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Theoretical Study of Nitrogen Heterocyclics. II. Molecular Diagrams and Carcinogenic Activities of Some Mono- and Dibenzocarbazoles

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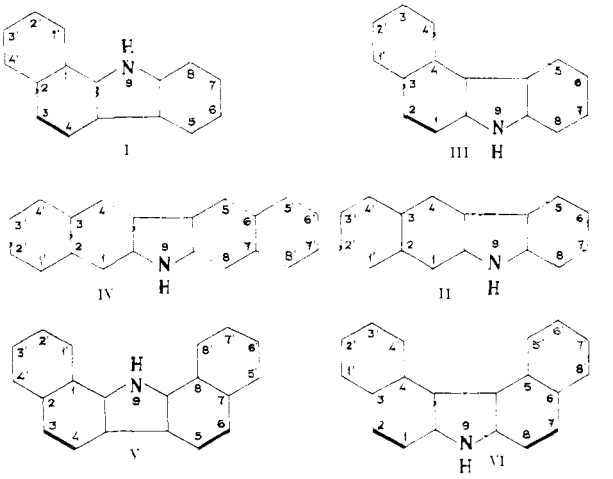
Molecular-orbital calculations of structural static parameters (bond orders, π-electron densities and free valences) and dynamic indexes (atom, *ortho*- and *para*-localization energies) are presented for a number of mono- and dibenzocarbazoles. The results are used to predict the chemical properties of the molecules. A correlation was found between carcinogenic activity and the static complex indexes used to characterize the K region.

Some years ago Longuet-Higgins and Coulson[1] calculated the molecular diagram of carbazole. Since then, little attention has been given to the theoretical study of carbazole and its derivatives and few molecular diagrams of these compounds have been calculated. Recently, Pullman and Pullman[2] published the molecular diagram for 3,4,5,6- and 1,2,7,8-dibenzocarbazoles, calculated by the MO method using the approximation, homocyclic conjugation[3,4]; in this approximation it is assumed that the atomic orbitals of all the atoms are equivalent, and. in consequence, the electron-pair of nitrogen atom is considered as belonging to the carbon atom which occupies its place. Their results are not satisfactory, because analysis of their molecular diagrams shows different gradations of the bond order and the π-electron density for the K region. Thus, they could not predict the chemical reactivity in this region for both molecules, and consequently could not predict their carcinogenic activities.

In contrast to the polycyclic carcinogenic compounds, the physiological activity of the carbazoles has attracted little attention. Recently, however, Buu-Hoï and his co-workers[5] have synthesized a great number of these derivatives, and Lacassagne and his co-workers[6] have published experimental results for 42 members of this series.

In this paper we present the molecular diagrams of the following compounds: 1,2- (I), 2,3- (II), 3,4-benzocarbazole (III), 2,3,6,7- (IV), 1,2,7,8- (V) and 3,4,5,6-dibenzocarbazole (VI). (The enumeration used in calculations and results is standard, as indicated in the respective diagrams.) From the calculated structural static and dynamic indexes, we have tried to establish a quantitative relation between carcinogenic activity and molecular structure.



(1) H. C. Longuet-Higgins and C. A. Coulson, *Trans. Faraday Soc.*, **43**, 87 (1947).

(2) A. Pullman and B. Pullman, "Cancérisation par les substances chimiques et structure moléculaire," Masson et Cie, Paris, 1955, p. 190.

(3) E. Huckel, *Z. Physik*, **70**, 242 (1931); **76**, 634 (1932); R. S. Mulliken, *J. Chem. Phys.*, **7**, 340 (1939).

(4) G. Berthier and B. Pullman, *Comp. rend.*, **231**, 774 (1950), have calculated by this approximation a molecular diagram for carbazole.

(5) N.-P. Buu-Hoï and P. Jacquignon, *J. Chem. Soc.*, 513 (1954), and former papers.

(6) A. Lacassagne, N.-P. Buu-Hoï, F. Zajdela and N. D. Kuong, *Bull. Cancer*, **42**, 3 (1955).

Method of Calculation.—We have used the MO method in the simplest LCAO approximation. We have not taken into account the overlap integrals between adjacent atomic oribitals, due to the complexity of the calculation, although the importance of this factor is admitted.[7] The three dibenzocarbazole molecules have the symmetry C_{2v}, which has been given consideration in the resolution of the corresponding secular determinants.

