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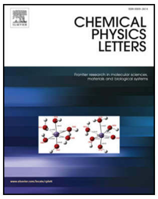

Research paper

The 3-D bonding morphology of the infra-red active normal modes of benzene

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HIGHLIGHTS

- Present a new vector-based interpretation of the chemical bond B{$\boldsymbol{p}$,$\boldsymbol{q}$,$\boldsymbol{r}$} for benzene.
- Provide a 3-D bonding morphology of the infra-red (IR) active normal modes of benzene.
- Show variation of the bond-path framework set B{$\boldsymbol{p}$,$\boldsymbol{q}$,$\boldsymbol{r}$} with frequency.
- Comprises the least ($\boldsymbol{p}$-), most preferred ($\boldsymbol{q}$-) directions of $\rho(\mathbf{r}_b)$ and the bond-path ($\boldsymbol{r}$).
- Show cooperative effects of the C—H and C—C bonds of the four IR active modes of benzene.

ABSTRACT

We present for the first time a visualization of the 3-D morphology of all the C—C and C—H bonds for the relaxed structures as well as four infra-red (IR) active normal modes of benzene using the complete bond-path framework set B = {$\boldsymbol{p}$,$\boldsymbol{q}$,$\boldsymbol{r}$} a vector-based interpretation of the chemical bond within the QTAIM framework. The bond-path framework set B = {$\boldsymbol{p}$,$\boldsymbol{q}$,$\boldsymbol{r}$} comprises three strands in the ground state, with the $\boldsymbol{r}$-path corresponding to the familiar QTAIM bond-path. The new $\boldsymbol{p}$- and $\boldsymbol{q}$-paths are formulated from the least and most preferred directions of electron density accumulation respectively.

Earlier, some of the current authors developed a methodology [1] that was created to gain new insights into the subtle details of the four infrared (IR) active normal modes of vibration of benzene [2–7]. This approach was based on bond or bond critical point (*BCP*) properties using the quantum theory of atoms in molecules QTAIM [8] and the stress tensor trajectories T_{σ} in the stress tensor eigenvector projection space U_{σ} [9,10]. We used this new *BCP* based methodology to explain the relative differences in the intensities of the IR active modes associated with changes in the dipole moment [3–5,11,12] where larger changes in the dipole moments led to greater intensities of the normal mode of vibrations. This work complemented earlier and extensive studies of the vibrational modes of benzene using both semi-empirical and *ab initio* methods [13–15] and theoretical treatments on the normal coordinate treatment of benzene [2,16,17], see Scheme 1.

Recently [18], the scalar properties in the forms of the lengths of H^* and H of the new $\boldsymbol{p}$- and $\boldsymbol{q}$-paths of the bond-path framework set B = {$\boldsymbol{p}$,$\boldsymbol{q}$,$\boldsymbol{r}$} were used as a sub-set of the vector-based interpretation of the chemical bond using the entire bond (bond-path). The entire length bond-path, as opposed to only the bond critical point, was investigated and the C—C and C—H bond-paths were found to be non-linear i.e. 3-D since they included bond curving and twisting for each of the four IR active normal modes and therefore demonstrated the inadequacy of the assumption of linear bonds. This assumption of bond linearity made by current mathematical models used for analyzing experimental vibrational spectra replies on the *ad-hoc* addition of anharmonic terms to correct the resulting spectra.

We will use QTAIM [8] to identify critical points in the total electronic charge density distribution $\rho(\mathbf{r})$ by analyzing the gradient vector field $\nabla\rho(\mathbf{r})$. These critical points can further be divided into four types of topologically stable critical points according to the set of ordered eigenvalues $\lambda_1 < \lambda_2 < \lambda_3$, with corresponding eigenvectors $\underline{\mathbf{e}}_1$, $\underline{\mathbf{e}}_2$, $\underline{\mathbf{e}}_3$ of the Hessian matrix. The eigenvector $\underline{\mathbf{e}}_3$ indicates the direction of the bond-path at the *BCP*. The most and least preferred directions of electron accumulation are $\underline{\mathbf{e}}_2$ and $\underline{\mathbf{e}}_1$, respectively [19–21]. The ellipticity, ε provides the relative accumulation of $\rho(\mathbf{r}_b)$ in the two directions perpendicular to the bond-path at a *BCP*, defined as $\varepsilon = |\lambda_1|/|\lambda_2| - 1$ where λ_1 and λ_2 are negative eigenvalues of the corresponding eigenvectors $\underline{\mathbf{e}}_1$ and $\underline{\mathbf{e}}_2$ respectively. In the limit that the forces on the nuclei become vanishingly small, an atomic interaction line [22] becomes a bond-path, although not necessarily a chemical bond [23]. The

