WaveMechanical Treatment of the Naphthalene Molecule

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The secular equation corresponding to the forty-two canonical structures for naphthalene has been set up and solved rigorously (except for the neglect of certain exchange integrals), the energy value obtained being 2.0400α greater than that corresponding to one of the unexcited structures, in which α is the single exchange integral between adjacent carbon atoms. The equation has also been solved by various simplified procedures, and it has been found that the assumptions made in the earlier treatment of Pauling and Wheland are to a considerable extent justified. The coefficients of the various structures in the wave function for the normal state have been evaluated. It has been found that of the three unexcited structures the symmetrical one makes approximately a 50 percent greater contribution to the wave function than either of the two unsymmetrical structures. Some further discussion of the magnitudes of the coefficients is given.

Introduction

A quantum-mechanical discussion of aromatic molecules has recently been given by Pauling and his co-workers.[1] The resonance energies of a number of molecules were obtained by setting up and solving the secular equations corresponding to the canonical structures for these molecules. The matrix elements in the secular matrix were calculated by the graphical method developed by Pauling.[2] Since the number of linearly independent structures increases very rapidly with increase in the size of the system, the secular equation is usually of very high degree. Thus for naphthalene the secular equation is of the forty-second degree and for anthracene it is of the four hundred twenty-ninth degree. In solving these equations, certain simplifying assumptions were made so as to reduce them to equations of low degree, the main assumption being suggested by chemical considerations; namely, that all first-excited structures (which contain one less than the maximum number of double bonds) could be given the same coefficient in the wave function for the normal state, and similarly for second-excited structures (which contain two less than the maximum

number of double bonds), etc. In addition it was assumed that for very complicated molecules the second- and higher-excited structures could be neglected entirely without introducing any appreciable error in the value of the energy.

It is the purpose of this paper to give a thorough treatment of the naphthalene molecule and to discuss the errors in the energy value and the wave function caused by these assumptions. It has been found that the earlier approximations are to a great extent justified.

The Secular Equation for Naphthalene

The secular equation for naphthalene is set up in the same manner as was done by Pauling and Wheland.[1] Each carbon atom is considered to possess two K electrons and four L electrons, one for each of the four orbital functions formed by a linear combination of one $2s$ and three $2p$ orbitals. Three of the L orbitals form single bonds to the attached hydrogen atom and the two adjacent carbon atoms. The fourth orbital for each atom is a pure p orbital projecting at right angles to the plane of the ring. Only the interactions of the electrons in these orbitals are considered and one electron is assigned to each orbital; i.e., naphthalene is treated as a ten-electron system with spin degeneracy only. Furthermore, all exchange integrals of unity and all exchange integrals of the energy except single exchange integrals between two adjacent atoms are neglected. These single exchange integrals

[1] L. Pauling and G. W. Wheland, J. Chem. Phys. **1**, 362 (1933).

L. Pauling and J. Sherman, J. Chem. Phys. **1**, 606, 679 (1933).

[2] L. Pauling, J. Chem. Phys. **1**, 280 (1933).

are all assumed to have the same value (although this is not required by the symmetry of the naphthalene molecule) and are denoted by the symbol α. The Coulomb integral is denoted by Q and the energy by W. The number of canonical (linearly independent) structures is forty-two, so that the secular equation is of the forty-second degree. This can be factored into a sixteenth, a fourteenth, and two sixth-degree factors by considering the symmetry of the molecule. The presence of the two planes of symmetry perpendicular to the plane of the ring makes it possible to form linear combinations of the forty-two structures which are symmetric-symmetric, anti-symmetric-antisymmetric, symmetric-antisymmetric, or antisymmetric-symmetric with respect to these two planes. The symmetric-symmetric combination, formed by giving all structures in a set related by these planes of symmetry the same coefficient, gives rise to the sixteenth-degree factor, and this alone need be considered in evaluating the energy of the normal state. The matrix elements of this sixteenth-degree equation, each divided by α, are given in Table I, the
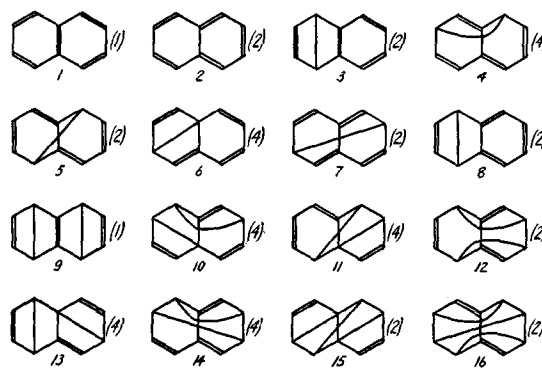

Fig. 1. Sets of canonical structures corresponding to the secular matrix given in Table I. The number in parenthesis following each structure denotes the number of structures in the set. The remaining structures are obtained from the given one by reflection through the two planes of symmetry perpendicular to the plane of the ring.

symbol x signifying $(Q-W)/\alpha$. The corresponding sets of structures are given in Fig. 1.

