Theoret. chim. Acta (Berl.) 7, 342—351 (1967)

# Sigma-Polarization in 5-Membered Heterocyclic Ring Systems*

WALDEMAR ADAM and ALEC GRIMISON**

Department of Chemistry and Puerto Rico Nuclear Center, University of Puerto Rico,
Rio Piedras, P. R. 00931

Received November 28, 1966

Extended Hückel calculations on the 5-membered heterocyclic molecules furan, pyrrole, imidazole, pyrazole, 1,2,3-triazole, and the four possible oxadiazoles suggest a significant polarization of the $\sigma$-framework. This $\sigma$-polarization appears to follow simple electronegativity considerations. The calculated $\pi$-polarizations are independent of, and may be opposed to, the corresponding $\sigma$-polarizations. For furan and pyrrole the above results reproduce the different direction of the experimental dipole moments of these two molecules. A good correlation is observed between the total ($\sigma + \pi$) calculated electron densities and the experimental proton and carbon-13 chemical shifts in all of the systems studied.

Rechnungen mit der erweiterten Hückel-Methode über die Fünferheterozyklen Furan, Pyrrol, Imidazol, Pyrazol, 1,2,3-Triazol und die vier möglichen Oxadiazole lassen eine beträchtliche Polarisation des $\sigma$-Gerüsts vermuten. Die $\sigma$-Polarisation scheint einfachen Elektronegativitätsbetrachtungen zu folgen. Die $\pi$-Polarisation ist unabhängig von der entsprechenden $\sigma$-Polarisation und kann entgegengesetzt gerichtet sein. Für Furan und Pyrrol reproduzieren die oben genannten Ergebnisse die verschiedenen Richtungen der experimentellen Dipolmomente beider Moleküle. Eine gute Korrelation wird zwischen der gesamten ($\sigma + \pi$)-Elektronendichte und der experimentellen chemischen Verschiebung für Protonen und $C^{13}$ in allen Systemen beobachtet.

Des calculs par la méthode de Hückel étendue portant sur les molécules à cycle pentagonaux: furane, pyrrole, imidazole, 1,2,3 triazole et les quatre oxadiazoles, suggèrent l'existence d'une polarisation significative du squelette $\sigma$. Cette polarisation $\sigma$ apparaît en accord avec de simples considérations d'électronégativité. Les polarisations $\pi$ calculées sont indépendantes des polarisations $\sigma$ correspondantes et peuvent leur être contraires. Pour le furane et le pyrrole les résultats ci-dessus reproduisent les directions différentes des moments dipolaires expérie mentaux des deux molécules. On observe une bonne corrélation entre les densités totales ($\sigma + \pi$) calculées et les déplacements chimiques expérimentaux du proton et du carbone 13 dans tous les systèmes étudiés.

The great majority of previous calculations on 5-membered heterocyclic ring compounds have been made in the $\pi$-electron approximation. Most of these calculations were of the Hückel Molecular Orbital (HMO) type [*1*], and only a few molecules, i.e., pyrrole [*2—4*], thiophene [*4, 8*], imidazole [*9*], and oxazole [*10*]

---

* This work was supported by a grant from the University of Puerto Rico. It was presented at the Fourth Caribbean Chemical Symposium, January 3—7, 1967, Kingston, Jamaica.

** The Puerto Rico Nuclear Center is operated by the University of Puerto Rico through a contract with the U. S. Atomic Energy Commission.

have been examined by various approximate self-consistent field methods. The difficulty of applying the $\pi$-electron approximation to overall molecular properties in heterocyclic molecules is well recognized [*11*]. While the use of a neutral $\sigma$-core gives excellent results for homonuclear systems [*12*], in heterocyclic molecules it is necessary to account for the polarization of the $\sigma$-framework caused by the heteroatom(s). In the HMO theory, for example, the electronegativity effect of the heteroatom is introduced by adjusting the Coulomb integral of the heteroatom, $\alpha_x$. This is generally done by using the expression $\alpha_x = \alpha_0 + h_x\beta_0$, where $\alpha_0$ and $\beta_0$ are the Coulomb integral for a neutral carbon atom, and the exchange integral for a carbon-carbon double bond, respectively, and $h_x$ is an arbitrary parameter related to the electronegativity of the atom in question [*13*].

