A Theoretical Interpretation of Dale's Rule for the Position of the Absorption Bands of Linear Conjugated Polyenes

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Dale^{1,2} has noticed that the wavelength of the p^{th} absorption band (λ_p) of a linear conjugated polyene containing n double bonds, is almost the same as that of the first absorption band of a polyene containing n/p double bonds. If p/n is not an integer then the wavelength for this hypothetical molecule is interpolated from the experimental curve relating λ_1 to n for the real polyenes. To explain this generalization Dale postulated a selection rule for the polyene transitions, namely that only the outermost π -electron shell could be excited. In the ground state of the polyenes the first n molecular orbitals are filled, so that Dale's selection rule means that the absorption bands arise from the transitions $n \rightarrow n+1$, $n \rightarrow n+2$, $n \rightarrow n+3$, etc., but that $n-1 \rightarrow n+1$, etc. are forbidden.

Dale's selection rule was derived from the free-electron-pattern of molecular orbital energies. He showed that the transition energy was given by the formula

$$\Delta E(n \rightarrow n+p) \propto \frac{p}{n} + \frac{p^2}{n^2} \quad (1)$$

if the free electron path was taken to be $2n$, and this formula explains his observations. However, the transitions from the other occupied orbitals of the ground state do not fall into this pattern, thus

$$\Delta E(n+1-p \rightarrow n+1) \propto \frac{p}{n} + \frac{p(2-p)}{n^2} \quad (2)$$

Kuhn and Bar³ have shown that even if the effect of bond alternation on the free electron potential is allowed for, the pattern of orbital energies explains the experimental results only if Dale's selection rule is adopted. However, just because an empirical theory gives results which agree with experiment that does not mean that it is correct. The agreement may be fortuitous. On the free electron theory the second absorption band should arise from the transition $n-1 \rightarrow n+1$, whether we have bond alternation or not, and there is no theoretical

justification behind Dale's selection rule, which removes this transition from the spectrum. In this note I shall show that Dale's observations can be explained without introducing any new selection rules.

Although a theory based on a one-electron Hamiltonian (e.g. free electron or Hückel theory) can correlate the position of a particular band (especially the first band) in a series of related molecules, it fails to explain the relative positions of successive bands in the spectrum. To do this the electron repulsion terms in the Hamiltonian have to be taken into account. A theory of polyene spectra which does include these terms, and which is justified for the polyenes because of the double bond localisation in these molecules, has been developed by Simpson^{4,5}. In this theory he just considers the electronic interaction between n coupled ethylene fragments, each of which has one excited state: that giving the strong band $V \rightarrow N$ of ethylene ($\lambda \sim 1700 \text{ \AA}$). If there is an interaction term of the Hamiltonian H' between two adjacent double bonds, then the energy of the p^{th} excited state can be shown to be⁶

$$E_p = E_0 - 2 |H'| \cos[\pi p/(n+1)] \quad (3)$$

where E_0 is the excitation energy of a single double bond. This formula gives fairly good agreement for the position of the fundamental and overtone bands of the linear polyenes; it therefore follows that it must also explain Dale's observations. From expression 3, the first band of the n/p polyene has an energy

$$\begin{aligned} E_1 &= E_0 - 2 |H'| \cos[\pi / (\frac{p}{n} + 1)] \\ &= E_0 - 2 |H'| \cos[\pi p/(n+p)] \end{aligned} \quad (4)$$

If p is significantly smaller than n , as it must be to see a band in the accessible ultra-violet region of the spectrum, then $\cos[\pi p/(n+p)] \sim \cos[\pi p/(n+1)]$. For example, for the 5th band of dodecaprenol- β -carotene ($n=19$), Dale calculates $\lambda_5 = 292 \text{ m}\mu$, and the observed value is $288 \text{ m}\mu$. But for this case $\cos(5\pi/20) = 0.71$ and $\cos(5\pi/24) = 0.79$, which are sufficiently close to explain Dale's observations.

Since Simpson's theory gives a satisfactory qualitative account of the polyene spectra, it must be assumed that a free electron theory which includes bond alternation and electron interaction would do so also, and in this theory Dale's selection rule would not be required.

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Received September 28, 1961.

On the Donor Strength of Amides

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It has previously been suggested¹ that two main effects can be predicted from a comparison of the strengths of ketones and esters as donor molecules. Accordingly the inductive effect associated with the substitution of the more electronegative methoxy group for a methyl group can be expected to reduce the donor strength, while this effect may be counteracted by the delocalization of one of the two lone pairs of electrons in the ether oxygen atom. The two effects seem to balance each other in this instance.

If the carbonyl oxygen atom in an amide acts as the donor, the same two effects can be assumed to influence the donor strengths when passing from ketones to amides. The inductive effect associated with the substitution of the $(\text{CH}_3)_2\text{N}$ group for a CH_3 group should reduce the donor strength while the delocalization of the lone pair electrons of the nitrogen atom should exert an opposing influence. In order to estimate the magnitude of the donor strength of amides compared with that of ketones, some reactions between tertiary amides and acetone as donors and SbCl_5 or SnCl_4 as acceptors have been studied by qualitative thermochemical measurements. The effect of further substitution leading to tetramethylurea was also studied.

Experimental. All chemicals used were commercial products which were further purified by distillation.

The thermochemical measurements were made in ethylene chloride solutions as described earlier², but with different concentrations.

Results and discussion. In each case the infrared spectra of the addition compounds formed in the systems studied (unpublished) show a decrease in the carbonyl bond frequency (in the free molecules situated in the range 1690–1650 cm^{-1}). In the compound formed between SbCl_5 and NN-dimethylformamide, however, this decrease is not significant, whereas in the compound formed with NN-dimethylacetamide the decrease is about 20 cm^{-1} . A decrease in the carbonyl bond frequency was earlier assumed to indicate that the carbonyl oxygen atom functioned as the donor. Although the negligible shift found in NN-dimethylformamide cannot be explained without further investigation, there is no prior reason to suspect that this compound would react differently from NN-dimethylacetamide. From the infrared spectra, therefore, it appears as though the carbonyl oxygen atom acts as the donor in all these molecules. It is further suggested that the oxygen atom in these amides functions as a donor in compounds formed with BCl_3 and BBr_3 ⁴ and with TiCl_4 ⁵.

The results from the thermochemical measurements are given in Table 1. From this table it appears that the amides are much better donor molecules than the ketone. If the inductive and the delocalization effects are the main influences on the relative donor strengths when passing from ketones to amides, the delocalization effects seems to be much more significant. With SbCl_5 tetramethylurea is a better donor than the amides. Other effects that can influence the donor strength cannot be excluded, but a discussion of these possible influences can only be made after further investigations of the compounds formed. In this connection a structure determination of the compound $\text{SbCl}_5 \cdot \text{HCON}(\text{CH}_3)_2$ using X-ray techniques has already been started at this institute.

A grant from the *Swedish Natural Science Research Council* is gratefully acknowledged.

Table 1.