SOLUTION OF THE SECULAR EQUATION

Method

The secular equation has been solved under the following procedures:

TABLE I. *Matrix elements in the secular equation for naphthalene.*

	1	2	3	4	5	6	7	8
1	$x+2$	$x/2+13/4$	$x+7/2$	$x/2+4$	$x/8+11/8$	$2x+7$	$x/2+5/2$	$x/4+2$
2	$x/2+13/4$	$17x/8+43/8$	$5x/4+11/2$	$5x/2+41/4$	$x+5$	$5x/2+11$	$x+5$	$5x/4+11/2$
3	$x+7/2$	$5x/4+11/2$	$5x/2+7/2$	$5x/4+31/4$	$x/2+4$	$2x+23/2$	$x/2+4$	$x+5$
4	$x/2+4$	$5x/2+41/4$	$5x/4+31/4$	$25x/4+53/4$	$5x/2+8$	$13x/4+65/4$	$5x/2+29/4$	$2x+17/2$
5	$x/8+11/8$	$x+5$	$x/2+4$	$5x/2+8$	$5x/2+7/2$	$x+13/2$	$5x/8+25/8$	$2x+4$
6	$2x+7$	$5x/2+11$	$2x+23/2$	$13x/4+65/4$	$x+13/2$	$7x+37/2$	$5x/2+8$	$5x/4+31/4$
7	$x/2+5/2$	$x+5$	$x/2+4$	$5x/2+29/4$	$5x/8+25/8$	$5x/2+8$	$17x/8+19/8$	$x/2+13/4$
8	$x/4+2$	$5x/4+11/2$	$x+5$	$2x+17/2$	$2x+4$	$5x/4+31/4$	$x/2+13/4$	$5x/2+7/2$
9	$x/4+5/4$	$x/2+5/2$	$x+2$	$x/2+4$	$x/2+5/2$	$x/2+4$	$x/8+11/8$	$x+2\iota$
10	$x+5$	$2x+17/2$	$x+8$	$7x/2+29/2$	$5x/4+25/4$	$5x+13$	$2x+7$	$x+13/2$
11	$x/2+4$	$5x/2+29/4$	$5x/4+31/4$	$13x/4+65/4$	$5x/2+8$	$13x/4+53/4$	$x+29/4$	$2x+17/2$
12	$x/8+11/8$	$x+17/4$	$x/2+13/4$	$5x/2+29/4$	$x+7/2$	$x+13/2$	$x+7/2$	$5x/4+5/2$
13	$x+5$	$2x+10$	$5x/2+8$	$7x/2+23/2$	$2x+7$	$7x/2+16$	$5x/4+25/4$	$5x/2+8$
14	$x/2+4$	$5x/2+29/4$	$5x/4+25/4$	$4x+31/2$	$x+13/2$	$13x/4+59/4$	$5x/2+29/4$	$5x/4+25/4$
15	$x/2+5/2$	$x+7/2$	$x/2+4$	$x+29/4$	$5x/8+25/8$	$5x/2+5$	$5x/8+31/8$	$x/2+13/4$
16	$x/8+11/8$	$x+7/2$	$x/2+5/2$	$5x/2+17/4$	$5x/8+25/8$	$x+13/2$	$x+7/2$	$x/2+13/4$

