

On the Quantum Mechanical Stability of a Benzol Molecule

M. Markov

Citation: [The Journal of Chemical Physics](#) **1**, 784 (1933); doi: 10.1063/1.1749245

View online: <http://dx.doi.org/10.1063/1.1749245>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/1/11?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Quantum mechanical study on the fragmentation of the POPOP molecule](#)

AIP Conf. Proc. **1504**, 1166 (2012); 10.1063/1.4772134

[Classical and quantum mechanics of diatomic molecules in tilted fields](#)

J. Chem. Phys. **122**, 184303 (2005); 10.1063/1.1888574

[A simplified quantum mechanical model of diatomic molecules](#)

Am. J. Phys. **46**, 889 (1978); 10.1119/1.11510

[The Quantum Mechanics of Collisions between Diatomic Molecules](#)

J. Chem. Phys. **21**, 2045 (1953); 10.1063/1.1698740

[QuantumMechanical Resonance between Identical Molecules](#)

J. Chem. Phys. **18**, 1150 (1950); 10.1063/1.1747904



On the Quantum Mechanical Stability of a Benzol Molecule

M. MARKOV, *Physical Institute, University of Moscow*

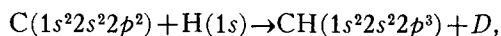
(Received August 28, 1933)

The Heitler-London-Rumer treatment of valence bonds is applied to the benzol molecule, considered as a system of six trivalent nitrogen-like CH groups. Partial solution of the secular equation of the thirty-fourth degree shows that this model of the benzol ring is thermodynamically

unstable relative to three acetylene molecules, in disagreement with experiment. The method does not take cognizance of the directional properties of valence bonds (Slater-Pauling). *Editors.*

AT the first attempt to approach the interpretation of the stability of a benzol molecule from the standpoint of Heitler-London's homopolar bending it is natural to start from the simplified model of a benzol molecule, namely, to assume that the benzol ring consists of six nitrogen-like atoms; that is, to take each of the CH groups that enter symmetrically into the structural formula of benzol as a single nitrogen-like trivalent atom.

The indication of the nitrogen-likeness of the CH molecule may be found, for instance, in the work of R. S. Mulliken,¹ who gives for the reaction of formation of CH the following formula:



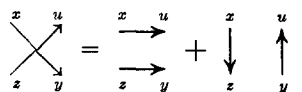
where D is the heat of dissociation and $1s^2$, $2s^2$, \dots , etc., are the current notations in the systematics of spectra. Thus, we replace all CH in the benzol molecule by nitrogen atoms in their fundamental states.

Following the usual method for solving such problems it is necessary to start from "eigenvalue problem" in the space of valency functions: $(\lambda - W)\varphi = 0$. In case of a cyclic chain of six trivalent atoms 1, 2, 3, 4, 5, 6 the operator W is equal to $T_{12} + T_{23} + T_{34} + T_{45} + T_{56} + T_{61}$, and T_{xy} is a differential operator of the kind² $T_{xy} = D_{xy}D_{yx} - 3$. In other words the "exchange integrals" between the neighboring atoms are

put equal to 1 and the interaction between the noncontiguous atoms is neglected.

Further, it is necessary to select independent valency functions φ_i ; "to build a basis"; i.e., to select a complete set of independent functions φ_i each of them being a product of symbols of the kind $([xy]; [xz] \dots)$. The symbol $([xy])$ corresponds to a valency bond between the atoms x and y and, moreover, to a valency bond having a definite sense (from x to y); i.e., to a valency arrow.

If one uses the methods developed by G. Rumer the building of the basis does not present any difficulty even in the case of such a complicated system as a benzol molecule. To build the basis one has according to Rumer³ to proceed as follows. Atoms are arranged arbitrarily along a circumference⁴ and linked up by valency arrows; each of the figures of this kind having no intersecting arrows then corresponds to an independent valency state, and all other figures with intersecting arrows (as shown for the general case by Rumer) represent superpositions of independent valency states. For example:



If the brackets of the kind $([xy])$ correspond to the valency arrows directed from X to Y ,

¹ R. S. Mulliken, *Phys. Rev.* **40**, 55; **41**, 49 (1932).

² M. Born, *Ergebnisse der Exakten Naturwissenschaften* Vol. 10, 1931,

³ G. Rumer: *Zur Theorie der Spinvalenz*, Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen. 1932. No. 27.

⁴ Generally along the convex side of the closed curve.

we can write the same in symbols: $[xy][zu] = [xu][zy] + [xz][yu]$.

In our case there are thirty-four independent valency states. They are given in Fig. 1.

