Bonding in Methyl- and Silyl-cyclopentadiene Compounds: A Study by Photoelectron Spectroscopy and *Ab Initio* Molecular-orbital Calculations

By **Stephen Cradock,* Robert H. Findlay,** and **Michael H. Palmer,** Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ

Photoelectron spectra of the cyclopentadiene derivatives RC_5H_5 (R = 1-Me, 2-Me, and 5-SiH_3) are reported. The observed ionisation potentials correlate well with orbital energies calculated by *ab initio* methods. Calculated total energies of the 1-, 2-, and 5-isomers show that the order of stability is 2-Me > 1-Me > 5-Me but 5-SiH_3 > 2-SiH_3 > 1-SiH_3. The Si–C bonding orbital in the 5-SiH_3 derivative is heavily involved in the π-system of the ring, and a high overlap integral exists between silicon and the *far* ring-carbon atoms. It is suggested that these features of the calculated eigenvectors are related to ' fluxional ' behaviour shown by the silyl (and related) compounds but not by the methyl derivatives.

THE 5-silyl and 5-germyl derivatives of cyclopentadiene have classical σ-bonded structures at low temperatures but exhibit n.m.r. spectra indicating ' fluxional ' behaviour, in which all five ring protons become equivalent, at room temperature.[1] Methylcyclopentadiene compounds do not show fluxional behaviour, but the 5-methyl and 5,5-dimethyl isomers rapidly convert to 1- or 2-substituted compounds;[2,3] thermal 1,5-prototropic shifts have also been observed in deuteriocyclopentadienes.[4] In an attempt to elucidate the reasons for this difference in behaviour, we investigated the extent of fluxional behaviour in compounds of the type $C_5H_5MX_n$ (M = Group IV or V element; X = H, halogen, *etc.*).[5] Here we describe studies on the ground states of some simple molecules of this type by photoelectron (p.e.) spectroscopy and non-empirical molecular-orbital calculations.

EXPERIMENTAL

5-Silylcyclopentadiene was prepared by reaction of silyl bromide with potassium cyclopentadienide, prepared by treating cyclopentadiene with potassium in liquid ammonia. It was purified by trap-to-trap or column fractionation at low temperature in a vacuum line and stored at 77 K. Methylcyclopentadiene was obtained by pyrolytic distillation of the commercial dimer; gas-chromatographic separation of the mixture, which consisted mainly of the 1-Me and 2-Me isomers in roughly equal proportions (in substantial agreement with earlier studies [2a,3c]), yielded the individual 1-Me and 2-Me isomers.

P.e. spectra were recorded on a Perkin-Elmer PS16 spectrometer with He(I) (21·22 eV) excitation. Compounds were admitted to the target chamber through a stainless-steel needle valve from a steel–glass–Teflon manifold. The experimental spectra are shown in Figure 1

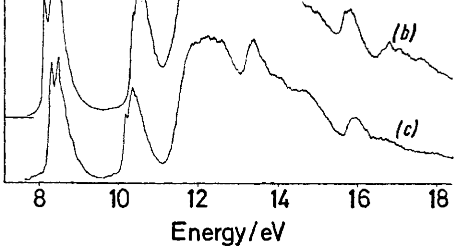

FIGURE 1 He(I) P.e. spectra of (*a*) 5-$(SiH_3)C_5H_5$, (*b*) 1-MeC_5H_5, and (*c*) 2-MeC_5H_5

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[1] A. P. Hagen and P. J. Russo, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 507; A. Davidson and P. E. Rakita, *J. Amer. Chem. Soc.*, 1968, **90**, 4479; *Inorg. Chem.*, 1970, **9**, 289; Yu. K. Griskin, N. M. Sergeyev, and Yu. A. Ustynyuk, *J. Organometallic Chem.*, 1970, **22**, 361; N. M. Sergeyev, G. I. Avramenko, and Yu. A. Ustynyuk, *ibid.*, pp. 63, 79; H. P. Fritz and C. G. Kreiter, *ibid.*, 1965, **4**, 313; F. A. Cotton, *J. Amer. Chem. Soc.*, 1968, **90**, 6230.