	9	10	11	12	13	14	15	16
1	$x/4+5/4$	$x+5$	$x/2+4$	$x/8+11/8$	$x+5$	$x/2+4$	$x/2+5/2$	$x/8+11/8$
2	$x/2+5/2$	$2x+17/2$	$5x/2+29/4$	$x+17/4$	$2x+10$	$5x/2+29/4$	$x+7/2$	$x+7/2$
3	$x+2$	$x+8$	$5x/4+31/4$	$x/2+13/4$	$5x/2+8$	$5x/4+25/4$	$x/2+4$	$x/2+5/2$
4	$x/2+4$	$7x/2+29/2$	$13x/4+65/4$	$5x/2+29/4$	$7x/2+23/2$	$4x+31/2$	$x+29/4$	$5x/2+17/4$
5	$x/2+5/2$	$5x/4+25/4$	$5x/2+8$	$x+7/2$	$2x+7$	$x+13/2$	$5x/8+25/8$	$5x/8+25/8$
6	$x/2+4$	$5x+13$	$13x/4+53/4$	$x+13/2$	$7x/2+16$	$13x/4+59/4$	$5x/2+5$	$x+13/2$
7	$x/8+11/8$	$2x+7$	$x+29/4$	$x+7/2$	$5x/4+25/4$	$5x/2+29/4$	$5x/8+31/8$	$x+7/2$
8	$x+2$	$x+13/2$	$2x+17/2$	$5x/4+5/2$	$5x/2+8$	$5x/4+25/4$	$x/2+13/4$	$x/2+13/4$
9	$x-1$	$x/4+11/4$	$x/2+4$	$x/2+1$	$x+5$	$x/2+5/2$	$x/8+11/8$	$x/8+11/8$
10	$x/4+11/4$	$11x/2+13/2$	$7x/2+10$	$5x/4+25/4$	$5x/2+25/2$	$7x/2+23/2$	$2x+4$	$5x/4+25/4$
11	$x/2+4$	$7x/2+10$	$25x/4+17/4$	$x+29/4$	$7x/2+23/2$	$5x/2+11$	$5x/2+11/4$	$x+23/4$
12	$x/2+1$	$5x/4+25/4$	$x+29/4$	$17x/8-5/8$	$5x/4+25/4$	$5x/2+17/4$	$x/4+11/4$	$x+7/2$
13	$x+5$	$5x/2+25/2$	$7x/2+23/2$	$5x/4+25/4$	$11x/2+13/2$	$2x+13$	$5x/4+25/4$	$5x/4+13/4$
14	$x/2+5/2$	$7x/2+23/2$	$5x/2+11$	$5x/2+17/4$	$2x+13$	$25x/4+23/4$	$x+23/4$	$5x/2+17/4$
15	$x/8+11/8$	$2x+4$	$5x/2+11/4$	$x/4+11/4$	$5x/4+25/4$	$x+23/4$	$17x/8-29/8$	$x/4+11/4$
16	$x/8+11/8$	$5x/4+25/4$	$x+23/4$	$x+7/2$	$5x/4+13/4$	$5x/2+17/4$	$x/4+11/4$	$17x/8-29/8$

I. All structures are taken into account in the following ways:

    a. The sixteenth-degree equation is solved rigorously by the method described by James and Coolidge.[3] The procedure consists in substituting two approximate values of the root into the determinant and then evaluating the determinant. A linear interpolation or extrapolation of these two values is then made in order to obtain a better approximation to the root.

    b. All first-excited structures are grouped together by giving them the same coefficient, and similarly for the second and third-excited structures. The resultant equation is of the fifth degree.

II. The third-excited structures only are neglected. The remaining structures are then grouped together as in the previous treatment. The resultant equation is of the fourth degree.

III. Only the unexcited and first-excited structures are considered. The following procedures are carried out:

    a. The resultant eighth-degree equation is solved rigorously.

    b. All first-excited structures are grouped together by giving them the same coefficient. The resultant equation is of the third degree.

    c. The individual sets of first-excited structures are first normalized and then grouped together to give a resultant equation of the third degree.

IV. The quadratic equation involving only the three unexcited structures is solved.

Results

The results obtained under the various procedures for solving the secular equation are summarized in Table II. It is seen that resonance among the three unexcited structures alone yields 1.3703α for the value of the resonance energy (procedure IV); this is only 67 percent of the total resonance energy. If the first-excited structures are now included, the resonance energy is increased to 2.0036α (procedure IIIa), each of the sixteen structures making an average contribution of 0.0396α as compared to the average contribution of each unexcited structure of 0.457α. This value of 2.0036α is only 2 percent less than the value 2.0400α obtained in the complete treatment. If the eighth-degree equation involving these structures is reduced to a

[3] H. M. James and A. S. Coolidge, J. Chem. Phys. 1, 825 (1933).

cubic by grouping together the first-excited structures (procedure IIIb), it is seen that the resultant energy value is only 0.0276α less than that obtained by solving the eighth-degree equation rigorously. If the second-excited structures are now included, the resonance energy is increased to 2.0172α (procedure II), each of the nineteen second-excited structures making an average contribution of only 0.0022α. If all the structures are considered, it is seen that the energy value resulting from the approximate treatment (procedure Ib) is 2.0175α, only 1 percent less than that obtained by solving the sixteenth-degree equation rigorously. The four third-excited structures make only a very small contribution, the average value per structure being only 0.00008α.

