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THE EFFECTS OF SUBSTITUENTS UPON THE ULTRAVIOLET SPECTRA OF CONJUGATED DIENES

THE APPLICABILITY OF WOODWARD'S RULES

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Abstract—Data on the electronic spectra of conjugated dienes di-substituted with saturated hydrocarbon chains of increasing length have been collected from the literature. One aspect of these spectra, the fact that the absorption maximum for a *cis–cis* compound lies at longer wavelengths than that for the corresponding *trans–trans*, has received some attention in the literature, but no quantitative explanation of the observation has been offered. A second fact, that increasing substituent chainlength results in a steady shift of the absorption maxima to long-wavelength limits of ~235 nm for *cis–cis*, ~233 nm for *cis–trans* and *trans–cis* and ~231 for *trans–trans*, appears to have gone unremarked in spite of the fact that, as a result, Woodward's rules are not obeyed by such compounds.

Quantitative interpretations of both these phenomena are described.

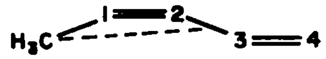
During a study of the rearrangements of prostaglandin dienes, we assembled data from the literature for the UV absorption maxima of long-chain dienes and noted the poor correspondence of the reported values with those predicted by Woodward's rules.[1] No mention is made of this phenomenon in the standard texts[2] and, since these rules are widely used, we were interested in the extent of, and the reason for, the discrepancies. We therefore collated the literature values for dienes of differing chain lengths by searching "Organic Electronic Spectral Data"[3] under appropriate molecular formulae.

As might be expected, there are erroneous, or at least highly suspect, values in the literature. The variations in wavelength maxima sought are not very large and the instrument-to-instrument variation even amongst professional users is often considerable, as collaborative trials have shown.[4] In general only those values have been chosen where comparative wavelength maxima have been reported, and where there is evidence of the purity and stereochemistry of the samples. It is hoped that the choice of values recorded in Table 1 and Fig. 1 has not been too subjective, but if all the values had been included it would merely have increased the spread of error without substantially altering the plots.

Two aspects of Fig. 1 require an explanation. Firstly, there is the fact that the *cis–cis*-dialkyl-*s-trans* dienes absorb at longer wavelengths than the corresponding *trans–trans* isomers; the *cis–trans* isomers lying between these two extremes. Secondly, there is the general shift to longer wavelength with increasing size of substituent and the consequent failure to obey Woodward's rules.[1]

These phenomena have been noted by others and, in particular, Crombie[5] proposed what we believe to be the correct explanation of the longer wavelength absorption of the *cis–cis* isomers as compared with the *trans–trans*. However, Crombie did not quantify his interpretation and it has been subsequently ignored and an alternative explanation proposed.[6] It appears worthwhile, therefore, to quantify and substantiate Crombie's proposal before turning to the second point noted above. First, however, we must briefly describe the alternative explanation put forward by Forbes[6] and explain why we believe it to be in error.

Forbes *et al.*[6] suggested that an interaction between a methyl group and the central C_2–C_3 bond in *cis* compounds (1) might be responsible for the longer-wavelength absorption of *cis* Me-substituted dienes.



(1)

Though the MO theory of electronic spectra is not in general sufficiently refined to interpret quantitatively the subtle effects with which we are dealing here,[7] we can attempt to estimate the magnitude of the effect proposed by Forbes as follows:

The mesomeric effect of a substituent upon the electronic spectrum of a π-electron system may be written in the form of eqn (1).[8]

$$\Delta E_\mu = C_\mu{}^2\beta^2\left\{\frac{4E}{4(E_c - E_d)^2 - E^2}\right\} \qquad (1)$$

ΔE_μ is the shift of the absorption band for a substituent attached at carbon atom μ, C_μ is the atomic orbital coefficient of the highest occupied MO at the position of substitution, E is the energy of the transition involved and $E_c - E_d$ is the energy difference between a carbon 2pπ atomic orbital and the donating orbital of the sub-