TABLE I

π-ELECTRON MOLECULAR-ORBITAL ENERGY LEVELS (E_i) IN ORDER OF INCREASING ENERGY

Benzocarbazole	i	Sym.[a]	$m_i = (E_i - \alpha)/\beta$	i	Sym.[a]	$m_i = (E_a - \alpha)/\beta$
3,4-	1		2.6547	6		1.0000
	2		2.1728	7		1.0000
	3		1.7886	8		0.5797
	4		1.4609	9		0.4941
	5		1.4142			
1,2	1		2.6596	6		1.1634
	2		2.1616	7		0.8574
	3		1.7186	8		.6801
	4		1.6225	9		.4339
	5		1.2649			
2,3	1		2.6428	6		1.1501
	2		2.1976	7		0.8631
	3		1.7641	8		.6842
	4		1.5442	9		.3798
	5		1.3031			
2,3,6,7-	1	S	2.6602	7	S	1.2454
	2	A	2.2700	8	S	1.0000
	3	S	2.0915	9	A	0.8592
	4	S	1.5792	10	A	.5206
	5	A	1.5094	11	S	.3467
	6	A	1.2798			
1,2,7,8-	1	A	2.6885	7	A	1.2094
	2	S	2.2700	8	A	1.0000
	3	A	1.9918	9	S	0.8592
	4	A	1.6634	10	S	.5206
	5	S	1.5094	11	A	.4434
	6	S	1.2798			
3,4,5,6-	1	S	2.6817	7	A	1.1798
	2	A	2.2440	8	A	1.0000
	3	S	2.0811	9	S	0.7845
	4	A	1.5801	10	S	.5858
	5	S	1.4791	11	A	.4434
	6	S	1.3763			

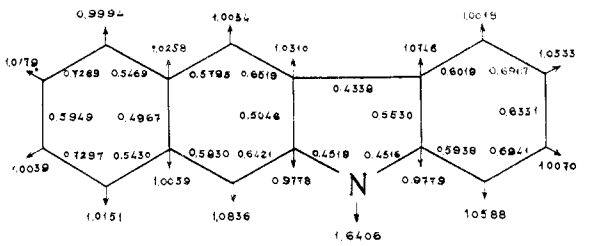
[a] The wave functions symmetrical in respect with the plane of symmetry are labeled S, those anti-symmetrical about the plane of symmetry are labelled A. Their correct designations according to group-theory, are A_2 and B_1, respectively. See H. Eyring, J. Walter and G. E. Kimball, "Quantum Chemistry," John Wiley and Sons, New York, N. Y., 1944, p. 376.

The Coulomb integral of the nitrogen atom, α_N, and the resonance integral for the CN bond, $\beta_{C,N}$, have the following form: $\alpha_N = \alpha_C + \delta\beta$ and $\beta_{C,N} = \rho\,\beta_{C,C}$, respectively. The selection of the best values for the δ and ρ parameters is a difficult question.[7-10] For our calculations we have chosen the parameters given by Fukui and his co-workers,[11] $\delta = 1$ and $\rho = 1$, *i.e.*, $\alpha_N = \alpha_C + \beta_{C,C}$ and $\beta_{C,N} = \beta_{C,C}$. (This value for δ is very near that adopted by Jaffé,[10] $\delta = 1.2$.) We have not taken the inductive effect into account.

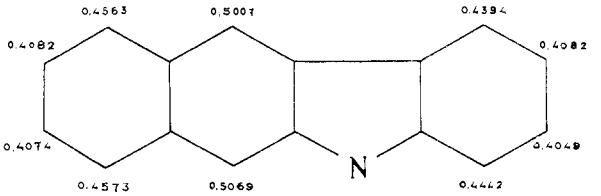
The molecular-orbital energies are indicated for the six compounds studied in Table I.

The MO coefficients being known, we have calculated the π-electron densities and the bond orders according to Coulson and Longuet-Higgins.[12] In spite of Moffitt's considerations,[13] we have adopted a single value for the maximum bond order,[14] $N_{max} = 3^{1/2}$, in the calculation of the free valences.

