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CNDO/2 Calculation of Prototropic Rearrangement in Cyclopentadiene

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A self-consistent procedure has been worked out for the optimisation of geometrical parameters of ground and transition states of molecular systems and chemical reactions. For cyclopentadiene molecule, the CNDO/2 method is used to calculate a number of the geometrical configurations which lie at the reaction co-ordinates corresponding to possible channels of the proton migration.

Deuteriated cyclopentadienes, as well as sigma-cyclopentadienyl compounds, were reported to rearrange through the 1,2 migration of proton or deuterium [1–3]. The rearrangement was proved to be intramolecular [4].

Various multi-centre mechanisms of the migration may be assumed. E.g., proton or deuterium may migrate in sigma-cyclopentadienyl compounds via the formation of two-centre (2C), three-centre (3C), and five-centre (5C) bonds between a hydrogen and the ring carbons.

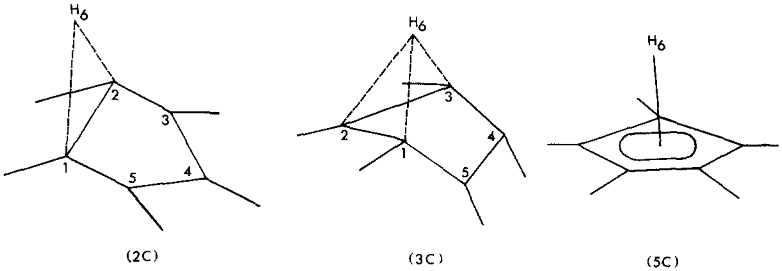


Fig. 1

The 3C and 5C transition states require that a usual carbon-hydrogen bond become much longer, hence a priori they must have greater energies.

Other transition states may also be possible, e.g. the 3CA state:

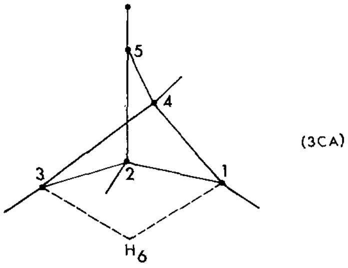
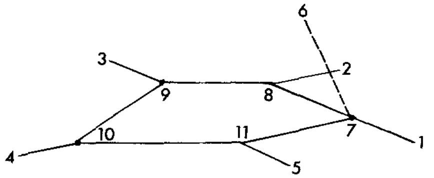


Fig. 2

In structural chemistry terms, however, the structures such as 3CA must have very high energies, in other words, the resulting C–C bonds would be subject to noticeable strain.

Cyclopentadiene is a simplest sigma-cyclopentadienyl molecule in which a prototropic rearrangement is possible.



(2)

Fig. 3.

We have calculated the ground state (GS) and the states 2C, 3C, and 5C, of the molecule by using a self-consistent optimisation of the geometrical parameters [5] with the total energy minimum obtained through CNDO/2 (Ref. [6]) serving as the criterion. GS has been approximated to have the C_{2v} symmetry, 2C and 3C states the plane of symmetry perpendicular to the lines C_1C_2 (for 2C) and $C_1C_1C_3$ (for 3C), the state 5C the C_{5v} symmetry.

The results are summarised in the Table. The Table also includes the microwave spectroscopy data [7]. When comparing these with the experiment, one comes to the conclusion (cf. the calculations by Fischer and Kollmar [8]) that CNDO/2 gives too low values for the C–C single bond while the calculation of shorter (double, one and one half) C–C bonds fits with the experiment somewhat better.

As for calculated CH bond lengths, they were reported to be on the average 0.01 Å higher than the experimental values [8]. This is the case with our calculation as well.

The 3C and 5C states are specific in that their H_6 atom is slightly attracted by the nearest hydrogen. E.g., H_2 in 3C declines from the $C_1C_3C_4C_5$ plane by ca. 2.1° towards the proton H_6. H_2, H_3, H_4, H_5, H in 5C decline along the same direction by 1.1°. For the 2C state the situation is as follows. The perpendicular dropped from the point H_6 to the line C_1C_2 forms the angle of 92.2° with the plane $H_2C_1C_2H_3$, the analogous angle is equal to 104.3° for the plane $C_5C_1C_2C_3$, and the H_6 atom is repulsed by the ring plane much stronger than it is by the hydrogens H_2 and H_3.

Further, the C_1C_2 bond length calculated for the 2C state is nearly equal to that for GS.

Total energy values listed in the Table show that proton is much more likely to migrate via the 2C state as compared with the states 3C and 5C, in other words, the migration consists in successive 1,2 shifts. These were verified experimentally. We plan to program the automatic search of the transition state responsible for the shift. This state is anticipated to resemble, or coincide with, the 2C state.

The 3C state is located, most probably, at the reaction co-ordinate responsible for the proton migration to the state 5C. This needs not be discussed in more

Table 1. The calculated geometry of various configurations of cyclopentadiene[a]

Variable	GS calcd.	GS exptl.	2C	3C	5C
1. (m, n)[b]					
(1, 7)	1.122	–	1.114	1.109	1.111
(2, 8)	1.112	–	1.111	1.114	1.111
(3, 9)	1.112	–	1.111	1.110	1.111
(6, 7)	1.122	–	1.595	1.229	1.477
(6, 8)	2.152	–	2.215	1.556	1.477
(6, 9)	3.080	–	1.279	1.840	1.477
(7, 8)	1.467	1.509	1.393	1.424	1.418
(8, 9)	1.348	1.342	1.404	1.413	1.418
(9, 10)	1.446	1.469	1.470	1.406	1.418
2. $(\bar{P}, q, r)$[c]					
(1, 7, 6)	106.2	–	157.6	123.0	–
(1, 7, 8)	111.7	–	124.6	116.0	–
(7, 8, 2)	122.6	–	126.9	126.5	126.0
(2, 8, 9)	127.9	–	125.6	125.8	126.0
(3, 9, 10)	124.0	–	125.5	127.3	126.0
(3, 9, 8)	127.3	–	126.0	124.2	126.0
(11, 6, 8)	64.7	–	62.4	95.4	–
(10, 6, 9)	27.2	–	70.2	44.9	–
(11, 7, 8)	103.8	102.5	110.9	107.9	108.0
(7, 8, 9)	109.5	109.2	107.5	107.1	108.0
(8, 9, 10)	108.7	109.2	107.1	108.5	108.0
3. (m, n) $(\bar{P}, q, r)$[d]					
(7, 1) (11, 7, 8)	53.1	–	− 0.8	− 0.2	1.1
(8, 2) (10, 8, 9)	0	–	− 0.6	2.1	1.1
(9, 3) (10, 8, 9)	0	–	− 10.5	0.4	1.1
4. $(\bar{P}, q, r)$ (s, t, u)[e]					
(6, 9, 10) (10, 9, 8)	–	–	104.3	–	–
(7, 8, 11) (11, 8, 9)	0	–	0.4	9.4	0
5. $-g$[f]					
	1088.67	–	1088.21	1086.02	1084.28

[a] Distances are in Å, angles in degrees. The atoms are numbered in the scheme (2).

[b] The internuclear distance between atoms numbered by m and n.

[c] The planar angle.

[d] The angle formed by bond (mn) and plane (p, q, r). The angle is arbitrarily assumed positive when the bond deviates towards H_6.

[e] The dihedral angles.

[f] Total energy multiplied by -1, eV.

detail since the total energies demonstrate that the 3C and 5C state are, in usual conditions, rather improbable.

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