

## Pariser-Parr-Pople Type SCF-MO-CI Calculations on Pentafluorobenzenes

C. L. KHETRAPAL\*

Physikalisches Institut, Universität Basel, Switzerland

D. K. RAI

Department of Spectroscopy, Banaras Hindu University, Varanasi-5, India

Received December 16, 1968

The  $\pi$ -electron densities at various atomic positions and the ground state bond orders have been calculated in several pentafluorobenzenes using Pariser-Parr-Pople method. The low lying excited energy states of these molecules obtained by a partial configuration interaction procedure involving only singly excited states are reported.

Die  $\pi$ -Elektronendichten an den verschiedenen Atomen sowie die Bindungsordnungen im Grundzustand sind in einer Reihe von Pentafluorbenzolen mittels der Methode von Pariser-Parr-Pople berechnet worden. Die untersten angeregten Zustände ergaben sich aus der Wechselwirkung mit einer beschränkten Anzahl einfach angeregter Konfigurationen.

La méthode de Pariser-Parr-Pople a été utilisée pour calculer les densités électroniques  $\pi$  et les indices de liaison dans l'état fondamental de plusieurs pentafluorobenzènes. Les états excités les plus bas de ces molécules ont été obtenus par interaction de configuration limitée aux états monoexcités.

### Introduction

The group of molecules obtained by substitution of hydrogen atoms in benzene by other atoms or groups are very interesting from the spectroscopic point of view. The spectral characteristics of all these molecules are very similar [1] and the differences in details are explained as being due to the different electronic properties of the substituent atoms and groups. This series of molecules are therefore suitable for studying the dependence of the spectra on the various parameters in a semi-empirical theory. This type of study has attracted the attention of several workers [2]. Most recently the spectral behaviour of several fluorobenzenes have been studied on the basis of semi-empirical methods by Ford [3]. No calculation of this type on substituted pentafluorobenzenes is available in the literature. It is however, expected that if one fluorine atom in hexafluorobenzene is replaced by another atom or group of atoms the spectra would show a slight change which may be qualitatively similar to the shift as compared to benzene in the spectra of mono-substituted benzenes. In the present communication we have applied the naive Pariser-Parr-Pople [4, 5] method to a number of mono-substituted pentafluorobenzenes.

\* Permanent address: Tata Institute of Fundamental Research, Bombay-5, India.

### Method of Calculation

The semi-empirical SCF MO method due to Pariser-Parr-Pople which has been shown to yield reasonable results in a large number of molecules has been used in these calculations. The molecules are assumed to be planar, and CCF and CCC angles were taken to be 120°. The bond distances were taken from the tables of interatomic distances [6]. When the substituent was CH<sub>3</sub> or OCH<sub>3</sub>, the H<sub>3</sub> group was treated as a pseudoatom contributing one  $\pi$ -electron to the conjugated system. The values of the ionisation potentials ( $I$ ) and electron affinities ( $E$ ) were taken for the appropriate valence states from the tables prepared by Hinze and Jaffé [7] and are reproduced in Table 1. The one centre core integrals were

Table 1. Ionisation potential and electron affinity of atoms

Atom or group	$I$ (eV)	$E$ (eV)	Atom or group	$I$ (eV)	$E$ (eV)
C (benzene)	11.16	0.03	Cl	26.37	11.05
C (C $\equiv$ N)	11.19	0.10	S(SH)	22.97	11.05
N (C $\equiv$ N)	14.18	1.66	Br	19.10	11.80
O(OH, OCH <sub>3</sub> )	34.19	14.61	I	19.40	10.60
F	39.64	18.11	H <sub>3</sub>	13.60	0.75

approximated as usual by  $I - E$ . The  $\beta$ -integrals were calculated using the formula [8]:

$$\beta_{rs} = KS_{rs}(I_r + I_s)$$

where  $S_{rs}$  is the overlap integral between the orbitals of atoms  $r$  and  $s$ ,  $I_r$  and  $I_s$  are the respective ionisation potentials. The constant ( $K$ ) of proportionality was evaluated by putting  $\beta_{C-C} = -2.39$  eV between two carbon atoms in benzene. This choice of  $\beta$  was the one suggested by Pariser and Parr [4] for getting the best fit to the lowest excited state of benzene.  $S_{rs}$  values were taken from the tables prepared by Mulliken *et al.* [9] using orbital exponents obtained using Slater's rules. The two centre coulomb  $\gamma$  repulsion integrals have been calculated using the following formula given by Mataga and Nishimoto [10].

$$\gamma(rr/ss) = \frac{14.3986}{R_{rs} + r} \text{ eV}$$

where  $r = \frac{14.3986}{\frac{1}{2}(I_r + I_s) - \frac{1}{2}(E_r + E_s)}$  and  $R_{rs}$  is the distance between  $r$  and  $s$ .