Operating on the valency functions by the operator W , using the notations of the valency functions of Fig. 1, and expressing the result by independent valency states, we obtain:

$$Wa_1 = 20a_1 + 18b_1 + 3l_1 - 8c_4 + j_1 + 3k_1,$$

$$Wc_1 = 16c_1 - 2i_2 - 6d_2 - 6d_5 - 18m_2 - 4a_4,$$

$$Wd_1 = 16d_1 + 12m_1 - 4m_2 + i_1 - 2c_2 - 2c_6 - 2l_2 + 6b_3 - 6b_2 + 2k_3,$$

$$Wb_1 = 10b_1 + a_1 - a_4 + 8m_1 - 8m_2 + 2d_3 - 2d_2 + 2d_5 - 2d_6,$$

$$Wl_1 = 22l_1 - 8d_6 + 8d_3 + 2c_1 - 2c_4 + 3a_1 - 3a_4 + 12b_1 + 4m_1 - 4m_2,$$

$$Wk_1 = 22k_1 - 8d_2 + 8d_5 + 2c_1 - 2c_4 + 3a_1 - 3a_4 + 12b_1 + 4m_1 - 4m_2,$$

$$Wj_1 = 30j_1 - 18a_4 + 18a_1,$$

$$Wi = 18i_1 - 9c_4 - 9c_6 - 9c_2,$$

$$Wm_1 = 6m_1 + 4b_1 - 4b_2 + 4b_3 - c_4 - c_6 - c_2.$$

Thus, generally speaking, we get a matrix of the thirty-fourth order. But as the operator W commutes with the cyclic operator Z , there is the possibility of reducing the order of the matrix. By the cyclic operator we understand the operator which acting on any function $\varphi_i(a_i; b_i; c_i \dots)$ represented in Fig. 1 changes it into φ_{i+1} if $i < n$ ($i = 1, 2 \dots n$) and into $+\varphi_1$ or $-\varphi_1$ if $i = n$.

Transforming the operator Z to the principal axes, we get:⁵

$$Z(a_1 + \sigma a_2 + \sigma^2 a_3 + \sigma^3 a_4 + \sigma^4 a_5 + \sigma^5 a_6) = \sigma^5(a_1 + \sigma a_2 + \sigma^2 a_3 + \sigma^3 a_4 + \sigma^4 a_5 + \sigma^5 a_6),$$

$$Z(a_1 + \sigma^2 a_2 + \sigma^4 a_3 + a_4 + \sigma^2 a_5 + \sigma^4 a_6) = \sigma^4(a_1 + \sigma^2 a_2 + \sigma^4 a_3 + a_4 + \sigma^2 a_5 + \sigma^4 a_6),$$

$$Z(a_1 + \sigma^3 a_2 + a_3 + \sigma^3 a_4 + a_5 + \sigma^3 a_6) = \sigma^3(a_1 + \sigma^3 a_2 + a_3 + \sigma^3 a_4 + a_5 + \sigma^3 a_6),$$

$$Z(a_1 + \sigma^4 a_2 + \sigma^2 a_3 + a_4 + \sigma^4 a_5 + \sigma^2 a_6) = \sigma^2(a_1 + \sigma^4 a_2 + \sigma^2 a_3 + a_4 + \sigma^4 a_5 + \sigma^2 a_6),$$

$$Z(a_1 + \sigma^5 a_2 + \sigma^4 a_3 + \sigma^3 a_4 + \sigma^2 a_5 + \sigma a_6) = \sigma(a_1 + \sigma^5 a_2 + \sigma^4 a_3 + \sigma^3 a_4 + \sigma^2 a_5 + \sigma a_6),$$

$$Z(a_1 + a_2 + a_3 + a_4 + a_5 + a_6) = 1(a_1 + a_2 + a_3 + a_4 + a_5 + a_6).$$

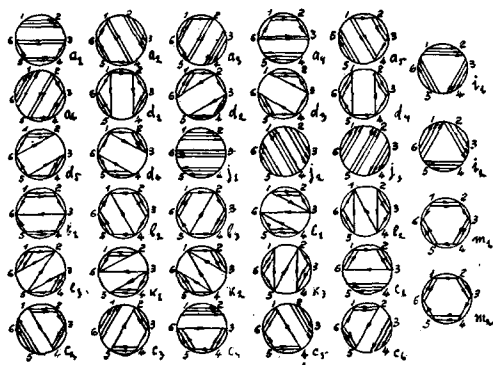


FIG. 1.

