Chapter 7

1,3,5-Cyclohexatriene captured in computro; the concept of aromaticity. †

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Abstract: The determination of the extra stability of benzene, due to resonance/delocalised \( \pi \)-electrons, is not straightforward, *e.g.* the energy of benzene, described by two Kekulé structures, should be compared to that of ‘hypothetical’ 1,3,5-cyclohexatriene, described by only one Kekulé structure. Using Valence Bond (VB) theory, the energies and geometries of two-Kekulé-structure benzene and one-Kekulé-structure 1,3,5-cyclohexatriene have been calculated. The vertical resonance energy of benzene is only -9.6 kcal/mol. Geometry optimisation of one-Kekulé-structure 1,3,5-cyclohexatriene leads to a \( D_{3h} \) symmetric structure with alternating bond lengths located 7.4 kcal/mol above benzene (-TRE). A calculation on deformed benzene (two Kekulé structures) in the 1,3,5-cyclohexatriene optimised geometry shows that it is still stabilised by resonance by 6.2 kcal/mol and is located only 1.2 kcal/mol above benzene itself. Upon geometry optimisation, \( D_{6h} \) symmetric benzene results. The resonance between the two Kekulé structures is thus necessary for the \( D_{6h} \) symmetric geometry of benzene.
1. Introduction

‘Bicarburet of hydrogen’ nowadays referred to as benzene (C\textsubscript{6}H\textsubscript{6}) continuously surprises the scientific community [1,2], since it was first isolated by Faraday in 1825 [3,4]. Despite its unsaturated character its properties differ from those of (conjugated) alkenes [5]. In fact, benzene has a very distinct chemical reactivity.

With the advance of quantum chemistry the peculiar behaviour of benzene could be qualitatively rationalised using a Valence Bond (VB) treatment, \textit{i.e.} by resonance between two Kekulé structures which provides extra stabilisation. In a Molecular Orbital (MO) approach the properties of benzene could be explained by \(\pi\)-electron delocalisation along its carbon perimeter. This has led to the famous Hückel 4n+2/4n rules, \textit{i.e.} monocyclic conjugated circuits (\([n]\)-annulenes) with 4n+2 \textit{(aromatic} character) and 4n \textit{(anti-aromatic} character) \(\pi\)-electrons \((n = 0, 1, 2, \text{etc.})\) are thermodynamically stabilised and destabilised, respectively [5]. The extra stabilisation of benzene due to the resonance between its two Kekulé structures or, equivalently, to its delocalised \(\pi\) system, is called the resonance (RE) or delocalisation energy. As a consequence benzene has a hexagonal geometry (\(D\textsubscript{6h}\) symmetry) with bond lengths (1.399 Å [6]) intermediate between regular single and double carbon-carbon bond lengths.

The determination of the resonance energy of benzene, which represents the energy criterion for aromaticity, is thus an important, but not straightforward issue. The problem is the inaccessibility of appropriate reference compounds [7]. For example, 1,3,5-cyclohexatriene with the same geometry as benzene, but lacking resonance/\(\pi\)-electron delocalisation would be an appropriate reference. However, it does not exist! The energy difference between benzene and this hypothetical 1,3,5-cyclohexatriene gives the vertical resonance energy (VRE). To circumvent this problem it was proposed to use polyenes as a reference [8], \textit{i.e.} the energy of benzene is compared to that of again a hypothetical cyclic polyene, 1,3,5-cyclohexatriene with \(D\textsubscript{3h}\) symmetry. Its energy is estimated by taking thrice the C=C and C-C increment [8]. This energy difference gives the theoretical resonance energy (TRE). In this case also a change in geometry \((D\textsubscript{6h} \rightarrow D\textsubscript{3h})\) is involved.
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Whereas the two reference points required for the determination of VRE or TRE of benzene are experimentally inaccessible, the best approach towards these reference compounds is by applying *Ab Initio* Valence Bond (VB) theory. A prerequisite is that optimised 1,3,5-cyclohexatriene (D$_{3h}$ symmetry) is within reach.

Here we report the results of VB calculations on benzene and the elusive reference points, viz. 1,3,5-cyclohexatriene in both the benzene as well as its optimised (‘true’ 1,3,5-cyclohexatriene) geometries. Besides giving values for the resonance energies VRE and TRE, the results also shed light on the recent proposal that the hexagonal geometry of benzene is a consequence of the symmetrising force of the $\sigma$-skeleton instead of resonance/delocalisation of the $\pi$-electrons [9,10].

2. Methods

Within the VB model the wave function describes the desired double and single bonds; the $\pi$-system is described within the non-orthogonal VB framework using p-like orbitals on the six carbon atoms. The $\sigma$-system consists of delocalised doubly occupied orbitals. In all calculations all orbitals are completely optimised.

