

# 1,3,5-Cyclohexatriene captured in computro; the importance of resonance

J.H. van Lenthe<sup>a,\*</sup>, R.W.A. Havenith<sup>a,b</sup>, F. Dijkstra<sup>a,1</sup>, L.W. Jenneskens<sup>b</sup>

<sup>a</sup> Debye Institute, Theoretical Chemistry Group, Utrecht University, Padualaan 14, 3584 CH Utrecht, The Netherlands

<sup>b</sup> Debye Institute, Department of Physical Organic Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands

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## Abstract

The geometry and energy of 1,3,5-cyclohexatriene, the reference molecule for the determination of the extra stabilization of benzene, have been calculated using an Ab Initio Valence Bond method. The theoretical resonance energy, according to Dewar, calculated as the energy difference between two-structure benzene and single-structure 1,3,5-cyclohexatriene, both with completely optimized geometries and orbitals, is only  $-12.05$  kcal/mol. Resonance energies of  $-25.37$  (local orbitals),  $-19.82$  (delocal orbitals) and  $-44.13$  (breathing orbitals) kcal/mol are found using the Pauling definition. The concept of the vertical resonance energy, however, is proven to be not tenable beyond a minimal basis. © 2002 Elsevier Science B.V. All rights reserved.

## 1. Introduction

The peculiar behavior of benzene has been rationalized by considering its  $D_{6h}$  symmetry delocalized  $\pi$  electron system, or equivalently, the resonance between two Kekulé resonance structures of equal weight [1]. The interaction between the two Kekulé resonance structures leads to stabilization of the molecule with respect to a one-structure description, in this case thus a 1,3,5-cyclohexatriene. This stabilization is the resonance energy ( $E_{res}$ ).

The determination of the resonance energy of benzene, which is an energy criterion for aromaticity, is an important issue. The resonance energy as defined by Pauling [2] can be calculated in a Valence Bond (VB) calculation as the energy difference between the total energy and the energy of the most stable structure in the same calculation (thus with the same orbitals). The energy difference between 1,3,5-cyclohexatriene with the same geometry as benzene, but lacking resonance, and benzene gives the vertical resonance energy (VRE) [3]. In this case, the orbitals are relaxed in the one-structure calculation.

Since 1,3,5-cyclohexatriene as such does not exist, it was proposed to compare the energy of benzene with that of a polyene-like 1,3,5-cyclohexatriene with  $D_{3h}$  symmetry [4]. In this case also a change in geometry ( $D_{6h} \rightarrow D_{3h}$ ) is involved.

\* Corresponding author. Fax: +30-253-7504.

E-mail address: [joop@chem.uu.nl](mailto:joop@chem.uu.nl) (J.H. van Lenthe).

<sup>1</sup> Present address: High Performance Computing Group, Utrecht University, Princetonplein 5, 3584 CC Utrecht, The Netherlands.

This gives the theoretical resonance energy (TRE) [5]. The energy of the hypothetical reference compound is now estimated by taking thrice the C=C and C—C increment [4]. We note in passing that the name 1,3,5-cyclohexatriene has been given to compounds that possess a benzene moiety distorted to a  $D_{3h}$  geometry; illustrative examples are tris(benzocyclobutadieno)- (bond alternation  $\Delta R$  0.159 Å [6]) and tris(bicyclo[2.1.1]hexeno)-benzene (bond alternation  $\Delta R$  0.089 Å [7]). However, also for these two similarly distorted benzenes the situation is more complicated. It was recently shown that the central benzene ring of the former lacks any conjugation [8], whereas the latter still possesses all the regular benzene properties [9]. Thus, the occurrence of bond alternation is not necessarily indicative of a lack or reduction of either aromaticity or resonance [10].

The reference points required for the determination of both VRE and TRE of benzene are experimentally inaccessible and standard MO theory is not capable to describe both benzene and 1,3,5-cyclohexatriene within a similar framework. Only within the framework of Ab Initio Valence Bond theory it is possible to describe 1,3,5-cyclohexatriene. This allows us to assess the importance of resonance in benzene and 1,3,5-cyclohexatriene. The best approach towards obtaining these reference compounds is to optimize their geometries ( $D_{6h}$  and  $D_{3h}$  symmetry) and orbitals.

