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A Self Consistent Reaction Field Study on Electrostatic Isopotential Maps

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The influence of a self consistent reaction field on the charge distribution of molecular systems is studied. Electrostatic isopotential maps are used to discuss the qualitative and quantitative aspects of such an influence.

INTRODUCTION

Several studies have been carried out in recent years using molecular electrostatic isopotential maps (EPM)[1]. The EPM produced by electrons and nuclei in the surrounding space is an effective tool in predicting the reactive behaviour towards electrophyles and protonation of simple systems. Furthermore, there has recently been proposed a procedure for using the EPM to predict and interpret nucleophylic processes[2].

It is well known that reaction field (RF) calculations are useful in providing information relative to changes in molecular properties and most of the usual parameters in the absence of direct interactions (hydrogen bonding, for instance). Since a self consistent reaction field (SCRF) is expected to modify the charge distribution of molecular systems, changes in the EPM should be anticipated.

The purpose of this paper is to study the qualitative aspects of this hypothesis. In order to develope this theme, we first study the influence of a RF in the EPM for a variety of molecules. We then examine some carbonylic compounds, especially cyclopropylketones, which, under a certain viewpoint, may be regarded as intermediate between aliphatic and aromatic[3]. Finally, we analyse the hydrogen bonding influence on these carbonylic compounds and the SCRF technique.

CALCULATION PROCEDURE

The EPM were determined using the charges provided by the SCRF-CNDO/2 technique as described by Tapia and Constanciel[4]. In this approach, the SCF procedure, including solvation effects, is based upon the following effective Fock operator containing the solvent interaction:

$$[h\,(r) - V\,(r) + \sum_{j} (2J_j - K_j)]\,\Phi_i\,(r) = \varepsilon_i\,\Phi_i\,(r) \tag{1}$$

where $h\,(r) + \sum_{j} (2J_j - K_j)$ denotes the usual Fock operator and $V\,(r)$ the solvent field one-electron operator. Expression (1) gives a new set of SCF equations from which the molecular orbitals and energies may be obtained. Within the CNDO scheme used here, the only terms modified in the Fock matrix are the diagonal ones. The modification is given by the following expression:

$$-V^{A} = f(D) \sum_{B} (Z_{B} - P^{B})\, \gamma_{AB}$$

where Z_B and P^B denote the nuclear and electronic charges respectively, γ_{AB} the two electron integrals and $f(D) = -(1 - 1/D)$ with D the square root of the dielectric constant. The EPM were generated by means of a Quantum Chemistry Exchange program[5]. In all cases, the geometries were optimized at the vacuum level, employing the previously reported geometries, except for small rings, where the MNDO technique[6] with the Davidon-Fletcher-Powell minimization procedure[7] was preferred. It is well known that these geometries are not properly described by the CNDO/2 method[8], whereas the MNDO method predicts them accurately.

RESULTS AND DISCUSSION

We have studied several molecules, with different functional groups (alcoholic, halogen derivates, cyano groups, aldehydic, ketonic, ethers, heteroaromatic compounds, etc.) There were no important changes observed in the qualitative aspects of the EPM, in most of the systems. Only significant changes were noticed in the carbonylic compounds, where direct interactions

