

# Origin of threefold methyl torsional potential in methylindoles

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**Abstract** In this article, we present a systematic study on mono-methylindoles to investigate the electronic origin of the threefold symmetric component ( $V_3$ ) of the methyl torsional potential barrier in the ground electronic state ( $S_0$ ). The structures and the torsional potential parameters of these molecules were evaluated from ab initio calculation using Hartree-Fock (HF), second order Moller Plesset perturbation (MP2) and B3LYP density functional level of theories and Gaussian type basis set 6-31G( $d, p$ ). Natural bond orbital (NBO) analysis of these molecules were carried out using B3LYP/6-31G( $d, p$ ) level of calculation to understand the formation of the threefold  $V_3$  term arising from the changes of various non-covalent interactions during methyl rotation. Our analysis reveals that the contributions from  $\pi$  orbitals play a dominant role in the barrier height determination in this class of molecules. The threefold term in the barrier arises purely from the interactions non-local to the methyl group in case when the methyl group has two single bonds vicinal to it. On the other hand, it is the local interaction that determines the potential energy barrier when the methyl group has one single bond and one double bond vicinal to it. However, in all these cases, the magnitude of the energy barrier depends on the resonance structure formation in the benzene ring frame upon rotation of the methyl group and, therefore, the energetics of the barrier cannot be understood without considering the molecular flexing during methyl rotation.

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## 1 Introduction

The hindered motion of the methyl group has drawn considerable interest since its first study by Kemp and Pitzer [1] in the simple molecule, ethane. Physical quantities associated with this motion such as the barrier height and the shape of the methyl torsional potential vary drastically depending on the local chemical environment of the methyl group. Subtle questions related to their structural dependence need answers from the energetic point of view. The much prevalent  $\pi$ -fragment model [2] propounded that the torsional barrier arises from the interactions between the out-of-plane hydrogen atoms of the methyl group and the vicinal  $\pi$  bond. However, Goodman et al. [3] showed that it was not the  $\pi$  electrons but the overwhelmed contribution of  $\sigma$  electrons that was responsible for the barrier formation in small conjugated molecules such as acetaldehyde and propene. They further emphasized that in order to understand the barrier energetics, the flexing of the molecular skeleton during methyl rotation should be taken into account [4–6]. Liljefors and Allinger [7] showed that the methyl torsional barrier in the aromatic molecules originated from the difference in the  $\pi$ -bond order between the two ring C–C bonds vicinal to the methyl group. This idea was further extended by George et al. [8] for toluene and several other aromatic hydrocarbons. Lu et al. [9] carried out extensive calculations for toluene and its cations to find a correlation between the barrier height and the difference between the two C–C bond orders vicinal to the methyl group. Sonoda et al. [10] on the other hand showed that the difference of the charge density between

the carbon atoms vicinal to the methyl group can be correlated with the barrier height. Nakai et al. [11–13] developed the energy density analysis for the potential barrier in substituted toluenes to establish the hydrogen bonding between the in-plane hydrogen atom of the methyl group and the fluorine atom in *o*-fluorotoluene. The role of remote substitution on the methyl torsional potential has also been studied in different para-substituted toluenes [14, 15].

The study of hindered motion of the methyl group in aromatic and heterocyclic molecules has important implications for the understanding of non-covalent electronic interactions. In our earlier work [16–18], we have studied some nitrogen heterocycles namely 1-methyl-2(1H)-pyridone (1MPY), 3-methyl-2(1H)-pyridone (3MPY) and 1-methyl-2(1H)-pyridinimine (1MPI) to understand the role of these basic interactions in the formation of the methyl torsional barrier. In the theoretical framework of natural bond orbital (NBO) analysis, bond–antibond and Lewis interaction energies were examined by partitioning these energies into the interactions associated with the methyl group (local) and others (non-local). It was shown that when the methyl group was attached to the nitrogen atom associated with the two vicinal single bonds, the torsional barrier calculated from the change in overall energy during methyl rotation was controlled by the non-local interactions. The flipping of the bond order due to resonance during methyl rotation was found to cancel the bond–antibond interactions between the methyl group and the vicinal bonds in case of 1MPY and 1MPI [16–18]. However, in 3MPY, the local interactions were the main contributors to the methyl torsional barrier. On the other hand in case of *p*-methylstyrene [15], the non-local interactions were shown to play a key role in the barrier formation because of the mutual cancelation of the local interactions upon flipping of the resonance during methyl rotation. In search for the generalities relating the origin of torsional barrier to various interactions in this class of molecules, we have extended our studies further to other heterocycles such as methyl substituted indoles, which are potential molecules in this regard.

Indole the chromophore of the amino acid tryptophan and its derivatives have attracted significant attention from spectroscopists. Bickel et al. [19] have studied one-photon resonant multiphoton ionization (MPI) and dispersed fluorescence of the supersonic jet cooled monomethyl indoles to understand the influence of the position of the methyl group on its torsional potential in both the ground and the excited states. The parameters of the torsional potential for 1-, 4-, 5-, 6- and 7-methylindole molecules were estimated in the excited electronic state from the MPI studies. The lack of sufficient dispersed fluorescence signal restricted the estimation of the ground state potential for 1-, 5- and 6-methylindole molecules. The motivation of these studies was to explore the change in the potential barrier upon electronic excitation.

Later, Sammeth et al. [20] studied 3- and 5-methylindole and their complexes with helium and water using the fluorescence excitation spectroscopy. The parameters of the ground state potential were estimated for 3-methylindole using the  $0a_1-1e$  splitting and the torsional transitions intensities [20]. In the light of these experimental observations, for developing a deeper understanding of the origin of the methyl torsion in terms of underlying electronic interactions in this class of molecules, we present here the results of our systematic studies using ab initio calculations and NBO analysis for seven methyl substituted indole derivatives. The importance of the pyrrol ring in the indole structure was focused upon to explore its role in the development of threefold barrier in these molecules compared to toluene, the parent molecule. The results have been compared with the previously reported methylpyridones to form a generalized picture in this class of *N*-heterocycles.