Since each bond in VB is described by a singlet coupled pair of orbitals, the reference points 1,3,5-cyclohexatriene in the benzene geometry (D$_{6h}$ symmetry) and in its optimised geometry (D$_{3h}$ symmetry) with double bonds between the carbon-atoms (1,2), (3,4) and (5,6), can be described by the following wave function:

$$\Psi_1 = |\sigma_{\text{core}}(p_1\overline{p}_2 - \overline{p}_1p_2)(p_3\overline{p}_4 - \overline{p}_3p_4)(p_5\overline{p}_6 - \overline{p}_5p_6)| = |\sigma_{\text{core}}(1,2)(3,4)(5,6)|$$

Thus the wave function in either case consists of only one Kekulé structure. In contrast, the wave function of regular benzene (D$_{6h}$ symmetry) and benzene deformed (D$_{3h}$ symmetry) in the optimised geometry of 1,3,5-cyclohexatriene will be obtained by adding the second Kekulé structure, giving

$$\Psi_2 = N(|\sigma_{\text{core}}(1,2)(3,4)(5,6)| + |\sigma_{\text{core}}(2,3)(4,5)(6,1)|)$$

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Note that two Kekulé structures are not orthogonal to each other (for benzene, the overlap is 0.66). This is both a consequence of the orbital overlap and an intrinsic property of the Rumer spin functions. Hence, the formal single bonds of 1,3,5-cyclohexatriene (one-Kekulé-structure calculations) will possess double bond character. So 1,3,5-cyclohexatriene is polyene-like.

In our VB description of benzene, the three Dewar benzene structures, viz. three additional covalent structures which contribute for less than 6-7% each [11,12] are excluded, to focus on the effect of resonance interactions between the possible Kekulé structures.

The VB wave functions will be denoted by the symmetry of the geometry and the number of structures employed. Thus a regular benzene calculation is denoted by $D_{6h}^2$. To obtain an estimate of the VRE, a one-Kekulé-structure calculation has been performed, viz. denoted by deformed 1,3,5-cyclohexatriene ($D_{6h}^1$). For the calculation of the TRE, the geometry of 1,3,5-cyclohexatriene ($D_{3h}^1$) has been optimised. A calculation on deformed benzene in the optimised 1,3,5-cyclohexatriene geometry ($D_{3h}^2$) has been performed to judge whether resonance is still important upon deformation of benzene.

In our VB approach, the p-orbitals are allowed to delocalise, though they are still predominantly atomic in nature (cf. Cooper et al. [11]). Thus completely optimised non-orthogonal atomic orbitals are used which have tails on the other atoms. This model was first used by Coulson and Fischer in their description of the $H_2$ molecule [13]. The geometries of benzene ($D_{6h}^2$, $\Psi_2$) and 1,3,5-cyclohexatriene ($D_{3h}^1$, $\Psi_1$) were optimised using gradient techniques [14]; a 6-31G basis set [15] was used. The calculations are performed using the *Ab Initio* Valence Bond program TURTLE [16], as integrated in the GAMESS-UK package [17].
3. Results and discussion

3.1. The geometries and resonance energies of (deformed) benzene ($D_{6h}$, $D_{3h}$) and (deformed) 1,3,5-cyclohexatriene ($D_{6h}$, $D_{3h}$)

The optimised geometries of benzene ($D_{6h}$) and its reference compound 1,3,5-cyclohexatriene ($D_{3h}$) are presented in Table 1, together with their total energies and the energy of their most stable Kekulé structure.

Scheme 1 The thermocycle of benzene, their relative energies (kcal/mol) and the weights (in *italics*) of the Kekulé structures.
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Table 1 The optimised structures of benzene (D$_{6h}$-2) and 1,3,5-cyclohexatriene (D$_{3h}$-1) together with their total VB energy (in Hartree) and energy of their most stable Kekulé structure (in Hartree), and those of their deformed counterparts D$_{6h}$-1 and D$_{3h}$-2.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>C$_1$-C$_2$(Å)</th>
<th>C$_2$-C$_3$(Å)</th>
<th>Total energy</th>
<th>Most stable structure energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzene (D$_{6h}$-2$^1$)</td>
<td>1.399</td>
<td>1.399</td>
<td>-230.693447</td>
<td>-230.661873</td>
</tr>
<tr>
<td>1,3,5-cyclohexatriene (D$_{3h}$-1$^2$)</td>
<td>1.369</td>
<td>1.433</td>
<td>-230.681589</td>
<td>-230.681589</td>
</tr>
<tr>
<td>deformed</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,3,5-cyclohexatriene (D$_{6h}$-1)</td>
<td>1.399</td>
<td>1.399</td>
<td>-230.678149</td>
<td>-230.678149</td>
</tr>
<tr>
<td>deformed benzene (D$_{3h}$-2)</td>
<td>1.369</td>
<td>1.433</td>
<td>-230.691547</td>
<td>-230.678195</td>
</tr>
</tbody>
</table>

In our calculations, the following results are obtained (Scheme 1). Benzene (D$_{6h}$-2) has a geometry with carbon-carbon bond lengths of 1.399 Å in excellent agreement with the experimental value (1.399 Å) [6]. Geometry optimisation of 1,3,5-cyclohexatriene (D$_{6h}$-1) starting at the benzene (D$_{6h}$-2) geometry leads to 1,3,5-cyclohexatriene (D$_{3h}$-1) with alternating bond lengths of 1.369 Å and 1.433 Å (Table 1), i.e. 1,3,5-cyclohexatriene (D$_{3h}$-1) is captured in computro (Scheme 1)! This relaxation of the 1,3,5-cyclohexatriene geometry (D$_{6h}$-1) from D$_{6h}$ symmetry to D$_{3h}$ symmetry (D$_{3h}$-1) is only moderately exothermic (-2.2 kcal/mol, Scheme 1). The calculated alternating bond lengths are in reasonable agreement with experimental values found in linear 1,3,5-hexatriene (1.368 Å and 1.458 Å [18]). The resemblance between the optimised geometry of 1,3,5-cyclohexatriene (D$_{3h}$-1) and related bond lengths in 1,3,5-hexatriene confirms the polyene character of the former.

