Theoret. chim. Acta (Berl.) 8, 341—357 (1967)

An Analysis of the Polarizabilities in Some Conjugated Molecules

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Received July 6, 1967

Atom-atom, atom-bond and bond-bond polarizabilities are calculated with a previously used LCAO approximation. Some properties of naphtalene, assumed as general for alternant hydrocarbons, seem to depend on the approximation employed. Atom-atom polarizabilities in azines are related to other theoretical and experimental quantities. In all the molecules studied, the part played by formal bonds is highly stressed.

Atom-Atom-, Atom-Bindungs- und Bindungs-Bindungs-Polarisierbarkeiten werden mit einem schon früher benutzten LCAO-Verfahren berechnet. Einige Eigenschaften von Naphthalin, die für alternierende Kohlenwasserstoffe als charakteristisch angesehen werden, scheinen von der benutzten Näherung abzuhängen. Atom-Atom-Polarisierbarkeiten in Azinen werden auf andere theoretische und experimentelle Größen zurückgeführt. In allen betrachteten Molekülen spielen formale Bindungen eine bedeutende Rolle.

Calcul des polarisabilités atome-atome, atome-liaison et liaison-liaison dans une approximation LCAO utilisée auparavant. Certaines propriétés du naphtalène, supposées générales pour les hydrocarbures alternants, semblent dépendre de l'approximation employée. Les polarisabilités atome-atome des azines sont reliées à d'autres grandeurs théoriques et expérimentales. Dans toutes les molécules étudiées, le rôle joué par les liaisons formelles est mis en relief.

1. Introduction

Few molecular polarizability calculations take into account the overlap integrals, introduction that modifies appreciably these quantities even for the case in which H and S commute [3, 15] (H, hamiltonian matrix; S, overlap matrix). The known polarizability estimations are usually referred to hydrocarbons. We shall calculate in this work, atom-atom, atom-bond and bond-bond polarizabilities by using the complete H and S matrices and Kohlrausch's nuclear effective charges. For the Coulomb (α) and exchange (β) integrals of the LCAO-MO method, we follow a semiempirical approximation based on electronegativity concepts [7]. We report here polarizabilities for naphtalene and monocyclic azines.

An advantage to our approximation is that it allows the calculation of absolute polarizabilities, not being expressed, as usual, in $1/\beta$ units. For instance, COULSON and LONGUET-HIGGINS [5] have found it difficult, when computing polarizabilities for butadiene, to decide which is the best β value to assume; they finally use the benzene value for the sake of uniformity. In other cases β may also be considered

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* With a fellowship from the Consejo Nacional de Investigaciones Científicas y Técnicas, Argentina.

** With a fellowship from the Centro Latino Americano de Física.

a parameter to fit [22], while in our calculation there remains no adjustable parameter.

Some properties of the polarizabilities are general, but others seem to depend on the approximation employed for their calculation. With this in mind, we analyse two theorems and show that they are not generally valid.

We have used CHIRGWIN and COULSON'S formulae for atom-atom ($\Pi_{\mu\nu}$), atom-bond ($\Pi_{\mu,\varrho\sigma}$) and bond-bond ($\Pi_{\mu\nu,\varrho\sigma}$) polarizabilities [3]:

$$\Pi_{\mu\nu} = 2 \sum_j \sum_k \frac{x_{j\nu}\, x_{k\mu}\, y_{j\mu}\, y_{k\nu} + x_{j\mu}\, x_{k\nu}\, y_{j\nu}\, y_{k\mu}}{E_j - E_k} \tag{1}$$

$$\Pi_{\mu,\varrho\sigma} = 2 \sum_j \sum_k \frac{x_{k\mu}\, y_{j\mu}\, (x_{j\varrho}\, y_{k\sigma} + x_{j\sigma}\, y_{k\varrho}) + x_{j\mu}\, y_{k\mu}\, (x_{k\varrho}\, y_{j\sigma} + x_{k\sigma}\, y_{j\varrho})}{E_j - E_k} \tag{2}$$

$$\Pi_{\mu\nu,\varrho\sigma} = \sum_j \sum_k \frac{(x_{j\mu}\, y_{k\nu} + x_{j\nu}\, y_{k\mu})\,(x_{k\varrho}\, y_{j\sigma} + x_{k\sigma}\, y_{j\varrho}) + (x_{k\mu}\, y_{j\nu} + x_{k\nu}\, y_{j\mu})\,(x_{j\varrho}\, y_{k\sigma} + x_{j\sigma}\, y_{k\varrho})}{E_j - E_k} \tag{3}$$

where $x_{j\mu}$ is the coefficient of atom μ in the wave function j (Greek suffixes mean atoms, and Latin suffixes wave functions); $y_{j\mu} = \sum_\nu S_{\mu\nu}\, x_{j\nu}$; $S_{\mu\nu}$ the matrix element of S; E_j the energy level corresponding to the wave function j. The sum over j is taken over the occupied levels and the sum over k runs over the unoccupied levels.

These formulae do not have the same physical meaning as the formulae without overlap. For now, if q_μ and $p_{\mu\nu}$ are charges and bond orders:

$$\Pi_{\mu\nu} = \frac{\partial q_\mu}{\partial H_\nu^\nu}; \quad \Pi_{\mu,\varrho\sigma} = \frac{\partial q_\mu}{\partial H_\varrho^\sigma} + \frac{\partial q_\mu}{\partial H_\sigma^\varrho}; \Pi_{\mu\nu,\varrho\sigma} = \frac{\partial p_{\mu\nu}}{\partial H_\varrho^\sigma} + \frac{\partial p_{\mu\nu}}{\partial H_\sigma^\varrho} \tag{4}$$

where

$$H_\nu^\mu = \sum_\varrho S^{\mu\varrho}\, H_{\nu\varrho} \tag{5}$$

and $S^{\mu\varrho}$ are the components of the tensor reciprocal to S.

The formulae without overlap formally resemble to (4):

$$\Pi_{\mu\nu} = \frac{\partial q_\mu}{\partial H_{\nu\nu}}; \quad \Pi_{\mu,\varrho\sigma} = \frac{\partial q_\mu}{\partial H_{\varrho\sigma}}; \quad \Pi_{\mu\nu,\varrho\sigma} = \frac{\partial p_{\mu\nu}}{\partial H_{\varrho\sigma}}\,. \tag{6}$$

But the H's in (4) and (6) are quite different physical quantities. On introducing overlap, the Coulomb integral is replaced by what CHIRGWIN and COULSON call the charge affinity of the atom; similarly, instead of the resonance integral we shall have H_ϱ^σ, the bond affinity of ϱ towards σ. These affinities refer to an atom (or a bond) *in the molecule.*

CHIRGWIN and COULSON have noted that there are non zero values of H_μ^ν even corresponding to positions between which the overlap was supposedly zero; and these elements were not at all negligible. Because we consider all the overlap integrals (and these have bigger values than usual with Kohlrausch's nuclear effective charges [7]), we expect to find an appreciable influence of the elements H_ϱ^σ when ϱ and σ are not neighbors.

