

## Bond Numbers and Bond Lengths in Tetrabenzo[*de,no,st,c<sub>1</sub>d<sub>1</sub>*]heptacene and Other Condensed Aromatic Hydrocarbons: A Valence-Bond Treatment

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### Abstract

Valence-bond calculations of bond lengths in tetrabenzo[*de,no,st,c<sub>1</sub>d<sub>1</sub>*]heptacene and several other condensed aromatic molecules are found to agree with observed values and with the values calculated by the molecular-orbital method to within about 0.010 Å, substantiating the conclusion reached by Cruickshank [*Tetrahedron* (1962), 17, 155–161]. For perylene and quaterrylene, which can be described as consisting of conjugated naphthalene residues, the valence-bond treatment is refined by the consideration of first-excited structures as well as unexcited structures.

### Introduction

In their recent report of the determination of the crystal structure of tetrabenzo[*de,no,st,c<sub>1</sub>d<sub>1</sub>*]heptacene, Ferguson & Parvez (1979) compared the observed values of bond lengths averaged over chemically equivalent bonds with values calculated by the Hückel molecular-orbital (HMO) method (Streitwieser & Brauman, 1965), and found a mean deviation of 0.026 Å. There is another way of calculating theoretical values of the bond lengths, based on valence-bond theory (Pauling, 1960, pp. 236–239). The mean deviation of the values calculated in this way from the observed values is only 0.011 Å, less than half that for the HMO method, and, moreover, the valence-bond calculation is far simpler than the HMO calculation. Only a brief discussion of the valence-bond theory of bond lengths in aromatic molecules has been previously published (Pauling, 1960); a more detailed discussion is given in the following paragraphs.

### The theory

In the valence-bond quantum-mechanical theory of benzene and the condensed aromatic molecules a canonical set of structures can be assigned by distributing the bonds in all the ways in which the bonds do not intersect (Pauling, 1933). The unexcited structures

are those in which there are no 'long bonds'; that is, in which all of the bonds are between adjacent atoms, the first-excited structures are those in which there is one long bond, and so on. Benzene has two unexcited structures (the two Kekulé structures) and three first-excited structures, and naphthalene has three unexcited structures, 16 first-excited structures, 19 second-excited structures, and 4 third-excited structures (Pauling & Sherman, 1933). For some properties a good approximation in a theoretical calculation is provided by consideration of the unexcited structures alone, whereas for others, such as those involving conjugation, other structures must be taken into consideration.

As a first approximation we assume that all of the unexcited structures have the same weight in contributing double-bond character to the bonds. For example, we examine the three unexcited structures of naphthalene shown in Fig. 1 and assign two-thirds double-bond character (bond number 1.667) to the bonds *b* and one-third to the others. A few minutes suffices to draw the four unexcited structures for anthracene, the five for phenanthrene, or the six for pyrene and to determine the bond numbers of the

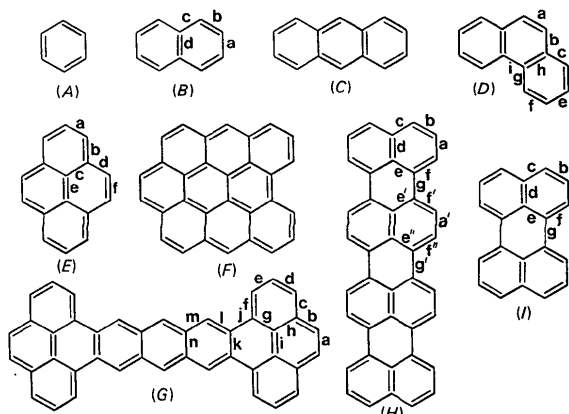


Fig. 1. Structural formulas, in each case showing one of the several ways of distributing the double bonds, of (A) benzene, (B) naphthalene, (C) anthracene, (D) phenanthrene, (E) pyrene, (F) 1:14-benzbisanthrene, (G) tetrabenzoheptacene, (H) quaterrylene, and (I) perylene.

various bonds; an hour or two might be needed for the 110 structures of tetrabenzoheptacene. In every case the calculation is far simpler, as well as more meaningful to chemists, than the corresponding HMO calculation.