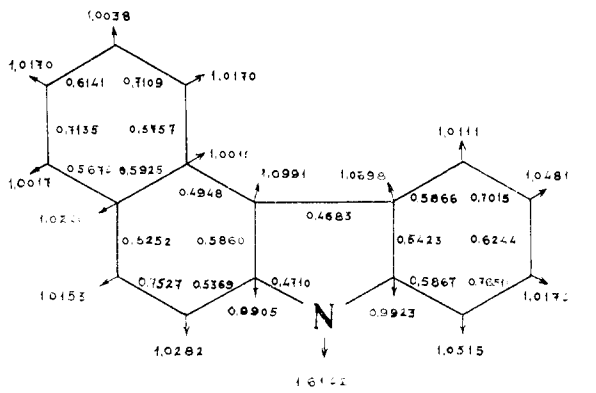
The bond orders and the π-electron densities for 1,2-benzocarbazole are shown in diagram VIIa, and the free valences in VIIb. VIIIa and VIIIb, and IXa and IXb give similar static indexes for 2,3- and 3,4-benzocarbazole, respectively. The structural static indexes are shown in X, XI and XII for 2,3,6,7-, 1,2,7,8- and 3,4,5,6-dibenzocarbazole; the values indicated by arrows (on the right of the figures) correspond to the π-electron densities and those on the left to the free valences.



VIIIa



VIIIb



IXa

(7) D. W. Davies, *Trans. Faraday Soc.*, **51**, 449 (1955), when previous references are given about the introduction of the overlap.

(8) L. E. Orgel, T. L. Cottrell, W. Dick and L. E. Sutton, *ibid.*, **47**, 1136 (1951).

(9) P.-O. Löwden, *J. Chem. Phys.*, **21**, 496 (1953).

(10) H. H. Jaffé, THIS JOURNAL, **77**, 4448 (1956).

(11) K. Fukui, T. Yonezawa, C. Nagata and H. Shingu, *J. Chem. Phys.*, **22**, 1433 (1954).

(12) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc. (London)*, **A191**, 39 (1947).

(13) W. E. Moffitt, *Trans. Faraday Soc.*, **45**, 373 (1949).

(14) H. H. Greenwood, *ibid.*, **48**, 677 (1952).

The atom localization energies, $A(-\beta)$, have been calculated by the standard method,[15] and those of the *ortho*-localization, $o(-\beta)$, and *para*-localization energies, $p(-\beta)$, by the methods described by Brown.[16]

TABLE II
ATOM LOCALIZATION ENERGIES

Benzocarbazole	Positions	$A_e(-\beta)$	$A_r(-\beta)$	$A_n(-\beta)$
2,3-	1	2.050	2.220	2.389
	1′	2.200	2.256	2.313
	2′	2.424	2.444	2.465
	4	2.068	2.113	2.157
	7	2.453	2.476	2.500
	8	2.196	2.366	2.535
1,2-	3	2.097	2.294	2.492
	4	2.346	2.362	2.377
	7	2.406	2.480	2.554
	8	2.225	2.362	2.499
3,4-	1	2.285	2.344	2.403
	2	2.230	2.281	2.332
	7	2.378	2.448	2.519
	8	2.223	2.361	2.500
Dibenzocarbazole				
2,3,6,7-	1	1.931	2.115	2.300
	1′	2.206	2.268	2.330
	2′	2.420	2.430	2.440
	3′	2.336	2.421	2.506
	4′	2.258	2.265	2.272
	4	2.097	2.119	2.141
1,2,7,8-	3	2.117	2.294	2.471
	4	2.328	2.351	2.374
3,4,5,6-	1	2.291	2.343	2.395
	2	2.190	2.264	2.338

TABLE III
ortho-LOCALIZATION ENERGIES

Benzocarbazole	Positions	$o(-\beta)$
2,3-	1′, 2′	1.232
	7, 8	1.360
1,2-	3, 4	1.139
	7, 8	1.343
3,4-	1, 2	1.129
	7, 8	1.339
Dibenzocarbazole		
2,3,6,7-	1′, 2′	1.236
	3′, 4′	1.234
1,2,7,8-	3, 4	1.131
3,4,5,6-	1, 2	1.124

TABLE IV
para-LOCALIZATION ENERGIES

Benzocarbazole	Positions	$p(-\beta)$
2,3-	1, 4	3.461
Dibenzocarbazole		
2,3,6,7-	1, 4	3.482
	1′, 4′	3.666
1,2,7,8-	1′, 4′	3.738
3,4,5,6-	1′, 4′	3.739

Chemical Reactivity.—Although little is known about the chemical behavior of the mono- and dibenzocarbazoles, we shall indicate, on the basis of our static (π-electron densities and free valences) and dynamic indexes (atom localization energies), in which positions the different types of substitution reactions should occur. Electrophilic attack should occur initially at the position (or positions) of maximum π-electron density and minimum A_e; nucleophilic substitution at the position of minimum π-electron density and A_n; and the radical attack at the position of maximum free valence and minimum A_r. These predictions are given for the carbazoles in Table V. Some results, however, cannot be considered as definitive because the entire localization energies have not been calculated.

