ELECTRONIC SPECTRA OF ORGANIC MOLECULES AND THEIR INTERPRETATION–IX*

SIDE CHAIN AND TERMINAL GROUP EFFECTS ON THE K AND B BANDS OF ANISOLE DERIVATIVES†

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Abstract—The effect of substituents X = OH, NH_2, NH_3^+, Ph, C≡N, Cl, Br, and I in the *o*-, *m*- and *p*-isomers of $MeOC_6H_4CH_2X$ on the K and B bands have been measured and interpreted qualitatively in terms of the hypotheses of terminal and side chain group effects. For the K bands the electron migration accompanying light absorption is along the long axis of molecule so that substituents orientated *para* to each other are terminal groups and can have a large effect on the K band whereas *ortho* and *meta* substituents are in the side chain and, in the absence of steric effects, have a relatively minor effect. For B bands the electron migration is perpendicular to that involved in the K band and consequently *ortho* substituents are terminal groups and strongly influence the intensity and wavelength of the B band while *para* groups have a small effect. For *m*-isomers the behaviour is intermediate between the *o*- and *p*-isomers but is more closely similar to the behaviour of the corresponding *o*-isomer than to the *p*-isomer. The effect of the CH_2Br and CH_2I groups is shown to be, for both K and B bands, very similar to the effects of groups such as carbonyl or vinyl group, which are capable of π–π interaction with the benzene ring.

INTRODUCTION

THE effect of substituents on the electronic spectra of conjugated hydrocarbons has been empirically classified[1] into terminal group effects and side chain group effects. Terminal group effects are those observed when a substituent group replaces a hydrogen at either the electron donating or electron accepting end of the electron migration caused by the light absorption in any allowed transition. Side chain effects are those observed when the substitution takes place at any other position along the path of the electron migration caused by the electronic excitation. For K bands the effect of terminal groups is now fairly well understood and a qualitative, but very detailed, analysis of the effects of different substituents has been given for a number of molecules.[2-5] This interpretation has been made in terms of two factors. (1) The extension of the highly polarizable aromatic conjugated systems by groups which

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[1] A. Burawoy, *Tetrahedron* 2, 122 (1958).
[2] A. Burawoy and A. R. Thompson, *J. Chem. Soc.* 4314 (1956).
[3] A. Burawoy, J. P. Critchley and A. R. Thompson, *Tetrahedron* 4, 403 (1958).
[4] A. Burawoy and J. P. Critchley, *Tetrahedron* 5, 340 (1959).
[5] R. W. H. Berry, P. Brocklehurst and A. Burawoy, *Tetrahedron* 10, 109 (1960).

contain multiple bonds,[2] unshared electrons or easily polarizable single bonds.[6] This has been called the polarizability effect and acts mainly by stabilizing the excited state. (2) The polar effect of the substituting group which is transmitted through the highly polarizable parent system and which is caused by the difference between the effective nuclear charges of the substituent group and the hydrogen which it replaces. The polarizability effect is also dependent in some degree on the effective positive charges on the nuclei and these change on substitution. Thus the separation into two effects is only a first approximation.

The effect of side chain groups, although recognized very early,[1] has been neglected in recent years. The present paper presents new experimental data on the K bands of *o*-, *m*- and *p*-methoxybenzyl derivatives which are used to clarify the different factors operating on both side chain and terminal group effects.

Since this work was completed[7] a paper on the effect on the electronic spectra of *p*-substituents of a similar type (i.e. CH_2X) has appeared.[8] However, the interpretation given there, although similar in some respects, is somewhat different in others to that given in the present series of papers and is confined solely to the K bands, whereas the emphasis in the present work is on the differences in the effect of the different substituents in the *o*-, *m*- and *p*-positions on both the K and B bands. It is gratifying to note that for the compounds common to this present work and Ref. 8, the experimental data, although determined independently on different instruments, agree very closely. This lends confidence to the reality of the small changes in the spectra with change of substituents for some of the substances discussed here.

The K bands of para-*substituted anisoles*

The results obtained for compounds of the type *p*-$MeOC_6H_4CH_2X$, X = H, Cl, Br, I, NH_2. $C{\equiv}N$, C_6H_5 and NH_3^+ are recorded in Table 1 together with similar results for *p*-aminobenzyl[9] and *p*-methoxyphenylbenzyl[9] derivatives.

