

An Approximate Expression of the Electrostatic Molecular Potential for Benzenic Compounds

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A method for getting approximate but realistic evaluations of the electrostatic molecular potential for benzene derivatives is presented and discussed. The method is based on a partition of the whole molecular observable into directly transferable contributions, which can be calculated without a previous knowledge of the molecular wavefunction. The algorithm, which probably is applicable also to other aromatic compounds, implements a preceding study concerning only unconjugated molecules.

Key words: Point charge description of chemical groups – Electrostatic molecular potential

In a couple of preceding papers [1, 2] we showed that a reasonable description of the electronic charge distribution of a molecule can be given in terms of directly transferable localized models of two- (or many-) electron groups, and that for the calculation of the electrostatic molecular potential V such models (expressed in a LCAO form) can be further approximated by simple point charge distributions. That analysis was limited to unconjugated compounds, because we had found at that time some difficulties for extending this approximation to conjugated molecules. In the present paper we report an extension of the method to molecules containing a benzenic ring.

For the elaboration of simple rules to get transferable models for these molecules we have found it convenient to treat the σ and the π electrons separately, adopting, as in the preceding papers, two electron local groups for the σ subsystem, including also the C—C and C—H bonds of the ring, and a unique group for the π electrons.

The main aim in our investigation on the determination of the point charge model of the π subsystem was directed to the development of a methodology general enough to be able to reproduce the main features of the electrostatic potential

and the variations in it due to changes in the ring substituents, but which should not require a previous knowledge of the wavefunction of the molecule under examination.

A preliminary step in this investigation consisted in comparing the performances of a hierarchy of models, composed of n , $2n$ or $3n$ couples of negative point charges symmetrically placed upon and above the ring plane and supplemented by n positive unit point charges placed at the positions of the n nuclei of the atoms involved in the π subsystem.

We have optimized these models using as independent parameters the charge of each couple, the distance $2h$ between the two charges of each couple and the position of each couple. As constraints we have imposed that the first set of n couples should be placed at the position of the nuclei, that the sum of the negative point charges should be equal to $-ne$, and the other constraints imposed by the symmetry of the C_6H_5X molecule¹.

In order to perform these optimizations we have calculated the electrostatic potential V of the models for a set of ≈ 2000 points evenly spaced but lying outside the van der Waals surface of the molecule. The optimization was obtained by allowing for the standard deviation of V of the model with respect to that obtained via direct calculation on the π portion of the molecular wavefunction (supplemented with n unit positive charges on the nuclei), and using the Simplex method [3]. Previous experience on analogous problems in our laboratory [4] showed that this method is more suitable for obtaining conditioned minima than other more straightforward methods.

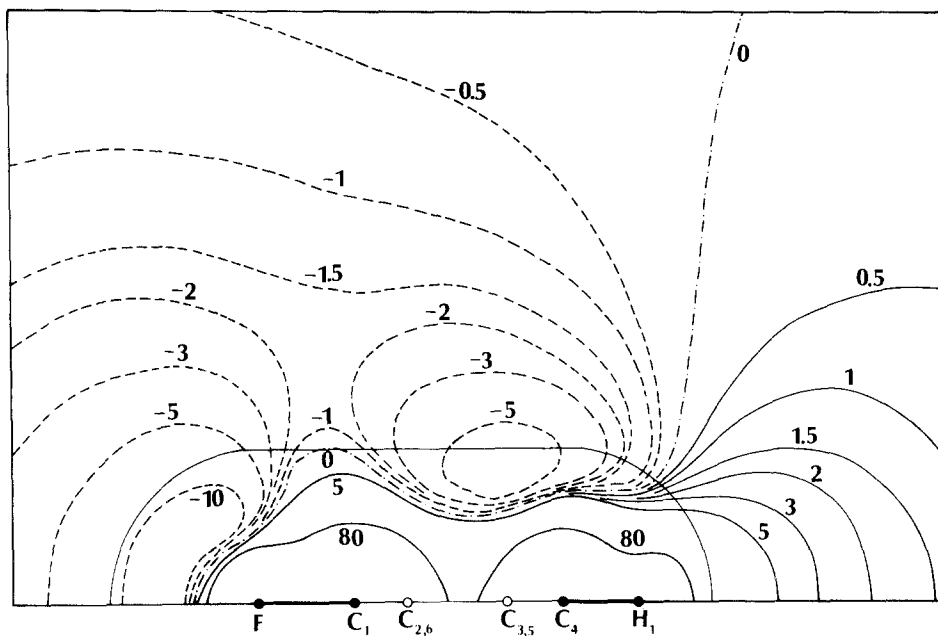
This preliminary investigation showed that it is quite easy to get models having a standard deviation (SD) less than 0.1 kcal/mole, that the performances of the models do not greatly improve in passing from $2n$ to $3n$ couples, and, as a more important result for our final aim, that it is possible to infer some simple rules for the construction of fairly accurate models.