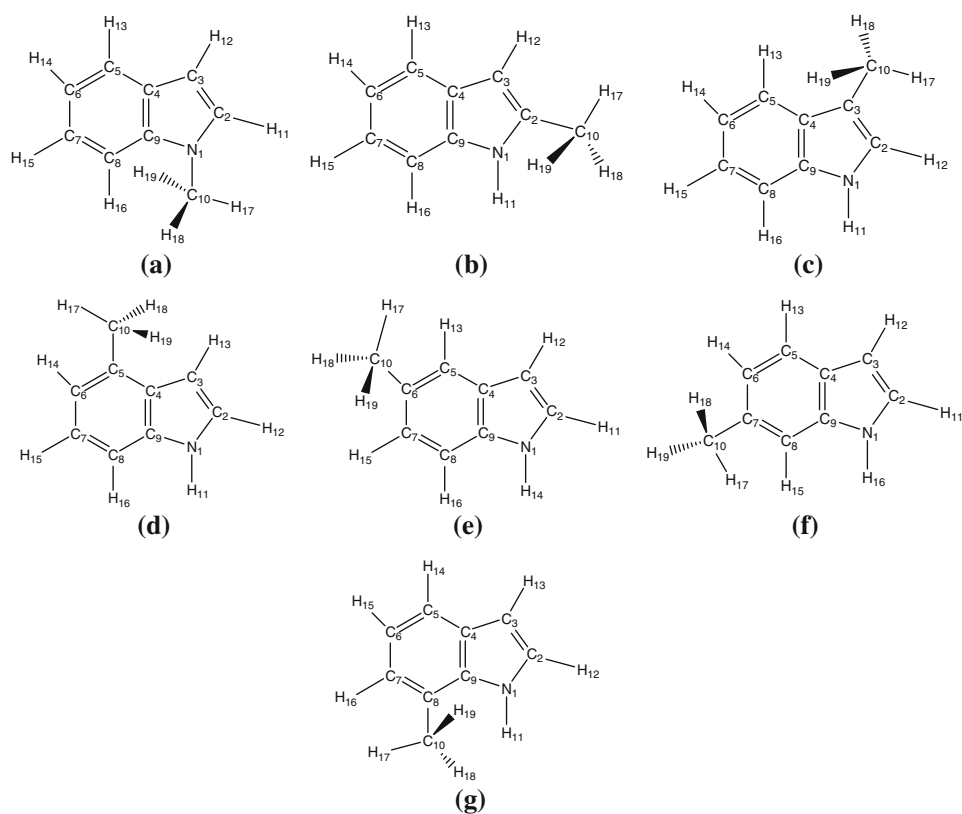
## 2 Results and discussions

### 2.1 Ab initio optimized molecular conformations and the torsional potentials

The ground state geometries of seven mono methyl indole molecules under consideration were optimized using 6-31G(*d*, *p*) basis set with Hartree-Fock (HF), second order Moller Plesset perturbation (MP2) and B3LYP density functional level of theories. The minimum energy conformations of the methyl group in all these molecules using B3LYP/6-31G(*d*, *p*) are shown in Fig. 1. The optimized geometrical parameters are listed in a tabular form (Table S1) as electronic supplementary materials. It can be seen that the ring frames are always planar and the methyl group attains a conformation in which one of its C–H bonds eclipses either the N–C bond in case of 1-methylindole or the C–C bond in other molecules. The localized molecular orbital (LMO) bond order calculations reveal that except 1-methylindole, the eclipsed C–H bond is always towards the C–C bond having higher  $\pi$  bond order, as pointed out by Lu et al. [9] using natural resonance theory (NRT). Individual LMO bond orders of bonds adjacent to the methyl group in 1- to 7-methylindoles calculated at B3LYP/6-31G(*d*, *p*) level of theory are listed in tabular form (Table S2) as electronic supplementary materials. In 1-methylindole, the two vicinal N–C bonds of the methyl group have bond orders close to one implying their single bond characters. It is to be noted that the in-plane C–H bond is towards the bond  $N_1C_2$ , which has an LMO bond order (0.7227) marginally lower than that of  $N_1C_9$ (0.7472).

The torsional potentials for all these molecules were calculated using fully relaxed model [3]. In this scheme, the rotational angle ( $\tau$ ) of the in-plane hydrogen of the methyl group in the minimum energy conformation of the  $S_0$  state

**Fig. 1** Minimum energy conformations of  
**a** 1-methylindole  
**b** 2-methylindole  
**c** 3-methylindole  
**d** 4-methylindole  
**e** 5-methylindole  
**f** 6-methylindole  
**g** 7-methylindole in the ground electronic state ( $S_0$ ) calculated with B3LYP/6-31G(*d*, *p*)



is defined as  $\tau = 0$  degree. The potential energy curve was obtained by constraining only the rotational angle ( $\tau$ ) of the methyl rotor to the local frame and then by optimizing the rest of the geometry to minimize the energy. The parameters of the torsional potential were obtained by fitting the energies derived from potential scan to one dimensional torsional potential of the form  $V(\tau) = (V_3/2)(1 - \cos 3\tau) + (V_6/2)(1 - \cos 6\tau)$  where  $V_3$  and  $V_6$  are the threefold and sixfold potential energy terms, respectively, and  $\tau$  is the torsional angle. Higher order terms in the potential functions were neglected because of their negligible contributions compared to the three and sixfold terms. The parameters of the torsional potential are given in Table 1 along with the experimental values for the ground state. For all these molecules under consideration,  $V_3$  terms are always at least one order of magnitude higher than  $V_6$  terms signifying the dominant threefold nature of the potential. The barrier height (magnitude of  $V_3$  term) increases from 1-methylindole to 3-methylindole. The methyl group experiences higher potential barrier in case of 4- and 7-methylindoles than that in 5- and 6-methylindoles. The calculated barriers with B3LYP/6-31G(*d*, *p*) are in reasonable agreement with the experimental values in all cases, while those predicted by HF and MP2 are always higher (Table 1). We have, therefore, used this level of theory to get further insight into the barrier formation mechanisms in these molecules.

## 2.2 NBO calculations

In the NBO framework, the total barrier energy of the molecules can be partitioned into the changes in the Lewis and the non-Lewis energies [21, 22] as

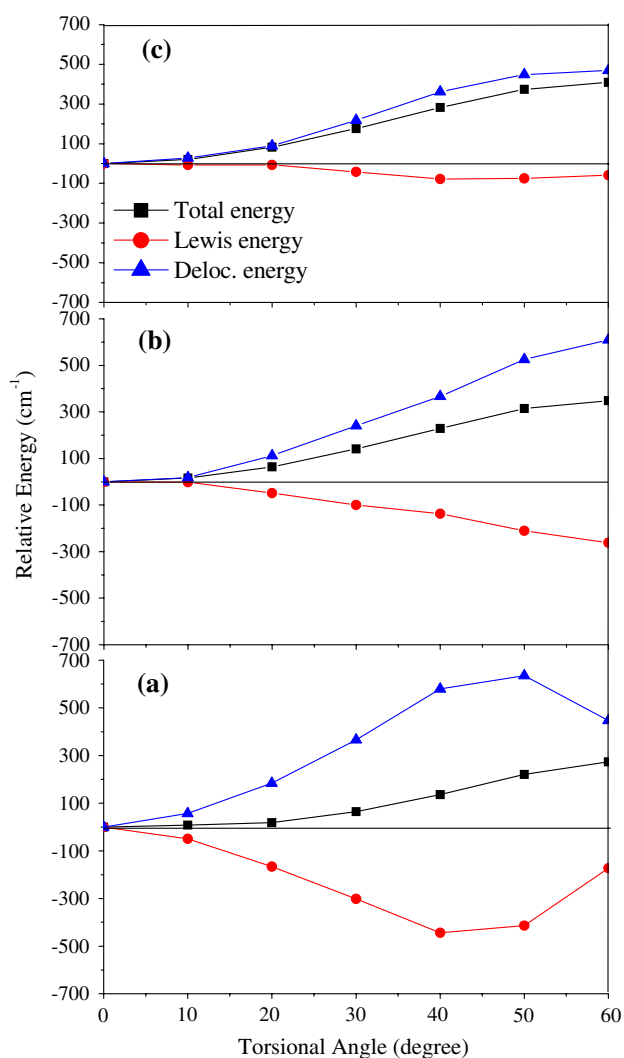
$$\Delta E_{\text{Barrier}} = \Delta E_{\text{Lewis}} + \Delta E_{\text{nonLewis}}$$

here, the Lewis energy is the energy of the localized species forming the Lewis structure and the non-Lewis energy represents the delocalization energy arising from the interactions between the bond–antibond, the lone pair–antibond and smaller antibond–antibond. In the NBO calculations, the diagonal and off-diagonal elements of Fock matrix represent the Lewis and delocalization energies, respectively. The Lewis and the overall delocalization energies can be separated by deleting all the off-diagonal elements of Fock matrix using NOSTAR option in the calculation.

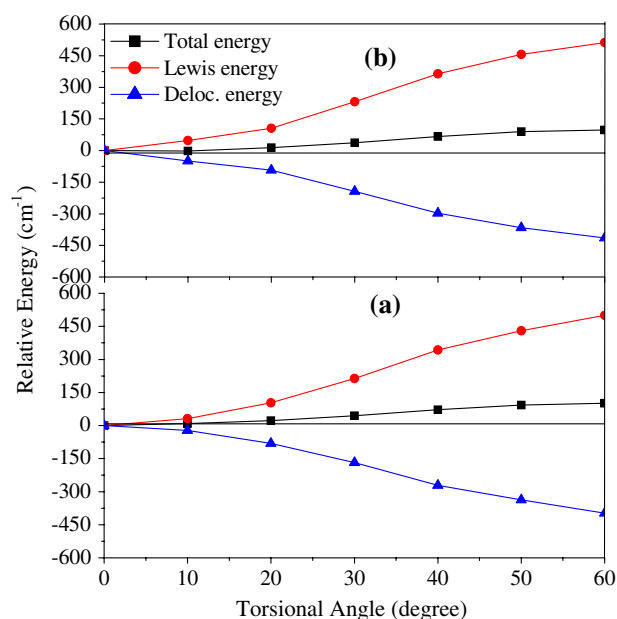
Figure 2 shows the barrier energy partitioning into Lewis and delocalization energies for 1-, 2- and 3-methylindoles. Figs. 3 and 4 represent the similar energy partition curves for 5- and 6-methylindoles and 4- and 7-methylindoles, respectively. In all these molecules, the Lewis and non-Lewis energy terms are opposite in sign and, thus, the net barrier energy stems from the resultant of these two terms. It is to be noted that when the methyl group is associated with the pyrrole ring as in case of 1-, 2- and 3-methylindole (Fig. 2), the change in Lewis energy is always antibarrier and the non-Lewis or the