The new results confirm the conclusion of Burawoy and Spinner[8,9] concerning the importance of polarizability effects since the red shift brought about by replacing one of the methyl hydrogens by different substituents X are in the polarizability order i.e.,

$$I > Br > Cl > NH_2 > CH$$
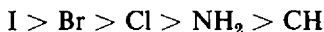
rather than in the inductive order as measured by Taft's o_1 values[10] i.e., in the order

$$C{\equiv}N > Cl > Br > I > OH > NH_2 > Ph$$

This would be the order expected if the only function of the substituent X is to alter the electron density of the benzylic carbon atom to give an excited state of the type I. A similar order for the halogens would also be expected to hold if the resonance structure II were important in determining the nature of the excited state where the negative charge on the para carbon atom is stabilized by the inductive effect of X.
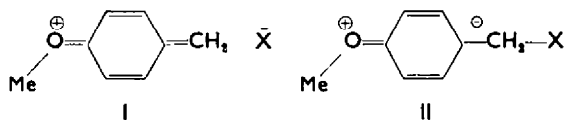
[6] P. Brocklehurst, A. Burawoy and A. R. Thompson, *Tetrahedron* 10, 602 (1960).

[7] J. E. Bloor, Ph.D. Thesis, University of Manchester, England (1959).

[8] E. Spinner, *Spectrochimica Acta* 17, 545 (1961).

[9] A. Burawoy and E. Spinner, *J. Chem. Soc.* 2557 (1955).

[10] R. W. Taft, *J. Phys. Chem.* 64, 1805 (1960).

The large magnitude of the shift brought about by the iodomethyl substituent —CH$_2$I on the K band of anisole is comparable with that brought about by electron attracting groups containing multiple bonds (Table 2) even though the former substituent is fully saturated and contains no π type bonds. This result shows that the distinction between the properties of sigma and pi electrons is not justified, even in qualitative discussions of electronic spectra, since the polarizabilities of sigma bonds between carbon atoms and atoms of high atomic number appear to be comparable magnitude to that of those bonds, e.g.

$$(>C=C<, \quad —C≡C—, \quad >C=0, \quad —C≡N)$$
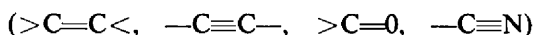
usually described by means of π type linkages. The effects of chloromethyl and bromide (Table 1) are of smaller, but still of considerable magnitude. The importance of the polarizability has also been emphasized by Spinner[8] and by Schubert.[11]

In the *p*-methoxyphenylbenzyl compounds the methoxyl group and the polar substitutent X are separated by two phenyl rings and their mutual interaction in the *ground* state is small so that the order of shifts for the groups of low polarizability is in the inductive order (Table 1). For groups of high polarizability (CH$_2$Br, CH$_2$I) it can be seen from Table 1 that the effects on the K band of *p*-methoxydiphenyl are smaller than on *p*-methoxybenzene; this is an example of the general rule that the larger the parent conjugated system the smaller the polarizability effect of a given substituent.[6]

For the effect of chlorine we find that the shift for the anisole derivative (100 Å) is the same as for the diphenyl derivative (110 Å) on replacing the hydrogen of the methyl by chlorine. In this case the mutual interaction between the two groups of opposing polarity, namely the methylene chloride group and the OMe group, reduces the already small polarizability effect of the CH$_2$Cl group, so that the total effect becomes comparable in magnitude to its effect on the methoxydiphenyl system, where the mutual interaction of the —OMe and —CH$_2$—Cl, now separated by two benzene rings, is much smaller.

The ammonium ion derivatives are of interest since these are one of the few examples where the spectra of the amino compound does not revert to that of the present hydrocarbon on acidification. Thus in the case of the *p*-aminobenzyl derivative the NH$_3$+ group causes a shift of 100 Å and in the case of the *p*-methoxybenzyl derivative the shift is 30 Å and in the case of the *p*-methoxybenzyl derivative the shift is 30 Å. When the NH$_3$+ group is not separated from the benzene ring by a CH$_2$ group the shift relative to anisole is 100 Å.