Table 1. Wavelengths of maximum absorption, extinction coefficients and molecular weights for conjugated dienes of the form: R_1–CH=CH–CH=CH–R_2

	R_1	R_2	M.Wt.	Conf.	λmax/nm	ε max	Solvent	Foot-note
1	H	H	54	-	217	20,900	EtOH	a
2	CH_3	H	68	-	223.5	22,900	EtOH	b
3	CH_3	CH_3	82	tt	227	22,500	EtOH	c
4	$OHCH_2$	CH_3	98	cc	230	14,700	EtOH	d
5				cc	231	16,850		
				ct	229	19,800		
				ct	229	22,100		
				tc	230	23,500		
				tc	229.5	21,450		
				tt	227	24,500		
				tt	227	25,500		
6	$OHCH_2$	CH_3	98	cc	231	16,850	EtOH	e
				ct	229.5	23,100		
				tc	229.5	21,450		
				tt	228	25,400		
7	$OHCH_2$	$OHCH_2$	114	tt	229	31,000	EtOH	c
8	CH_3CH_2CHOH	CH_3	126	tt	229	28,400	EtOH	f
9	$OHCH_2$	n-C_5H_{11}	154	cc	233	20,000	EtOH	g
				ct	232	24,000		
				tc	232	22,100		
				tt	230	30,600		
10	$CH_3CO_2CH_2$	n-C_3H_7	168	tc	233	19,000	EtOH	h
				tt	228	17,000		
11	$CH_3CO_2CH_2$	n-C_7H_{15}	224	tc	233	17,000	EtOH	h
				tt	229	14,000		
12	HCO_2CH_2	n-C_8H_{17}	224	cc	235		C_6H_{14}	i
				ct	233			
				tc	233			
				tt	229			
13	$CH_3CO_2CH_2$	n-C_8H_{17}	238	cc	234	29,000	C_5H_{12}	i
				ct	231.5	29,000	C_6H_{14}	
				tc	231.5	27,000	C_5H_{12}	
				tt	229	28,000	C_6H_{14}	
14	$C_2H_5CO_2(CH_2)_7$	CH_3	238	ct	230	25,700	EtOH	
				tt	228	27,200		
15	$OH(CH_2)_9$	n-C_3H_7	238	cc	235	27,500	EtOH	j
				ct	232.5	26,200		
				tc	232.5	26,800		
				tt	230.5	31,500		
16	$OH(CH_2)_9$	n-C_3H_7	238	cc	236	27,500	EtOH	k
				ct	233	26,000		
				tc	234	26,300		

Table 1. (*Contd*)

				tt	230.5	32,000		
17	$CH_3CO_2(CH_2)_8$	n-C_3H_7	266	cc	236	28,000	EtOH	k
				ct	233	26,000		
				tc	233	25,000		
				tt	231	32,000		
18	$HCO_2(CH_2)_7$	n-C_6H_{13}	280	tc	232.5	24,360$^+$	EtOH	l
				tt	231	31,500		
19	$HCO_2(CH_2)_8$	n-C_5H_{11}	280	ct	232	26,600	EtOH	l
				tt	231	32,200		
20	$OHCH_2(CH_2)$ CHOH	n-C_5H_{11}	282	tt	231	19,360	EtOH	m
21	$C_2H_5CO_2(CH_2)_8$	n-C_5H_{11}	294	cc	235	24,100	EtOH	n
				ct	231.5	——		
22	$HCO_2(CH_2)_8$	$CH_3(CH_2)_3$ CHOH	296	tt	231		EtOH	f
23	$CH_3CO_2(CH_2)_7$ CHOH	n-C_5H_{11}	310	tt	231	27,900	EtOH	m