Denoting linear combinations of the kind a_i by A_i , C_i , etc., we have in case of c_i and d_i also:

$$ZC_1 = \sigma^5 C_1, \quad ZD_1 = \sigma^5 D_1,$$

$$ZC_2 = \sigma^4 C_2, \quad ZD_2 = \sigma^4 D_2,$$

$$ZC_3 = \sigma^3 C_3, \quad ZD_3 = \sigma^3 D_3,$$

$$ZC_4 = \sigma^2 C_4, \quad ZD_4 = \sigma^2 D_4,$$

$$ZC_5 = \sigma C_5, \quad ZD_5 = \sigma D_5,$$

$$ZC_6 = 1C_6, \quad ZD_6 = 1D_6.$$

$$\sigma^3 = -1.$$

In case of b_i :

$$Z(b_1 + \sigma b_2 + \sigma^2 b_3) = -\sigma^2(b_1 + \sigma b_2 + \sigma^2 b_3),$$

$$Z(b_1 - \sigma^2 b_2 - \sigma b_3) = \sigma(b_1 - \sigma^2 b_2 - \sigma b_3),$$

$$Z(b_1 - b_2 + b_3) = -1(b_1 - b_2 + b_3).$$

Denoting the corresponding combinations of the kind b_i by capital letters B_i etc. for l_i ; k_i ; j_i we get:

$$ZL_1 = -\sigma^2 L_1; \quad ZK_1 = -\sigma^2 K_1; \quad ZJ_1 = -\sigma^2 J_1;$$

$$ZL_2 = \sigma L_2; \quad ZK_2 = \sigma K_2; \quad ZJ_2 = \sigma J_2;$$

$$ZL_3 = -1L_3; \quad ZK_3 = -1K_3; \quad ZJ_3 = -1J_3;$$

and finally:

$$Z(i_1 + i_2) = 1(i_1 + i_2); \quad Z(m_1 + m_2) = 1(m_1 + m_2);$$

$$Z(i_1 - i_2) = -1(i_1 - i_2); \quad Z(m_1 - m_2) = -1(m_1 - m_2).$$

Thus our matrix of the thirty-fourth order may be decomposed into six matrices: one of the

ninth, two of the seventh, two of the third, and one of the fifth order. Each of these matrices corresponds to a definite eigenvalue λ_i of the operator W . Acting with the operator W on the functions denoted by capital letters we obtain the following matrices:

$$\begin{vmatrix} 6-\lambda & 0 & 0 & 1 & 0 \\ 0 & 18-\lambda & 0 & 9 & 0 \\ 0 & 0 & 20-\lambda & 8 & 0 \\ 54 & 6 & 4 & 16-\lambda & 12 \\ 24 & 3 & 0 & 4 & 16-\lambda \end{vmatrix} = 0, \quad (1)$$

$$\begin{vmatrix} 20-\lambda & -8 & 0 \\ -4 & 16-\lambda & 6 \\ 0 & 2 & 16-\lambda \end{vmatrix} = 0 \quad (2)$$

$$\begin{vmatrix} 20-\lambda & -8 & 0 \\ -4 & 16-\lambda & 6 \\ 0 & 2 & 16-\lambda \end{vmatrix} = 0, \quad (3)$$

$$\begin{vmatrix} 10-\lambda & 0 & 0 & 0 & 1 & 0 & -2 \\ 12 & 22-\lambda & 0 & 0 & 3 & 2 & -8\sigma \\ 0 & 0 & 30-\lambda & 0 & 18 & 0 & 0 \\ 12 & 0 & 0 & 22-\lambda & 3 & 2 & 8\sigma^2 \\ 36 & 6 & 2 & 6 & 20-\lambda & 8 & 0 \\ 0 & 0 & 0 & 0 & 4 & 16-\lambda & -6 \\ -12 & 4\sigma^2 & 0 & -4\sigma & 0 & -2 & 16-\lambda \end{vmatrix} = 0, \quad (4)$$

$$\begin{vmatrix} 10-\lambda & 0 & 0 & 0 & 1 & 0 & -2 \\ 12 & 22-\lambda & 0 & 0 & 3 & 2 & 8\sigma^2 \\ 0 & 0 & 30-\lambda & 0 & 18 & 0 & 0 \\ 12 & 0 & 0 & 22-\lambda & 3 & 2 & -8\sigma \\ 36 & 6 & 2 & 6 & 20-\lambda & 8 & 0 \\ 0 & 0 & 0 & 0 & 4 & 16-\lambda & -6 \\ -12 & -4\sigma & 0 & 4\sigma^2 & 0 & -2 & 16-\lambda \end{vmatrix} = 0, \quad (5)$$

$$\begin{vmatrix}
 6-\lambda & 0 & 8 & 0 & 0 & 0 & 0 & 1 & 0 \\
 0 & 18-\lambda & 0 & 0 & 0 & 0 & 0 & 9 & 0 \\
 24 & 0 & 10-\lambda & 0 & 0 & 0 & 1 & 0 & 4 \\
 12 & 0 & 12 & 22-\lambda & 0 & 0 & 3 & 2 & 8 \\
 0 & 0 & 0 & 0 & 30-\lambda & 0 & 18 & 0 & 0 \\
 12 & 0 & 12 & 0 & 0 & 22-\lambda & 3 & 2 & 8 \\
 0 & 0 & 36 & 6 & 2 & 6 & 20-\lambda & 8 & 0 \\
 54 & 6 & 0 & 0 & 0 & 0 & 4 & 16-\lambda & 12 \\
 48 & 3 & 24 & 4 & 0 & 4 & 0 & 4 & 16-\lambda
 \end{vmatrix} = 0. \quad (6)$$

