

# A SELF CONSISTENT FIELD MOLECULAR ORBITAL TREATMENT OF FURAN INCLUDING ALL VALENCE ELECTRONS

D. T. CLARK

Department of Chemistry, The University, Durham

(Received in the UK 18 October 1967; accepted for publication 4 November 1967)

**Abstract**—The electronic structure of furan has been investigated using a semi empirical self consistent field MO method including all valence electrons. The calculated pi electron distribution has been compared with that obtained using the PPP SCF MO method. The calculation gives satisfactory agreement with experiment for the total dipole moment and first ionization potential of furan.

## INTRODUCTION

IN PREVIOUS papers we have investigated the electronic structure of the 5-membered ring heterocyclic molecules thiophene<sup>1</sup> and pyrrole<sup>2</sup> by a self consistent field MO method including all valence electrons. In continuance of this work we report here the results of similar calculations on furan (Fig. 1).

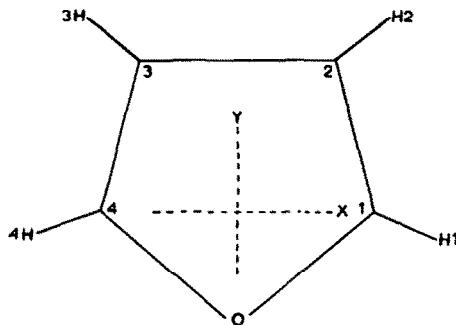


FIG. 1 Co-ordinate axes and numbering system for furan.

The pi electronic structure of furan has been investigated thoroughly<sup>3-7</sup> using the Pariser-Parr-Pople self consistent field MO method,<sup>8,9</sup> however there have been no serious attempts to study the sigma electronic structure of this molecule. The polarized sigma core will obviously affect the pi electron distribution and *vice versa* and hence the calculations which have been carried out on the pi electronic structure of furan neglecting this factor must be treated with caution. A further criticism which may be levelled at previous MO treatments of furan is the neglect of non nearest neighbour  $\beta$ 's, which for a small ring compound such as furan is an important omission.<sup>10</sup> In the light of this discussion a self consistent field MO calculation, including all valence electrons, on furan is clearly worthwhile.

### Method of calculation

The calculations have been carried out using the Pople-Segal Complete Neglect of Differential Overlap Method II.<sup>11-13</sup> One centre core and repulsion integrals were estimated from spectroscopic data as described previously.<sup>1,2</sup> Two centre repulsion integrals were calculated from the one centre integrals using the refined Mataga procedure.<sup>14,15</sup> The two centre core integrals were calculated from the relevant valence state ionization potentials and overlap integrals and the Mulliken-Wolfsberg-Helmholtz equation.<sup>16</sup> The overlap integrals were calculated using Slater orbitals with orbital exponents obtained using Slater's rules as modified by Burns.<sup>17</sup> The parameters employed in these calculations are shown in Table 1. Bond lengths and bond angles for furan were taken from Ref. 18.

TABLE 1. PARAMETERS USED IN THE CALCULATION ON FURAN

| Orbital | Atom | Z effective | $-I_{\mu\mu}$ | $-U_{\mu\mu}$ | $\gamma_{\mu\mu}$ |
|---------|------|-------------|---------------|---------------|-------------------|
| 1s      | H    | 1.2         | 13.60         | 13.60         | 12.848            |
| 2s      | C    | 3.150       | 20.07         | 50.69         | 10.207            |
| 2p      | C    | 2.800       | 10.91         | 41.53         |                   |
| 2s      | O    | 4.400       | 33.18         | 101.31        | 13.625            |
| 2p      | O    | 3.950       | 16.16         | 84.28         |                   |

### RESULTS AND DISCUSSION

#### A. Charge distribution and dipole moment of furan

Tables 2 and 3 show the distribution of charge between the atomic orbitals of furan and the total  $\sigma$  and  $\pi$  charge distributions. For comparison the results of two recent PPP SCF calculations on the pi electron distribution in furan are also included in Table 3.

