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# AN MO STUDY OF THE SUBSTITUENT EFFECT IN BENZENE RADICAL IONS

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**Abstract**—The effect of various types of substituents (X = OH, $CH_3$, CN, $SiH_3$) in benzene radical cations and anions have been investigated using INDO–SCF computations with and without $\pi$ conjugation admitted between the substituent and the adjacent substrate. The inductive effect of the substituent has been found to play a minor role in determining the more stable configuration, the latter being determined in all cases investigated by the $\pi$ conjugative interactions. A OEMO analysis of such interactions provides a better understanding of the key factors controlling the configuration preferentially stabilized in the various cases.

## INTRODUCTION

Qualitative MO models have proved to be very useful for rationalizing and elucidating a variety of chemical problems. In recent years significant progress has been made in such areas, particularly through the application of Perturbational Molecular Orbital (PMO) theory. On the other hand, it is also important to test quantitatively these models through explicit calculations in order to assess their validity. An approach on these lines is that based on the combined use of SCF–MO calculations and One Electron MO (OEMO) analyses. Such an approach has already been used successfully to investigate various structural and reactivity problems.[1]

In this paper we report the results obtained in an application of such a combined approach to the study of the substituent effect in mono-substituted benzene radical cations and anions. The ground states of the two benzene radical ions are doubly degenerate and the introduction of a substituent removes the degeneracy, as revealed by the change of the spin density distribution with respect to the parent radical. This effect, which is well known from the earliest papers concerned with electron spin resonance, has been widely discussed in the literature.[2] The relative stabilization or destabilization of one configuration with respect to the other, has in some cases been interpreted in terms of the conjugative properties of the substituent,[2] and in other cases the inductive effect[2,3] or the participation of the 3d orbitals of the substituent[2] has been invoked to account for the experimental results.

The object of this paper is to present a detailed quantitative theoretical investigation, based on SCF–MO computations at the INDO level,[4] on the relative importance of the conjugative and inductive effects of various kinds of substituents in lifting the degeneracy. Here we denote with the term inductive effect all effects, exerted by the substituent, other than the $\pi$ conjugative one. Furthermore a computational procedure has been developed which allows for decoupling of the $\pi$ interactions occurring between the substituent and the adjacent fragment and therefore to obtain separate quantitative information about the conjugative and inductive effects of the substituents. The former one is also analyzed in terms of a OEMO treatment focusing upon the $\pi$ interactions occurring between the $\pi$ MO's of the substituent and those of the two configurations of the benzene ions. The main difference between this OEMO analysis and previous similar investigations[3] is that here we have considered all the various $\pi$ interactions between substituent and the adjacent fragment, and not only those between the $\pi$ MO's of the substituent and the singly occupied MO of the benzene ion as reported in previous papers. The conclusions reached on this basis do not necessarily parallel those obtained considering just the stabilization or destabilization of the singly occupied MO of the benzene ion.

## DISCUSSION

*Computational results.* INDO SCF–MO calculations have been carried out for a series of mono substituted benzene radical cations $(C_6H_5-X)^{\dagger}$ and anions $(C_6H_5-X)^{\overline{\cdot}}$, with X = OH, $CH_3$, CN and $SiH_3$. These substituents have been chosen in order to examine situations where the magnitude and type of the inductive and conjugative effects are significantly different.

We first investigated the unsubstituted benzene radical cation and anion. In benzene the two highest occupied MO's (HOMO's) and the two lowest unoccupied MO's (LUMO's) are degenerate, both having $\pi$ symmetry; therefore in the corresponding cation one electron can be removed from either of the two degenerate HOMO's, while in the anion the extra electron can occupy either of the two degenerate LUMO's. With respect to a perpendicular plane of symmetry passing through $C_1$ (the carbon at which substitution will occur) and $C_4$, the two degenerate HOMO's and LUMO's are either symmetric (S) or antisymmetric (A). We shall denote the lowest energy configurations where the singly occupied MO is symmetric or antisymmetric $\Psi_S$ and $\Psi_A$ respectively.

In the absence of the perturbation due to the substituent, the two configurations $\Psi_S$ and $\Psi_A$ are degenerate in both benzene radical anion and cation. The effect of the substituent is to remove the degeneracy by stabilizing (or destabilizing) preferentially one of these two configurations, so that the ground state will be represented at this theoretical level just by the lowest energy configuration.