An incidental consequence of the preceding is that it will not be possible using simple expressions such as

$$\delta q_\mu = \sum_\nu \Pi_{\mu\nu}\, \delta\alpha_\nu + \sum_{\varrho\sigma} \Pi_{\mu,\varrho\sigma}\, \delta\beta_{\varrho\sigma}$$

to calculate q_μ or $p_{\mu\nu}$ for a given molecule starting from the data for a parent molecule.

2. Naphtalene

a) Atom-atom Polarizabilities

In an alternant hydrocarbon (AH), two sets of atoms are defined, namely the "starred" and "unstarred" ones (see Fig. 1). It has been shown [4] that in an AH, the mutual polarizability of atoms μ and ν has a negative value when the two atoms are identical or when they belong to the same set, and a positive value when they belong to different sets [13]. We see in Tab. 1 that this is not our case for $\Pi_{10,1}$ (and therefore $\Pi_{4,9}$ etc.). This difference in sign with respect to $\Pi_{1,1}$ and $\Pi_{3,1}$ although refering to a small quantity, cannot be ascribed to rounding in calculation, for we may calculate accurately to five decimal places.

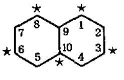


Fig. 1

The above theorem, as other theorems concerning AH, lies upon a special form of the secular determinant; this form depends on the approximation used. We have already remarked [11] that our secular determinant does not reduce to that form. Hence, it is possible that the alternation in sign will not appear.

Apart from the self-polarizabilities, the polarizabilities also have an appreciable value between first neighboring atoms, and are low for second neighbors. Among higher order neighbors, the only significant values correspond to the canonical structures of naphtalene which had an expressive weight [11, 12].

Fig. 2 shows $\Pi_{\mu\nu}/\Pi_{\nu\nu}$, together with the corresponding values of Coulson and Longuet-Higgins [4]. The absolute value of $\Pi_{\mu\nu}$ does not always decrease with increasing distance between μ and ν [13]. For example, $|\Pi_{3,1}| < |\Pi_{4,1}|$. On the other hand, $\Pi_{1,2}$ is roughly twice $\Pi_{3,2}$; and $\Pi_{2,1} \gg \Pi_{9,1}$. This means that a substitution, an addition or the introduction of an nuclear heteroatom in 2 should affect the electronic density in 1 more than 3. This is the case, for example, with the charge distribution reported by Pullman [18] for isoquinoline, where the neighboring carbon-1 to nitrogen has $q = 0.916$, while the carbon-3 has $q = 0.957$.

Table 1. *Atom-atom polarizabilities in naphtalene*

	1	2	9
1	−1.29169	0.61909	0.23652
2	0.61909	−1.19923	−0.02458
3	−0.06234	0.27316	0.15098
4	0.39765	−0.06234	0.00206
5	0.05270	−0.01590	0.00206
6	−0.01590	0.15210	0.15098
7	0.10749	−0.00078	−0.02458
8	−0.04558	0.10749	0.23652
9	0.23652	−0.02458	−0.87784
10	0.00206	0.15098	0.14787

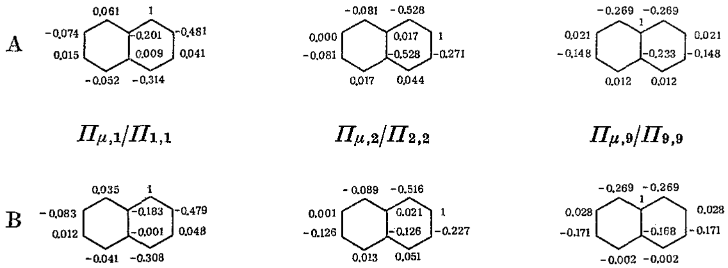


Fig. 2. $\Pi_{\mu\nu}/\Pi_{\nu\nu}$ for naphtalene, A) Coulson and Longuet-Higgins [4], B) this work

If the heteroatom introduction takes place at position 1, the charge over carbon-2 should vary more than the charge at 9. This is verified for quinoline [18], where $q_2 = 0.916$ and $q_9 = 0.965$.

Coulson and Longuet-Higgins obtain $\Pi_{1,2} = \Pi_{10,2}$. For these two we have quite different values, i.e. $|\Pi_{1,2}| > |\Pi_{10,2}|$; also, we find $\Pi_{10,2} = \Pi_{6,2}$ which is not true in their case.

As in the calculations without overlap, our absolute values of naphtalene's 1- and 2-self-polarizabilities verify the relation [13]

$$|\Pi_{1,1}| > |\Pi_{2,2}| > |\Pi_{\mu\mu}|_{\text{benzene}}$$

being $\Pi_{\mu\mu}$ for benzene, with our approximation, -1.19489.

b) Atom-bond Polarizabilities

When $q_\mu = 1$, $\Pi_{\mu,\varrho\sigma}$ must be zero [13] and it is usually assumed so [21]. But this theorem is also a consequence of the special form assumed for the secular determinant. As we have obtained for naphtalene an uneven charge distribution [11], we have for $\Pi_{\mu,\varrho\sigma}$ non-zero values. Therefore, with our approximation, variations in bond affinity must produce fluctuations in electron density and since atom-bond polarizabilities are twice the bond-atom polarizabilities $\partial p_{\varrho\sigma}/\partial H^{\mu}_{\mu}$, variations in the charge affinity alter the values of the bond orders. For example, the introduction of a substituent into a certain position of naphtalene, which varies the charge affinity of that position and, to a lesser degree, those of all positions, shall alter the bond orders and in consequence the interatomic distances in the molecule. It would not then be altogether correct to use for the interatomic distances of a molecule those determined for a derivative.

Large values for $\Pi_{\mu,\varrho\sigma}$ are also found in a table calculated by V. W. Maslen and C. A. Coulson [15]. Their appearance is due to the fact that, instead of having $q_\mu = 1$, they have the addition of the atom and bond charges equal unity.