The point charge couples can be placed on the ring periphery and on the straight line connecting X to the ring. The first set of n couples q_i being placed at the positions of the nuclei, the second set, q_{ij} , may be placed at the midpoint of the segment connecting two linked nuclei.

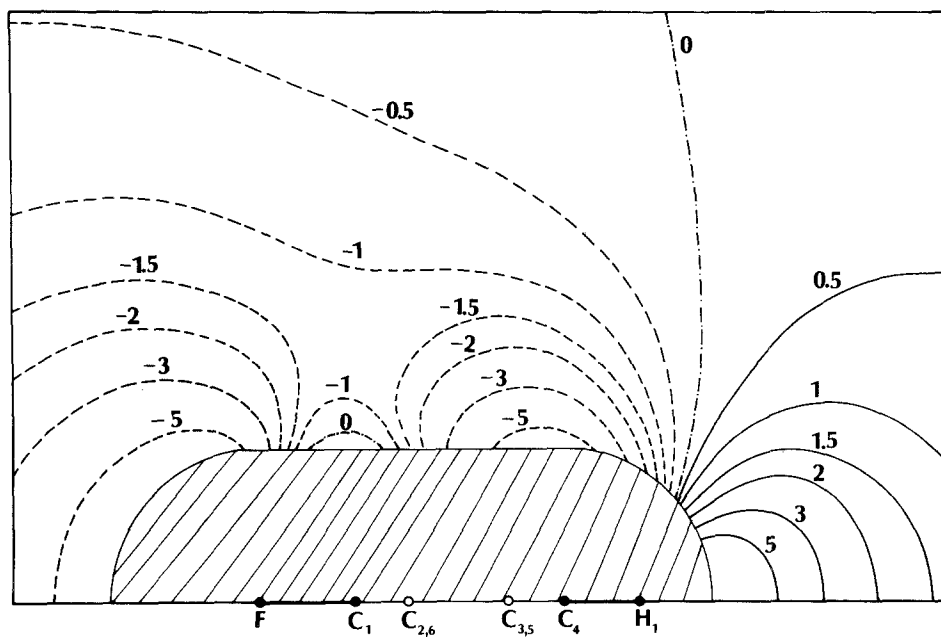
Further checks on this simplified model performed over a small set of C_6H_5X compounds ($X = H, F, OH, NH_2$) indicate in addition that one can use a fixed h_i distance for each couple placed on the nuclei, this distance being dependent only on the nature of the nucleus ($h_C = 0.564 \text{ \AA}$, $h_N = 0.460 \text{ \AA}$, $h_O = 0.406 \text{ \AA}$, $h_F = 0.364 \text{ \AA}$)², while the distances h_{ij} of second set of couples can be put equal to 0.46 \AA irrespective of the nature of atoms i and j .

¹ In many C_6H_5X compounds the symmetry of an actual geometry generally is quite low. Some numerical checks indicated that for our purposes it is appropriate enough to assume a local C_{2v} symmetry for the ring portion of the charge models.