In order to understand the key factors operating in these charged radicals, we have carried out the SCF computations for both $\Psi_S$ and $\Psi_A$ in all cases investigated and the computed energy differences are listed in Table 1. Standard geometries have been used. The results of these calculations show that in the radical cations, the symmetric configuration $\Psi_S$ is more stable in all cases, while in the radical anions, the antisymmetric configuration $\Psi_A$ is more stable when X = OH, and the symmetric $\Psi_S$ is lower in energy for all other substituents.

In order to assess quantitatively the relative importance of the conjugative and inductive effects of each substituent in stabilizing one particular electronic configuration, we have used a computational procedure that allows decoupling the conjugation between substituent and the adjacent residue. This consists of an additional SCF computation for both configurations where (i) all non-diagonal matrix elements between atomic orbitals of R and X having $\pi$ symmetry are set equal to zero, and (ii) the MO's of $\sigma$ symmetry are kept, during this additional SCF procedure, fixed in the form obtained in the full SCF computation. This procedure differs from that used by Baird[5] and Schweig[6] because the $\sigma$ MO's here are not allowed to change. This constraint has been introduced in order to keep the extent of the inductive effect to the same order of magnitude as in the full SCF computation. The results of these additional calculations are also listed in Table 1. They provide information about the preferential stabilizing effect exerted by a substituent and due solely to its inductive effect. The results of this analysis can be summarized as follows: (i) in the radical cations, $\pi$ conjugative interactions always favour a preferential stabilization of the symmetric configuration while the substituent's inductive effect favour the anti-symmetric one irrespective of the nature of the substituent; (ii) in the radical anions, with X = $CH_3$ and CN both the $\pi$ conjugative and inductive interactions favour a preferential stabilization of the symmetric configuration, while with X = OH and $SiH_3$ they have the opposite effect; (iii) the energy changes associated with the $\pi$ conjugative interactions are always much larger than those associated with the inductive effect. Consequently, when $\pi$ conjugative and inductive effects act in opposite directions, the former one is dominant and therefore in all cases the preferential stabilization can be assessed considering the conjugative interactions only.

Table 1. Energy differences $\Delta E = E_S - E_A$ (kcal/mole) of the symmetric (S) and antisymmetric (A) configurations of various monosubstituted benzene radical cations and anions computed with ($\Delta E_\pi$) and without ($\Delta E_0$) $\pi$ conjugation between the substituent and the adjacent substrate

| Substituent | Energy differences | Cations | Anions |
|---|---|---|---|
| OH | $\Delta E_\pi$ | −45.65 | 7.99 |
| | $\Delta E_0$ | 31.31 | −0.46 |
| $CH_3$ | $\Delta E_\pi$ | −19.00 | −4.75 |
| | $\Delta E_0$ | 1.21 | −2.37 |
| CN | $\Delta E_\pi$ | −17.65 | −13.86 |
| | $\Delta E_0$ | 3.71 | −1.67 |
| $SiH_3$ | $\Delta E_\pi$ | −15.15 | −16.10 |
| | $\Delta E_0$ | 1.86 | 3.28 |

*OEMO analysis of the conjugative interactions.* Since the $\pi$ conjugative interactions appear to be the dominant factor in determining the preferential stabilization of one of the two configurations, it becomes important to have a better understanding of the effects associated with these interactions. Useful information can be obtained by focusing upon the $\pi$ interactions occurring between the $\pi$ MO's of the substituent X and those of the adjacent benzene ring (R). In the course of such analysis we shall make use of the following results of OEMO theory consistent with an Unrestricted Hartree–Fock procedure,[7] where the contributions associated with the interactions between MO's of $\alpha$ spin and those between MO's of $\beta$ spin are computed separately. Since the occupation of a spin MO can be 0 or 1, we have to consider only two kinds of interactions, i.e. a stabilizing one-electron two-orbital interaction $\Delta E^1_{12}$ ($\alpha$ or $\beta$) given by the following expression where $\eta$ denotes $\alpha$ or $\beta$ spin

$$\Delta E^1_{12}(\eta) = (H_{12}(\eta) - S_{12}(\eta)\epsilon_1(\eta))^2/(\epsilon_1(\eta) - \epsilon_2(\eta)) \qquad (1)$$

and a destabilizing two-electron two orbital interaction $\Delta E^2_{12}$ ($\alpha$ or $\beta$) given by the following expression:

$$\Delta E^2_{12}(\eta) = 2[S^2_{12}(\eta)\epsilon_0(\eta) - S_{12}(\eta)H_{12}(\eta)]/(1 - S^2_{12}(\eta)). \qquad (2)$$

