381. *Colour and Constitution. Part II.* The Effect of the Common Monatomic Substituents on the Ultraviolet Spectrum of Alternant Hydrocarbons.*

By David Peters.

The Hückel L.C.A.O. molecular-orbital theory is shown to provide a quantitative account of the bathochromic shifts observed in the ultraviolet spectrum of alternant hydrocarbons on the introduction of the common monatomic † substituents.

In Part I,* the bathochromic shifts in the *p*-band ‡ of the ultraviolet spectrum which result from the introduction of a methyl group into an alternant hydrocarbon were discussed in terms of the Hückel L.C.A.O. molecular-orbital theory, and it was shown that a simple explanation of the origin and magnitude of these shifts is available. It is now of interest to examine how far this method is applicable to other common substituents. The available information on the effect of the common monatomic substituents (hydroxyl, methoxyl, amino, and the halogens) on the ultraviolet spectrum of alternant hydrocarbons, much of which is due to Jones[1] and to Friedel and Orchin,[2] is less complete that that for the methyl group, but is adequate for the present purpose.

While there is no difference from a theoretical viewpoint in the complexity of the problems of monatomic substituents and of the methyl group, in practice the former case is rather more difficult for several reasons. Monatomic substituents, particularly the amino-group, affect the ultraviolet spectrum to a greater degree, the bathochromic shifts being larger, and the general shape and fine structure of the *p*-band being often substantially or completely distorted. On occasion, when the bathochromic shift is very large, and the fine structure of the *p*-band of the parent hydrocarbon is completely absent in the derivative, the curves of the hydrocarbon and the derivative differ completely in appearance and no relation between them is apparent. This situation is fortunately rare and, where the bathochromic shift due to the substituent is small and the *p*-band of the derivative retains fine structure, there can be little doubt as to the close relation. Often, the larger the bathochromic shift, the more complete is the destruction in the derivative of both the fine structure and the general shape of the *p*-band. Several examples will be found below. A minor difficulty arises with large shifts in that their exact magnitude cannot be determined from the published curves. This is rarely serious as the estimate which can be made is usually of sufficient accuracy to test the predictions.

---

* Part I, *J.*, 1957, 646.

† Monatomic substituents are those contributing one *p*-orbital to the mesomeric system of the hydrocarbon.

‡ The nature and origin of the *p*-band are discussed in Part I.

[1] Jones, *J. Amer. Chem. Soc.*, (*a*) 1945, **67**, 2127; (*b*) 1941, **63**, 151; (*c*) 1940, **62**, 148; (*d*) *Chem. Revs.*, 1947, **41**, 353.

[2] Friedel and Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, New York, 1951.

The nature of the hydrocarbon is also important in determining how far the spectrum of the derivative retains fine structure. Substituted anthracenes are particularly prone to this distortion of the *p*-band, the well-developed fine structure of the hydrocarbon being replaced by a smooth, broad curve whose centre can be estimated only roughly.

Another difficulty, related to the α-band, arises on occasion. In the hydrocarbon, the α-band is usually at longer wavelength and less intense than the *p*-band. These differences are often reduced or eliminated in the derivative, the α-band having nearly the same wavelength but greater intensity and the *p*-band being shifted bathochromically but being unchanged in intensity. In extreme cases, the two effects combine to produce a complete merging of the *p*- and the α-band.

In spite of these complications, the size of the shift resulting from the introduction of the substituent can usually be estimated from the published curves sufficiently accurately to test the theoretical method.

As with the methyl substituent, the shifts exhibit certain regularities. It is commonly accepted [3] that these substituents exert a bathochromic effect and the data collected in Table 2 substantiate this, although there are one or two cases in which one cannot be sure that a small hypsochromic shift is not occurring. No clear case of such a shift has been found, however, and the generalisation seems correct.

Method.—The effect of the monatomic substituents on the ultraviolet spectrum of alternant hydrocarbons has been discussed in terms of the simple Hückel L.C.A.O. molecular-orbital theory.[4] The introduction into the hydrocarbon of the single *p*-orbital of the substituent is regarded as a perturbation of the molecular orbitals of the former. It has been shown theoretically,[5] and supported by experimental evidence (cf. Part I and refs. 1*a* and 6), that the inductive effect of a substituent, represented by a change in the coulomb integral of the carbon atom to which it is attached, has little or no effect on the energy of the *p*-transition. The conjugative effect is dealt with by supposing that the result of the addition of the single *p*-orbital, of coulomb integral α, to the molecular orbitals of the hydrocarbon, is a perturbation of the latter orbitals. The resulting change in the energy of the *j*th molecular orbital ($\delta\varepsilon_j$) is given by the familiar expression of perturbation theory: [7]