The K bands of ortho-*substituted anisoles*

The effect of *o*-methyl- substituents on the K bands of monosubstituted benzene derivatives has often previously[12] been interpreted on the assumption that the K bands

[11] W. M. Schubert, H. Steadly and J. M. Craven, *J. Amer. Chem. Soc.* **82,** 1353 (1960).
[12] E. A. Braude and E. S. Wright, *Progress in Stereochemistry* (Edited by W. Klyne) Vol. I, Butterworths, London (1954).

of o- and p-disubstituted isomers would be similar in the absence of steric and other short-range interactions. Braude[13] suggested that the relationship given by Eq. (1) may be used to determine the angle θ through which the π electron system of the primary substituent is rotated by steric interaction with an o-methyl group. ε is the observed molecular extinction coefficient of the o-isomer and ε_0 is the observed molecular extinction coefficient of the p-isomer.

$$\frac{\varepsilon}{\varepsilon_0} = \cos^2 \theta \tag{1}$$

Such an interpretation does not allow for any difference between the electronic effects of side chain and terminal groups. Since the existence of such a difference is basic to the interpretation proposed in the present paper it is of importance to examine the validity of Eq. (1), making use, if possible, of unambiguous experimental data. Such data is only available for the case of substituted benzonitriles. The triple bond of the nitrile group is cylindrically symmetrical about the carbon bond which joints it to the benzene ring, so that twisting it about this bond does not change the amount of overlap between the π electrons of the substituent and the benzene ring. As a consequence of this, the predicted effect of an o-methyl group on the extinction coefficient, if the assumptions underlying the use of Eq. (1) are valid, should be similar to the effect of a p-methyl group and $\varepsilon/\varepsilon_0$ should be unity. The results of Table 2 show that there is a quite definite decrease in the intensity of the o-isomer as compared to the p-isomer corresponding, according to Eq. (1), to a steric twisting of 34°. Such a result shows that the assumption that the electronic effect of a substituent is independent of whether it is placed *ortho* or *para* to a primary* substituent, is incorrect. Moreover, the magnitude of the angle θ calculated by Eq. (1) i.e., 34° is similar in magnitude to the angle calculated by Braude (13) for o-methylstyrene (28°), o-methylbenzaldehyde (21°) and o-methylacetophenone (40°). Thus there seems to be no doubt that a substantial part of the intensity decrease observed on o-methyl substitution compared to p-methyl substitution is really due to the normal electronic differences exerted by the methyl group in the o-position and not, as has been previously supposed, entirely due to steric interactions. Thus, it appears that the angles of twist calculated by the use of (1) are too large. Objections to Braude's theory on other grounds have also been made recently by Suzuki.[14]

In order to elucidate more clearly the nature of the difference between the effects of a secondary substituent in different positions relative to a primary substituent we have prepared and examined the spectra of a number of o-, m- and p-methoxybenzyl compounds (III) $MeOC_6H_4CH_2X$. The results for the K bands are set out in Table 3. The effect of a methyl group (III, X = H) in the o-position to a methoxyl group is probably a mixture of steric and electronic effects which at present are impossible to disentangle. However, models show that replacing one of the hydrogens of the methyl

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* We have adopted the convention of referring to the two substituents in a disubstituted benzene as the primary substituent and the secondary substituent, where the primary substituent is that substituent of the two which, on being substituted into benzene, produces the largest shift of the K band (2000 Å).

[13] E. A. Braude and F. Sondheimer, *J. Chem. Soc.* 754, 3773 (1955).
[14] H. Suzuki, *Bull. Chem. Soc., Japan* 33, 619 (1960).

by another substituent do not increase the steric effects, if the CH_2X group takes up a configuration in which the X group is away from the methoxyl oxygen and the ether methyl group is twisted away from the CH_2X group. We can expect therefore, by choosing the methyl group as our reference compound, to observe only the electronic effects of the different substituents (III, $X = Cl$, Br, I, OH, $C\equiv N$, NH_2, Ph, NH_3^+).

