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A CNDO/2 CALCULATION OF A REARRANGEMENT IN CYCLOPENTADIENYLSILANE*

G.A. SHCHEMBELOV and Yu.A. USTYNYUK
NMR Laboratory, Chemical Department, Moscow State University, Moscow B-234 (U.S.S.R.)

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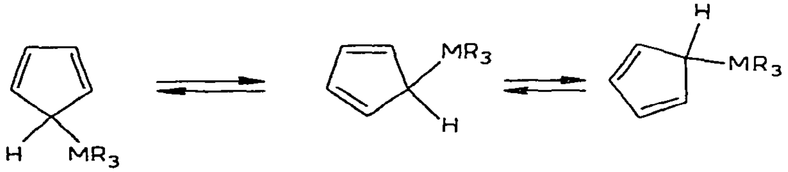
Summary

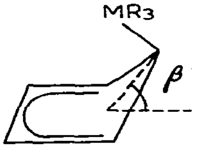
The ground state geometry of cyclopentadienylsilane and the transition state geometry for SiH_3 group migration have been calculated by the CNDO technique, a semi-empirical version of the LCAO MO SCF approach.

Introduction

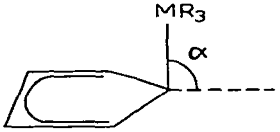
h^1-Cyclopentadienyl compounds of silicon and other Group IVB elements have been shown to undergo a degenerate intramolecular rearrangement [2].



Earlier we discussed [3, 4] a model of the rearrangement in which we assumed that the MR_3 group migrated through a transition state in which additional donor—acceptor bonds were formed by interaction of the lower energy vacant *d*-orbitals of the element with the π-orbitals of the cyclopentadienyl.



(I)



(II)

We used a π-version of the Wolfsberg-Helmholtz method [5] to estimate the energies necessary for distorting the initial geometry to give structures (I) and (II), and the donor—acceptor interaction energies. The results led to the following conclusions.

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(*i*) The MR_3 migration activation energy should be lower than the proto migration energy.

(*ii*) The metallotropic rearrangement activation energy should decrease along the series Si, Ge, Sn for the respective $C_5H_5MR_3$ compounds.

(*iii*) No considerable perturbations of the ring plane are possible in a trai sition state.

Conclusions (*i*) and (*ii*) were later verified experimentally [2, 6].

After the completion of our previous studies [3, 4], electronography of $C_5H_5MR_3$ (M = Si, Ge, Sn) showed [7—9] that the σ-cyclopentadienyl ring attached to the Group IVB element was envelope-shaped, that is, it had structure (I) with β being about 20° even in the ground state. In contrast, σ-cyclopentadienyl derivatives of such transition metals as iron [10], titanium [11], and molybdenum [12] have planar σ-cyclopentadienyls as shown by X-ray da Recently, a paper by Bentham and Rankin [13] reported electronography da for cyclopentadienylsilane, $C_5H_5SiH_3$, which suggest that the cyclopentadier is planar. More recent experimental data suggest that the more accurate quantum-chemical technique should be applied and we have used this technique tc calculate the ground state (GS) geometry for $C_5H_5SiH_3$, the simplest representative of the series, and the geometries corresponding to the transition stat possible for metallotropic rearrangement in the molecule. The CNDO/2 technique, a semi-empirical version of the LCAO MO SCF approach, has been use together with complete optimisation of the geometrical variables [15]. Such technique was employed successfully by us previously [16] for calculating th GS and transition state geometries associated with prototropic rearrangement in cyclopentadiene.

Results and discussion

SiH_3 migration may be approximated to a first order reaction. The proc is degenerate, so the transition states should have, at least, a symmetry plane. Qualitatively, the most energetically favourable transition states are (2C) (for the 1,2 shift of SiH_3), (3C) (for the 1,3 shift), and (5C) (for the 1,2 and 1,3 migration). See Scheme 1.

C_5 local site symmetry was assumed for (5C), and six geometrical variables were minimized. Twenty variables were minimised for the other states (tl C_s symmetry).

The values of the geometrical parameters listed in Table 1 have been calc lated through the CNDO/2 technique together with the self-consistent optimi tion [15]. Vacant orbitals have been neglected [14]. Table 1 also contains th experimental data reported by Bentham and Rankin.

The calculated C—H bond lengths agree well with the experimental value for the C—C bonds and the valence angles, agreement is satisfactory, the dieni part of the ring clearly being "butadienic". The greatest deviations fall on the C—Si bond length (0.137 Å) and the $R(9,10)$ values (0.05 Å). In contrast to t experimental data, calculations require that the ring should deviate somewhat from planar geometry while the SiH_3 groups should be drawn to the plane of the diene (β 3.2°). Note also that hydrogens $H_{2(5)}$ and $H_{3(4)}$ deviate away froi the plane in opposite directions.

