Ab initio studies on the electronic structure of some substituted benzenes

O P SINGH and J S YADAV*

Department of Physics, Banaras Hindu University, Varanasi 221 005, India

Abstract. *Ab initio* Molecular orbital (MO) calculations with the 4-31G, 6-31G (split valence) and 6-31G* (split valence + polarized) basis sets have been carried out on monofluorobenzene and *o-*, *m-*, *p*-difluorobenzenes to study ground state properties such as orbital energies, gross orbital charges, net atomic charges and dipole moments. The redistribution of charges consequent to excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) has also been calculated. The results so obtained have been compared and discussed in the light of semi-empirical calculations and available experimental observations. The present study suggests the intermingling of the σ and π orbitals; however, the highest occupied and lowest unoccupied molecular orbitals are of π-symmetry indicating that most of the chemical and spectroscopic properties are controlled by π-electrons. It is also noted that the substituent fluorine is a weak π-donor and a strong σ-attractor. On exciting an electron from HOMO to LUMO it is observed that certain reactions may proceed through excited states. Though, in general, the semi-empirical and *ab initio* methods predict the same trend, the latter should be applied in order to explore the finer details of the chemical properties for the molecules considered in the present investigation.

Keywords. Orbital energies; gross orbital charges; net atomic charges; dipole moments; excited states.

1. Introduction

A knowledge of the electronic structure of substituted benzenes is of basic importance for a deeper understanding of their reactivities and spectral properties. Therefore, the study of their electronic structures has received much attention at every stage of the development of the molecular orbital theory. The method developed by Pariser-Parr and Pople (PPP) provides a fairly satisfactory description of both the ground and the excited state properties of substituted benzenes (Misra and Rai 1970, 1972). Though several features of the electronic structure can be understood with the help of these calculations, several equally important aspects cannot be satisfactorily explained. These latter aspects include contributions from the so-called inductive effects of the substituent and correspond to the changes in the σ-electron framework of the compounds. Therefore, an extensive application of the all valence electrons molecular orbital method was carried out on substituted benzenes (Yadav *et al* 1972a, b, 1973a, b, 1975). The general agreement between both the π-electrons method and the all valence electrons molecular orbital approximation is encouraging. However, the approximate all valence electrons method also did not reproduce all the experimental results since the parameters suitable for some properties were not exactly suitable for the other

---

* To whom all correspondence should be addressed.

indices. Also different sets of parameters were suggested in a particular approximation by different workers (Del Bene and Jaffee 1968). Furthermore, different approximate methods (Pople and Beveridge 1970) were available with varying degrees of reliability and success. Moreover some workers in the field are of the opinion that semi-rigorous procedures are no longer adequate for molecular electronic structure calculations (Kaufman 1979).

The fourth generation in computers has made available quantum chemical programs which include all electrons of the system wherein all electron integrals were evaluated analytically. This prompted several investigators to apply *ab initio* methods to some substituted benzenes (Hehre *et al* 1972b; Binning and Sando 1980; Boggs *et al* 1982). The computations due to Hehre *et al* (1972b) were carried out on a STO-3G basis set for a fixed geometry whereas Binning and Sando (1980) applied a double zeta contracted gaussian basis set. Recently several workers (Boggs *et al* 1982) and (Nagi-Felsobuki *et al* 1982) in their separate communications have reported structures of some substituted benzenes with 4-21G and STO-3G, 4-31G basis sets respectively. None of these studies included the systematic applications of double zeta plus polarised basis sets to the electronic structure of these molecules. It was therefore thought worthwhile to apply gaussian series of programs (Binkley *et al* 1977, 1983) at split valence and split valence plus polarized basis sets to some substituted benzenes as we have a long standing interest in quantum chemical calculations on these molecules (Misra and Rai 1970, 1972; Yadav *et al* 1972a,b, 1973a,b, 1975) hoping that the inclusion of polarised functions will improve the quality of the results.