We can sum up these considerations concerning chemical reactivity by plotting the static indexes against the dynamic, *e.g.*, Fig. 1 in which the values

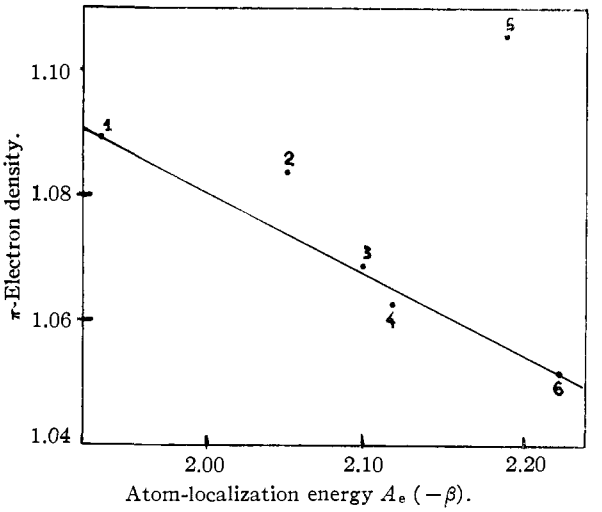
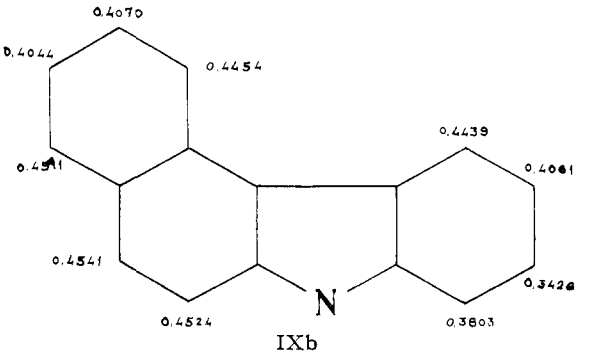
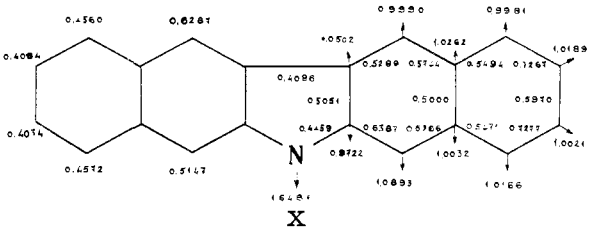


Fig. 1.—Variation of the π-electron densities with the atom localization energies for the position of initial electrophilic attack: (1) 2,3,6,7-dibenzocarbazole; (2) 2,3-benzocarbazole; (3) 1,2-benzocarbazole; (4) 1,2,7,8-dibenzocarbazole; (5) 3,4,5,6-dibenzocarbazole; (6) 3,4-benzocarbazole.

of the π-electron density are plotted against A_e for the positions of the initial electrophilic attack. The agreement between these indexes is excellent, with the exception of 3,4,5,6-dibenzocarbazole.



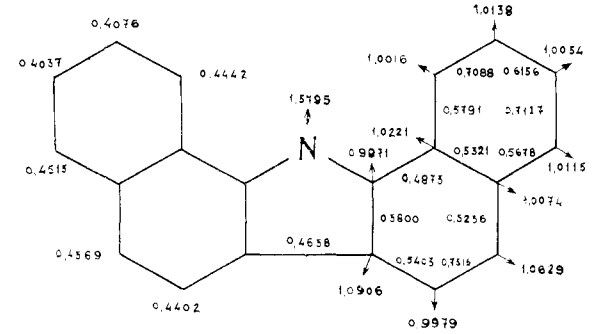
IXb



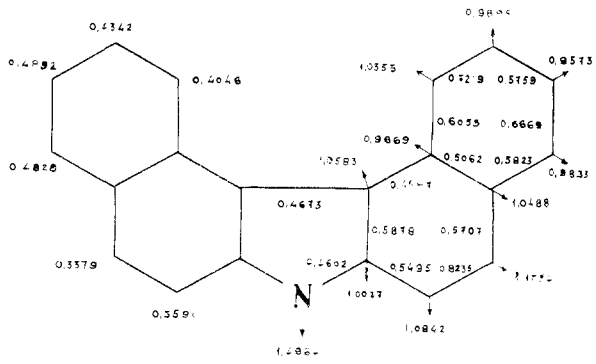
X

(15) G. W. Wheland, THIS JOURNAL, **64**, 900 (1942).