The importance of resonance may already be derived without calculations. Consider the wavefunction of benzene as a mixture of the Kekulé structures  $\Phi_1$  and  $\Phi_2$ ;

$$\Psi = c_1\Phi_1 + c_2\Phi_2. \quad (1)$$

The resonance between the two structures is given by the matrix element  $\langle\Phi_1|H|\Phi_2\rangle$ . If there is no resonance this matrix element is zero. In this case one of the structures will become dominant and will enforce  $D_{3h}$  symmetry [11,12]. Any size of the matrix element will make a  $D_{6h}$  symmetry structure possible. So resonance is a necessary requirement for obtaining a fully symmetric benzene molecule. A non-zero resonance is not sufficient, though, since its size will determine if the  $D_{6h}$  geometry has preference over the  $D_{3h}$  structure.

## 2. Methods

Within the non-orthogonal VB framework the  $\pi$ -system, comprising the double bonds, is described using singly occupied p-like atomic orbitals on the six carbon atoms. These p-orbitals are allowed to delocalize, though they are still predominantly atomic in nature (cf. [13]). Alternatively, we can restrict the p-orbitals to their atoms (strictly local). This restriction of the orbitals has the advantage, that the wavefunction is apparently more easily interpretable. However, this division of the orbital space is in the end not tenable if the basis set is enlarged. The local approach gives a higher total energy than the delocal approach and is thus inferior. The  $\sigma$ -system consists of delocalized doubly occupied orbitals. All orbitals are completely optimized.

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 optimized geometry ( $D_{3h}$  symmetry) with double bonds between the carbon atoms (1,2), (3,4) and (5,6), is described by the following wavefunction:

$$\begin{aligned} \Psi_1 &= |\sigma_{\text{core}}(1,2)(3,4)(5,6)| \\ &= \left| \sigma_{\text{core}}(\bar{1}\bar{2}-\bar{1}\bar{2})(\bar{3}\bar{4}-\bar{3}\bar{4})(\bar{5}\bar{6}-\bar{5}\bar{6}) \right| \end{aligned} \quad (2)$$

in which the core comprises all doubly occupied  $\sigma$  orbitals, and  $(\bar{1}\bar{2}-\bar{1}\bar{2})$  denotes the singlet spin-coupling between the singly occupied p-orbitals on carbon atom 1 and 2. Thus the wavefunction in either case consists of only *one* Kekulé structure. In contrast, the wavefunction of regular benzene ( $D_{6h}$  symmetry) and benzene deformed in the optimized geometry of 1,3,5-cyclohexatriene ( $D_{3h}$  symmetry) will be obtained by adding the *second* Kekulé structure, giving

$$\begin{aligned} \Psi_2 &= N(c_1|\sigma_{\text{core}}(1,2)(3,4)(5,6)| \\ &\quad + c_2|\sigma_{\text{core}}(2,3)(4,5)(6,1)|) \end{aligned} \quad (3)$$

In our VB description of benzene, the three Dewar benzene structures, viz. the three additional covalent structures, which contribute for less than 6–7% each [13,14], are excluded, to focus on the effect of resonance interactions between the two Kekulé structures.

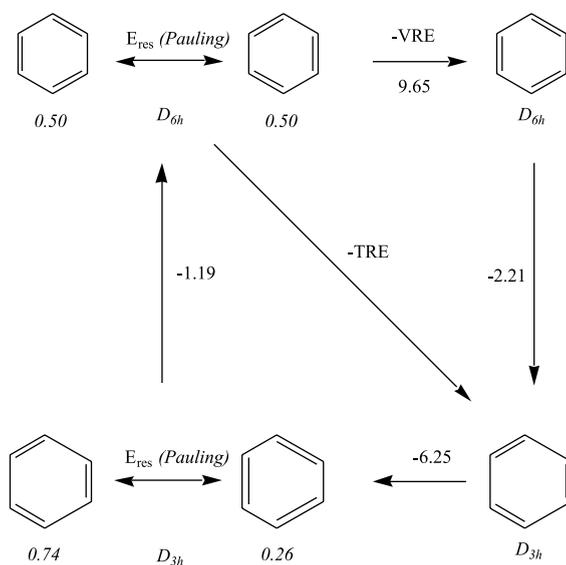
The calculations are denoted by the symmetry of the geometry and the number of structures employed. Thus a regular benzene calculation is denoted by  $D_{6h}$ -2. To obtain an estimate of the VRE, a one-Kekulé-structure calculation has been performed to access the energy of deformed 1,3,5-cyclohexatriene ( $D_{6h}$ -1). For the calculation of the TRE, the geometry of 1,3,5-cyclohexatriene ( $D_{3h}$ -1) has been optimized. A calculation on deformed benzene in the optimized 1,3,5-cyclohexatriene geometry ( $D_{3h}$ -2) has been performed to judge whether resonance is still important after deformation of benzene.