In both equations $\epsilon_1$ and $\epsilon_2$ denote the orbital energies of the two interacting spin MO's, $\psi_1$ and $\psi_2$, $S_{12}$ their overlap integral and $H_{12}$ their matrix element, and $\epsilon_0$ denotes the mean of the energies of $\epsilon_1$ and $\epsilon_2$. The quantities involved in the two equations refer to a canonical basis; on the other hand it has been shown that the values of the core elements in the INDO as well as CNDO methods are closer to the values in a symmetrically orthonormalized basis than to the values in a canonical basis.[8] Consequently we have transformed the Fock matrices and the spin MO's obtained in the INDO computations with and without $\pi$ conjugation admitted to the canonical basis. We denote here with $F$ and $F_0$, $C$ and $C_0$ the Fock matrices and the coefficient matrices over the canonical basis with and without $\pi$ conjugation admitted. The interaction matrix and the overlap matrix over the fragment molecular basis can be obtained, following the suggestion of Wolfe *et al.*,[9] from the relations below:

$$H = C_0^+(F - F_0)C_0$$
$$S = C_0^+SC_0$$

where S is the overlap matrix over the canonical basis. The orbital energies of the fragment MO's prior to interaction are obtained from the computations without $\pi$ conjugation admitted.

The combination of the terms referring to $\alpha$ spin and $\beta$ spin will provide values for the energy variations. In particular an estimate of the one electron stabilization $\Delta E^1_{12}$ associated with the interaction between a singly occupied MO and an empty MO will be obtained directly from $\Delta E^1_{12}(\alpha)$, that of the two-electron stabilization $\Delta E^2_{12}$

associated with the interaction between a doubly occupied MO and an empty MO summing up the two stabilizing contributions $\Delta E^1_{12}(\alpha)$ and $\Delta E^1_{12}(\beta)$, that of the four-electron destabilization $\Delta E^4_{12}$ associated with the interaction of two doubly occupied MO's summing up the two destabilizing contributions $\Delta E^2_{12}(\alpha)$ and $\Delta E^2_{12}(\beta)$, and that of the energy variation $\Delta E^3_{12}$ associated with a three-electron two-orbital interaction summing up the two contributions $\Delta E^2_{12}(\alpha)$ and $\Delta E^1_{12}(\beta)$. Depending on the relative absolute values of these two quantities, $\Delta E^3_{12}$ will be stabilizing or destabilizing. The results of this analysis are reported in Table 2, where the symbols referring to the interacting orbitals are specified in Figs. 1 and 2 for the radical cations and anions respectively. For the sake of simplicity the ordering of the $\pi$ MO-'s of the benzenic fragment in these figures is that at the Huckel level, while the positioning of the $\pi$ MO's of the substituent is just schematic.

From these two interaction diagrams, and on the basis of the data reported in Table 2, the following information can be obtained: (i) in the radical cations, the key interaction is $\chi_1 - \varphi_n$: this is a three-electron two-orbital interaction in the $\Psi_S$ configuration and a four-electron two-orbital interaction in the $\Psi_A$ configuration. Since the latter is in all cases destabilizing and the former stabilizing because of the small energy gap,[10] this interaction favours a preferential stabilization of $\Psi_S$. With substituents having a filled–unfilled $\pi$ system also $\varphi_n - \chi_2$ might in principle have a certain importance; this is a two-electron interaction in $\Psi_A$ and a one-electron inter-

