o-Nitro-*t*-butylbenzene	~260s (I)[b]	~2.0	
p-Nitrotoluene	273.5 (M)	9.7	1.50
	264 (I)[b]	10.25	
p-Nitro-*t*-butylbenzene	265 (I)[b]	10.7	

[a] s = shoulder or inflection; solvent: M, methanol; E, 96% ethanol; I, isoöctane. [b] Ref. 1. [c] Ref. 2. [d] $l.\ cm.^{-1}/mole\ cm. \times 10^{-7}$.

Such secondary resonance and inductive effects on ground state electron density at C_4 may also serve to explain the relative positions of λ_{max} for other *m*-substituted nitrobenzenes. C_3-Substituents which, like nitro, decrease the ground state C_4-electron density, as evidenced by their being ring-deactivating toward electrophilic substitution, shift λ_{max} hypsochromically relative to nitrobenzene. Conversely, ring-activating C_3-substituents increase the C_4-electron density and shift the maximum bathochromically (Table II). Generally the magnitudes of the shifts correlate well with σ_{para} for the substituents.[7]

Table II

Spectra of *m*-Substituted Nitrobenzenes in Methanol

$3\text{-}YC_6H_4NO_2$ Y =	λ_{max}, mμ	log ε	σ_{para}
NO_2	234	4.23	+1.27
NH_3^+	252.5[a]	3.92	+0.9[c]
COOH	256.5	3.87	+ .73
Cl	257	3.88	+ .23
Br	259	3.84	+ .23
H	259.5	3.91	0
CH_3	265	3.89	−0.17
OH	269[a]	3.77	−0.36
O^-	288[b]	3.60	−1.00

[a] Solvent: 90% methanol, 1.2 *N* HCl. [b] Solvent: 90% methanol, 0.1 *N* KOH. [c] Estimated to be similar to value for Me_3N^+.

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(5) W. F. Forbes, *Can. J. Chem.*, **36**, 1350 (1958); W. F. Forbes, A. S. Ralph and R. Gosine, *ibid.*, **36**, 868 (1958). Forbes' interpretation of effects of *m*-substituents on nitrobenzene spectra, although not explicitly stated in the same manner, appears on the whole to agree with our own (present report and ref. 8).

(6) We had at one time considered that the approximate 1/2/3 ratio of ϵ_{max} for mono-, di- and trinitrobenzene might be directly related to the number of mutually equivalent transition axes, especially inasmuch as other such series, *e.g.*, (biphenyl, *m*-terphenyl, 1,3,5-triphenylbenzene) appear to show the same 1/2/3 relationship. Since half-band integrated intensities, which are less influenced by band overlap than ϵ_{max}, show a relative ratio of 1/2.8/4.8, we now feel that the ϵ_{max} ratio cannot be so simply explained.

(7) Relationships between the various substituent constants and spectra of nitroaromatic compounds will be discussed in detail in a forthcoming paper.

A similar argument has been advanced by Kamlet and Glover[8] to account for the hypsochromic displacement of λ_{max} for *p*,β-dinitrostyrene relative to β-nitrostyrene and the bathochromic displacement of λ_{max} for 3,4-methylenedioxy-β-nitrostyrene relative to *p*-methoxy-β-nitrostyrene.

In relating the alkyltrinitrobenzene spectra to that of the parent compound, it is evident that the transition $(C_4^+ \rightarrow C_1{=}NO_2^-)$ is no longer exactly equivalent with the transitions $(C_6^+ \rightarrow C_3{=}NO_2^-)$ and $(C_2^+ \rightarrow C_5{=}NO_2^-)$. These may be considered as giving rise to two discrete N → V bands, labeled A for the transition in the alkyl-nitro axis, B for the transitions in the other axes. Over-all substituent effects on spectra may then be treated as summations of the effects on the individual bands.