We show in the Tab. 2 $\Pi_{1,\varrho\sigma}$ as an example of the influence of the variation of bond affinity over the most active position. The bonds among first neighbors seem to have little influence over atom 1 (Tab. 2 A); only the left-hand side of the ring to which 1 belongs, together with bond 8–9 (i.e. bonds involving a tertiary carbon) have an effect on it.

The variation in bond affinity involving second neighbors has the greatest influence over the electronic density in position 1 (Tab. 2 B). Some of these polarizabilities have quite unexpected values. The "bonds" having the biggest effect

Table 2. *Values of* $\Pi_{1,\mu\nu}$ *for naphtalene.* A: *$\mu\nu$, first neighbors*; B: *$\mu\nu$, second neighbors*; C: *$\mu\nu$, higher neighbors*

A			B			C		
μ, ν	$\Pi_{1,\mu\nu}$	$p_{\mu\nu}$	μ, ν	$\Pi_{1,\mu\nu}$	$p_{\mu\nu}$	μ, ν	$\Pi_{1,\mu\nu}$	$p_{\mu\nu}$
1,2	−0.00806	0.726	1,3	0.46937	0.036	1,4	0.29253	−0.337
2,3	−0.07649	0.584	1,10	0.25974	−0.047	1,5	−0.13649	0.050
3,4	0.00942	0.726	1,8	0.45501	−0.053	1.6	−0.24278	0.023
4,10	0.12460	0.559	2,4	−0.97374	0.036	1,7	0.08108	−0.196
5,10	−0.02634	0.559	2,9	0.76478	0.007	2,10	−0.19978	−0.228
5,6	0.01707	0.726	3,10	−0.04241	0.007	2,5	0.28500	0.023
6,7	−0.05049	0.584	4,5	−0.26217	−0.053	2,6	0.12447	0.197
7,8	0.08474	0.726	4,9	−0.59260	−0.047	2,7	−0.49920	−0.002
8,9	−0.17582	0.559	5,7	−0.13976	0.036	2,8	−0.22909	−0.196
1,9	0.17346	0.559	5,9	0.16096	−0.047	3,9	−0.08460	−0.228
9,10	−0.14430	0.505	6,8	0.05422	0.036	3,5	0.01800	−0.196
			6,10	0.00922	0.007	3,6	0.06778	−0.002
			7,9	−0.29847	0.007	3,7	0.01998	0.197
			8,10	−0.01622	−0.047	3,8	−0.11675	0.023
						4,6	−0.08272	−0.196
						4,7	0.41517	0.023
						4,8	0.13635	0.050
						5,8	−0.02124	−0.337
						6,9	0.09211	−0.228
						7,10	0.07122	−0.228

over position 1 are those belonging to the triangle 2–4–9; the least effect is provided by the triangle 6–8–10. Next in influence to the first triangle come "bonds" 1,8 and 1,3. The right-hand ring prevails generally over the left one for this position.

When we consider the "bonds" between higher order neighbors (Tab. 2 C), we see that the most influential are 2,7 and 4,7. We notice that, when these long "bonds" are formed by two shorter "bonds" they have an appreciable effect if one of these has, in turn, a sizeable value.

On comparing Tabs. A, B and C, it is enlighting to calculate the mean absolute values of $\Pi_{1,\varrho\sigma}$ and $p_{\varrho\sigma}$ for each table (Π^*, p^*):

$$\Pi^*_{\text{A}} = 0.08098\ ; \qquad p^*_{\text{A}} = 0.619$$
$$\Pi^*_{\text{B}} = 0.32133\ ; \qquad p^*_{\text{B}} = 0.030$$
$$\Pi^*_{\text{C}} = 0.16082\ ; \qquad p^*_{\text{C}} = 0.148\,.$$

We see that the greater is p^*, the less is Π^*. Surprisingly, Π^*_{C} is very closely twice Π^*_{A}, and this, in turn, is still more closely twice the value of Π^*_{B}.

Another general feature is that $\Pi_{1,2\sigma}$ has, as expected, larger values than $\Pi_{1,3\sigma}$. There is also a tendency for $\Pi_{1,9\sigma}$ to be larger than $\Pi_{1,10\sigma}$.

Finally, let us remark that not only "bonds" between non-neighboring atoms must be considered, but their variations have a greater influence over the calculated $\Pi_{\mu,\varrho\sigma}$ values than the variations in the usual bonds.

c) Bond-bond Polarizabilities

We show in Tab. 3 our mutual bond polarizabilities (m.b.p.) for bonds between neighboring atoms, in order to compare them with the results of Coulson and

Table 3. *Mutual bond polarizabilities in naphtalene, being μ and ν neighboring atoms*

μ, ν	10,9	9,1	1,2	2,3
10,9	−0.72998	0.29297	−0.19999	0.12640
9,1	0.29297	−0.82089	0.54967	−0.34515
1,2	−0.19999	0.54967	−0.62550	0.62482
2,3	0.12640	−0.34515	0.62482	−0.92607
3,4	−0.19999	0.22296	−0.36727	0.62482
4,10	0.29297	−0.25688	0.22296	−0.34515
10,5	0.29297	0.07771	−0.07216	0.14624
5,6	−0.19999	−0.07216	0.06789	−0.12987
6,7	0.12640	0.14624	−0.12987	0.15132
7,8	−0.19999	−0.18337	0.11110	−0.12987
8,9	0.29297	0.40428	−0.18337	0.14624

LONGUET-HIGGINS (Hückel approximation) [5] and those of MASLEN and COULSON [15], who also took into account overlap in applying Pauling and Wheland's approximation.

Mutual bond self-polarizabilities (m.b.s.p.) have of course the greatest absolute values. We have obtained in this case the usual alternation in sign.

For MASLEN and COULSON the introduction of overlap generally results in a lowering of the absolute values. The effect mentioned by COULSON and LONGUET-HIGGINS about the influence of one ring over the other, is stressed by the introduction of the whole overlap matrix with Kohlrausch's nuclear effective charges; this is because these charges decrease with increasing distance more slowly than Slater's [7].

It is curious that we find again $|\Pi_{23,12}| \cong |\Pi_{12,12}|$; this relation disappeared on passing from the Hückel to the Pauling and Wheland approximation.

The introduction of overlap with our approximation sets up a difference between the influence of bonds 6–7 and 7–8 over 1–2 and 2–3; this was not appreciable in the former estimations. The same thing, to a lesser extent, happens with bonds 10–5 and 5–6 over 9–1.