Different values of the parameter $h_x$ must be chosen for a "pyrrole-type" nitrogen and a "pyridine-type" nitrogen in order to account adequately for the difference between the $\sigma$-bond environment of the nitrogen atom in each situation [*14*]. Similarly in approximate SCF calculations, it is necessary to choose different Coulomb repulsion parameters for a "pyrroletype" and a "pyridine-type" nitrogen, since the valence state of the nitrogen atom depends on the $\sigma$-framework in question [*15*]. Such parametrization can be carried out with a greater or lesser degree of arbitrary choice, and is capable of giving excellent accord with certain molecular properties depending specifically on the $\pi$-electrons, such as the energy of $\pi$-electron excitations [*16*]. However, the application of such methods to overall molecular properties is more suspect, and actually precludes obtaining information about the $\sigma$-bond polarization from the calculation.

Previous publications have described the application of the Extended Hückel Theory (EHT), in the form developed by HOFFMANN [*17*] to specific heterocyclic molecules or groups of molecules [*18—20*]. This method uses an extended basis set including all valence electrons, and can give information on $\sigma$-electron, as well as $\pi$-electron, effects. The results obtained from EHT calculations on pyridine, quinoline, and isoquinoline [*18*], and on imidazole [*20*], suggested (i) that a considerable polarization of the $\sigma$-framework occurs, and (ii) that such a polarization may be opposite in direction to that of the $\pi$-framework, and greater, so that the $\sigma$-polarization can predominate in the overall molecular polarization. This important suggestion of independent, or even opposed, $\sigma$- and $\pi$-polarizations has been discussed previously by CLEMENTI [*21*], PETERS [*22*], and POPLE [*23*].

The main purpose of the work reported here was to investigate the generality of the phenomenon of independent $\sigma$- and $\pi$-polarizations for a wide range of nitrogen and oxygen five-membered heterocyclic ring systems, using the Extended Hückel Theory. The molecules specifically considered were furan, pyrrole, pyrazole, imidazole, oxazole, isoxazole, the triazoles, and the oxadiazoles. Except for pyrrole [*24*] and imidazole [*20*], no all-valence-electron calculations appear to have been reported on these molecules.

## Details of the Calculation

The Extended Hückel Theory, an LCAO MO method developed by HOFFMANN [*17*], simultaneously calculates $\sigma$- and $\pi$-electron distributions. In this method, the basis set for the linear combination of atomic orbitals $\psi_i = \sum_r c_{ir}\,\phi_i$

is extended to include all valence shell atomic orbitals. Thus, in the case of furan, the 1*s* Slater orbitals for hydrogen, and the 2*s* and three 2*p* Slater orbitals for carbon and oxygen, are used. Minimization of the total energy, in the Hückel approximation of the total Hamiltonian as a sum of one-electron effective Hamiltonians, gives the secular determinant

$$\det [H_{ij} - E\, S_{ij}] = 0$$

where $i$, $j$ go from 1 to $n$, i.e., through the total number of valence atomic orbitals. All overlap integrals $S_{ij}$ are retained, and are calculated from standard sources [*25*]. The exchange integrals $H_{ij}$ are computed using the approximation

$$H_{ij} = 0.5\,\mathrm{K}\,(H_{ii} + H_{jj})\,S_{ij}, \text{ where } K = 1.75\,.$$

The Coulomb integrals $H_{ii}$ are taken as the valence state ionization potentials. A Mulliken Population Analysis [*26*] finally yields the $\sigma$- and $\pi$-electron densities. A program for carrying out these calculations on the IBM 7094 computer has been described [*27a*], and is available [*27b*].

The geometries of the 5-membered rings were approximated as regular pentagons. All ring bond lengths were taken as 1.40 Å, and all carbon-hydrogen and nitrogen-hydrogen bond lengths as 1.10 Å. The valence state ionization potentials were taken as H(1*s*): −13.6 eV, C(2*s*): −21.4 eV, C(2*p*): −11.4 eV, N(2*s*): −26.0 eV, N(2*p*): −13.4 eV, O(2*s*): −32.30 eV, and O(2*p*): −14.80 eV. The Slater orbital exponents were H: 1.00, C: 1.625, N: 1.950, and O: 2.275.