When using the mirror symmetry K_i and L_i the order of the latter matrix may be lowered by a unit, and we obtain

$$\begin{vmatrix}
 6-\lambda & 0 & 8 & 0 & 0 & 0 & 1 & 0 \\
 0 & 18-\lambda & 0 & 0 & 0 & 0 & 9 & 0 \\
 24 & 0 & 10-\lambda & 0 & 0 & 1 & 0 & 4 \\
 24 & 0 & 24 & 22-\lambda & 0 & 6 & 4 & 16 \\
 0 & 0 & 0 & 0 & 30-\lambda & 18 & 0 & 0 \\
 0 & 0 & 36 & 6 & 2 & 20-\lambda & 8 & 0 \\
 54 & 6 & 0 & 0 & 0 & 4 & 16-\lambda & 12 \\
 48 & 3 & 24 & 4 & 0 & 0 & 4 & 10-\lambda
 \end{vmatrix} = 0 \quad (6')$$

and $\lambda_9 = 22$.

As the energy of three N_2 -like molecules is equal to -9 we are interested only in matrices whose roots lie in the region of negative λ and especially in the region lower than -9 , for only these values for the energy secure mechanical and (in case $\lambda < -9$) thermodynamical stability of the benzol molecule as well.⁶

It is quite evident that all the matrices with the exception of the last one have no roots in the region $\lambda < -9$. In fact, the proper values $\lambda_1; \lambda_2 \cdots \lambda_n$ of matrices in the general case (in case of complex matrix elements a_{ik}) lie only within a certain closed region (in a complex plane) made up by circles K_i ($i=1, 2, \cdots n$) with centers in a_{ii} and radii:

$$R = \Sigma' |a_{ik}|,$$

⁶ The minus sign before the "exchange integral" indicates attraction.

where Σ' means the sum over all k with exception of $k=i$.⁷ Transforming our matrices in a suitable way (by multiplying rows and columns by certain numbers) we can slightly narrow the region of proper values of these matrices deduced directly from 1, 2, 3, 4, 5, 6.

The proper values of the transformed matrix of the fifth order lie between $-6 < \lambda_i < 36$, of the third between $6 < \lambda_i < 28$, of the seventh between $-8 < \lambda_i < 40$, of the eighth between $-17 < \lambda_i < 54$. Matrices (2) and (3), (4) and (5) have the same roots. The root in question hence can arise only from the last matrix (6'), which when transformed may be written:

⁷ S. Gerschgorin: *Über die Abgrenzung der Eigenwerte einer Matrix*, Bulletin de l'Académie des Sciences de U. S. S. R., 1931.

$$\begin{vmatrix}
 6-\lambda & 0 & 16 & 0 & 0 & 0 & 6 & 0 \\
 0 & 18-\lambda & 0 & 0 & 0 & 0 & 9 & 0 \\
 12 & 0 & 10-\lambda & 0 & 0 & 3 & 0 & 12 \\
 2 & 0 & 4 & 22-\lambda & 0 & 3 & 2 & 8 \\
 0 & 0 & 0 & 0 & 30-\lambda & 18 & 0 & 0 \\
 0 & 0 & 12 & 12 & 2 & 20-\lambda & 8 & 0 \\
 9 & 6 & 0 & 0 & 0 & 4 & 16-\lambda & 12 \\
 8 & 3 & 8 & 8 & 0 & 0 & 4 & 16-\lambda
 \end{vmatrix} = 0.$$

The direct substitution of definite values of λ_i shows that the lowest proper value of this matrix lies between -8 and -9 ; hence in the model chosen by us the benzol molecule is stable mechanically but not thermodynamically.

We may suppose that this thermodynamical instability is the result of the incompleteness of our model of the benzol molecule. We have assumed the nitrogen-like atoms replacing CH in our model of the benzol ring to be in the state

4S ; we have further assumed the benzol model to be flat while we had to refer to it as to a space one, in fact it is known that N does not enter NH_3 in its fundamental state and that NH_3 (as the result of the absence of spherical symmetry of N) has not a plane structure, but a pyramidal one.

In conclusion I wish to offer my best thanks to Professor Rumer for the suggestion of the problem and for his continued help in this work.