Electrophilic Substitution Sites of Aromatic Compounds in Terms of Perturbation Theory

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Commencing from qualitative ab initio calculations on the molecules benzene, toluene and fluorobenzene, the corresponding favoured positions of electrophilic substitution are discussed in terms of perturbation theory including the electrostatic molecular potential and polarisation.

1. Introduction

There are basically two quantum chemical methods which differ essentially in the amount of work required and which can give some insight into reactions particularly in the sense of selectivity. These are the population analysis, using one MO calculation, and the pointwise energy hypersurface, if these two methods can be compared at all.

A desirable method would be one with the work of the population analysis (one MO calculation), and with results which approach an energy hypersurface or, at least, which can be discussed in terms of an energy surface. As a first move in this direction, Scrocco et al. have used the electrostatic molecular potential

$$E_{\mathrm{stat}}(\boldsymbol{R}) = \sum_k Z_k / |\boldsymbol{R}_k - \boldsymbol{R}| - 2 \sum_i^{\mathrm{occ}} \langle \Phi_i | 1/|\boldsymbol{r} - \boldsymbol{R}| | \Phi_i \rangle$$

which represents the interaction energy of a molecule with a proton at $\boldsymbol{R}$ in the first order perturbation theory[1]. Meanwhile numerous results, also on large molecules, give some guide to the informative value of the electrostatic molecular potential, in particular to the occasional breakdown of population analysis in this context[2]. The limits of application of the electrostatic molecular potential have been examined, until now, by means of the formamide molecule[3]. It has been found that with significant protonation sites, obtained from the first order approximation, the second order contributions cannot change the first order results qualitatively. The main contribution of second order results is the polarisation of the molecule by the proton. Charge transfer, dispersion forces and, in most cases, the deformation of the attacked molecule play a negligible role. The basic principle for the use of perturbation theory for reactivity is always the assumption that the mutual initial interaction of two approaching reagents determines the further progress of the reaction. Thus, the aim of the calculations is not the structure and the energy of the transition state.

2. Method of Calculation

The second order polarisation energy is given by

$$E_{\mathrm{pol}}(\boldsymbol{R}) = 2 \sum_i^{\mathrm{occ}} \sum_j^{\mathrm{vir}} \left| \langle \Phi_i | 1/|\boldsymbol{r} - \boldsymbol{R}| | \Phi_j \rangle \right|^2 / (e_i - e_j)$$

where $|\boldsymbol{r} - \boldsymbol{R}|$ is the distance of the proton to the electron; Φ_i are the common HF orbitals and e_i the corresponding energies. The calculation of this contribution does not need additional integrals with respect to E_{stat}. It is, therefore, unwarranted that usually only the first order approximation has been used until now. The sometimes criticized use of virtual Hartree Fock orbitals for second order perturbation theory may be the reason. However, it is shown by the benzene molecule that this objection may be overruled. In Fig. 1 the approximated polarizability α, obtained from the above formula and the relation $E_{\mathrm{pol}} = 1/2\, \alpha F^2$, is drawn over the distance R (proton – centre of the molecule) assuming an in plane attack. For the electrical field strength F, the field of the proton at the centre of the molecule was taken. With increasing distance, R, the field in the molecule becomes homogeneous, and therefore the curve approaches the real second order polarizability. This is seen to agree quite well with the exact polarizability obtained by the complete consideration of the homogeneous field in the Fock matrix. The calculated polarizability is found to be only 30% below the experimental[4].

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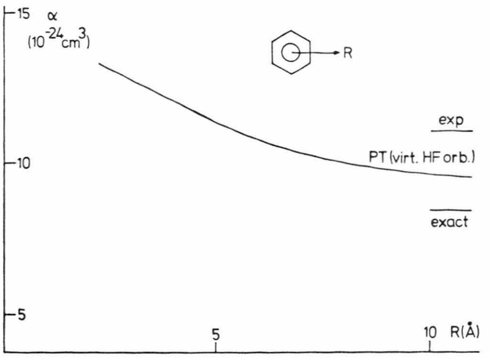

Fig. 1. Polarizability of the benzene molecule by the second order perturbation theory (PT) including virtual HF orbitals versus the exact HF value (see text) and the experimental value [4].