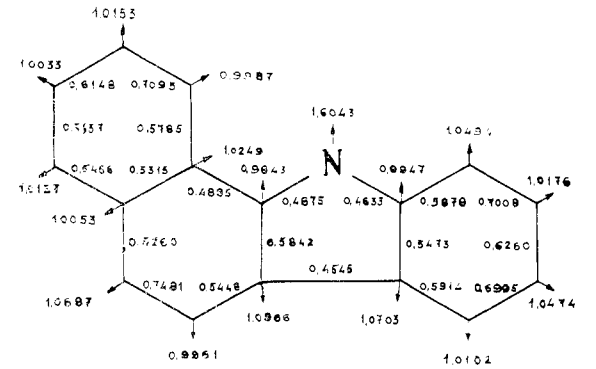
(16) R. D. Brown, *Australian J. Sci. Res.*, **A2**, 564 (1949); *J. Chem. Soc.*, 691 (1950).



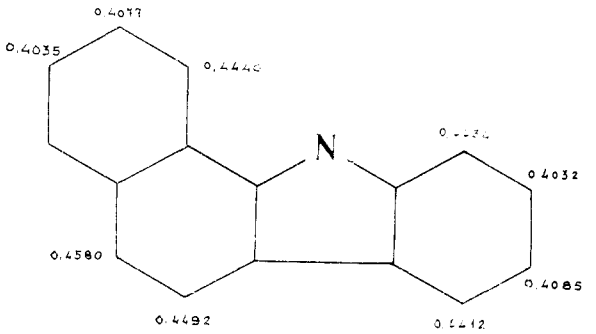
XI



XII



VIIa



VIIb

From their study of the ultraviolet absorption spectra of the benzocarbazoles, Clemo and Felton[17] have postulated that the electronic polarization leads to a *p*-quinoid structure, which indicates the initial position at which substitution by electrophilic reagents should take place; for 2,3-benzocarbazole

(17) G. R. Clemo and D. G. I. Felton, *J. Chem. Soc.*, 1658 (1952).

TABLE V

POSITIONS AT WHICH SUBSTITUTION REACTIONS SHOULD OCCUR INITIALLY

	Type of substitution reaction		
Benzocarbazole	Electrophilic Position	Nucleophilic Position	Radical Position
2,3-	1	4′[a]	1
1,2-	3	4	4′[a]
3,4-	8	1′[a]	2
Dibenzocarbazole			
2,3,6,7-	1, 8	4, 5	4, 5
1,2,7,8-	3, 6	4, 5	3, 6
3,4,5,6-	2, 7	2′,[a] 7′[a]	2′,[b] 7′[b]

[a] Uncertain, since A_n for this position is unknown. [b] Uncertain, since A_r for this position is unknown.

electrophilic attack should occur at position 6, for 3,4-benzocarbazole at position 2, and for 1,2-benzocarbazole at position 3. Their conclusions agree with the theoretical results (π-electron densities) of Longuet-Higgins and Coulson,[1] and also with the experimental findings. They agree with our results only for 1,2-benzocarbazole. Similar results were obtained by Felton[18] for 1,2,7,8-, 3,4,5,6- and 1,2,5,6-dibenzocarbazole.

Carcinogenic Activity and Molecular Structure.—We have tried to establish a quantitative relationship between the molecular structure of these mono- and dibenzocarbazoles and their carcinogenic activity.

It is well known that condensed carbazoles (especially derivatives of 1,2-benzocarbazole[19]) and the di-angular benzocarbazoles[6,20] (particularly 3,4,5,6-dibenzocarbazole) show marked carcinogenic activity. All theories which relate molecular structure to the carcinogenic activity of the nitrogen heterocyclics are based on the assumption that carcinogenically active molecules possess—in a form similar to the polycyclic aromatic hydrocarbons—a *meso*-phenanthrenic region called the K region, which is chemically very active, and is the seat of physiological activity. Furthermore, according to Pullman and Pullman,[21] if the molecule has a *meso*-anthracenic region, called the L region, the latter must have little activity; otherwise, the K region cannot enter into the carcinogenic process.

