The trimerization of acetylene to benzene has been studied along an hypothetical concerted reaction pathway belonging to the $D_{3h}$ symmetry point group. This can be conveniently described in terms of a Z-matrix, where the reaction coordinate (RC) is defined as the distance of the C≡C acetylene bonds to the center of symmetry, see below for an example.

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The making of ring currents

Electron Delocalization and Aromaticity: Celebrating the 150th Anniversary of the Kekulé Benzene Structure

Guglielmo Monaco and Riccardo Zanasi

Department of Chemistry and Biology “Alfredo Zambelli”, University of Salerno, via Giovanni Paolo II 132, 84084 Fisciano, Italy.

Benzene
Distances are in Å and angles in degrees.

For each selected value of the reaction coordinate, only three geometrical parameters have to be optimized, i.e., the C-C and C-H bond lengths and the HCC bond angle of the acetylene units. This has been done assuming a singlet closed-shell electronic configuration at the density functional theory (DFT) level of approximation, combining the B97-2 functional with the cc-pVTZ basis set and using the Gaussian 09 suite of programs. At this level of theory, the RC value for the $D_{6h}$ benzene equilibrium geometry is 1.203 Å, which correspond to a C-C bond length of 1.389 Å. Reaction steps have been taken every 0.05 Å up to RC=2.00 Å, with a few finer exceptions.

Table 1: B97-2/cc-pVTZ optimized geometrical parameters and energies for the various steps of the hypothetical concerted trimerization of acetylene to benzene along the pathway of $D_{3h}$ symmetry. RC is the reaction coordinate in Å; C≡C, C-H and HCC are bond lengths (Å) and angle (degree) of the acetylene units; C···C is the length of the forming bond; $E$ is the energy of the whole system in hartree. Equilibrium bond lengths and energy of acetylene at the same level of calculation are: C≡C=1.197 Å, C-H=1.062 Å, $E = -77.32865994 \, E_h$.

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Figure 1: the animation shows the π electron first-order current density induced by a perpendicular magnetic field in points at 1 \( a_0 \) above the plane where the hypothetical \( 3C_2H_2 \rightarrow C_6H_6 \) concerted reaction takes place. The modulus of the current density is proportional to the area of the plotted fat arrows with a fixed length/width ratio. The phase portrait of the current density vector field is also shown. Calculations have been performed using the continuous transformation of the origin of the current density (CTOCD-DZ2) method and the B97-2/cc-pVTZ combination of functional and basis set, as implemented in the SYSMO package. Singularities of the current density vector field are marked by green/red dots denoting diatropic/paratropic vortex centers and by blue crosses denoting saddle points. Black lines connect saddle points; these are trajectories of current density that represent the boundary of current domains. Current susceptibilities in nA T\(^{-1}\) are reported on the left for the forming C···C bonds and on the right for the C≡C acetylene bonds. Positive/negative values are relative to diatropic/paratropic current density cross sections.
Planar cyclooctatetraene (COT)

Similarly, the tetramerization of acetylene to planar cyclooctatetraene (COT) has been studied along an hypothetical concerted reaction pathway belonging to the $D_{4h}$ symmetry point group. Also in this case, a Z-matrix can be written where the reaction coordinate (RC) is defined as the distance of the C≡C acetylene bonds to the center of symmetry.

\[
\begin{array}{cccccc}
X0 & X12 & X0 & RC & X12 & a90 \\
X34 & X0 & RC & X34 & a90 & X12 \text{ d180} \\
X56 & X0 & RC & X56 & a90 & X34 \text{ d180} \\
C1 & X12 & CC2 & X0 & a90 & X34 \text{ d0} \\
C2 & X12 & CC2 & X0 & a90 & X78 \text{ d0} \\
H1 & C1 & CH & X12 & HCC & X34 \text{ d180} \\
H2 & C2 & CH & X12 & HCC & X78 \text{ d180} \\
C3 & X34 & CC2 & X0 & a90 & X12 \text{ d0} \\
C4 & X34 & CC2 & X0 & a90 & X56 \text{ d0} \\
H3 & C3 & CH & X34 & HCC & X12 \text{ d180} \\
H4 & C4 & CH & X34 & HCC & X78 \text{ d180} \\
C5 & X56 & CC2 & X0 & a90 & X34 \text{ d0} \\
C6 & X56 & CC2 & X0 & a90 & X78 \text{ d0} \\
H5 & C5 & CH & X56 & HCC & X34 \text{ d180} \\
H6 & C6 & CH & X56 & HCC & X78 \text{ d180} \\
C7 & X78 & CC2 & X0 & a90 & X56 \text{ d0} \\
C8 & X78 & CC2 & X0 & a90 & X12 \text{ d0} \\
H7 & C7 & CH & X78 & HCC & X56 \text{ d180} \\
H8 & C8 & CH & X78 & HCC & X12 \text{ d180} \\
\end{array}
\]

Variables:
CC2 0.69
CH 1.0817
HCC 117.1663

Constants:
RC 2.00
a90 90.0
d180 180.0
d0 0.0

Distances are in Å and angles in degrees.