The geometries of benzene ( $D_{6h}$ -2,  $\Psi_2$ ) and 1,3,5-cyclohexatriene ( $D_{3h}$ -1,  $\Psi_1$ ) were optimized using gradient techniques [15]; a 6-31G basis set [16] was used. The calculations were performed using the Ab Initio Valence Bond program TUR-TLE [17], as integrated in the GAMESS-UK package [18].

### 3. Results and discussion

The optimized geometries and energies of benzene ( $D_{6h}$ -2) and 1,3,5-cyclohexatriene ( $D_{3h}$ -1) using either local or delocal p-orbitals, and different orbitals for the two different structures (vide infra) are presented in Table 1. In Scheme 1 and in our discussion we present the relative energies of the different isomers using the delocal orbital method. Finally all the resonance energies, that were calculated, are collected in Table 2.

Benzene ( $D_{6h}$ -2) has a geometry with carbon-carbon bond lengths of 1.399 Å, in excellent agreement with the experimental value [19,20].



Scheme 1. The thermocycle for benzene, relative energies (in kcal/mol) using the delocal orbital model and the weights (*in italics*) of the Kekulé structures.

Both structures are degenerate and have equal weights, as expected. An  $E_{\text{res}}$  value of  $-19.82$  kcal/mol is found in good agreement with the result of Cooper et al. ( $-20$  kcal/mol [21]). In the absence of the second Kekulé resonance structure ( $E_{\text{res}} = 0$ ), deformed 1,3,5-cyclohexatriene in the benzene geometry ( $D_{6h}$ -1) results, which is located only 9.65 kcal/mol ( $-VRE$ ) above benzene ( $D_{6h}$ -2). This low value compared to the Pauling resonance energy must be attributed to orbital relaxation. This suggests that the intuitive correspondence between VRE and Pauling resonance is not maintained if the orbitals are allowed to relax. Subsequent geometry optimization of 1,3,5-cyclohexatriene

Table 1  
Results of geometry optimizations<sup>a</sup> of benzene ( $D_{6h}$ -2) and 1,3,5-cyclohexatriene ( $D_{3h}$ -1) (Ångstroms/degrees; energies in hartrees)

Method	Orbitals	Energy	CC1	CC2	HC	$\angle CCH$	
$D_{6h}$	HF	Delocal	-230.624474	1.388	1.388	1.073	120.0
$D_{6h}$ -2	Two-struct. VB	Local	-230.548734	1.426	1.426	1.071	120.0
$D_{6h}$ -2	Two-struct. VB	Delocal	-230.693447	1.399	1.399	1.073	120.0
$D_{6h}$ -2	Two-struct. VB	Breathing	-230.700800	1.398	1.398	1.074	120.0
$D_{3h}$ -1	One-struct. VB	Local	-230.530694	1.368	1.509	1.071	118.6
$D_{3h}$ -1	One-struct. VB	Delocal	-230.681589	1.369	1.433	1.073	119.4

<sup>a</sup> The breathing orbitals did not influence the geometry significantly, so for the  $D_{6h}$  calculations the geometries from the delocal orbitals were used for the breathing calculations.

Table 2

Resonance energies for benzene ( $\mathbf{D}_{6h}$ -2) and benzene at the 1,3,5-cyclohexatriene geometry ( $\mathbf{D}_{3h}$ -1) calculated with different methods, orbitals and wavefunctions (in kcal/mol)

Symmetry	Method	Orbitals	Energy
$\mathbf{D}_{6h}$	Pauling	Local	-25.37
$\mathbf{D}_{6h}$	Pauling	Delocal	-19.82
$\mathbf{D}_{6h}$	Pauling	Breathing	-44.13
$\mathbf{D}_{6h}$	VRE	Local	-25.13
$\mathbf{D}_{6h}$	VRE	Delocal	-9.65
$\mathbf{D}_{6h}$	VRE	Breathing	-14.26
$\mathbf{D}_{6h}$	Bond-distorted VRE <sup>a</sup>		-62.80
$\mathbf{D}_{6h}$	TRE	Local	-11.32
$\mathbf{D}_{6h}$	TRE	Delocal	-7.44
$\mathbf{D}_{6h}$	TRE	Breathing	-12.05
$\mathbf{D}_{3h}$	Pauling	Local	-7.74
$\mathbf{D}_{3h}$	Pauling	Delocal	-8.38
$\mathbf{D}_{3h}$	Pauling	Breathing	-29.53
$\mathbf{D}_{3h}$	Bond-distorted VRE <sup>a</sup>		-49.78

<sup>a</sup> See text.