## Results and Discussion

The net $\sigma$-, $\pi$-, and ($\sigma + \pi$)-charges are summarized in Tab. 1. The values of the $\sigma$-charges are exceedingly important in that they suggest a pronounced polarization of the $\sigma$-bond framework. In all cases studied, the $\sigma$-charges are larger than the corresponding $\pi$-charges. If attention is focussed on the formal $\sigma$-charges on the heteroatoms, it can be seen that they exclusively follow the sequence of electronegativities, i.e., $\mathrm{O} > \mathrm{N} > \mathrm{C}$. For example, the $\sigma$-charges in the isoelectronic series furan, pyrrole, and cyclopentadienyl anion [*17*], are −0.94, −0.77, and −0.10 electrons for the oxygen, nitrogen, and carbon atoms, respectively. When more than one heteroatom is present in the ring, as in pyrazole, imidazole, oxazole, isoxazole, the triazoles, and the oxadiazoles, the most electronegative atom still bears the greatest negative $\sigma$-charge, but the degree of charge localization also depends on the electronegativity of the neighboring atoms. In Tab. 2 the averaged $\sigma$-charges on oxygen, nitrogen, and carbon are arranged according to their neighboring atoms. The surprising constancy of these charges may be due to the use of identical, ideal geometries for all molecules. This simplifies discussion of these results, since only the immediate neighbors have to be considered. For example, three arrangements are possible for the oxygen atom: C–O–C in furan, oxazole, and 3,4-oxadiazole, N–O–C in isoxazole, 2,3- and 2,4-oxadiazole, and N–O–N in 2,5-oxadiazole. The averaged formal $\sigma$-charges are −0.92, −0.68, and −0.42 electrons, respectively. This indicates that the oxygen atom localizes electronic charge most effectively when flanked by two carbon atoms, and that the polarity of the $\sigma$-bonds decreases in the order C–O–C, C–O–N, and N–O–N. For nitrogen it is necessary to distinguish between the "pyrrole-type" nitrogen, and

Table 1. *Calculated* EHT *Net Charges*

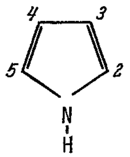
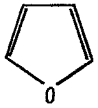
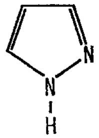
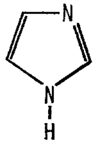
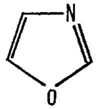
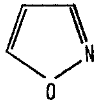
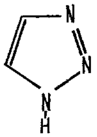
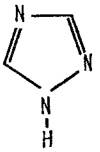
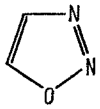
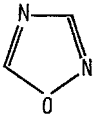
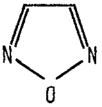
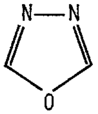
| Molecule | Position | $\varrho_\sigma$ | $\varrho_\pi$ | $\varrho_{\sigma+\pi}$ | $\varrho_H$ |
|---|---|---|---|---|---|
|  | 1 | −0.77 | +0.36 | −0.41 | +0.304 |
| | 2,5 | +0.15 | −0.05 | +0.10 | +0.095 |
| | 3,4 | −0.04 | −0.14 | −0.18 | +0.029 |
|  | 1 | −0.94 | +0.18 | −0.76 | — |
| | 2,5 | +0.36 | −0.02 | +0.34 | +0.105 |
| | 3,4 | −0.10 | −0.07 | −0.17 | +0.106 |
|  | 1 | −0.49 | +0.43 | −0.06 | +0.292 |
| | 2 | −0.28 | −0.54 | −0.82 | — |
| | 3 | +0.15 | +0.11 | +0.26 | +0.112 |
| | 4 | −0.12 | −0.11 | −0.23 | +0.110 |
| | 5 | +0.11 | +0.10 | +0.21 | +0.112 |
|  | 1 | −0.74 | +0.48 | −0.26 | +0.293 |
| | 2 | +0.36 | +0.15 | +0.51 | +0.110 |
| | 3 | −0.50 | −0.52 | −1.02 | — |
| | 4 | +0.14 | −0.06 | +0.08 | +0.111 |
| | 5 | +0.11 | −0.06 | +0.05 | +0.111 |
|  | 1 | −0.91 | +0.23 | −0.68 | — |
| | 2 | +0.57 | +0.33 | +0.90 | +0.124 |
| | 3 | −0.49 | −0.50 | −0.99 | — |
| | 4 | +0.14 | −0.03 | +0.11 | +0.115 |
| | 5 | +0.33 | −0.04 | +0.29 | +0.122 |
|  | 1 | −0.68 | +0.19 | −0.49 | — |
| | 2 | −0.04 | −0.56 | −0.60 | — |
| | 3 | +0.15 | +0.25 | +0.40 | +0.114 |
| | 4 | −0.12 | −0.07 | −0.19 | +0.114 |
| | 5 | +0.34 | +0.19 | +0.53 | +0.122 |
|  | 1 | −0.49 | +0.61 | +0.12 | +0.295 |
| | 2 | −0.04 | −0.39 | −0.43 | — |
| | 3 | −0.24 | −0.39 | −0.63 | — |
| | 4 | +0.10 | +0.09 | +0.19 | +0.115 |
| | 5 | +0.14 | +0.08 | +0.22 | +0.116 |
|  | 1 | −0.50 | +0.47 | −0.03 | +0.295 |
| | 2 | −0.28 | −0.50 | −0.78 | — |
| | 3 | +0.39 | +0.26 | +0.65 | +0.118 |
| | 4 | −0.50 | −0.50 | −1.00 | — |
| | 5 | +0.36 | +0.27 | +0.63 | +0.116 |
|  | 1 | −0.67 | +0.28 | −0.38 | — |
| | 2 | +0.19 | −0.35 | −0.16 | — |
| | 3 | −0.22 | −0.23 | −0.45 | — |
| | 4 | +0.14 | +0.07 | +0.21 | +0.119 |
| | 5 | +0.33 | +0.21 | +0.54 | +0.124 |