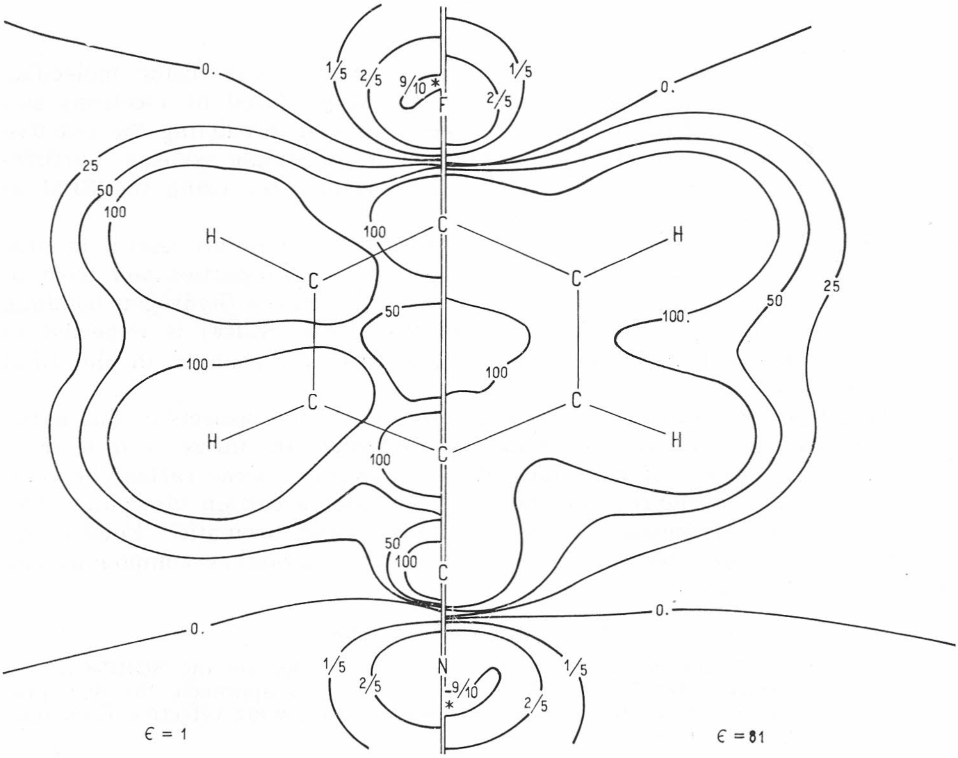

Figure 1. EPM for *p*-fluorobenzonitrile. Left hand side: vacuum level, right hand side: dielectric constant equal to 81. The positive part of the isoenergetic curves are indicated, and the energy values of the system on the curve are given in Kcal/mole. The fractions denote decimal fractions minimum energy for the zones of charge excess. The asterisk shows the position of the minimum.

(such as hydrogen bonding) also have a marked influence. Bifunctional systems, such as *p*-fluorobenzonitrile for instance, with two withdrawing groups, may be strongly affected, as well as the localization of the minimum energy position, which may be significatively changed. As it may be seen, a system like this may be protonated on either of the withdrawing groups, depending on the dielectric constant of the medium (Figure 1).

The EPM of a series of cyclopropyl ketones were obtained. The energy difference between the cis and the trans conformers is almost maintained, as the dielectric constant is increased, the stabilization being slightly greater for the cis geometry. (the cis conformation is found experimentally to be the most stable[9]). Although the correlation amongst the EPM parameters (energy minimum, distance between the oxygen and the minimum energy position, etc.) between the members of the family remains unchanged, the value of the minimum is at least duplicated, and the distance between the O and the minimum is reduced by about 25%. The qualitative differences are evident, and they are shown in Figure 2. It may be seen that the EPM for a dielectric constant 10 is closer to that of dielectric constant 81 than to that of dielectric constant 1. This behaviour has been previously noted, and it can be attributed to the marked dependence of the Fock matrix elements on the dielectric constant.

It was formerly remarked other dependence between the dielectric constant and the Fock matrix elements may be used[10], although its meaning is not so clear as the one proposed by Constanciel and Tapia[4].

In the figures, we do not reproduce the values at the minimum since the semiempirical techniques (such as CNDO) do not provide accurate quantitative values; they may simplly be considered as methods elaborated in order to get proper qualitative correlations.

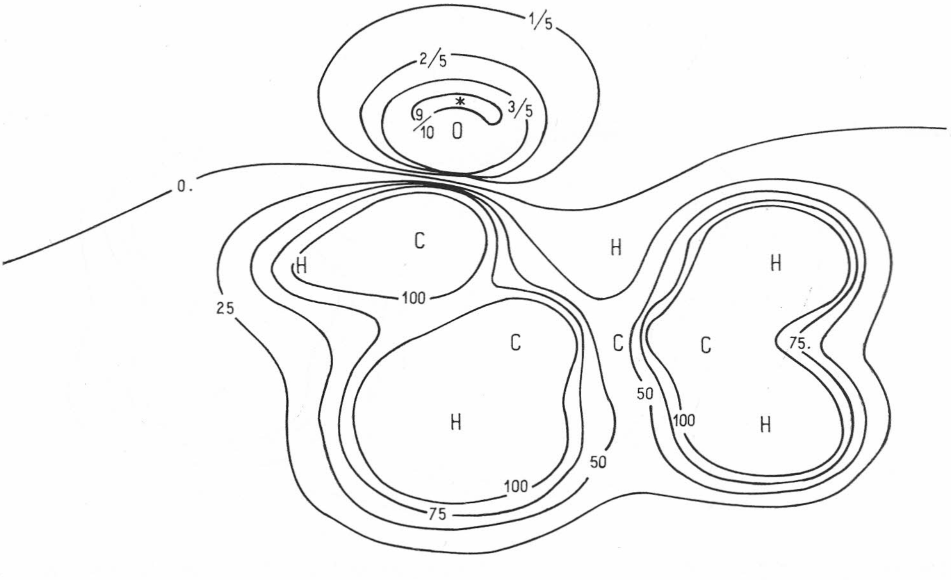

Figure 2a.