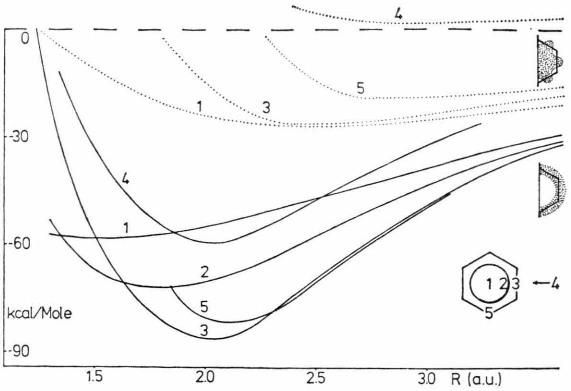

Fig. 2. E_{stat} (dotted lines) and $E_{\text{stat}}+E_{\text{pol}}$ (full lines) for various paths of attack towards benzene. (R: distance of the proton to the plane of the molecule for 1, 2, 3, 5 (attack perpendicular to the molecular plane) and to the centre of the molecule for 4 (planar complex).

All the calculations were performed ab initio by use of the SCF-MO method using pure Gaussians [5]. In order to construct symmetry adapted basis functions, it should be noted that with pure Gaussians and with the simulation of Cartesian 2p functions it is, in general, impossible to obtain equivalent descriptions for equivalent atoms. Therefore, with benzene, the sp^2 hybrids were simulated instead of Cartesian 2p functions. Starting with a $\{4s, 1p\}$ basis on carbon, this basis is modified as follows: 3 s-type functions describe the s-core, 3 functions describe the 3 sp^2 hybrids and one pair of functions are for the π contribution. Altogether, two functions per atom are saved. Summarizing, the main advantage of this basis is the equivalent atoms, furthermore the computer time is reduced drastically for larger molecules, without any essential loss of total energy.

3. Results

3.1. Benzene

For the protonated benzene molecule, ab initio treatments predict the σ complex as the most stable conformation [6]. In spite of this, the possible importance of a π (C_{6v} symmetry) or π' complex (one bridged C=C bond) at an early stage of the reaction is not yet clear. With the first order approximation, the π and the π' complex turn out to be almost equal in energy, and an in plane attack is seen to be repulsive (Figure 2). With the consideration of polarisation, however, the π complex seems to be among the most unfavourable possibilities of attack. The most probable path of attack proceeds perpendicular to the plane of the molecule towards the ring, whereby the π' complex seems not to play a significant role. An alternative possibility of attack with less energy is an in plane path, owing to the high in plane polarizability of the aromatic system. Summarizing, it should be noticed that with benzene, and most probably with all other aromatic compounds, the contribution of polarisation yields essential changes of those results which were obtained from only the first order approximation. Although the perturbation theory would fail in the range of bond distances, the interaction energies are drawn also for short distances in order to compare the results with those of the literature [7].

3.2. Toluene

The paths of attack chosen for the toluene molecule proceed perpendicular to the plane of the aromatic system towards the midpoints of the various C=C bonds (π' complexes, Fig. 3), and towards the C atoms (Figure 4). The slightly favoured site of electrophilic charge controlled attack is seen to be the ortho position, as is also confirmed by population analysis (Table 1). Contrary to this, the corresponding orbital controlled attack, which is given by the highest occupied MO, takes place at the para position [8]. The range of the distance proton – molecule which is used for the discussion was chosen at about 2 Å. For those distances the perturbation theory seems to provide useful results and the chemical bond starts to be formed.