[2] (*a*) S. McLean and P. Haynes, *Tetrahedron Letters*, 1964, 2385; (*b*) V. A. Mironov, E. V. Sobolev, and A. N. Elizarova, *Tetrahedron*, 1963, **19**, 1939.

[3] (*a*) S. McLean and D. M. Findlay, *Canad. J. Chem.*, 1970, **48**, 3107; (*b*) J. W. de Haan and H. Kloosterziel, *Rec. Trav. chim.*, 1968, **87**, 298; (*c*) S. McLean and P. Haynes, *Canad. J. Chem.*, 1963, **41**, 1231.

[4] W. R. Roth, *Tetrahedron Letters*, 1964, 1009; R. K. Lyon, *J. Chem. Phys.*, 1967, **46**, 4504; S. McLean, C. J. Webster, and R. J. D. Rutherford, *Canad. J. Chem.*, 1969, **47**, 1555.

[5] J. E. Bentham, E. A. V. Ebsworth, H. Moretto, and D. W. H. Rankin, *Angew. Chem. Internat. Edn.*, 1972, **11**, 640 and unpublished observations.

and the vertical ionisation potentials are included in Table 1 and Supplementary Publication No. SUP 21024 (2 pp.).[*]

TABLE 1

Calculated eigenvalues (eV), observed ionisation potentials (eV), and orbital types

$\mathrm{C_5H_6}$ (planar)

Calc.	Obs.	Orbital	Type
8·88	8·56	$1a_2$	π
11·74	10·72	$2b_1$	$\pi - \mathrm{CH_2}$
13·69	12·2	$6b_2$	CC,CH
13·80	12·6	$9a_1$	C,CH
14·26	13·2	$8a_1$	CC,$\mathrm{CH_2}$
15·19	13·8	$5b_2$	CC,CH
16·63	15·0	$1b_1$	$\mathrm{CH_2} + \pi$
18·92	16·5	$7a_1$	CH
19·30	17·5	$4b_2$	CH,CC
20·15	18·4	$6a_1$	C_{2s}
25·75	22·0	$5a_1$	C_{2s},$\mathrm{CH_2}$
26·13	22·3	$3b_2$	C_{2s}
31·50	26·0	$4a_1$	C_{2s}

1-$\mathrm{MeC_5H_5}$ (planar)

Calc.	Obs.	Orbital	Type
8·45	8·40	$4a''$	π
11·49	10·60	$3a''$	$\pi - \mathrm{CH_2}$
12·62	11·7	$18a'$	CC,CH
13·30	12·2	$17a'$	CC,CH
13·68	12·8	$16a'$	CC
14·83	13·4	$15a'$	CC,CH
15·07		$2a''$	$\mathrm{CH_3}(e) - \mathrm{CH_2} - \pi$
15·58	13·9	$14a'$	$\mathrm{CH_3}(e)$
16·37	14·9	$1a''$	$\mathrm{CH_3}(e) + \mathrm{CH_2} + \pi$
17·97	15·9	$13a'$	CH
19·02	16·9	$12a'$	CH,CC
20·60	17·7	$11a'$	C_{2s}
24·40		$10a'$	$\mathrm{CH_3}(a) - \mathrm{C}_{2s}$
25·53		$9a'$	C_{2s},$\mathrm{CH_2}$
2·720		$8a'$	$\mathrm{CH_3}(a) + \mathrm{C}_{2s}$
30·79		$7a'$	C_{2s}

2-$\mathrm{MeC_5H_5}$ (planar)

Calc.	Obs.	Orbital	Type
8·87	8·45	$4a''$	π
11·37	10·36	$3a''$	$\pi - \mathrm{CH_2}$
12·75	11·8	$18a'$	CC,CH
13·17	12·25	$17a'$	CC,CH
13·91	12·6	$16a'$	$\mathrm{CH_3}(e) - \mathrm{CC}$
15·05	13·4	$15a''$	CC,CH
15·14		$2a''$	$\mathrm{CH_3}(e) - \mathrm{CH_2} - \pi$
15·91	13·9	$14a'$	$\mathrm{CH_3}(e) + \mathrm{CC}$
16·10	14·7	$1a''$	$\mathrm{CH_3}(e) + \mathrm{CH_2} + \pi$
17·94	15·9	$13a'$	CH
19·15	16·6	$12a'$	CH,CC
21·20	17·8	$11a'$	C_{2s}
24·18		$10a'$	$\mathrm{CH_3}(a) - \mathrm{C}_{2s}$
25·32		$9a'$	$\mathrm{CH_3}(a) - \mathrm{C}_{2s}$
27·09		$8a'$	$\mathrm{CH_2}(a) + \mathrm{C}_{2s}$
31·58		$7a'$	C_{2s}