In diagrams I, II, V and VI, we represent the *K* region by a thick line. As 2,3-benzocarbazole and 2,3,6,7-dibenzocarbazole are not carcinogenic, we cannot properly speak of their K region; however, for comparative purposes we designated 1′, 2′ as the K region for 2,3-benzocarbazole, and 1′, 2′ and 7′, 8′ as the K region for 2,3,6,7-dibenzocarbazole.

The chemical reactivity for the K region can be characterized by the bond order (static index) and by the *ortho*-localization energy (dynamic index).

(18) D. G. I. Felton, *ibid.*, 1668 (1952).

(19) O. Schurch and A. Winterstein, *Z. physiol. Chem.*, **236**, 79 (1935); A. Lacassagne, N.-P. Buu-Hoï, R. Royer and F. Zajdela, *C. R. Soc. Biol.*, **141**, 635 (1947).

(20) E. Boyland and A. M. Brues, *Proc. Roy. Soc. (London)*, **B122**, 429 (1937); E. Boyland and E. H. Mawson, *Biochem. J.*, **32**, 1460 (1938); G. M. Badger, J. W. Cook, C. L. Hewett, E. L. Kennaway, N. M. Kennaway, R. H. Martin and A. M. Robinson, *Proc. Roy. Soc. (London)*, **B131**, 170 (1942); A. H. Kirby and P. R. Peacock, *Brit. J. Exp. Path.*, **27**, 179 (1946).

(21) Ref. 2, Conts. III and IV.

The bond orders *versus* the *ortho*-localization energies are represented in Fig. 2, which shows that the two types of structural indexes vary in a linear manner. The exception is 3,4,5,6-dibenzocarbazole, for which the bond order value is probably high; it should be recalled that this compound showed a marked deviation from the curve of Fig. 1.

The bond orders values p_K, the π-electron densities for the K region (the sum of the corresponding values of the two carbon atoms that delineate it) q_K, the π-electron density of the nitrogen atom q_M, and the carcinogenic activity are shown in Table VI.

TABLE VI

RELATION OF q_K AND q_N WITH CARCINOGENIC ACTIVITY

Compound	Bond	p_K	q_K	q_N	Carcinogenic activity[a]
2,3,6,7-Dibenzocarbazole	1', 2'	0.7277	2.0187	1.6481	−
2,3-Benzocarbazole	1', 2'	.7297	2.0190	1.6406	−
3,4-Benzocarbazole	1, 2	.7527	2.0455	1.6142	+
1,2,7,8-Dibenzocarbazole	3, 4	.7515	2.0608	1.5795	+
1,2-Benzocarbazole	3, 4	.7481	2.0648	1.6043	+
3,4,5,6-Dibenzocarbazole	1, 2	.8235	2.1896	1.4964	+++

[a] We used the notation of Pullman and Pullman, ref. 2, p. 16. From these results we can draw the following conclusion: the larger the q_K, the greater is the carcinogenic activity; and conversely, the larger the q_N, the smaller is this activity.

The relation between q_K and carcinogenic activity allows us to define the latter quantitatively. In fact, the two physiologically inactive derivatives are characterized by a q_K value of approximately 2.02 π-electrons; q_K is more or less equal to 2.06 for the three weakly active compounds and, finally, q_K has an approximate value of 2.20 for 3,4,5,6-dibenzocarbazole, which is very active.

Thus there exists a marked difference in the q_K values of the three groups, which was not found for the methylated derivatives of the angular benzacridines; Chalvet and his co-workers[22] report a difference of only 0.3% in π-electron density for q_K between a very active substance (3,10-methyl-7,8-benzacridine) and an inactive one (2-methyl-7,8-benzacridine).

The two types of complex static structural indexes, $2p_K + q_K$ and $2p_K + q_K + F_K$ (where F_K is the sum of the free valences of the two carbon atoms that delineate the K region) and the carcinogenic activity are given in Table VII. The results indicate that these static complex indexes vary with the carcinogenic activity; the three groups of compounds (inactive, weakly carcinogenic and strongly carcinogenic) have different values of the indexes, particularly $2p_K + q_K$.