SCHEME 1

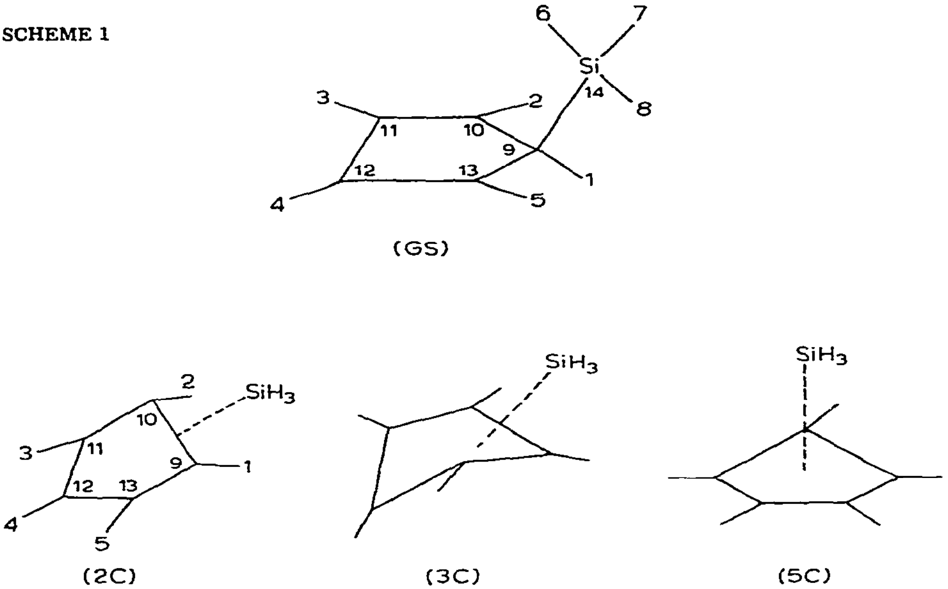

TABLE 1

GEOMETRIC VARIABLES [a], NET ATOMIC CHARGES (q), AND TOTAL ENERGIES (E, eV), AFTER OPTIMISATION

	GS calcd.	GS exptl.	(2C)	(5C)
$R(1,9)$ [b]	1.122	1.11	1.117	1.113
$R(2,10)$	1.114	1.11	1.117	1.113
$R(3,11)$	1.113	1.11	1.112	1.113
$R(9,10)$	1.450	1.50	1.456	1.416
$R(10,11)$	1.363	1.39	1.403	1.416
$R(11,12)$	1.429	1.436	1.395	1.416
$R(6,14)$	1.617		1.615	1.641
$R(7,14)$	1.617		1.621	1.641
$R(9,14)$	2.117	1.88	2.268	2.419
$\varphi(10,9,13)$ [c]	105.1	100.3 ± 1.5	108.3	108.0
$\varphi(2,10,11)$	126.9		125.4	126.0
$\varphi(3,11,10)$	128.0		124.9	126.0
$\varphi(6,14,7)$	108.9		109.3	102.4
$\varphi(7,14,8)$	107.4		107.0	102.4
$\varphi(7,6,8)$	121.0		118.1	120.0
$\alpha(1,\mathrm{Cp})$ [d]	−31.5		−1.3	−2.4
$\alpha(2,\mathrm{Cp})$	−3.1		−1.3	−2.4
$\alpha(3,\mathrm{Cp})$	−1.3		−12.5	−2.4
$\alpha(14,\mathrm{Cp})$	70.7	73.5 ± 0.7	72.0	
β [e]	3.2	0	0	0
$q(\mathrm{H}_1)$	−0.008		−0.022	−0.007
$q(\mathrm{H}_2)$	−0.019		−0.016	−0.007
$q(\mathrm{H}_3)$	−0.015		−0.010	−0.007
$q(\mathrm{H}_6)$	−0.117		−0.135	−0.212
$q(\mathrm{H}_7)$	−0.134		−0.130	−0.212
$q(\mathrm{C}_9)$	−0.031		−0.022	−0.076
$q(\mathrm{C}_{10})$	−0.027		−0.022	−0.067
$q(\mathrm{C}_{11})$	−0.029		−0.077	−0.072
$q(\mathrm{Si})$	0.590		0.671	1.023
$-E$(eV)	1233.96		1233.70	1232.70

[a] Numbering of the atoms is given in Scheme 1. Distances are in Å, angles in degrees. [b] Distance between the atoms. [c] Planar angle between the bonds. [d] Angle between the bond and the ring plane. [e] Dihedral angle between the C(9)C(10)C(13) and C(13)C(10)C(11)C(12) planes (for GS) or the C(11)C(12)C(13) and C(9)C(10)C(11)C(13) planes [for (2C)].