The main purpose of this study is to extend our calculations upto the *ab initio* level and to provide reliable and fairly accurate information on the electronic structures of these molecules. The present paper deals with studies on mono-fluorobenzene and isomeric di-fluorobenzenes. The results will be discussed in the light of available experimental and other non- and semi-empirical results.

2. Method of calculation

All the molecules have been taken as planar, the bond angles as 120° and the bond lengths C–C, C–H and C–F as 1·397, 1·084 and 1·350 Å respectively. The calculations were performed on a CYBER 175 computer using Gaussian-76 Program (Binkley *et al* 1977) with 4-31G basis set (Ditchfield *et al* 1971) of 160 and 176 primitive gaussians contracted to 73 and 80 basis functions, a 6-31G basis set (Hehre *et al* 1972a) of 174 and 192 primitive gaussians contracted to 73 and 80 basis functions and Gaussian-82 Program (Binkley *et al* 1983) with 6-31G* basis set (Hariharan and Pople 1973) of 216 and 240 primitive gaussians contracted to 115 and 128 basis functions for the mono-fluorobenzene and the di-fluorobenzenes respectively. A calculation of the redistribution of charges has also been made on exciting an electron from HOMO to LUMO, the elements of the density matrix are changed according to the equation:

$$P'_{\mu\nu} = 2 \sum_{i}^{occ} C_{\mu i} C_{\nu i} - (C_{\mu})_{\text{HOMO}} (C_{\nu})_{\text{HOMO}} + (C_{\mu})_{\text{LUMO}} (C_{\nu})_{\text{LUMO}}$$

The elements of the newly constructed density matrix multiplied by their respective overlap integrals give the new Mulliken's population from which the charges on each atomic site were computed.

3. Results and discussions

3.1 *Orbital energies*

The energies for five highest occupied and five lowest unoccupied molecular orbitals and their symmetry types have been presented in table 1.

The general observation regarding the σ-π separability in the present non-empirical study and our earlier semi-empirical investigation is almost the same. However, some noticeable differences are present. For instance, the second HOMO is of π-symmetry in all the molecules of the present study whereas in INDO and CNDO/2 calculations (table 1), they are of σ-symmetry in monofluorobenzene and p-difluorobenzene. Furthermore, in p-difluorobenzene the third and fourth HOMO have π and σ symmetries respectively in 6-31G* but their symmetries are reversed in 4-31G and 6-31G methods. It is also interesting to mention that in all the *ab initio* methods the third and fourth HOMO have nearly the same energy though their symmetries are σ and π respectively. Thus *ab initio* results very clearly suggest that σ and π orbitals could have similar energies. The same mixing appears also in non-empirical (Clementi 1967) and semi-empirical studies on nucleic acid bases (Prettre and Pullman 1968).

The symmetry of the HOMO, an indication of the symmetry of the ionized species, is found to be of π-symmetry in all the methods. This is in agreement with the usual assumption that the excitation and ionization mechanisms are mainly controlled by π-electrons in conjugated and aromatic molecules.

The ionization potential, the energy of the HOMO, obtained from the improved basis set 6-31G* is in excellent agreement with the experimental value (table 1). The energy difference between HOMO and LUMO decreases from 4-31G to 6-31G to 6-31G*. The examination of atomic orbital coefficients reveals that it is not possible to speak of fluorine lone-pairs in the context of the present calculations since they appear to be strongly mixed with other atomic orbitals in molecular orbitals.

3.2 *Gross-orbital charges*

The following conclusions can be drawn from the study of the orbital populations of carbon, fluorine and hydrogen atoms.

1. The assumption of sp^2 hybridization on the carbon atoms implies the charge population described as $2s^1$, $2p_x^1$, $2p_y^1$ and $2p_z^1$. The present calculations do show a similar distribution of charges except on the carbon to which the substituent fluorine is attached. There is a deficit of about $\cdot85\ e$ (approximately the same in all calculations) in the $2s$ atomic orbitals of all the carbon atoms as compared to a free carbon atom. This deficit which represent promotion from a $2s$ to a $2p$ orbit is explained as being due to the ensuing energy gains from sp^2 hybridization.

