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ARTICLE *in* JOURNAL OF MOLECULAR STRUCTURE THEOCHEM · OCTOBER 2000

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Lowest singlet excited state geometries, rotational constants and molecular electrostatic potentials of some substituted benzenes: an ab initio study

D.M. Upadhyay, M.K. Shukla, P.C. Mishra*

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

Received 23 August 1999; accepted 25 February 2000

Abstract

Ground and lowest singlet excited state geometries of certain substituted benzenes (fluorobenzene, chlorobenzene, *p*-difluorobenzene, *p*-dichlorobenzene, *p*-fluorochlorobenzene and aniline) were optimized using the ab initio RHF procedure employing the 6-31+G* basis set. The calculations were also carried out using the 6-311++G** basis set for two molecules. Excited states were generated using configuration interaction involving singly excited configuration (CIS). The calculated lowest singlet transition energies of the molecules agree with experimental ones satisfactorily. It is found that our calculations reproduce the ground and excited state rotational constants A, B and C of the molecules obtained from high-resolution spectroscopy quite well. Excited state geometries of the molecules have not been determined experimentally precisely but certain approximate estimates of the changes in bond lengths and bond angles consequent to excitation are available in the literature. There is a satisfactory agreement between these and our calculated changes in ring bond lengths and bond angles of the molecules consequent to excitation. Studies of excited state molecular electrostatic potential (MEP) maps are scarce in the literature. Our study of ground and excited state MEP maps of the molecules has revealed several interesting features some of which, e.g. the *ortho*, *para* directing property of the substituents in the ground state, are in agreement with experiment. It is indicated that reactions at the *ortho*, *para* positions in the ground state would take place in planes located much above the ring planes and there is an appreciable modification in this respect following excitation of the molecules. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Excited states; Molecular electrostatic potentials; Ab initio calculations; Excited state geometries; Electronic spectra

1. Introduction

An experimental study of excited state geometries of molecules requires rotational analyses of their electronic absorption or fluorescence excitation spectra at high resolution followed by interpretation of the observed changes in rotational constants in terms of changes in molecular geometry consequent

to excitation [1]. This approach would lead to unambiguous results for excited state geometries of highly symmetric molecules like benzene where there are only three geometrical parameters to be determined but for asymmetric polyatomic molecules, it involves many difficulties. The basic problem in the study of molecules of low symmetry is that the number of bond lengths, bond angles and dihedral angles to be determined is usually much larger than the number of available conditions in terms of changes of rotational constants under excitation. To

* Corresponding author. Fax: + 91-542-317468.

E-mail address: pcmishra@banaras.ernet.in (P.C. Mishra).

overcome this difficulty, one would be required to study rotational spectra of a sufficiently large number of isotopically substituted molecules, which is a difficult job. This problem becomes formidable and almost impossible to solve for complex heterocyclic or biologically important molecules, the rotational or even vibrational details in the electronic spectra of which cannot be resolved satisfactorily. However, knowledge about the excited states of many such molecules is important from the points of view of photophysics, photochemistry and photobiology. Therefore, alternative approaches which can be helpful in the study of excited state molecular geometries and properties need to be developed and evaluated. Ab initio molecular orbital theory can serve as a universally applicable technique to study not only excited state geometries of molecules but also other excited state properties like dipole and higher electrical moments simultaneously. In dealing with excited states of large molecules, configuration interaction involving single electron excitations (CIS) is frequently used [2]. Other methods to study excited states of molecules using ab initio calculations include multireference configuration interaction (MRCI) [3], complete active space method (CAS) [4], coupled cluster theory [5] etc. but calculations using these methods for complex molecules are comparatively more difficult than those using CIS. Therefore, it is desirable that usefulness of the CIS approach to study excited states of molecules be evaluated rigorously. Many calculations using CIS have already appeared in the literature and in most cases this method has yielded good results [2,6–9]. For benzene and its derivatives, the CIS approach underestimates the splitting between the lowest two singlet excited states but the properties of the two individual states may still be described by it, at an approximate level, satisfactorily. This, however, has not been tested thoroughly earlier. In order to evaluate reliability of the CIS method for calculating lowest singlet excited state geometries, we have applied it to the excited states of some substituted benzenes since experimentally determined ground and excited rotational constants and some approximate estimates about the excited state geometries of these molecules are available [1]. Using bond order bond length relationships and vertical π -electron excitation calculations, some approximate changes in the molecular geometries of

some substituted benzenes were obtained long back [10]. It is desirable that this aspect be studied using excited state geometry optimization at the ab initio level, and particularly, it is desirable to examine if the CIS procedure yields satisfactory results in this context. Molecular electrostatic potential (MEP) maps of molecules are found to be very useful with regard to the description of long range intermolecular interactions involving them e.g. hydrogen bonding [11–13]. While there are numerous studies on ground state MEP maps of molecules including those dealing with drug design [12,13], studies of excited state MEP maps are scarce. The *ortho*, *para* directing property of certain substituents e.g. the substitution of fluorine in benzene, was explained earlier on the basis of calculated net charges [10]. It should be possible to explain this aspect of molecules in a much better way using MEP mapping. In this work, we aim to study the ground and lowest singlet excited state geometries, rotational constants and MEP maps of some substituted benzenes. These aspects of the higher electronic transitions of the molecules will, however, not be discussed here.

2. Method of calculations

Ground state molecular geometries were optimized at the ab initio SCF level. Excited states were generated using the CIS procedure, starting with the ground state geometry and subsequently excited state molecular geometries, were also optimized. Vibrational frequency analysis was carried out in all the cases in order to ensure that the optimized geometries really corresponded to total energy minima. The 6-31+G* basis set was employed in all the cases while for two cases, for reasons explained in Section 3, additional calculations were also carried out using the 6-311++G** basis set. Transition energies were calculated as vertical energy differences from the optimized ground state (denoted by ΔE^{gv}) and these were suitably scaled for convenience of comparison with experimental results. Transition energies were also calculated as differences of total energies of the separately optimized ground and excited states (denoted by ΔE^{ge}). MEP values were computed at a large number of points inside a cube enclosing a given molecule using continuously distributed charges

Table 1

Calculated and observed lowest singlet transition energies (eV) and oscillator strengths of substituted benzenes. The basis set used was 6-31+G*, unless otherwise specified. Scaled transition energies are given in parentheses

Molecule	Calc. vert. excit. ener. from ground state (ΔE^{gv})	Calc. excit. ener. using opt. gr. and excit. states (ΔE^{ge})	Oscillator strength corresponding to		Experiment ^a	
			(ΔE^{gv})	(ΔE^{ge})	Exc. ener.	Osc. str.
Fluoro-benzene	6.19 (4.62) 6.16 ^b	5.92 (4.47) 5.88 ^b	0.0191	0.028	4.69	0.0072
Chloro-benzene	6.11 (4.56)	5.86 (4.37)	0.0005	0.0017	4.59	0.0012
<i>p</i> -Difluoro-benzene	6.14 (4.58) 6.10 ^b	5.80 (4.33) 5.75 ^b	0.0614	0.0833	4.57	0.0204
<i>p</i> -Dichloro-benzene	6.03 (4.49)	5.74 (4.28)	0.0022	0.0062	4.43	0.0048
<i>p</i> -Fluoro-chloro-benzene	6.09 (4.54)	5.73 (4.28)	0.0220	0.0367	4.50	
Aniline	5.77 (4.31)	5.07 (3.80)	0.0614	0.0000	4.22	0.0224

^a From Refs. [15,16].

^b The basis set used in these cases was 6-311++G**.

given by the corresponding SCF or the SCF-CIS wavefunction. These MEP data were analyzed to locate the minima or lowest MEP values and to plot isopotential contours. All the calculations were performed using the Windows version of the GAUSSIAN 94 program [14], except those of analysis of MEP data and plotting of MEP maps which were carried out using a program developed locally.