Table 4. $\Pi_{23,\mu\nu}$ *values for naphtalene*

$\mu - \nu$	$\Pi_{23,\mu\nu}$	$\mu - \nu$	$\Pi_{23,\mu\nu}$
1 – 2	0.62482	2 – 7	−0.08614
1 – 3	−0.07856	2 – 8	−0.26943
1 – 4	0.55675	2 – 9	0.04515
1 – 5	−0.21571	2 – 10	−0.03609
1 – 6	0.00295	5 – 6	−0.12987
1 – 7	0.29910	5 – 7	0.02565
1 – 8	0.07222	5 – 8	0.09159
1 – 9	−0.34515	5 – 9	−0.01957
1 – 10	−0.03088	5 – 10	0.14624
2 – 3	−0.92607	6 – 7	0.15132
2 – 5	0.10209	6 – 9	−0.14588
2 – 6	0.15251	6 – 10	−0.00999
		9 – 10	0.12640

Table 5. *Some "bond"-"bond" polarizability values*

$\mu\nu,\varrho\sigma$	$\Pi_{\mu\nu,\varrho\sigma}$	$\mu\nu,\varrho\sigma$	$\Pi_{\mu\nu,\varrho\sigma}$
13, 13	−1.30692	15, 26	0.60319
13, 24	0.31416	15, 28	−0.45976
13, 45	0.35009	15, 2 − 10	0.38700
13, 47	−0.49519	15, 48	0.35207
13, 49	0.62659	16, 16	−1.26048
13, 79	0.30241	17, 17	−1.13709
14, 14	−0.89404	17, 28	0.62270
14, 2 − 10	0.36118	18, 18	−1.33727
15, 15	−1.23899	1 − 10, 1 − 10	−1.05535

We see in Tab. 4 the influence of all "bonds" over one particular bond, 2–3. The variation of 1–4 has an even greater effect than that of 1–9 on 2–3. "Bonds" 1–5, 1–7 and 2–8 have lesser influence, but quite appreciable. We may also consider 2–5, 2–6 and 6–9, with 6–9 having an influence greater than 5–6 and nearly equal to 5–10.

Let us now reproduce some other m.b.p. which have absolute values greater than 0.30 (Tab. 5). Among these, the self-polarizabilities are larger than those corresponding to bonds between neighboring atoms.

3. Monocyclic Azines

a) Atom-atom Polarizabilities

Tab. 6 shows the atom-atom polarizabilities in monocyclic azines. We see that in each molecule self-polarizabilities (s.p.) of the nitrogen atoms, except for *s*-triazine, have greater absolute values than those of the carbon atoms. If we draw a graph for $-\sum \Pi_{\mu\mu}$ as a function of the number of neighboring nitrogen atoms (n)-taking the sequence benzene, pyridine, pyridazine, *v*-triazine, *v*-tetrazine and pentazine – we obtain a straight line (Fig. 3). *V*-triazine falls out of this line, whose equation is:

$$-\sum \Pi_{\mu\mu} = 0.29\,n + 7.17\,.$$

It is known that in AH there exists a close correlation between self-polarizabilities and free valence (F). For azines [8]:

$$\text{pyridine}\left\{\begin{array}{l}\Pi_{22} > \Pi_{44} > \Pi_{33}\\ F_2 > F_4 > F_3\end{array}\right. \qquad v\text{-triazine}\left\{\begin{array}{l}\Pi_{33} > \Pi_{44}\\ F_3 > F_4\end{array}\right.$$

$$\text{pyridazine}\left\{\begin{array}{l}\Pi_{22} > \Pi_{33}\\ F_3 > F_2\end{array}\right. \qquad as\text{-triazine}\left\{\begin{array}{l}\Pi_{66} > \Pi_{22} > \Pi_{33}\\ F_2 > F_6 > F_3\end{array}\right.$$

$$\text{pyrimidine}\left\{\begin{array}{l}\Pi_{11} > \Pi_{33} > \Pi_{44}\\ F_2 > F_3 > F_4\end{array}\right.$$

The correlation is broken only for pyridazine and for positions 2 and 6 in *as*-triazine. However, this inversion takes place for very similar values: in pyridazine both Π and F values are very close to one another; and this is also true for *as*-triazine.

Table 6. *Atom-atom polarizabilities in monocyclic azines*

molecule	atom	$\Pi_{\mu,\mu}$	$\Pi_{\mu,\mu+1}$	$\Pi_{\mu,\mu+2}$	$\Pi_{\mu,\mu+3}$	$\Pi_{\mu,\mu+4}$	$\Pi_{\mu,\mu+5}$
 pyridine	1	−1.39846	0.47773	−0.03341	0.50982		
	2	−1.25470	0.49722	−0.05093	0.29503	0.03566	
	3	−1.14175	0.42035	−0.03743			
	4	−1.24866					
 pyridazine	1	−1.49251	0.52876	−0.05648	0.44390	0.03787	0.53846
	2	−1.18569	0.44832	−0.05108	0.22182		
	3	−1.18104	0.39638				
 pyrimidine	1	−1.30888	0.52455	0.00253	0.25488		
	2	−1.34398	0.45756	−0.04118	0.43919	−0.03615	
	3	−1.28859	0.45122	−0.06180			
	4	−1.07508					
 pyrazine	1	−1.46857	0.43183	−0.05761	0.71999		
	2	−1.17431	0.53742		0.25268	0.00999	
 *v*-triazine	1	−1.38006	0.50127	0.00699	0.36353		
	2	−1.35693	0.49404	−0.04816	0.35686	0.05293	
	3	−1.22662	0.42372	−0.05499			
	4	−1.11465					
 *s*-triazine	1	−1.35726	0.49899	−0.01790	0.39501		
	2	−1.29986		−0.04660			
 *as*-triazine	1	−1.41667	0.42713	−0.05617	0.64839	−0.06703	0.46435
	2	−1.21506	0.48574	−0.07132	0.38815	−0.01464	
	3	−1.11138	0.47496	0.00870	0.19814		
	4	−1.55775	0.50882	−0.00310			
	5	−1.42043	0.58178				
	6	−1.22653					
 *v*-tetrazine	1	−1.47910	0.54999	−0.01373	0.31731	0.00592	0.61961
	2	−1.47853	0.45084	−0.06066	0.53243		
	3	−1.14624	0.45249				
 *s*-tetrazine	1	−1.48218	0.51609	−0.08542	0.58090	−0.02107	0.49168
	2	−1.15189			0.16185		
 *as*-tetrazine	1	−1.66397	0.55518	−0.02037	0.59434		
	2	−1.36656	0.54614	−0.06684	0.32072	0.01136	
	3	−1.26640	0.44790	−0.02799			
	4	−1.35648					
 pentazine	1	−1.18862	0.49290	−0.03245	0.26772		
	2	−1.42269	0.52572	−0.02044	0.50140	−0.07690	
	3	−1.58179	0.60919	−0.02207			
	4	−1.44523					

