

## The Molecular Diagram Method

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## The Molecular Diagram Method

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The "importance" of various valence bond formulas, including monoexcited and diexcited formulas, is calculated for a number of resonating organic molecules. By "importance" is meant the square of the coefficient of its wave function. Several applications of the derived values are discussed.

### METHOD OF CALCULATION

OBSERVING that naphthalene is representable by means of the three Kékulé formulas (see Formula 1), Pauling represents<sup>1</sup> naphthalene with the diagram shown in Formula 2, which, for each bond, gives its double-bond character.

The excited formulas are not introduced in this diagram. It is possible to introduce them in the following way. Let us consider a Kékulé or an excited formula representing an aromatic molecule, and possessing a double bond between the two atoms  $l$  and  $m$ . Let  $S_l$  be its importance (proportional to the square of the coefficient of its wave function). The number:  $I_{lm} = \sum_i S_i$  represents the importance of the sharing between the atoms  $l$  and  $m$ ; we call it the *indice de liaison* of the bond  $l-m$ .<sup>2a</sup> Let  $S_j$  be the importance of a formula possessing an ineffective bond (i.e., a bond between two non-adjacent carbons) leading to a certain atom  $l$ . The number  $J_l = \sum_j S_j$  represents the amount of unshared electrons existing in the atom  $l$ . It gives quantitatively the Thiele notion of free half-valence;

we call it the *indice de valence libre*<sup>2b</sup> of the atom  $l$ . For each molecule it is possible to make a diagram which represents these indices.

If we use the importances calculated by Pauling, we get for benzene the diagram shown in Formula 3. For more complicated molecules the number of the formulas which we must use to construct the diagrams rapidly becomes great and the calculation of the importances is very laborious. The importances of the formulas of naphthalene have been calculated by Sherman.<sup>3</sup> Jonnson<sup>4</sup> and Svartholm<sup>5</sup> have calculated those of anthracene and benzanthracene, but they used only the Kékulé and monoexcited formulas, neglecting the diexcited formulas.

Pauling and Wheland's method has been a little simplified, systematized,<sup>6</sup> and used<sup>7</sup> to determine the importances of the formulas (including the diexcited formulas), which represent anthracene and naphthacene. Table I and the

<sup>1</sup> Linus Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1944).

<sup>2a</sup> Pauling, Brockway and Beach, *J. Am. Chem. Soc.* **57**, 2705 (1935).

<sup>2b</sup> R. Daudel and A. Pullman, *Comptes Rendus* **220**, 888 (1945); *ibid.* **222**, 663 (1946); P. Daudel, R. Daudel, R. Jacques, and M. Jean, *Rev. Scientifique* (1946); P. Daudel, *Comptes Rendus* **223**, 947 (1946).

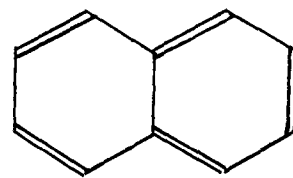
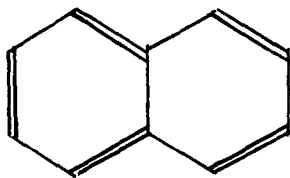
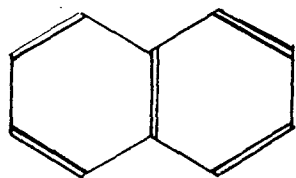
<sup>3</sup> J. Sherman, *J. Chem. Phys.* **2**, 488 (1934).

<sup>4</sup> Jonnson, *Ark. f. Kem. Min. Geol.* **15A**, No. 14 (1941).

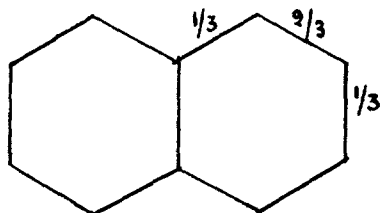
<sup>5</sup> Svartholm, *Ark. f. Kem. Min. Geol.* **15A**, No. 13 (1941).

<sup>6</sup> R. Daudel and A. Pullman, *J. de Phys.* **59-64**, 74-83, 105-111 (1946).