3. Results and discussion

3.1. Transition energies

The calculated scaled and unscaled lowest singlet transition energies (ΔE^{gv} and ΔE^{ge}) of fluorobenzene (FB), chlorobenzene (ClB), *p*-difluorobenzene (PFB), *p*-dichlorobenzene (PClB), *p*-fluorochlorobenzene (PFCIB) and aniline are presented in Table 1. The former of these transition energies (ΔE^{gv}) would correspond to peaks in electronic absorption spectra while the latter (ΔE^{ge}) would, under the assumption of equal zero point energies of the ground and excited states, correspond to (0,0) bands of the absorption or fluorescence transitions. We find that both the types of calculated transition energies (ΔE^{gv} and ΔE^{ge}) are appreciably larger than the observed ones [15,16]. We may compare the qualitative trends in the calculated and observed transition energies or, for convenience in this context, scale down the calculated

transition energies suitably, as done earlier [17]. However, if scaling is adopted, it should be noted that the actual calculated transition energies are differences between the excited and ground state total energies of molecules, and the optimized molecular geometries, vibrational frequencies and other molecular properties are consistent only with the corresponding total energies. Thus transition energies obtained as scaled total energy differences have to be taken cautiously. We used scaling with this understanding and found that a scaling constant equal to 1.34 was suitable to scale down the computed lowest singlet transition energies (ΔE^{gv}) in all the cases uniformly. The scaled calculated lowest singlet transition energies (ΔE^{gv}) agree with the observed ones satisfactorily (rms error ~ 0.16 eV). The transition energies obtained as differences of total energies corresponding to the optimized ground and excited state geometries (ΔE^{ge}) are somewhat less than the corresponding vertical ones (ΔE^{gv}). However, the trend found in going from one molecule to another in ΔE^{gv} is similar to that in ΔE^{ge} . If the latter total energy differences (ΔE^{ge}) are compared with the experimental ones and if scaling is used, a different scaling constant would be required than the one mentioned above. As shown by two examples, i.e. FB and PFB (Table 1), we note that the calculated transition energies and oscillator strengths do not change appreciably when the basis set is enhanced from 6-31+G* to 6-311++G**. However, as we

Table 2

Calculated and observed ground and lowest singlet excited state rotational constants of substituted benzenes (cm^{-1}) (the basis set used was 6-31+G* except for the constants given in parentheses for which the 6-311++G** basis set was used)

Molecule	State	Rot. const. A			Rot. const. B			Rot. const. C		
		Calc.	Obs.	%Error	Calc.	Obs.	%Error	Calc.	Obs.	%Error
Fluoro-benzene	S ₀	0.1917 (0.1923)	0.18892	1.4 (1.8)	0.0869 (0.0872)	0.08575	1.3 (1.7)	0.0598 (0.0600)	0.05897	1.4 (1.8)
	S ₁	0.1822 (0.1827)	0.1777	2.5 2.8	0.0864 (0.0868)	0.08474	2.0 2.4	0.0586 (0.0588)	0.05738	2.2 2.5
Chloro-benzene	S ₀	0.1920	0.18923	1.6	0.0527	0.05260	0.2	0.0413	0.04115	0.5
	S ₁	0.1842	0.1797	2.5	0.0525	0.05230	0.4	0.0408	0.04051	0.8
Aniline	S ₀	0.1901	0.18738	1.5	0.0873	0.08652	0.9	0.0599	0.05928	1.1
	S ₁	0.1824	0.1762	3.4	0.0905	0.08788	3.0	0.0605	0.05869	3.1
<i>p</i> -Difluoro benzene	S ₀	0.1913 (0.1920)	0.1881	1.7 2.1	0.0482 (0.0484)	0.04764	1.3 1.7	0.0385 (0.0387)	0.03801	1.3 1.7
	S ₁	0.1803 (0.1809)	0.1762	2.3 2.6	0.0488 (0.0490)	0.04787	1.9 2.4	0.0384 (0.0386)	0.03765	2.0 2.4
<i>p</i> -Dichloro-Benzene	S ₀	0.1919	0.1887	1.7	0.0224	0.02236	0.01	0.0200	0.01999	0.2
	S ₁	0.1830	0.1782	2.7	0.0225	0.02253	0.05	0.0201	0.02000	0.3
<i>p</i> -Fluoro-chloro-benzene	S ₀	0.1916	0.1884	1.7	0.0321	0.03190	0.5	0.0275	0.02728	0.7
	S ₁	0.1815	0.1772	2.4	0.0324	0.03215	0.9	0.0275	0.02721	1.1

shall discuss, this change of basis set was required for satisfactory excited state geometry optimization in PFB. The calculated and observed oscillator strengths (Table 1), as usual, do not agree quantitatively but they agree qualitatively satisfactorily. Further, the calculated as well as the observed oscillator strengths are all small which is reminiscent to the fact that the corresponding transition in benzene is forbidden.

3.2. Rotational constants

The calculated and observed ground (S_0) and lowest singlet excited (S_1) state rotational constants of FB, CIB, PFB, PCIB, PFCIB and aniline are presented in Table 2. We find that the observed ground and excited state rotational constants of the molecules [16,18–23] are reproduced by theory fairly accurately. We make the following specific observations regarding differences between the calculated and observed rotational constants. (a) Usually the errors in excited state rotational constants are more than those in the corresponding ground state rotational constants, the largest errors in the ground and excited state rotational constants being less than 2 and 3.5%, respectively. (b) The errors in the rotational constants of FB and PFB obtained with the enhanced basis set (6-311++G**) are more than those in the rotational constants

obtained with the comparatively smaller basis set (6-31+G*). It can be understood in terms of the fact that the observed rotational constants correspond to zero-point structures [1], while the calculated ones correspond to potential energy surface minima, and also it appears that there is some sort of cancellation of errors when the smaller basis set is used, in comparison to the situation when the higher basis set is used. (c) The largest error in the excited state rotational constants is for the excited state of aniline but among the ground state rotational constants of all the molecules, the error is largest for PFB. (d) Usually, percentage errors are less in the rotational constants B and C than those in the constant A. (e) In FB and CIB, all the rotational constants A, B and C decrease both according to theory and experiment in going from the ground state to the excited state. However, in each of aniline and the three disubstituted benzenes, A decreases while B increases and C increases or decreases following excitation of the molecule.

3.3. MEP maps

The ground and excited state MEP values near the different sites of the molecules obtained using the 6-31+G* basis set are presented in Table 3. The MEP patterns obtained for FB and PFB using the

Table 3

MEP values near the substituted benzenes obtained using the 6-31+G* basis set

Molecule	State	MEP value (kcal/mol)	Minimum or lowest ^a	Height ^b (Å), near atom	Angle (ϑ) (°) ^c
Fluoro-benzene	S ₀	−23.3	Lowest	0.0, F	82°
		−24.7	Minimum	1.02, F	Single
		−12.7	Lowest	1.95, C4	
		−11.1	Lowest	1.95, C2, C6	
	S ₁	−17.1	Lowest	0.0, F	73°
		−18.0	Minimum	1.05, F	Single
		−10.0	Lowest	2.01, C2C3 bond	
		−7.7	Lowest	2.01, C4	
Chloro-Benzene	S ₀	−12.6	Lowest	0.0, Cl	126°
		−16.7	Minimum	1.80, Cl	Single
		−11.3	Lowest	1.92, C4	
		−10.7	Lowest	1.92, C2, C6	
	S ₁	−8.3	Lowest	0.0, Cl	126°
		−11.4	Minimum	1.92, Cl	Single
		−7.7	Lowest	2.04, C4	
		−9.3	Lowest	1.98, C2C3 bond	
Aniline	S ₀	0.5	Positive	0.0	Single
		−58.1	Minimum	1.32, N	Single
		−23.2	Lowest	1.80, C4	
		−22.3	Lowest	1.80, C2, C6	
	S ₁	−8.0	Lowest	0.0, H(NH2)	121°
		−19.4	Minimum	2.8, N	Single
		−3.5	Lowest	4.01, C2C3 bond	
<i>p</i> -Difluoro-benzene	S ₀	−19.8	Lowest	0.0, F	77°
		−21.3	Minimum	1.05, F	Single
		−5.3	Lowest	1.92, C2C3 bond	
	S ₁	−12.6	Lowest	0.0, F	92°
		−13.4	Minimum	1.05, F	Single
		−6.3	Lowest	1.92, C2C3 bond	
<i>p</i> -Dichloro-benzene	S ₀	−8.2	Lowest	0.0, Cl	130°
		−12.4	Minimum	1.83, Cl	Single
		−3.1	Lowest	1.83, C2C3 bond	
	S ₁	−4.7	Lowest	0.0, Cl	130°
		−7.5	Minimum	1.95, Cl	Single
		−5.8	Lowest	2.04, C2C3 bond	
<i>p</i> -Fluoro-chloro-benzene	S ₀	−18.3	Lowest	0.0, F	87°
		−9.1	Lowest	0.0, Cl	110°
		−19.6	Minimum	1.02	Single
		−13.6	Lowest	1.83, Cl	
		~−3.4	Contour ^d	1.89, C2C3 bond	
	S ₁	−13.1	Lowest	0.0, F	96°
		~−3.3	Contour ^d	0.0, Cl	132°
		−13.9	Minimum	1.05	Single
		−6.4	Lowest	1.95, F, Cl	
		−6.8	Lowest	1.95, C2, C5	