Upon inclusion of resonance, deformed benzene (D$_{3h}$-2) is located 1.2 kcal/mol above benzene. Geometry optimisation leads immediately back to D$_{6h}$-2. These results indicate that resonance between the two Kekulé structures is necessary for obtaining the D$_{6h}$ symmetric geometry of benzene (cf. [19]).

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$^1$ Other structural features of D$_{6h}$-2: C-H 1.073 Å; $\angle$ C-C-H 120.0°.

$^2$ Other structural features of D$_{3h}$-1: C-H 1.073 Å; $\angle$ C$_1$-C$_2$-H 120.6°; $\angle$ C$_2$-C$_3$-H 119.4°.
According to Pauling, the resonance energy (RE) of a molecule is defined as the energy difference between the total energy of the molecule and the energy of its most stable Kekulé structure [20]. For benzene (D₆ᵥ-2), both structures are degenerate and have equal weights. A RE value of -19.8 kcal/mol is found (Scheme 1). Upon deformation of benzene towards the 1,3,5-cyclohexatriene geometry (D₃ᵥ-2), the weights of both structures become 0.74 and 0.26 (Scheme 1). The Pauling RE of deformed benzene (D₃ᵥ-2) is still -8.4 kcal/mol. While a significant resonance stabilisation is present in deformed benzene (D₃ᵥ-2), it is located above D₆ᵥ benzene (D₆ᵥ-2, Scheme 1). The small endothermicity (1.2 kcal/mol, Scheme 1) of the deformation of benzene to the 1,3,5-cyclohexatriene optimised structure (D₆ᵥ-2 → D₃ᵥ-2) and the fact that resonance still is important in deformed benzene (D₃ᵥ-2) suggest that the (magnetic) properties of deformed benzene are similar to those of benzene (D₆ᵥ-2) itself. Indeed, for even stronger distortions of the benzene geometry towards a D₃ᵥ structure with alternating bond lengths, the magnetic properties, are nearly identical to those of benzene [21].

A VRE of only -9.6 kcal/mol is found for benzene (D₆ᵥ-2) (Scheme 1). The VRE of deformed benzene (D₃ᵥ-2) is only 3.4 kcal/mol lower than that of benzene (D₆ᵥ-2), viz. -6.2 kcal/mol. According to our VB calculations, the TRE of benzene is only -7.4 kcal/mol (Scheme 1). These values for both the VRE and TRE are considerably lower than most previously reported values (range 5 - 95 kcal/mol [7,22-24]). This discrepancy can be attributed to the fact that in previous calculations the VRE and TRE were calculated using either calculations with pre-determined ethene π orbitals [23] or CASSCF wave functions that were transformed to a VB space of all covalent VB determinants [22]. Hence the 1,3,5-cyclohexatrienes (D₆ᵥ-1 and D₃ᵥ-1) were accessed with non-optimised orbitals. In the most recent VB calculations [24] 175 different (ionic) structures for benzene (D₆ᵥ-2) while for (deformed) 1,3,5-cyclohexatriene (D₆ᵥ-1 and D₃ᵥ-1) only 27 (ionic) structures were taken into account. This may well be an unbalanced view, and e.g. affect the energies.

The calculated VRE of benzene is also considerably lower than the resonance energy according to the Pauling definition. The optimisation of the wave function in the case of the one-structure calculation lowers the energy by 10.2 kcal/mol in comparison
with the energy of one single structure in the corresponding two-structure calculation. We attribute this to the fact that deformed 1,3,5-cyclohexatriene (D$_{6h}$-1) does not possess isolated double bonds but possesses polyene character.

4. Conclusions

The Valence Bond calculations show that benzene is stabilised with respect to the elusive reference molecule 1,3,5-cyclohexatriene (D$_{3h}$-1) by 7.4 kcal/mol (TRE), which is much smaller than most earlier suggestions. 1,3,5-Cyclohexatriene (D$_{3h}$-1) is accessed in computer experiments. At this geometry, benzene still possesses a considerably degree of π-electron delocalisation. The second Kekulé structure is responsible for the relaxation of D$_{3h}$-2 to benzene, thus resonance is necessary for obtaining the D$_{6h}$ symmetric geometry of benzene.

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It is derived from the original GAMESS code due to M. Dupuis, D. Spangler and J. Wendolowski, *NRCC Software Catalog, Vol. 1, Program No. QG01 (GAMESS) 1980*.