Conclusions

The above results indicate that the best approximate solution of the secular equation is obtained when all of the canonical structures are taken into account by grouping together all first-excited structures, all second-excited structures, etc., as was done by Pauling and Wheland. This procedure seems reasonable from chemical

TABLE II. *Resonance energy of naphthalene.*

	Total energy	Resonance energy
Single unexcited structure	$Q+2\alpha$	0
I. All structures are considered		
a. rigorous solution of the complete equation	$Q+4.0400\alpha$	2.0400α
b. all first-excited structures are assumed to have the same coefficient and similarly for higher-excited structures	$Q+4.0175\alpha*$	$2.0175\alpha*$
II. Third-excited structures are neglected. Remaining structures are grouped as in Ib.	$Q+4.0172\alpha$	2.0172α
III. Only unexcited and first-excited structures are considered		
a. rigorous solution of eighth degree equation	$Q+4.0036\alpha$	2.0036α
b. all first-excited structures are assumed to have the same coefficient	$Q+3.9760\alpha$	1.9760α
c. each set of first-excited structures is normalized and then all are grouped together	$Q+3.9682\alpha$	1.9682α
IV. Only the unexcited structures are considered	$Q+3.3703\alpha$	1.3703α

* These values differ from those given by Pauling and Wheland (reference 1) because of an error in one of the matrix elements of their equation, and also because they solved the fifth-degree equation only approximately. In the secular equation given on page 366, the 3,4 and 4,3 matrix elements should be corrected to read $(531/8)(Q-W)+2175\alpha/8$.

considerations, inasmuch as all first-excited structures have one less than the maximum number of double bonds and may therefore be expected to contribute about equally to the energy of the normal state. In naphthalene the error introduced in the energy value by this procedure is only 1 percent of the resonance energy. It may be expected to increase slowly with the size of the molecule.

Although the error introduced by neglecting all second and higher-excited structures in naphthalene is only 2 or 3 percent, this error may be expected to increase fairly rapidly as we go to more complicated molecules, inasmuch as the number of these higher-excited structures increases very rapidly relative to the increase in the number of first-excited structures. Thus, in anthracene the total number of canonical structures (429) is slightly more than ten times the number of naphthalene (42). However, the number of first-excited structures increases only three-fold (48/16) whereas the total number of higher-excited structures increases more than sixteen-fold (377/23).

The Wave Function for the Normal State

Having solved the secular equation for the energy of the normal state, the coefficients of the structures in the wave function can then be evaluated in the usual manner. The results (before normalizing) obtained under the various assumptions used in solving the secular equation are tabulated in Table III. It is seen that when all the structures are taken into account, as in procedure Ib, the coefficients approximate the values obtained in the complete treatment rather closely, and, moreover, neglect of the third-excited structures (II) produces only a small change. On the other hand the rougher

TABLE III. *Relative values of the coefficients of the canonical structures of naphthalene in the wave function for the normal state.*

Structures in set	Ia	Ib	Coefficients under assumption II	IIIa	IIIb	IIIc	IV
1	1	1	1	1	1	1	1
2	0.654	0.618	0.623	0.993	0.851	0.854	0.876
3	.453	.228	.229	.744	.303	.521	0
4	.283	.228	.229	.428	.303	.521	0
5	.259	.228	.229	.352	.303	.521	0
6	.245	.228	.229	.588	.303	.521	0
7	.238	.228	.229	.237	.303	.521	0
8	.218	.228	.229	.451	.303	.521	0
9	.206	.084	.085	0	0	0	0
10	.114	.084	.085	0	0	0	0
11	.106	.084	.085	0	0	0	0
12	.076	.084	.085	0	0	0	0
13	.069	.084	.085	0	0	0	0
14	.046	.084	.085	0	0	0	0
15	.055	.016	0	0	0	0	0
16	.011	.016	0	0	0	0	0

approximations lead to large errors even in the relative values of the coefficients for the unexcited structures.

It is striking that of the three unexcited structures, the symmetrical one makes a 50 percent greater contribution to the wave function than either of the two unsymmetrical structures, the relative values of the coefficients in the complete treatment being 1 to 0.654. It is also to be noticed that the coefficient of the symmetrical second-excited structure labelled 9 is nearly twice as great as the next largest coefficient for a second-excited structure and is only slightly less than the smallest coefficient of the first-excited structures. The coefficient of the third-excited structures in set 15 is seen to be greater than that for the second-excited structures in set 14.

The above results indicate that the procedure which yields the most nearly correct value of the energy also yields the best approximation to the values of the coefficients.