^a When the MEP is: (i) negative and lowest in a given plane in the given regions, and (ii) its magnitude increases in going to other planes or heights from the molecular plane than the given one, it is called a minimum. However, when the condition (i) is satisfied but not (ii), the MEP is said to be lowest.

^b Height of the plane in question measured with respect to the molecular plane. In those cases where the MEP feature is located above the molecular plane, the projection of the feature is considered in specifying the atom near which the feature is located.

^c The angle ϑ is given for the equivalent lowest MEP values. For MEP minima, such an angle would be zero, and, therefore, for them, the word 'single' is used. C2C3 bond implies above the centers of the C2C3 and C5C6 bonds.

^d A contour of the given MEP value passes by the specified region. No minimum or lowest MEP could be located.

6-311++G** basis set were similar to those obtained using the 6-31+G* basis set. The MEP maps for FB and PFB obtained using only the 6-31+G* basis set are presented here since this basis set was used in all the other cases also due to which a meaningful quantitative comparison between the MEP values around the different molecules can be made. In the following discussion, the term ‘minimum’ of MEP would be used when the MEP is found to be negative and minimum by analysis of MEP data in different planes above or below the molecular ring plane. The term ‘lowest’ MEP value or ‘localized’ negative MEP region would be used to describe the situation where the MEP is lowest negative in some specific region in a given plane lying above or below the molecular plane, and the magnitude of MEP while it continues to be negative, does not decrease in going further above and below the given plane. The MEP maps of the molecules in different planes are presented as figures and discussed so that a direct comparison between them can be made visually. We computed the MEP map of benzene also as a reference case. We make the following observations from the computed MEP results for benzene and substituted benzenes (Table 3).

(i) In the ground state of benzene, the MEP

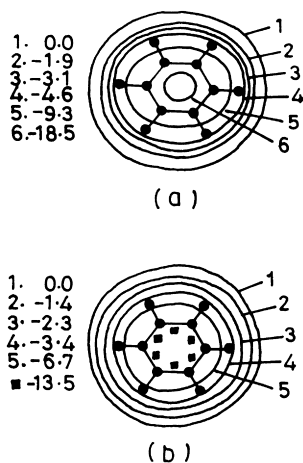


Fig. 1. (a) Ground state MEP map of benzene projected in the molecular plane showing the MEP minimum in the form of a circular ring located at a height of 1.84 Å from the plane. (b) Excited state MEP map of benzene projected in the molecular plane showing six distinct MEP minima located at a height of 1.98 Å from the molecular plane.

minimum computed using the 6-31+G* basis set occurs at a height of about 1.84 Å above the molecular plane in the form of a circular ring, the minimum MEP value being -18.5 kcal/mol (Fig. 1a). In an earlier work [24], in the ground state of benzene, when the 6-31G** basis set was used, the minimum MEP was reported to be -20.17 kcal/mol at a height of 1.69 Å and the appearance of the MEP minimum region was similar to that found here i.e. as a circular ring inside the benzene ring. In fact, there are only six MEP minima near the CC bond centers inside the benzene ring [24] but the MEP values at the nearby points over a circular ring are quite close, due to which the MEP minimum region appears in the form of a circular ring. The distance of the MEP minimum region from the CC bond centers as obtained using the 6-31+G* basis set was about 0.53 Å and a similar value for this distance was found earlier [24,25]. In going from the ground to the lowest singlet excited state of benzene, the following differences in the MEP pattern of benzene as calculated using the 6-31+G* basis set were found (a). The MEP minimum occurs at a height of about 1.98 Å from the molecular plane in the excited state, and thus the height of the minimum from the molecular plane is increased appreciably consequent to excitation. (b) The minimum MEP value in the excited state obtained using the 6-31+G* basis set was found to be -13.4 kcal/mol the magnitude of which is much less than that of the ground state minimum MEP value. (c) There are six disconnected distinct equivalent MEP minima near the CC bond centers inside the ring in the excited state of benzene (Fig. 1b) instead of a circular ring. The distance of each excited state MEP minimum from the corresponding CC bond center as obtained using the 6-31+G* basis set is almost half of that in the ground state (Fig. 1b).

(ii) In FB, the MEP minimum was found at the height of about 1.02 Å from the molecular plane, the projection of which in the molecular plane lies near the fluorine atom (Fig. 2a) (Table 3). In the molecular plane, there are two equivalent lowest MEP values near the fluorine atom (Fig. 2b), the difference between any of these MEP values and the minimum MEP value found at the height of about 1.02 Å being about 1.4 kcal/mol. The angle ABA' (henceforth denoted by ϑ), where A and A' represent the locations of the two equivalent lowest MEP values near the

fluorine atom in the molecular plane and B represents the location of the fluorine atom of FB in the molecular plane, was found in the ground state to be around 82° . In the lowest singlet excited state of FB also, the MEP minimum occurs at a height very close to that in the ground state but the excited state minimum MEP magnitude is reduced by about 6.7 kcal/mol in comparison to that in the ground state (Fig. 2c). In the excited state, in the molecular plane, the MEP

pattern is similar to that in the ground state, the lowest excited state MEP magnitude being less than that of the corresponding minimum by about 1 kcal/mol (Fig. 2d). The angle ϑ in the excited state of FB was found to be about 73° i.e. about 9° less than the ground state value. Further, in the ground state of FB, localized negative MEP regions are found inside the ring near the *ortho* and *para* carbon atoms at a height of about 1.95 \AA from the molecular plane with MEP

