Possibility of proton oscillations through the benzene ring

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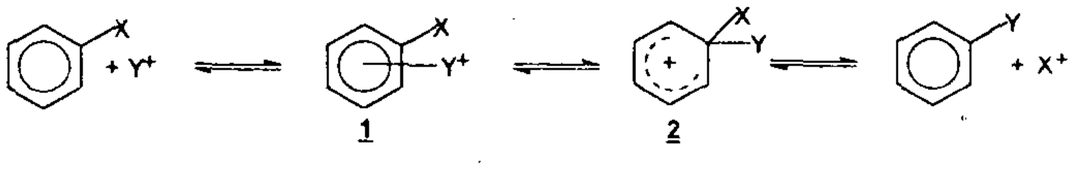
The possibility of proton oscillations above and below the plane of the benzene ring, through its centroid, in protonated benzene is pointed out, in this communication.

PROTONATION of benzene and other aromatic hydrocarbons has been studied over the years by a variety of methods[1]. The nature of the arenium ion that is formed as the transition state in an electrophilic aromatic substitution has been the focus of attention of a number of experimental and theoretical studies (for example, see ref. 2 and references therein). It is generally believed that a π-complex (**1**) is formed first and then it rearranges into a σ-complex (**2**) before it results in products.



When $X = Y = H$, there is an interesting possibility: the proton in (**1**) could lie either above or below the plane of the benzene ring and it could undergo an oscillatory motion between the two positions, through the centre of the ring.

In order to examine such a possibility we have computed the H^+–C_6H_6 interaction energy keeping C_6H_6 in its equilibrium geometry[3] ($r_{C-C} = 1.386$ Å, $r_{C-H} = 1.076$ Å) and varying the distance (Z) of H^+ from the centre of the C_6H_6 plane by the LCAO–MO–SCF approach using the 6-311G basis set and the Gaussian 94 set of programs[4].

It is clear from the results shown in Figure 1 that there is a potential well of depth of 4.38 eV, with the minimum at $Z = \pm 1.1$ Å and that we are dealing with a stable ionic species that is likely to be found in nature. Mulliken population analysis reveals that there is substantial charge transfer between C_6H_6 and H^+ at such short distances.

Geometry optimization calculations reveal that even when the proton is at the centre of the ring, the ring is only slightly enlarged ($r_{C-C} = 1.424$ Å; $r_{C-H} = 1.068$ Å) and that the energy difference between the distorted and the undistorted geometries is only 0.23 eV, implying that the proton can go through the centre of ring. It is worth emphasizing that the energy of the $C_6H_7^+$ ion with an H in the geometric centre of the benzene ring is well below (– 1.8 eV) that for the separated $C_6H_6 + H^+$ and that there are several bound states corresponding to the oscillatory motion above and below the plane of the ring as can be seen from Figure 1. These bound states were computed using the Fourier grid Hamiltonian approach[5]. A close examination of the figure suggests three types of oscillations. For $0 \le V \le -1.8$ eV, there would be 'free' oscillation of the proton between the two sides of the ring. For energies just below the barrier (– 1.8 eV), there is the possibility of tunneling. For energies well below the barrier, the proton would oscillate about the equilibrium position on either side.

In order to make sure that our findings are not dependent on the quality of the basis set, we have computed the entire potential-energy curve shown in Figure 1 using 6-311G** basis set, which includes polarization functions. While the depth of the well and the height of the barrier in between change in magnitude with the basis set, the major features of the double well potential remain the same.

It is worth pointing out that several semiempirical and *ab initio* calculations (for example, see ref. 6) on $C_6H_7^+$ have shown that the σ complex (**2**) is more stable than the π complex (**1**), in the context of electrophilic aromatic substitution. But that is not quite relevant to the present investigation which focuses attention on the penetration of the ring by a proton.

The possibility of the charge transfer ($C_6H_6^+ + H$) channel suggests that the proton undergoing oscillatory motion between the two sides of the benzene ring may not stay attached to the ring forever. The lifetime of the species would depend on the crossing (or avoided crossing) between the potential energy curves for $C_6H_6 - H^+$ and $C_6H_6^+ - H$ interaction. Investigation of this aspect of the problem is presently being taken up. Regardless of the nature of the crossing between the two curves, the

