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. 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⁺–C₆H₅ interaction energy keeping C₆H₅ in its equilibrium geometry (r_C–C = 1.386 Å, r_C–H = 1.076 Å) and varying the distance (Z) of H⁺ from the centre of the C₆H₅ plane by the LCAO–MO–SCF approach using the 6-311G basis set and the Gaussian 94 set of programs.

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 = ±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 C₆H₅ 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 C₆H₅⁺ ion with

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Figure 1. The interaction potential for H⁺–C₆H₅ with the zero of energy corresponding to the asymptotically separated H⁺ and C₆H₅ in its equilibrium geometry. For reference, the energy of C₆H₅⁺+H state is included in the figure.
proposed structure can be expected to play an important role in proton–benzene collisions. Also, under conditions as in a mass spectrometer or in interstellar clouds, C₇H₅ 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 show that there are no significant minima but there exist barriers to penetration through the ring in the interaction of C₇H₅ 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.

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


ACKNOWLEDGEMENTS. We are grateful to Dr S. Manogaran for stimulating discussions and for a critical reading of the manuscript. We thank Dr Sumathy for pointing out some of the crucial references on C₇H₅. This study was supported in part by a grant from the Commission of European Communities.

Received 22 March 1996; revised accepted 13 June 1996

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 DNFM, 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 bacterial phage 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, euarykaryotic and prokaryotic sequences exhibit hierarchy in the frequencies of appearance of most dinucleotides. Instances of distinct bias in dinucleotide usage in genomic sequences include underrepresentation of TₐA and over-representation of GₜC in most temperate bacteriophage sequences, CₜG suppression in vertebrate non-coding sequences, animal mitochondrial genomes and many thermophilic bacterial sequences and abundance of GₜG/CₜC in animal mitochondrial genomes and chloroplast genomes. A revealing contrast in statistical composition is often observed for long versus short DNA sequences, primarily because of the presence of local signals 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. Interpretation to such compositional heterogeneity usually centres on structural or conformational preferences, context-dependent mutational events, methylation effects processes of rep-