Table 2. Interaction energies† (eV) associated with the various $\pi$ orbital interactions occurring in the various mono-substituted benzene radical cations and anions

| Substituents | Interaction | Cations | | Anions | |
|---|---|---|---|---|---|
| | | S | A | S | A |
| OH | $\chi_1 - \varphi_n$ | −5.4736 | 1.0799 | 1.0401 | 1.0274 |
| | $\chi_1 - \varphi_{n+1}$ | −1.4215 | −0.7752 | 0.1795 | −0.5217 |
| $CH_3$ | $\chi_1 - \varphi_n$ | −0.5591 | 1.1556 | 1.1297 | 1.0792 |
| | $\chi_1 - \varphi_{n+1}$ | −0.4129 | −0.2985 | 0.3077 | −0.1802 |
| | $\varphi_n - \chi_2$ | −0.0519 | −0.1123 | −0.2699 | −0.2073 |
| | $\varphi_{n+1} - \chi_2$ | — | — | −0.3239 | — |
| CN | $\chi_1 - \varphi_n$ | −1.1213 | 0.8733 | 0.8254 | 0.7976 |
| | $\chi_1 - \varphi_{n+1}$ | −0.4362 | −0.2857 | 0.2422 | −0.1693 |
| | $\varphi_n - \chi_2$ | −0.1075 | −0.2363 | −0.5748 | −0.4228 |
| | $\varphi_{n+1} - \chi_2$ | — | — | −0.8165 | — |
| $SiH_3$ | $\chi_1 - \varphi_n$ | −1.0767 | 0.5787 | 0.5238 | 0.5055 |
| | $\chi_1 - \varphi_{n+1}$ | −0.2063 | −0.1321 | 0.1256 | −0.0733 |
| | $\varphi_n - \chi_2$ | −0.0397 | −0.0898 | −0.4250 | −0.2499 |
| | $\varphi_{n+1} - \chi_2$ | — | — | −1.5884 | — |

†A positive value corresponds to destabilization energy, while a negative value to stabilization energy.

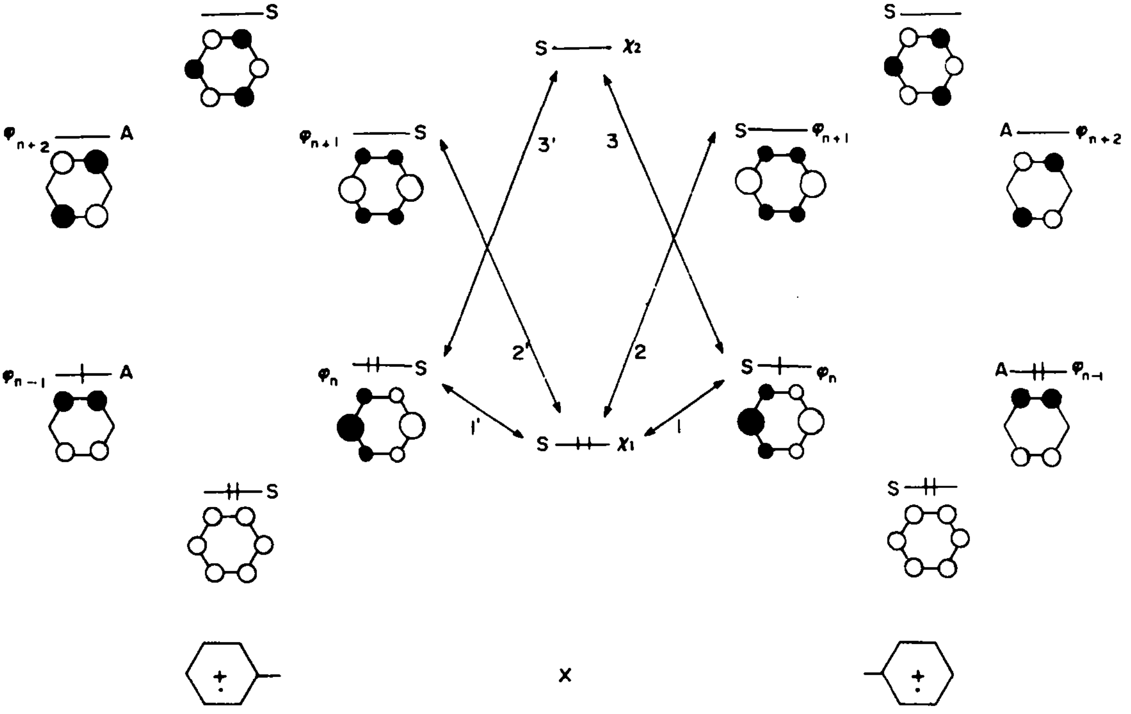

Fig. 1. $\pi$ Orbital interactions between the substituent X and the adjacent benzenic fragment occurring in the $\Psi_S$ and $\Psi_A$ configurations of monosubstituted benzene radical cations.