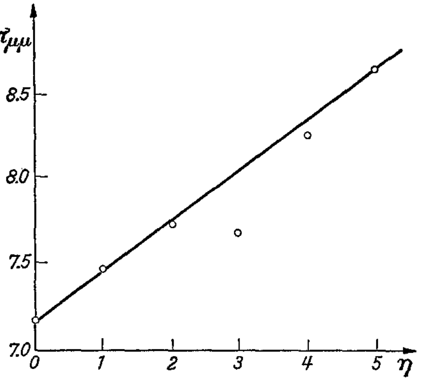


Fig. 3

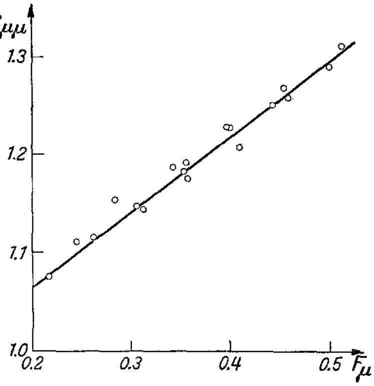


Fig. 4

Fig. 3. Sum of all the atom-atom self-polarizabilities in a molecule, as a function of the neighboring nitrogen atoms (read $\Pi_{\mu\mu}$ instead of $\pi_{\mu\mu}$)

Fig. 4. Self-polarizability as a function of free valence for the carbon atoms of monocyclic azines (read $\Pi_{\mu\mu}$ instead of $\pi_{\mu\mu}$)

The approximately linear correlation between F_μ and $\Pi_{\mu\mu}$ found for hydrocarbons [17], appears also clearly for the carbon atoms in monocyclic azines (Fig. 4), which have:

$$-\Pi_{\mu\mu} = 0.743\ F_\mu + 0.917\ .$$

However, this correlation is not found for the N atoms; in this case the dispersion of the points around a straight line is too great.

Recently, CARBÓ [1] has calculated with a SCHMO method the self-polarizability values for pyridine and diazines (in $1/\beta$ units):

pyridine: $\Pi_{11} = 0.325$; $\Pi_{22} = 0.480$; $\Pi_{33} = 0.522$; $\Pi_{44} = 0.502$
pyridazine: $\Pi_{11} = 0.339$; $\Pi_{22} = 0.460$; $\Pi_{33} = 0.508$
pyrimidine: $\Pi_{11} = 0.387$; $\Pi_{22} = 0.324$; $\Pi_{33} = 0.444$; $\Pi_{44} = 0.529$
pyrazine: $\Pi_{11} = 0.328$; $\Pi_{22} = 0.482$.

We see that his sequence is, for each molecule, exactly opposite to ours; nitrogen, for instance, has the lowest self-polarizability values.

All $\Pi_{\mu,\mu+3}$ values in Tab. 6 are large. It is possible to establish a sequence for $\Pi_{\mu,\mu+3}$, which depends on the kind of atoms they involve:

$$\Pi_{\mathrm{NN}} > \Pi_{\mathrm{CN}} > \Pi_{\mathrm{CC}}\ .$$

Some of these values are even greater than those corresponding to neighboring atoms. For instance, in pyridine, pyrazine, *as*-triazine and *as*-tetrazine, $\Pi_{14} > \Pi_{12}$; in *v*-tetrazine, $\Pi_{25} > \Pi_{23}$; and in *sim*-tetrazine $\Pi_{14} > \Pi_{16}$.

If in the pyridine nucleus another nitrogen is introduced in position 3, the corresponding variation in its charge affinity shall cause a bigger change in position 2 than in position 4 ($\Pi_{23} > \Pi_{34}$). The Δq of the corresponding positions of pyrimidine (1 and 3) with respect to those of pyridine (2 and 4) are consistent with what precedes; the values of Δq are: $\Delta q_1 = 0.066$ and $\Delta q_3 = 0.057$ [8] (the numbering refers to pyrimidine).

The values of pyrimidine's self-polarizabilities can be applied to the qualitative prediction of nitrogen charges in triazines. Introducing into pyrimidine a third nitrogen atom at positions 1, 3 or 4, we shall obtain respectively *v*-triazine, *as*-triazine and *s*-triazine. Paying attention to the corresponding numbering, we have respectively $\Delta q = 0.207$, 0.201 or 0.185, according to the sequence $|\Pi_{11}| > |\Pi_{33}| > |\Pi_{44}|$.

Similarly, *as*-triazine gives *v*-tetrazine, *s*-tetrazine or *as*-tetrazine, depending on whether the fourth nitrogen enters at position 6, 2 or 3; it is verified that $|\Pi_{66}| > |\Pi_{22}| > |\Pi_{33}|$, and accordingly $\Delta q = 0.202$, 0.189 or 0.187.

The experimental difficulty encountered in the halogenation of pyridine is well known. However, the introduction of an amino group facilitates this process; for example, 2-amino-pyridine halogenates in positions 3 and 5 [6]. This is in agreement with our appreciable values of the polarizabilities involving 2, i.e. Π_{32} and Π_{52}.

In the same way, 1-amino-pyrimidine or 1-3-diamino-pyrimidine halogenates in position 4 [6], the only one predicted by the $\Pi_{\mu\nu}$ values.

In Figs. 5 A and B basic strength (pK_a) values of some methyl pyridines and pyrimidines are shown as functions of $-\sum \Pi_{\mu\mu}$ of the corresponding azine, this sum being taken over the positions where a methyl radical has entered. Fig. 5 A shows this for pyrimidine, and Fig. 5 B for pyridine. Obviously, mono-, di-, and tri-methyl derivatives are quite separate. It is possible to draw three parallel straight lines corresponding to each group. If we assume that the slope is the same for both pyrimidine and pyridine, this would permit, knowing the pK_a value of an azine methyl derivative, to determine roughly the pK_a of another derivative of the same group, with the aid of Tab. 6. We may furthermore predict that, for example, 2–5 and 2–6 dimethyl pyrazine have the same pK_a, supported by the fact that 2–3 and 2–5 dimethylpyridine have practically equal values; both these cases exhibit the equality of the corresponding $-\sum \Pi_{\mu\mu}$.