Variation of the angle α(Si, Cp) gives no energy minimum for (3C). Possibly, this state lies on the reaction coordinate corresponding to the transition from GS to (5C).

Collation of the GS, (2C), and (5C) energies shows that the difference $E_1 = E_{(2C)} - E_{GS}$ is 6 kcal/mole. The difference $E_2 = E_{(5C)} - E_{GS}$ is 29 kcal/mole and is thus much higher than E_1. Consequently, the 1,2 shift of SiH_3 is much more probable than 1,2 and 1,3 migration, which agrees with experimental data [2]. E_1 is half the activation energy usually observed for metallotropic rearrangements in silicon cyclopentadienyls [2]. When we compare (2C) with GS we see that R(9,10) remains almost unaffected while the other C—C bond lengths are very close. The charge at Si is higher for (2C) and (5C) compared with GS, which reflects the tendency to form the C_5H_5 anion. However, the C—Si bonds show covalency in these transition states as well.

We have extended the study by using 3*d* orbitals according to the Santry and Segal [17] procedure. At a constant angle α(14, Cp) 70.7°, minimisation of the other variables leads to R(9,14) (the Si—C bond length) equal to 1.90 Å. The calculated dihedral angle β is 16° but these values may be inaccurate since optimisation of all the variables in GS, including α(14, Cp) and 3*d* orbitals, gives (5C) as the structure which corresponds to the total energy minimum. Variation of exchange integrals and optimisation of the Slater ζ parameter do not affect the result. Thus, the silicon 3*d* orbitals contribute to the total energy somewhat excessively, which is a drawback of the CNDO/2 technique using vacant orbitals.

Scanning and optimization of angle β with the CNDO/2 technique (in which the 3*d* orbitals were not included) for $C_5H_5Si(CH_3)_3$ gave β equal to 3.8°. The state in which β is equal to 20° brings about an energy loss of 9 kcal/mole.

References

1 Yu.A. Ustynyuk, N.M. Sergeyev, A.V. Kisin, Yu.A. Grishin, N.N. Veniaminov and G.A. Shchembelov, 5th International Conference on Organometallic Chemistry, Moscow, August 1971, Abstracts, Vol. II, p. 271.
2 N.M. Sergeyev, G.I. Avramenko, A.V. Kisin, V.A. Korenevsky and Yu.A. Ustynyuk, J. Organometal. Chem., 32 (1971) 55, and refs. therein.
3 G.A. Shchembelov and Yu.A. Ustynyuk, Dokl. Akad. Nauk SSSR, 173 (1967) 847.
4 G.A. Shchembelov and Yu.A. Ustynyuk, Dokl. Akad. Nauk SSSR, 173 (1967) 1364.
5 M. Wolfsberg and L. Helmholz, J. Chem. Phys., 20 (1957) 837.
6 G.I. Avramenko, N.M. Sergeyev and Yu.A. Ustynyuk, J. Organometal. Chem., in press; A.I. Ashe III, J. Amer. Chem. Soc., 92 (1971) 1233.
7 N.N. Veniaminov, Yu.A. Ustynyuk, Yu.T. Struchkov, N.V. Alekseyev and I.A. Ronova, Zh. Strukt. Khim., 11 (1970) 117.
8 N.N. Veniaminov, Yu.A. Ustynyuk, Yu.T. Struchkov, N.V. Alekseyev and I.A. Ronova, J. Organometal. Chem., 22 (1970) 551.
9 N.N. Veniaminov, Yu.A. Ustynyuk, N.V. Alekseyev, I.A. Ronova and Yu.T. Struchkov, Dokl. Akad. Nauk SSSR, 199 (1971) 346.
10 M.J. Bennett, F.A. Cotton, A. Davison, J.W. Faller, S.J. Lippard and S.M. Morehouse, J. Amer. Chem. Soc., 88 (1966) 4371.
11 J.L. Calderon, F.A. Cotton, B.G. Deboer and J. Takats, J. Amer. Chem. Soc., 93 (1971) 3592.
12 J.L. Calderon, F.A. Cotton and P. Legzdins, J. Amer. Chem. Soc., 91 (1969) 2528).
13 J.E. Bentham and D.W.H. Rankin, J. Organometal. Chem., 30 (1971) C54.
14 J.A. Pople and G.A. Segal, J. Chem. Phys., 44 (1966) 3289.
15 G.A. Shchembelov and Yu.A. Ustynyuk, J. Amer. Chem. Soc., submitted.
16 G.A. Shchembelov and Yu.A. Ustynyuk, Theor. Chim. Acta, 24 (1972) 389.
17 D.P. Santry and G.A. Segal, J. Chem. Phys., 47 (1967) 158.