For single-bond:double-bond resonance with  $n - 1$  double-bond character (bond number  $n$ ) an equation for the bond length was derived by assuming the potential energy to be the sum of two parabolas, with their minima at the single-bond and double-bond distances, respectively, and their curvatures in the ratio of the force constants, taken as 1.84 (Pauling, 1960, p. 235). This equation is

$$D = D_1 - (D_1 - D_2) \frac{1.84(n - 1)}{0.84n + 0.16}, \quad (1)$$

in which  $D$  is the value of the bond length for bond number  $n$ ,  $D_1$  is that for a single bond (1.504 Å for aromatic molecules), and  $D_2$  is that for a double bond (1.334 Å). The line in Fig. 2 represents this equation.

### Results

Twenty years ago (Pauling, 1960, pp. 237–239) I compared values given by equation (1) with values of  $n$  assigned by giving equal weights to the unexcited valence-bond structures with the experimental values for anthracene (Cruickshank, 1956, 1957) and for 1:14-benzbisanthrene (Trotter, 1958). The values are plotted in Fig. 2. The mean deviation is 0.008 Å for anthracene and 0.007 Å for 1:14-benzbisanthrene. The observed value for benzene, 1.397 Å, is also shown; it is 0.003 Å above the curve.

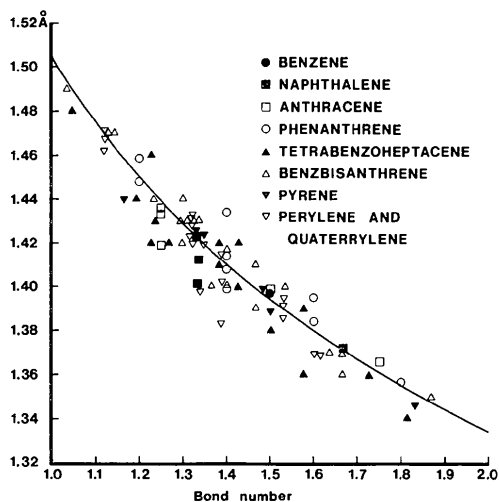


Fig. 2. The curve gives the values of the carbon-carbon bond length for single-bond:double-bond resonance as a function of the bond number  $n$  (1 plus the fraction of double-bond character). The indicated points are the observed values of bond lengths at the values of  $n$  calculated by the valence-bond theory.

Observed values for naphthalene (Pawley & Yeats, 1969) and for phenanthrene (Kay, Okaya & Cox, 1971) are compared with the calculated values in Tables 1 and 2. The observed values for phenanthrene are the means for two X-ray diffraction studies and one neutron diffraction study. Values obtained by an MO calculation (Trotter, 1963) are also given. The mean deviations are 0.008 Å for naphthalene (VB) and 0.009 Å (VB) and 0.013 Å (MO) for phenanthrene.

Hazell, Larsen & Lehmann (1972) made a neutron-diffraction determination of the structure of pyrene and compared the results with those found in two X-ray studies of the crystal and for three other substances: pyrene-TCNE, 2,7-di-*tert*-butylpyrene, and pyrene-PMDA. Averages of the sets of six values, with mean deviations about 0.008 Å, are given in Table 3, together with the values calculated by the valence-bond method with use of the six unexcited structures and averages of seven MO calculations (mean deviation about 0.007 Å) given, with references, in the paper by Hazell *et al.* The VB and MO values differ from one

Table 1. Comparison of calculated and observed values of bond lengths in naphthalene

Bond	Bond number	Bond length	
		Calculated	Observed
<i>a</i>	1.333	1.421 Å	1.401 Å
<i>b</i>	1.667	1.371	1.372
<i>c</i>	1.333	1.421	1.423
<i>d</i>	1.333	1.421	1.412

Table 2. Comparison of calculated and observed values of bond lengths in phenanthrene