Table 1. (continued)

| Molecule | Position | $\varrho_\sigma$ | $\varrho_\pi$ | $\varrho_{\sigma+\pi}$ | $\varrho_H$ |
|---|---|---|---|---|---|
|  | 1 | −0.68 | +0.22 | −0.46 | — |
| | 2 | −0.04 | −0.54 | −0.58 | — |
| | 3 | +0.40 | +0.35 | +0.75 | +0.126 |
| | 4 | −0.49 | −0.47 | −0.96 | — |
| | 5 | +0.57 | +0.44 | +1.01 | +0.121 |
|  | 1 | −0.46 | +0.21 | −0.25 | — |
| | 2,5 | −0.03 | −0.37 | −0.40 | — |
| | 3,4 | +0.15 | +0.26 | +0.41 | +0.119 |
|  | 1 | −0.90 | +0.26 | −0.64 | — |
| | 2,5 | +0.56 | +0.37 | +0.93 | +0.127 |
| | 3,4 | −0.24 | −0.50 | −0.74 | — |

The numbering indicated for pyrrole applies to all other molecules.

the "pyridine-type" nitrogen atoms. Although identical values were employed for the Slater exponents and Valence State Ionization Potentials, the final results discriminate between the two types of nitrogen atoms. The σ-charges on the "pyrrole-type" nitrogen are consistently more negative than those of the "pyridine-type" nitrogen. This can be reconciled with a greater demand for electronic charge in the >N–H group compared to the >N: group due to electron withdrawal by hydrogen in forming the nitrogen-hydrogen bond. This is recognized implicitly in the HMO theory by the use of a higher value of $h_x$ for a pyrrole nitrogen [*14*].

The calculated π-charges, contrary to the σ-charges, do not reflect the electronegativity values of the heteroatoms. For example, in the isoelectronic series furan, pyrrole, and cyclopentadienyl anion [*17*], the π-charges on oxygen, nitrogen, and carbon, are respectively +0.18, +0.36, and −0.20, whereas the previously mentioned σ-charges were respectively −0.94, −0.77, and −0.10. There is complete disagreement with the electronegativity sequence $O > N > C$, but more importantly, for the heteroatoms oxygen and nitrogen the π-charges are of opposite

Table 2. *Averaged σ-Charges (in Electrons) as a Function of the Electronegativity of the Neihgboring Atoms*

| Molecular Environment | σ-Charges of Central Atom | | | |
|---|---|---|---|---|
| | X=C | X=N | X=NH | X=O |
| C–X–C | −0.10 | −0.50 | −0.76 | −0.92 |
| C–X–NH | +0.13 | −0.28 | — | — |
| C–X–N | +0.14 | −0.23 | −0.49 | −0.68 |
| C–X–O | +0.34 | −0.04 | — | — |
| NH–X–N | +0.37 | −0.04 | — | — |
| N–X–N | +0.40 | — | — | −0.46 |
| N–X–O | +0.57 | +0.19 | — | — |

sign to the σ-charges. The overall charge distribution, given by the sum of the σ- and π-charges, is thus dominated by the σ-charge distribution in these molecules.

