# Energy Levels of Aromatic Hydrocarbons

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July 20, 1949

SOME current theories of the $\pi$-electron energy levels of aromatic molecules[1-3] start from a scheme of one-electron molecular orbitals and work from the supposition that the lower absorption bands record transitions, by one electron, from one molecular orbital to another. According to this view a molecular state can be described by a single "configuration," or assignment of electrons to molecular orbitals, the latter being either made up from atomic orbitals[1,2] or chosen in some other way[3] to fit a potential having the symmetry of the molecule. Evidently, it is essential for a theory built up in this way that there should be no large interaction terms between different configurations; this has usually been taken for granted, perhaps from the fact that in atomic theory "configuration interaction" can often be neglected.

There are indications however that configuration interaction in molecular theory does not play the same minor role as it does in atomic theory, and that calculations neglecting it may go seriously wrong. The subject has been explored in benzene[4] by setting up a number of wave functions, corresponding to different configurations but of the same symmetry, and using them as a basis for a variation calculation with electron repulsion as the perturbing potential. The procedure is an extension of the method of Goeppert-Mayer and Sklar[1] in benzene and follows it closely in technique: Goeppert-Mayer and Sklar calculated the effect of electron repulsion on single configurations, and the extension is to work out as well the degree to which electron repulsion causes the mixing of different configurations. A measure of the importance of this mixing is the depression in the energy, measured relative to the most stable single configuration, caused by other configurations.

| Symmetry | Lowest config-uration energy | Energy in-cluding config. interaction | Depression rel-ative to lowest configuration |
|---|---|---|---|
| $A_{1g}$ | 0 | 0 | 2.0 ev |
| $B_{2u}$ | 3.7 ev | 1.2 ev | 4.5 ev |
| $B_{1u}$ | 4.2 ev | 3.3 ev | 2.9 ev |
| $E_{2g}$ | 6.1 ev | 3.0 ev | 5.1 ev |

Interactions are considered between configurations whose energies fall within 10 ev of the lowest of any one symmetry type. The effect varies strongly between symmetries, and to put the magnitudes in their proper perspective it may be noted that the depressions are comparable with spectral intervals.

The calculations are being published in detail.[4] As is to be expected in any non-empirical theory, good agreement with experiment will have to await inclusion of many-center integrals and perhaps some more subtle refinements. The chief interest of the work at this stage is to suggest that a basis of single configurations in one-electron molecular orbitals is not likely to prove well suited to the discussion, even qualitatively, of excited states and spectral bands of aromatic molecules. Physically it must be the case that the electron motions depart considerably from the uncorrelated motions implicit in any theory of single configurations, and therefore have to be described as a linear combination of configurations. It follows that a satisfactory theory will need either to include configuration interaction within a basis of several configurations, or to start from a different basis altogether, such as electron-pair wave functions or some elaboration of them.

There is one spectral assignment in benzene, previously made on the basis of Goeppert-Mayer and Sklar's work, which these calculations call seriously in question. It is the assignment $A_{1g}-B_{1u}$ for the 2000A band. Under configuration interaction, an $E_{2g}$ state is depressed very strongly relative to the $B_{1u}$, suggesting that some

attention should be paid to the alternative assignment $A_{1g}-E_{2g}$ which was mentioned as a possibility some years ago by Nordheim, Sponer, and Teller.[5] It is a significant, and perhaps hopeful, sign that this assignment agrees with valence-bond theory including polar structures,[4] and an experimental decision would greatly assist in sifting the claims of present theories.

[1] M. Goeppert-Mayer and A. L. Sklar, J. Chem. Phys. 6, 645 (1938).
[2] Coulson, Proc. Phys. Soc. 60, 257 (1948).
[3] John R. Platt, J. Chem. Phys. 17, 484 (1949).
[4] D. P. Craig, to be published.
[5] Nordheim, Sponer, and Teller, J. Chem. Phys. 8, 455 (1940).

## Mass Spectra of *cis*- and *trans*-Decahydronaphthalene

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October 3, 1949

MASS spectra of many *cis*- and *trans*-isomers of hydrocarbons have been measured and, in general, there is very little difference between the two isomers.[1] A notable exception is the *cis*- and *trans*-forms of decahydronaphthalene. Recently, pure NBS standard samples of these two isomers have become available and we have measured the spectra for publication in the API Catalog.[1] Spectra were measured with a Consolidated mass spectrometer following standard procedures except that pressure in the reservoir was measured by a micromanometer to obtain the sensitivity (current per unit pressure) at the maximum peaks.

Table I lists some of the larger and more distinctive peaks ob-

TABLE I. Mass spectra of *cis*- and *trans*-decahydronaphthalene.

| m/e | Formula | Relative intensities cis | trans |
|---|---|---|---|
| 138 | $C_{10}H_{18}$ | 71.8 | 85.5 |
| 123 | $C_9H_{15}$ | 0.90 | 0.93 |
| 110 | $C_8H_{14}$ | 7.3 | 6.9 |
| 109 | $C_8H_{13}$ | 30.8 | 16.7 |
| 97 | $C_7H_{13}$ | 9.7 | 8.0 |
| 96 | $C_7H_{12}$ | 88.4 | 62.9 |
| 95 | $C_7H_{11}$ | 52.1 | 63.7 |
| 83 | $C_6H_{11}$ | 11.2 | 14.1 |
| 82 | $C_6H_{10}$ | 64.2 | 68.2 |
| 81 | $C_6H_9$ | 88.6 | 57.0 |
| 69 | $C_5H_9$ | 22.5 | 49.7 |
| 68 | $C_5H_8$ | 42.3 | 100.0 |
| 67 | $C_5H_7$ | 100.0 | 96.3 |
| 55 | $C_4H_7$ | 47.6 | 43.7 |
| 54 | $C_4H_6$ | 29.2 | 23.9 |
| 41 | $C_3H_5$ | 85.1 | 86.9 |
| 39 | $C_3H_3$ | 46.8 | 46.5 |
| 29 | $C_2H_5$ | 30.1 | 29.6 |
| 28 | $C_2H_4$ | 12.9 | 11.9 |
| 27 | $C_2H_3$ | 44.4 | 42.9 |
| Sensitivity relative to *n*-butane | | 0.432 | 0.555 |

tained with 70 volts ionizing voltage. The most conspicuous difference between the spectra occurs on the 68$^+$ and 67$^+$ peaks but there are large differences on all the larger peaks heavier than 68, while on all the lighter peaks differences are small. It is rather surprising that the most probable ionization processes give ions with five carbon atoms for three C—C bonds must be broken to give $C_5$ ions while only two bonds need to be broken to give other ions.

[1] Catalog of Mass Spectral Data. API Research Project 44, Nat. Bur. of Standards.