[a] K. Bowden, E. A. Braude, E. R. H. Jones and B. C. L. Weedon, *J. Chem. Soc.* 45 (1946). [b] E. A. Braude and C. J. Timmons, *J. Chem. Soc.* 2007 (1950). [c] E. B. Bates, E. R. H. Jones and M. C. Whiting, *J. Chem. Soc.* 1854 (1954). [d] L. Crombie, S. H. Harper and R. J. D. Smith, *J. Chem. Soc.* 2754 (1957). (measurements made on samples synthesised by different routes.) [e] A. Butenandt, E. Hecker and H.-G. Zachau, *Chem. Ber.* 88, 1185 (1955). [f] R. L. Lohmar, C. R. Smith and T. L. Wilson, *J. Org. Chem.* 25, 2034 (1960). [g] L. Crombie, *J. Chem. Soc.* 1007 (1955). [h] W. D. Celmer and I. A. Solomons, *J. Am. Chem. Soc.* 75, 3430 (1953). [i] J. O. Rodin, M. A. Leaffer and R. M. Silverstein, *J. Org. Chem.* 35, 3152 (1970). [j] A. Butenandt, E. Hecker, M. Hopp and W. Koch, *Ann. Chem.* 658, 39 (1962). [k] E. Truscheit and E. Eiter, *Ann. Chem.* 658, 65 (1962). (The acids corresponding to the esters gave identical results.) [l] P. L. Nichols, S. F. Herb and R. W. Riemenschneider, *J. Am. Chem. Soc.* 73, 247 (1951). (Data estimated from Fig. 3. + This material was stated to be impure.) [m] C. R. Smith, T. L. Wilson, E. H. Melvin and I. A. Wolff, *J. Am. Chem. Soc.* 82, 1417 (1960). [n] R. R. Allen, *J. Org. Chem.* 21, 143 (1956).

stituent group, Me in the present case. β is the resonance integral between the π-symmetry orbital of the Me group and the $2p\pi$ orbital of the C atom to which it is attached. Clearly, the terms in parentheses do not change on changing the position of substitution, and we may estimate the magnitude of Forbes' effect, ΔE_F, by consider-

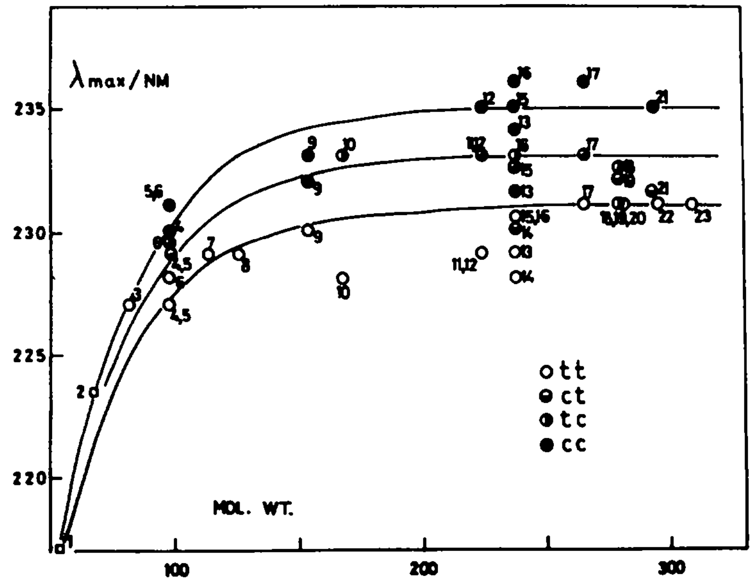


Fig. 1. The wavelength of maximum absorption for disubstituted conjugated dienes plotted against molecular weight. The solid curves join the theoretical points, calculated according to eqn (12), for symmetrically substituted di-n-alkyl dienes. The numbers correspond to Table 1.

ing changes in $C_\mu{}^2\beta^2$ on going from a conventional position of substitution to the type of interaction envisaged by Forbes; i.e. eqn (2)

$$\Delta E_\mu/\Delta E_F = C_\mu{}^2\beta_\mu{}^2/C_F{}^2\beta_F{}^2 \sim \beta_\mu{}^2/\beta_F{}^2. \qquad (2)$$