Using these values for the integrals the Pople equations for eigenfunctions and eigen-values are solved iteratively till self consistency is reached. To calculate the singlet and triplet excitation energies the expressions given by Pople [11] are used. All configurations obtained by single excitation of electrons from filled molecular orbitals to empty molecular orbitals have been included. All calculations were made on a CDC-3600 computer at the University of Uppsala data centre.

### Results and Discussion

The numbering of various atoms and the bonds in the various pentafluorobenzenes studied are given in Fig. 1. The charge densities at various positions and the ground state bond orders are given in Tables 2 and 3 respectively. It can be noticed from Tables 2 and 3 that the  $\pi$ -electron densities at the various fluorine

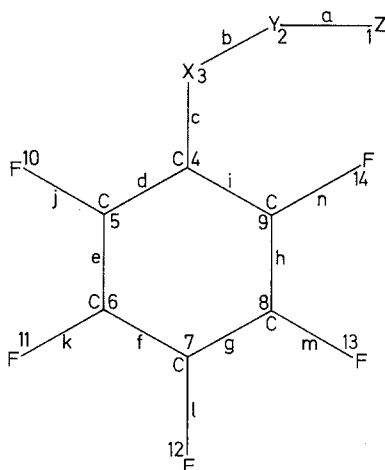


Fig. 1. Numbering of atoms and bonds in pentafluorobenzenes

atoms and the C–F bond orders are the same in all the molecules considered here (1.964 and 0.186 respectively). The  $\pi$ -electron densities of the halogen substituted compounds follow a regular sequence. The C–C bond orders remain almost unaffected by the substituent except for the bond nearest to the substituent. The double bond character of this bond ( $d$ ) decreases when the substituent is  $\text{OCH}_3$  or CN.

The energy values of the lowest lying states obtained after including configuration interaction are shown in Table 4 along with their oscillator strength.

Table 2.  $\pi$ -electron densities at various positions in several pentafluorobenzenes

Substituent XYZ	$\pi$ -electron densities at position													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
$\text{OCH}_3$	1.002	1.060	1.870	1.037	1.048	1.033	1.042	1.033	1.052	1.965	1.964	1.964	1.964	1.965
SH			1.974	1.060	1.020	1.038	1.029	1.038	1.020	1.963	1.964	1.964	1.964	1.963
$\text{CH}_3$		0.923	1.078	1.064	1.007	1.040	1.023	1.040	1.007	1.962	1.964	1.963	1.964	1.962
Cl			1.972	1.054	1.024	1.038	1.031	1.038	1.024	1.964	1.964	1.964	1.964	1.964
Br			1.989	1.064	1.003	1.055	1.021	1.055	1.003	1.958	1.961	1.959	1.961	1.958
I			2.000	1.086	0.997	1.057	1.017	1.057	0.997	1.957	1.961	1.963	1.961	1.957
F			1.964	1.036	1.036	1.036	1.036	1.036	1.036	1.964	1.964	1.964	1.964	1.964
CN		1.225	0.830	1.085	0.985	1.039	1.004	1.039	0.985	1.960	1.964	1.962	1.964	1.960
H				1.071	1.006	1.039	1.021	1.039	1.006	1.962	1.964	1.963	1.964	1.962

It is observed that there are two weak transitions below 6 eV. The calculations give two intense transitions in the neighbourhood of 6.5 eV. In Table 4 only the mean of the two excitation energies is given. The fact that these transitions for all the compounds lie in a rather narrow energy range is significant and shows that