² These h_i values, obtained with independent optimizations are remarkably close to one third of the mean radius \bar{r} of the $2p$ orbital [5].



a



b

Fig. 1. Comparison of the electrostatic molecular potential maps for fluorobenzene in the perpendicular symmetry plane: a) SCF STO-3G calculation, b) point charge models (2n model for the π subsystem). The isopotential curves are given in kcal/mole

The charges q_i of the first set of couples are very close to one-half of the net charge of the corresponding atom, and can be safely put equal to this quantity. The quality of the results does not depend heavily upon the values assigned to the q_{ij} charges. A practical rule could consist in adopting charges near to $-0.10e$ but with actual values such as to ensure the electroneutrality of the whole system. The typical values of the SD for these models are in the interval 0.2–0.5 kcal/mole.

We report in Table 1 the actual values of the charges of the models for some selected molecules and we give in Fig. 1 a comparison of a map of V calculated with the SCF wavefunction and with the model point (for the point description of the σ portion of the molecule, see later). The numerical results refer to standard geometries and to calculations performed with the STO-3G basis set [6].

The definition of the simplified $2n$ models does not seem to meet with our initial prerequisite of obtaining a rule for building up models without knowing the corresponding SCF wavefunction. This objection is only partially valid, because our experience, though limited, indicates that in general the description of the π contributions to the potential depends only on the nature of the group directly attached to the ring (for example, the $2n$ model for $C_6H_5CH_2OH$ can be used also for $C_6H_5CH_2OCH_3$, $C_6H_5CH_2OC_2H_5$, etc., without a substantial increase in the SD) and that the model can be easily arranged also for the case of multiple substitutions on the ring. The charges q_i of the model for the C_6H_4XY systems may

Table 1. The $2n$ point charge model for benzene and some simple derivatives^a

	C_6H_6	C_6H_5F	C_6H_5OH	$C_6H_5NH_2$
q_1	0.407	0.392	0.374	0.421
q_2	0.407	0.419	0.433	0.377
q_3	0.407	0.386	0.383	0.439
q_4	0.407	0.405	0.415	0.352
q_x	—	0.953	0.939	0.929
h_1	0.564	0.564	0.564	0.564
h_x	—	0.364	0.406	0.460
q_{12}	0.093	0.104	0.103	0.106
q_{23}	0.093	0.104	0.103	0.106
q_{34}	0.093	0.104	0.103	0.106
q_{1x}	—	0.016	0.022	0.030
h_{ij}	0.462	0.462	0.462	0.462
h_{1x}	—	0.462	0.462	0.462
SD ^b (π system)	0.18	0.30	0.31	0.36
SD ^b (σ system)	0.56	0.94	0.77	0.84

^a The charges q_i (expressed in $-e$ units) are placed in couples above and below the i nucleus at a distance of h_i Å from the ring plane. The charges q_{ij} are placed in couples in correspondence of the middle of the segment connecting nuclei i and j at a distance of h_{ij} Å from the ring plane. The numbering of the ring atoms starts from the atom where the substitution occurs.

All geometries are standard and the NH_2 group in aniline is planar.

^b Standard deviation in kcal/mole.

be obtained from those of C_6H_5X and C_6H_5Y as arithmetic mean. A typical example is given by the catechol (ortho-dihydroxybenzene): by averaging the charges of two phenols, shifted by one position around the ring, one obtains a model with $SD = 0.60$ while for phenol itself the SD is 0.31 kcal/mole.

This model could be considered too cumbersome (the number of point charges for each ring is 24) and a simpler version could consist in a n couple model, with couples placed on the nuclei at the same heights h_i as above and charges q_i equal to the gross subtotal π populations. The SD obviously increases (0.5 – 1.5 kcal/mole), but the differential features of V (location of the nodal planes etc.) are fairly well reproduced. This model could be used particularly for the evaluation of V at relatively large distances from the ring, where the recipe given in Ref. [2], (i.e. a transferable LCAO description of the group near to the zone under investigation supplemented with suitable point charge descriptions of the more distant groups) should be employed. We give in Table 2 the point charges q_i of this model for the rings of a few C_6H_5X systems.