( $\mathbf{D}_{6h}$ -1) leads to a 1,3,5-cyclohexatriene ( $\mathbf{D}_{3h}$ -1) with alternating bond lengths of 1.369 and 1.433 Å, in line with experimental values found for linear polyenes (1.368 and 1.458 Å) [22].

The relaxation of the 1,3,5-cyclohexatriene geometry ( $\mathbf{D}_{6h}$ -1) from  $\mathbf{D}_{6h}$  symmetry to  $\mathbf{D}_{3h}$  symmetry ( $\mathbf{D}_{3h}$ -1) is exothermic by 2.21 kcal/mol. Benzene ( $\mathbf{D}_{6h}$ -2) is thus stabilized by 7.44 kcal/mol (–TRE) with respect to the optimized geometry of 1,3,5-cyclohexatriene ( $\mathbf{D}_{3h}$ -1). These values for both the VRE and TRE are considerably lower than most previously reported values (range –5 to –95 kcal/mol [5,23–26]). In previous calculations, however, the 1,3,5-cyclohexatrienes ( $\mathbf{D}_{6h}$ -1 and  $\mathbf{D}_{3h}$ -1) were accessed with non-optimized, fixed orbitals [24], e.g., with pre-determined ethene  $\pi$  orbitals [25]. Recent VB calculations [5] yielded a VRE of –74.3 kcal/mol. The balance between benzene (175 different (ionic) structures) and (deformed) 1,3,5-cyclohexatriene (only 27 (ionic) structures) was sacrificed. The lack of a simple model and of orbital optimization made these results unfortunately dependent on chemical intuition and preference (cf. [27]).

The observation that our  $\mathbf{D}_{6h}$ -1 calculation is energetically so close to the full  $\mathbf{D}_{6h}$ -2 result is an indication that the orbital optimization in the one-

structure calculation is able to recover a significant amount of energy, thus compensating for the lack of the resonance. Thus in absence of the other structure, one structure is able to describe a considerable part of the total two-structure bonding. This is caused by the non-orthogonality of the resonance structures. Already the *spin-functions* in the two Kekulé structures have an overlap of 25%, without any orbital overlap at all. In a two-structure, delocalized calculation the overlap between the structures is 66%. If the two structures are optimized in separate calculations an overlap as large as 89% results. This means that one structure is able to capture a significant part of the effect of the other one and even more so in the single-structure calculation. Therefore our VRE value, calculated with delocal orbitals, has to deviate considerably from the Pauling resonance energy. *This suggests that the concept behind the vertical resonance energy is not tenable beyond a minimal basis.* The fact that the single structure contains part of its counterpart may be considered to be delocalization, but not resonance since the latter is an interaction between structures. This effects both TRE and VRE.

Recently Mo et al. and Shaik et al. considered the resonance energy of benzene and noted the compensating effect of delocalization. They therefore used two-center bond-distorted orbitals [28] in the one-structure calculation and completely delocalized orbitals in the full benzene calculation [29,30] to arrive at a VRE-value of –65 kcal/mol [26], which fortuitously agrees with previous estimates (cf. [5,23–26]). Following this recipe, we find resonance energies of –62.80 kcal/mol for benzene ( $\mathbf{D}_{6h}$ ) and –49.78 kcal/mol for benzene in the 1,3,5-cyclohexatriene geometry, using a two-structure delocalized wavefunction for benzene. Unfortunately, the use of these two-center orbitals does not exclude the  $\pi$ -bonding between the not-connected centers completely, since that is already contained in the spin-functions, nor are the two-center orbitals orthogonal to their counterparts (vide infra). The use of different orbital optimization models for different structures will introduce a further orbital dependent arbitrariness in the calculation of the resonance energy.