Bond	Bond number	Bond length		
		VB	Observed	MO
<i>a</i>	1.80	1.355 Å	1.357 Å	1.378 Å
<i>b</i>	1.20	1.450	1.448	1.426
<i>c</i>	1.40	1.410	1.434	1.413
<i>d</i>	1.60	1.380	1.384	1.390
<i>e</i>	1.40	1.410	1.395	1.405
<i>f</i>	1.60	1.380	1.395	1.391
<i>g</i>	1.40	1.410	1.408	1.411
<i>h</i>	1.40	1.410	1.414	1.419
<i>i</i>	1.20	1.450	1.459	1.434

Table 3. Comparison of calculated and observed values of bond lengths in pyrene

Bond	Bond number	Bond length		
		VB	Observed	MO
<i>a</i>	1.500	1.394 Å	1.390 Å	1.394 Å
<i>b</i>	1.500	1.394	1.403	1.401
<i>c</i>	1.333	1.421	1.423	1.415
<i>d</i>	1.167	1.459	1.440	1.445
<i>e</i>	1.333	1.421	1.424	1.428
<i>f</i>	1.833	1.351	1.346	1.361

another by a mean of 0.007 Å and differ from the observed values by means of 0.007 Å (VB) and 0.006 Å (MO).

Values of bond numbers and bond lengths calculated for the 110 unexcited valence-bond structures of tetrabenzoseptacene are given in Table 4. These unexcited structures are easily constructed by noting that there are 100 structures (the product of 5 for each of two phenanthrene groups at the ends and 4 for the central anthracene group) in which the bonds *j* are single bonds, and 10 structures in which the bonds *j* at one end or the other are double bonds, giving a single quinone-like structure to that end of the molecule. Observed values of the bond lengths and the MO values reported by the investigators are also given in Table 4. The mean deviation of the VB values from the observed values, 0.012 Å, is only half that for the MO values, 0.024 Å.

The valence-bond values agree with the observed values to within their reported standard error of 0.020 Å except for *d* and *n*, which are high by 0.024 Å. Five of the MO values (*b, c, i, j, k*) deviate by more than the standard error (0.040, 0.030, 0.030, 0.060, and 0.050 Å, respectively). It is hard to understand why the MO calculation should give values so much different from those given by the VB calculation, deviation 0.070 Å

Table 4. Comparison of calculated and observed values of bond lengths in tetrabenzo[de,no,si,c<sub>1</sub>d<sub>1</sub>]heptacene

Bond	Bond number	VB	Bond length	
			Observed	MO
<i>a</i>	1-809	1.354 Å	1.34 Å	1.36 Å
<i>b</i>	1-191	1.452	1.44	1.40
<i>c</i>	1-427	1.407	1.42	1.39
<i>d</i>	1-573	1.384	1.36	1.38
<i>e</i>	1-427	1.407	1.40	1.38
<i>f</i>	1-573	1.384	1.39	1.39
<i>g</i>	1-382	1.413	1.42	1.40
<i>h</i>	1-382	1.413	1.41	1.40
<i>i</i>	1-236	1.442	1.43	1.40
<i>j</i>	1-045	1.490	1.48	1.42
<i>k</i>	1-227	1.444	1.46	1.41
<i>l</i>	1-727	1.364	1.36	1.38
<i>m</i>	1-273	1.436	1.42	1.40
<i>n</i>	1-227	1.444	1.42	1.41
<i>o</i>	1-500	1.394	1.38	1.39

for *j*, for example, inasmuch as the values given by the two theories usually agree to within 0.020 Å.

#### Inclusion of excited structures in the valence-bond calculation

For some molecules consideration of the unexcited valence-bond structures does not suffice to explain the observed values of the bond lengths, enthalpy of formation, conformation, and other properties. The simplest example is butadiene. The normal structure, =-=-, must be combined with the excited structure ·-=-· to account for the planarity, increased stability, and decreased length of the 2,3 bond. For many molecules with conjugated double bonds the observed carbon-carbon distances for the 'single' bonds lie between 1.46 and 1.48 Å, average 1.47 Å, corresponding to 12% double-bond character.