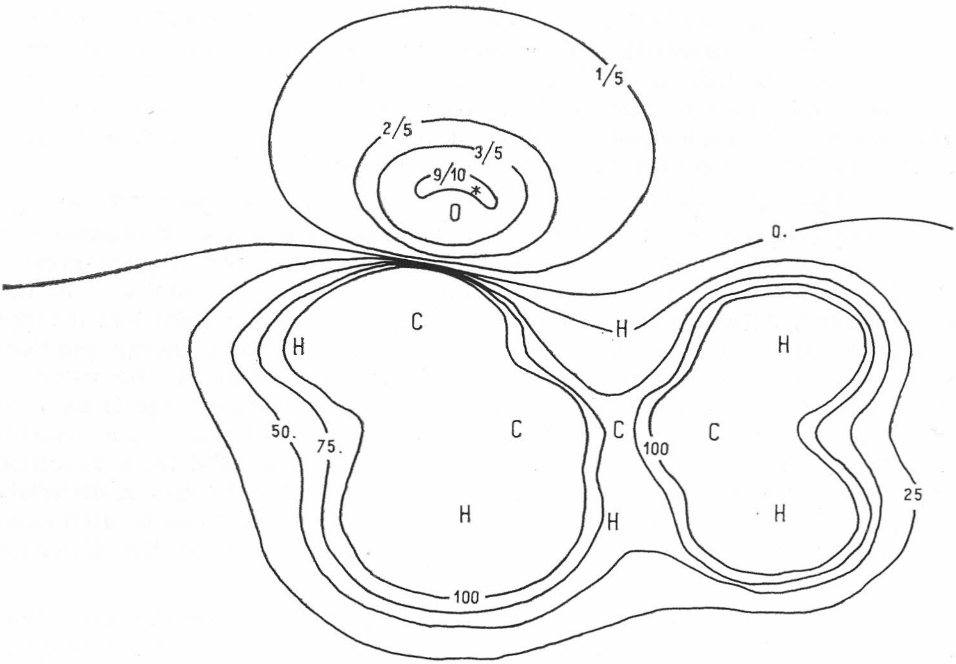

Figure 2b.

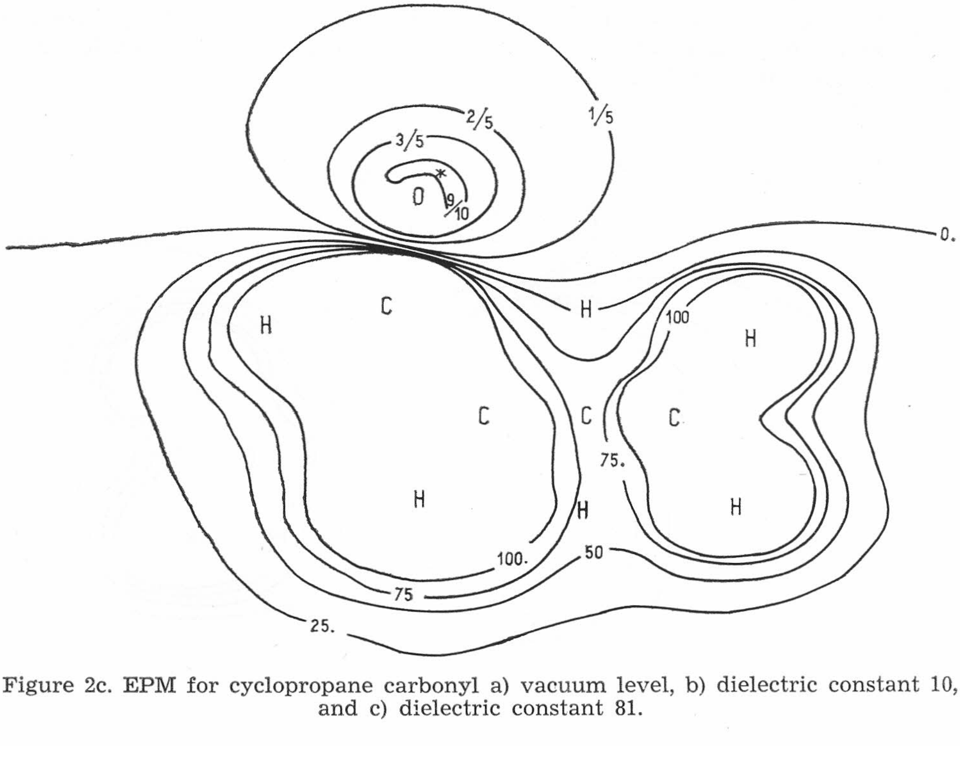

Figure 2c. EPM for cyclopropane carbonyl a) vacuum level, b) dielectric constant 10, and c) dielectric constant 81.