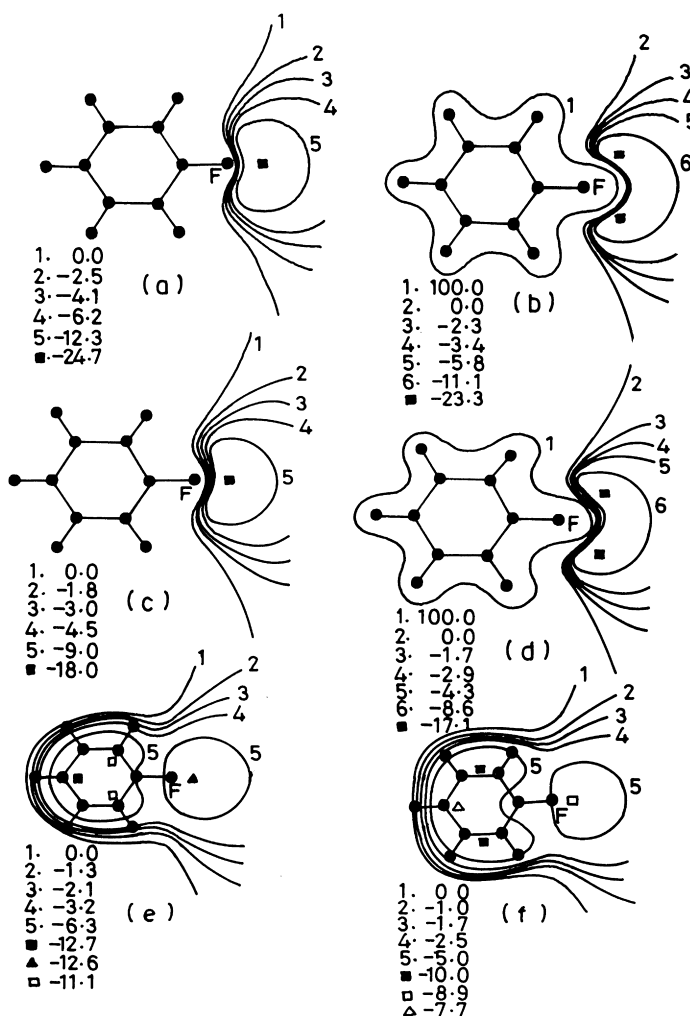


Fig. 2. (a) Ground state MEP map of fluorobenzene projected in the molecular plane, the MEP minimum being located at a height of 1.02 \AA from the plane. (b) Ground state MEP map of fluorobenzene in the molecular plane. (c) Excited state MEP map of fluorobenzene projected in the molecular plane, the MEP minimum being located at a height of 1.05 \AA from the plane. (d) Excited state MEP map of fluorobenzene in the molecular plane. (e) Ground state MEP map of fluorobenzene projected in the molecular plane, the MEP features corresponding to a height of 1.95 \AA from the plane. (f) Excited state MEP map of fluorobenzene projected in the molecular plane, the MEP features corresponding to a height of 2.01 \AA from the plane.

magnitudes which are close to half of the corresponding MEP minimum (Fig. 2e). These results conform to the well known *ortho*, *para* directing property of fluorine for electrophiles and show that the reactions at the *ortho* and *para* positions in FB would not take place in the molecular plane but in a region appreciably away from the molecular plane. In the excited state of FB, at a height of about 2 Å from the molecular plane, a lowest negative MEP region occurs almost above the centers of the C2C3 and C5C6 bonds and also there is a localized negative MEP

region near the *para* carbon atom (Fig. 2f). Thus though the *para*-directing property is partly retained by the fluorine substituent, its *ortho*-directing property seems to be lost consequent to excitation.

In PFB, in the ground state, two equivalent MEP minima occur at a height of about 1.05 Å from the molecular plane the projections of which in the molecular plane lie near the fluorine atoms (Fig. 3a) (Table 3). In the molecular plane of PFB in the ground state, two equivalent lowest MEP regions occur near each of the fluorine atoms the angle θ being about 77°

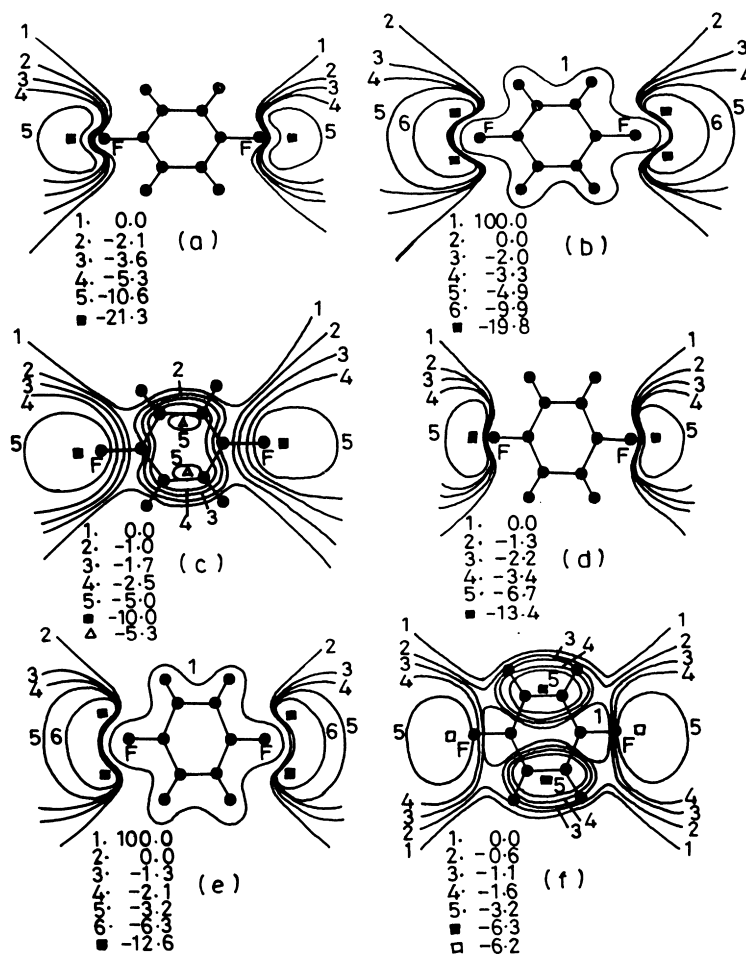


Fig. 3. (a) Ground state MEP map of *p*-difluorobenzene projected in the molecular plane, the MEP minimum being located at a height of 1.05 Å from the plane. (b) Ground state MEP map of *p*-difluorobenzene in the molecular plane. (c) Ground state MEP map of *p*-difluorobenzene projected in the molecular plane, the MEP features corresponding to a height of 1.92 Å from the plane. (d) Excited state MEP map of *p*-difluorobenzene projected in the molecular plane, the MEP minimum being located at height of 1.05 Å from the plane. (e) Excited state MEP map of *p*-difluorobenzene in the molecular plane. (f) Excited state MEP map of *p*-difluorobenzene projected in the molecular plane, the MEP features corresponding to a height of 1.92 Å from the plane.

and the magnitudes of these MEP values differing from the minima by about 1.5 kcal/mol (Fig. 3b). At a height of about 1.92 Å from the molecular plane of PFB in the ground state, a localized negative MEP region occurs above the C2C3 and C5C6 bond centers (Fig. 3c). Qualitatively similar MEP features are found in the excited state of PFB also as in the ground

state but there are significant quantitative differences between the two sets of results (Fig. 3c–f). Thus the minimum MEP magnitude in the excited state of PFB is less than that in the ground state by about 8 kcal/mol and angle ϑ is larger in the excited state by about 15° than the ground state value (Fig. 3d and e). Further, in the excited state of PFB, equivalent