<sup>7</sup> A. Pullman, Thèse, Paris, 1946.



FORMULA 1.



FORMULA 2.

curves of Fig. 1, representing the results obtained, show that the diexcited formulas are very important and that it is not correct to neglect them.

It is pointed out that when the number of rings in an aromatic molecule increases the polyexcited formulas become very important, which leads to very laborious calculations. By using the importances under consideration we obtain the diagram for naphthalene and anthracene shown in Formula 4. Some other diagrams have been calculated in this way.<sup>7</sup>

#### APPLICATION TO THE STUDY OF THE CHEMICAL PROPERTIES OF MOLECULES

Let us study, for example, the addition of a diatomic molecule  $AA$  to an aromatic molecule. Let us consider the approach of  $AA$  to the aromatic molecule.

To each formula possessing a double bond between the two atoms  $C$  and  $D$  (type I, Formula 5) it is possible to associate a formula of type II, Formula 5, using the mesomerism method in order to study the dynamics of the chemical reactions. Let  $S_i$  be the importance of the  $i$ th formula (type I). If the molecule  $AA$  is far from the aromatic molecule, it is possible to admit

TABLE I.

Substances	Unexcited formulas	Importances of monoexcited formulas	Diexcited formulas
Benzene	78	22	0
Naphthalene	54	41	5
Anthracene	10	60	30
Naphthacene	0	40	60

that the part  $CD$  is only disturbed; with this condition it is normal to conclude that the importance  $C_i$  of the associated formula (type II) is given by the relation

$$C_i = aS_i,$$

where  $a$  does not depend on the chosen formula of type I but only on the position of the molecule  $AA$ . So, it is possible to write

$$\sum_i C_i = a \sum_i S_i = aI_{cd}.$$

But  $\sum_i C_i$  represents roughly the attraction which appears between the molecule  $AA$  and the part  $CD$  of the aromatic molecule. Since this number is proportionate to  $I_{CD}$  we can say:

1. The greater the *indice de liaison* of a bond, the more the molecule which possesses this bond is apt to react by addition.

It is possible to show in the same way that:

2. The addition or the substitution of an atom on a molecule is facilitated by the presence in this molecule of an atom possessing a great *indice de valence libre*.

3. The addition of a diatomic molecule to another molecule is facilitated by the presence in this molecule of two atoms possessing a great *indice de valence libre*.