5-$\mathrm{MeC_5H_5}$ (planar)

Calc.	Orbital	Type
8·77	$8a''$	π
11·61	$14a'$	$\pi - \mathrm{CC}$
12·96	$7a''$	CC,CH
12·90	$13a'$	CC
14·03	$12a'$	CC
14·71	$11a'$	$\mathrm{CH_3}(e) - \mathrm{CH} - \pi$
15·12	$6a''$	CC,CH
15·43	$5a''$	$\mathrm{CH_3}(e)$
16·57	$10a'$	$\mathrm{CH_3}(e) + \mathrm{CH} + \pi$
18·84	$9a'$	CH
19·49	$4a''$	CH
19·86	$8a'$	C_{2s}
23·41	$7a'$	$\mathrm{CH_3}(a) - \mathrm{C}_{2s}$
26·11	$3a''$	C_{2s}
27·22	$6a'$	$\mathrm{CH_3}(a) + \mathrm{C}_{2s}$
31·69	$5a'$	C_{2s}

5-$\mathrm{SiH_3C_5H_5}$ (planar)

Calc.	Obs.	Orbital	Type
9·09	8·7	$10a''$	π
11·09	10·2	$16a'$	$\pi - \mathrm{SiC}$
12·67	12·0	$15a'$	$\mathrm{SiC} + \pi$
12·72		$9a''$	$\mathrm{SiH_3}(e)$
13·18		$14a'$	
13·88	12·8	$8a''$	CC
14·72	13·9	$13a'$	CC,CH
15·56	14·1	$7a''$	CC,CH
15·65		$12a'$	$\mathrm{CH} + \pi$
18·53	16·5	$11a'$	$\mathrm{CH} - \mathrm{SiH_3}(a)$
19·53	17·0	$6a''$	CH
19·34		$10a'$	$\mathrm{CH} + \mathrm{SiH_3}(a)$
21·47		$9a'$	C_{2s}
25·39		$8a'$	C_{2s}
26·57		$5a''$	C_{2s}
31·74		$7a'$	C_{2s}

Computation.—The LCGO (linear combination of gaussian orbital) method used was that described previously.[6] The scaled hydrocarbon basis, used earlier[6] on norbornadiene, was of 7,3,3 type for $1s_C + 2s_C,2p_C,1s_H$. A silicon best-atom basis[7] of 10,6 type ($1s + 2s + 3s,2p + 3p$) was scaled for optimum energy in silane, with simultaneous scaling of $1s_H$; then six $3d_{ab}$ orbitals,[†] where $a,b = x$, y, or z, were added and the optimum energy obtained with a *d*-orbital exponent of 0·3533. The energy obtained (Table 2) compared well with most previous calculations,[8] except those of Schaefer *et al.*[9a] whose basis sets were much larger. As a check that the basis was adequate for use on silylcyclopentadiene compounds, a calculation on methylsilane was carried out using the geometry adopted by Liskow and Schaefer[9b] so that direct comparison with their data was possible. Despite their much larger basis sets for all atoms, our total energy (Table 2) was only 0·17% poorer, which, although considerable (15·4 eV), can almost all be accounted for in terms of core energy levels. In the valence shell the average difference between our results and those from Liskow and Schaefer's largest basis set was 0·14 eV. The present basis led to very satisfactory values of a range of one-electron operators.

Our computations for silylcyclopentadiene compounds were made with three different basis sets for Si: using the (10,6) basis only (*sp*); with the addition of an extra $3s'$ function ($sp + s'$); and with the addition of the six $3d_{ab}$ functions ($spd + s'$). Eigenvalues and eigenvectors of the occupied levels did not differ significantly between the three sets of calculations, while small improvements in total energies for the larger basis sets did not alter relative energies of the isomers or conformations (Table 3).