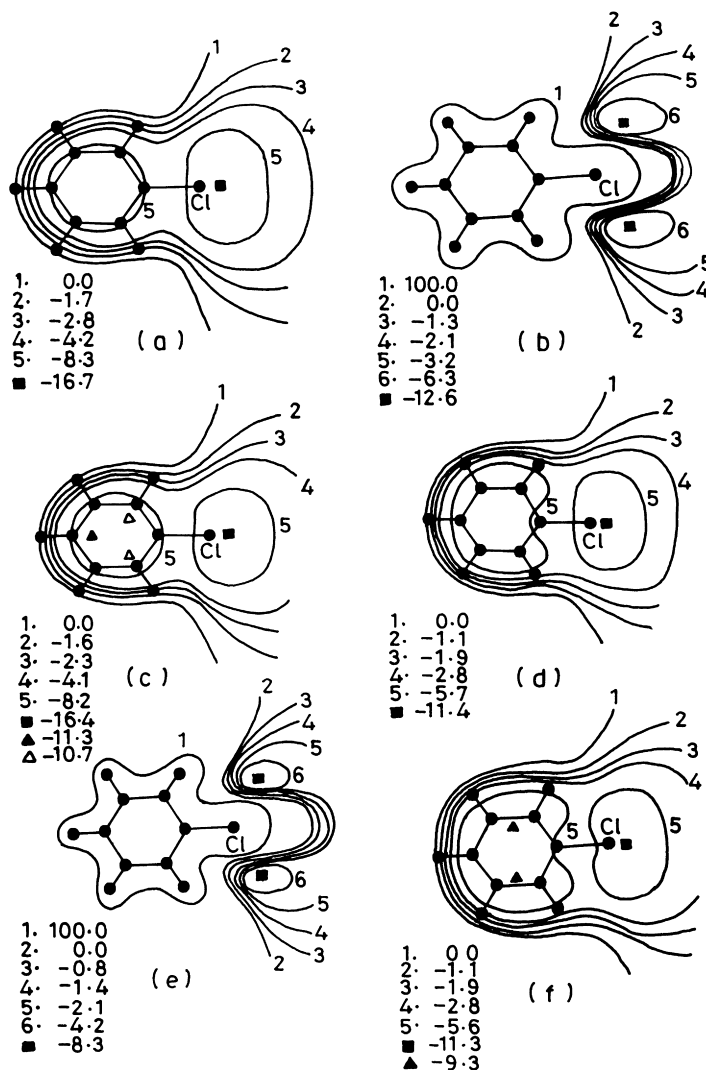


Fig. 4. (a) Ground state MEP map of chlorobenzene projected in the molecular plane, the MEP minimum being located at a height of 1.80 Å from the plane. (b) Ground state MEP map of chlorobenzene in the molecular plane. (c) Ground state MEP map of chlorobenzene projected in the molecular plane, the MEP features corresponding to a height of 1.92 Å from the plane. (d) Excited state MEP map of chlorobenzene projected in the molecular plane, the MEP minimum being located at height of 1.92 Å from the plane. (e) Excited state MEP map of chlorobenzene in the molecular plane. (f) Excited state MEP map of chlorobenzene projected in the molecular plane, the MEP features corresponding to a height of 1.98 Å from the plane.

lowest negative MEP regions are located above the C2C3 and C5C6 bond centers at a height of about 1.92 Å each, the MEP magnitude being close to that near the fluorine atom at the same height (Fig. 3f).

(iii) In the ground state of CIB, the MEP minimum occurs at a height of 1.8 Å the projection of which in the molecular plane lies near the chlorine atom (Fig. 4a) (Table 3). This height of MEP minimum is much larger than that found in FB and, moreover, the minimum MEP magnitude in CIB is much less than that in FB. In the molecular plane of CIB, there are

two equivalent lowest negative MEP regions near the chlorine atom in the ground state, the magnitudes of the MEP values being about 4 kcal/mol less than that of the corresponding MEP minimum (Fig. 4b). At a height of about 1.92 Å from the molecular plane in the ground state, a localized negative MEP region occurs near the C4 atom while another similar region at almost the same height occurs near the C2 atom (Fig. 4c). These localized negative MEP regions conform to the *ortho*, *para* directing property of chlorine and show that the reactions at the *ortho*,

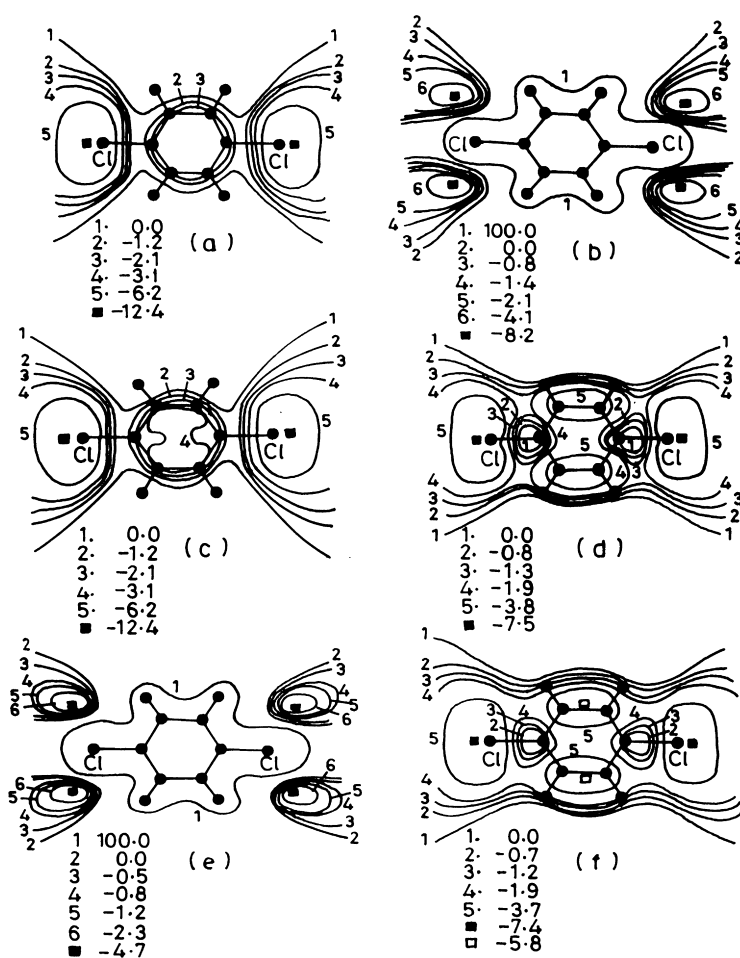


Fig. 5. (a) Ground state MEP map of *p*-dichlorobenzene projected in the molecular plane, the MEP minimum being located at a height of 1.83 Å from the plane. (b) Ground state MEP map of *p*-dichlorobenzene in the molecular plane. (c) Ground state MEP map of *p*-dichlorobenzene projected in the molecular plane, the MEP features corresponding to a height of 1.83 Å from the plane. (d) Excited state MEP map of *p*-dichlorobenzene projected in the molecular plane, the MEP minimum being located at height of 1.95 Å from the plane. (e) Excited state MEP map of *p*-dichlorobenzene in the molecular plane. (f) Excited state MEP map of *p*-dichlorobenzene projected in the molecular plane, the MEP features corresponding to a height of 2.04 Å from the plane.

para sites would take place in a region appreciably away from the molecular plane of CIB. The height of the MEP minimum in CIB from the molecular plane is about 0.1 Å higher in the excited state than that in the ground state and its projection in the molecular plane lies near the chlorine atom (Fig. 4d). The angle ϑ in the molecular plane of CIB was found to be about 126° in both the ground and excited states, the magnitude of the excited state MEP value being about 4.3 kcal/mol less than that of the ground state value (Fig. 4e). In the excited state of CIB, at a height of about 1.98 Å from the molecular plane, a localized negative MEP region occurs near the center of each of the C2C3 and C5C6 bonds (Fig. 4f), while another localized negative MEP region occurs near the C4 atom at a height of about 2.04 Å from the molecular plane (Table 3). This result is similar to that found in FB and shows that the *para*-directing property is retained by the chlorine substituent but its *ortho*-directing property appears to be lost consequent to excitation.

In PCIB, the ground state MEP minimum occurs at a height of about 1.83 Å from the molecular plane the projection of which in the plane lies near each chlorine atom, the MEP magnitude being about 4.3 kcal/mol less than that in CIB (Fig. 5a) (Table 3). There are two equivalent lowest MEP regions near each chlorine atom, the angle ϑ being about 130° and the MEP magnitudes being less than the corresponding minimum by 4.2 kcal/mol (Fig. 5b) in the ground state of PCIB. At the height of about 1.83 Å from the molecular plane in this case, a negative MEP contour passes through the region lying above both the C2C3 and C5C6 bonds with a MEP magnitude which is much smaller than the corresponding MEP minimum (Fig. 5c). In the excited state of PCIB, the MEP minimum occurs at a height of about 1.95 Å from the molecular plane the projection of which lies near each chlorine atom, the MEP magnitude being about 5 kcal/mol less than that in the ground state (Fig. 5d). In the molecular plane of PCIB in the excited state, two equivalent lowest negative MEP regions occur near each chlorine atom with a MEP magnitude which is less than that of the excited state MEP minimum by about 2.8 kcal/mol, the angle ϑ being almost the same as that in the ground state (Fig. 5e). At a height of about 2.04 Å from the molecular plane in the excited state of PCIB, a localized negative MEP region occurs above the center of each

of the C2C3 and C5C6 bonds with a MEP magnitude which is about 1.7 kcal/mol less than that of the excited state MEP minimum (Fig. 5f). The isopotential contours in the MEP maps of the ground and excited states of PCIB in the planes, which contain the MEP minima, form quite different patterns (Fig. 5a and d).