$$\delta\varepsilon_j = \frac{c_{jr}^2}{\varepsilon_j - \alpha} \cdot \beta_{rs}^2 \quad . \; . \; . \; . \; . \; . \; . \quad (1)$$

where c_{jr} is the atomic orbital coefficient of the *j*th molecular orbital at atom *r*, and β_{rs} is the resonance integral between the substituent(s) and the ring carbon atom (*r*). Applied to both the highest bonding (*i*) and the lowest antibonding molecular orbital of an alternant hydrocarbon, the change in energy (δE) of the *p*-transition is found to be:

$$\delta E = -c_{ir}^2 \, . \, \beta_{rs}^2 \, . \, 2\varepsilon_i/(\varepsilon_i^2 - \alpha^2) \quad . \; . \; . \; . \; . \; . \; . \quad (2)$$

Since $\alpha^2 > \varepsilon_i^2 > 0$, and ε_i is a negative quantity, the shift is bathochromic. The usual values for the constants being inserted, the bathochromic shift ($\delta\lambda$ in mμ) is

$$\delta\lambda = 475 \, . \, c_{ir}^2 \cdot \frac{1}{\varepsilon_i(\varepsilon_i^2 - \alpha^2)} \cdot (\beta_{rs}/\beta)^2 \quad . \; . \; . \; . \; . \; . \quad (3)$$

where ε_i and α are expressed in units of β. β = 30,000 cal. per mole.

---

[3] Braude, *Ann. Reports*, 1945, **42**, 105.

[4] Pullman and Pullman, "Les Theories Electronique de la Chimie Organique," Masson et Cie, Paris, 1952; Dewar, "Progress in Organic Chemistry," Butterworths Scientific Publ., London, 1953, Vol. II, p. 1.

[5] Longuet-Higgins and Sowden, *J.*, 1952, 1404; Coulson, *Proc. Phys. Soc.*, 1952, **65**, *A*, 933.

[6] Epsztein, *Mém. Services chim. Etat*, 1951, **36**, 235.

[7] Coulson and Longuet-Higgins, *Proc. Roy. Soc.*, 1947, *A*, **191**, 39; Dewar, *J. Amer. Chem. Soc*, 1952, **74**, 3341.

TABLE 2. *Bathochromic shifts, resulting from the introduction of monatomic substituents, in the p-band.*

(*a*) *Substituent* : OH and OMe

Posn. of subst.	λ (mμ) of parent	Shift (mμ) Calc.	Shift (mμ) Obs.	Ref.
Naphthalene				
1	276	17	13—17	2, *a*
2		6	0	2
Phenanthrene				
1	293	11	11—14	2
2		0	0	2
3		9	—	
4		5	—	
9		16	12—16	2
Pyrene *				
1	333	10	13	2
3		15	13, 17	1*a*, *b*
4		0	2	1*a*, *b*
Chrysene *				
1	319	6	7	*c*
2		15	12	*c*
3		9	16	*c*
4		1	0	*c*
5		6	9	*c*
6		6	15	*c*
1 : 2-Benzanthracene				
3	341	10	Small	1*b*
9		18	11	*d*
10		23	12	1*a*, 2
4′		3	Small	*e*

(*b*) *Substituent* : NH_2

Posn. of subst.	λ (mμ) of parent	Shift (mμ) Calc.	Shift (mμ) Obs.	Ref.
Naphthalene				
1	276	36	30—40	*a*
2		14	5—10	*a*
Phenanthrene				
1	293	23	—	
2		0	0—1	6
3		20	30—35	6
4		11	—	
9		34	*ca.* 30	6
Pyrene *				
1	333	18	—	
3		29	25—35	1*a*, *b*
4		0	4	1*a*, *b*
Anthracene				
1	339	21	—	
2		11	14	1*d*
9		43	*ca.* 50	*f*
1 : 2-Benzanthracene				
3	341	18	Small	1*b*
8		20	30—50	1*a*
10		44	40—60	1*b*

(*c*) *Substituent* : Cl and Br

Posn. of subst.	λ (mμ) of parent	Shift (mμ) Calc.	Shift (mμ) Obs.	Ref.
Naphthalene				
1	276	9	10, 11	*a*
2		3	3, 4	*a*
Anthracene				
1	374	5	7, 8	*g*, *h*
2		3	3	*h*
9		11	10—12	*i*
Naphthacene				
5	471	11	13, 14	*g*
Phenanthrene				
1	293	6	—	
2		0	1, 2	2
3		5	—	
4		3	—	
9		9	9	2
Pyrene *				
3	333	7	10	*b*
1 : 2-Benzanthracene				
6	341	2	5—6	2
10		11	14—15	*d*

(*d*) *Substituent* : F

Posn. of subst.	λ (mμ) of parent	Shift (mμ) Calc.	Shift (mμ) Obs.	Ref.
Naphthalene				
1	276	5	5—6	*j*
2		2	Small	*j*
Phenanthrene				
1	293	3	3	*k*
2		0	1·5	*k*
3		2·5	0	*k*
4		1·5	4	*k*
9		4·5	4	*k*
Pyrene *				
1	333	3	4—5	*k*

* Ring Index numbering.