The linear correlation between σ_μ (the substitution constant of Hammett's equation) and $\Pi_{\mu\mu}$ for AH [20] is well known. Not having enough experimental data available for σ_μ, we shall not correlate σ_μ for carbon positions in azines with our $\Pi_{\mu\mu}$. Even for pyridine, where several groups of σ_μ values exist, difficulties in their determination have been pointed out [14, 19]. We expect to consider this problem in the future.

b) Comparison with Golebiewski's Formulae

A. GOLEBIEWSKI [9] gives simple empirical formulae to calculate $\Pi_{\mu\nu}$ knowing $p_{\mu\nu}$. His treatment lies on Hückel's approximation, and is succesfully applied to hydrocarbons. He proposes that

$$\Pi_{\mu\nu} = A_1[\exp(A_2\, p_{\mu\nu}^2) + A_3]$$

where A_1, A_2 and A_3 depend on whether the carbons considered are secondary or tertiary, on the number of bonds separing the atoms and on the range of $p_{\mu\nu}^2$.

We have tried to extend this formula to azines, where of course the A's shall depend also on the kind of atoms involved and their values will be different even for the pair CC. The following A's are those which best fitted the $\Pi_{\mu\nu}$ numerical values:

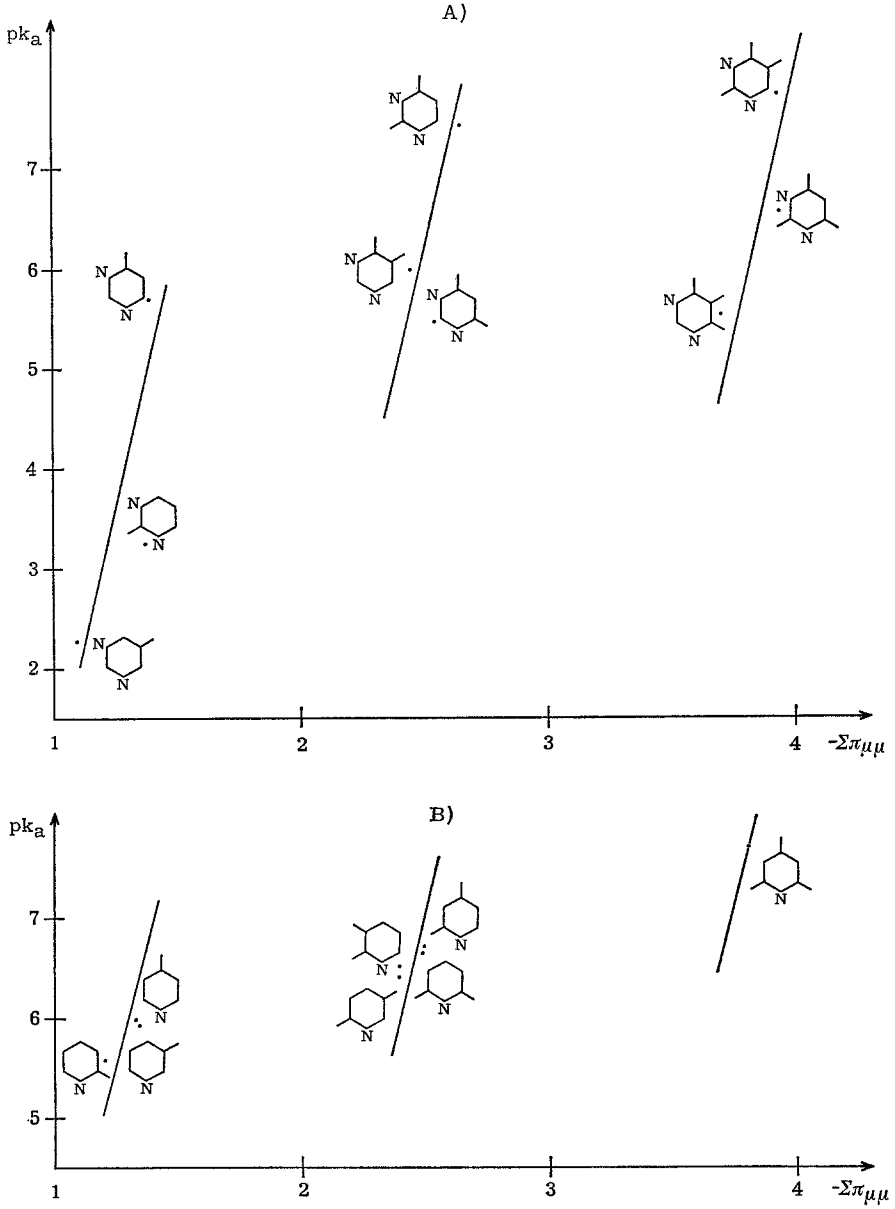


Fig. 5. Basic strength (pK_a) values of methyl pyridines (5 B) and methyl pyrimidines (5 A) as a function of $-\Sigma\,\Pi_{\mu\mu}$ of the corresponding azine. The sum is taken over the positions where a methyl radical has entered. (Data for A quoted from [2] and for B from [16]. Read $\Pi_{\mu\mu}$ instead of $\pi_{\mu\mu}$, and pK_a instead of pk_a)

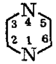
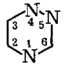
For first neighbors:

$$A_1 = 0.1976;\ A_3 = 0.054$$
$$A_2 = 1.74\ (\mathrm{CC});\ 2.1\ (\mathrm{CN});\ 2.5\ (\mathrm{NN})\,.$$

For third neighbors:

$$A_1 = 0.1628;\ A_3 = -0.0899$$
$$A_2 = 7.27\ (\mathrm{CC});\ 7.4\ (\mathrm{CN});\ 7.8\ (\mathrm{NN})\,.$$