Comparison of the shifts $\Delta\lambda$ obtained for the effect of X in the o-isomer with the effect of X in the p-isomer (Table 3) shows that although the o-shifts are bathochromic in nature they are much smaller than the shifts for the corresponding p-isomers. This is in complete agreement with the hypothesis that, for the K band p-substituents are terminal groups and o-substituents are side chain groups which have little effect. This is clearly shown in the replacement of hydrogen by chlorine (III, $X = Cl$). For the p-isomer there is a considerable wavelength shift ($\Delta\lambda = 100$ Å) and the maximum extinction coefficient is almost doubled for the K band, but for the o-isomer the observed change (Table 3) on replacing H by Cl is well within the experimental error. This latter result also applies to the substituents $X = NH_2$, OH, $C\equiv N$ and NH_3^+. For $X = Br$ and I, the o-isomer wavelength changes appear to be quite large. However for these compounds the CH_2X group is almost certainly the terminal group with the OMe group in the side chain [$\lambda_{max}(C_6H_5 OMe) = 2205$ Å, $\lambda_{max}(C_6H_5CH_2Br) = 2245$ Å, $\lambda_{max}(C_6H_5CH_2I) = 2320$ Å]. With the CH_2X compounds as reference molecules the shifts on *ortho* OMe substitution become 85 Å for $X = Br$ and 110 Å for $X = I$, compared to shifts of 215 Å and 285 Å for the corresponding p-isomers. The *ortho* effect of the OMe group on the K band of the benzyl iodide and bromide is similar in magnitude to the effect of this substituent on the K band of benzaldehyde ($\Delta\lambda = 50$ Å). This again emphasises the similarity between the CH_2—X grouping, with no π electrons to interact with the benzene ring and the grouping $C = Y$ with a multiple bond containing electrons capable of interacting with the benzene π electrons.

The K bands of meta-*substituted anisoles*

When the CH_2X group, where X is one of the weakly interacting groups Cl, OH, NH_2, NH_3^+, $C\equiv N$ and Ph, is in the m-position to the methoxyl group, the effect of X on the K band is similar to the effect it would have in the o-isomer. For each of the two m-isomers $X = Br$ and $X = I$ however two K bands are observed (Table 3). One of these is at 2120 Å ($X = Br$) and 2170 Å ($X = I$) and probably corresponds to a transition with the OMe group as a terminal group and the other one is a shoulder appearing at 2220 Å ($X = Br$) and 2300 Å ($X = I$) and is probably the K band of the unsubstituted benzyl halide modified by an OMe group in the side chain. A similar interpretation has been given previously by Forbes for m-substituted compounds where one of the substituents is electron donating and one electron attracting. This interpretation is also supported by molecular orbital calculations to be reported elsewhere.[17]

B bands of substituted anisoles

The effects of the groups $X = OH$, NH_2, NH_3^+ and $C\equiv N$ in III on the wavelength maxima of the B bands of the three methyl cresyl ethers are very small and it is not possible from these results to come to any reliable conclusions concerning the effects of these substituents on the B bands. For chlorine, although the effect is small, the

vibrational fine structure is kept for the p-isomer on replacing H by Cl and it is there-fore possible to state definitely that the B band is moved to shorter wavelengths with a small reduction in intensity. For the o-isomer the fine structure is lost but λ_{max} is the same as for the p-isomer. For the molecules X = Br and I there is a long wave-length shift of the B band for the o-isomer relative to X = H ($\Delta\lambda = 80$ Å for X = Br and $\Delta\lambda = 150$ Å for X = I) and a considerable increase in intensity (Table 3); as expected if the hypothesis that o-substituents are terminal groups for B bands is correct. Unfortunately, for the p-isomers, the K band has moved to obscure the B band so it is only possible to state that the B band has moved less than for the o-isomer and *much* less than the corresponding K band for the p-isomer, again in agree-ment with the terminal group/side chain group hypothesis.

For the m-isomers the results of Table 4 show that for X = OH, NH_2, NH_3^+, Ph and C≡N the effect of the substituent on the B band is very small while for the substituents X = Cl, Br and I the effects on the B band are similar to the o-isomer but smaller in magnitude. We can therefore conclude that the effects of a substituent on the intensity and the wavelength shift of the B band of disubstituted benzenes are in the order,

$$o > m > p$$

compared to the order for K bands which is

$$p > o > m$$

This difference in order between o-, m- and p-isomers can be seen in many examples in the literature, e.g. for substituted benzaldehydes[15,16] and benzonitriles[17] where the substituents are in direct conjugation with the ring.

GENERAL DISCUSSION

The difference in behaviour between o-, m- and p-derivatives is also clearly brought out in theoretical molecular orbitals calculations on disubstituted benzenes.[17,18] However, these theoretical calculations are limited to cases where the main interactions are between the π electrons of the substituent and the π electrons of the benzene ring and are not applicable to groups such as CH_2X. Spinner[8] has recently extended his theory of intramolecular London–van der Waals interaction forces to this type of substituent. This theory at the present time is only qualitative in nature and predicts that groups such as CH_2I and CH_2Br will give rise to stabilization of the ground state similar to those produced by substituents containing conjugatable π electrons. In an attempt to test this prediction we have measured the IR stretching frequencies and intensities of a number of nitrobenzenes substituted in the p-position by CH_2X groups.[19] The effect of the groups CH_2Br, CH_2I on the stretching frequency of nitro-benzene (1349 cm^{-1}) is found to be much smaller than that for the OH or OMe group ($\nu_{pOMe} = 1341$ cm^{-1}; $\nu_{pCH_2I} = 1347$ cm^{-1}) indicating very little interaction in the ground state. Such a conclusion is strengthened by the fact that the C^{13} NMR

[15] M. R. Padhye and B. G. Viladkav, *J. Sci. Ind. Res., India* **20B**, 530 (1961).