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[*] For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue (items less than 10 pp. are supplied as full-size copies).

[†] The use of six *d*-type GTO s (gaussian type orbitals) is conventional and preserves the 3-fold symmetry of the indexing sequences in calculation. For the silylcyclopentadiene compounds these six functions were contacted to five $3d$ orbitals and a further *s* orbital ($3s' \equiv d_{x^2+y^2+z^2}$) to give the '$spd + s'$' basis. This was not done for silane or methylsilane since the process does not alter total or orbital energies.

[6] M. H. Palmer, A. J. Gaskell, and M. S. Barber, *Theoret. Chim. Acta*, 1972, **26**, 357; M. H. Palmer and R. H. Findlay, *Chem. Phys. Letters*, 1972, **15**, 416.

[7] B. Roos and P. Siegbahn, *Theoret. Chim. Acta*, 1970, **17**, 209.

[8] W. G. Richards, T. E. H. Walker, and R. K. Hinkley, 'A Bibliography of *Ab Initio* Molecular Wave Functions,' Clarendon Press, Oxford, 1971.

[9] (*a*) S. Rothenberg, R. H. Young, and H. F. Schaefer, *J. Amer. Chem. Soc.*, 1970, **92**, 3243; (*b*) D. H. Liskow and H. F. Schaefer, *ibid.*, 1972, **94**, 6641.

RESULTS

The Geometry of Methyl- and Silyl-cyclopentadiene Compounds.—The microwave (rotation) spectrum of cyclopentadiene has been incompletely analysed,[10] but the planarity of the carbon skeleton is established. Electron-diffraction studies of the 5-silyl compound [11] show the C_5 ring to be planar, but less-sophisticated analysis [12] of similar results for 5-(trimethylsilyl)cyclopentadiene indicates that the ring is far from planar with two planes intersecting at 158°. No evidence as to the structures of the methyl compounds seems to be available.

We used two distinct geometries for the 5-isomers in the present study, one with a planar ring skeleton and one with the non-planar ring described above. The dimensions of the ring were otherwise kept unchanged throughout the series of compounds, and standard geometries were also used for methyl and silyl groups. Conformations of silyl and methyl groups were chosen so as to minimise computation; other studies have shown that LCGO methods give total and orbital energies that do not change greatly with conformation.[13] The conformations adopted all result in a single mirror plane, the only molecular symmetry element, passing through the MH_3 group. In the non-planar ring 5-isomers the MH_3 group may be axial (*cis*) or equatorial (*trans*) in configuration; calculations were performed for both forms.

TABLE 3

Total energies (a.u.) for cyclopentadienes

C_5H_6 (non-planar)	−192·2849
C_5H_6 (planar)	−192·3016
5-MeC_5H_5 (*trans*)	−231·2153
(*cis*)	−231·2258
(planar)	−231·2345
1-MeC_5H_5 (planar)	−231·3644
2-MeC_5H_5 (planar)	−231·3741

	sp Basis	*sp* + *s'* Basis	*spd* + *s'* Basis
1-SiH_3 (planar)	−481·9505	−481·9903	−482·0500
5-SiH_3 (*trans*)	−481·9541	−481·9949	−482·0588
2-SiH_3 (planar)	−481·9658	−482·0055	−482·0651
5-SiH_3 (planar)	−481·9738	−482·0144	−482·0780
(*cis*)	−481·9748	−482·0152	−482·0791

The results of our calculations of total energy (Table 3) show that for the parent cyclopentadiene and for 5-methylcyclopentadiene the planar skeleton is preferred, but for 5-silylcyclopentadiene the *cis* non-planar form is most stable. The very small energy difference found in the last case, and the fact that we did not optimise any other geometrical parameters in the calculations, may serve to account for the apparent discrepancy between calculated and experimental structures. The energy difference amounts only to *ca.* 3 kJ mol^{-1}, which is comparable to vibrational energies. We did not make calculations for 1- and 2-isomers with non-planar rings.