TABLE 2. THE DISTRIBUTION OF ELECTRONS BETWEEN THE ATOMIC ORBITALS OF FURAN

(The Z axis is perpendicular to the molecular plane, the co-ordinate system is defined in Fig. 1).

| Atom and orbital                 |                 | electron population |
|----------------------------------|-----------------|---------------------|
| H <sub>1</sub> (H <sub>4</sub> ) | 1s              | 0.9844              |
| H <sub>2</sub> (H <sub>3</sub> ) | 1s              | 0.9731              |
| C <sub>1</sub> (C <sub>4</sub> ) | 2s              | 1.0251              |
|                                  | 2p <sub>x</sub> | 0.8073              |
|                                  | 2p <sub>y</sub> | 0.9059              |
|                                  | 2p <sub>z</sub> | 1.0674              |
| C <sub>2</sub> (C <sub>3</sub> ) | 2s              | 1.0100              |
|                                  | 2p <sub>x</sub> | 0.9955              |
|                                  | 2p <sub>y</sub> | 0.9941              |
|                                  | 2p <sub>z</sub> | 1.0803              |
| O                                | 2s              | 1.5238              |
|                                  | 2p <sub>x</sub> | 1.3512              |
|                                  | 2p <sub>y</sub> | 1.7342              |
|                                  | 2p <sub>z</sub> | 1.7046              |

TABLE 3. TOTAL SIGMA, PI, CHARGE DISTRIBUTION IN FURAN

| Atom                             | Electron population | Charge   | Ref. 6  | Ref. 7 |
|----------------------------------|---------------------|----------|---------|--------|
| H <sub>1</sub> (H <sub>4</sub> ) | 0.98437             | +0.01563 |         |        |
| H <sub>2</sub> (H <sub>3</sub> ) | 0.97307             | +0.02693 |         |        |
| C <sub>1</sub> (C <sub>4</sub> ) | σ 2.7383            | +0.2617  |         |        |
|                                  | π 1.0674            | -0.0674  | -0.0401 | -0.046 |
| C <sub>2</sub> (C <sub>3</sub> ) | σ 2.9996            | +0.0004  |         |        |
|                                  | π 1.0803            | -0.0803  | -0.0351 | -0.056 |
| O                                | σ 4.6093            | -0.6093  |         |        |
|                                  | π 1.7046            | +0.2954  | +0.1504 | +0.205 |

The hydrogen atoms all carry a small positive charge, which is of the same order of magnitude as that calculated for pyrrole.<sup>2</sup> Carbon atoms 1 and 4 are sigma electron donors and pi electron acceptors and overall are positively charged. The total charge on these atoms is +0.1943 and this may be compared with +0.0775 in the case of pyrrole.<sup>2</sup> Carbon atoms 2 and 3 are virtually neutral as far as the sigma electron distribution is concerned, but they are pi electron acceptors, so overall are negatively charged. Oxygen is a powerful sigma electron acceptor and weak pi electron donor and hence carries a substantial negative charge. Particularly noteworthy in Table 2 is the large population of the 2p<sub>z</sub> orbital on oxygen, which contributes significantly to the lone pair orbital. The order of pi electron density C<sub>2</sub>(C<sub>3</sub>) > C<sub>1</sub>(C<sub>4</sub>) is in agreement with Ref. 7. Preliminary calculations on potential energy surfaces indicates that this is not inconsistent with the fact that electrophilic substitution with a wide variety of electrophiles occurs predominantly at C<sub>1</sub>(C<sub>4</sub>).<sup>19</sup> There is an interesting variation in the order of pi electron densities at the ring carbon atoms in going from thiophene → pyrrole → furan. For thiophene C<sub>1</sub>(C<sub>4</sub>) > C<sub>2</sub>(C<sub>3</sub>) for pyrrole C<sub>1</sub>(C<sub>4</sub>) ≈ C<sub>2</sub>(C<sub>3</sub>) and for furan C<sub>1</sub>(C<sub>4</sub>) < C<sub>2</sub>(C<sub>3</sub>).

The overall charge distribution in a molecule is reflected in some measure by the total dipole moment. The calculated total dipole moment is 0.94 Debye with oxygen at the negative end. This is in satisfactory agreement with the experimental value ~0.7 Debye<sup>20</sup> in the same sense.

### B. Orbital energies

Table 4 gives the calculated eigen values together with the appropriate symmetry classification (σ' is defined with respect to the *xy* plane).

