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Electrostatic Potential for Some Non-Spherical Organic Molecules: An Oblate-Spheroidal Dipolar Approximation

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A spheroidal dipolar expansion is used for the determination of the electrostatic potential due to three non-spherical organic molecules: toluene, phenol and cyclohexanone. The agreement of experimental facts with the prediction of the most probable reactive sites on each molecule deduced from calculated equipotential maps is discussed.

Key words: Electrostatic potential – Non-spherical molecules.

1. Introduction

The determination of the electrostatic potential field outside a molecular charge distribution is a fundamental problem in the theory of intermolecular forces. The knowledge of an approximation of the electrostatic potential due to an isolated molecule has been proved [1, 2] to be useful for the understanding and the prediction of the a priori most probable reactive sites on the molecule. It should be noted that short-range effects such as exchange and charge transfer as well as long-range second-order effects as polarization involved in the interaction of a substrate with a reagent do not change in most cases the prediction obtained from the electrostatic model [3].

Outside the molecular charge distribution, the electrostatic potential can be expressed in terms of the permanent electric multipole moments of the

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molecule [4, 5]. In the conventional two-centre expansion in polar coordinates the charge distribution is assumed to be inscribable in a sphere. This spherical model which by nature is unable to describe anisotropies is unapplicable in regions close to non-spherical molecules, however the knowledge of the electrostatic potential in these regions is highly desirable. Following the pioneer work of Stiles (1975) [6, 7] Aubert–Frécon [8] has recently proposed a spheroidal multipolar expansion for the electrostatic potential due to a non-spherical charge distribution. For non-spherical molecules such a spheroidal formalism which is available outside the smallest ellipsoid of revolution (prolate or oblate) encapsulating the molecular charge distribution is applicable in larger regions than the spherical one.

This note presents as a straight forward application of the spheroidal formalism an analytical approximate determination of the electrostatic potential due to non-spherical organic molecules: toluene, phenol and cyclohexanone. Only the first non-zero term which is the dipolar one for each molecule investigated here is taken into account in the multipolar spheroidal expansion of the electrostatic potential.

After a brief recall of the spheroidal electrostatic potential presented in Sect. 2, the results are displayed and discussed in Sect. 3.

2. Electrostatic Potential Due to an Oblate-Spheroidal Dipolar Charge Distribution

The three molecules considered are dipolar ones and can be shaped by oblate ellipsoids. The electrostatic potential Φ produced by an oblate dipolar charge distribution at an arbitrary point external to the distribution is given by [for details see Ref. [8]] (S. I. units):

$$\Phi = -12\{Q_1^0(i\lambda)\mathcal{P}_1^0(\mu)\cdot\mu_z + Q_1^1(i\lambda)\mathcal{P}_1^1(\mu)[\cos\phi\cdot\mu_x + sin\,\phi\cdot\mu_y]\}/4\pi\varepsilon_0\, d^2 \tag{1}$$

where the distance d between the foci of the ellipse generating the ellipsoid is chosen so that it defines the smallest spheroid encapsulating the molecule. The oblate spheroidal coordinates (λ, μ, ϕ) (see Fig. 1) of the point considered are defined by their relationship with the corresponding cartesian coordinates $\{x, y, z\}$:

$$\lambda = \left(\frac{r^2 - d^2/4 + [(r^2 - d^2/4)^2 + d^2 z^2]^{1/2}}{d^2/2}\right)^{1/2} \tag{2a}$$

$$\mu = 2z/d\lambda \tag{2b}$$

$$\phi = \text{arctg}\,(y/x) \tag{2c}$$

where $r^2 = x^2 + y^2 + z^2$.

The symmetrized associated Legendre functions of the first kind $\mathcal{P}_l^m(\mu)$ and of

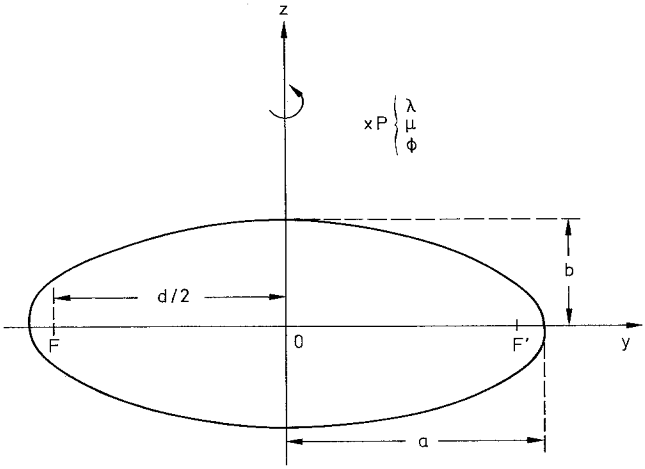

Fig. 1. Oblate-Spheroidal coordinates. *F* and *F'* are the foci of the ellipse generating the oblate ellipsoid. *Oz* is the rotational axis

the second kind $Q_l^m(i\lambda)$ are given by:

$$\mathcal{P}_1^0(\mu) = \mu, \qquad \mathcal{P}_1^1(\mu) = [(1-\mu^2)/2]^{1/2} \tag{3a}$$

$$Q_1^0(i\lambda) = \lambda \text{ arcotg } \lambda - 1,$$

$$Q_1^1(i\lambda) = [(\lambda^2-1)/2]^{1/2}\{\text{arcotg } \lambda - \lambda/(\lambda^2-1)\} \tag{3b}$$