Recent molecular orbital calculations on formaldehyde, in which σ-electrons have been explicitly included, bear out the same point. First, an "ab initio" calculation by Foster and Boys [*28*], then an approximate self-consistent field calculation (CNDO method) by Pople [*29*], and finally a simulated Hartree-Fock calculation by Lipscomb et al. [*24*] all suggest that the carbon-oxygen bond in formaldehyde is $\overset{\oplus}{C} - \overset{\ominus}{O}$ polarized in the σ-orbital, but of opposite polarity in the π-orbital.

It is obviously desirable to check the conclusions of these theoretical calculations as far as possible with experimental data on the 5-membered heterocyclic ring systems. Considerable experimental data on reactivity can be found in the literature [*30*], but this is of no direct relevance to the isolated molecule calculations reported here without specific consideration of the nature of the transition state in each case, as shown previously for imidazole [*20*]. In Tab. 3 the calculated σ-, π-, and total dipole moments are summarized together with the experimental values, for all molecules on which data is available. The calculated dipole moments are much too large, a discrepancy shared by dipole moments calculated from exact SCF wave functions [*31*]. A more important result is that the correct direction of the dipole is obtained for furan and pyrrole. The calculations indicate that in furan the dipole points towards the oxygen atom, while in pyrrole it points in the opposite direction, towards the $C_3$–$C_4$ bond. This is in excellent agreement with the experimental results [*32*—*35*]. As illustrated in Fig. 1, the most interesting result is that the calculated σ- and π-dipole moments are in opposite directions to each other in both furan and pyrrole. However, in furan the overall dipole direction is that of the larger σ-moment, while in pyrrole the π-moment is larger, and gives the direction of the overall dipole moment. This is presented as strong evidence that independent σ- and π-polarization is a real phenomenon in these systems.

Table 3. *Dipole Moments (in Debye)*[a]

| Molecule | $\mu_{exp}$ | $\mu_\pi$ | | $\mu_\sigma$ | | $\mu_{\sigma+\pi}$ | |
|---|---|---|---|---|---|---|---|
| Furan | 0.70[b] | 1.60 | (270°) | 4.44 | (90°) | 2.83 | (90°) |
| Pyrrole | 1.80[b] | 3.82 | (270°) | 0.65 | (90°) | 3.17 | (270°) |
| Imidazole | 3.99[c] | 5.62 | (275°) | 2.00 | (321°) | 7.17 | (286°) |
| Pyrazole | 1.47[d] | 3.24 | (327°) | 2.79 | (34°) | 5.05 | (358°) |
| 1,2,3, -Triazole | 1.79[d] | 6.03 | (314°) | 4.20 | (352°) | 8.09 | (330°) |
| Izoxazole | 2.76[d] | 3.01 | (7°) | 5.61 | (66°) | 7.63 | (46°) |
| 1,2,5, -Oxadiazole | 3.38[e] | 2.43 | (90°) | 6.34 | (90°) | 8.77 | (90°) |

---

[a] Numbers in parenthesis represents the angle that the dipole moment makes with the positive X-axis in the clockwise sense in the coordinate system of Fig. 1.

[b] Ref. [*31*—*34*].

[c] CA 62, $3494_g$.

[d] McClellan, A. L.: Tables of experimental dipole moments. San Francisco: W. H. Freeman and Co. 1963.

[e] Ref. [*39* f].