The effects on band B, the original 224 mμ band of nitrobenzene, may readily be discerned as following those described for the *o*-alkylnitrobenzenes,[1] *i.e.*, a progressive diminution in intensity with increasing bulk of the alkyl group until, in the case of isopropyltrinitrobenzene (IV), the band persists only as an inflection superimposed on the tail of a high-intensity shorter-wave length transition and, in the case of the *t*-butyl derivative V, even the inflection has disappeared. Steric inhibition of resonance in the classical sense, involving the C_3- and C_5-nitro groups, offers an adequate explanation for this behavior. The increasingly bulkier alkyl groups progressively force these nitro groups further out of coplanarity with correspondingly decreasing band B transition probabilities. Since the band-heights and half-band integrated intensities are affected to a strong but undetermined extent by band-overlap with both the high-shorter-wave length transition and the emerging band A, the semi-quantitative relationship $[\cos^2 \theta = \epsilon/\epsilon_0]$[9] would lead to fallacious estimates of the degree of non-coplanarity of the C_3- and C_5-nitro groups. In a qualitative sense, however, relative effects of substituents in this series and the *o*-alkylnitrobenzene series appear to parallel one another.

To evaluate substituent effects on band A, two factors must be considered: (1) the normal bathochromic–hyperchromic influence of *p*-alkyl substituents such as causes a shift in λ_{max} (ϵ) from 259.5 mμ (8100) in nitrobenzene to 273.5 mμ (9700) in *p*-nitrotoluene and (2) the decreasing "electronic suppression of resonance interaction" which accompanies increasing ground state electron density at C_4 as the C_3- and C_5-nitro groups are forced from coplanarity. The latter effect is "steric enhancement of resonance."

The first factor undoubtedly contributes to the bathochromic position of the maximum of II relative to I and the broadening of the spectral envelope. In comparing II, III, IV and V, however, any further effect on the A band should be no greater than is evident from the very slight difference in the spectra of *p*-nitrotoluene and *p*-nitro-*t*-butylbenzene in isoöctane (Table I).

The further displacements to longer wave lengths of the band-edges of III-V relative to II and the emergence of inflections in III and IV which grow to a full maximum in V we attribute solely to steric enhancement of resonance which may be detailed as: C_3- and C_5-nitro groups may withdraw electrons from C_4 by two mechanisms, induction (the −I effect of Ingold[10]) and mesomerism (the −M effect). As the nitro groups are forced from coplanarity, orbital overlap decreases as does the −M effect until, when the nitro groups are completely non-coplanar, only the −I effect is in operation. As a consequence, a non-coplanar nitro group decreases ground state electron density at C_4 to a lesser extent than a coplanar nitro group, the energy of the $(C_4^+ \rightarrow C_1{=}NO_2^-)$ electronic transition is diminished and band A is shifted toward the red.

Relative magnitudes of electron withdrawal by coplanar and non-coplanar conjugating substituents may be evaluated by comparing σ_{para} and σ_I, σ_{para} being a measure of combined inductive and mesomeric effects and σ_I measuring the pure inductive contribution to the substituent constant.[11] For the nitro group these values[12] are +1.27 and +0.63,[11] so that non-coplanar nitro groups at C_3 and C_5 should reduce electron density at C_4 to about half the extent of coplanar nitro groups.

In trinitrobenzene the nitro groups at C_3 and C_5 are essentially coplanar; in *t*-butyltrinitrobenzene (V) they are completely non-coplanar. It is a constructive exercise to assume that the blue-shifts of the maxima of the former compound relative to nitrobenzene and of the latter compound relative to *p*-nitro-*t*-butylbenzene should be proportional to these effects[7] and to compare the predicted position of λ_{max} of V with its observed position. For quantitative transition energy comparisons, computations are best carried out in terms of energy-proportional γ_{max}.[13]

For nitrobenzene, ν_{max} = 38,500 cm.$^{-1}$; for trinitrobenzene, ν_{max} = 44,500 cm.$^{-1}$, $\Delta\nu_{max}$ = 6,000 cm.$^{-1}$. For *p*-nitro-*t*-butylbenzene,[4] ν_{max} = 36,400 cm.$^{-1}$, $\Delta\nu_{max}$ (predicted) = (0.63/1.27) (6,000) = 3,000 cm.$^{-1}$. This leads to a predicted value of ν_{max} of 39,400 cm.$^{-1}$ for V, corresponding to λ_{max} = 254 mμ. This compares, probably more nicely than it should, with the observed value of 255 mμ.