For perylene and quaterrylene, for example, the bonds *g* and *g'* (Fig. 1) remain single bonds for all of the unexcited structures; these molecules might be described as conjugated sets of naphthalene residues, rather than as condensed aromatic hydrocarbons. For perylene, in addition to the 9 unexcited structures, with 10 double bonds, there are 98 first-excited structures with one double bond in one of the *g* positions and 8 in the naphthalene residues. There is uncertainty about the relative weights to give the first-excited and unexcited structures. I have accepted the usual value 1.470 Å for the bonds *g*, which corresponds to 12% contribution of the excited structures and to the ratio 0.030. With this assumption, consideration of the distribution of double bonds in the 9 unexcited and 98 first-excited structures leads to the values given in Table 5 for the bond numbers and bond lengths *a* to *g*. The effect of conjugation is seen in the deviation of the bond numbers from the values 1.667, 1.333, and 1.000 given by the unexcited structures alone.

The observed values of the bond lengths for perylene (Camerman & Trotter, 1964) are given in the fourth column of Table 5. In the next column there are given the corresponding values for quaterrylene (Kerr, Ashmore & Speakman, 1975). For some sets of bonds, such as *f*, *f'*, and *f''*, consideration of the excited structures indicates that they contribute the same

Table 5. Comparison of calculated and observed values of bond lengths in perylene and quaterrylene

Bond	Bond number	VB	Bond length		
			Perylene	Quaterrylene	MO
<i>a</i>	1-390	1.412 Å	1.415 Å	1.402, 1.383 Å	1.402, 1.394 Å
<i>b</i>	1-610	1.379	1.369	1.369	1.377
<i>c</i>	1-339	1.421	1.398	1.420	1.422
<i>d</i>	1-322	1.427	1.421	1.420, 1.432	1.425, 1.427
<i>e</i>	1-322	1.427	1.428	1.433, 1.433, 1.432	1.431, 1.431, 1.431
<i>f</i>	1-558	1.386	1.394	1.385, 1.385, 1.391	1.395, 1.398, 1.397
<i>g</i>	1-120	1.470	1.471	1.468, 1.462	1.469, 1.468

amounts to  $n$ , to within the reliability of the calculation, as is seen also from the MO values in the last column, which are the averages of two MO sets given by Kerr *et al.*

The mean deviation of the VB and MO bond lengths is 0.005 Å, and those with the observed values are 0.007 Å (VB) and 0.006 Å (MO). The average standard error of the observed bond lengths is 0.004 Å.

### Conclusion

The valence-bond method of calculating bond numbers and bond lengths is simple and straightforward. The calculated values of the bond lengths are found to agree with experimental values for several aromatic hydrocarbons to within about 0.010 Å and also to agree within the same amount with those calculated by the molecular-orbital method. This conclusion agrees with that reached by Cruickshank (1962).

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## The Structure and Absolute Configuration at Low Temperature of the Acetate Derivative of Plexauroalone, a Marine Cembranoid

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### Abstract

The crystal structure and absolute configuration at low temperature of the acetate derivative of plexauroalone, a marine cembranoid isolated from a *Plexaura*-related species, have been determined and refined using three-dimensional X-ray diffraction data. The compound crystallizes in space group  $P2_1$  with two molecules per asymmetric unit and with cell dimensions  $a = 21.215$  (5),  $b = 9.322$  (1),  $c = 11.327$  (3) Å and  $\beta = 99.30$  (1)° at 138 K. The absolute configuration was determined using the anomalous scattering of the O atoms. The final  $R$  value for all 4851 data is 5.3%. Comparison of geometrical parameters using half-normal probability plots indicates that the standard deviations are not underestimated. Because the olefinic

unsaturation at position 7 is absent in plexauroalone, the configuration convention is not directly applicable. Evaluation of its oxygen substitution pattern in view of a proposed extension of the convention places plexauroalone in the  $\alpha$  series. Plexauroalone thus appears to be the first  $\alpha$ -cembranoid isolated from a Caribbean gorgonian.

### Introduction

In a continuation of our study of the Caribbean gorgonians, we have isolated a new cembranoid diterpene, plexauroalone (1), from an as yet undescribed gorgonian which appears to be related to the genus *Plexaura*. Plexauroalone was first discovered in