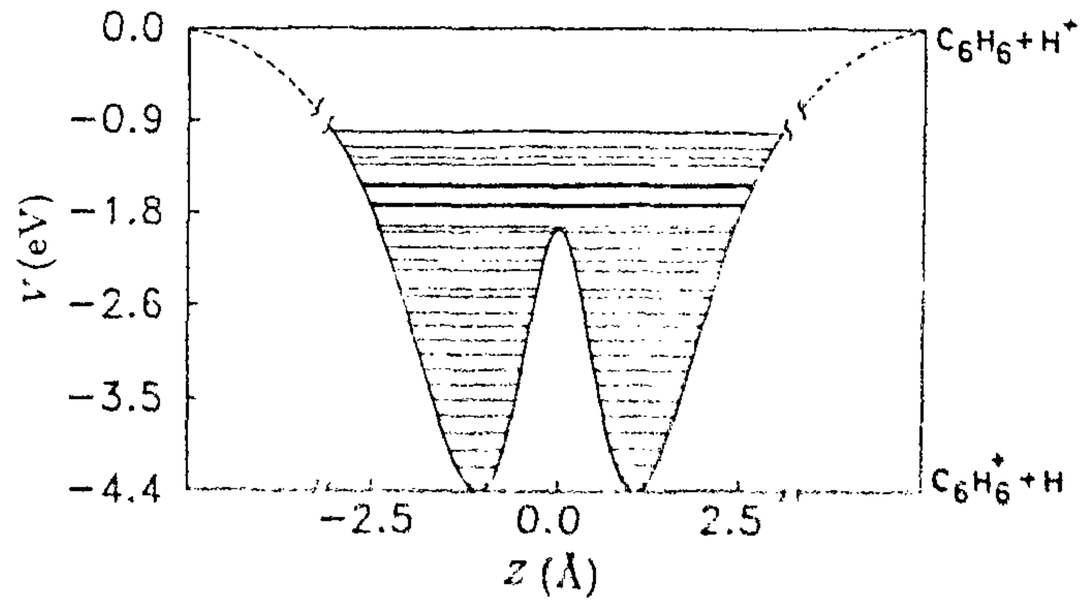


Figure 1. The interaction potential for H^+-C_6H_6 with the zero of energy corresponding to the asymptotically separated H^+ and C_6H_6 in its equilibrium geometry. For reference, the energy of $C_6H_6^+ + H$ state is included in the figure.

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proposed structure can be expected to play an important role in proton–benzene collisions[7]. Also, under conditions as in a mass spectrometer or in interstellar clouds[8] $C_6H_7^+$ could live for a sufficiently long time and transitions between its electronic states and also between the bound states supported by the double well potential could account for some of the hitherto unaccounted emissions, particularly in the long wavelength regions.

Preliminary calculations[9] show that there are no significant minima but there exist barriers to penetration through the ring in the interaction of C_6H_6 with H, H^- and He, thus making H^+ a unique partner in exhibiting such an oscillatory motion.

If such a motion could exist in protonated benzene, it could exist in a variety of other protonated aromatic hydrocarbons such as naphthalene, anthracene, etc. We have indeed found this to be the case[9].

There has been a lot of interest in collisions of neutrals and charged species with fullerenes and the possibility of trapping atoms/ions inside the cage[10]. In this context the possibility of proton motion through the ring becomes quite relevant.

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Nucleotide frequency map: A new technique for pictorial representation of dinucleotide frequencies

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In this communication, a method of presentation of dinucleotide frequencies in the form of a contour diagram (map), designated as dinucleotide frequency map (DNFM), has been used for the first time to analyse the compositional bias of different nucleic acid sequences. Such maps provide a method of visualization of the nucleotide usage at a glance and allow simultaneous representation and comparative analysis of multiple sequences of different origins. Using the technique of DNFMs, it has been shown that the dinucleotide frequency distribution profile of any nucleotide sequence often exhibits distinct statistical bias, which is not predictable from the knowledge of its base composition. Analysis of bacterial rDNA operons showed that 16S and 23S rRNA genes of such species, in general, follow similar dinucleotide patterns, which are different from those of the intervening regions. The technique of DNFM has also been applied to analyse the compositional heterogeneity of the genomic sequence of the bacteriophage lambda to show that the dinucleotide frequencies vary along the phage genome depending on the distribution of open reading frames.

COMPOSITIONAL heterogeneity is an intrinsic feature of natural nucleic acid sequences. At the genome level, eukaryotic and prokaryotic sequences exhibit hierarchy in the frequencies of appearance of most dinucleotides[1]. Instances of distinct bias in dinucleotide usage in genomic sequences include underrepresentation of T_pA and overrepresentation of G_pC in most temperate bacteriophage sequences[2], C_pG suppression in vertebrate non-oncogenes[3,4], animal mitochondrial genomes and many thermophilic bacterial sequences[2] and abundance of G_pG/C_pC in animal mitochondrial genomes and chloroplast genomes[5]. A revealing contrast in statistical composition is often observed for long versus short DNA sequences, primarily because of the presence of local signals[2] such as promoter, enhancer and termination signals, or genetic mosaicism resulting from horizontal gene transfer, transposition or recombination events and also due to the fact that coding and non-coding regions of any sequence, in general, have distinct bias in short oligonucleotide distributions[6,7]. Interpretation to such compositional heterogeneity usually centres on structural or conformational preferences[2], context-dependent mutational events[8,9], methylation effects[2,10] processes of rep-