research work spanning nearly three decades, is in the application of NMR technique for the study of phase transition in solids, fast ionic conductors and high temperature superconductors. R. S. Sirohi has distinguished himself in the field of applied optics. He has used modern optical techniques to make precision mechanical measurements.

Interferometry, speckle phenomena, holography and ellipsometry have been effectively used coupled with electronic instrumentation, computing techniques and metrological principles.

The awards were presented on 6 September 2001, by V. S. Rama Devi, Governor of Karnataka, who presided over the function. R. Chidambaram, Homi

Bhabha Professor, BARC, and former Chairman of the Atomic Energy Commission was the chief guest. He gave away the scrolls and cheque to the awardees.

J. Shashidhara Prasad and **M. A. Sridhar,** Department of Physics, Mysore University, Mysore 570 006, India

RESEARCH NEWS

A revised look at π-electron delocalization in benzene

G. Narahari Sastry

Aromaticity occupies a central place in chemical thought. Aromaticity as such, is not an experimental quantity and no generally acceptable definition has been established to quantify this property[1-3]. Conventionally, it is associated with conjugated π-systems with very high stability, planarity, delocalization with small bond length alternation, preference for substitution reactions over the addition reactions, and exalted diamagnetic susceptibilities. Aromaticity is associated with cyclic arrays of mobile electrons with favourable symmetries, leading to fully delocalized structures with equal bond lengths. Benzene is a seminal example of aromaticity[4]. Antiaromatic systems are characterized by localized rather than delocalized electronic and geometric structures. π-bonding and σ–π separation in the planar conjugated systems are an integral part of contemporary chemical thinking[5]. The σ–π separation was the basis for the famous Huckel rules which account for the special stability for closed shell $4n + 2$ π-electron systems and instability for $4n\pi$-electron systems. The stability of cyclopropenyl cation and the apparent instability of cyclobutadiene laid strong foundations to the $4n + 2$ rule for aromaticity, and the $4n$ rule for antiaromaticity. These Huckel rules have become among the most powerful paradigms of chemistry, in general and organic chemistry, in particular. Consequently, aromatic species

are associated with highly delocalized π-electronic component, with equal bond lengths, and special stability relative to an open-chain reference. In contrast, antiaromatic systems exhibit bond localizations and their geometries are non-uniform, exhibiting alternating C–C bond lengths. π-delocalization and geometry have thus found a strong link in the aromatic and antiaromatic organic compounds. This led to a 'popular belief' that symmetric geometries, with equal C–C bond lengths, in species such as benzene or allyl are due to the inherent tendency of π-electrons for strong delocalization in the aromatic species. Apparently, these ideas have become so popular and powerful and also an integral part of our thinking in structural organic chemistry, without any concrete proof.

Early recognition of π-distortivity paradox

While the π-delocalization in benzene became standard textbook material, some theoretical and spectroscopic studies led to a contrary viewpoint, namely these results pointed out that π-electrons in benzene are distortive in nature. Longuet–Higgins and Salem recognized as early as in 1959, that distortivity of π-electrons exists already in benzene, using the Huckel theory with a variable, β (ref. 2). A similar

argument was used to account for the low experimental frequency of the b_{2u} vibrational mode in benzene, by postulating that the bond alternation caused by the distortion lowers the π-electron energy[6]. Shaik and Bar[7] also came to the same conclusion based on qualitative VB ideas, that the π-component in benzene is distortive. The valence-bond treatments by Mazumdar and Dixit[8] as well as Soos and Ramasesha[9], of Hubbard and extended Hubbard rings, essentially predict the distortion. However, these views which were familiar to the spectroscopic community have not gained much ground in organic chemistry, which accumulated tremendous support for the special stability of benzene and association of this stability with the 'aromatic behaviour of π-electrons' in the light of Huckel rules.

Thus, although the recognition of π-distortive tendency is quite old, significant effort was not taken to probe this problem and convince the traditional organic chemistry community about this seemingly unbelievable hypothesis that π-electrons have inherent distortive propensity in benzene.

