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# Computer simulation of the mechanisms and energetics of circumambulatory rearrangements of Dewar furan, thiophene and selenophene

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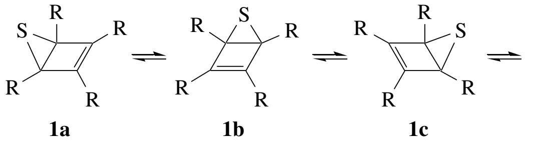
**By *ab initio* [MP2(fc)/6-311+G**] and DFT (B3LYP/6-311+G**) calculations, energy barriers to thermal walk rearrangements of the Dewar type isomers of the aromatic five-membered heterocycles were found in the range of 16–22 kcal mol$^{-1}$.**

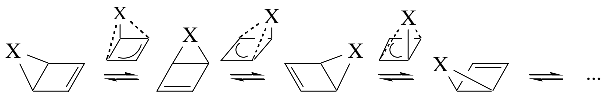
Circumambulatory (merry-go-round) rearrangements due to the rapid displacement of transition metal- or main group element-centered migrants around the periphery of a cyclopolyenyl ring, in particular, those related to cyclopentadiene derivatives, represent a comprehensively explored area of the dynamic stereochemistry of structurally non-rigid compounds.[1,2] The principal mechanism that governs the fluxional behaviour of these compounds is controlled by [1,j]-sigmatropic shifts of a migrating group to the adjacent position of the ring. For the derivatives of electrically neutral even-membered ring cyclopolyenyl systems, this mechanism consists in the rearrangements of bicyclic structures, *e.g.*, bicyclo[2.1.0]pent-2-enes and bicyclo[4.1.0]-hepta-2,4-dienes (norcaradienes). The rearrangements of this type, which are also classified as walk rearrangements,[3] are usually associated with the energy barriers exceeding those (≤ 20–25 kcal mol$^{-1}$) measurable with the aid of the dynamic NMR technique. An exception to this tendency is the very low free energy barrier (~7 kcal mol$^{-1}$ at –136 °C)[4] found for the circumambulatory rearrangement of the S-oxide of a tetra(trifluoromethyl) derivative of Dewar thiophene, whereas an analogous degenerate rearrangement of parent compound **1** (R = H) requires overcoming a free energy barrier of 22.1 kcal mol$^{-1}$ (at 157 °C).[3]



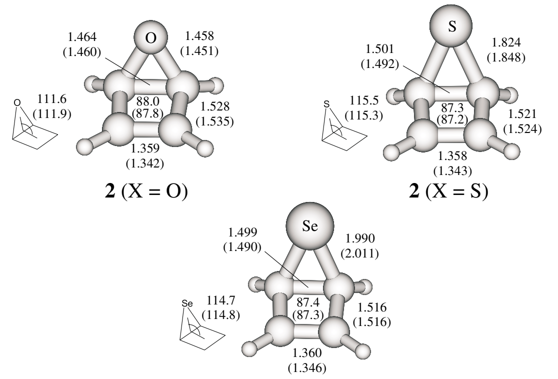
**1a** **1b** **1c**

$R = CF_3$

Walk rearrangements leading to the scrambling of ring atoms are considered as an important mechanistic route of the photochemical isomerizations of cyclopentadienes and five-membered heterocycles.[5] At the same time, no additional experimental data are currently available on the mechanism and energetics of thermal walk rearrangements of the bicyclic structures derived from parent five-membered heterocycles: furan, thiophene and selenophene. The only computational studies of these rearrangements are restricted to the early PRDDO calculations[6] of Dewar's pyrrole and furan. These calculations predicted very high energy barriers (68 and 76 kcal mol$^{-1}$, respectively) to the displacements of heteroatoms along the four-membered ring. Here we report on the *ab initio* [MP2(fc)/6-311+G**] and DFT (B3LYP/6-311+G**) theoretical study of the critical parts of the ground state potential energy surfaces (PESs) related to the degenerate thermally induced circumambulatory (walk) rearrangements of Dewar furan (X = O), thiophene (X = S) and selenophene (X = Se) **2**.



**2a** **2b** **2c** **2d**

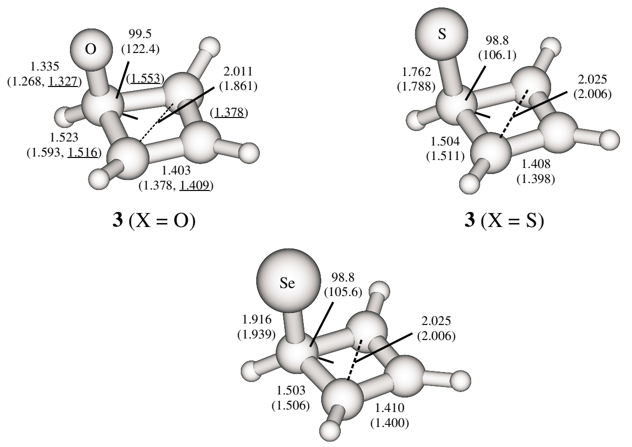


**2** (X = O) **2** (X = S) **2** (X = Se)

**Figure 1** MP2(fc)/6-311+G** and B3LYP/6-311+G** (in parentheses) optimised geometries (bond lengths in Angström units and angles in degrees) of Dewar furan **2** (X = O), thiophene **2** (X = S) and selenophene **2** (X = Se).