Table 1. Population analysis (q_{tot}) and coefficients of the HOMO (c_{HOMO}) at the C atoms in the aromatic ring (s: C atom at which the substituent is attached; o: ortho; m: meta; p: para).

	s	o	m	p	
q_{tot}	5.925	6.269	6.124	6.193	C_6H_5F
c_{HOMO}	−0.352	−0.356	0.184	0.492	
q_{tot}	5.983	6.173	6.152	6.163	$C_6H_5CH_3$
c_{HOMO}	−0.498	−0.277	0.239	0.507	

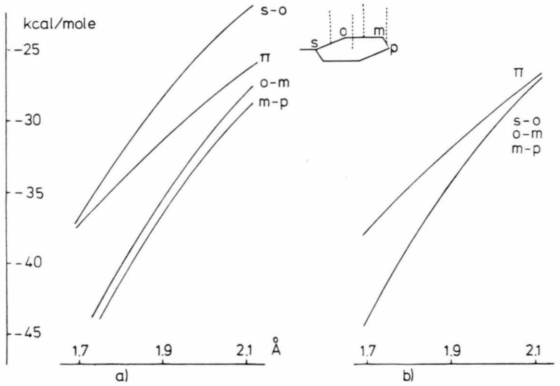

Fig. 3. $E_{\text{stat}}+E_{\text{pol}}$ for various π' complexes and the π complex for a) fluorobenzene and b) toluene. (s: C atom at which the substituent is attached, o: ortho-, m: meta-, p: para-C atom; the distance of the proton is referred to the corresponding C=C midpoint.)

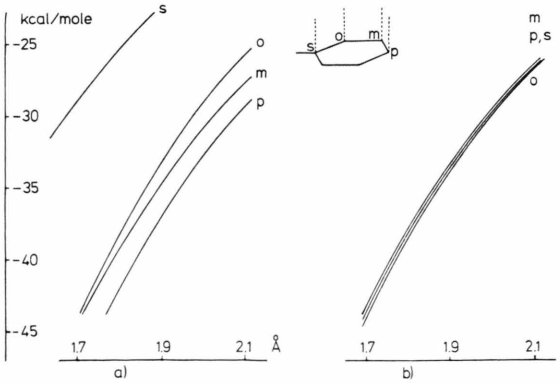

Fig. 4. $E_{\text{stat}}+E_{\text{pol}}$ for various paths of attack perpendicular towards a) fluorobenzene and b) toluene. (The distance of the proton is referred to the corresponding C atom.)

3. 3. Fluorobenzene

The fluorobenzene molecule has already been investigated by means of the electrostatic molecular potential, in order to describe electrophilic substitution sites [7, 9]. These authors have used a {7s, 3p} basis for the atoms C and F, and their results for population analysis and molecular potential are in full agreement with those of the present work, and therefore they should not be repeated in full here. The insensibility of these quantities to the choice of the basis has already been remarked upon [10]. The consideration of polarisation does not change the suggestion of the para position as the most favoured electrophilic attack, but the π complex becomes quite unimportant. The orbital controlled attack takes place also in para position owing to the coefficients in the HOMO. The population analysis cannot be used to indicate the most favoured site of an electrophilic substitution (Table 1). The reason for this breakdown is seen to be that the steric arrangement of the charges is neglected. Consequently the population analysis is unable to describe just the crude effects.

4. Conclusions

All the reported results are in accord with the experimental findings on electrophilic substitution which should encourage us to investigate more detailed problems [11, 12]. Meanwhile an improvement of the second order perturbation contribution has been carried out by means of improved virtual orbitals which were obtained by removing one electron in the Fock operator. Although the polarisation energy is considerably increased, the qualitative results, concerning chemical selectivity, remain unchanged. The disregard of the molecular deformation can be justified by the existence of equivalent competing reaction sites. More general statements must take into account solution effects by means of point charges as has recently been suggested again in this context [13].

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