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Unidirectional migration of the iodine atom over a cyclopentadiene ring in a rotating electric field

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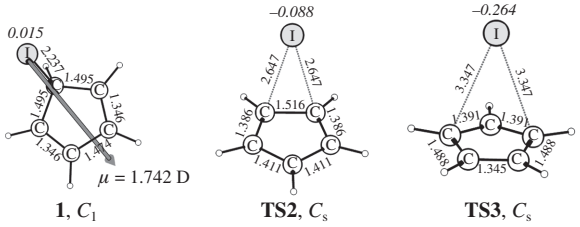
The DFT, B3LYP/Gen and 6-311++G(d,p)/SDD calculations of the reaction paths of a circumambulatory rearrangement of 5-iodocyclopentadiene showed that, under the application of a rotating electric field, the molecule behaves as a rotor-type molecular motor with the unidirectional motion of the iodine atom along the perimeter of the five-membered ring (k_{298} = 630 s^{-1}).

Progress in the development of nanotechnological equipment for manipulations with individual molecules has stimulated interest in molecular devices closely resembling macroscopic machines and their units. An essential component of such nanosized and microscopic objects is a molecular motor capable of converting heat, light, electric or chemical energy into mechanical motion energy.[1,2] In the case of rotary nanomotors, conditions must be fulfilled for unidirectional rotation of a rotor about a stator moiety of molecular or nanocluster species in order to deliver useful work. Recently, a plausible solution to this problem has been proposed and computationally substantiated based on the example of the fluxional behavior of a B_{13}^+ nanocluster, in which the constant unidirectional rotation of the outer B_{10}^+ ring relative to the inner B_3 ring was initiated by the application of an external laser field.[3] On the molecular level, the degenerate rearrangements of B_{13}^+ imitate motions similar to those of the Wankel engine.[4]

Fluxional cyclopolyenes, which are prone to the circumambulation of organic and organometallic groups along the perimeters of cyclopropene, cyclopentadiene and cycloheptatriene rings, can also be considered as the molecular prototypes of gear rotary motors.[5,6] The energy barriers and dynamics of motion of a covalently interlocked migratory group (rotor) over the carbocycle (stator) depend on the migrant and can be regulated by temperature.[7–11] To impart the properties of a molecular motor to cyclopolyene systems, it is necessary to ensure conditions for the unidirectional migration of the functional group. This problem can be solved based on the proper design of asymmetric migrants and the substituted cyclopolyene ring similar to the approach implemented in the light-driven rearrangements of overcrowded chiral alkenes.[12] However, no examples of such a structural design of cyclopolyene systems capable of controlled intramolecular motion have been documented so far. Here, we report the testing of another approach suggested by Zhang *et al*.,[3] which implies the triggering unidirectional circumambulation of the iodine atom of 5-iodocyclopentadiene **1** under the action of a rotating electric field applied to the ring plane of the molecule. The kinetics of circumambulatory rearrangement of 5-iodocyclopentadiene has not been studied in detail, but experiments on the transfer of magnetization in a solution of C_5H_4DI[13] showed that the migration of iodine is very fast at room temperature ($\Delta G^{\neq}_{298}$ ~ 14 kcal mol^{-1}) and the motion of iodine over the ring slows down totally only at about –40 °C. With the use of the density functional theory method (DFT, B3LYP/Gen, 6-311++G(d,p)/SDD), we calculated the reaction paths of iodine atom migration in **1** in a gas phase under the application of an external electric field.†



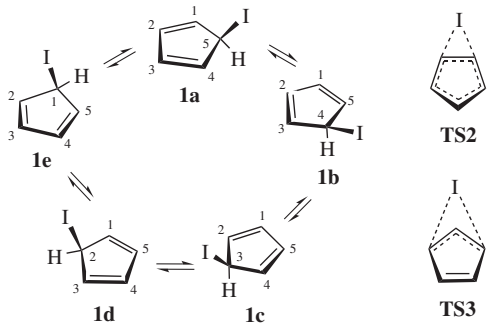
1, C_1 **TS2**, C_s **TS3**, C_s

Figure 1 Geometrical parameters of the ground state structures of **1a** and transition states **TS2** for 1,5- and **TS3** for 1,3-sigmatropic shifts of the iodine atom calculated by B3LYP/Gen and 6-311++G(d,p)/SDD. Hereinafter, bond distances are given in angstrom units. Charges are shown as italicized numbers.