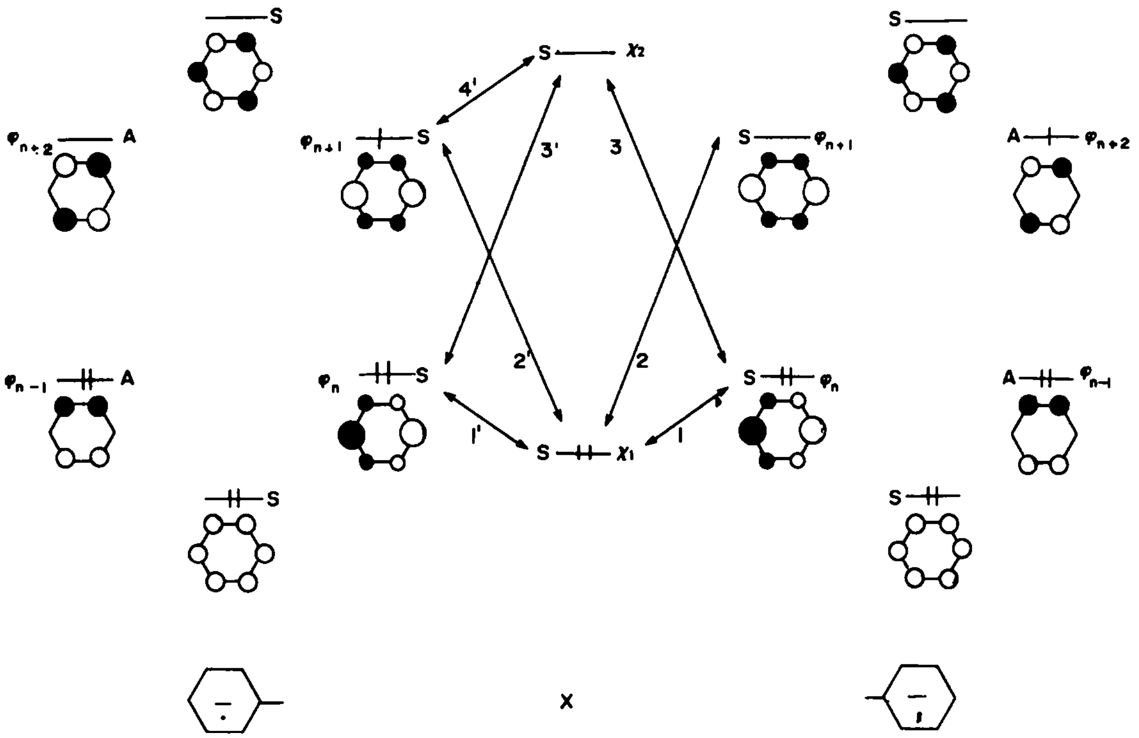

Fig. 2. $\pi$ Orbital interactions between the substituent X and the adjacent benzenic fragment occurring in the $\Psi_S$ and $\Psi_A$ configurations of monosubstituted benzene radical anions.

action in $\Psi_S$ and therefore favours a preferential stabilization of $\Psi_A$. However the energy gap between these two interacting MO's is so large that the related stabilizing effects become negligible, as shown by the values listed in Table 2, as compared with the energy effects associated with the $\chi_1 - \varphi_n$ interaction; (ii) in the radical anions, with substituents having just a lone pair (i.e. X = OH) the key interaction is $\chi_1 - \varphi_{n+1}$, which is a three electron interaction in $\Psi_S$ and a two-electron interaction in $\Psi_A$. The latter is always stabilizing, while the former has a small destabilizing effect because of the large energy gap.[10] Therefore this interaction will favour a preferential stabilization of $\Psi_A$, in agreement with the computed results listed in Table 1. With substituents having a filled–unfilled $\pi$ system another important interaction has to be considered, i.e. the one-electron stabilizing interaction $\varphi_{n+1} - \chi_2$ that occurs only in the $\Psi_S$ configuration. The associated stabilizing effect will increase decreasing the energy of $\chi_2$ and eventually $\varphi_{n+1} - \chi_2$ can become the dominant interaction dictating a preferential stabilization of $\Psi_S$. This is just what happens in the radical anions with X = $CH_3$, CN and $SiH_3$ (see Tables 1 and 2), where the energy of $\chi_2$ varies in the following way:

$$\chi_2(CH_3) = 0.5097 \text{ a.u.}, \quad \chi_2(CN) = 0.4460 \text{ a.u.}, \quad \chi_2(SiH_3) = 0.3128 \text{ a.u.}$$

*Inductive effect of the various substituents.* Even if the inductive effect of the substituent seems to play a secondary role in determining the preferential stabilization of one of the two configurations, nevertheless it is interesting to know which type of inductive effect is exerted by the various substituents in these radical ions. This may be determined by examining the sign of the change in energy of a given benzene MO, $\Delta E_\mu$, due to the introduction of a substituent when $\pi$ conjugation is not admitted. We expect that a substituent exerting a withdrawing electron inductive effect causes the adjacent carbon atoms to become partially positive, with consequent increase of the absolute magnitude of the carbon's Coulomb integrals and therefore decrease of the $\pi$ MO's orbital energy. The opposite effect, i.e. an increase of the $\pi$ MO's orbital energy, is caused by a substituent exerting an electron releasing inductive effect. On this basis, and from the comparison of the orbital energies listed in Table 3 where we have focused our attention only on the singly occupied symmetric benzene $\pi$ MO, the following observations can be made; (i) in the radical cations, OH and CN exert an electron withdrawing inductive effect, while $CH_3$ and $SiH_3$ an electron releasing inductive effect; (ii) in the radical anions, the substituents OH, $CH_3$, CN exert an electron withdrawing inductive effect, while $SiH_3$ an electron releasing effect. The most interesting result concerns the methyl group which shows opposite effects in the negatively and positively charged species.

*Comparison with experiments.* The INDO predictions on the effect of a substituent in stabilizing one particular

Table 3. Orbital energies (a.u.) of the symmetric singly occupied MO in benzene radical cations and anions

| Substituent | HOMO† | LUMO‡ |
|---|---|---|
| H | −0.8035 | 0.1104 |
| OH | −0.8378 | 0.0932 |
| $CH_3$ | −0.8028 | 0.1017 |
| CN | −0.8231 | 0.0937 |
| $SiH_3$ | −0.7982 | 0.1191 |

†Singly occupied MO in benzene radical cations.
‡Singly occupied MO in benzene radical anions.

electronic configuration of benzene may be compared with experiment by examining the spin density distributions of the pertinent radical ions as determined from their ESR spectra. Since the antisymmetric HOMO and LUMO have a node through the 1 and 4 positions, hyperfine splitting constants relatively large (5–6 G) at the *ortho* and *meta* protons together with a small splitting at the *para* position are taken as evidence for the preferential stabilization of $\Psi_A$. On the other hand a large (7–8 G) *para* and moderate (2 G) *ortho* and *meta* splittings are indicative of the preferential stabilization of the symmetric configuration $\Psi_S$. In some cases, as for toluene, a direct comparison with the experimental results can be made since the ESR spectra of the corresponding radical ions are known. In other cases, the theoretical results may be tested by referring to related compounds having similar electronic properties. For instance the radical anion of phenol has never been prepared, while the anion of anisole is known. Since it is quite reasonable to assume that the OH and OMe groups will produce an analogous lifting of the degeneracy of the benzene orbitals, the theoretical calculations on the former compound will be compared with the experimental results for the latter one. Also radical ions of *para*-disubstituted benzenes will be taken as reference terms as, given the symmetry of the benzene orbitals, two equivalent substituents are expected to reinforce their effect when they are introduced at the 1 and 4 positions.