In order to estimate the ratio of β_μ to β_F two relationships between β and internuclear distance, d, are used, eqns (3)[9] and (4).[10]

$$\beta = -67.753\exp(-d/0.3727) \qquad (3)$$

$$\beta = -17.464/d^6. \qquad (4)$$

In these equations d is to be entered in Å and β is found in eV. As an estimate of d for Forbes' interaction, we take the distance from the Me carbon to carbon atom 2 in structure 1 and obtain, using eqns (2) and (3),

$$\Delta E_\mu/\Delta E_F \sim (20.2)^2 \sim 408$$

and using eqns (2) and (4).

$$\Delta E_\mu/\Delta E_F \sim (37.5)^2 \sim 1406.$$

Since the spectral shift for single Me substitution, ΔE_μ is 5 nm by Woodward's rules[1] it is quite clear that, unless the mechanism of the Forbes interaction is very different from that assumed here, no observable shift will result from it.

The explanation proposed by Crombie[5] is a steric one. He noted that in the case of the deca-2:4-dienols and methyl decadienoates, the wavelength of maximum absorption for the *trans–trans* isomers lies at significantly shorter wavelengths than for the *cis–cis*, and further that models of the compounds showed significant steric hindrance in the *cis* structures. Crombie pointed out that such steric hindrance could be relieved by in-plane or out-of-plane distortions of the diene system. The latter involves a twisting of the double bond, or bonds, and we can estimate the spectral shift caused by such a twisting in the following way:

Symmetry requires that the form of the π-electron molecular orbitals, ψ_m, of *s-trans*-butadiene be written as follows in terms of carbon $2p_z$ atomic orbitals, ϕ_μ.

$$\text{Energy}\uparrow\quad\begin{array}{ll}\psi_4 = a\phi_1 - b\phi_2 + b\phi_3 - a\phi_4 & b_g\\ \psi_3 = b\phi_1 - a\phi_2 - a\phi_3 + b\phi_4 & a_u\\ \psi_2 = b\phi_1 + a\phi_2 - a\phi_3 - b\phi_4 & b_g\\ \psi_1 = a\phi_1 + b\phi_2 + b\phi_3 + a\phi_4 & a_u\end{array}$$

The orbitals are classified with respect to the point symmetry group C_{2h}. The values of the coefficients a and b do not vary widely with different levels of MO theory. Thus a self-consistent field calculation by Kon[10] gives a = 0.4397 and b = 0.5538 whilst the Hückel orbitals have a = 0.3718 and b = 0.6015.

The lowest energy singlet excited state is obtained by promoting an electron from ψ_2 to ψ_3, ${}^1\chi_2{}^3$, and is of B_u symmetry. Configuration interaction can mix it with ${}^1\chi_1{}^4$. The effect of steric distortion upon the energies of these transitions may be assessed by use of eqn (5)

$$E_i = \sum_\mu C_{i\mu}^2\alpha_\mu + \sum_\mu\sum_{\mu\neq\nu} C_{i\mu}C_{i\nu}\beta_{\mu\nu} \qquad (5)$$

in which the $C_{i\mu}$ are atomic orbital coefficients and α_μ and $\beta_{\mu\nu}$ are core integrals.[11] Assuming that α_μ is the same for all μ and $\beta_{\mu\nu} = 0$ when μ is not bonded to ν we obtain eqn (6)

$$\Delta E_{32} = E_3 - E_2 = -8ab\beta_{12} + 4a^2\beta_{23} \qquad (6)$$

in which we have used the fact that $\beta_{12} = \beta_{34}$. ΔE_{32} is not the energy difference between the ground state and the excited state ${}^1\chi_2{}^3$, there are significant electron-repulsion terms which are not included in eqn (6). However, provided that any steric distortions are sufficiently small that the atomic orbital coefficients a and b may be considered to be unchanged by them, the change in energy brought about by twisting through an angle θ, $\Delta\Delta E_{32}^\theta$, may be expressed by means of eqn (7)

$$\Delta\Delta E_{32}^\theta = \Delta E_{32}(\theta = 0) - \Delta E_{32}(\theta = \theta). \qquad (7)$$

