

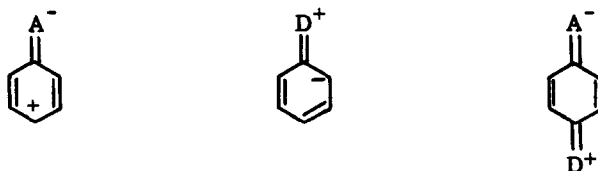
## THE DESCRIPTION OF THE EXCITED STATES OF AROMATIC MOLECULES CONTAINING MESOMERIC SUBSTITUENTS

R. Grinter and E. Heilbronner, Organisch-chemisches Laboratorium der Eidgenössischen Technischen Hochschule Zürich, and

M. Godfrey and J. N. Murrell, Dept. of Chemistry, The University, Sheffield.

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IT has become established to formulate the excited states of aromatic molecules containing mesomeric groups by means of resonance structures of the following type:



A and D are respectively electron accepting ( $-M$ ) and electron donating ( $+M$ ) groups.

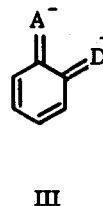
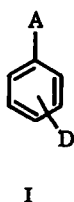
If this formulation is adopted, it leads to certain conclusions concerning the relative energies and the charge distributions of these excited states. In this way it is possible to understand general properties such as the bathochromic shift of the absorption spectrum of an aromatic nucleus on substitution with either an A or a D, and the fact that molecules containing donor groups, for example  $\text{ArOH}$ ,  $\text{ArNHR}$ ,  $\text{ArNR}_2\text{H}^+$  and  $\text{ArSH}$ , are stronger acids in the first excited states than in the ground states whereas those containing acceptor groups for example  $\text{ArCOOH}$ ,  $\text{ArCR}=\text{OH}^+$  and  $\text{ArCR}=\text{NRH}^+$  become weaker acids in the excited states.<sup>1</sup>

<sup>1</sup> A. Weller, Progress in Reaction Kinetics 1, 187 (1961).

On the other hand, it should be emphasised that the resonance theory fails badly when called upon to predict more detailed results such as the relative excitation energies of polysubstituted aromatic systems and the detailed excited state electron distribution in the aromatic fragment. However these detailed results, as well as the general results, can readily be understood on the basis of a molecular orbital model incorporating locally excited and charge transfer states.

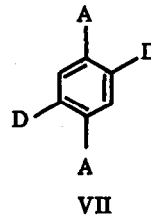
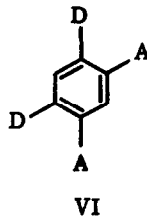
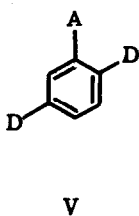
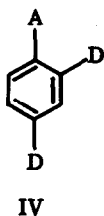
**Example 1.**

The spectra of the ortho and meta isomers of molecules of the type I are quite similar to each other but different from those of the para isomers. Also the former generally absorb at longer wavelengths than the latter:



This cannot be understood on the basis of resonance theory which would lead one to expect that the meta compounds should be the odd ones out, as no structures of the type II or III can be drawn for them.

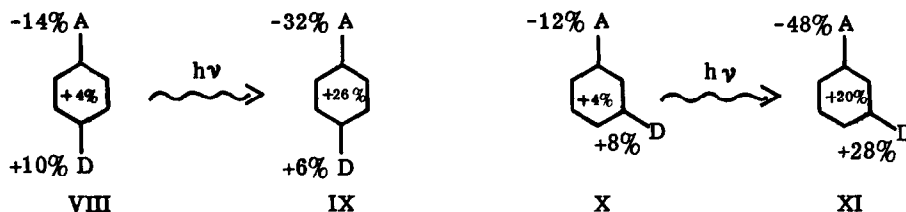
Likewise, in polysubstituted molecules such as IV to VII, those with the donating groups in para relationship absorb at the longest wavelength, even though fewer polar resonance structures without long bonds can be drawn for them.



The molecular orbital theory however is in agreement with all the above experimental results.

### Example 2.

Zimmerman<sup>2</sup> has reported that a solution of meta-nitrophenyl-tritylether in aqueous dioxane, though almost completely unreactive in the dark, hydrolyses rapidly when irradiated. The para isomer however, which reacts in the dark, hydrolyses only a little faster on irradiation. Similar results have been obtained by Havinga<sup>3</sup> on the photochemical hydrolysis of meta and para-nitrophenyl-phosphates. These results which are diametrically opposed to the resonance expectation are again easily explained by the above molecular orbital model. In formulae VIII to XI the change in electron density on going from the ground to the excited state is given for a typical model (electron affinity  $E_A = -1$  ev, ionisation potential  $I_D = 10$  ev).



### Example 3.

An estimate of the change, on excitation, of the charge density at a particular atom in an aromatic system may be obtained from the effect of introducing a more electronegative atom at that position. The absorption spectra of 2- and 3-nitropyridines are similar to each other and different

2 H. Zimmerman, Chem. and Eng. News July 17, 1961, p.46.

3 E. Havinga, R. O. De Jongh and W. Dorst, Rec. Trav. Chim. 75, 378 (1956); E. Havinga, Koninkl. Nederl. Akad. Wetenschappen 70, 52 (1961), and personal communication.

from that of 4-nitropyridine.<sup>4</sup> The same is true for the aminopyridines.<sup>5</sup> The spectral shifts which occur on the protonation of an amino-aza-compound are also contrary to the resonance picture. For example the red shift of the first bands of 6- and 7-aminoquinolines on protonation are approximately equal.<sup>6</sup> Again these results are to be expected on the basis of a molecular orbital model.

A detailed theoretical treatment of the excited states of these compounds will be published by us in the near future.

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4 W. Gruber, Canad. J. Chem. 31, 1020 (1953).

5 E. A. Steck and G. W. Ewing, J.A.C.S. 70, 3397 (1948).

6 J. N. Murrell, J. Chem. Soc. 296 (1959).