2. It is clear that the accepted concept of fluorine being a strong σ-attractor and a weak π-donor (back donation effect) is well borne out by the detailed charge distribution pattern in all the molecules. The amount of π-charges donated to the ring by the fluorine is approximately $\cdot06\ e$ in all the *ab initio* methods, however the σ-charges attracted by the fluorine from the ring tend to decrease as the basis sets improve. This type of back donation has been propounded in the theory of geminal proton-proton spin coupling constants (Pople and Bothner-by 1965) and semi-empirical methods (Doraiswamy and Sharma 1983).

Table 1. Orbital energies (a.u.)† for five highest occupied and five lowest unoccupied MO.

Molecules	Methods MO	Present calculation			Experimental	Earlier calculation (Semi-empirical)		
		4-31G	6-31G	6-31G*		PPP**	CNDO/2***	INDO***
		-0.527σ	-0.528σ	-0.526σ		—	—	—
		-0.508π	-0.509π	-0.501π		—	—	—
		-0.501σ	-0.503σ	-0.501σ		-0.481π	-0.526π	-0.507π
		-0.351π	-0.352π	-0.345π		-0.378π	-0.516σ	-0.500σ
	HOMO	-0.341π	-0.342π	-0.333π	-0.340[a] / -0.354[b]	-0.367π	-0.490π	-0.467π
Monofluoro-benzene	LUMO	+0.132π	+0.127π	+0.131π		-0.028π	+0.130π	+0.148π
		+0.143π	+0.139π	+0.145π		-0.023π	+0.136π	+0.156π
		+0.225σ	+0.225σ	+0.228σ		+0.085π	+0.242σ	+0.245π
		+0.279π	+0.279π	+0.284σ		—	—	—
		+0.294σ	+0.293π	+0.298σ		—	—	—
		-0.550σ	-0.551σ	-0.546σ		—	—	—
		-0.528σ	-0.530σ	-0.524σ		—	—	—
		-0.519π	-0.520π	-0.509π		-0.473π	-0.533π	-0.517π
		-0.365π	-0.366π	-0.355π		-0.371π	-0.525π	-0.505π
	HOMO	-0.355π	-0.356π	-0.344π	-0.341[a]	-0.359π	-0.488π	-0.464π
o-difluoro-benzene	LUMO	+0.118π	+0.114π	+0.122π		-0.023π	+0.116π	+0.133π
		+0.129π	+0.125π	+0.136π		-0.018π	+0.122σ	+0.140π
		+0.211σ	+0.210σ	+0.216σ		+0.088π	+0.244σ	+0.218π
		+0.274σ	+0.273σ	+0.278σ		—	—	—
		+0.289σ	+0.286σ	+0.297σ		—	—	—
		-0.552σ	-0.554σ	-0.547σ		—	—	—
		-0.532σ	-0.533σ	-0.528σ		—	—	—

m-difluoro-benzene	−0·518π	−0·519π	−0·509π		−0·471π	−0·537σ	−0·523σ
	−0·366π	−0·367π	−0·356π		−0·370π	−0·523π	−0·305π
HOMO	−0·355π	−0·357π	−0·344π	−0·343ª	−0·360π	−0·494π	−0·471π
LUMO	+0·118π	+0·114π	+0·123π		−0·023π	+0·116π	+0·123π
	+0·129π	+0·126π	+0·137π		−0·018π	+0·123π	+0·142π
	+0·219π	+0·218σ	+0·223σ		+0·088π	+0·236σ	+0·210σ
	+0·281σ	+0·279σ	+0·286σ		—	—	—
	+0·287σ	+0·286σ	+0·294σ		—	—	—
	−0·586σ	−0·589σ	−0·580σ		—	—	—
	−0·518π	−0·519π	−0·513σ		—	—	—
p-difluoro-benzene	−0·517σ	−0·519σ	−0·508π		−0·471π	−0·543π	−0·526π
	−0·371π	−0·372π	−0·361π		−0·375π	−0·519σ	−0·503σ
HOMO	−0·350π	−0·351π	−0·338π	−0·335ª	−0·355π	−0·477π	−0·453π
LUMO	+0·122π	+0·108π	+0·115π		−0·026π	+0·112π	+0·129π
	+0·135π	+0·132π	+0·143π		−0·015π	+0·126π	+0·144π
	+0·219σ	+0·219σ	+0·223σ		+0·088π	+0·240π	+0·219π
	+0·269σ	+0·269σ	+0·276σ		—	—	—
	+0·298σ	+0·295σ	+0·299σ		—	—	—