(iv) In the ground state of PFCIB, a MEP minimum (V1) is found at a height of about 1.02 Å from the molecular plane the projection of which in the molecular plane lies near the fluorine atom and another MEP minimum (V2) is found at a height of about 1.83 Å from the molecular plane the projection of which in the molecular plane lies near the chlorine atom, the magnitude of V2 being less than that of V1 by about 6 kcal/mol (Fig. 6a(i,ii)) (Table 3). In the molecular plane, two equivalent lowest negative MEP regions occur near each of the fluorine and chlorine atoms, the angles ϑ in the two cases being about 80 and 110°, respectively, and the lowest MEP magnitude near fluorine being almost twice that near chlorine (Fig. 6b). At a height of about 1.83 Å from the molecular plane, in the ground state, a contour with the MEP value of about -3.4 kcal/mol passes nearby the C2, C3, C5 and C6 atoms (Fig. 6a(ii)). Qualitatively similar features were found in PCIB also but in PFB localized negative MEP regions occur above the C2C3 and C5C6 bonds, as discussed earlier. In the excited state of PFCIB, a MEP minimum occurs at a height of 1.05 Å above the molecular plane the projection of which lies near fluorine (Fig. 6c). In the molecular plane, in the excited state of PFCIB, two equivalent lowest negative MEP regions are located near each of the fluorine and chlorine atoms, the MEP values near the two atoms differing by about 10 kcal/mol (Fig. 6d). Further, in the excited state of PFCIB, at a height of about 1.95 Å from the molecular plane, the lowest MEP values lying near the fluorine and chlorine atoms are nearly equal while near the C2C3 and C5C6 bond centers, the magnitudes of the lowest negative MEP are only slightly different from those near the fluorine and chlorine atoms (Fig. 6e).

(v) The amino group of aniline in the ground state is pyramidal. In this case, the MEP values in the ring plane are all positive and the MEP minimum occurs at a height of 1.32 Å from the ring plane on the side on which the nitrogen atom is located (Fig. 7a) (Table 3).

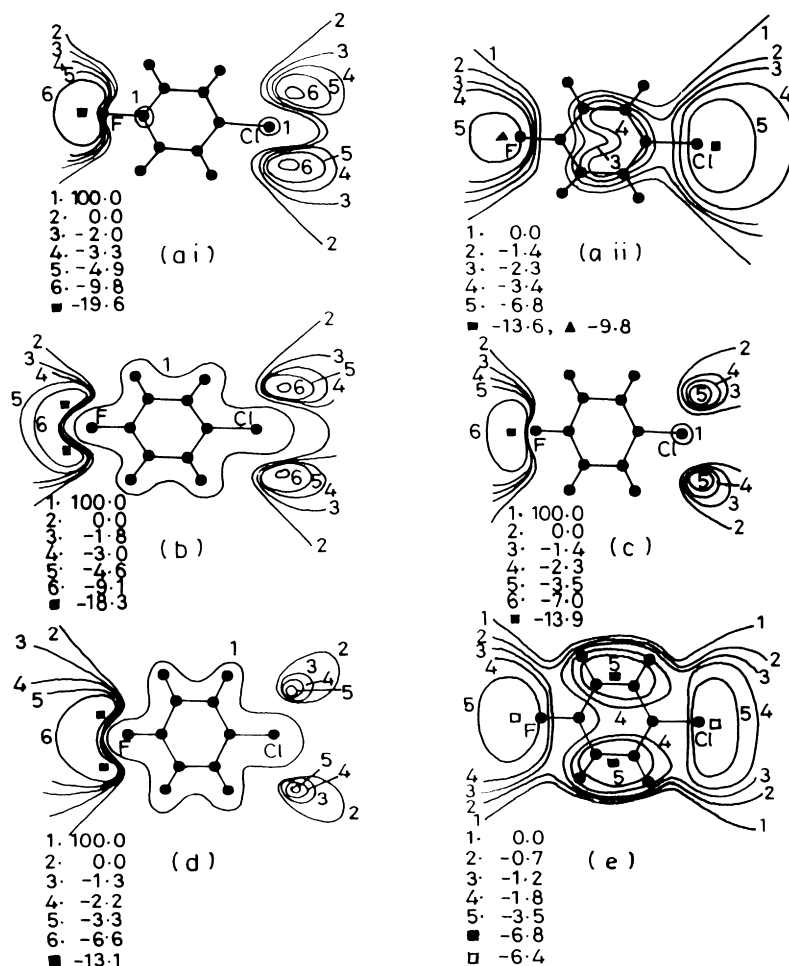


Fig. 6. (a) (i) Ground state MEP map of *p*-fluorochlorobenzene projected in the molecular plane, the MEP minimum being located at a height of 1.02 Å from the plane. (ii) Ground state MEP map of *p*-fluorochlorobenzene projected in the molecular plane, the MEP minimum being located at a height of 1.83 Å from the plane. (b) Ground state MEP map of *p*-fluorochlorobenzene in the molecular plane. (c) Excited state MEP map of *p*-fluorochlorobenzene projected in the molecular plane, the MEP minimum being located at height of 1.05 Å from the plane. (d) Excited state MEP map of *p*-fluorochlorobenzene in the molecular plane. (e) Excited state MEP map of *p*-fluorochlorobenzene projected in the molecular plane, the MEP features corresponding to a height of 1.95 Å from the plane.

The MEP values in the ring plane of aniline are all positive. In the ground state of aniline, at a height of about 1.8 Å from the ring plane, localized negative MEP regions occur near the C2, C6 and C4 atoms with appreciable MEP magnitudes (Fig. 7b). This is in conformity with the *ortho*, *para* directing property of the NH₂ group. In the excited state of aniline, the amino group is planar [16]. The MEP minimum in the excited state of this molecule lies at a height of about 2.8 Å from the ring plane almost above the nitrogen

atom and this minimum MEP magnitude is strongly reduced in comparison to that in the ground state (Fig. 7c). Interestingly, even in the ring plane in the excited state of aniline, two equivalent lowest negative MEP regions occur in the directions of the NH bonds of the amino group of the molecule (Fig. 7d).

3.4. Excited state geometries

The optimized ground and excited state bond

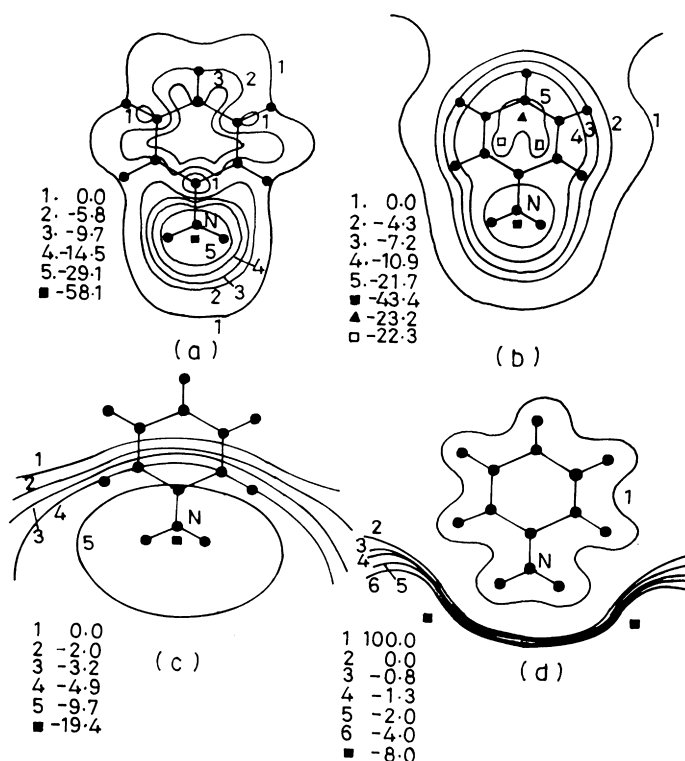


Fig. 7. (a) Ground state MEP map of aniline projected in the ring plane, the MEP minimum being located at a height of 1.32 Å from the plane. (b) Ground state MEP map of aniline projected in the ring plane, the MEP features corresponding to a height of 1.80 Å from the plane. (c) Excited state MEP map of aniline projected in the molecular plane, the MEP minimum being located at height of 2.8 Å from the plane. (d) Excited state MEP map of aniline in the molecular plane.