Main results of the calculations are given in Table 1 and Figures 1–4. The geometries of the ground state structures of bicyclic compounds **2** are shown in Figure 1. The values of $E_{\text{rel}}$ in Table 1 indicate that Dewar isomers **2** of the aromatic five-membered heterocycles are considerably strained compared to the latter, with the strain progressively decreased with the size of the heteroatom. The calculations predict that all compounds **2** are susceptible to sufficiently low-energy barrier walk rearrangements occurring as the sequence of [1,3]-sigmatropic shifts around the periphery of the four-membered cyclobutene rings. The geometries of the transition state structures corresponding to a step in these rearrangements are shown in Figure 2.

The topology of the PESs of the walk rearrangements of **2**, which is generally common to all the compounds, is portrayed by Figure 3. The minimal energy reaction paths for the rearrangements are stretched along the slopes of the rather high



**3** (X = O) **3** (X = S) **3** (X = Se)

**Figure 2** MP2(fc)/6-311+G** and B3LYP/6-311+G** (in parentheses) optimised geometries (bond lengths in Angström units and angles in degrees) of the transition state structures for the thermal walk rearrangements of Dewar furan **3** (X = O), thiophene **3** (X = S) and selenophene **3** (X = Se). Structural parameters of the intermediate corresponding to a shallow minimum on the B3LYP/6-311+G** PES in the vicinity of the transition state structure are given underlined.

**Table 1** Total energies plus zero point energy (ZPE) corrections, relative energies of furan, thiophene, selenophene, their Dewar type isomers **2**, transition state structures **3** and stationary points **4** corresponding to a top on the hill at the PES (Figure 3) for walk rearrangements of **2** calculated by MP2(fc)/6-311+G** and B3LYP/6-311+G** methods.

| Structure | $-(E_{\text{tot}} + \text{ZPE}^a)$ (a.u.) | | $E_{\text{rel}}$/kcal mol$^{-1}$ | | $\lambda^b$ (i$\omega$/cm$^{-1}$) | |
|---|---|---|---|---|---|---|
| | MP2(fc)/6-311+G** | B3LYP/6-311+G** | MP2(fc)/6-311+G** | B3LYP/6-311+G** | MP2(fc)/6-311+G** | B3LYP/6-311+G** |
| Furan | 229.36820 | 230.01950 | –65.6 | –67.8 | 0 | 0 |
| **2** (X = O) | 229.26371 | 229.91149 | 0 | 0 | 0 | 0 |
| **3** (X = O) | 229.22947 | 229.89216 | 20.5 | 22.1 | 0$^c$ | 1 (i210) |
| **4** (X = O) | 229.03974 | 229.77247 | 140.5 | 87.2 | 2 | 3 |
| Thiophene | 551.97962 | 553.00808 | –57.3 | –58.5 | 0 | 0 |
| **2** (X = S) | 551.88833 | 552.91483 | 0 | 0 | 0 | 0 |
| **3** (X = S) | 551.84635 | 552.88990 | 16.3 | 15.7 | 1 (i594) | 1 (i294) |
| **4** (X = S) | 551.76674 | 552.79888 | 76.3 | 72.8 | 2 | 2 |
| Selenophene | 2554.22535 | 2556.33600 | –40.6 | –52.5 | 0 | 0 |
| **2** (X = Se) | 2554.16068 | 2556.33601 | 0 | 0 | 0 | 0 |
| **3** (X = Se) | 2554.11052 | 2556.23201 | 31.5 | 22.8 | 1 (i556) | 1 (i288) |
| **4** (X = Se) | 2554.03849 | 2556.15234 | 76.7 | 62.8 | 2 | 2 |

[a] Zero point vibration energy factors for MP2 (0.9748) and DFT (0.9806) calculations are taken according to ref. 7. [b] The number of negative eigenvalues of the Hessian matrix. [c] An intermediate corresponding to a very shallow minimum on the PES.