$\beta_{\mu\nu}$ may be taken to be proportional to the cosine of the angle of twist, θ[12] (eqn 8),

$$\beta_{\mu\nu}^\theta = \beta_{\mu\nu}^0\cos\theta \qquad (8)$$

so that $\Delta\Delta E_{32}^\theta$ is given by eqn (9) for a simultaneous twisting of bonds 1–2 and 3–4, and by eqn (10) for the

Table 2. Calculated shifts of the longest-wavelength diene absorption band for varying angles of twist of the formal double bonds

Angle of twist/ degrees	$\Delta\Delta E_{32}$/eV	Shift from 227 nm	Band position/ nm
0	0	0	227
2.5	0.005	0	227
5.0	0.021	1	228
7.5	0.048	2	229
10.0	0.085	4	231
12.5	0.133	6	233
15.0	0.191	8	235
17.5	0.260	11	238
20.0	0.339	15	242

twisting of the central bond, 2–3.

$$\Delta\Delta E^{\circ}_{32} = 8ab\beta^{\circ}_{12}(\cos\theta - 1) \qquad (9)$$

$$\Delta\Delta E^{\circ}_{32} = 4a^2\beta^{\circ}_{23}(1 - \cos\theta). \qquad (10)$$

$\Delta\Delta E^{\circ}_{41}$ is also given by eqn (9) for 1–2 and 3–4 twisting. For 2–3 twisting it is given by eqn (11).

$$\Delta\Delta E^{\circ}_{41} = 4b^2\beta^{\circ}_{23}(\cos\theta - 1). \qquad (11)$$

Equations (9)–(11) simply express in quantitative form the well-known result that the twisting of noded bonds decreases the energy of an orbital while the twisting of non-noded bonds increases it. We therefore expect ΔE_{32} to decrease for 1–2 and 3–4 twisting but to increase for 2–3 twisting. ΔE_{41} too decreases for 1–2 and 3–4 twisting and it is also decreased by 2–3 twisting. Since ${}^1\chi_2{}^3$ will make a larger contribution to the lowest-energy excited state than ${}^1\chi_1{}^4$, whilst the coefficient b is greater in magnitude than a, the effect of twisting the central bond on the energy of the long-wavelength absorption band will be rather finely balanced and we do not expect 2–3 twisting to have a significant effect on diene spectra for small angles of twist.

The effect of 1–2 and 3–4 twisting, on the other hand, is clearly in the required direction and a quantitative estimate of the effect may be made if β°_{12} is known. Since $\Delta\Delta E_{32}$ and $\Delta\Delta E_{41}$ are both given by eqn (9) the effects of configurational mixing of ${}^1\chi_2{}^3$ and ${}^1\chi_1{}^4$ do not affect our argument at this level of approximation. Taking Kon's values for a, b and β°_{12}[10] we obtain the results given in Table 2.

The numerical values in Table 2 are clearly of the correct order and strongly substantiate Crombie's proposal.[5] Angles of twist of the order of 10° are sufficient to explain the observed differences in the spectra of *cis–cis* and *trans–trans* isomers. We also note that twisting of the formal double bonds, by lowering the overlap between the carbon $2p\pi$ atomic orbitals at either end of the bond, should decrease the transition dipole moment of the component ethylene units[13] and hence the extinction coefficient of the diene absorption.[14] This prediction stands in good accord with the observation that for most of the compounds measured the extinction coefficient of the *trans–trans* isomer is significantly larger than that of the *cis–cis* with the *cis–trans* and *trans–cis* isomers lying in between.

It would make our explanation of the spectral differences between *cis–cis* and *trans–trans* isomers more convincing if other evidence for the twisting of the formal double bonds could be obtained, and there is such evidence. Crombie[5] noted that the C=C stretching bands of methyl decadienoates move to lower frequencies on going from *trans–trans*, through *cis–trans* and *trans–cis*, to *cis–cis*, which implies a weakening of the C=C bonds in this series. Similar results were found for the *p*-bromophenacyl esters.[5] Bacon and Maciel[15] have interpreted the proton NMR spectra of alkyl-substituted butadienes in terms of such an effect, together with an in-plane deformation. We discount the possibility that the spectral shifts discussed above could be caused by in-plane deformations, even if small distortions of this type are present, since much larger in-plane than out-of-plane movements would be necessary to cause appreciable changes in π-electron energy.