† Underlined values represent the first ionisation potential of the molecule; ª Brolsfond *et al* (1960); ᵇ Morrison and Nicholson (1952); ** Misra (1970), semi-empirical molecular orbital calculations on some substituted benzenes; *** Yadav (1973), molecular orbital study of electronic structure, spectra and excited state geometry of some substituted benzenes.

3.3 *Net atomic charges*

The net atomic charges at various atomic sites are presented in figure 1. The conclusions drawn from these calculations are:

1. We observe that qualitatively the results obtained by 4-31G, 6-31G and 6-31G* methods are similar but quantitatively the magnitude of the net charges on each atomic site of the carbon in the 4-31G and 6-31G methods is less than in the 6-31G* method whereas this order is reversed for the substituent fluorine. However, the magnitude of the net charges on the hydrogen atoms attains approximately the same value in all the methods.

2. A very interesting aspect of these results is that the hydrogen atoms, which in π-electron approximations were not considered and carry only a small amount of
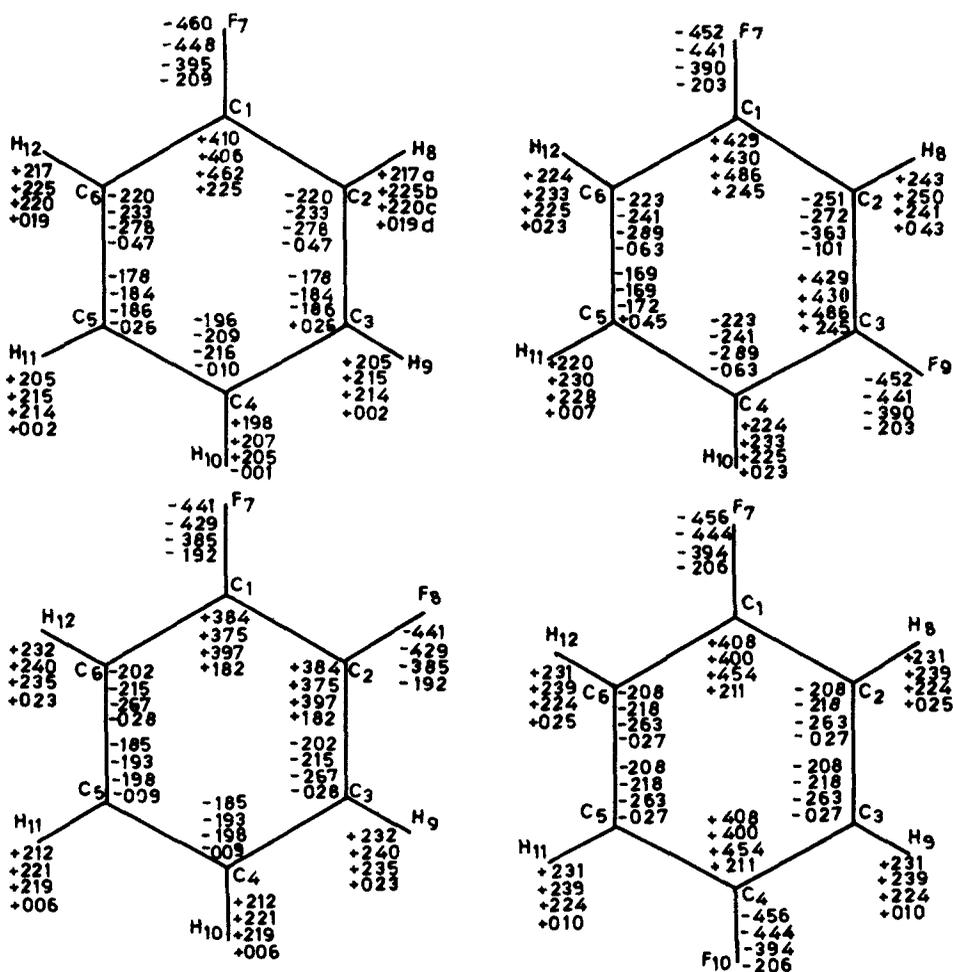
Figure 1. Net atomic charges in units of 10^{-3} electrons: (a) 4-31G (b) 6-31G (c) 6-31G* (d) CNDO/2 electron distributions (the values shown by the side of each atom refer to those obtained by methods a, b, c and d, respectively, from top to bottom).