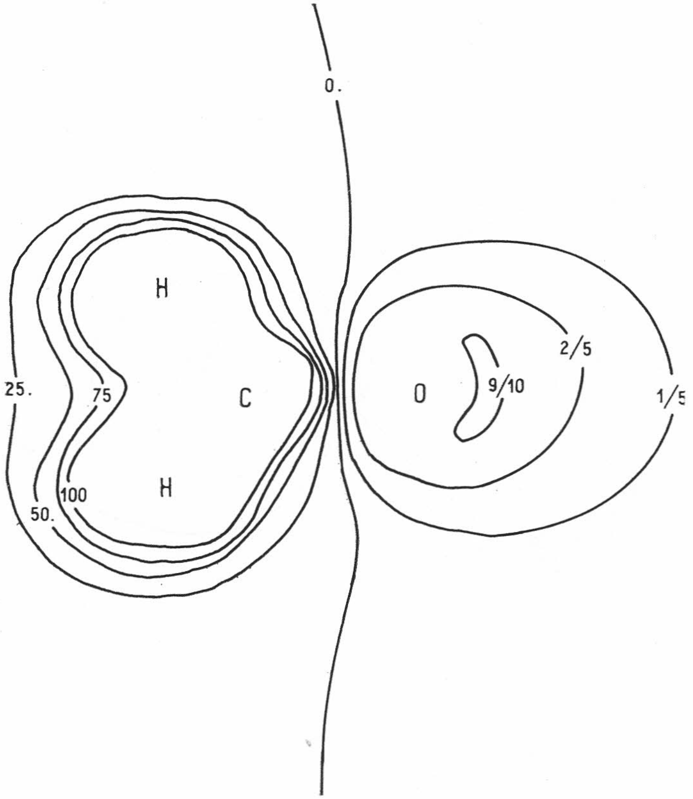

Figure 3a.

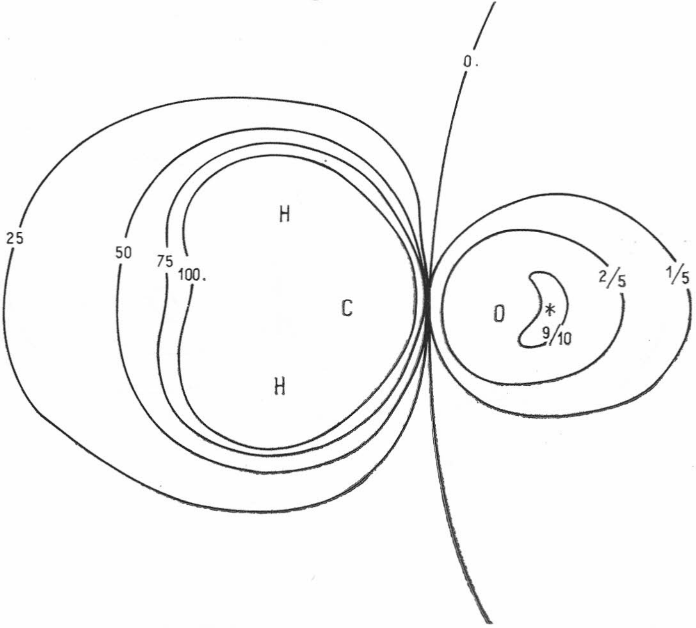

Figure 3b. EPM for isolated H_2CO, a) vacuum level, b) dielectric constant 81.