We have not yet considered the point charge description of the σ subsystem. To get the transferable models we have adopted the technique given in Ref. [2], i.e. we put for each σ orbital two unit point charges on the nuclear axis a Å apart with respect to the charge center of the corresponding mean LO, and for each lone pair a $-2e$ charge at the position of the LO charge center. We give in Table 3 the numerical parameters of the ring C—C and C—H bonds. For the X groups we

Table 2. The ring parameters for the n point charge model of the system of some C_6H_5X molecules. All the couples of ring charges are placed at a distance $h = 0.564$ Å above and below the relevant nucleus. Hyperconjugation has not been included in the π model

Molecule	q_1	q_2	q_3	q_4
$C_6H_5CH_3$	0.485	0.509	0.496	0.505
$C_6H_5NH_2$	0.472	0.544	0.487	0.528
C_6H_5OH	0.488	0.534	0.488	0.520
C_6H_5F	0.504	0.521	0.492	0.511
$C_6H_5CH_2NH_2$	0.488	0.509	0.495	0.504
$C_6H_5CH_2OH$	0.493	0.504	0.498	0.503
$C_6H_5CH_2F$	0.494	0.506	0.496	0.502
$C_6H_5NHCH_3$	0.475	0.543	0.487	0.528
$C_6H_5NHNH_2$	0.477	0.538	0.489	0.527
C_6H_5NHOH	0.479	0.540	0.487	0.526
$C_6H_5OCH_3$	0.492	0.532	0.489	0.519
$C_6H_5ONH_2$	0.496	0.524	0.493	0.517
$C_6H_5CH=CH_2$	0.498	0.501	0.499	0.500
$C_6H_5CH=NH$ (<i>syn</i>)	0.507	0.492	0.502	0.494
C_6H_5CHO	0.510	0.491	0.501	0.491
$C_6H_5COCH_3$	0.510	0.491	0.501	0.492
C_6H_5COOH	0.520	0.485	0.503	0.488
$C_6H_5N=CH_2$	0.510	0.502	0.497	0.499
$C_6H_5N=NH$ (<i>trans</i>)	0.525	0.484	0.504	0.489
$C_6H_5N=NH$ (<i>cis</i>)	0.517	0.499	0.495	0.492
C_6H_5CN	0.528	0.488	0.500	0.486
$C_6H_5NO_2$	0.545	0.479	0.502	0.479

Table 3. Location of the point charges in the models of the LO's of the ring

	R^a	P^b	a^c
σ_{CC}	1.530	0.765	0.185
σ_{CH}	1.102	0.761	0.185

^a Length of the A—B bond.

^b Distance of the charge center from the heavier nucleus.

^c Magnitude of the symmetric displacement of the point charges from P . All values are in Å.

have directly employed the parameters given in Ref. [2] the only exception being the F atom, where it was found more profitable to reduce by 10° the angle between the point charges of the two lone pairs, with respect to the angle between the corresponding LCAO charge centers.

This description gives SDs of the order of 0.5–0.9 kcal/mole for the whole set of benzene derivatives we have examined, but probably a further refinement could improve the fitting.

To conclude, it seems to us that the models we have proposed can be of some aid in estimating the electrostatic reactivity of large molecules containing one or more benzenic groups. This method of construction of point charge models should be valid also for other aromatic systems containing heteroatoms or condensed rings (see for this last case, the analysis of the LO's made by Ruedenberg and coworkers [7] which could constitute the starting point for a different approach to this problem). As we have remarked in Ref. [2] this kind of utilization requires a passable knowledge of the contributions to V also of groups not very near to the portion of space under investigation. The SD values we have given in this paper mainly depend on the values of V in regions near the ring and underestimate the accuracy of the model for the study of the properties of other zones of the molecular space. The validity of the model in assessing the electrostatic characteristics of the aromatic group itself deserves further checks: some tests performed on systems already studied with *ab initio* SCF wavefunctions in our laboratory [8–10] indicate that the $2n$ model can give reasonable results.

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