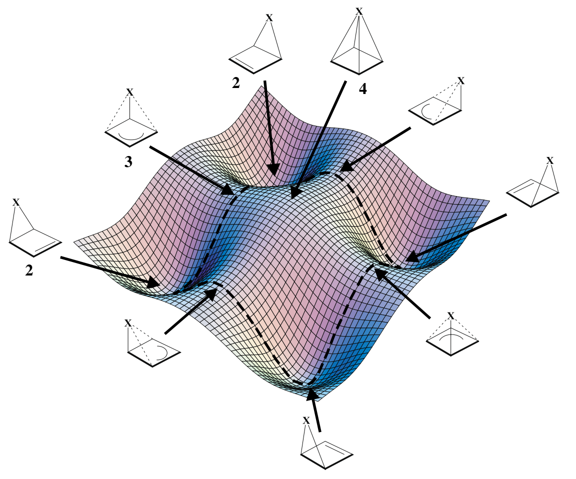
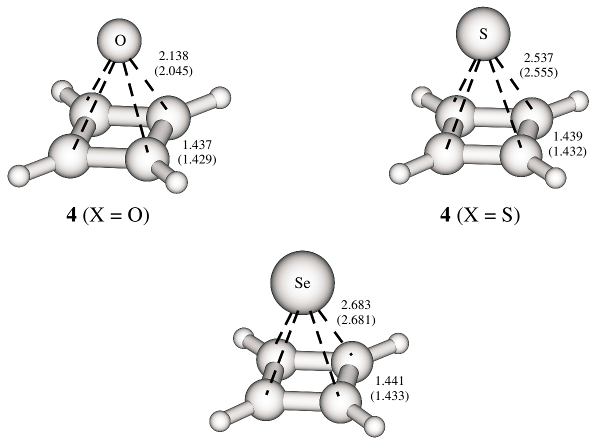


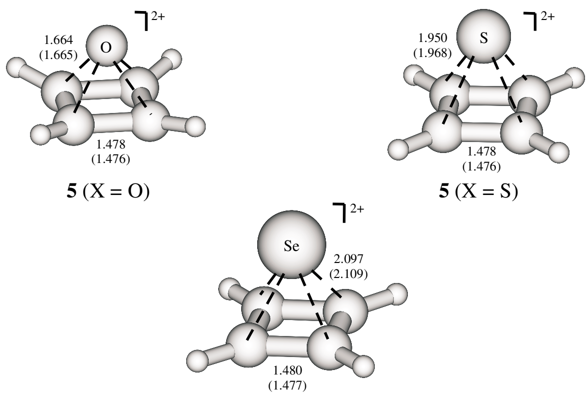
**Figure 3** The pattern of the lowest singlet PESs of the walk rearrangements of Dewar furan (X = O), thiophene (X = S) and selenophene (X = Se). The minimal energy reaction path is indicated by a dashed line.

(see Table 1) hill with square-pyramidal $C_{4v}$ structures **4** on its top. Structures **4** may be considered as $D_{4h}$ cyclobutadiene capped by an oxygen (X = O) or a chalcogen (X = S, Se) atom. It was found that stable structures of the $C_{nv}$ type must contain no more than eight electrons (8e rule) in the valence orbitals of their fragments: π-MOs of the basal ring and valence AOs of the apical atom or σ-bonded group.[8] Thus, the instability of structures **4** is caused by an excessive number of electrons (10) on these orbitals. In accordance with the 8e rule, the removal of two electrons from the MOs of **4** may lead to the formation of stable $C_4H_4X^{2+}$ dications **5**. This expectation was previously tested by semiempirical calculations[8,9] and verified by *ab initio* and DFT calculations carried out in this work. All the $C_{4v}$ dications correspond to sufficiently deep local minima on the respective PESs. The calculated geometries of structures **4** and **5** are shown in Figures 4 and 5, respectively. The essential difference in the geometries of unstable $C_{4v}$ structures **4** and stable $C_{4v}$ dications **5** consists in the substantial (0.4–0.6 Å) shortening of the C–X distances in the latter, which are ~0.2 Å longer than the standard $C_{sp^2}$–X bonds.



**4** (X = O) **4** (X = S) **4** (X = Se)

**Figure 4** MP2(fc)/6-311+G** and B3LYP/6-311+G** (in parentheses) of the optimised geometries (bond lengths in Angström units) of unstable structures **4** corresponding to a top on the hills on the PESs for the walk rearrangements of Dewar furan (X = O), thiophene (X = S) and selenophene (X = Se) shown in Figure 3.



**5** (X = O) **5** (X = S) **5** (X = Se)

**Figure 5** MP2(fc)/6-311+G** and B3LYP/6-311+G** (in parentheses) optimised geometries (bond lengths in Angström units) of square-pyramidal dications **5**.

All the calculations were performed using the Gaussian 98[10] program with the 6-311+G** basis set. Electron correlation was accounted for in the second order Møller–Plesett perturbation theory approximation. In the DFT calculations, the B3LYP exchange-correlation functional was employed. All the stationary points in the PES were identified by calculations of the force constant matrix (Hessian). Zero point energies (ZPE) were corrected[7] by multiplying them by 0.9748 [MP2(fc)/6-311+G** level] and 0.9806 (B3LYP/6-311+G** level).

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