lengths and bond angles in all the molecules and dihedral angles for the amino group hydrogens of aniline are presented in Table 4. As discussed earlier, the ground and excited state bond lengths calculated using the 6-31+G* basis set are usually somewhat larger than those obtained using the 6-311++G** basis set. The average difference between the experimentally observed gas phase bond lengths and bond angles [26] and the calculated ones using the 6-31+G* basis set for fluorobenzene is about 0.009 Å and 0.3°, respectively, and, approximately speaking, the same is likely to be true for the other molecules also. In going from the ground to the excited state of benzene, according to experiment [27], the CC bond lengths are increased by 0.038 Å and the CH bond lengths are decreased by 0.014 Å while all the bond angles remain at 120°. According to our calculations, the CC bond lengths of benzene increase by about 0.027 Å, the CH bond lengths

decrease by about 0.003 Å and all the bond angles remain at 120° following excitation of the molecule. Thus although these calculations predict the changes in the CC and CH bond lengths of benzene consequent to excitation qualitatively in the right direction, they underestimate the changes in both the bond lengths, particularly in the CH bond lengths. The changes in CH bond lengths in all the substituted benzenes studied here consequent to excitation are underestimated in the same way as for benzene. For two fluorine-substituted molecules (FB and PFB), the calculations were carried out using two basis sets: 6-31+G* and 6-311++G** while in the other cases (CIB, PCIB, PFCIB and aniline), the calculations were performed using only the former basis set. The reason for using two basis sets for the two fluorine-substituted molecules was that when the 6-31+G* basis set was used for PFB, a slight nonplanarity was being predicted in its excited state geometry

Table 4

Ground and excited state optimized geometries of substituted benzenes (the basis set used was 6-31+G*, except for the values given in the parentheses for which the basis set used was 6-311++G**: Å and degree)

Bond length/bond angle ^a	Fluorobenzene ^b		Chlorobenzene	
	S ₀	S ₁	S ₀	S ₁
C1C2	1.379 (1.377) [1.383]	1.407 (1.406)	1.384	1.412
C2C3	1.387 (1.386) [1.395]	1.412 (1.410)	1.387	1.414
C3C4	1.388 (1.386) [1.397]	1.417 (1.415)	1.387	1.413
C2H11	1.074 (1.074) [1.081]	1.072 (1.072)	1.074	1.072
C3H12	1.075 (1.075) [1.083]	1.073 (1.072)	1.075	1.073
C4Y8	1.075 (1.075) [1.084]	1.074 (1.074)	1.075	1.074
C1X7	1.334 (1.328) [1.354]	1.319 (1.313)	1.745	1.719
C6C1C2	122.6 (122.5) [123.4]	124.2 (124.2)	121.3	122.0
C1C2C3	118.4 (118.4) [117.9]	117.6 (117.6)	119.1	118.7
C2C3C4	120.5 (120.5) [120.5]	119.6 (119.5)	120.4	119.9
C3C4C5	119.7 (119.7) [119.8]	121.5 (121.5)	119.8	120.7
X7C1C2	118.7 (118.8)	117.9 (117.9)	119.4	119.0
X7C1C6	118.7 (118.8)	117.9 (117.9)	119.4	119.0
C1C2H11	119.8 (119.8) [120.0]	119.7 (119.6)	120.1	120.1
H11C2C3	121.9 (121.8)	122.7 (122.7)	120.8	121.2
C2C3H12	119.5 (119.4)	120.3 (120.4)	119.5	119.9
H12C3C4	120.0 (120.1) [119.9]	120.1 (120.1)	120.2	120.2
	<i>p</i> -Difluorobenzene		<i>p</i> -Dichlorobenzene	
C1C2	1.379 (1.377)	1.408 (1.407)	1.384	1.411
C2C3	1.387 (1.385)	1.409 (1.407)	1.386	1.412
C3C4	1.379 (1.377)	1.408 (1.407)	1.384	1.411
C2H11	1.074 (1.074)	1.072 (1.071)	1.074	1.072
C3H12	1.074 (1.074)	1.072 (1.071)	1.074	1.072
C4Y8	1.334 (1.329)	1.315 (1.308)	1.741	1.715
C1X7	1.334 (1.329)	1.315 (1.308)	1.742	1.715
C6C1C2	122.2 (122.1)	124.8 (124.8)	120.9	122.4
C1C2C3	118.9 (118.9)	117.6 (117.6)	119.6	118.8
C2C3C4	118.9 (118.9)	117.6 (117.6)	119.6	118.8
C3C4C5	122.2 (122.1)	124.9 (124.8)	120.9	122.4
X7C1C2	118.9 (118.9)	117.6 (117.6)	119.6	118.8
X7C1C6	118.9 (118.9)	117.6 (117.6)	119.6	118.8
C1C2H11	119.9 (119.8)	119.7 (119.6)	120.2	120.2
H11C2C3	121.2 (121.2)	122.7 (122.8)	120.2	121.0
C2C3H12	121.2 (121.2)	122.7 (122.8)	120.2	121.0
H12C3C4	119.9 (119.8)	119.7 (119.6)	120.2	120.2

Table 4 (continued)

Bond length/bond angle ^a	Fluorobenzene ^b		Chlorobenzene	
	S ₀	S ₁	S ₀	S ₁
	<i>p</i> -Fluorochlorobenzene		Aniline	
C1C2	1.378	1.406	1.394	1.434
C2C3	1.387	1.409	1.386	1.365
C3C4	1.384	1.414	1.387	1.401
C2H11	1.074	1.072	1.077	1.070
C3H12	1.074	1.071	1.076	1.073
C4Y8	1.743	1.714	1.075	1.074
C1X7	1.332	1.315	1.398	1.312
X7H13			0.998	1.006
X7H14			0.998	1.006
C6C1C2	122.2	124.4	118.8	119.3
C1C2C3	118.8	117.6	120.4	119.5
C2C3C4	119.7	118.4	120.9	120.5
C3C4C5	120.9	123.0	118.7	120.7
X7C1C2	118.9	117.8	120.6	120.3
X7C1C6	118.9	117.8	120.6	120.3
C1C2H11	120.0	119.9	119.7	118.9
H11C2C3	121.3	122.5	119.9	121.7
C2C3H12	120.2	121.5	119.2	119.8
H12C3C4	120.1	120.1	120.0	119.7
C3C4Y8	119.6	118.5		
Y8C4C5	119.6	118.5		
C1X7H13			114.4	121.5
H14X7C6C1			−26.9	000.0
H14X7C1C6			155.9	180.0

^a X and Y stand for the substituents F, Cl, N(NH₂) or H in general. In *p*-fluorochloro-benzene, X = F and Y = Cl. In aniline, X = N(NH₂) and Y = H.

^b Experimental bond lengths and bond angles are from Ref. [26].

which was against the experimental results and also the lowest vibrational frequency was nearing to be imaginary. However, this nonplanarity vanished and the lowest vibrational frequency came out to be real when the higher basis set was used. However, the calculated bond lengths and bond angles of FB and PFB with the two basis sets were found to be very similar. The ground and excited state geometries of FB were also studied along with those of PFB using the higher basis set so that the effect of basis set on mono- and di-fluoro substitution in benzene on the calculated ground and excited state molecular geometries may be analyzed.