TABLE VII

RELATION BETWEEN THE STRUCTURAL COMPLEX STATIC INDEXES FOR THE *K* REGION AND THE CARCINOGENIC ACTIVITY

Compound	Bond	$2p_K + q_K$	$2p_K + q_K + F_K$	Carcinogenic activity
2,3,6,7-Dibenzocarbazole	1', 2'	3.4741	4.3387	−
2,3-Benzocarbazole	1', 2'	3.4784	4.3431	−
3,4-Benzocarbazole	1, 2	3.5489	4.4554	+
1,2,7,8-Dibenzocarbazole	3, 4	3.5638	4.4609	+
1,2-Benzocarbazole	3, 4	3.5610	4.4682	+
3,4,5,6-Dibenzocarbazole	1, 2	3.8366	4.5335	+++

(22) O. Chalvet, R. Daudel, M. Pagés, M. Roux, N.-P. Buu-Hoï and R. Royer, *J. chim. phys.*, **51**, 548 (1955).

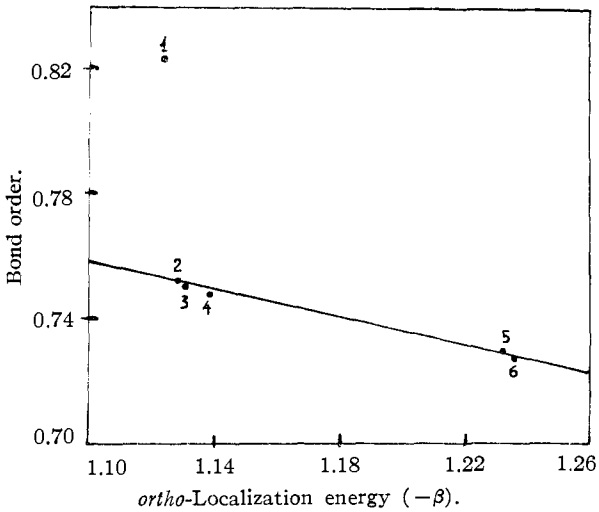


Fig. 2.—Variation of the bond orders with the *ortho*-localization energies for the K region: (1) 2,3,5,6-dibenzocarbazole; (2) 3,4-benzocarbazole; (3) 1,2,7,8-dibenzocarbazole; (4) 1,2-benzocarbazole; (5) 2,3,6,7-dibenzocarbazole; (6) 2,3-benzocarbazole.

The latest theories relate the structural dynamic indexes instead of the static indexes to carcinogenic activity.[21] Before applying them to our carbazole derivatives, in the form developed by Pullman and Pullman,[21] several remarks are necessary. First, the use of the dynamic indexes requires that a distinction be made between the unsubstituted hydrocarbons, and the substituted hydrocarbons and heterocyclics. For the former, according to Wheland's theorem, the value of the atom localization energy for a given carbon is independent of the nature of the substitution reaction (electrophilic, radical or nucleophilic); this is not true for the two other types of compounds. Consequently, in this study relations are established between the structural dynamic indexes for both electrophilic and radical reactions and carcinogenic activity. Since most addition reactions take place in two steps,

TABLE VIII

RELATION BETWEEN CARCINOGENIC ACTIVITY AND STRUCTURAL INDEXES OF BENZO- AND DIBENZOCARBAZOLES FOR THE K REGION IN ELECTROPHILIC (ELECTRO) AND RADICAL (RAD) REACTIONS

I = inactive, W = weakly carcinogenic and S = strongly carcinogenic.

Compound	Carcinogenic activity	Bond	K Region Electro. $o(-\beta) + A_{em}(-\beta)$	Rad. $o(-\beta) + A_{rm}(-\beta)$
2,3,6,7-[a]	I	1', 2'	3.441	3.503
2,3-[b]	I	1', 2'	3.432	3.488
3,4-	W	1, 2	3.359	3.410
1,2,7,8-	W	3, 4	3.248	3.425
1,2-	W	3, 4	3.236	3.433
3,4,5,6-	S	1, 2	3.314	3.388

[a] For the L region (carbons 7,8), $p(-\beta) + A_{em}(-\beta) = 5.413$; $p(-\beta) + A_{rm}(-\beta) = 5.597$. [b] For the L region (carbons 1,4), $p(-\beta) + A_{em}(-\beta) = 5.511$.