The computational process is straight forward. Each molecule is roughly encapsulated in an oblate ellipsoid characterized by three parameters: the distance *d* between foci involved in (1) and (2), the major semi-axis *a* and the minor semi-axis *b*. It should be noted that the knowledge of the quantities *a* and *b* is not necessary for the evaluation of Φ but it defines the volume inside which our model is not available. The three cartesian components μ_x, μ_y and μ_z of the permanent molecular dipole been known (experimentally or by calculation or estimated from the method suggested by Flygare et al. [9]), the electrostatic potential is given by a direct evaluation of (1) for any point $\{x, y, z\}$ outside the molecular ellipsoid.

3. Results and Discussion

Toluene and phenol are molecules for which the assumption of an oblate-spheroidal shape is a reasonable one and they possess two reactive sites: ortho and para, so they constitute good examples to test our model.

The toluene molecule is shaped as an oblate ellipsoid characterized by $d = 0.584$ nm, $a = 0.337$ nm and $b = 0.084$ nm.

Equipotential contours are drawn in Fig. 2 in a plane parallel to the ring at $z = 0.22$ nm and for x (nm) $\in \{-0.3, +0.3\}$, y (nm) $\in \{-0.34, +0.46\}$. The following values have been used for the dipole moment (in 10^{-30} Cm): $\mu_x = 0$, $\mu_y = 1.13$ and $\mu_z = 0.40$.

Fig. 2 shows that carbons in ortho position are in the repulsive part of the electrostatic potential while carbons in para position are in the attractive region. Consequently electrophilic substitution would be favoured at the para position. This is in qualitative agreement with the experimental result of Olah *et al.* [10] (1972) who have shown by NMR that toluene protonates in the para position when dissolved in supraacid. It should be noted that electrostatic potentials calculated from the method proposed by Scrocco et al. [1] are seen to be repulsive for all the reactive sites of toluene [11] and one has to consider the movement of an hydrogen atom out of the ring-plane to obtain a path of negative potential leading to the para carbon atom.

The phenol molecule is shaped as an oblate ellipsoid characterized by $d = 0.584$ nm, $a = 0.337$ nm and $b = 0.168$ nm. Equipotential contours are drawn in Fig. 3 in a plane parallel to the ring at $z = 0.22$ nm and for x (nm) $\in \{-0.3, +0.3\}$, y (nm) $\in \{-0.34, +0.46\}$. The following values have been used for the dipole moment (in 10^{-30} Cm): $\mu_x = 5.42$, $\mu_y = 2.40$ and $\mu_z = 0$.

Fig. 3 shows an attractive region surrounding the carbon 6 in ortho position. Therefore it is to be expected that ortho substitution will occur at orthoposition. This is in qualitative agreement with the experimental fact that phenol can be chlorinated exclusively in the ortho position by reaction with Cl_2 in a diluted non polar solvent [12]. It should be noted that in a concentrated solvent as well as in a polar medium, the para position is experimentally found to be the most reactive. Our calculations in which the molecule is considered as isolated are by nature unable to reproduce such interactions.

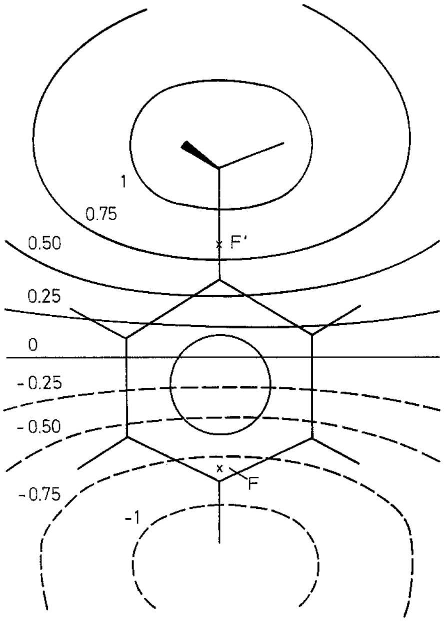

Fig. 2. Equipotential map for toluene in a plane parallel to the ring at $z = 0.22$ nm. The values of the potential are in kcal mole^{-1} (= 4.184 kJ mole^{-1}), negative values in broken lines, positive values in full lines