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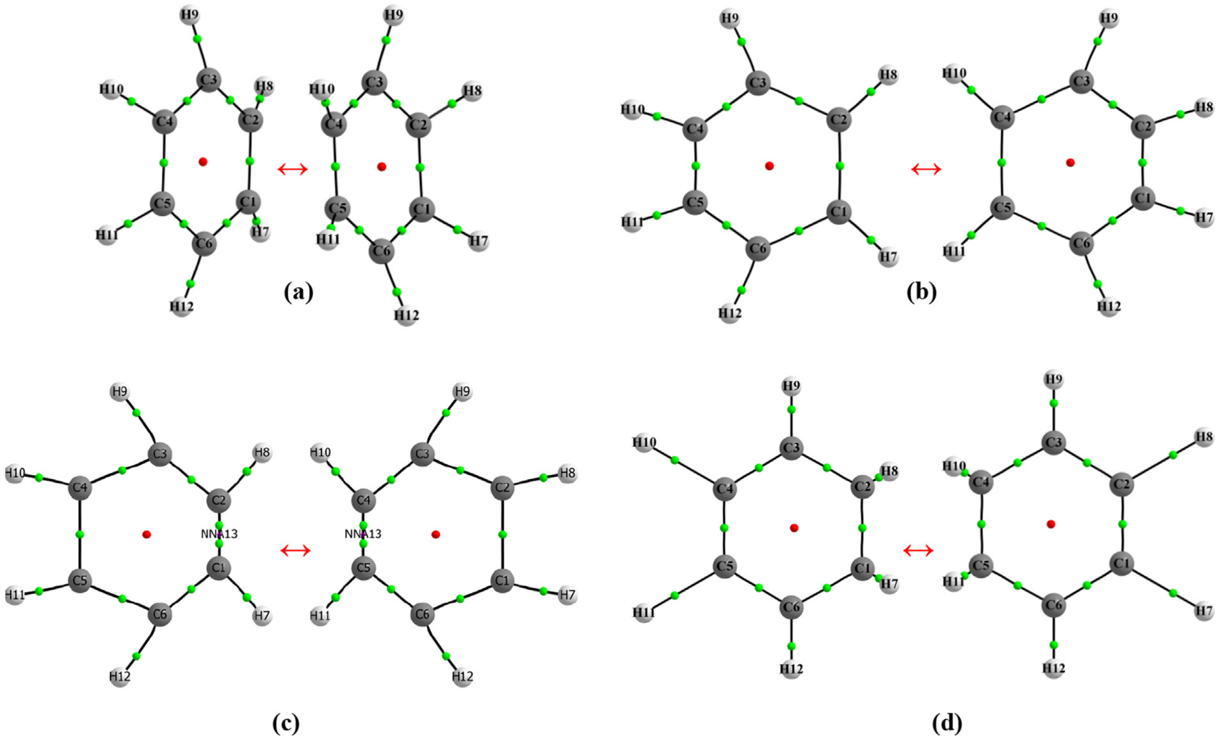


Scheme 1. The molecular graphs of the four infrared active modes of benzene; benzene_0005(721.568 cm^{-1}), benzene_0014(1097.691 cm^{-1}), benzene_0021(1573.927 cm^{-1}) and benzene_0028(3298.320 cm^{-1} are presented in sub-figures (a) to (d) respectively. The undecorated green and red spheres represent the *BCP*s and *RCP*s respectively, see Scheme 1 of the main text.

complete set of critical points together with the bond-paths of a molecule or cluster is referred to as the molecular graph.

The bond-path length (BPL) is defined as the length of the path traced out by the $\underline{\mathbf{e}}_3$ eigenvector of the Hessian of the total charge density $\rho(\mathbf{r})$, passing through the *BCP*, along which $\rho(\mathbf{r})$ is locally maximal with respect to any neighboring paths. The deviation from linearity of a bond-path separating two bonded nuclei is defined as the dimensionless ratio:

$$(\mathrm{BPL}-\mathrm{GBL})/\mathrm{GBL} \tag{1}$$

where BPL is as the associated bond-path length and the geometric bond length GBL is the inter-nuclear separation. The BPL often exceeds the GBL particularly in for weak or strained bonds and unusual bonding environments [24]. We start by choosing the length traced out in 3-D by the path swept by the tips of the scaled $\underline{\mathbf{e}}_2$ eigenvectors of the λ_2 eigenvalue, the scaling factor being chosen as the ellipticity ε.