**Table 1** Potential parameters ( $\text{cm}^{-1}$ ) for methylindoles calculated at 6-31G(*d*, *p*) basis set

Molecules	HF		MP2		B3LYP		Experiment [19,20]	
	$V_3$	$V_6$	$V_3$	$V_6$	$V_3$	$V_6$	$V_3$	$V_6$
1-methylindole	340	-70	321	-80	274	-70	282.2	-55.8
2-methylindole	461	-26	369	-60	348	-27	-	-
3-methylindole	557	-10	427	-16	419	-11	443.2	-
4-methylindole	373	-13	393	-58	335	-17	-	-
5-methylindole	142	-7	147	-31	109	-8	132.7	-8.1
6-methylindole	142	-8	140	-33	104	-10	123.1	-6.2
7-methylindole	488	-37	501	-100	418	-44	-	-

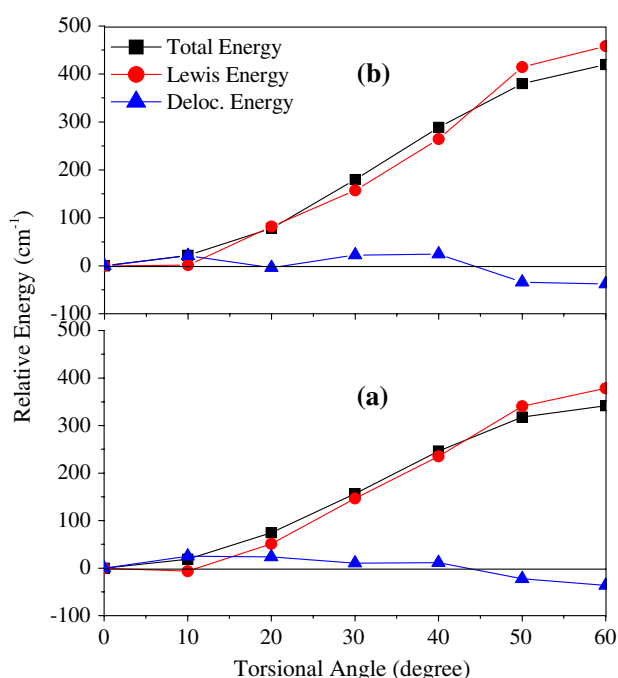
**Fig. 2** Contributions of Lewis and delocalization energy to the barrier for **a** 1-methylindole **b** 2-methylindole and **c** 3-methylindole

delocalization energy change is the barrier-forming term. On the other hand when the methyl group is associated with the benzene ring as in the case of 4-, 5-, 6- and 7-methylindoles,

**Fig. 3** Contributions of Lewis and delocalization energy to the barrier for **a** 5-methylindole and **b** 6-methylindole

the barrier results from the positive energy change of the Lewis energy. In case of 5-methylindole and 6-methylindole (Fig. 3), the overall delocalization energy is antibarrier and plays a significant role in determining the magnitude of the barrier by canceling partially the barrier forming contribution from Lewis energy. However, in case of 4-methylindole and 7-methylindole (Fig. 4), the delocalization energy plays a minimal role and the barrier energy largely stems from the Lewis energy change.

To get an insight into the mechanism of the torsional barrier formation, barrier energy was further partitioned depending on the adjacent electronic environment of the methyl group. For 1-, 2- and 3-methylindoles, the electronic interactions were studied with respect to the position of the methyl group. The contributions to the barrier energy arising from the vicinity of the methyl group were considered as local interactions. The importance of the other interactions present



**Fig. 4** Contributions of Lewis and delocalization energy to the barrier for **a** 4-methylindole and **b** 7-methylindole

in the molecule termed as non-local were also sought to understand the formation of the methyl torsional barrier. The molecules 4-, 5-, 6- and 7-methylindoles were considered as the asymmetric substitution of the pyrrol ring in the toluene, and hence the asymmetric contributions of the interactions arising from the two sides of the molecular frame with respect to the methyl rotor axis were investigated to understand the evolution of the threefold barrier in this category of molecules.

The delocalization energy contributions to the barrier arising from various individual orbital interactions were investigated using a single deletion procedure [23]. The barrier contribution from the delocalization energy change of a particular bond–antibond interaction can be extracted using the relation,

$$\Delta^2 E[F_{ij*}^{\text{del}}] = \Delta E - \Delta E[F_{ij*}^{\text{del}}]$$

where  $\Delta E = E_t - E_m$  is the barrier energy calculated without deletion of any bond–antibond interaction and  $\Delta E[F_{ij*}^{\text{del}}] = E_t[F_{ij*}^{\text{del}}] - E_m[F_{ij*}^{\text{del}}]$  is the barrier energy with the Fock matrix element ( $F_{ij*}$ ) deleted. The subscript t and m represent the top of the barrier and the minimum energy conformations of the molecule, respectively. Subscripts  $i$  and  $j^*$  signify bonding and antibonding orbitals, respectively.

The Lewis energy term ( $\Delta E_{\text{Lewis}}$ ), which represents the energy changes in the Fock matrix elements of doubly occupied bond orbitals was further partitioned into structural and

steric exchange energies under the following scheme

$$\Delta E_{\text{Lewis}} = \Delta E_{\text{struc}} + \Delta E_{\text{steric}}$$

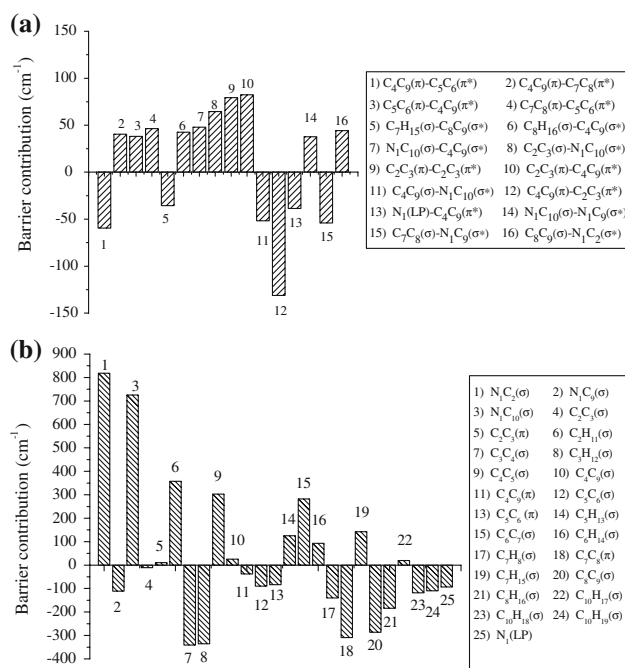
where  $\Delta E_{\text{struc}}$  is the change in structural energy corresponding to the energy change due to all the interactions within and between bonds and  $\Delta E_{\text{steric}}$  is the change in steric exchange repulsion. Since  $\Delta E_{\text{struc}}$  corresponds to the change of the Fock matrix elements of the Lewis structure, the reasonable approximation is  $\Delta E_{\text{struc}} \approx \Delta E_{\text{bond}} = \Delta\omega$  where  $\Delta\omega$  is the pNBO energy change corresponding to individual bond energy change accompanying rotation. The structural energy change ( $\Delta\omega$ ) can be obtained using the relation

$$\Delta\omega = \varepsilon_t N_t - \varepsilon_m N_m$$

where  $\varepsilon_t$  and  $\varepsilon_m$  are the NBO energies of the top of the barrier and the minimum energy conformers, respectively, and  $N_t$  and  $N_m$  are the corresponding NBO occupancies.