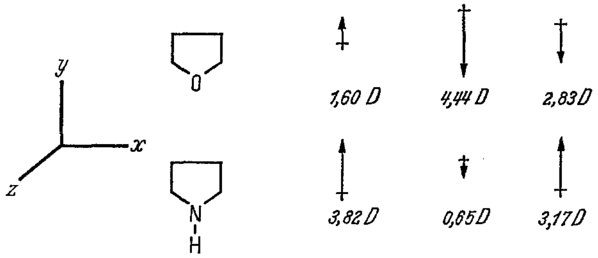


Fig. 1. Dipole Moments of Furan and Pyrrole

A further useful test of the validity of the calculated charge distributions is the comparison between total electron densities and corresponding nuclear magnetic resonance chemical shifts. For homocyclic aromatic systems, a linear relationship has been established between proton chemical shifts and the $\pi$-electron density of the carbon atom to which the proton is bonded [*36*]. An attempt to extend this correlation to heterocyclic systems has lead in one instance to the conclusion that "the proton chemical shifts appear to be a somewhat unreliable measure of $\pi$-electron densities, especially in positions adjacent to a nitrogen atom" [*37*]. However, we have indicated previously [*18*, *20*] that a linear correlation exists between EHT total electron densities in heterocyclic systems and experimental proton chemical shift. The carbon-13 chemical shift should be an even more direct measure of the electron density of a carbon atom [*38*], so that a similar correlation has been tested between EHT total electron densities and Carbon-13 chemical shifts.

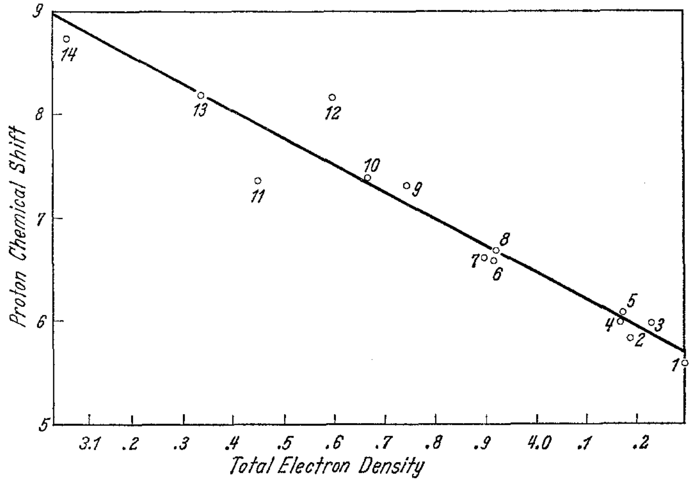


Fig. 2. Proton Chemical Shifts (ppm) of Heterocyclic Molecules versus EHT Total Electron Densities. In the index below, the first number indicates the particular point on the figure, while the number in parenthesis designates a particular position in the ring. 1. Cyclopentadienyl anion, [*39a*]; 2. Isoxazole (4 –), [*39b*]; 3. Pyrazole (4 –), [*39c*]; 4. Furan (3 –), [*39d*]; 5. Pyrrole (3 –), [*39d*]; 6. Imidazole (4 –), [*39c*]; 7. Pyrrole (2 –), [*39d*]; 8. Methyl Sydnone (4 –), [*39e*]; 9. Pyrazole (3 –), [*39c*]; 10. Furan (2 –), [*39d*]; 11. Imidazole (2 –), [*39c*]; 12. Furazan (3 –), [*39f*]; 13. 1,2,4, -Triazole (3 –), [*39g*]; 14. 1,3,4, -Oxadiazole (2 –), [*39h*]

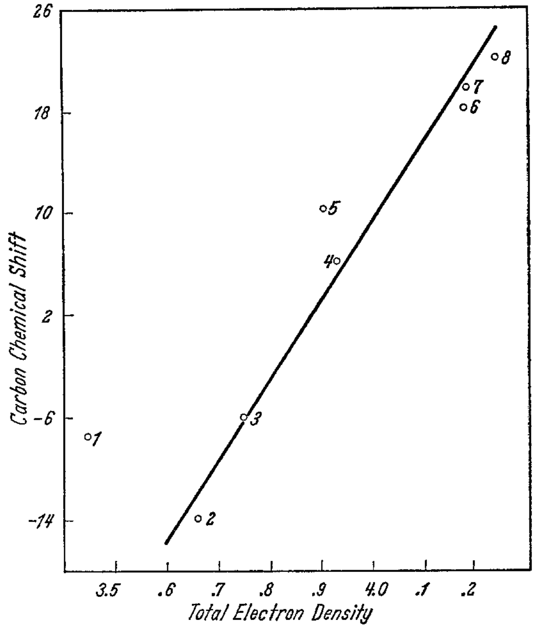


Fig. 3. Carbon-13 Chemical Shifts (ppm) relative to benzene of 5-membered heterocyclic molecules versus EHT Total Electron Densities. In the index below, the first number indicates the point on the figure, while the number in the parentheses designates a particular position in the ring [*40*]. 1. Imidazole (2 –); 2. Furan (2 –); 3. Pyrazole (3 –); 4. Imidazole (4 –); 5. Pyrrole (2 –); 6. Furan (3 –); 7. Pyrrole (3 –); 8. Pyrazole (4 –)