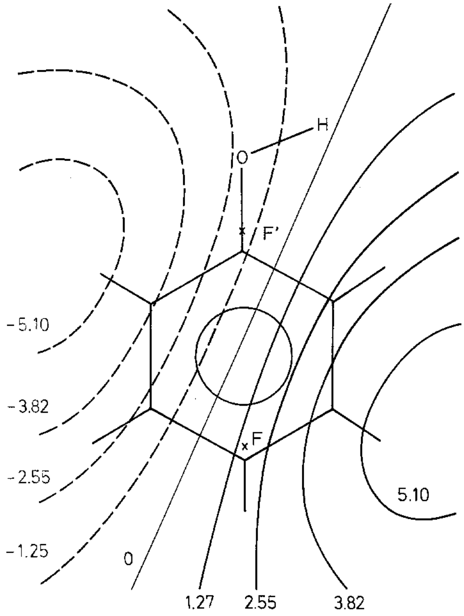

Fig. 3. Equipotential map for phenol in a plane parallel to the ring at $z = 0.22$ nm. [See caption of Fig. 2]

The cyclohexanone molecule is also worthy to be investigated as a test of our model because the reduction of the carbonyl group of this ketone can occur a priori either axially or equatorially. The cyclohexanone molecule is encapsulated in an oblate ellipsoid with the characteristic values $d = 0.663$ nm, $a =$ 0.6 nm and $b = 0.5$ nm. Equipotential contours are drawn in Fig. 4 in a plane parallel to the yoz plane at $x = 0.25$ nm and for y (nm)$\in\{-0.6, +0.4\}$ and $z \in \{-0.5, +0.5\}$. The following values have been used for the dipole moment (in 10^{-30} Cm): $\mu_x = 0$, $\mu_y = 9.47$ and $\mu_z = 2.10$. Fig. 4 shows that the

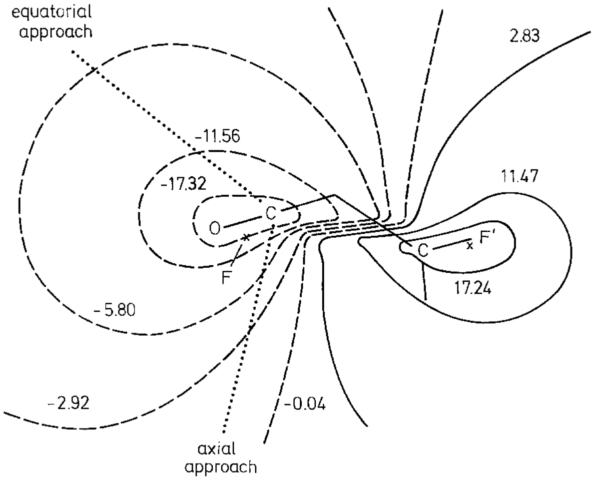

Fig. 4. Equipotential map for cyclohexanone in a plane parallel to the yoz plane at $x = 0.25$ nm. [See caption of Fig. 2]

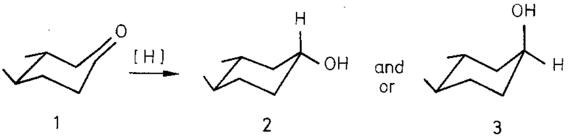

Fig. 5. Stereochemically different products in reduction of cyclohexanones

potential surrounding the carbonyl group is dissymmetrical, its values are smaller in the axial direction than in the equatorial one, so the axial approach should be favored. In fact it is well known that reduction of cyclohexanones 1 (see Fig. 5) by hydride-ions gives essentially the equatorial alcohols 2 [13]. For instance reduction of cholestan-3-one by sodium borohydride gives a 94% predominance of axial attack yielding the equatorial alcohol. A similar example is the reduction of 4-*t*-butylcyclohexanone by the same reductant giving a 86% predominance of trans-4-*t*-butylcyclohexanol.

4. Conclusion

Being analytical our model of determination of the electrostatic potential due to a molecular non-spherical charge distribution is a very cheap one. Furthermore, as long as we are not interested in the true values of the potential but only in the general behaviour of the equipotential maps, our results are seen to be equivalent to those obtained from more elaborated methods [11, 12, 14] needing some knowledge of the wavefunction.

The results are dependent on the choice of the ellipsoid encapsulating the molecule under investigation so, in order to check the importance of this arbitrariness we have re-calculated the electrostatic potential due to the phenol molecule with a significantly modified value of d: $d = 0.66$ nm (variation of 18%). The equipotential map is unchanged. In the same way, the behaviour of the equipotential map has been seen to be not significantly dependent on the quality of the values used for the dipole moment of phenol, so that values estimated from Flygare's method could be sufficient.

The spheroidal formalism we have used for the determination of the electrostatic potential is also available for the interaction energy between two non-overlapping charge distributions, one of which at least being non-spherical [8]. It has been used for the determination of the lattice energy of the orthorhombic structure of the acetylene crystal [15] and of the benzene crystal [16]. Similar work on the phenol crystal is undertaken.

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