### 2.2.1 1-methylindole

The methyl group in 1-methylindole has two adjacent single N–C bonds similar to the case of *N*-methylpyrrol and 1MPY. In *N*-methylpyrrol, the barrier to the methyl internal rotation is sixfold symmetric [24], as the threefold barrier term vanishes due to equal and opposite energy contributions from two sides of the molecule about the methyl rotor axis. Whereas, in the case of 1MPY, a finite threefold symmetric potential was observed [18]. The origin of this threefold potential in 1MPY is predominantly due to the asymmetry of the electronic environment in the molecule about the methyl rotor axis. Similarly in 1-methylindole, the experiment [19] and the ab initio calculations show a moderate threefold potential. The calculated  $282\text{ cm}^{-1}$  threefold potential term with B3LYP/6-31G( $d, p$ ) is in good agreement with the experimental value of  $274\text{ cm}^{-1}$ , as mentioned earlier. To understand the role of interactions stemming from various parts of the molecule in this barrier formation, we have analyzed separately the energy changes in the benzene ring, pyrrol ring and the structure adjacent to the methyl group. In the course of methyl rotation, small changes in the bond angles ( $\Delta\angle\text{C}_7\text{C}_6\text{C}_5 = -0.20$ ,  $\Delta\angle\text{C}_8\text{C}_7\text{C}_6 = 0.11$  and  $\Delta\angle\text{C}_9\text{C}_8\text{C}_7 = 0.22$  degree between the top of the barrier and minimum energy conformer) in the benzene ring are observed, while the methyl group experiences major structural changes. The  $\text{N}_1\text{C}_{10}$  bond length increases by  $0.002\text{ \AA}$ , and the bond angles  $\angle\text{C}_{10}\text{N}_1\text{C}_9$  and  $\angle\text{H}_{17}\text{C}_{10}\text{N}_1$  increase by  $1.44$  and  $0.38$  degree, respectively, from the minimum energy to the top of the barrier conformations. The contribution to the barrier arising from changes in the individual bond–antibond (hyperconjugation) interaction energies evaluated using single deletion procedure are shown in Fig. 5a. Relevant interactions larger than  $0.1\text{ kcal/mole}$  only are listed here. In this figure, interactions 1–6, 7–12 and 13–16 are associated with the benzene ring,



**Fig. 5** Individual delocalization energy contributions **a** and structural energy contributions **b** to the barrier energy in 1-methylindole

pyrrol ring and others, respectively. It can be seen that the contributions from bond–antibond energy changes in the benzene ring (interactions 1–6) are collectively barrier forming in nature with a magnitude of  $72\text{ cm}^{-1}$ . The other non-local interactions (interactions 7–12) arising from the pyrrol ring ( $90\text{ cm}^{-1}$  in aggregate) are also barrier forming in nature. The methyl group contribution in delocalization energy is not significant, whereas the interaction of the nitrogen lone pair with the antibonding  $\pi$  orbital of  $C_4C_9$  (interaction 13) is anti barrier with a small magnitude ( $-38\text{ cm}^{-1}$ ). Therefore, the contribution from the pyrrol ring together with the benzene ring (all non-local to the methyl group) constitutes the overall change in delocalization energy as barrier-forming term. It is to be noted that a similar phenomenon was observed in case of 1MPY and 1MPI [18] where the contributions to the barrier energy local to the methyl group was antibarrier and the non-local bond–antibond interactions were large enough to make the total delocalization term barrier forming.

The structural energy contributions to the barrier from change in individual bond energies are shown in Fig. 5b. The overall structural energy change is positive ( $651\text{ cm}^{-1}$ ) and hence favor the barrier. However, the contributions from the CH bonds of the methyl group (22–24 in Fig. 5b), the benzene ring (9–21) and the contribution from the lone pair (25) are negative and thus antibarrier with their respective magnitude  $209$ ,  $160$  and  $93\text{ cm}^{-1}$ . The change in structural energies of the pyrrol ring is barrier forming and is dominated by the energy change in  $N_1C_2$  and  $N_1C_{10}$  (1 and 3 in Fig. 5b). In order to probe the source of this change in structural energy

in the pyrrol ring, first, the angle  $\angle C_{10}N_1C_9$  was kept fixed to its value corresponding to the minimum energy conformation, and bond energies were recalculated. It was observed that the overall structural energy remained unchanged except for the change in bond energies of  $N_1C_2$  and  $N_1C_9$ . By fixing this angle, the bond energy of  $N_1C_9$  increased, whereas the bond energy of  $N_1C_2$  decreased keeping the total contribution from these two interactions unchanged.

In the second step, the bond length  $N_1C_{10}$  was kept pegged to its value corresponding to the minimum energy conformation and the energy was recalculated. The effect of this appeared in the bond energy of  $N_1C_{10}$ . The bond energy of  $N_1C_{10}$  decreased by  $570\text{ cm}^{-1}$ , which was very close to the magnitude of the total structural energy change. Therefore, the positive structural energy contribution to the barrier energy is due to the change in local structure, particularly, bond length increment of  $N_1C_{10}$  during the methyl rotation. Thus, the positive contribution from the structural energy implies that the steric energy change is antibarrier and its magnitude is greater than the structural energy to form the total Lewis energy term negative.

### 2.2.2 2-methylindole and 3-methylindole

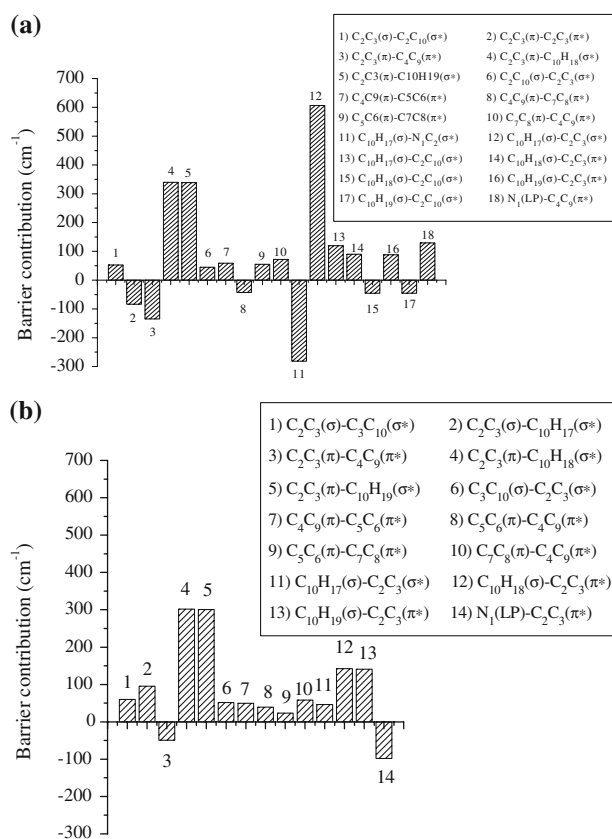
The methyl group in 2- and 3-methylindole has one single N–C/C–C bond and one double C–C bond adjacent to it as is the case for methyl group in the previously studied molecule 3MPY [18]. Threefold potential term for 3-methylindole calculated with B3LYP/6-31G(*d*, *p*) ( $419\text{ cm}^{-1}$ ) is very close to that in 3MPY calculated with the same level of theory and basis set ( $403\text{ cm}^{-1}$ ). The  $V_3$  term, on the other hand, for 2-methylindole is  $71\text{ cm}^{-1}$  lower than that for 3-methylindole. This difference in magnitude of the  $V_3$  term for these two cases stems from the changes in various structural parameters and electronic interactions. The important geometrical changes observed in 2- and 3-methylindole from the minimum energy conformation to the top of the torsional barrier conformation are given in Table 2. In both these molecules, the change in the bond length of the C–C bond between the methyl group and the pyrrol ring are nearly same with a magnitude of  $0.0048$  and  $0.0046\text{ \AA}$  for 2- and 3-methylindoles, respectively. The major differences in the structural changes in these two molecules appear in the angle change of  $\angle H_{ip}C_mC_r$  (*ip* = in plane; *m* = methyl and *r* = ring). In 2-methylindole, this angle ( $\angle H_{17}C_{10}C_2$ ) increases by  $1.32$  degree whereas in 3-methylindole, this angle ( $\angle H_{17}C_{10}C_3$ ) decreases by  $0.33$  degree. This change in the  $\angle H_{ip}C_mC_r$  angle may be responsible for the change in the orbital interactions or the bond energies in the molecule. The contributions from the energy change in individual bond–antibond interactions during methyl group rotation are shown in Fig. 6a and b for 2- and 3-methylindoles, respectively. The sum of these individual energies is positive and thus barrier