In the case of the radical cations the experimental results that may be employed to test our calculations are those reported for toluene[11] and hydroquinone.[12] In both cases the measured hyperfine splitting constants indicate that the lowest energy configuration is $\Psi_S^+$ in agreement with the SCF results. On the other hand radical anions are known for all the compounds we have examined, except phenol which may be compared with anisole. For both benzonitrile[13] and phenylsilane[14] the experimental spin density distribution shows that the unpaired electron occupies the symmetric LUMO in agreement with the INDO calculations. It is worthwhile to point out that in the case of phenylsilane the stabilization of the $\Psi_S^-$ configuration was explained by admitting delocalization of $\pi$ electrons into the silicon 3d orbitals[14] while our INDO results predict correctly the symmetry of the lowest energy configuration without including d orbitals in the calculations. Consistency between theory and experiment is also found for the negatively charged phenol when the experimental hyperfine splittings used in the comparison are those obtained for the radical anion of anisole.[15] The situation is less clear for the radical anion of toluene.[16] In fact, the experimental splitting constants determined by ESR in solution denote occupation by the unpaired electron of the antisymmetric LUMO of benzene, while the INDO calculations show that the symmetric configuration is more stable by 4.75 kcal.

It has recently been found that the relative stability of the anions alkylbenzenes and benzene display opposite ordering in the gas phase and in solution,[17] the difference being attributed to solvation energies which oppose the intrinsic gas phase ordering of this class of negative ions. In the light of these data it was suggested that the location of the symmetric $\Psi_S$ above the antisymmetric state $\Psi_A$ found in solution, may be the result of solvation effects. The present INDO calculations give some support to this hypothesis and therefore, although in disagreement with the ESR results, may not be incorrect.

## CONCLUSIONS

The analysis of the effect of substituents in benzene radical ions has shown various interesting points that can be summarized as follows: (i) the inductive effect of the substituent plays a minor role in determining the more stable configuration; the latter is, in all cases investigated, controlled by the conjugative effect; (ii) a OEMO analysis of the $\pi$ interactions occurring between the substituents and the adjacent fragment has revealed that in the radical cations the interaction $\chi_1 - \varphi_n$ (i.e. that between the HOMO of the substituent and the benzene symmetric HOMO) dictates the preferential stabilization of the $\Psi_S$ configuration, irrespective of the substituent. Support for this rule comes from the ESR spectra of the cation radical of aniline,[18] *p*-dimethoxybenzene[19] and *p*-bis(methylthio)benzene[19] all showing spin density distributions typical for the symmetric configuration. No examples where the $\Psi_A$ configuration is more stable are known; (iii) in the radical anions the key orbital interaction determining the more stable configuration depends on the nature of the substituent. With substituents having just a lone pair, the key orbital interaction is $\chi_1 - \varphi_{n+1}$ that favours $\Psi_A$. This expectation is confirmed by the ESR spectrum of the *p*-difluorobenzene negative ion[20] which gives proton hyperfine splittings of 5.30 G.

With substituents having a filled–unfilled $\pi$ system, one has to consider also the effect of the stabilizing interaction $\varphi_{n+1} - \chi_2$ that favours $\Psi_S$. Therefore in these cases there are two opposite effects, one favouring $\Psi_A$ and one favouring $\Psi_S$. With substituents having a vacant $\pi$ MO located at low energy such as CN and $SiH_3$ the latter effect dominates and consequently $\Psi_S$ is the more stable configuration. The same clearly occurs with the radical anions of trimethylsilylbenzene and trimethylgermyl benzene[14] for which, as for phenylsilane, the stabilization of the symmetric configuration may be explained without invoking participation of 3d orbitals to the $\pi$-system.

The behaviour of the methyl group is rather peculiar since, in this case, there is not a largely dominant effect. However, even if the prediction of the more stable configuration is incorrect, such computations are of significance since they point out this balanced situation. It follows that the experimental results in this system can be very sensitive to factors that may affect the balance such as solvation or, even more, ion pairing. In solution, in fact, we can expect a relative lowering of the set of orbital energies of the benzenic fragment because of the decrease of the negative charge of this fragment caused by the interactions with the solvent or the positive counterion. Consequently, the key interaction will tend to become $\chi_1 - \varphi_{n+1}$, favoring thus $\Psi_A$ over $\Psi_S$, as experimentally observed.

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