Cvitaš et al. [1] have attempted to develop models for the excited state geometries of some substituted benzenes using experimentally determined rotational constants and some assumptions. For fluorine-

substituted benzenes, they have suggested two possible sets of changes in the bond lengths and bond angles due to excitation. In the absence of better experimental results than those given by Cvitaš et al. [1], it is appropriate that we compare our calculated results with those obtained by these authors. According to them, there would be decrease in the CF bond length of FB by 0.009 or 0.028 Å. Our calculated value using the 6-311++G** basis set for decrease in the CF bond length of FB was found to be 0.015 Å which lies between the above two values. The CC bond length changes in FB were found by us (Table 4) to be close to that in benzene, and Cvitaš et al. [1] also assumed the same. The bond angle C6C1C2 in FB, according to the models of Cvitaš et al. [1], would increase either by 3.7 or 1.3°. Our calculated increase in this bond angle was found to be 1.7°

which lies between the two values suggested by Cvitaš et al. [1]. Our calculated increase in the C3C4C5 bond angle is close to that of C6C1C2 while Cvitaš et al. [1] had given two possible changes in this angle, i.e. 0 or 2.3°. According to our calculations, both the bond angles C1C2C3 and C2C3C4 decrease by about 0.8 and 0.9°, respectively. No estimates for the changes in these bond angles were given by Cvitaš et al. [1]. According to Cvitaš et al. [1], the CCl bond length in chlorobenzene would decrease consequent to excitation by about 0.039 Å, the C6C1C2 bond angle would increase by about 1.2° while the other bond lengths and bond angles would change by negligible amounts. According to our calculation, the CCl bond length decreases by about 0.026 Å, the C6C1C2 and C3C4C5 bond angles increase by about 0.7 and 0.9°, respectively, while the other ring bond angles decrease by about 0.4 to 0.5°. Cvitaš et al. [1] suggested a similar change in the geometry of aniline consequent to excitation as that in chlorobenzene except that the CN(NH₂) bond length was found to decrease by 0.08 Å and the C6C1C2 bond angle was found to increase by 4.1°. Our calculated decrease in the CN(NH₂) bond length is 0.086 Å which is close to that due to Cvitaš et al. [1] but our calculated increase in the C6C1C2 bond angle is only about 0.6° which is much smaller than that due to Cvitaš et al. [1]. Further, according to our calculation, the C3C4C5 bond angle of aniline increases consequent to excitation by about 2° while the bond angles C1C2C3 and C2C3C4 decrease by about 0.9 and 0.36°, respectively. The experimental value of the HNC1C2 dihedral angle (C1 being bonded to N and C2 being bonded to C1) in the ground state of aniline is 42° [28,29], while our calculated value of the same is 26.9°. Further, according to a recent experimental study [16], the amino group of aniline is flat (planar) in the lowest singlet excited state and exactly the same result is predicted by our calculations also (Table 4). The above comparison of our calculated changes in the molecular geometries of benzene, FB, ClB and aniline with those obtained on the basis of experimental rotational constants and assumed models by Cvitaš et al. [1] reveals that the present theoretical calculations reveal the trend of geometrical changes in going from the ground to the excited states of the molecules correctly. Further, the present calculations show that the C3C4C5 bond angle would increase by a similar

amount as the bond angle C6C1C2 consequent to excitation, or even by a larger amount than the latter. However, the models due to Cvitaš et al. [1] do not take this possibility into account. The bond angles C1C2C3 and C2C3C4 decrease by similar amounts in all the cases, usually within 1°, consequent to excitation and, therefore, the approximation made by Cvitaš et al. [1] for a negligible change in these bond angles under excitation was not totally unjustified.

The calculated changes in the geometry of PFB using the 6-311++G** basis set following excitation are as follows. The CF bond length decreases by 0.021 Å, i.e. appreciably more than that in FB, C1C2 bond length increases by 0.030 Å which is close to the corresponding value in benzene or FB while the C2C3 bond length increases by 0.022 Å, i.e. by a smaller amount than that in benzene or FB. The bond angle C6C1C2 of PFB increases by about 2.6° while the bond angle C1C2C3 decreases by about 1.3° following excitation. Cvitaš et al. [1] have suggested two possible models for the change of geometry of PFB consequent to excitation: According to the first model by these authors, the CF bond length decreases by 0.009 Å, the bond angle C6C1C2 increases by 2.4°, the bond length C2C3 increases by 0.011 Å while the C1C2 and C3C4 bond lengths increase by 0.038 Å, the CH bond lengths decreasing by 0.014 Å, as in benzene. The second model due to these authors for the change of geometry of PFB under excitation, differs from the first one given above only in two respects i.e. decrease in the CF bond length by 0.028 Å instead of 0.009 Å and increase in the C2C3 bond length by 0.033 Å instead of 0.011 Å. In view of our calculated results, the second model due to Cvitaš et al. [1] appears to be better than the first one. Further, our calculations and the models due to Cvitaš et al. [1] qualitatively agree that the C2C3 bond length increases by a smaller amount than the C1C2 bond consequent to excitation of PFB.

For PCIB, Cvitaš et al. [1] have suggested the following changes in molecular geometry consequent to excitation: The CCl bond length decreases by 0.039 Å, the C2C3 bond length increases by 0.031 Å which is smaller than the increase in the other CC bonds (0.038 Å), the C6C1C2 and C3C4C5 bond angles increase by 1.3° each while the other bond angles remain unchanged. According to our calculations, the

CCl bond length in PCIB decreases by 0.027 Å, the C2C3 bond length increases by 0.026 Å while the C1C2 bond length increases by about 0.027 Å, the C6C1C2 and C3C4C5 bond angles increase by about 1.5° each while the C1C2C3 bond angle decreases by about 0.8°. Thus in PCIB, the agreement between our calculated values and those given by Cvitaš et al. [1] is satisfactory. For PFCIB, as for FB and PFB, Cvitaš et al. [1] have suggested two possible sets of changes in molecular geometry following excitation. According to their second model, the CCl bond length decreases by 0.039 Å, the CF bond length decreases by 0.028 Å, the C2C3 bond length increases by 0.029 Å i.e. by a smaller amount than the other CC bonds, the C6C1C2 bond angle (near Cl) increases by 1.2° while the C3C4C5 bond angle (near F) increases by 2.5°. According to our calculations on PFCIB, the CCl bond length decreases by 0.029 Å, the CF bond length decreases by 0.017 Å, the C2C3 bond length increases by 0.022 Å while the other CC bonds increase by about 0.028 Å each, the bond angle C6C1C2 (near Cl) increases by 2.1° while the C3C4C5 bond angle (near F) increases by 2.2°. Thus while the calculated changes in ring bond angles near F and Cl are similar, those due to Cvitaš et al. differ appreciably. However, the overall agreement between our calculated changes in the molecular geometry of PFCIB following excitation and those obtained by Cvitaš et al. [1] is satisfactory.

4. Conclusions

We arrive at the following conclusions from this study:

- (i) The trends in the calculated lowest singlet transition energies of the molecules agree with those in the experimental ones satisfactorily.
- (ii) The present calculations reproduce the ground and excited state rotational constants A, B and C of the molecules obtained from high-resolution spectroscopy within the error limit of less than 3.5%.
- (iii) There is a satisfactory qualitative agreement between our calculated changes in ring bond lengths and bond angles of the molecules consequent to excitation and those estimated using experimentally determined rotational constants and approximate models. The CX (X = F, Cl, NH₂)

bond lengths decrease and the CC bond lengths increase appreciably in all the cases consequent to excitation, the increase being the least in the C2C3 bond lengths of *p*-disubstituted benzenes, according to both theory and experiment. The calculated changes in CH bond lengths are, however, much smaller than those obtained experimentally.

(iv) The study of ground and excited state MEP maps of the molecules has revealed several interesting features some of which e.g. the *ortho*, *para* directing property of the substituents in the ground state, are in agreement with experiment. It is indicated that reactions at the *ortho*, *para* positions in the ground state would take place in planes far away from the ring planes. The MEP patterns are appreciably modified following excitation of the molecules.

Acknowledgements

The authors are thankful to the Council of Scientific and Industrial Research (New Delhi) and the University Grants Commission (New Delhi) for financial support.

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