Figure 1 shows the calculated geometries of compound **1** and the structures of **TS2** and **TS3**, transition states for 1,5- and 1,3-sigmatropic shifts of iodine along the perimeter of a five-membered ring (Scheme 1), respectively. The calculated energy barrier for the symmetry allowed 1,5-shifts of iodine, $\Delta E^{\neq}_{ZPE}$ = = 15.4 kcal mol^{-1} (Table 1), is consistent with experimental data[13] on the fast migration of iodine over the ring. The symmetry forbidden reaction path for the 1,3-shifts of iodine requires overcoming a much higher energy barrier ($\Delta E^{\neq}_{ZPE}$ = 38.9 kcal mol^{-1}) and cannot compete with the symmetry allowed alternative.

Obviously, the clockwise and anticlockwise thermally controlled 1,5-shifts of the iodine atom in **1** are equivalent as are also all five possible degenerate isomers equilibrated in the statistic ratio **1a**:**1b**:**1c**:**1d**:**1e** = 0.2:0.2:0.2:0.2:0.2 (Scheme 1). To compose a molecular motor based on this system, it is necessary to disturb equilibrium by an external electric field that would

† Quantum chemical computations were performed by DFT with B3LYP three-parameter potential and combined basis (Gen): for the iodine atom – the SDD basis set with effective core potential, for the rest atoms – the split-valence basis set 6-311++G(d,p) in the gas phase with the use of the Gaussian 03 software package. The Gaussian keyword FIELD was used to apply an external electric field to the test system. All stationary points were identified by the computation of a Hessian matrix. Charges on atoms were calculated by the Mulliken method.



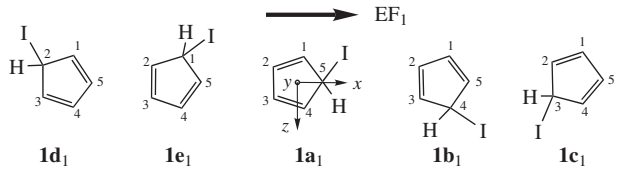
Scheme 1

Table 1 Total and relative energies of the ground state structures of 5-iodocyclopentadiene isomers and transition states for iodine atom migration in a gas phase in the absence and presence of an electric field calculated by B3LYP/Gen and 6-311++G(d,p)/SDD.[a]

Structure	E_{tot}/a.u.	E_{ZPE}/a.u.	ΔE_{ZPE}/kcal mol^{-1}	ω_1/cm^{-1}
1a–e	–204.9673	–204.8847	0	120
TS2	–204.9417	–204.8602	15.4	–362
TS3	–204.9017	–204.8227	38.9	–404
$\mathbf{1b}_2$	–204.9782	–204.8957	0	123
TS4	–204.9506	–204.8693	16.6	–316
$\mathbf{1a}_2$	–204.9730	–204.8906	3.2	119
TS5	–204.9445	–204.8632	20.4	–370
$\mathbf{1e}_2$	–204.9687	–204.8863	5.9	118

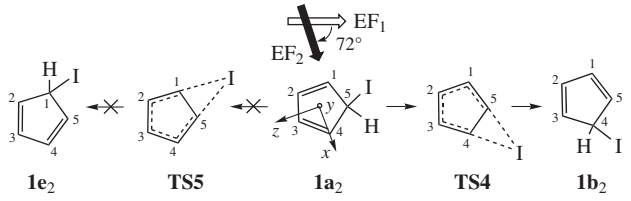
[a] E_{tot} is the total energy, 1 a.u. = 627.5095 kcal mol^{-1}; E_{ZPE} is the sum of total and zero-point energies; ΔE_{ZPE} is the relative E_{ZPE}; ω_1 is the least value of harmonic oscillation frequency or the value of the only imaginary harmonic oscillation frequency.

lock the molecule in the energy preferable orientation with respect to the applied field corresponding to the only isomer and provide for the unidirectional iodine circumambulation. A way to experimentally perform such a process is the fixation of a cyclopentadiene moiety of the molecule (stator) by means of intermolecular interactions on the insulating surface between nanoelectrodes arranged in a proper manner to generate a rotating electric field. The calculations showed that the application of external electric field EF_1 = 0.01 a.e. (5.14×10^9 V m^{-1}) to the system **1a–e** in the positive direction of the *x* axis (in the ring plane normally from the C^2–C^3 bond to the C^5 atom) (Scheme 2) leads to the energy preference of the molecule orientation corresponding to isomer $\mathbf{1a}_1$ as compared with the couples of isomers $\mathbf{1b}_1$, $\mathbf{1e}_1$ and $\mathbf{1c}_1$, $\mathbf{1d}_1$ by 3.2 and 5.9 kcal mol^{-1}, respectively (henceforth, subscripts are added to indicate the positions of a degenerate isomer with respect to the applied field). These energy differences of the isomers inhibit the circumambulation of iodine along the perimeter of the five-membered ring.