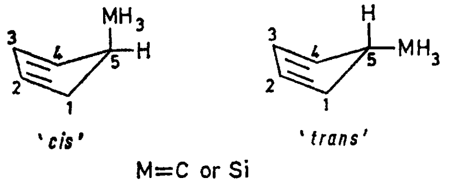

TABLE 2

Energy levels (eV) and total energies (a.u.) [a]

Methane		Silane			Methylsilane		
Calc.	Obs.[b]	Calc.	Obs.[c]	Orbital type	Calc.	Obs.[d]	Orbital
		1 865		$1s_{Si}$	1 865		$1a_1$
305·1	290·8			$1s_C$	304·7		$2a_1$
		161·7		$2s_{Si}$	161·4		$3a_1$
		113·9		$2p_{Si}$	113·6		$4a_1$
					113·6		$1e$
25·3	23·0			$2s_C + 1s_H$	25·39		$5a_1$
		19·62	18·16	$3s_{Si} + 1s_H$	18·58	17·1	$6a_1$
14·85	13·0			$2p_C + 1s_H$	15·35	14·3	$2e$
		13·31	12·2	$3p_{Si} + 1s_H$	12·66	12·1	$3e$
				$3p_{Si} + 2p_C$	12·39	11·8	$7a_1$

[a] Total energies for methane, silane, and methylsilane are −40·1032, −290·7650, and −329·7326 a.u. respectively; 1 a.u. ≈ 2 625·5623 kJ mol^{-1}. [b] D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, 'Molecular Photoelectron Spectroscopy,' Wiley, New York, 1970. [c] S. Cradock, *J. Chem. Phys.*, 1971, **55**, 980. [d] Ref. 18.

The reason for stabilisation of the *cis*-form over the planar form for the silyl compound appears to be an increased overlap integral between silicon and the *far* ring carbon atoms,* associated with mixing of the Si–C σ-bonding orbital with π-bonding (b_1) levels of the ring. An electrostatic effect may also assist the stabilisation; the *cis*-silyl group carries a net positive charge of 0·29 e, while the ring carbon atoms are negatively charged. As the methyl group in the *cis* 5-methyl isomer is effectively neutral this effect is absent (see Table 4).

TABLE 4

Net atomic populations for 5-silyl- and 5-methyl-cyclopentadiene

5-Silyl [a]		5-Methyl	
Si	+0·695	$C_{(H_3)}$	−0·435
H_{Si}	−0·138, −0·138, −0·131	H_c	+0·163, +0·163, +0·172
C_5	−0·375	C_5	−0·221
$C_{1(4)}$	−0·164	$C_{1(4)}$	−0·126
$C_{2(3)}$	−0·172	$C_{2(3)}$	−0·167
$H_{1(4)}$	+0·161	$H_{1(4)}$	+0·144
$H_{2(3)}$	+0·155	$H_{2(3)}$	+0·142

[a] The figures are not significantly changed with basis set.

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* 'Non-bonded' overlap integrals are almost universally small and *negative*; the value for overlap of the methyl carbon with the far ring carbon atoms in 5-MeC_5H_5 is −0·080. For the corresponding Si compound the value rises to +0·005, which, while small numerically, is significantly larger in absolute terms.

[10] V. W. Laurie, *J. Chem. Phys.*, 1956, **24**, 635; L. H. Scharpen and V. W. Laurie, *ibid.*, 1965, **43**, 2765.

[11] J. E. Bentham and D. W. H. Rankin, *J. Organometallic Chem.*, 1971, **30**, C54.

[12] N. N. Veniaminov, Yu. A. Ustynynk, N. V. Alekseev, J. A. Ronova, and Y. T. Struchkov, *J. Organometallic Chem.*, 1970, **22**, 551.

[13] E. Clementi and D. R. Davies, *J. Chem. Phys.*, 1966, **45**, 2593.

It is clear from Table 3 that the calculated total energies are generally consistent with the experimental observations that the 5-methyl isomer is less stable than the 1- and 2-methyl compounds whereas the 5-silyl compound is the most stable, being the only isomer detected.

Assignment of Experimental Spectra.—The p.e. spectrum of cyclopentadiene to *ca.* 27 eV has been analysed by Lindholm and his co-workers in terms of extended Hückel (EHM)[14] and spectroscopically parameterised INDO (SPINDO)[15] calculations.* The SPINDO and our LCGO calculations were in almost complete agreement in (*a*) orbital ordering (only the nearly degenerate pair $9a_1$ and $6b_2$ is reversed), (*b*) the major character of the orbitals, and (*c*) the major groupings of lines (1 : 1 : 5 : 3 : 2 : 1) in the spectrum. The SPINDO results are thus a considerable improvement over those of EHM which do not correlate well with the LCGO method in respect of any of these features. It remains open to question whether the parameterisation required in the SPINDO calculation can be extended to reproduce non-empirical calculations in systems containing other elements or in molecules of lower symmetry.