Having discussed the spectral differences within groups of isomers we now turn our attention to the behaviour of the diene absorption with increasing size of substituent group. Each type of isomer shows the same behaviour, the absorption maximum shifting to longer wavelengths as the length of the substituent chain increases. This behaviour, which is contrary to Woodward's rules, does not proceed indefinitely however; the curves approach asymtotes at ~235 nm, ~233 nm and ~231 nm for the *cis–cis*, *cis–trans* and *trans–cis* and *trans–trans* isomers respectively.

It is tempting at first sight to seek an explanation of this phenomenon in terms of increasing steric hindrance, but on closer examination this explanation seems unlikely for two reasons. Firstly, it appears unreasonable to assume that steric hindrance will continue to increase as a straight-chain hydrocarbon substituent is augmented by $-CH_2-$ groups beyond n-propyl. Secondly, if our discussion above has any substance, then the *cis–cis* series would be expected to behave differently from the *trans–trans* if steric hindrance were the essential factor. In fact, however, the curves for the two series of isomers are closely parallel. We therefore neglect steric hindrance as an interpretation of the shift to longer wavelength with increasing substituent chain length, and seek the explanation in terms of the weak and slowly attenuating mesomeric effect of the substituent groups on the diene spectra.[16]

We take as our starting point eqn (12) in which the wavelength of maximum absorption, λ, of a symmetrically disubstituted diene is expressed as 217 nm, the value of λ for *s-trans*-butadiene, plus the sum of a geometric progression.

$$\lambda_{\alpha\beta} = 217 + \sum_{n=1}^{m} a_{\alpha\beta} r^{n-1} \qquad (12)$$

$\alpha\beta$ indicates the conformation of the diene and m is the number of Me or methylene groups in each of the two saturated chains attached to the diene, i.e. there are 2 m Me or methylene groups in total.

For 1,4-dimethylbutadiene, for example, m = 1 and

$$\lambda_{tt} = 217 + a_{tt} = 227\ \text{nm}$$

giving $a_{tt} = 10$ nm in accord with Woodward's rules. r, which does not depend upon the conformation of the diene, represents the factor by which the effect of the Me or methylene group upon λ attenuates as the group moves further away from the diene unit. It must therefore be less than unity and we can consequently express the asymptotic limit of $\lambda_{\alpha\beta}$, $\lambda_{\alpha\beta}(\infty)$, by means of eqn (13)

$$\lambda_{\alpha\beta}(\infty) = 217 + a_{\alpha\beta}/(1 - r). \qquad (13)$$

Since we have three different values of $\lambda_{\alpha\beta}(\infty)$ we clearly require three different values of $a_{\alpha\beta}$. Alternatively, one might fix $a_{\alpha\beta}$ and chose different values of r, but this would imply that the transmission of the effect on the spectrum through a methylene group at some distance from the diene system is different for different conformations of that diene. This seems most unlikely and we have not considered this possibility further.

In order to determine $a_{\alpha\beta}$ and r we first consider the *tt* series for which we have most data and a rather definite indication (Fig. 1) that $\lambda_{tt}(\infty) = 231$ nm. We now choose a_{tt} and r in such a way that the correct value of $\lambda_{tt}(\infty)$ is obtained from eqn (13) while, at the same time, a good fit

Table 3. Wavelengths of maximum absorption, calculated using eqn (12), for conjugated dienes of the form: R–CH=CH–CH=CH–R