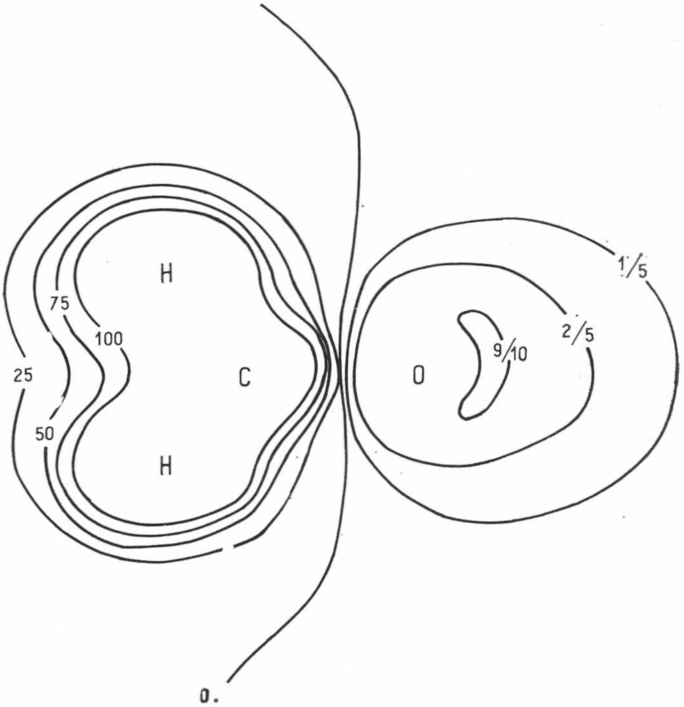

Figure 4a.

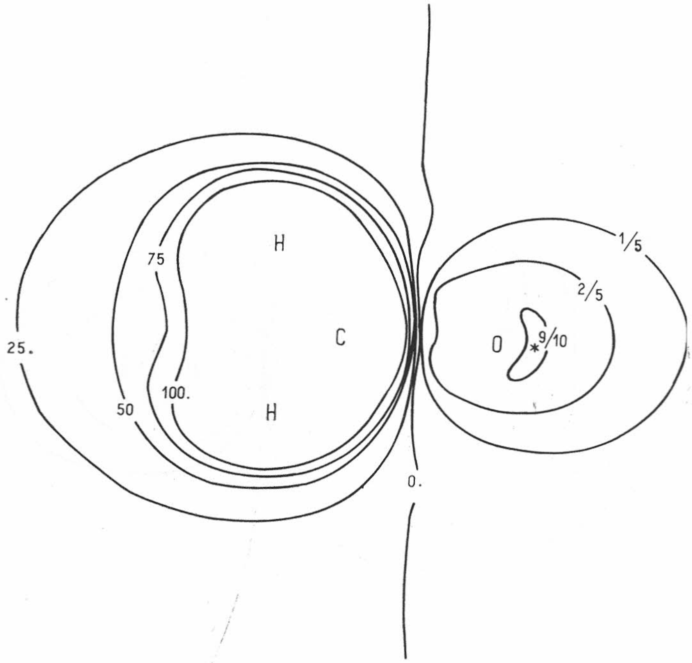

Figure 4b. EPM for H_2CO perturbed by a H_2O molecule, a) vacuum level, b) dielectric constant 81.

DIRECT INTERACTIONS AND REACTION FIELD CALCULATIONS. RESULTS AND DISSCUSSION

In this section we shall deal strictly with the water formaldehide interaction, and its relation with RF calculations and EPM of the latter. When a water molecule approaches formaldehyde, the CNDO/2 method reproduces a minimum, as expected experimentally because of the hydrogen bonding. This minimum is deeper the greater the dielectric constant, and it also depends on the hydrocarboned moiety, so that the stability of the hydrogen bond with a proton donor is a function of both of these properties. In Figure 3 we show the isolated formaldehyde molecule and consider its interaction with a reaction field generated by a medium with a dielectric constant 1 (part a) and 81 (part b).

In Figure 4 a similar study is carried out, but for a water molecule with its mass center placed at 3.75 Å from the mass center of formaldehyde, and in such a way that both molecular planes are orthogonal. The *strongest changes* amongst the four pictures occur for those which consider a reaction field and those which do not. From the EPM the direct interactions seem to be of second order with respect to the RF studies. Obviously the consideration of a single water molecule will certainly not simulate the main contribution to the polarization of the system. The molecule which interacts directly, generating a hydrogen bond, will surely be the most important for a shell surrounding the molecule under study, but only the consideration of at least a pair of solvation shells would provide an approximately accurate description of what really happens. On the other hand the consideration of this interacting molecule may affect the EPM as may be seen through the border lines between the positive and negative zones of the molecules.

Both the direct interactions and the RF should be considered in the study of a system where direct interactions may exist.

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SAŽETAK

Studij elektrostatičkih izopotencijalnih mapa s pomoću samousklađenoga reakcijskog polja

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Proučavan je utjecaj samousklađenog polja na raspodjelu naboja u molekulskim sustavima. Upotrijebljene su elektrostatičke izopotencijalne mape za diskusiju o kvalitativnim i kvantitativnim aspektima tih utjecaja.