In Figs. 2 and 3 the calculated total electron densities of carbon atoms in the various heterocyclic rings are plotted against the available experimental proton chemical shifts [*39*], and carbon-13 chemical shifts [*40*], respectively. A reasonable correlation is obtained in both cases, indicating that the total electron densities calculated from EHT wave functions are qualitatively reliable.

Point 1 in Fig. 3, which represents the 2-position in imidazole, is rather far from the straight line in a direction suggesting overestimation of the electron withdrawal from this carbon atom by the flanking nitrogen atoms. Similar discrepancies have been observed here in other systems [*41*], when a carbon atom is in the $\alpha$-position to two nitrogen atoms. The extension of these NMR chemical shift correlations is currently underway in these laboratories. Preliminary Carbon-13 chemical shifts calculated by the KARPLUS and DAS [*42*] and POPLE [*43*] equations using EHT wavefunctions are in a reasonable correspondence with the experimental values for a wide range of heterocyclic molecules [*44*].

In summary, these EHT calculations on five-membered heterocyclic ring systems suggest pronounced, and independent, $\sigma$- and $\pi$-electron polarizations. The results are supported by the correlations between chemical shifts and calculated total electron densities, as well as by the agreement between the direction of the calculated and experimental dipole moments for furan and pyrrole. The calculations strongly suggest that the use of simple electronegativity considerations, while giving a reasonable guide to the $\sigma$-polarization, may lead to erroneous conclusions for the $\pi$-polarization, or indeed for the overall molecular polarization, in such molecules.

*Acknowledgements.* We wish to thank Dr. Roald Hoffmann for helpful discussions, and Mr. Angel López for computational assistance.