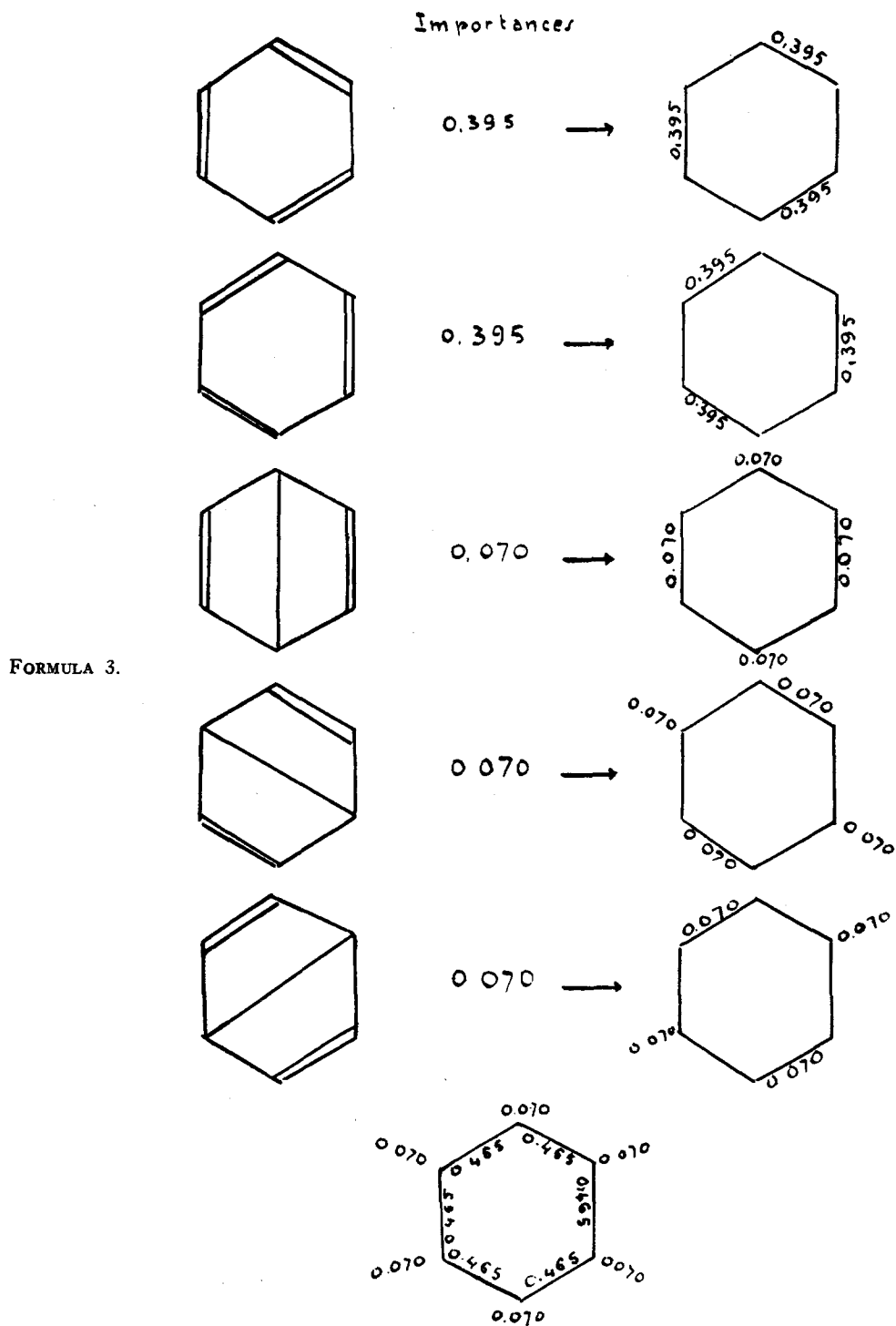
These are the specific rules of the molecular diagram theory.<sup>8</sup> They have been used in order to study the general reactivity of the aromatic molecules,<sup>8</sup> the diene synthesis,<sup>9</sup> the hydrogenation.

TABLE II.

Bond	$I_{lm}$	$J_l$	$J_m$	$Y_{lm}$	$E_{lm}$	Number of bond	Energy
$\alpha\beta$	527	123	97	582	30.5	4	122
$\alpha O$	350	123	67	397	23	4	92
$OO$	233	67	67	266	17	1	17
$\beta\beta$	376	97	97	424	24.5	2	49
Bond energy of the $\pi$ -electrons							280

<sup>8</sup> R. Daudel and A. Pullman, *Comptes Rendus* **221**, 201 (1945).

<sup>9</sup> R. Daudel and A. Pullman, *Comptes Rendus* **222**, 86 (1946).



**FORMULA 3.**

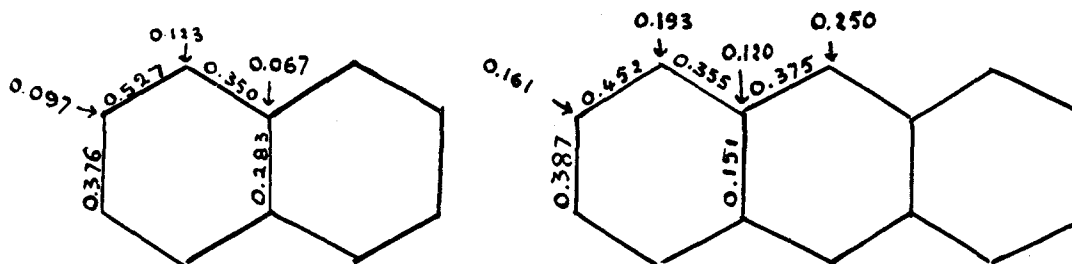
tion of naphthalene,<sup>10</sup> quinolin, and the diexcited states of molecules.<sup>11</sup>

<sup>10</sup> A. Pullman and R. Daudel, *Comptes Rendus* **221**, 218 (1945).