+ ve and − ve charges in semi-empirical all valence electron SCF calculations (Yadav *et al* 1972a), tend to acquire very high values of only the positive charge indicating migration of electronic charge from hydrogen atoms to the ring.

3. We observe that whereas the substituent fluorine carries a net positive charge in π-electron calculations, they are negatively charged in our semi-empirical studies and the present study. This is because where π-electrons migrate from the fluorine to the ring making the former deficient in π-electrons, there is a large migration of the σ-electrons resulting in a net acquisition of negative charge by the fluorine. The fact that the fluorine carries a net negative charge and the hydrogen also has a net charge is not consistent with π-electron theories.

4. The semi-empirical all valence electrons calculations (Yadav *et al* 1973a) and even the π-electron calculations carried out in the variable electronegatively formalism (Misra and Rai 1970, 1972), lead to some activation of the *m*-position in monofluorobenzene, but in the *ab initio* calculations no similar activation is obtained. However, if we disregard the charges migrating from the hydrogen to the carbon at the *m*-position, the *m*-position does get a small negative charge. It is also observed that the *o*-, *p*-, directing property of this fluorine atom is mainly associated with the π-electron cloud of the system. The σ-charges do not correlate well with this property.

5. A comparison of the net charges on the fluorine atoms shows that they are modified substantially in difluorobenzenes as compared to the monoderivative. The magnitude of the net charges on fluorine atoms increases from *ortho* to *para* but it is maximum in monofluorobenzene. This mutual interaction of the substituents is exhibited clearly in all *ab initio* as well as semi-empirical CNDO/2 methods (figure 1).

3.4 *Dipole moments*

Calculated dipole moments have been presented in table 2 and compared with semi-empirical calculations and experimental values. The calculated dipole moments are very large compared to their experimental values, however, the trends are reasonably well produced. The dipole moment corresponding to the polarized basis set 6-31G* are almost the same as the CNDO/2 (table 2) method and are close to experimental values. Similar values of the dipole moments of monofluorobenzene and *m*-difluorobenzene (MB) have also been calculated by Boggs *et al* (1982) using the 4-21G basis set for optimized geometries.

Table 2. Dipole moments (Debye).

Method	Present calculation			Experimental	Earlier calculation (semi-empirical)	
Molecule	4-31G	6-31G	6-31G*		CNDO/2[b]	INDO[b]
Monofluorobenzene	2·32	2·32	1.81	1.66[a]	1.76	1.85
o-difluorobenzene	3·98	3·98	3.11	2.59 ± 0.02[c]	3.06	3.22
m-difluorobenzene	2·31	2·31	1·80	1·51 ± 0·02[c]	1·74	1·81

[a] Dekowalewski *et al* (1959); [b] Yadav *et al* (1972b); [c] Nygaard *et al* (1967).

3.5 *Excited state*

The redistribution of charges at various atomic sites of the molecules have been calculated by exciting an electron from HOMO to LUMO. As it is clear from table 1 that HOMO and LUMO are of π-symmetry, the change in orbital populations as compared to its ground state will take place in π-orbitals only. The redistribution of charges in the π-orbitals has been presented in figure 2.