## References

*1.* Pullman, A., and B. Pullman: Quantum biochemistry, New York: J. Wiley and Sons 1963, give an excellent discussion of the application of this method to heterocyclic systems.
*2.* Dahl, J. P., u. A. E. Hansen: Theoret. chim. Acta (Berlin) **1**, 199 (1963).
*3.* Brown, R. D., and M. L. Heffernan: Austral. J. Chem. **12**, 319 (1959).
*4.* Solony, N., F. W. Birss, and J. B. Greenshields: Canad. J. Chem. **43**, 1569 (1965).
*5.* Orloff, M. K., and D. D. Fitts: J. chem. Physics **38**, 2334 (1963).
*6.* Pujol, L., u. A. Julg: Theoret. chim. Acta (Berlin) **2**, 125 (1964).
*7.* Sappenfield, D. S., and M. Kreevoy: Tetrahedron **19**, Suppl. 2, 157 (1963).
*8.* Mangini, A., and C. Zauli: J. chem. Soc. **1960**, 2210.
*9.* Brown, R. D., and M. L. Heffernan: Austral. J. Chem. **12**, 543 (1959).
*10.* Orloff, M. K., and D. D. Fitts: Tetrahedron **19**, 1691 (1963).
*11.* Lykos, P. G.: Adv. Quantum Chem., I, 171 (Ed. by P. O. Löwdin). New York: Academic Press 1964.
*12.* Parr, R. G.: Quantum theory of molecular electronic structure, Chapter III. New York: W. A. Benjamin 1963.
*13.* Moffat, J. B.: Canad. J. Chem. **42**, 1323 (1964).
*14.* Streitwieser, A. Jr.: Molecular orbital theory for organic chemists, p. 135. New York: John Wiley and Sons 1962.
*15.* Orloff, M. K., and O. Sinanoǧlu: J. chem. Physics **43**, 49 (1965).
*16.* Mataga, N., u. K. Nishimoto: Z. physik. Chem. **13**, 140 (1957).
*17.* Hoffmann, R. A.: J. chem. Physics **39**, 1397 (1963).
*18.* Adam, W., and A. Grimison: Tetrahedron **21**, 3417 (1965).
*19.* Hoffmann, R. A.: Tetrahedron **22**, 539 (1966).
*20.* Adam, W., and A. Grimison: Tetrahedron **22**, 835 (1966).
*21.* Clementi, E., and H. Clementi: J. chem. Physics **36**, 2824 (1962).
*22.* Peters, D.: J. chem. Soc. **1963**, 2015.
*23.* Pople, J. A., and G. A. Segal: J. chem. Physics **43**, S136 (1965).
*24.* Newton, M. D., F. P. Boer, and W. N. Lipscomb: J. Amer. Chem. Soc. 88, 2367 (1966).
*25.* Roothaan, C. C. J.: J. chem. Physics **19**, 1445 (1951).
*26.* Mulliken, R. S.: J. chem. Physics **23**, 1833, 2338, 2343 (1955).
*27a.* Hoffmann, R., and W. N. Lipscomb: J. chem. Physics **36**, 2179; **37**, 2872 (1962).
*27b.* Quantum Chemistry Program Exchange, Chemistry Department, Indiana University, QCPE No. 30.
*28.* Foster, J. M., and S. F. Boys: Rev. mod. Physics **32**, 303 (1960).
*29.* Pople, J. A., D. P. Santry, and G. A. Segal: J. chem. Physics **43**, S139 (1965).
*30.* Ridd, J. H.: Physical methods in heterocyclic chemistry, Vol. 1, pp. 109—160 (Ed. by A. R. Katritsky). New York: N. Y., Academic Press 1963.
*31.* Ransil, B. J.: Rev. mod. Physics **32**, 245 (1960).
*32.* Bak, B., D. Christensen, L. Hansen-Nygaard, and J. Rastrup-Anderson: J. molecular Spectroscopy **7**, 58 (1961).
*33.* — — — — J. chem. Physics **24**, 720 (1956).
*34.* —, L. Hansen, and J. Rastrup-Anderson: Disc. Faraday Soc. **19**, 30 (1955).
*35.* Koford, H., L. E. Sutton, and G. Jackson: J. chem. Soc. **1952**, 1467.
*36.* Fraenkel, G., R. E. Carter, A. McLachlan, and J. H. Richards: J. Amer. chem. Soc. 82, 5846 (1960).
*37.* Gawer, A. H., and B. P. Dailey: J. chem. Physics **42**, 2658 (1965).
*38.* Stothers, J. B.: Quart. Rev. (London) **19**, 144 (1965).

*39* a) SHAEFFER, T., and W. G. SCHNEIDER: Canad. J. Chem. **41**, 966 (1963).
b) FEUER, H., and S. MARKOFSKY: J. org. Chem. **29**, 935 (1964).
c) KATRITSKY, A. R.: Physical methods in heterocyclic chemistry, Vol. 2, Chapter 9. New York: Academic Press 1963.
d) JACKMAN, L. M.: Application of nuclear magnetic resonance in organic chemistry. New York: Macmillan Co. 1959.
e) LAWSON, K. D., W. S. BREY, and L. B. KIER: J. Amer. chem. Soc. **86**, 463 (1964).
f) OLOFSON, R. A., and J. S. MICHELMAN: J. org. Chem. **30**, 1854 (1965).
g) POTTS, K. T., and T. H. CRAWFORD: J. org. Chem. **27**, 2631 (1962).
h) AINSWORTH, C.: J. Amer. chem. Soc. **87**, 5800 (1965).
*40*. GRANT, D. M., and R. J. PUGMIRE: Private communication.
*41*. ADAM, W., A. GRIMISON, and G. RODRIGUEZ: Tetrahedron **23** (1967) (In press).
*42*. KARPLUS, M., and T. P. DAS: J. chem. Physics **34**, 1683 (1961).
*43*. POPLE, J. A.: Proc. Roy. Soc. (London) **A 239**, 541, 550 (1957).
*44*. ADAM, W., A. GRIMISON, and G. RODRIGUEZ: Unpublished data.

Prof. W. ADAM
Department of Chemistry
University of Puerto Rico
Rio Piedras, P. R. 00931
Puerto Rico