**Table 2** Major geometrical changes in 2- and 3-methylindole in top of barrier and minimum energy conformations (bond lengths are in Å and bond angles are in degree)

2-methylindole		3-methylindole	
C <sub>3</sub> C <sub>2</sub>	0.0012	C <sub>3</sub> C <sub>2</sub>	0.0012
C <sub>10</sub> C <sub>2</sub>	0.0048	C <sub>10</sub> C <sub>3</sub>	0.0046
H <sub>17</sub> C <sub>10</sub>	0.0025	–	–
H <sub>18</sub> C <sub>10</sub>	–0.0022	–	–
H <sub>19</sub> C <sub>10</sub>	–0.0022	∠C <sub>5</sub> C <sub>4</sub> C <sub>3</sub>	0.1281
∠C <sub>10</sub> C <sub>2</sub> C <sub>3</sub>	0.2802	∠C <sub>10</sub> C <sub>3</sub> C <sub>2</sub>	0.1599
∠H <sub>11</sub> N <sub>1</sub> C <sub>2</sub>	–0.3348	∠H <sub>12</sub> C <sub>2</sub> N <sub>1</sub>	–0.2126
∠H <sub>12</sub> C <sub>3</sub> C <sub>2</sub>	0.2163	∠H <sub>13</sub> C <sub>5</sub> C <sub>4</sub>	0.1111
∠H <sub>17</sub> C <sub>10</sub> C <sub>2</sub>	1.3201	∠H <sub>17</sub> C <sub>10</sub> C <sub>3</sub>	–0.3299
∠H <sub>18</sub> C <sub>10</sub> C <sub>2</sub>	–0.3834	∠H <sub>18</sub> C <sub>10</sub> C <sub>3</sub>	0.4035
∠H <sub>19</sub> C <sub>10</sub> C <sub>2</sub>	–0.3913	∠H <sub>19</sub> C <sub>10</sub> C <sub>3</sub>	0.4043

forming. This is in accordance with the barrier partitioning obtained using NOSTAR option. The major positive contributions to the barrier are from the interactions of bonding and antibonding  $\pi$  orbitals of C<sub>2</sub>C<sub>3</sub> with the antibonding and bonding  $\sigma$  orbitals of the out-of-plane CH bonds of the methyl group. In 2-methylindole, these interactions (4, 5, 14 and 16 in Fig. 6a) are C<sub>2</sub>C<sub>3</sub>( $\pi$ )–C<sub>10</sub>H<sub>18</sub>( $\sigma^*$ ), C<sub>2</sub>C<sub>3</sub>( $\pi$ )–C<sub>10</sub>H<sub>19</sub>( $\sigma^*$ ), C<sub>10</sub>H<sub>18</sub>( $\sigma$ )–C<sub>2</sub>C<sub>3</sub>( $\pi^*$ ) and C<sub>10</sub>H<sub>19</sub>( $\sigma$ )–C<sub>2</sub>C<sub>3</sub>( $\pi^*$ ) making a contribution of 857 cm<sup>–1</sup> to the barrier. Whereas, in the case of 3-methylindole these interactions (4, 5, 12 and 13 in Fig. 6b) are C<sub>2</sub>C<sub>3</sub>( $\pi$ )–C<sub>10</sub>H<sub>18</sub>( $\sigma^*$ )–C<sub>2</sub>C<sub>3</sub>( $\pi$ )–C<sub>10</sub>H<sub>19</sub>( $\sigma^*$ ), C<sub>10</sub>H<sub>18</sub>( $\sigma$ )–C<sub>2</sub>C<sub>3</sub>( $\pi^*$ ) and C<sub>10</sub>H<sub>19</sub>( $\sigma$ )–C<sub>2</sub>C<sub>3</sub>( $\pi^*$ ) making 886 cm<sup>–1</sup> contribution to the barrier. All these major interactions are associated with the methyl group. Apart from these major interactions, interactions 11 and 12 (Fig. 6a) in 2-methylindole are collectively barrier forming. These interactions are between  $\sigma$  bonding of CH<sub>ip</sub> and antibonding orbitals of NC and CC bonds of the pyrrol ring. This is a consequence of the molecular flexing during methyl rotation.

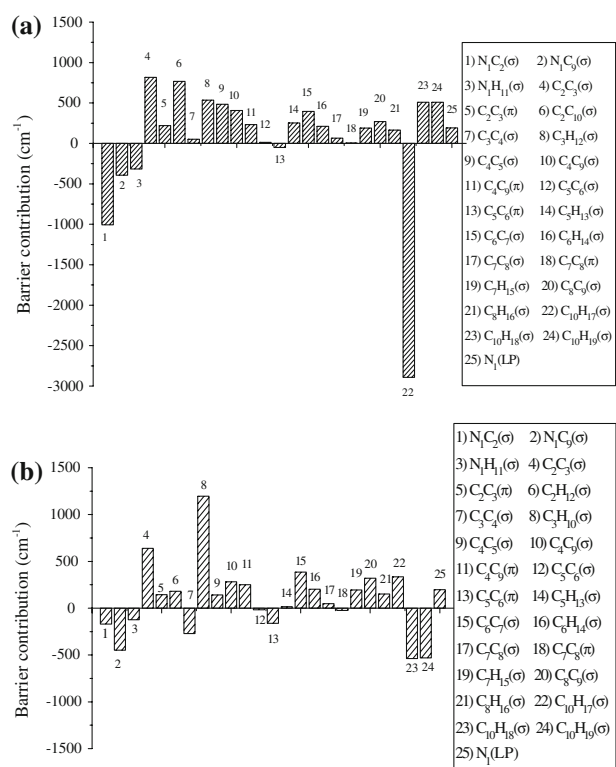
The structural energy contributions for these two molecules are shown in Fig. 7a and b. The overall contribution from the structural energy is positive, indicating a major role of the steric energy in ascertaining the magnitude of the barrier. In 2-methylindole, the large negative change in bond energy of C<sub>10</sub>H<sub>17</sub> (22 in Fig. 7a) makes the energy contribution from the methyl group in this molecule antibarrier in nature. This could be due to the opening of the angle  $\angle$ H<sub>17</sub>C<sub>10</sub>C<sub>2</sub>. The structural contribution from the pyrrol ring is negligible and the overall positive contribution comes from the aggregate of the small changes in the bond energies associated with the benzene ring. For 3-methylindole again, the overall structural energy change is positive and the methyl group contribution is negative. However, the extent of

**Fig. 6** Individual delocalization energy contributions to the barrier in a 2-methylindole and b 3-methylindole

antibarrier contribution from the methyl group is not as much as in the case of 2-methylindole. The contribution from the bond energy change of C<sub>3</sub>C<sub>10</sub> (8 in Fig. 7b) in the pyrrol ring favors the barrier. The many small positive bond energy changes from the benzene ring make the overall structural energy positive.