For each selected value of the reaction coordinate, the C-C and C-H bond lengths and the HCC bond angle of the acetylene units have been optimized, with the same assumptions as in the previous case of benzene. At this level of theory, the RC value for the planar $D_{4h}$ COT equilibrium geometry is 1.708 Å, which correspond to a C=C double bond length of 1.338 Å and a C–C single bond length of 1.469 Å.
Table 2: B97-2/cc-pVTZ optimized geometrical parameters and energies for the various steps of the hypothetical concerted tetramerization of acetylene to planar COT along the pathway of $D_{4h}$ symmetry. RC is the reaction coordinate in Å; C≡C, C-H and HCC are bond lengths (Å) and angle (degree) of the acetylene units; C···C is the length of the forming bond; $E$ is the energy of the whole system in hartree.

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<th>C-H</th>
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</table>
Figure 2: the animation shows the $\pi$ electron first-order current density induced by a perpendicular magnetic field in points at 1 \(a_0\) above the plane where the hypothetical \(4\text{C}_2\text{H}_2 \rightarrow \text{C}_8\text{H}_8\) concerted reaction takes place. See the caption of the previous animation for other details.
Borazine

The simplest iminoborane, HBNH, is isoelectronic with acetylene, and an hypothetical concerted trimerization of HBNH to borazine can be devised along a reaction pathway belonging to the $C_{3h}$ symmetry point group. As in the previous cases, a Z-matrix can be written where the reaction coordinate (RC) is defined as the distance of the $\text{B} \equiv \text{N}$ iminoborane bonds to the center of symmetry, see below.

\begin{verbatim}
X0
X12 X0 RC
X34 X0 RC X12 a120
X56 X0 RC X12 a120 X34 d180
N1 X12 NX12 X0 a90 X34 d0
B2 X12 BX12 X0 a90 X56 d0
H1 N1 NH X12 BNH X34 d180
H2 B2 BH X12 HBN X56 d180
N3 X34 NX12 X0 a90 X56 d0
B4 X34 BX12 X0 a90 X12 d0
H3 N3 NH X34 BNH X56 d180
H4 B4 BH X34 HBN X12 d180
N5 X56 NX12 X0 a90 X12 d0
B6 X56 BX12 X0 a90 X34 d0
H5 N5 NH X56 BNH X12 d180
H6 B6 BH X56 HBN X34 d180

Variables:
BX12 0.7527
NX12 0.6572
BH 1.1874
NH 1.0031
HBN 129.3318
BNH 120.9993

Constants:
RC 1.60
a120 120.0
a90 90.0
d180 180.0
d0 0.0

Distances are in Å and angles in degrees.

Owing to the lower symmetry with respect to benzene and planar COT, a few more geometrical parameters have been optimized, retaining the same assumptions as in the previous cases, for each selected value of the reaction coordinate. These are: the $\text{B} \equiv \text{N}$, B-H and N-H bond lengths and the HBN, BNH bond angles of the iminoborane units. At this level of theory, the RC value for the $D_{3h}$ borazine equilibrium geometry is 1.235 Å, which correspond to a B-N bond length of 1.428 Å.

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Table 3: B97-2/cc-pVTZ optimized geometrical parameters and energies for the various steps of the hypothetical concerted trimerization of iminoborane to borazine along the pathway of $C_{3h}$ symmetry. RC is the reaction coordinate in Å; $\equiv N$, $B-H$, $N-H$, $\hat{H}B\hat{N}$ and $B\hat{N}$ are bond lengths (Å) and angle (degree) of the iminoborane units; $B\cdot\cdot\cdot N$ is the length of the forming bond; $E$ is the energy of the whole system in hartree. Equilibrium bond lengths and energy of iminoborane ($BH_2N$) at the same level of calculation are: $B-N=1.234$ Å, $B-H=1.170$ Å, $N-H=0.988$ Å, $E=-80.80243798 E_h$.

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Figure 3: the animation shows the $\pi$ electron first-order current density induced by a perpendicular magnetic field in points at 1 $a_0$ above the plane where the hypothetical $3\text{BH}_2\text{N} \rightarrow \text{B}_3\text{H}_6\text{N}_3$ concerted reaction takes place. See the caption of the previous animation for other details.
Figure 4: An example of the integration domains of the current density cross section for the calculation of the \( \text{C}\equiv\text{C} \) bond current strength of a distorted acetylene molecule. The inducing magnetic field is perpendicular to the molecular plane.
Figure 5: An example of the integration domains of the current density cross section for the calculation of the C≡C and C–C bond current strengths in one step of the trimrization of acetylene to benzene. The inducing magnetic field is perpendicular to the molecular plane.