Shaik–Hiberty approach

However, in early the 1980s, Sason Shaik examined the process of interconversion between the two Kekule structures as a reaction, using his, then

recently developed, curve-crossing model[10]. In this model, there exist two possibilities for the π-electron component of benzene as illustrated in Figure 1. A very high vertical energy gap (Figure 1 a) results in the distortive nature of the π-electrons or localized double bonds. However, if the vertical gap is very small, a fully delocalized mode is energetically more stable for the π-component (Figure 1 b). The vertical excitation gap is roughly proportional to three times the singlet–triplet energy difference of a C=C. Thus, a stronger bond exhibits higher propensity towards a localized (distorted) structure, while weaker bonds show relatively higher preference for delocalization (Scheme 1). Considering the fact that C=C is a relatively strong bond, Sason Shaik concluded that π-electrons are distortive in benzene; these results were also supported by computations. Later, he started collaboration with Philippe Hiberty and used σ–π separation techniques and theoretical tools of various sophistication to test these qualitative ideas[11]. Each time they studied this problem with a different theoretical approach, their confidence levels enhanced in the π-distortivity. Expectedly, their conclusions met with criticisms[12], each of which was successfully rebutted by Shaik, Hiberty and coworkers[13]. According to this viewpoint, in aromatic systems the symmetrizing σ-component is dominating (Figure 2), whereas in the antiaromatic systems, the distortive π-component is dominating (Figure 2).

While there is a general consensus about the theoretical description of π-electron distortivity, the idea appeared to have little or no impact on experimental chemistry.

However around the same time, Haas and Zilberg[14] have observed a significant frequency exaltation selectively for the bond alternation mode (called b_{2u}) in the first excited state of β-methyl styrene and connected their findings to earlier ones found for benzene. These results can readily be explained by the curve-crossing model of Shaik which maintains that π-electrons, in the symmetric geometry, will have a transition state nature in the ground state and the nature of minima in the excited state[15]. This observation and corroboration of exaltation of the b_{2u} mode in the excited state of benzene with Kekule crossing model, provided the missing link between theory and experiment and effectively provided the experimental
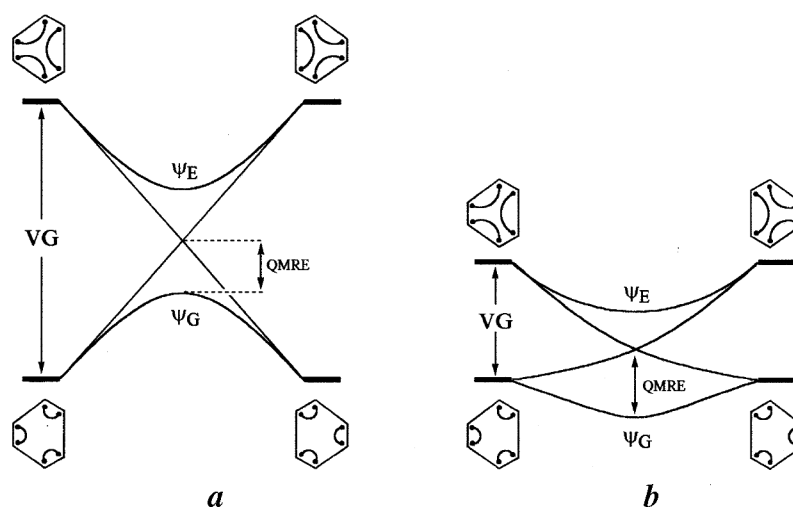

Figure 1. Valence bond curve–crossing diagram for the interconversion of two Kekule structures along the bond alternating coordinate (referring only to πelectrons). VG is the vertical gap and QMRE the quantum mechanical resonance energy or avoided crossing energy. ψ_G and ψ_E correspond to ground and excited states for the πelectron component. In (a) where VG is substantial, the avoided crossing results in transition state, implying the distortive tendency of the πcomponent. In contrast, (b) gives a minimum for the symmetrical structure which corresponds to the delocalization.
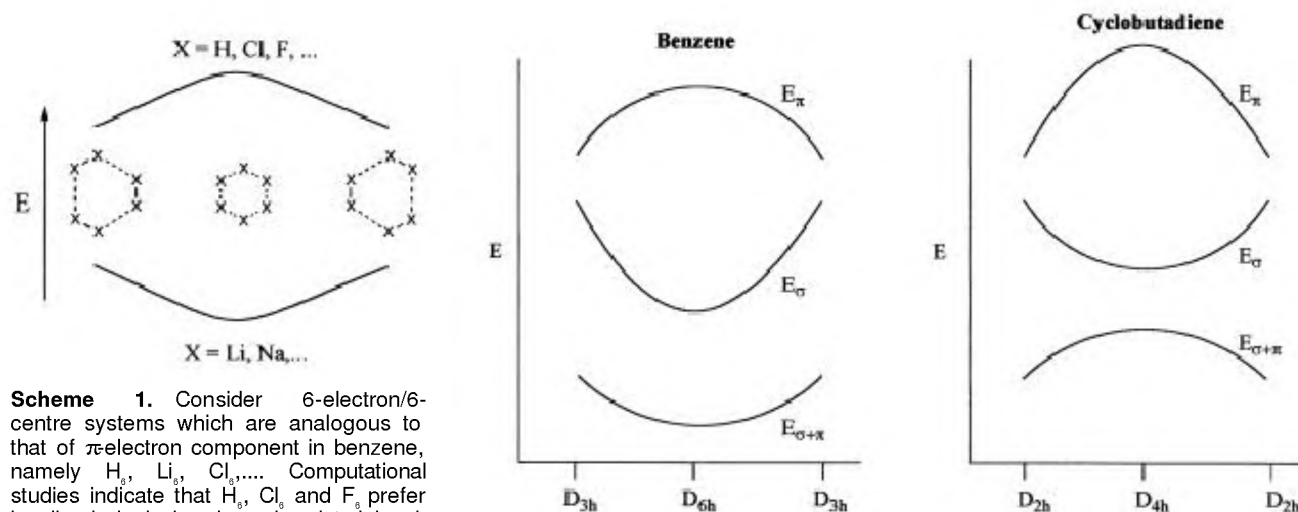
Scheme 1. Consider 6-electron/6-centre systems which are analogous to that of πelectron component in benzene, namely H_6, Li_6, Cl_6,.... Computational studies indicate that H_6, Cl_6 and F_6 prefer localized single bonds and resist delocalization. In contrast, Li_6, Na_6 prefer D_{6h} and fully delocalized structures. Weaker bonds prefer delocalization and stronger bonds prefer localization.