<sup>11</sup> A. Pullman and R. Daudel, *Comptes Rendus* 222, 288 (1946).

## APPLICATION TO THE CALCULATION OF RESONANCE ENERGY AND INTERATOMIC DISTANCES

When the polyexcited formulas are introduced it is possible to generalize Pauling's notion of



FORMULA 4.



FORMULA 5. The diagram on the left is type I; the one on the right, type II.

double-bond character by the following number:

$$y_{lm} = I_{lm} + a(J_l + J_m/2),$$

which introduces the *indice de liaison* and the *indices de valence libre* in the same time.

In the case of benzene we must obtain  $y = \frac{1}{2}$ ; it is held necessary to take  $a = \frac{1}{2}$ .

It is possible to establish a relation between the character of a bond and its heat of formation. The consideration of experimental values of the heats of formation of symmetric molecules, such as benzene, leads to the curve shown in Fig. 2.

With it, we can calculate the "resonance energy" of aromatic molecules when we know their diagrams. For naphthalene we obtain Table II.

We see that the bond energy of the  $\pi$ -electrons is 280 kcal./mole. If naphthalene could be represented by a Kékulé-like formula this energy would be

$$41.4 \times 5 = 207 \text{ kcal./mole.}$$

The difference (73 kcal./mole) represents the resonance energy, and leads to a good agreement with the experimental value (75 kcal./mole). For anthracene we find a resonance energy of 104.2 kcal./mole and the experimental value is 105.

Using the importances calculated by the mesomerism theory, the molecular diagram leads to better results than those of the simple mesomerism theory because the molecular diagram introduces empirically the variation of the exchange integral  $\alpha$  with the interatomic distance.

These interatomic distances can be evaluated with the Pauling curve when we know the molecular diagrams which give the double bond characters  $y$ . We obtain, for example, the fol-

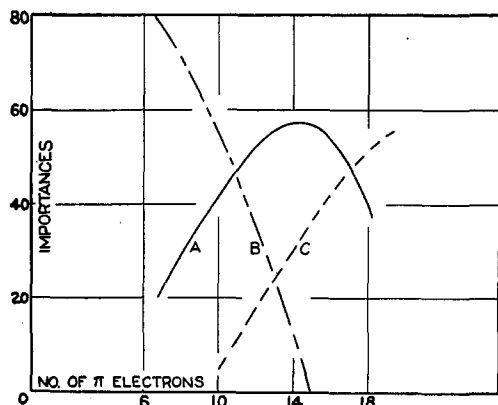


FIG. 1. A—Monoexcited formulas;  
B—unexcited formulas;  
C—diexcited formulas.

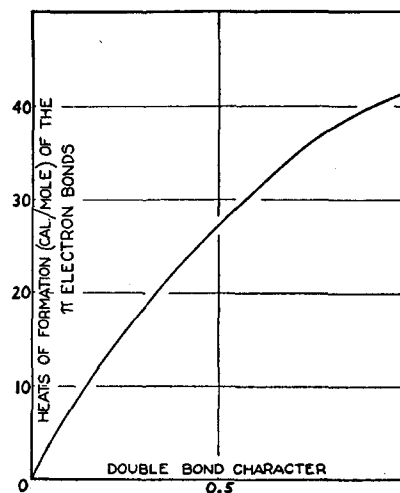


FIG. 2.

TABLE III.