The examination of MFB in figure 2 suggests that the *meta* carbon which was positively charged in the ground state gets negatively charged after exciting an electron from HOMO to LUMO. Correspondingly, the *para* carbon looses a considerable amount of charge in this process making it positively charged. Also the carbon at the *ortho* position becomes more negatively charged as compared to its value in the ground state.
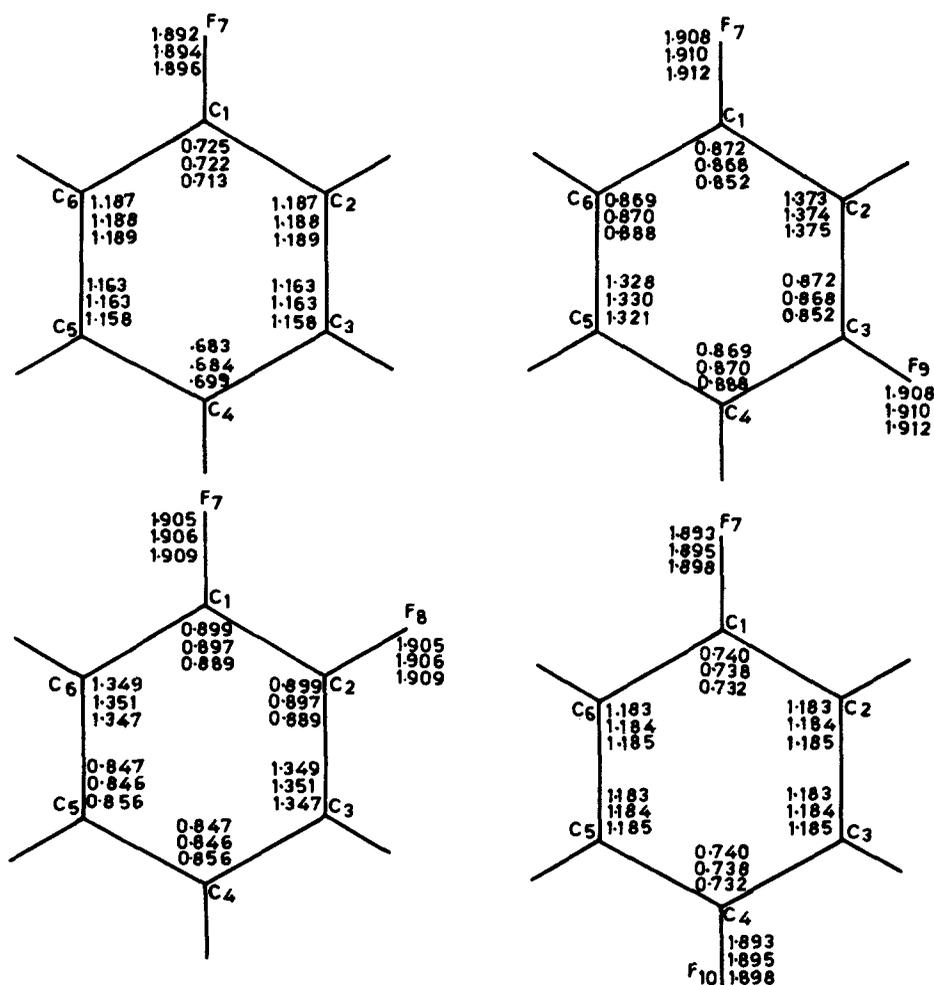

Figure 2. Redistribution of charges in the π orbitals at various atomic sites after exciting an electron from HOMO to LUMO (other orbitals are unaffected). The values by the side of each atom are obtained by the 4-31G (top), the 6-31G (middle) and the 6-31G* (bottom) methods.

However, the increase in the *ortho* position is less than that at the *meta* position. This *meta* directing features of fluorine in the excited state obtained by exciting an electron from HOMO to LUMO is found in all the three *ab initio* methods. Similar suggestions have been made (Del Bene and Jaffe 1968) on a large number of substituted benzenes using the CNDO/2 method. This suggests that certain reactions may proceed through excited states.