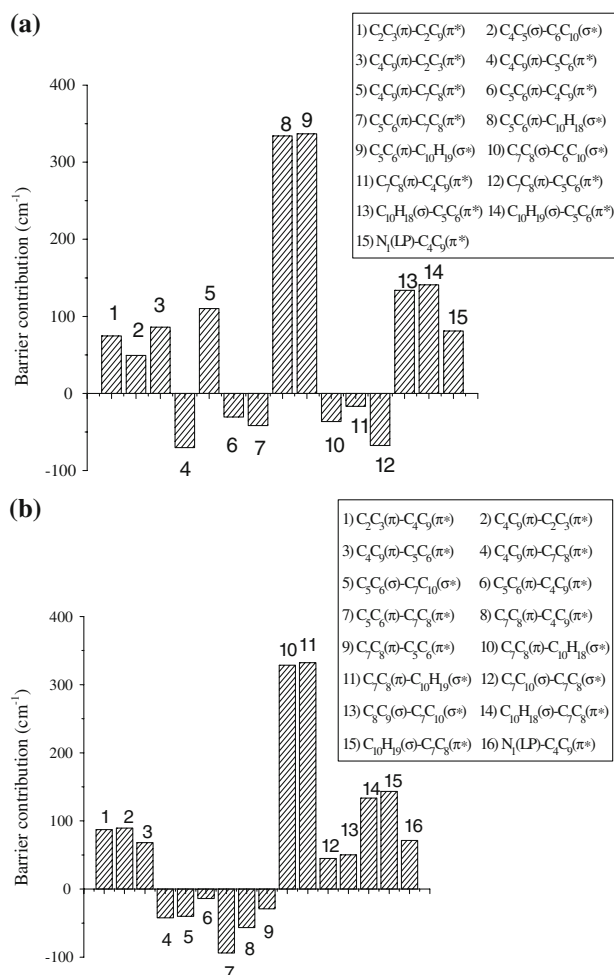
### 2.2.3 5-methylindole and 6-methylindole

The methyl group in these two molecules is attached to the benzene ring and resembles toluene as regard to the electronic environment adjacent to the methyl group. In toluene, a resonance structure forms in the course of rotation of the methyl group from 0 degree conformation to 180 degree conformation. Due to this resonance structure formation, there is an alternation of CC bond length by  $\sim$ 0.005 Å. This resonance structure formation is also revealed by the NBO analysis in the form of alternation of  $\pi$  bond character. Due to this, the energies from the individual bond–antibond interactions of the two sides of the methyl rotor axis cancel each other yielding a null threefold term. On the contrary, in 5- and 6-methylindoles, a finite threefold symmetric barrier is observed experimentally [19] and has been calculated



**Fig. 7** Individual structural energy contributions to the barrier in **a** 2-methylindole and **b** 3-methylindole

theoretically in Sect. 2.1. To figure out the reason for the appearance of the threefold term, the geometrical changes in these two molecules were compared with those in toluene. An alternation in the CC bond length of benzene ring is observed, but the extent of this change is 0.002 and 0.003 Å only in 5- and 6-methylindoles, respectively, as against 0.005 Å in the case of toluene. Due to this, there is no clear shift of the  $\pi$  bond character observed in the NBO analysis of these two molecules. The  $\angle C_{\text{methyl}} CC$  angle change is only 0.59 degree in 5-methylindole and 0.72 degree in 6-methylindole, unlike in toluene with 0.93 degree. We investigated the major changes observed in individual hyperconjugative bond–antibond interaction energies (larger than 0.10 kcal/mole) from the top of the barrier to the minimum energy conformation. These are presented in Fig. 8a and b, respectively. The contributions from the interactions involving out-of-plane CH bond of the methyl group and antibonding and bonding  $\pi$  orbitals of the CC bond of the benzene ring are barrier-forming positive terms. These interactions are  $C_5C_6(\pi)–C_{10}H_{18}(\sigma^*)$ ,  $C_5C_6(\pi)–C_{10}H_{19}(\sigma^*)$ ,  $C_{10}H_{18}(\sigma)–C_5C_6(\pi^*)$  and  $C_{10}H_{19}(\sigma)–C_5C_6(\pi^*)$  corresponding to 8, 9, 13 and 14, respectively, in Fig. 8a for 5-methylindole. The same is also observed for 6-methylindole where the interactions are  $C_7C_8(\pi)–C_{10}H_{18}(\sigma^*)$ ,  $C_7C_8(\pi)–C_{10}H_{19}(\sigma^*)$ ,  $C_{10}H_{18}(\sigma)–C_7C_8(\pi^*)$  and  $C_{10}H_{19}(\sigma)–C_7C_8(\pi^*)$  corresponding to 10, 11, 14 and 15, respectively in Fig. 8b. These interactions



**Fig. 8** Individual delocalization energy contributions to the barrier in **a** 5-methylindole and **b** 6-methylindole

are local to the methyl group. The overall energy change for all the bond–antibond interactions is  $1,083 \text{ cm}^{-1}$  for 5-methylindole (Fig. 8a) and  $1,072 \text{ cm}^{-1}$  for 6-methylindole (Fig. 8b). However, in the energy partitioning using NO-STAR option, it was observed that the overall delocalization energy is antibarrier in nature. In the individual interaction analysis of the delocalization energy contribution, the energies from antibond–antibond interactions and interactions involving core and Rydberg orbitals are neglected. Thus, for these two molecules, where the barrier energy is low, the interactions other than bond–antibond also play a crucial role in switching the total delocalization energy from barrier-forming to antibarrier term.

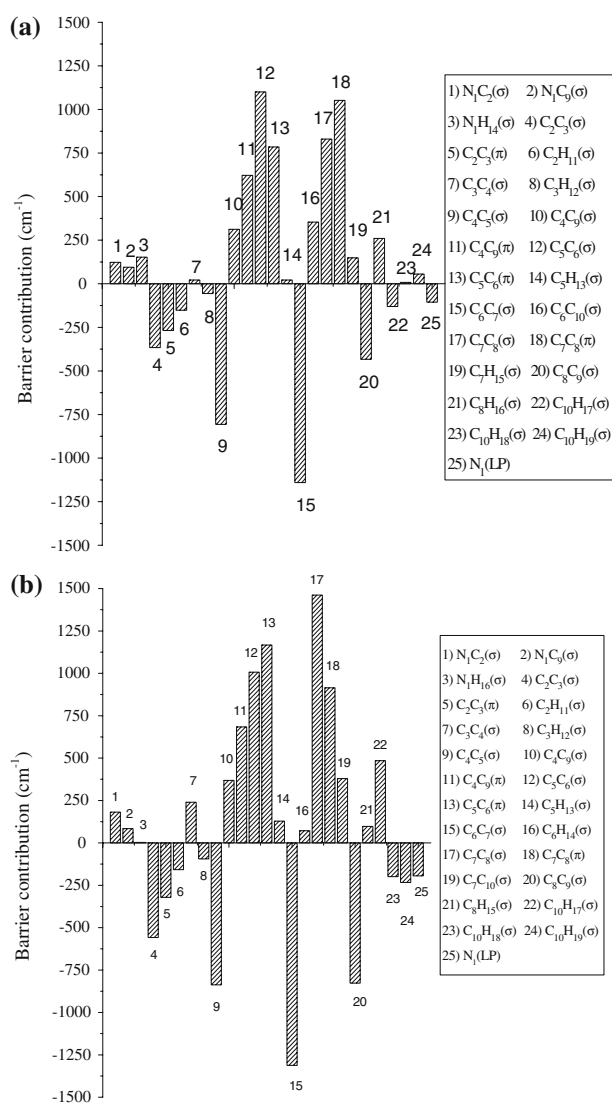
The structural energy contributions to overall barrier for 5- and 6-methylindole are shown in Fig. 9a and b, respectively. The overall contribution from the structural energy is positive for both these molecules. For 5-methylindole, total structural energy is  $2,488 \text{ cm}^{-1}$ , whereas for 6-methylindole it is  $2,535 \text{ cm}^{-1}$ . The pyrrol ring contribution to the structural