[16] I. A. Rao and V. R. Rao, *J. Sci. Ind. Res., India* **20B**, 145 (1961).

[17] J. E. Bloor and F. Peradejordi, *Theoret. Chim. Acta, Berl* 1, 83, (1962) and unpublished work.

[18] J. N. Murrell, *Royal Institute of Chemistry Lectures* No. 2 (1963).

[19] J. E. Bloor and H. W. Wilson, Unpublished work.

TABLE 1.—MAXIMA* OF K BANDS OF p-DISUBSTITUTED COMPOUNDS IN Å

X	MeO—⟨C6H4⟩—CH2X			H2N—⟨C6H4⟩—CH2X			MeO⟨C6H4⟩-⟨C6H4⟩CH2X		
	λ†	ε†	Δλ	λ‡	ε‡	Δλ	λ†	ε†	Δλ†
H	2235	7,350	0	2355	11,000	0	2602	23,600	0
OH	2265	7,600	30	2410	12,000	55	2638	24,500	36
NH₂	2255	9,400	20	2410	10,500	55	—	—	—
NH₃⁺	2270	13,000	35	2455	11,500	100	— ·	—	—
C≡N	2260	8,000	25	2424	10,500	79	2657	23,000	55
C₆H₅	2270	6,150	35	2400	13,000	45	2632	28,000	30
Cl	2335	13,000	100	—	—	—	2712	23,000	110
Br	2460	12,000	225	—	—	—	2767	23,500	165
I	2605	10,340	360	—	—	—	2910	23,500	308

* Maxima are used throughout since only in a very few of the compounds is there vibrational fine structure.
  † Measured in *n*-hexane.
  ‡ Measured in ethanol.

spectra[20] of benzyl iodide is very little different from toluene although if the CH₂I group was interacting with the benzene π electrons in the ground state we would expect the chemical shift for the *para* carbon atom to be considerably different in the latter compound from that in the former compound. These experimental facts support Burawoy's original contention that the interaction between the CH₂X group and the benzene molecule is almost completely an excited state interaction. Work is in progress in an attempt to give a semiquantitative interpretation to the qualitative theory results using an exciton model similar to that used by Simpson[21] for the interpretation of the

TABLE 2.—K AND B BAND MAXIMA IN Å AND MOLECULAR EXTINCTION COEFFICIENTS OF METHYL BENZONITRILES IN ISOCTANE

Substance	K band				B band*		
	λ	ε	Δλ	θ†	λ	ε	Δλ
Benzonitrile	2200	12,200	0		2755	960	0
	2250	12,600	0				
	2290	12,200	0				
p-Tolunitrile	2290	16,500	90		2780	800	35
	2320	16,700	70				
	2370	15,100	80				
m-Tolunitrile	2255	11,000	55	35°	2820	1320	65
	2260	11,500	10	34°			
	2310	10,420	20	34°			
o-Tolunitrile	2240	11,700	40	32°	2820	1700	65
	2270	11,700	20	33°			
	2326	9,200	36	38°			

* Considerable fine structure. Only the *o–o* transition given.
  † Calculated using Eq. (1). If oscillator strengths are used instead of *f* values then $\theta = 44°$ for the *o*-isomer and 48° for the *m*-isomer.

[20] W. G. Schneider. Private communication.
[21] M. B. Robin and W. T. Simpson, *J. Chem. Phys.* **36**, 580 (1962).