An interesting feature here is the low lying πB<sub>1</sub> orbital at -19.610 eV and the proximity of the top-occupied sigma and pi orbitals. This suggests that excited states involving sigma orbitals will probably be of considerable importance in any interpretation of the electronic spectra of furan. Preliminary calculations which we have carried out shows this to be the case, and an adequate account of the electronic spectra of furan necessitates the consideration of excited states involving sigma orbitals.

The ionization potential of furan has been measured and is 8.98 eV.<sup>21</sup> Applying Koopmans theorem the calculated ionization potential is 10.13 eV in satisfactory agreement for this type of calculation. This compares very favourably with the value 11.74 eV obtained by Solony<sup>6</sup> and co-workers using the PPP method.

TABLE 4. CALCULATED EIGEN VALUES FOR FURAN

| $\sigma A_1$   | $\sigma B_2$   | $\pi A_2$      | $\pi B_1$      |
|----------------|----------------|----------------|----------------|
| -52.876        | -33.702        | <u>-10.128</u> | -19.610        |
| -37.071        | -23.846        | 3.192          | <u>-12.079</u> |
| -24.252        | -14.109        |                | 1.632          |
| -21.574        | <u>-12.480</u> |                |                |
| -12.905        | 5.655          |                |                |
| <u>-12.184</u> | 6.252          |                |                |
| 5.909          | 6.939          |                |                |
| 6.602          | 7.319          |                |                |
| 7.438          | 8.231          |                |                |
| 7.830          |                |                |                |

**Acknowledgements**—The calculations were carried out on the University of Newcastle's KDF9 computer using a program kindly supplied by Drs. P. G. Perkins and D. H. Wall. The initial H matrix was calculated using a separate program and used as input data together with atomic co-ordinates, gammas and core charges. 25 Iterations were sufficient to obtain density matrix elements self consistent to seven decimal places.

## REFERENCES

- 1 D. T. Clark, *Tetrahedron* **24**, 2663 (1968).
- 2 D. T. Clark, submitted for publication.
- 3 M. K. Orloff and D. D. Fitts, *J. Chem. Phys.* **38**, 2334 (1963).
- 4 L. Pajol and A. Julg, *Theoret. Chim. Acta* **2**, 125 (1964).
- 5 D. S. Sappenfield and M. Kreevoy, *Tetrahedron* **19**, Suppl. 2, 157 (1963).
- 6 N. Solony, F. W. Birss and J. B. Greenshields, *Canad. J. Chem.* **43**, 1569 (1965).
- 7 P. J. Black, R. D. Brown and M. L. Heffernan, *Austral. J. Chem.* **20**, 1325 (1967).
- 8 R. Pariser and R. G. Parr, *J. Chem. Phys.* **21**, 466 (1953).
- 9 J. A. Pople, *Trans. Faraday Soc.* **49**, 1375 (1953).
- 10 e.g. R. L. Flurry, Jr., and J. J. Bell, *J. Am. Chem. Soc.* **89**, 525 (1967).
- 11 J. A. Pople, D. P. Santry and G. A. Segal, *J. Chem. Phys.* **43**, 5129 (1965).
- 12 J. A. Pople and G. A. Segal, *Ibid.* **43**, 5136 (1965).
- 13 J. A. Pople and G. A. Segal, *Ibid.* **44**, 3289 (1966).
- 14 N. Mataga and K. Nishimoto, *Z. Phys. Chem. Frankfurt* **13**, 140 (1957).
- 15 K. Ohno, *Theoret. Chim. Acta* **2**, 219 (1964).
- 16 M. Wolfsberg and L. Helmholz, *J. Chem. Phys.* **20**, 837 (1952).
- 17 G. Burns, *Ibid.* **41**, 1521 (1964).
- 18 B. Bak, D. Christensen, W. B. Dixon, L. Hansen-Nygaard, J. Rastrup Adersen and M. Scholtlaender, *J. Mol. Spectr.* **9**, 124 (1962).
- 19 R. M. Acheson *An Introduction to the Chemistry of Heterocyclic Compounds*. Interscience, New York (1960).
- 20 A. L. McClellan *Tables of Experimental Dipole Moments*. Freeman, San Francisco (1963).
- 21 K. Watanabe and T. Nakayama, *J. Chem. Phys.* **29**, 48 (1958).