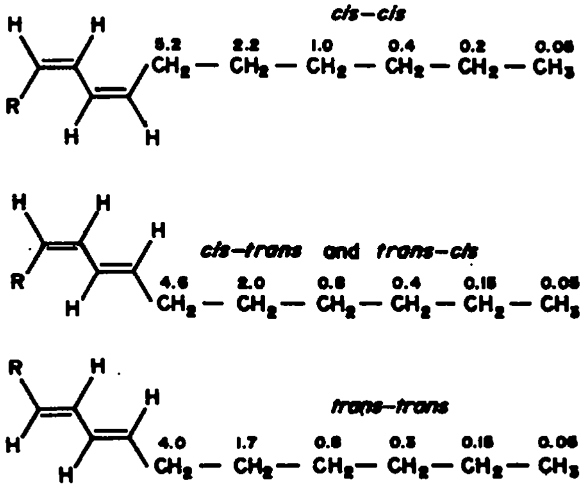
m	R	M.Wt.	λ(cc)/nm	λ(ct,tc)/nm	λ(tt)/nm
	H	54	217	217	217
1	CH_3	82	227.3	226.1	225
2	$(CH_2)_2H$	110	231.7	230.1	228.4
3	$(CH_2)_3H$	138	233.6	231.7	229.9
4	$(CH_2)_4H$	166	234.4	232.5	230.5
5	$(CH_2)_5H$	194	234.8	232.8	230.8
6	$(CH_2)_6H$	222	234.9	232.9	230.9
7	$(CH_2)_7H$	250	235.0	233.0	231.0
	Value of $a_{\alpha\beta}$ /nm		10.3	9.1	8.0
	Value of r		0.429	0.429	0.429

to the data for *tt* compounds absorbing at shorter wavelengths is obtained with eqn (12).

The intermediate region raises problems in so far as the molecules for which we have data represent a wide variety of chain lengths, and groupings etc (Table 1). We have therefore used the simple property of molecular weight as abscissa. This procedure gives value of a_{tt} = 8.0 nm and r = 0.429. Substitution of this value of r into eqn (13) with the experimental results for $\lambda_{cc}(\infty) = 235$ nm and $\lambda_{ct}(\infty) = \lambda_{tc}(\infty) = 233$ nm gives values of $a_{cc} = 10.3$ nm and $a_{ct} = a_{tc} = 9.1$ nm. The continuous lines in Fig. 1 join the points calculated for the above values of the parameters $a_{\alpha\beta}$ and r for the compounds listed in Table 3.

The results may also be usefully illustrated by means of the following diagrams. The figures above each methylene or Me group give that part of the spectral shift, in nm, to be attributed to that particular group in a symmetrically disubstituted *s-trans*-butadiene. Since the other chain makes an identical contribution, the total observed shift is given by the combined sums of the figures for the two chains.

It is interesting to compare the value of r with a result due to Jaffé for the transmitting effects of alkyl groups as measured by the Hammett relation.[17] He states that these average 0.410 for $-CH_2-$ and 0.206 for $-CH_2CH_2-$; figures which might be compared with 0.429 and $(0.429)^2 = 0.184$ of the present work. This close agreement with Jaffé's independent assessment, and the way in which the theoretical lines in Fig. 1 reflect the general trend of the experimental data provide strong confirmation that our interpretation of the basic phenomenon is correct. At this point we should perhaps reiterate that, although we have discounted the effect of steric hindrance as the prime cause of the spectral shift of diene absorption with increasing substituent chain-length for the molecules discussed here, we recognize the dominant role which steric hindrance plays in many aspects of the spectroscopy of polyenes. We believe that in general the electronic effect to which we have drawn attention in the second part of this paper must be combined with steric effects, such as that discussed in the first part, in any interpretation of the UV spectra of such systems. Thus the quantity $a_{\alpha\beta}$ which we have used is a



Structure 2

composite parameter, and the values which we have determined for it reflect both a steric and an electronic (mesomeric) component. We therefore expect that for other positions of substitution, for example, the value of $a_{\alpha,\beta}$ will change for both steric and electronic reasons. The parameter r, on the other hand, is purely electronic and is expected to be transferable within n-alkyl chains.