TABLE 3.—K BAND MAXIMA IN Å OF o-, m- AND p-ISOMERS OF MeOC₆H₄CH₂X

X	p-isomer			m-isomer			o-isomer		
	λ	Σ	Δλ	λ	Σ	Δλ	λ	Σ	Δλ
H	2235	7,350	0	2200	5,600	0	2190	6,000	0
	2240*	6,750	0	2200*	5,500	0	2195*	5,800	0
OH	2265	7,600	30	2190	6,500	−10	2205	5,700	15
NH₂	2255	6,000	20	—	—	—	2200	6,000	10
	2260*	7,300	20*	—	—	—	2200*	6,100	5*
NH₃⁺*	2270*	6,500	30*	2300*	7,700	100	2215*	6,500	20*
C≡N	2260	8,000	25	2230	6,100	30	2200	6,000	10
C₆H₅	2270	6,150	35	—	—	—	—	—	—
Cl	2335	13,000	100	2215	7,350	15	2220	6,350	30
Br	2460	12,000	235	2120	7,700	−80	2330	6,580	140
				2220†	4,000				
	2605	10,300	370	2170	11,300	−30	2430	6,470	240
				2300†	5,000				

* Measured in ethanol, other data measured in n-hexane.

† Shoulder or inflection.

TABLE 4.—THE B BAND MAXIMA I Å* OF THE o-, m- AND p-ISOMERS OF MeOC₆H₄CH₂X COMPOUNDS IN n-HEXANE

X	p-isomer			m-isomer			o-isomer		
	λ	ε	Δλ	λ	ε	Δλ	λ	ε	Δλ
H	2790	2300	0	2730	1500	0	2720	2010	0
	2830	2700	0	2790	1520	0	2780	1900	0
OH	2760	1680	−30	2730	1600	0	2710	1740	−10
	2820	1400	−10	2800	1400	10	2765	1740	−15
NH₂	2760	1600	−30	2730	1900	0	2720	2000	0
	2830	1300	0	2800	1800	10	2780	1830	0
NH₃⁺†	2740	1300	−50	2810	2000	80	2735	1500	15
	2800	1150	−30						
C≡N	2770	1560	−60	2740	1500	10	2710	2140	−10
				2800	1300	10	2770	1964	−10
C₆H₅	2760	1100	+30	2740	2200	10	2720	1800	0
	2800	1030	−30	2810	2400	20	2790	1700	10
Cl	2760	1740	−20	2780	2080	−10	2770	2500	−10
	2800	1630	0						
Br	2860	1800	30	2830	2300	40	2860	3260	80
I	—	—	—	2860	2140	70	2930	5180	150

* Where only one peak is observed Δλ is arbitrarily given relative to the lowest λ_{max} of the parent.

† Measured and compared with the parent in ethanol.

electronic spectra of dyes. However, at the present time one must conclude that the effects of CH₂X groups on the K and B bands of aromatic molecules are understood only in an empirical qualitative manner, whereas in the case of compounds where X is directly attached to an aromatic ring the effect of X on the K and B bands can be semiquantitatively interpreted in terms of conventional molecular orbital theories.

EXPERIMENTAL

The spectra were determined with a Hilger Uvispeck Photoelectric Spectrophotometer. All the investigated substances were prepared in a high state of purity, analyses being made immediately

before the spectra were measured. With the exception of the methoxybenzyl iodides the synthetic methods employed were taken from the literature and used directly or with slight modification. Full experimental details of the analyses and physical constants have been reported elsewhere.[7] The m.p. of p-methoxybenzyl chloride was recorded as 39–39·5°C (Found: C, 61·2; H, 5·8; Cl, 22·4. C_8H_9OCl requires: C, 61·3; H, 5·7; Cl, 22·6%). Lit. value,[8] mp-1°C.

o-*Methoxybenzyl iodide.* o-Methoxybenzyl bromide (100 g) was dissolved in acetone (20 ml) and added to a solution of KI (17 g) in acetone (100 ml)–water (12 ml) mixture. The solution was left in the dark for 24 hr and the brownish red liquid decanted, from the precipitated KBr, into ice cold water containing $Na_2S_2O_3$. After stirring for 10 min the precipitate was filtered off and recrystallized at low temp (using a solid carbon dioxide–methanol cooling mixture) from ether. Colourless light sensitive needles were obtained in 40% yield. m.p. 37°. (Found: C, 39·0; H, 3·6; I, 51·0. Calc. for C_8H_9OI: C, 38·7; H, 3·6; I, 51·2%).

m-*Methoxybenzyl iodide.* m-Methoxybenzyl bromide was treated in the same way as the o-methoxy benzyl bromide in the preparation of the o-isomer. White crystals were obtained. m.p. 40°. (Found: C, 38·8; H, 3·7; I, 50·5. Calc. for C_8H_9OI: C, 38·7; H, 3·6; I, 51·2%).