Table 7. *$\Pi_{\mu\nu}$ between first and third neighbors, calculated with Golebiewski formulae (1) and with Chirgwin and Coulson's (2)*

molecule	First neighbors									Third neighbors								
	C–C			C–N			N–N			C–C			C–N			N–N		
	$\Pi_{\mu\nu}$	(1)	(2)	$\Pi_{\mu\nu}$	(1)	(2)	$\Pi_{\mu\nu}$	(1)	(2)	$\Pi_{\mu\nu}$	(1)	(2)	$\Pi_{\mu\nu}$	(1)	(2)	$\Pi_{\mu\nu}$	(1)	(2)
	Π_{23} Π_{34}	0.474 0.421	0.497 0.420	Π_{12}	0.478	0.478				Π_{25}	0.295	0.295	Π_{14}	0.525	0.506			
	Π_{23} Π_{34}	0.448 0.405	0.448 0.396	Π_{12}	0.538	0.529	Π_{16}	0.518	0.538	Π_{25}	0.240	0.222	Π_{14}	0.428	0.444			
	Π_{34}	0.452	0.451	Π_{12} Π_{23}	0.527 0.464	0.524 0.457				Π_{14}	0.261	0.255	Π_{25}	0.425	0.439			
	Π_{23}	0.515	0.537	Π_{12}	0.452	0.432				Π_{25}	0.258	0.253				Π_{14}	0.875	0.720
	Π_{34}	0.435	0.424	Π_{23}	0.508	0.494	Π_{12}	0.602	0.501				Π_{14} Π_{25}	0.357 0.340	0.363 0.324			
				Π_{12}	0.504	0.499							Π_{14}	0.344	0.395			
	Π_{23}	0.482	0.486	Π_{12} Π_{34} Π_{56} Π_{16}	0.424 0.504 0.594 0.488	0.427 0.475 0.582 0.466	Π_{45}	0.500	0.509	Π_{36}	0.218	0.198	Π_{25}	0.362	0.381	Π_{14}	0.710	0.648
	Π_{34}	0.466	0.452	Π_{23}	0.457	0.451	Π_{12} Π_{16}	0.574 0.672	0.550 0.620				Π_{14}	0.297	0.317	Π_{25}	0.525	0.532
				Π_{12}	0.526	0.516	Π_{16}	0.485	0.492	Π_{25}	0.194	0.162				Π_{14}	0.578	0.581
				Π_{23} Π_{34}	0.529 0.472	0.546 0.448	Π_{12}	0.563	0.555				Π_{25}	0.297	0.321	Π_{14}	0.597	0.594
				Π_{12}	0.527	0.493	Π_{23} Π_{34}	0.526 0.645	0.526 0.609				Π_{14}	0.264	0.268	Π_{25}	0.465	0.501

We have used the bond orders previously calculated [7, 8]. The results are shown on Tab. 7. Between first neighbors, the correlation obtained is satisfactory, particularly for C–C and C–N bonds, where the errors do not exceed 5%; for N–N bonds the errors do nat exceed 10%. For third neighbors, the errors are generally less than 10% for C–C and C–N, but the N–N bonds are more difficult to fit.

As for the second neighbors, GOLEBIEWSKI could not extrapolate formulae valid for them, because he had bond orders equal to zero. Even though we have bond orders different from zero, it is apparent, looking both at the errors just obtained and at the small values of these polarizabilities, that we will not be able to fit the parameters in formulae of this kind.

We conclude that the variation of $\Pi_{\mu\nu}$ as $\exp(Ap^2_{\mu\nu})$ may be extended to monocyclic azines in bonds between first and third neighbors.

c) *Atom-bond Polarizabilities*

The $\Pi_{1,\mu\nu}$ values for pyridine and pyrimidine (Tab. 8), are examples of the influence of the bond affinities in a molecule over a carbon atom and over a nitrogen atom. To show a complete table, we have reported in Tab. 9 all the $\Pi_{\mu,\varrho\sigma}$ values for *sim*-tetrazine.

Table 8. *Atom-bond polarizabilities* $\Pi_{1,\mu\nu}$ *in pyridine* (A) *and pyrimidine* (B)

		μ	ν				
			2	3	4	5	6
A		1	0.44900	0.39875	0.03278		
		2		−0.15086	−1.00518	−0.15086	0.95547
		3			0.08281	−0.06682	
B		1	−0.13044	0.37661	0.35464		
		2		−0.26496	−0.73906	−0.26496	1.04898
		3			0.15613	0.00503	

Table 9. *Atom-bond polarizabilities* $\Pi_{\varrho,\mu\nu}$ *for s-tetrazine*

ϱ		μ	ν				
			2	3	4	5	6
1		1	0.25147	0.58400	0.18527	0.35183	0.23665
		2		−0.01131	−1.07258	−0.16745	1.00591
		3			−0.06920	−0.10153	−0.01783
		4				0.13124	−1.07902
		5					−0.17751
2		1	−0.27034	1.03217	−0.16745	−0.55884	−0.16745
		2		−0.27034	0.37521	0.33489	0.37521
		3			−0.16745	−0.55884	−0.16745
		4				0.07644	−0.04213
		5					0.07644

If we look at the values that measure the influence of an effective bond (between neighboring atoms) on the charge of an atom at the end of the bond, we notice that:

$$\Pi_{\mathrm{C,CC}} < 0; \quad \Pi_{\mathrm{C,CN}} < 0; \quad \Pi_{\mathrm{N,NC}} > 0; \quad \Pi_{\mathrm{N,NN}} > 0 .$$

This is common to all monocyclic azines, i.e. it is also verified for the values not reported in these tables. A C–N bond affinity thus modifies in one sense the charge at one end of the bond, and in the opposite sense the charge at the other end. These variations differ not only in sign. In sim-tetrazine, $\Pi_{1,12} = 0.25147$ and $\Pi_{2,12} = -0.27034$. However, in pyrimidine $\Pi_{2,23} = 0.31961$ and $\Pi_{3,23} = -0.01979$; and in *v*-triazine $\Pi_{2,23} = 0.17190$ and $\Pi_{3,23} = -0.07465$.

The equality of the coefficients [see formulae (2)] causes some physically unexpected identities. In pyridine and pyrimidine $\Pi_{1,23} = \Pi_{1,25}$. In sim-tetrazine, $\Pi_{2,14} = \Pi_{2,16}$.

Some particular values exceed the others considerably. In pyridine and pyrimidine, they are the values of $\Pi_{1,24}$ and $\Pi_{1,26}$. It is surprising that this occurs in both molecules, since for one of them the influence is exerted on a nitrogen atom, and for the other on a carbon atom, and the "bonds" concerned are also quite different in nature. As for sim-tetrazine, these large values are $\Pi_{1,24}$; $\Pi_{1,26}$; $\Pi_{1,46}$ and $\Pi_{2,13}$.