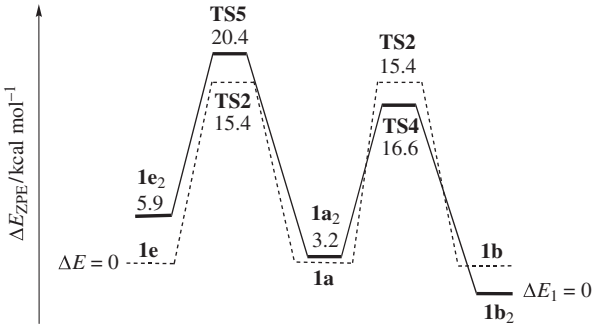
Scheme 2

The clockwise 72° turn of the electric field in the ring plane (EF_2, Scheme 3) leads to the molecule-field configuration $\mathbf{1a}_2$ which is energy equivalent to $\mathbf{1e}_1$ ($\mathbf{1b}_2$ – to $\mathbf{1a}_1$, $\mathbf{1e}_2$ – to $\mathbf{1d}_1$). The energy barrier $\Delta E^{\neq}_{ZPE}$ calculated for the clockwise 1,5-shift of iodine in isomer $\mathbf{1a}_2$ *via* transition state **TS4** resulting in more energy preferable molecule-field configuration isomer $\mathbf{1b}_2$ is



Scheme 3

13.4 kcal mol^{-1}, while that for the anticlockwise motion *via* transition state **TS5** to less energy favorable $\mathbf{1e}_2$ is notably higher and equal to 17.2 kcal mol^{-1} (Schemes 3, 4, Table 1). Consequently, isomer $\mathbf{1a}_2$ will pass to $\mathbf{1b}_2$ by means of unidirectional 1,5-shifts of the iodine atom.



Scheme 4

Scheme 4 shows the energy profile for the consequent 1,5-shifts of iodine under the application of electric field EF_2. The profile in the absence of the field is pictured in a dotted line. The energy barrier for the clockwise motion of iodine along the perimeter of the five-membered ring (in the field direction) $\mathbf{1a}_2 \rightarrow \mathbf{1b}_2$ is 2.0 kcal mol^{-1} lower than that in the absence of the field, whereas the barrier for the anticlockwise migration (against the field direction) $\mathbf{1a}_2 \rightarrow \mathbf{1e}_2$ is 1.8 kcal mol^{-1} higher than that in the absence of the field.

Figure 2 depicts the calculated structures corresponding to $\mathbf{1b}_2$, $\mathbf{1a}_2$ and $\mathbf{1e}_2$ minima and transition states **TS4** and **TS5** under the application of the field EF_2. It is interesting that a negative charge on the iodine atom (–0.138 *e*) in $\mathbf{1b}_2$ significantly exceeds that in **1** in the absence of field (–0.015 *e*) and in $\mathbf{1a}_2$ (–0.035 *e*), $\mathbf{1e}_2$ (0.109 *e*). In **TS4** structure corresponding to the motion in the field direction, the iodine atom bears a negative charge (–0.226 *e*), whereas charge division between the iodine atom and the ring is almost absent in **TS5** (against the field direction) and **TS2**

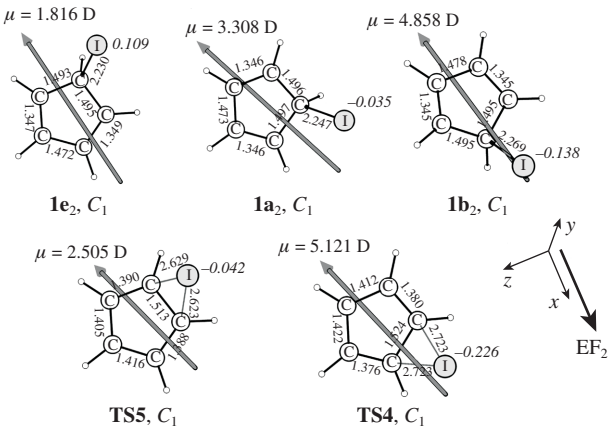
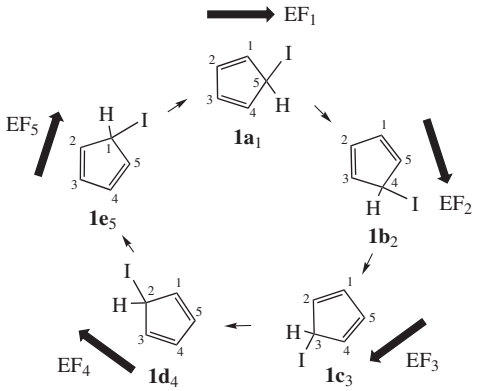


Figure 2 Geometrical parameters of the ground state structures of isomers $\mathbf{1e}_2$, $\mathbf{1a}_2$, $\mathbf{1b}_2$ and transition states **TS4** and **TS5** for 1,5-shifts of the iodine atom under application of external electric field EF_2 calculated by B3LYP/Gen and 6-311++G(d,p)/SDD.