Refs. : (*a*) de Laszlo, *Proc. Roy. Soc.*, 1926, *A*, **111**, 355. (*b*) Förster and Wagner, *Z. phys. Chem.*, 1937, **37**, *B*, 353. (*c*) Holiday and Jope, *Spectrochim. Acta*, 1950, **4**, 157. (*d*) Badger and Pearce, *J.*, 1950, 3072. (*e*) Holiday, *Cancer Res.*, 1943, **3**, 689. (*f*) Craig and Short, *J.*, 1945, 419. (*g*) Clar and Marschalk, *Bull. Soc. chim. France*, 1950, **17**, 433. (*h*) Conrad-Billroth, *Z. phys. Chem.*, 1936, **33**, *B*, 133. (*i*) Etienne and Le Grand, *Bull. Soc. chim. France*, 1953, **20**, 108. (*j*) Ferguson, *J.*, 1954, 304. (*k*) Bavin and Dewar, *J.*, 1955, 4486.

When it is seen that equation (3) is identical with that derived for the methyl substituent, the close relation between the bathochromic effects of the two classes of substituents becomes clear. Within a given hydrocarbon, the factor determining the size of the bathochromic shift at any position is the atomic orbital coefficient of the top bonding molecular orbital at the ring carbon atom concerned, the energy term being constant.

In equation (3) there are two quantities which must be assigned for each substituent, the coulomb integral α, and β_{rs}/β. The values chosen for these terms are set out in Table 1.

TABLE 1.

Substituent	N	O	Cl	Br	F
Coulomb integral	$1{\cdot}0\beta$	$1{\cdot}3\beta$	$1{\cdot}0\beta$	$1{\cdot}0\beta$	$1{\cdot}5\beta$
β_{rs}/β	0·4	0·4	0·2	0·2	0·25

The choice of the coulomb integrals is governed by the accepted order of the electronegativities [8] and, as with the methyl substituent, the values of β_{rs}/β have been chosen to reproduce the α-naphthalene results. The resulting values are reasonable, and, in any case, no rational choice of these parameters would give results outisde of the correct order of magnitude.

The results calculated from equation (3) are compared with the available experimental data in Table 2.

DISCUSSION

The bathochromic shifts of the monatomic substituents are quite similar to those of the methyl group. In both instances, the *meso*-positions of anthracene and similar positions show large shifts, while the β-position of naphthalene and similar positions show small shifts. The identical expressions derived for both classes of substituents explain this position exactly. The differences in absolute magnitude arise from the differing coulomb integrals of the heteroatoms and from the differing resonance integrals between these atoms and the ring carbon atom.

Hydroxy- and Methoxy-substituents.—These groups give rise to very similar shifts. The methoxy-shifts seem slightly larger than the hydroxy-shifts, and this may be due to a reduction in the coulomb integral of the oxygen atom by the methyl group. The effect is quite small, however, and the groups are not distinguished further.

The bathochromic shifts in the *p*-band introduced by the hydroxy- or methoxy-group for naphthalene follow the generalisation just given. There is some distortion of the fine structure of the *p*-band in the 1-hydroxy-compound but almost none in the 2-hydroxy-derivative, in conformity with the previous statement that the greater the bathochromic shift, the greater the distortion. The ultraviolet spectra of the hydroxyanthracenes are unknown, but experimental data are available for three of the hydroxyphenanthrenes. The 1- and the 9-hydroxy-compound show considerable distortion of the fine structure and general shape of the *p*-band, but the shifts can be determined with sufficient accuracy to show the agreement with the calculations. In 2-hydroxyphenanthrene, the zero bathochromic shift is accompanied by excellent retention of the fine structure of the *p*-band.

A very small bathochromic shift and good retention of the fine structure are also shown by 4-hydroxypyrene, while 1- and 3-hydroxypyrene show larger shifts and there is concomitant distortion of the fine structure. The calculated and experimental shifts are again in good agreement.