All these considerations apply, by definition, on discussing bond-atom polarizabilities, that is, the influence of charge affinity over bond order. Because these values are quite far from negligible, we may repeat that, as for naphtalene, it would not be valid to take for the distances in one of these molecules those determined for a derivative.

d) Bond-bond Polarizabilities

Tab. 10 shows the mutual bond self-polarizabilities (m.b.s.p.). The m.b.s.p. seem to have smaller absolute values among neighboring atoms than for the other "bonds", particularly for $(\mu, \mu + 2)$ and $(\mu, \mu + 4)$. That is, $p_{\mu,\mu+2}$ and $p_{\mu,\mu+4}$ are the most sensitive to changes in the bond affinities; the higher is the order of a "bond", the lower is its self-polarizability. This has been noticed for the case of styrene and polyenes [5], and we have verified it for naphtalene (Section 2-c).

Looking then for a simple quantitative relationship, we verified that $\Pi_{\mu\nu,\mu\nu}$ behaves roughly as $1/\sqrt{|p|}$, within errors that generally do not exceed 10%. GOLEBIEWSKI [10] has proposed an empirical relationship, with $\Pi_{\mu\nu,\varrho\sigma}$ proportional to *ShQ* or to Q, Q being a combination of products $p_{\mu\nu}\, p_{\varrho\sigma}$.

It is interesting to look at values of $\Pi_{\mu\nu,\varrho\sigma}$ for cases other than the m.b.s.p. We have reported for three molecules the most expressive values (see Tab. 11), the observed features being common to all the monocyclic azines. The highest values correspond to $\Pi_{13,46}$ and $\Pi_{35,26}$, that is the mutual influence of two parallel "bonds" between second neighboring atoms. In particular, the two parallel "bonds" may coincide, leading to what we have just pointed out for the m.b.s.p.

The influence of an effective bond over another effective bond at a distance of two bonds gives a negative $\Pi_{\mu\nu,\varrho\sigma}$ value, which means that in this case an increase in the $\varrho\sigma$ bond affinity will decrease the $\mu\nu$ bond order.

Table 10. *Mutual bond self-polarizabilities in monocyclic azines*

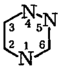
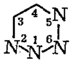
molecule	atom	$\Pi_{\mu,\mu+1;\mu,\mu+1}$	$\Pi_{\mu,\mu+2;\mu,\mu+2}$	$\Pi_{\mu,\mu+3;\mu,\mu+3}$	$\Pi_{\mu,\mu+4;\mu,\mu+4}$	$\Pi_{\mu,\mu+5;\mu,\mu+5}$
 pyridine	1	−0.87349	−1.32965	−0.82840		
	2	−0.69925	−1.30280	−0.90071	−1.21904	
	3	−0.77346	−1.17918			
 pyridazine	1	−0.81221	−1.39954	−0.88290	−1.32685	−0.95405
	2	−0.73980	−1.23566	−0.96387		
	3	−0.78466				
 pyrimidine	1	−0.83971	−1.29736	−0.92537		
	2	−0.87251	−1.27048	−0.90292	−1.38001	
	3	−0.72228	−1.35045			
 pyrazine	1	−0.90801	−1.41591	−0.74857		
	2	−0.63695		−0.92163	−1.16436	
 *v*-triazine	1	−0.86924	−1.30478	−0.85657		
	2	−0.79213	−1.28072	−0.94037	−1.30401	
	3	−0.74546	−1.28161			
 *s*-triazine	1	−0.84906	−1.37516	−0.96516		
	2		−1.34646			
 *as*-triazine	1	−0.90021	−1.35478	−0.83543	−1.48515	−0.90198
	2	−0.67770	−1.47633	−0.93691	−1.23782	
	3	−0.85339	−1.27529	−0.96778		
	4	−0.97934	−1.43748			
	5	−0.76174				
 *v*-tetrazine	1	−0.93432	−1.32342	−0.97863	−1.47541	−0.85949
	2	−0.85257	−1.38590	−0.94609		
	3	−0.69375				
 *s*-tetrazine	1	−0.82287	−1.56760	−0.90128	−1.37571	−0.99050
	2			−0.99004		
 *as*-tetrazine	1	−0.94956	−1.50312	−0.89940		
	2	−0.77698	−1.42821	−1.01623	−1.35520	
	3	−0.88929	−1.29439			
 pentazine	1	−0.82152	−1.42834	−1.05066		
	2	−0.97369	−1.45673	−0.99630	−1.49959	
	3	−0.90609	−1.60386			

Table 11. *The most expressive $\Pi_{\mu\nu,\varrho\sigma}$ values (other than* m.b.s.p.*), for pyridine, pyrimidine and pyridazine*

			
$\mu\nu$, $\varrho\sigma$	$\Pi_{\mu\nu,\varrho\sigma}$	$\Pi_{\mu\nu,\varrho\sigma}$	$\Pi_{\mu\nu,\varrho\sigma}$
12, 16	0.59851	0.77941	0.66403
12, 23	0.69751	0.64107	0.71106
12, 34	−0.53695	−0.36503	−0.48674
12, 36	0.48403	0.48797	0.45840
12, 56	−0.38675	−0.50644	−0.31497
13, 46	0.84503	0.82956	0.91592
14, 23	0.40588	0.45959	0.41015
14, 25	0.40588	0.45959	0.45508
23, 16			−0.50899
23, 34	0.64917	0.65874	0.61713
23, 45	−0.38852	−0.48174	−0.33733
25, 16			0.56663
25, 36	0.48035	0.41553	
34, 25	0.41441	0.40198	0.39724
34, 45	0.61158	0.64373	
35, 26	0.79224	0.89668	0.80911

4. Conclusion

In an alternant hydrocarbon, the alternation in sign of the atom-atom polarizability generally found on passing from atoms belonging to the same set to atoms belonging to different sets, depends on the approximation used. That is, it is not a general property of alternant hydrocarbons.

For naphtalene, the atom-bond polarizabilities are not at all negligible; this is consistent with the non-uniform charge distribution previously obtained.

The linear correlation between self-polarizabilities and free valence, which is known for hydrocarbons, is extended to the carbon atoms in azines. The empirical expression proposed by GOLEBIEWSKI for $\Pi_{\mu\nu}$ as a function of $p_{\mu\nu}$ in hydrocarbons is also extended to first and third neighbors in azines.

The Π values permit qualitative considerations concerning certain experimental properties of azines.

It is found that the part played by variations in bond affinities corresponding to formal bonds is highly stressed.

The authors gratefully acknowledge the helpful discussions with Dr. J. BRIEUX and Lic. H. C. GONZÁLEZ, who has besides collaborated in part of the calculations.

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