It should be kept in mind that the positions of all of these maxima are displaced to a greater or lesser extent by band-overlap and that reliance on such

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[8] M. J. Kamlet and D. J. Glover, *J. Am. Chem. Soc.*, **77**, 5696 (1955).

[9] E. A. Braude in E. A. Braude and F. C. Nachod, "Determination of Organic Structures by Physical Methods," Academic Press, Inc., New York, N. Y., 1955, p. 174.

[10] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Section 7.

[11] R. W. Taft and I. C. Lewis, *J. Am. Chem. Soc.*, **80**, 2436 (1958).

[12] Since the C_3- and C_5-nitro groups may conjugate directly with C_4, the value is used as it applies to nitroanilines and nitrophenols.

[13] We regret the imposition on the reader to convert his thinking from wave lengths to wave numbers in mid-argument. In an overwhelming majority of the organic and physical-organic chemical literature dealing with ultraviolet spectra, measurements are expressed on a wave length basis. The average practitioner, to whose convenience we defer in this and other papers, is accustomed to thinking in such terms. We recognize, however, that since transition energies are proportional to wave numbers or frequencies, quantitative interrelationships are meaningful only on the latter bases. With the growing utilization of integrated intensities, also meaningful only when expressed in energy-proportional terms, the literature in the field is bound to become increasingly confusing.

simplified calculations can lead to serious misinterpretations. The comparison of half-band integrated intensities of V and *p*-nitro-*t*-butylbenzene (Table I and footnote 4) indicates that this factor does not shift the observed position of the maximum of V very far from its "true" position, but it is impossible to judge to what extent the maxima of the reference compounds have been displaced.

Summations of these effects on the alkyltrinitrobenzene spectra are: band B in II is shifted to the blue by 3–5 $m\mu$ with strongly diminished intensity relative to I due to steric inhibition of resonance; band A is displaced to the red by 10–15 $m\mu$ with slightly increased intensity as a consequence of factor 1, and somewhat further to the red due to steric enhancement of resonance. The resultant is still a fused band with λ_{max} displaced to a slightly greater wave length, strongly reduced ϵ_{max} and a broadened spectral envelope. Going to III, slightly more steric inhibition in band B and steric enhancement in band A have compensating effects on half-band integrated intensity. There is further separation between band B and band A so that band A begins to emerge as an inflection. Steric inhibition decreases band B absorption intensity in IV to the point where the transition is discernible only as an inflection on the tail of a high-intensity shorter-wave length band; steric enhancement causes a bathochromic–hyperchromic displacement of band A with further broadening of the spectral envelope. In V, steric inhibition has caused complete disappearance of band B; steric enhancement has caused band A to emerge as a full maximum whose half-band integrated intensity exceeds that of *p*-nitro-*t*-butylbenzene. The spectrum has become a composite of band A and the tail of the high-intensity shorter-wave length band with no contribution from band B.

Steric enhancement of resonance appears to be a fairly prevalent phenomenon. Further examples will be discussed in subsequent papers of this series.

Experimental

1-Ethyl-2,4,6-trinitrobenzene (III)[14] and 1-*t*-butyl-2,4,6-trinitrobenzene (V)[15] were prepared by literature methods. In the preparation of 2,4,6-trinitrocumene (IV) it was found that better yields (up to 60%) resulted if the crude oil obtained by the method of Fittig, Schaeffer and Koenig[16] was renitrated as follows: 30 g. of the oil dissolved in a mixture of 120 ml. of 90% nitric acid and 600 ml. of 96% sulfuric acid was heated to 115° whereupon a vigorous reaction ensued. After holding the temperature between 120 and 130° for 30 minutes the reaction mixture was drowned on ice and the precipitate recrystallized three times from ethanol. The product had m.p. 107–110°. Other materials were commercially available and were purified by standard methods to meet conventional criteria of purity.