energy is slightly negative and the major positive contribution comes from the bonds having  $\pi$  character in the benzene ring. In the light of the cancellation of the structural energy seen in toluene, we compare the structural contribution for these molecules on the two sides of the methyl rotor axis. For both these molecules, the energy contribution from the  $\sigma$  bond energy cancels on the two sides. In 5-methylindole, the positive  $\sigma$  bond energy contributions from C<sub>4</sub>C<sub>9</sub>, C<sub>5</sub>C<sub>6</sub> and C<sub>7</sub>C<sub>8</sub> corresponding to 10, 12, 17 in Fig. 9a are cancelled by the negative contributions from C<sub>8</sub>C<sub>9</sub> (20), C<sub>6</sub>C<sub>7</sub> (15) and C<sub>4</sub>C<sub>5</sub> (9), respectively. The overall contribution from these six bond energies is antibarrier with a magnitude of 137 cm<sup>-1</sup>. However, the  $\pi$  bond energies from C<sub>4</sub>C<sub>9</sub> (11), C<sub>5</sub>C<sub>6</sub> (13) and C<sub>7</sub>C<sub>8</sub> (18) are positive and are the major contributors to the overall structural energy (2,458 cm<sup>-1</sup>). The same is also observed for 6-methylindole (Fig. 9b) where positive  $\sigma$  bond energy contributions from C<sub>4</sub>C<sub>9</sub> (10), C<sub>5</sub>C<sub>6</sub> (12) and C<sub>7</sub>C<sub>8</sub> (17) are balanced by the negative contributions from C<sub>4</sub>C<sub>5</sub> (9), C<sub>8</sub>C<sub>9</sub> (20) and C<sub>6</sub>C<sub>7</sub> (15), respectively. For this molecule also, the total energy contribution from these bonds is antibarrier with a magnitude of 141 cm<sup>-1</sup>. Thus, the  $\pi$  bond energy contribution from benzene ring again plays a role similar to that in 5-methylindole with a magnitude of 2,764 cm<sup>-1</sup>. In the structural energy, the methyl group does not play any significant role (energy contribution is -66 cm<sup>-1</sup> in 5-methylindole and 52 cm<sup>-1</sup> in 6-methylindole) in the barrier formation. In view of the dominant positive contribution from the structural energy, the steric energy change is negative to make the magnitude of the Lewis energy change lesser than the total structural energy change.

#### 2.2.4 4-methylindole and 7-methylindole

The electronic environment vicinal to the methyl group in these two molecules also resembles that in toluene. Hence, the resonance structure formation is likely to be similar to that in toluene. However, it is to be noted that the pyrrole ring in these two molecules is two bonds away from the methyl group, whereas it is three bonds away in 5- and 6-methylindoles. Consequently, a large change in the three-fold potential is observed for these molecules as against 5- and 6-methylindoles. The calculated threefold torsional potential term [with B3LYP/6-31G(*d*, *p*)] for 4-methylindole is 335 cm<sup>-1</sup> and it is 418 cm<sup>-1</sup> for 7-methylindole (see Sect. 2.1). Moreover, the barrier energy of 7-methylindole is 83 cm<sup>-1</sup> higher than that of 4-methylindole, even though the electronic environment adjacent to the methyl group is similar in both these molecules. This increase in the barrier energy of 7-methylindole compared to that of 4-methylindole could be due to the presence of nitrogen atom in the vicinity of methyl group in case of 7-methylindole. The important changes in geometry are listed in Table 3. No clear alternation of bond lengths in the benzene ring was observed for any

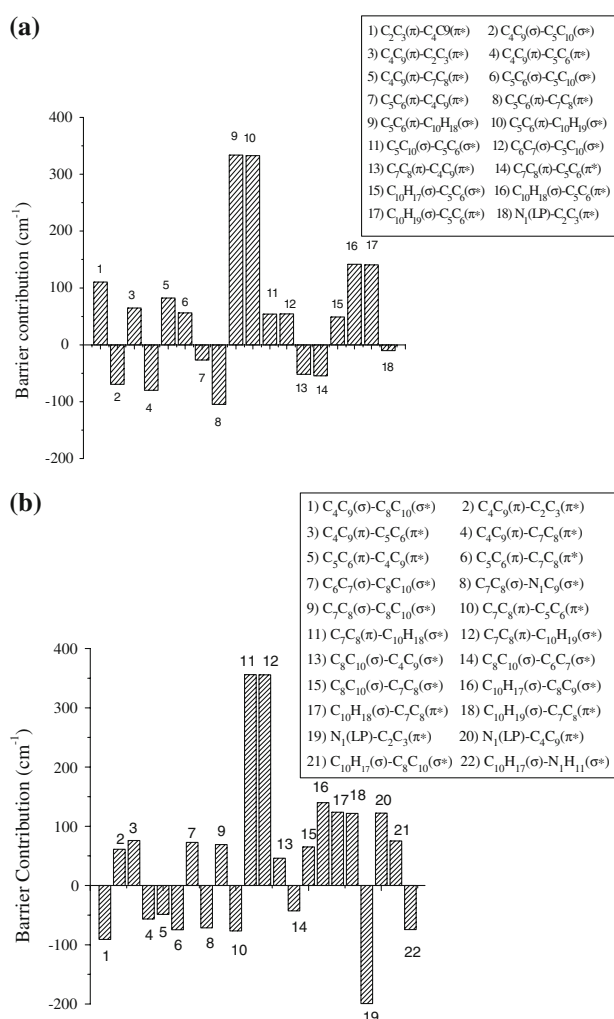


**Fig. 9** Individual structural energy contributions to the barrier in **a** 5-methylindole and **b** 6-methylindole

of these molecules, unlike toluene. Further, the change in the bond angles involving methyl C–H bonds are prominent in 7-methylindole. We investigated only those individual bond–antibond interactions, which undergo large energy changes upon methyl group rotation as shown in Fig. 10. As in the case of 5- and 6-methylindole, the contribution arising from the interactions of out-of-plane C–H bonds of the methyl group with the  $\pi$  orbitals of C–C bonds of the benzene ring is positive and hence barrier favoring. These interactions are C<sub>5</sub>C<sub>6</sub>( $\pi$ )–C<sub>10</sub>H<sub>18</sub>( $\sigma^*$ ), C<sub>5</sub>C<sub>6</sub>( $\pi$ )–C<sub>10</sub>H<sub>19</sub>( $\sigma^*$ ), C<sub>10</sub>H<sub>18</sub>( $\sigma$ )–C<sub>5</sub>C<sub>6</sub>( $\pi^*$ ) and C<sub>10</sub>H<sub>19</sub>( $\sigma$ )–C<sub>5</sub>C<sub>6</sub>( $\pi^*$ ) corresponding to 9, 10, 16 and 17 in Fig. 10a for 4-methylindole and C<sub>7</sub>C<sub>8</sub>( $\pi$ )–C<sub>10</sub>H<sub>18</sub>( $\sigma^*$ ), C<sub>7</sub>C<sub>8</sub>( $\pi$ )–C<sub>10</sub>H<sub>19</sub>( $\sigma^*$ ), C<sub>10</sub>H<sub>18</sub>( $\sigma$ )–C<sub>7</sub>C<sub>8</sub>( $\pi^*$ ) and C<sub>10</sub>H<sub>19</sub>( $\sigma$ )–C<sub>7</sub>C<sub>8</sub>( $\pi^*$ ) corresponding to 11, 12, 17 and 18 in Fig. 10b for 7-methylindole. Along with these interactions, in 7-methylindole, the interactions of the lone pair with

**Table 3** Major changes in the geometry of 4- and 7-methylindole upon rotation of methyl group from 0 degree conformation to 180 degree conformation