Table 3. *Ground state bond orders in some pentafluorobenzenes*

Substituent XYZ	Ground state bond order of the bond													
	a	b	c	d	e	f	g	h	i	j	k	l	m	n
OCH <sub>3</sub>	0.964	0.250	0.262	0.631	0.646	0.643	0.642	0.646	0.630	0.183	0.186	0.184	0.186	0.182
SH			0.154	0.647	0.644	0.644	0.644	0.644	0.647	0.189	0.185	0.187	0.185	0.189
CH <sub>3</sub>		0.984	0.159	0.646	0.644	0.644	0.644	0.644	0.644	0.193	0.184	0.189	0.184	0.193
Cl			0.161	0.646	0.644	0.644	0.644	0.644	0.644	0.188	0.185	0.187	0.185	0.188
Br			0.099	0.649	0.640	0.641	0.641	0.640	0.649	0.191	0.185	0.188	0.185	0.191
I			0.064	0.650	0.640	0.641	0.641	0.640	0.650	0.207	0.192	0.202	0.192	0.207
F			0.186	0.641	0.641	0.641	0.641	0.641	0.641	0.186	0.186	0.186	0.186	0.186
CN		0.929	0.310	0.619	0.619	0.640	0.640	0.649	0.649	0.201	0.186	0.195	0.186	0.201
H				0.654	0.653	0.644	0.644	0.643	0.654	0.193	0.185	0.189	0.185	0.193

the transitions are of similar type in all compounds. No detailed experimental data on the spectrum of these molecules is so far available. Recent work [12] on pentafluoroanisole and pentafluorotoluene shows two absorption peaks near 4.8 eV and 5.4 eV in both cases. More detailed experimental work is in progress and we hope to have more data for comparison.

Table 4. *Low lying singlet states of some substituted pentafluorobenzenes*

Substituent XYZ	1st excited state		2nd excited state		3rd excited state	
	Energy eV	Oscillator strength	Energy eV	Oscillator strength	Energy eV	Oscillator strength
OCH <sub>3</sub>	4.55	0.003	5.51	0.232	6.23	0.920
SH	4.62	0.001	5.72	0.017	6.53	1.160
CH <sub>3</sub>	4.61	0.007	5.67	0.110	6.42	1.140
Cl	4.63	0.001	5.78	0.002	6.62	1.260
Br	4.66	0.004	5.82	0.002	6.61	1.240
I	4.66	0.006	5.83	0.005	6.68	1.230
F	4.63	0.000	5.71	0.000	6.64	1.253
CN	4.39	0.037	5.19	0.501	6.17	0.750
H	4.67	0.008	5.84	0.009	6.70	1.230

*Acknowledgements:* The work was performed while the authors were guests of the Quantum Chemistry Group Uppsala for the Summer School Aug.—Sept. 1967. It is a great pleasure to thank Professors P. O. Löwdin and J. L. Calais for their keen interest and helpful discussion. Our thanks are also due to Dr. Olle Mårtensson for his help. D.K.R. is thankful to N.B.S. (USA) for a travel grant which enabled him to attend the Summer School.

### References

1. Platt, J. R. ed.: Source book on spectra of conjugated molecules. New York: J. Wiley, Specially papers by Petruska and Stevenson.
2. Mataga, N.: Bull. chem. Soc. Japan **36**, 1607 (1963). — Clark, D. T., and J. M. Elinsley: Molecular Physics **12**, 365 (1967).
3. Ford, B.: Theoret. chim. Acta (Berl.) **10**, 342 (1968).
4. Pariser, R., and R. G. Parr: J. chem. Physics **21**, 466, 767 (1953).
5. Pople, J. A.: Trans. Faraday Soc. **49**, 1315 (1953). See also: Parr, R. G.: Molecular electronic structure. New York: W. A. Benjamin 1963.
6. Sutton, L. E., ed.: Interatomic distances: Chemical Society Special Publication No. 11 (1958).
7. Hinze, J., and H. H. Jaffé: J. Amer. chem. Soc. **84**, 540 (1962).
8. Wolfsberg, M., and L. Helmholz: J. chem. Physics **20**, 837 (1952).
9. Mulliken, R. S., C. A. Rieka, D. Orloff, and H. Orloff: J. chem. Physics **17**, 1248 (1949).
10. Mataga, N., and K. Nishimoto: Z. physik. Chemie **13**, 140 (1957).
11. Pople, J. A.: Proc. physic. Soc. **68** A, 81 (1955).
12. Amini, R., and K. P. R. Nair: Unpublished work.

Dr. D. K. Rai  
Department of Spectroscopy  
Banaras Hindu University  
Varanasi-5, India