The monomethoxychrysenes are remarkably free from distortion of the fine structure of the *p*-band. The steric bathochromic shift found in 6-methylchrysene occurs in 6-methoxychrysene. 3-Methoxychrysene also shows a larger bathochromic shift than the calculations suggest, but in the remaining four positions agreement is good.

In the monomethoxy-1 : 2-benzanthracenes, quantitative agreement between the

---

[8] Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, New York, 1945, p. 60.

calculated and experimental shifts is inferior to that found with the other hydrocarbons. The 9- and the 10-methoxy-compound show very severe distortion of the fine structure of the *p*-band.

. The conversion of a phenol into its anion causes a bathochromic shift of the *p*-band.[1a, 2] This may be due either to an increase in the resonance integral of the bond between the oxygen atoms and the ring, or to a decrease in the coulomb integral of the oxygen atom. The latter interpretation is preferred since an increase in negative charge on an atom is commonly supposed to decrease the coulomb integral.[9]

The Amino-substituent.—This often causes very large shifts with severe distortion of the fine structure of the *p*-band and of the general appearance of the spectrum. Thus, in α-naphthylamine, the clear distinction of the *p*- and the α-band is lost and the bathochromic shifts cannot be estimated accurately. The spectrum of β-naphthylamine is less distorted and the shift is of the calculated size.

The published spectrum of 2-aminoanthracene is abnormal in that the fine structure of only one half of the *p*-band is destroyed, that of the short-wavelength portion being retained very well, undoubtedly because the intensified α-band emerges beneath the long-wavelength portion of the *p*-band. From the remaining fine structure, it is not possible to decide which of two vibrational peaks is derived from a given peak of the parent hydrocarbon. One assignment leads to a bathochromic shift of 14 mμ while the alternative is a hypsochromic shift of 3 mμ: the calculated shift of 11 mμ shows that the first alternative is correct. The spectrum of 9-aminoanthracene is very badly distorted but the bathochromic shift seems to be of the calculated size.

The calculated and experimental shifts of the known monoaminophenanthrenes agree satisfactorily; the inversion in the order of the shifts of the 3- and the 9-compound may be due to the rather bad distortion of the spectra and the resulting difficulty in estimating the shifts.

4-Aminopyrene exhibits a very small shift and excellent retention of the fine structure of the *p*-band, while the 3-compound shows a larger shift and substantial distortion of the fine structure. Both results agree well with the calculations.

Very severe distortion of the fine structure of the *p*-band of 8- and 10-amino-1 : 2-benzanthracene prevents an accurate estimate of their bathochromic shifts. The spectrum of 3-amino-1 : 2-benzanthracene exemplifies a situation which has been noted previously (Part I): the 3- and the 4-derivative are calculated to show quite large shifts, as would be expected from their relation to the 9- and 10-position of phenanthrene, but the experimental result is that 3-amino-1 : 2-benzanthracene shows a small shift.

The Halogen Substituent.—This causes rather small shifts, accompanied by very good retention of the fine structure of the *p*-band. There is good agreement between the experimental and the calculated results for naphthalene and for the known phenanthrenes. The ultraviolet spectra of all of the monofluorophenanthrenes have been recorded. In the phenanthrene ring, the 4-position is unreliable for comparison between theory and experiment owing to the probable intervention of steric effects. For three of the remaining four positions, there is good agreement between experimental and calculated values; the exception is the 3-position, where theory suggests a moderate shift but no shift is found in practice; there is no apparent explanation of this anomoly, and it would be of interest to examine the spectra of the other halogenophenanthrenes.

Other Substituents.—There seems no reason why the current method should not be extended to other, more complex substituents, and the literature has been surveyed with respect to the vinyl, carbonyl, and cyano-substituents. These naphthalene derivatives show the expected results, the bathochromic shifts of the *p*-band being several times greater in the 1- than in the 2-position,[2, 10] but data are scanty. More complex substituents containing four or more *p*-orbitals are in principle amenable to the method, but

---

[9] Bassett, Brown, and Penfold, *Chem. and Ind.*, 1956, 892 and refs. therein.

[10] Ref. *a* of Table 2.

the large size of their shifts, the extensive distortion of the fine structure of the *p*-band, and the increased arithmetical manipulation restrict the utility of the method.

It seems, then, that at least an approximate value is available for the bathochromic shifts due to the common monatomic substituents, in the ultraviolet spectra of alternant hydrocarbons. The method should prove of value in interpreting the spectrum of new compound of unknown orientation of the substituents.

The author is indebted to Professor M. J. S. Dewar for reading the manuscript and for advice and encouragement.

"BRENTWOOD," PLASKYNASTON LANE,
CEFN MAWR, WREXHAM, DENBIGHSHIRE.

[*Received, December 6th,* 1956.]