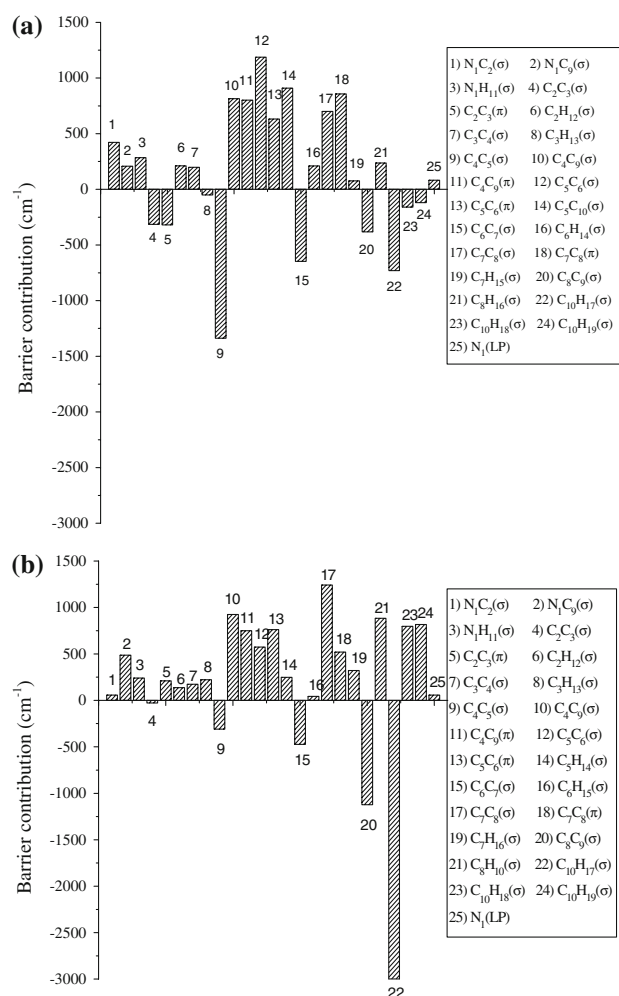
4-methylindole				7-methylindole			
Bonds	Bond length(Å)	Bond angle	Degree	Bonds	Bond length (Å)	Bond angle	Degree
C <sub>3</sub> C <sub>2</sub>	−0.0014	C <sub>5</sub> C <sub>4</sub> C <sub>3</sub>	0.3449	–	–	C <sub>5</sub> C <sub>4</sub> C <sub>3</sub>	−0.3364
C <sub>4</sub> C <sub>3</sub>	0.002	–	–	–	–	C <sub>8</sub> C <sub>7</sub> C <sub>6</sub>	0.1335
C <sub>5</sub> C <sub>4</sub>	−0.0019	C <sub>10</sub> C <sub>5</sub> C <sub>4</sub>	1.0373	C <sub>5</sub> C <sub>4</sub>	−0.0019	C <sub>10</sub> C <sub>8</sub> C <sub>7</sub>	−1.4076
C <sub>6</sub> C <sub>5</sub>	0.0025	H <sub>13</sub> C <sub>3</sub> C <sub>2</sub>	−0.2426	C <sub>6</sub> C <sub>5</sub>	0.0011	H <sub>11</sub> N <sub>1</sub> C <sub>2</sub>	−0.3073
C <sub>7</sub> C <sub>6</sub>	−0.003	H <sub>17</sub> C <sub>10</sub> C <sub>5</sub>	0.589	C <sub>7</sub> C <sub>6</sub>	−0.0026	H <sub>17</sub> C <sub>10</sub> C <sub>8</sub>	1.6145
C <sub>8</sub> C <sub>7</sub>	0.0016	H <sub>18</sub> C <sub>10</sub> C <sub>5</sub>	−0.1261	C <sub>7</sub> C <sub>8</sub>	0.0022	H <sub>18</sub> C <sub>10</sub> C <sub>8</sub>	−0.4324
C <sub>9</sub> C <sub>8</sub>	−0.0021	H <sub>19</sub> C <sub>10</sub> C <sub>5</sub>	−0.1222	C <sub>9</sub> C <sub>8</sub>	−0.0009	H <sub>19</sub> C <sub>10</sub> C <sub>8</sub>	−0.4535
C <sub>10</sub> C <sub>5</sub>	0.004	–	–	C <sub>10</sub> C <sub>8</sub>	0.0043	–	–

**Fig. 10** Individual delocalization contributions to the barrier in **a** 4-methylindole and **b** 7-methylindole

the antibonding  $\pi$  orbital of C<sub>2</sub>C<sub>3</sub> and C<sub>4</sub>C<sub>9</sub> (interactions 19 and 20) are larger in magnitude than that corresponding to 4-methylindole. The total contribution of these two inter-

actions involving nitrogen lone pair is negative and hence antibarrier in nature. The overall energy change for all the bond–antibond interactions shown in Fig. 10a is 1,022 cm<sup>-1</sup> for 4-methylindole and in Fig. 10b it is 948 cm<sup>-1</sup> for 7-methylindole. However, in the interaction deletion procedure using NOSTAR option, the delocalization contribution to the barrier is negligible compared to the Lewis energy contribution. Therefore, the contributions from interactions other than bond–antibond are important in determining the sign of total delocalization contribution in these two molecules also. The individual structural energy contributions for 4- and 7-methylindole are shown in Fig. 11a and b, respectively. The overall contribution from the structural energy change is positive and hence barrier forming. This is in accordance with the barrier partitioning using NOSTAR option as discussed in Sect. 2.2. The overall structural contribution in 4-methylindole is 3,765 cm<sup>-1</sup> while it is 4,540 cm<sup>-1</sup> for 7-methylindole. These are relatively large compared to that seen in 5- and 6-methylindoles. Net contribution of the pyrrol ring (1–8 and 25 in Fig. 11) is positive with a magnitude of 718 cm<sup>-1</sup> for 4-methylindole and for 7-methylindole it is 1,559 cm<sup>-1</sup>. The cumulative contribution from the benzene ring and the methyl group (9–24) is 3,047 cm<sup>-1</sup> for 4-methylindole and 2,980 cm<sup>-1</sup> for 7-methylindole. Thus, in 7-methylindole, the additional energy change compared to 4-methylindole is due to the bond energy change in the pyrrol ring.

The  $\sigma$  bond energy changes in the benzene ring are less. It is 335 cm<sup>-1</sup> for 4-methylindole and 834 cm<sup>-1</sup> for 7-methylindole. This is because in both these molecules, the positive contributions due to  $\sigma$  bond energy changes from C<sub>5</sub>C<sub>6</sub> (12), C<sub>4</sub>C<sub>9</sub> (10) and C<sub>7</sub>C<sub>8</sub> (17) are balanced by changes in bond energies of C<sub>4</sub>C<sub>5</sub> (9), C<sub>6</sub>C<sub>7</sub> (15) and C<sub>8</sub>C<sub>9</sub> (20). However, the dominant contribution is from the energy change of the bonds having the  $\pi$  character in the benzene ring. For 4-methylindole, this contribution is 2,288 cm<sup>-1</sup> arising from C<sub>4</sub>C<sub>9</sub> (11), C<sub>5</sub>C<sub>6</sub> (13) and C<sub>7</sub>C<sub>8</sub> (18), whereas for



**Fig. 11** Individual structural energy contributions to the barrier in **a** 4-methylindole and **b** 7-methylindole

7-methylindole it is  $2,030\text{ cm}^{-1}$ . The contribution to the structural energy from the C–H bonds of the methyl group (22, 23 and 24) is negative for both the molecules and hence antibarrier in nature. For 4-methylindole, it is  $-1,008\text{ cm}^{-1}$ , and for 7-methylindole it is  $-1,385\text{ cm}^{-1}$ , in contrast to the extremely small contribution in case of 5- and 6-methylindoles. In view of the positive and barrier-forming contribution from the structural energy, it is obvious that the steric energy is antibarrier and plays an important role in the determination of the magnitude of the barrier.

### 3 Conclusions

From the detailed ab initio calculations on the methylindoles, it is observed that all these molecules show significant threefold potential term. The preferred conformation for all the molecules has C–H bond of the methyl group in plane with the molecular frame. Our analysis reveals that for the mole-

cules having two single bonds adjacent to the methyl group, the difference in their bond orders does not play any decisive role in the determination of the preferred methyl group conformation as against the molecules with one single and one double bond adjacent to the methyl group where the in-plane C–H bond always eclipses the bond having a higher  $\pi$  bond order. In this kind of molecules, the torsional potential arises due to the hyperconjugative interactions non-local to the methyl group. For the molecules having toluene like vicinal environment to the methyl group, the contributions from  $\pi$  orbitals play a dominant role in the barrier height determination. The magnitude of the threefold barrier depends on the resonance structure formation in the benzene ring frame upon rotation of the methyl group. The major contributions to the hyperconjugative energies in these molecules are from the local interaction of the out-of-plane CH bonds with the bonding and antibonding orbitals of the adjacent double bonds. It is seen that the molecular flexing during the course of methyl rotation in all these molecules plays a crucial role in barrier determination. Therefore, the origin of overall barrier cannot be explained completely without considering the molecular flexing, hyperconjugative interactions and the steric effects.

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