Absorption spectra over the range 214 to 400 $m\mu$ were determined in methanolic solutions using a Cary model 14 spectrophotometer with matched 1-cm. silica cells. Concentrations were 3 to 10 $\times 10^{-5}$ *M*. Previously described precautions[17] were taken to guard against photochemical transformations. Data of Table II are from single determinations: data of Table I in each case represent averages of two complete replicate determinations which agreed to within 1% near the maxima and to within 2% on band-edges. We are satisfied that the relative positions of the band edges of II, III and IV between 260 and 280 $m\mu$ are as shown in Fig. 1.

Half-band integrated intensities were determined as follows: Molar absorbancy index was plotted as a function of wave-number on 10 × 10 to the half-inch graph paper, Keuffel and Esser No. 359-11, 100 × 100 unit squares of which (representing 10^8 l. cm.$^{-1}$/mole cm.) weighed 754 ± 1 mg. The spectra were cut vertically at ν_{max} and the spectral envelopes from ν_{max} toward the red were carefully cut out and weighed. Weights were: nitrobenzene, 97 mg.; dinitrobenzene, 276 mg.; I, 468 mg.; II, 390 mg.; III, 381 mg.; V, 124 mg.; *p*-nitrotoluene, 113 mg.

Acknowledgments.—Helpful comments and suggestions by Drs. D. V. Sickman, J. C. Dacons and L. A. Kaplan are gratefully acknowledged. The work was done under NOL Task FR-44.

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[14] A. Gay-Lussac and H. Ficheroulle, *Mém. poudres*, **36**, 71 (1954).

[15] E. Liss and K. Lohmann, *Ber.*, **89**, 2546 (1956).

[16] R. Fittig, Schaeffer and Koenig, *Ann.*, **149**, 328 (1869).

[17] M. J. Kamlet and L. A. Kaplan, *J. Org. Chem.*, **22**, 576 (1957)

[Joint Contribution from the Department of Chemistry, Fordham University, New York, N. Y., and the Division of Protein Chemistry, C.S.I.R.O., Melbourne, Australia]

Steric Interactions in the Absorption Spectra of 2,2'-Diaroylbiphenyls and Related Compounds. IV.[1] Absorption Spectra and Electronic Interactions in Halogen-substituted Benzophenones

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The infrared and ultraviolet absorption spectra of a number of halogen-substituted benzophenones have been determined. The main ultraviolet absorption bands can be rationalized in terms of locally excited states; that is, it is assumed that the molecule does not preferentially absorb as one conjugated system. The reason for this may be the non-planarity of the molecule. In 2-halogen-substituted benzophenones this non-planarity is clearly indicated by the spectral data. For 4-halogen substituted benzophenones the ultraviolet data indicate an order of apparent mesomeric (resonance) interaction of I > Br > Cl > F in the electronic excited state. Information concerning the actual conformation of some of the benzophenones is also deduced using infrared data. This indicates that a number of substituted benzophenones exist in more than one conformation. In most of the monosubstituted benzophenones investigated, the unsubstituted benzene ring is probably more coplanar with the carbonyl group. As a preliminary observation it is reported that some of the halogen-substituted benzophenones in the solid state afford a strong e.s.r. signal on irradiation with 2537 Å. light.

Introduction

Halogen-substituted benzophenones, like other compounds discussed in this series of papers, are of interest because they represent examples of conjugated molecules which do not absorb ultra-

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[1] Part III, E. J. Moriconi, W. F. O'Connor and W. F. Forbes, *J. Am. Chem. Soc.*, **82**, 5454 (1960).

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