Scheme 5

(in the absence of field). The notable polarization of $\mathbf{1b}_2$ and **TS4** structures resulting in their stabilization and higher dipole moments is caused by the most favorable conditions for interaction with the applied electric field.

Repeated clockwise 72° field turns $EF_2 \rightarrow EF_3 \rightarrow EF_4 \rightarrow EF_5 \rightarrow \rightarrow EF_1$ result in unidirectional 1,5-sigmatropic shifts of the iodine atom along the perimeter of the five-membered ring $\mathbf{1b}_2 \rightarrow \mathbf{1c}_3 \rightarrow \rightarrow \mathbf{1d}_4 \rightarrow \mathbf{1e}_5 \rightarrow \mathbf{1a}_1$ and full rotation of iodine along the perimeter of the 5-iodocyclopentadiene ring (Scheme 5). Under electric field rotation with the same speed as that of iodine atom migration ($\mathbf{1a}_2 \rightarrow \mathbf{1b}_2$, k_{298} = 630 s^{-1}, $\Delta G^{\neq}_{298}$ = 13.6 kcal mol^{-1}), the migrant makes 126 turns per second.

In summary, the results of the calculations demonstrate the potential of the circumambulatory rearrangements of functionalized cyclopolyene systems for the design of rotary molecular motors. The computed behavior of 5-iodocyclopentadiene in the presence of a rotating electric field corresponds to minimum requirements for a molecular rotary motor, including the most important of those – unidirectional rotation.[14]

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References

1 G. S. Kottas, L. I. Clarke, D. Horinek and J. Michl, *Chem. Rev*., 2005, **105**, 1281.
2 S. Brydges, L. E. Harrington and M. J. McGlinchey, *Coord. Chem. Rev*., 2002, **233–234**, 75.
3 J. Zhang, A. P. Sergeeva, M. Sparta and A. N. Alexandrova, *Angew. Chem. Int. Ed*., 2012, **51**, 8512.
4 G. Merino and T. Heine, *Angew. Chem. Int. Ed*., 2012, **51**, 10226.
5 I. D. Gridnev, M. Karenina and C. Rosario, *Organometallics*, 2005, **24**, 4519.
6 R. E. Bulo, F. Allaart, A. W. Ehlers, F. J. J. de Kanter, M. Schakel, M. Lutz, A. L. Spek and K. Lammertsma, *J. Am. Chem. Soc.*, 2006, **128**, 12169.
7 V. I. Minkin, I. E. Mikhailov, G. A. Dushenko, I. A. Yudilevich, R. M. Minyaev, A. Zschunke and C. Mugge, *J. Phys. Org. Chem.*, 1991, **4**, 31.
8 V. I. Minkin, I. E. Mikhailov, G. A. Dushenko, I. D. Sadekov, A. A. Maksimenko and Yu. E. Chernysh, *Dokl. Akad. Nauk*, 1992, **322**, 706 (in Russian).
9 V. I. Minkin, I. E. Mikhailov, G. A. Dushenko, O. E. Kompan and A. Zschunke, *Russ. Chem. Bull*., 1998, **47**, 884 (*Izv. Akad. Nauk, Ser. Khim*., 1998, 913).
10 G. A. Dushenko, I. E. Mikhailov, A. Zschunke, G. Reck, B. Schulz and V. I. Minkin, *Mendeleev Commun.*, 1999, 222.
11 V. I. Minkin, I. E. Mikhailov, G. A. Dushenko and A. Zschunke, *Russ. Chem. Rev*., 2003, **72**, 867 (*Usp. Khim*., 2003, **72**, 978).
12 N. Koumura, E. M. Geertsema, M. B. van Gelder, A. Meertsma and B. L. Feringa, *J. Am. Chem. Soc*., 2002, **124**, 5037.
13 R. Breslow and J. W. Canary, *J. Am. Chem. Soc.*, 1991, **113**, 3950.
14 E. R. Kay, D. A. Leigh and F. Zerbetto, *Angew. Chem. Int. Ed*., 2007, **46**, 72.

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