Figure 2. Idealized σ and πcomponents of energy for benzene and cyclobutadiene. The total energy is taken as the sum of the σ and π. In benzene, the symmetrizing σcomponent overrides the πdistortive propensity. However, in cyclobutadiene the σcomponent is not strong enough to resist πdistortivity.

evidence for the π-electron distortivity. The exaltation of the frequency corresponding to the Kekule mode, particularly in benzene and the aromatic hydrocarbons in general, have given importance to the appreciation of the effect of π-electron distortivity in the ground states and higher propensity of π-delocalizations in the excited states of aromatic hydrocarbons. Later, Shaik and Shurki showed that the distorted C_6 nucleus in the newly synthesized trisubstituted benzene adopts its geometry due to the π-distortivity, while the first excited state restores the six-fold symmetry[16]. These two findings marked the beginning of a new chapter in the story of benzene.

What determines the D_{6h} geometry of benzene?

There is a strong preference by the σ-framework towards the D_{6h} over D_{3h}. This symmetrizing force is responsible for the bond length equalization in benzene. Thus, benzene has a D_{6h} equilibrium structure because its σ-resistance to the localizing (distortive) mode exceeds the π-distortivity by a significant margin.

'Benzene possesses a unique delocalized π-component which has a dual nature; at any geometry of $(CH)_6$ structure, the π-electrons are strongly stabilized by quantum mechanical resonance energy (QMRE), and at the same time, they possess a global distortive tendency toward a D_{3h} structure'. The delocalized π-electronic component of benzene is unstable towards a localizing distortion and is at the same time stabilized by resonance relative to the localized reference structure. Therefore, in spite of the distortive nature, the π-electron component enjoys substantial stabilization due to the quantum mechanical resonance energy in the symmetrical D_{6h} geometry.

A fine balance between the distortive π-component and the symmetrizing σ-frame is operative in any conjugated system. For example, in allylic species

and in benzene, the σ-frames win and the species remain symmetrical. In contrast, in cyclobutadiene the σ-resistance is not sufficient and the structure relaxes to a rectangular geometry (Figure 2). So the bottom line is that if a conjugated system is symmetric, then the σ-framework is stronger; a distorted structure means that the σ-framework is not strong enough to circumvent π-distortivity. The avoided crossing of the Kekule structures and π-distortivity of the ground state will be manifested as a low-frequency Kekule mode in the ground state and a high frequency for the same mode in the twin excited state. This is expected to be a general signature of the Kekule-avoided crossing and π-distortivity.

Although the π-electron energy favours a distorted structure, the QMRE resonance energy favours a symmetrical geometry. Experimental determinations such as relative heats of formation, reactivity, spectroscopy and magnetism deal only with the QMRE property of benzene. The σ-frame restricts the geometries which are very close to the perfect hexagon, where QMRE is large. Therefore, the D_{6h} benzene can behave as a stable species with lower energy compared to the corresponding open chain polyene, even with a distortive π-component. Obviously, QMRE is higher for a symmetrical (D_{6h}) benzene compared to the Kekule form, which accounts for the definitive link between the aromaticity and π-electron delocalization.

However, Shaik, Hiberty and co-workers have proved beyond doubt that the preference of π-electrons for delocalized geometries in the aromatic hydrocarbons is a mis-concept.

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G. Narahari Sastry is in the Department of Chemistry, Pondicherry University, Pondicherry 605 014, India e-mail: gnsastry@yahoo.com