We are confident that we can now assign the experimental ionisation potentials of cyclopentadiene to the LCGO eigenvalues by use of Koopmans' theorem. Since the gradient of a correlation line is largely determined from data at the ends of the line rather than at the centre, minor reassignments will not lead to a substantially different line, which for cyclopentadiene is I.P.$_{\text{obs}}$ = 0·80 I.P.$_{\text{calc}}$ + 1·3 eV. This line is similar to that found for azoles,[17] except that an intercept is now apparent; this may be due to the separate scaling adopted for carbon and hydrogen exponents to saturated and unsaturated centres.

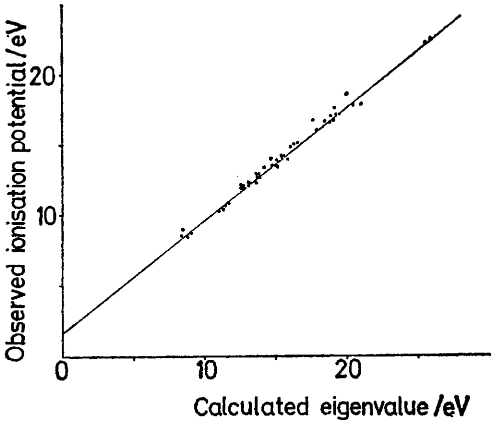

FIGURE 2 Correlation between calculated eigenvalues and observed vertical-ionisation potentials

The spectra of the substituted compounds (Figure 1) did not show such clearly separated bands in the 12—16 eV region as are found in the parent cyclopentadiene. This makes assignment more difficult, but by use of unambiguous points at each end of the correlation line and the calculated line groupings, which are generally consistent with the observed spectra, we obtained an overall correlation line, shown in Figure 2, for all four compounds corresponding to the equation I.P.$_{\text{obs}}$ = 0·78$_4$ I.P.$_{\text{calc}}$ + 1·65 eV. Assignment of the observed bands to molecular orbitals shown in Table 1 follows from this linear correlation.

DISCUSSION

The electronic structure of cyclopentadiene, in terms of atomic-orbital contributions to the various molecular energy levels, is now well defined; our results agree closely with those of Lindholm and his co-workers[15] and may be expressed in abbreviated form as shown in Table 1. The effects of substituting methyl or silyl groups in the 1-, 2-, or 5-positions may now be discussed; the results are summarised in Table 1 and SUP 21024.

Our computations on methane, silane, and methylsilane, required for checking the scaling parameters used, provide information on levels associated with the methyl and silyl groups (Table 2). A complication arises in that, although all the substituted molecules may be treated as having a mirror plane (C_s point group), the orientation of this plane varies relative to the ring. For the 1- and 2-substituted compounds it contains the ring atoms and σ- and π-orbitals of the ring remain strictly separated, whereas for the 5-substituted isomers the plane is perpendicular to the ring. Nevertheless inspection of the eigenvectors shows that, even in the latter case, the σ–π-separation associated with the ring is maintained to a high degree of accuracy. The effect of the single mirror plane passing through the MH_3 group is to lift the double degeneracy of levels of e-symmetry species in axial environments, into a' and a'' components. For 1- and 2-substituted compounds these correlate respectively with σ- and π-orbitals of the ring, but for the 5-isomers no such separate correlation is possible.

In C_s symmetry the methyl group will have two a' orbitals in the valence shell near 25 and 15 eV (calculated, see Table 2) derived largely from C 2*s* and 2*p* orbitals respectively, and one a'' orbital near 15 eV derived from C 2*p*. For the SiH_3 group the corresponding eigenvalues are 19 and 13 eV (a') and 13 eV (a''). We expect to find these ' group orbitals ' mixing significantly with orbitals, of the same symmetry and similar energy, associated with the cyclopentadiene group.