The π-orbital charges on the fluorine atoms and carbon atoms attached to the substituent in these molecules decrease from their ground state values. The difference between the two π-orbital charges on the fluorine and the carbon atoms attached to substituents are in the order *mono > para > ortho > meta*. The redistribution of the π-charge on the fluorine atom indicates that the π-electron donating capacity of the fluorine atom is more pronounced in such excitations and also that the carbon at the *meta* position in MFB is more populated.

4. Concluding remarks

The present study completes our MO calculations on mono- and difluorobenzenes. A detailed comparison of the results of different semi-empirical (both π-electrons and all valence electrons approximation) methods with the *ab initio* procedure suggests the same trend for the electronic properties of aromatic systems. However, the latter should be applied in order to explore the finer details of their chemical and spectroscopic properties.

References

Binkley J S, Frisch M, Raghavachari K, Defrees D, Schlegel H B, Whiteside R, Fluder E, Seegar R and Pople J A 1983 Gaussian 82, Release A, Department of Chemistry, Carnegie Mellon University, Pittsburg
Binkley J S, Whitehead R A, Hariharan P C, Seegar R, Pople J A, Hehre W J and Newton M D 1977 QCPE Program No. 368, Gaussian 76, Department of Chemistry, Indiana University, Bloomington, IN 47405, USA
Binning R C and Sando K M 1980 *J. Am. Chem. Soc.* **9** 2948
Boggs J E, Pang F and Pulay P 1982 *J. Comput. Chem.* **3** 344
Brolsfond R, Harris P V and Price 1960 *Proc. R. Soc.* **A258** 459 WC
Clementi E 1967 *J. Chem. Phys.* **46** 4731, 4737
Dekowalewski D G, Kokeritz P and Selen H H 1959 *J. Chem. Phys.* **31** 1438
Del Bene J and Jaffee H H 1968 *J. Chem. Phys.* **49** 1221
Ditchfield R, Hehre W J and Pople J A 1971 *J. Chem. Phys.* **54** 724
Doraiswamy S and Sharma S D 1983 *J. Mol. Struct.* **94** 63
Hariharan P C and Pople J A 1973 *Theor. Chim. Acta* **28** 213
Hehre W J, Ditchfield R and Pople J A 1972a *J. Chem. Phys.* **56** 2257
Hehre W J, Radom L and Pople J A 1972b *J. Am. Chem. Soc.* **5** 1496
Kaufman J J 1979 *Int. J. Quantum Chem.* **15** 221

Misra P C 1970 *Semi-empirical molecular orbital calculations on some substituted benzenes* Ph.D. thesis, Department of Physics, Banaras Hindu University, Varanasi, India

Misra P C and Rai D K 1970 *J. Mol. Struct.* **6** 246

Misra P C and Rai D K 1972 *Int. J. Quantum. Chem.* **6** 47

Morrison J D and Nicholson A J 1952 *J. Chem. Phys.* **20** 1021

Nagi-Felsobuki E V, Topson R W, Pollack S and Taft R W 1982 *J. Mol. Struct.* **88** 255

Nygaard L, Ridby H, Lykke H R, Rastrup A J and Sorensen G O 1967 *Spectrochim. Acta* **A23** 2813

Pople J A and Beveridge D L 1970 *Approximate molecular orbital theory* (New York: McGraw-Hill)

Pople J A and Bothner-by A A 1965 *J. Chem. Phys.* **42** 1339

Prettre C G and Pullman A 1968 *Theor. Chim. Acta* **9** 279

Yadav J S 1973 *Molecular orbital study of electronic structure, spectra and excited state geometry of some substituted benzenes* Ph.D. thesis, Department of Physics, Banaras Hindu University, Varanasi, India

Yadav J S, Misra P C and Rai D K 1972a *J. Mol. Struct.* **13** 253

Yadav J S, Misra P C and Rai D K 1972b *J. Mol. Struct.* **13** 311

Yadav J S, Misra P C and Rai D K 1973a *Mol. Phys.* **26** 193

Yadav J S, Misra P C and Rai D K 1973b *Chem. Phys. Lett.* **29** 445

Yadav J S, Misra P C and Rai D K 1975 *Chem. Phys. Lett.* **37** 129