		Double-bond character (direct method)	Double-bond character (Coulson's method)
Benzene		0.465	0.465
Naphthalene		$\alpha\beta$ bond 0.582	0.575
		$\beta\beta$ bond 0.397	0.450
		$\alpha O$ bond 0.266	0.365
		OO bond 0.424	0.400
Anthracene		$\alpha\beta$ bond 0.540	0.590
		$\alpha O$ bond 0.435	0.385
		Om bond 0.467	0.450
		OO bond 0.211	0.340
		$\beta\beta$ bond 0.467	0.435

lowing results:

$\alpha\beta$ bond of naphthalene	1.37A
$\beta\beta$ bond of naphthalene	1.40
$\alpha\beta$ bond of anthracene	1.38
$\beta\beta$ bond of anthracene	1.395

C. A. Coulson has developed another method<sup>12</sup> of determining molecular diagrams, based upon the orbital method. It is possible to establish a correspondence between Coulson's bond orders and the double bond-characters by noting that Coulson finds a bond order of 0.667 for benzene and a bond order of 0.525 for graphite.

Using the bond order diagrams, it is possible to calculate the double-bond characters. Table III compares the results obtained in this way with the numbers directly calculated by the mesomerism method. The agreement is moderately good and it seems that the double-bond character can be placed by decreasing values in the following order:

Naphthalene and anthracene  $\alpha\beta$  Benzene  
 Naphthalene and anthracene  $\beta\beta$  and anthracene Om  
 Naphthalene and anthracene  $\alpha O$   
 Naphthalene OO  
 Anthracene OO

#### GENERALIZATION OF THE METHOD

The method has been generalized by the use of the electro-valency formulas<sup>13</sup> in order to

<sup>12</sup> For the references see C. A. Coulson, P. Daudel, and R. Daudel, *Rev. Scientifique* (1947).

TABLE IV.

	Charge of the re- active part*	Carcino- genic power**
5,9,10-methyl-1,2-benzanthracene	2.054	50
9,10-methyl-1,2-benzanthracene	2.043	50
5,6-methyl-1,2-benzanthracene	2.029	27
10-methyl-1,2-benzanthracene	2.027	23
5-methyl-1,2-benzanthracene	2.016	23
7-methyl-1,2-benzanthracene	2.014	0
8-methyl-1,2-benzanthracene	2.011	0
0-methyl-1,2-benzanthracene	2.000	0

\* Calculated by M. Martin.

\*\* These numbers are the index evaluated by Rudali à l'Institut de Radium de Paris (Laboratoire de A. Lacassagne).

study the substituted and heterocyclic<sup>14</sup> aromatic molecules and inorganic molecules.

This method has been used to study the phenomena of oxidation-reduction,<sup>15</sup> the  $p_H$ ,<sup>16</sup> the synergie and the free radicals.<sup>17</sup>

#### APPLICATION TO THE STUDY OF THE PHYSIOLOGICAL PROPERTIES OF THE MOLECULES

O. Schmidt<sup>18</sup> has supposed that the carcinogenic molecules possess a part rich in  $\pi$ -electrons. Svartholm<sup>19</sup> thought that they must tend to react by addition. These two hypotheses<sup>20</sup> have been studied by the molecular diagram method. It seems that there is a good agreement between these hypotheses and the experiments.

With electronic density of the reactive part of the molecules equal, the carcinogenic power increases roughly with the power of addition. With power of addition equal, the carcinogenic power seems to increase with the  $\pi$ -electron charge of the reactive part of the molecule, as is pointed out by Table IV.

<sup>13</sup> P. Daudel and R. Daudel, *Comptes Rendus* **222**, 738 (1946).

<sup>14</sup> R. Daudel, *Comptes Rendus* **222**, 798 (1946); Buu Hoi and R. Daudel, *Ann. des Pays Bas* (1946); R. Daudel, *Rev. Scientifique*, 229 (1946).

<sup>15</sup> J. Bellugue and R. Daudel, *Rev. Scientifique* (1946).

<sup>16</sup> Reference 15 and P. Daudel, *Comptes Rendus* **222**, 799 (1946).

<sup>17</sup> R. Daudel, *Trans. Faraday. Soc.*, "The Labile Molecule" (in press).

<sup>18</sup> For references see R. Daudel, *Rev. Scientifique*, 37 (1946).

<sup>19</sup> Svartholm, *Ark. f. Kem. Min. Geol.* **15A**, No. 13 (1941).

<sup>20</sup> Reference 18 and A. Pullman, Thèse, Paris, 1946 and R. Daudel, *Bulletin du Cancer* (in press).