With n scaled eigenvector $\underline{\mathbf{e}}_2$ tip path points $\boldsymbol{q}_\mathrm{i}$ on the path $\boldsymbol{q}$ where ε_i = ellipticity at the i^{th} bond-path point $\boldsymbol{r}_i$ on the bond-path $\boldsymbol{r}$, the form of $\boldsymbol{p}_\mathrm{i}$ and $\boldsymbol{q}_\mathrm{i}$ defined as follows:

$$\boldsymbol{p}_i = \boldsymbol{r}_i + \varepsilon_i \underline{\mathbf{e}}_{1,i} \tag{2a}$$

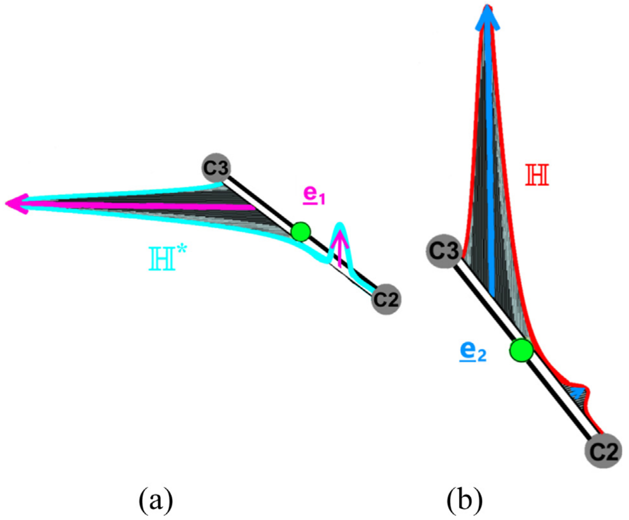
$$\boldsymbol{q}_i = \boldsymbol{r}_i + \varepsilon_i \underline{\mathbf{e}}_{2,i} \tag{2b}$$

Analogously, equation (2a), is used for the $\underline{\mathbf{e}}_1$ tip path points we have $\boldsymbol{p}_\mathrm{i} = \boldsymbol{r}_i + \varepsilon_i \underline{\mathbf{e}}_{1,i}$ on the $\boldsymbol{p}$-path where ε_i = ellipticity at the i^{th} bond-path point $\boldsymbol{r}_i$ on the bond-path $\boldsymbol{r}$. It should be noted that the bond-path is associated with the λ_3 eigenvalues of the $\underline{\mathbf{e}}_3$ eigenvector does not take into account differences in the λ_1 and λ_2 eigenvalues of the $\underline{\mathbf{e}}_1$ and $\underline{\mathbf{e}}_2$ eigenvectors.

We will refer to the new QTAIM interpretation of the chemical bond as the *bond-path framework set* that will be denoted by B, where B = {p, q, r}. This effectively means that in the most general case a bond is comprised of three 'linkages'; p, q and r associated with the $\underline{\mathbf{e}}_1$, $\underline{\mathbf{e}}_2$ and $\underline{\mathbf{e}}_3$ eigenvectors respectively.

From this we shall define eigenvector-following paths with lengths H^* and H, see Scheme 2:

$$H^* = \sum_{i=1}^{n-1} |p_{i+1} - p_i| \tag{3a}$$



Scheme 2. The pale-blue line in sub-figure (a) represents the path, referred to as the eigenvector-following path length H^*, swept out by the tips of the scaled $\underline{\mathrm{e}}_1$ eigenvectors, shown in magenta, and defined by equation (3a). The red path in sub-figure (b) corresponds to the eigenvector-following path length H, constructed from the tips of the scaled $\underline{\mathrm{e}}_2$ eigenvectors, shown in mid-blue and is defined by equation (3b). The pale-blue and mid-blue arrows representing the $\underline{\mathrm{e}}_1$ and $\underline{\mathrm{e}}_2$ eigenvectors are scaled by the ellipticity ε respectively, where the vertical scales are exaggerated for visualization purposes. The green sphere indicates the position of a given *BCP*. Details of how to implement the calculation of the eigenvector-following path lengths H^* and H are provided in the Supplementary Materials S1.