In the methyl cyclopentadiene compounds the cyclopentadiene orbitals $5a_1$ (25·76 eV) and $3b_2$ (26·13 eV) are closest in energy to the 25 eV methyl orbital; in the 1-methyl compound, $5a_1$, which has a very small eigenvector at C_1, is hardly affected, while $3b_2$ interacts strongly. In the 5-methyl compound $3b_2$ is unaffected, being of a'' symmetry, whereas $5a_1$ is split by *ca.* 4 eV by the interaction; in the 2-methyl compounds both

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* The ring numbering system used in Lindholm's work has the CH_2 group at the 1-position, and the orbitals (nX) of representation X were sequenced to correspond to those of earlier work[16] on furan. In our discussion the I.U.P.A.C. numbering is used and the orbitals were resequenced conventionally so that binding energy decreased as n increased in a given representation.

[14] P. J. Derrick, L. Åsbrink, O. Edqvist, B.-Ö. Jonsson, and E. Lindholm, *Internat. J. Mass Spec. Ion Phys.*, 1971, **6**, 203.

[15] C. Fridh, L. Åsbrink, and E. Lindholm, *Chem. Phys. Letters*, 1972, **15**, 408.

[16] P. J. Derrick, L. Åsbrink, O. Edqvist, B.-Ö. Jonsson, and E. Lindholm, *Internat. J. Mass Spec. Ion Phys.*, 1971, **6**, 161.

[17] S. Cradock, R. H. Findlay, and M. H. Palmer, *Tetrahedron*, 1973, **29**, 2173.

levels show the effects of interaction, because the eigenvectors at C_2 are high for both orbitals in cyclopentadiene. The methyl-group orbitals near 15 eV (a' and a'') are mixed quite extensively with cyclopentadiene orbitals such as $1b_1$ (16·63 eV), $5b_2$ (15·19 eV), and $8a_1$ (14·26 eV). In addition the ring-methyl σ-bond orbital is involved in various levels in the 13—15 eV region, but mixes only slightly with the ' π '-orbital derived from $2b_1$.

The SiH_3-group orbital near 19 eV interacts most strongly with $7a_1$ of cyclopentadiene in each of the silyl compounds; the effect is least in the 5-silyl compound. Silyl-group orbitals near 13 eV seem to be essentially unperturbed by ring orbitals, while the C–Si σ-bond is represented almost entirely by a single molecular orbital in the 1- and 2-isomers, though heavily delocalised over the ' π-system ' of the ring in the 5-silyl compound. This observation appears to offer the key to understanding the fluxional behaviour of 5-silylcyclopentadiene. Mixing of the C–Si bond with $2b_1$ of cyclopentadiene is associated with the high overlap noted above between silicon and the far ring carbon atoms; such overlap could afford a path for a 1,3-shift of the silyl group. Further investigation of the ' energy surface ' for such processes is planned.

Finally, this interpretation suggests that the observed correlation between the separation of the first two bands of spectra of substituted cyclopentadiene compounds and their fluxional or non-fluxional behaviour [18] is best regarded as related to the degree of mixing of the C–M (M = C or Si) bond orbital with the ' π-system ', and is thus physically reasonable.

Conclusions.—We believe that the calculations reported here, and the experimental p.e. spectra that these enable us to interpret in detail, afford a firm foundation for consideration of the differences in fluxional behaviour of a variety of cyclopentadiene derivatives of main-group elements. We have identified one factor that we believe to be of outstanding significance; this is the involvement of the C–Si bonding level in 5-silylcyclopentadiene in the ' π-system ' of the ring. Such involvement is much smaller in the methyl compound, where fluxional behaviour is not found.

The observed difference in structures of the most stable isomers (5-silyl, but 1- and 2-methyl) are also largely reproduced by the calculations of total energy. Much greater mixing of methyl-group orbitals with those of the ring suggests that the difference is due to destabilisation of the 5-methyl isomer rather than any special stabilisation of the 5-silyl compound. The ' normal ' order of stability would thus be that predicted for the silyl compounds ($5 > 2 > 1$), which is consistent with observations on many σ-cyclopentadiene compounds, all of which, except the methyl compounds, have the 5-isomer predominating.

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[18] S. Cradock, unpublished work.