In conclusion, in view of the continuing interest in Woodward's rules and the spectra of polyenes, particularly in connexion with conformational analysis,[18,19] it appears worthwhile to record the following observations. Firstly, trends very similar to those noted above are found in a wide variety of similarly di-substituted dienes which could not be included in the analysis because they absorb at much longer wavelengths on account of further conjugation, frequently to a carbonyl group. The following papers are of interest in this connexion; Crombie,[5] Elvidge *et al.*,[20] Allan *et al.*,[21] Wailes[22] and Fegley *et al.*[23]

Mono- and poly-substituted dienes, trienes[24,25] and tetraenes[26] also appear to show similar trends in their spectra, but insufficient data for a meaningful general analysis were found. Furthermore, polysubstituted compounds are those most likely to show λ values influenced by both electronic and steric factors, thus making interpretation particularly difficult. For example, this might well be the case with the data reported by Julia *et al.*[27]

REFERENCES

[1] R. B. Woodward, *J. Am. Chem. Soc.* **64**, 72 (1942).

[2a] J. J. Jaffé and M. Orchin, *Theory and Application Ultraviolet Spectroscopy*. Wiley, London (1962); [b] J. N. Murrell, *The Theory of the Electronic Spectra of Organic Molecules*. Methuen, London (1963); [c] A. I. Scott, *Interpretation of the Ultraviolet Spectra of Natural Products*. Pergamon, Oxford (1962); [d] A. E. Gillam and E. S. Stern, *An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry*. (2nd Edn). Arnold, London (1962).

[3] *Organic Electronic Spectral Data*, Vols. I–XIII. Wiley, Interscience (1960–78).

[4] *Photoelectric Spectrometry Group Bull.* **16**, 441 (1965).

[5] L. Crombie, *J. Chem. Soc.* 1007 (1955).

[6] W. F. Forbes, R. Shilton and A. Balasubramanian, *J. Org. Chem.* **29**, 3527 (1964).

[7] Ref. 2*b*, p. 225.

[8] Ref. 2*b*, p. 222.

[9] H. C. Longuet-Higgins and L. Salem, *Proc. Roy. Soc.* **A251**, 172 (1959).

[10] H. Kon, *Bull. Chem. Soc. Japan* **28**, 275 (1955).

[11] Ref. 2*b*, p. 109.

[12] Ref. 2*a*, p. 389.

[13] R. S. Mulliken, *J. Chem. Phys.* **7**, 20 (1939).

[14] Ref. 2*b*, p. 150.

[15] M. Bacon and G. E. Maciel, *Mol. Phys* **21**, 257 (1971).

[16] Ref. 2*b*, Chap. 10.

[17] H. H. Jaffé, *Chem. Revs.* **53**, 191 (1953); *J. Chem. Phys.* **21**, 415 (1953).

[18] N. L. Allinger and J. C. Tai, *J. Am. Chem. Soc.* **99**, 4256 (1977).

[19] T. Liljefors and N. L. Allinger, *Ibid.* **100**, 1068 (1978).

[20] J. A. Elvidge, R. P. Linstead, P. Sims and B. A. Orkin, *J. Chem. Soc.* 2235 (1950).

[21] J. L. H. Allan, E. R. H. Jones and M. C. Whiting, *Ibid.* 1862, (1955).

[22] P. C. Wailes, *Austral. J. Chem.* **12**, 173 (1959).

[23] M. F. Fegley, N. M. Bortnick, C. H. McKeever and F. B. Farnum, *J. Am. Chem. Soc.* **79**, 4734 (1957).

[24] L. Crombie and A. G. Jacklin, *J. Chem. Soc.* 1632 (1957).

[25] K. Alder and H. von Brachel, *Ann. Chemie* **608**, 195 (1957).

[26] D. Holme, E. R. H. Jones and M. C. Whiting, *Chem. & Ind.*, 928 (1956).

[27] M. Julia, Ch. Descoins and C. Rissé, *Tetrahedron* Supplement **8**, 443 (1966).