Pullman and Pullman,[21] in characterizing the K and L regions, employed a complex index which includes the atom localization energy having the lowest value for the two carbon atoms which define the corresponding region, A_m. Finally, it should be stated that to avoid undue computation, only the *para*-localization energies were calculated for the non-angular derivatives; the free valences indicated that the remaining compounds studied possess relatively inactive L regions.

In Table VIII the corresponding values for the electrophilic and radical reactions are shown.

A comparison of the results in Table VIII shows that the variation of the complex index that characterizes the K region is more uniform for radical reactions than for electrophilic ones. For the latter, 3,4,5,6-dibenzocarbazole, the most carcinogenic of these compounds, should have the minimum index value, but 1,2-benzocarbazole and 1,2,7,8-dibenzocarbazole have even smaller values. On the other hand, there is no marked difference in the index values of the three groups of compounds (inactive, weakly and strongly carcinogenic). Thus, the complex dynamic indexes do not permit us to define threshold values from which we can predict whether a compound of this type is carcinogenic.

From these results, we conclude that there is a better correlation between the carcinogenic activity and the static complex indexes of these carbazole derivatives than between the carcinogenic activity and the dynamic complex indexes; however, more results are necessary to establish this finding for the nitrogen heterocyclics.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF MARYLAND]

Characteristic Integrated Intensities of Bands in the Infrared Spectra of Carboxylic Acids[1]

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The integrated intensities of the free and bonded hydroxyl and carbonyl stretching bands in the spectra of carboxylic acids were measured and found to be characteristic properties of acids. The bands were all more intense in acids in which the carbonyl function was part of a conjugated system. In all cases there was an increase in intensity when the absorbing group was hydrogen-bonded. The integrated intensities of the free hydroxyl bands were 1.2 units for non-conjugated acids and 1.7 units for acids in which the carbonyl function was part of an aromatic or dienoic system. The corresponding intensities for the associated hydroxyl bands were 10.6 and 15.5 units. The integrated intensities of the free carbonyl stretching bands were 3.6 and 4.6 units and for the associated carbonyls 4.5 and 5.9 units for the two types of acids. Each carbon–hydrogen bond in the acids studied absorbed with an intensity of about 0.46 unit near 3000 cm.$^{-1}$. Equilibrium constants for the dimerization of several acids were determined spectroscopically. These dissociation constants were near 4.5×10^{-4} mole/l. for the non-conjugated acids and near 2.2×10^{-4} mole/l. for the conjugated acids.

Introduction

In drawing conclusions from the frequencies of infrared absorption maxima one uses only part of the information available from infrared spectra. Further information about the identity and nature of the absorbing material may be obtained from a consideration of band intensities. It is true that until recently it has been difficult to evaluate the absolute intensities of infrared bands. Ramsay[3] has shown, however, how to calculate intensities from the infrared spectra of compounds in solution. The increased reliability and improved dispersion of the infrared instruments currently available, moreover, make it possible to obtain reproducible measurements.

The utility of intensity measurements in the characterization of unknown structures depends upon the relationship between the intensity and the nature of an absorbing group. If the absolute intensity of an infrared band can be shown to be characteristic of a functional group or of the molecular environment of such a group, it will be possible to use such data to supplement band frequency measurements.

The absolute intensity, A, of an infrared band is defined by the expression

$$A = \int \alpha d\nu = 1/Cl \int \ln I_0/I d\nu \qquad (1)$$

where α is the molar absorption coefficient, C is the concentration of the solution in moles/liter, l is the sample thickness in cm., I/I_0 is the transmittance of the solution and ν is the frequency in cm.$^{-1}$. The units of A are cm.$^{-2}$ mole^{-1} l. For convenience, an "intensity unit" is defined as 10^4 cm.$^{-2}$ mole^{-1} l. The quantity A has been evaluated for various bands by two methods. The first involves the measurement of the area under a plot of log I_0/I against frequency and the direct calculation of A through eq. 1. The second method[3] assumes a symmetrical shape for the infrared band in question and requires the measurement of only two quantities from the experimentally determined spectrum: the value of ln I_0/I at the band maxi-

(1) Taken from a thesis submitted by Joseph Wenograd to the Graduate School of the University of Maryland as partial fulfillment of the requirements for the degree of Doctor of Philosophy. This investigation received the generous financial support of the Office of Army Ordnance. A portion of this work was presented before the Eighth Symposium on Molecular Structure and Spectroscopy, June, 1954, at Columbus, Ohio.

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(3) D. A. Ramsay, THIS JOURNAL, 74, 72 (1952).