A further way to restrict the orbitals is to use strictly atomic (local) orbitals. Then a nearly identical Pauling and vertical resonance energy are obtained (Table 2). The local orbital model offers no freedom to the orbitals to adapt to the one-structure wavefunction. We note that a completely unrestricted model is the only one possible option in the limit of a full (one-center) basis.

However, the use of a common set of orbitals in the two-structure calculation, is not a completely balanced approach either. The restriction of identical orbitals for different structures is imposed only in the two-structure calculation, but not in the one-structure case. Borrowing the concept of breathing orbitals [31,32], we combined the two structures and optimized the orbitals, allowing different  $\pi$ -orbitals for each structure in the two-structure calculation. Then the overlap between the structures decreases from 89% to 55%. This means that the one-structure calculations, in the absence of resonance, exaggerate the delocalization into the space of the missing structure. The total energy is only 4.61 kcal/mol lower than that of the delocal calculation. The Pauling resonance energy, however, is now  $-44.13$  kcal/mol. This implies that using completely separate structures the total energy is optimized by optimizing the resonance energy. This is done by making each structure more local as is indicated by the decreased overlap (from 89% to 55%) between the structures. The self-repulsion of the structures is now higher making the individual structure energies higher. The locality of the resonating structures was forced in the calculations by Mo et al. [5,28] and Shaik et al. [26,29] by making use of only partially delocalized p-orbitals. In their approach the aim was just to reduce the delocalization of the orbitals. This approach would actually yield some 'resonance' for the ethane molecule as the energy of a single determinant with doubly occupied two-center orbitals lies above that of the fully optimized determinant [33]. In our case the locality of the structures is not artificially forced, but it emerges automatically from the calculation. A breathing orbital calculation at the 1,3,5-cyclohexatriene geometry gives a Pauling resonance energy of  $-29.53$  kcal/mol with an overlap of still 54%. Even for this distorted geometry there is

considerable resonance and a sizeable part of one structure present in the other one.

Our geometry-optimized calculations on benzene ( $\mathbf{D}_{6h-2}$ ) and 1,3,5-cyclohexatriene ( $\mathbf{D}_{3h-1}$ ) show that the two-structure calculation allows a much more contracted geometry of benzene. Upon inclusion of the second Kekulé resonance structure, in going from  $\mathbf{D}_{3h-1}$  to  $\mathbf{D}_{3h-2}$ , deformed benzene ( $\mathbf{D}_{3h-2}$ ) results, which is only 1.19 kcal/mol located above benzene. Shaik et al. [34] also found a small value (7.2 kcal/mol) for the distortion of benzene towards the 1,3,5-cyclohexatriene geometry. The weights of both structures in deformed benzene ( $\mathbf{D}_{3h-2}$ ) become 0.74 and 0.26 and a Pauling resonance energy of  $-8.38$  kcal/mol is found. Thus, in line with the findings of Shaik et al. [34], benzene ( $\mathbf{D}_{6h-2}$ ) can easily distort towards the 1,3,5-cyclohexatriene geometry ( $\mathbf{D}_{3h-2}$ ). This, however, is not a sign that resonance is unimportant, but should instead be attributed to the fact that resonance is still an important factor even in deformed benzene ( $\mathbf{D}_{3h-2}$ ) [9,10] (see also [35]).

#### 4. Conclusions

The geometry and energy of the hypothetical molecule 1,3,5-cyclohexatriene, the reference molecule of choice for the determination of the extra stabilization of benzene, have been determined. The calculation of the seemingly trivial defined concept of the resonance energy is hampered by the arbitrariness in the choice of orbitals. Depending on the orbital optimization model chosen, we find resonance energies of  $-25.37$  (local),  $-19.82$  (delocal) and  $-44.13$  (breathing) kcal/mol, using the Pauling definition [2]. The last one employs the most extended wavefunction with the lowest total energy, and currently represents the best result. Our TRE (Dewar), calculated by complete optimization of both geometries and wavefunctions, is  $-12.05$  (breathing) kcal/mol, and is substantially lower than previous estimates. A single-structure calculation always includes a part of the other structure as a consequence of both the spin and space non-orthogonality of the structures. The qualitative trends in resonance energies, however, are the same for all VB orbital optimi-

zation models. Furthermore, the results show that resonance between the two Kekulé structures is a necessary, and sufficient condition for obtaining the  $D_{6h}$  symmetric geometry of benzene.

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