Photoelectron Spectra and Fluxional Behaviour in some σ-Cyclopentadienes

By **Stephen Cradock, E. A. V. Ebsworth, Hans Moretto,** and **David W. H. Rankin,** Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ

A close correlation is shown to exist between fluxional behaviour in the σ-cyclopentadienes 5-RC_5H_5 (R = H, CH_3, SiH_3, GeH_3, or SiF_3) and the relative positions of the two photoelectron bands due to the ring π-bonding electrons. For R = PF_2 and $SiCl_3$ interactions between the second ring level and non-bonding orbitals of R have to be taken into account. It is suggested that the fluxional behaviour arises from interaction of R–C_5 σ-bonding level with the symmetric ring π-bonding level, which is greatest in those compounds that show fast fluxional behaviour.

THE fluxional behaviour of a number of cyclopentadiene derivatives of main-group elements is now well established.[1-3] We have investigated the photoelectron (p.e.) spectra of a selection of cyclopentadienes, some of which exhibit fluxional behaviour, to try to elucidate the effect of the substituent on the rate of fluxional motion. Detailed *ab initio* calculations have been reported[4] that suggest that the major electronic difference between 5-silylcyclopentadiene and the 5-methyl derivative is that the Si–C bonding orbital is significantly mixed with the ring π-system. This may provide a pathway for the fluxional behaviour, and we shall show here that the same sort of interaction may be important in other molecules of this type.

EXPERIMENTAL

The 5-substituted cyclopentadienes RC_5H_5 (R = SiH_3, GeH_3, $SiCl_3$, and PF_2) were prepared[5] by reaction of $K^+C_5H_5^-$ with the halides RCl or RBr. 5-$SiF_3C_5H_5$ Was obtained by halogen exchange between 5-$SiCl_3C_5H_5$ and SbF_3. Compounds were purified by trap-to-trap or column distillation under vacuum. Identity and purity were confirmed by i.r., n.m.r., and mass spectroscopy.

Cyclopentadiene and methylcyclopentadienes were prepared by cracking the commercially available dimers. The methyl compound obtained in this way consists of a mixture of the 1- and 2-isomers, with at most a small

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equilibrium concentration of the 5-isomer. The 1- and 2-isomers were separated by gas chromatography.[4]

P.e. spectra were recorded with He^{I} (21·22 eV) excitation using a Perkin-Elmer PS16 spectrometer. Samples were admitted from a vacuum system through a stainless-steel needle valve.

N.m.r. spectra were recorded at various temperatures on a Varian HA100 spectrometer. For each compound the effect of solvent and concentration on the ' coalescence ' temperature was found to be negligible. The results of these studies are being reported separately; for the purposes of this paper we may divide the compounds into three groups with distinctive coalescence temperatures as shown below. For our purpose a ' characteristic ' temperature T_c is taken as that at which the *olefinic* signals begin to broaden significantly as the temperature rises.

Group A: Fast fluxional behaviour (characteristic temperature $T_c \sim -25$ °C)
$R = PF_2$, SiH_3, and GeH_3.
Group B: Slow fluxional behaviour ($T_c \sim 0$ °C)
$R = SiF_3$.
Group C: Very slow fluxional behaviour ($T_c > 50$ °C)
$R = SiCl_3$, CH_3, and H.

In the last group effects of fluxional behaviour were not observed in the n.m.r. spectra up to 50 °C; dimerisation and isomerisation (involving proton shifts) occur before fluxional behaviour as the temperature is raised.

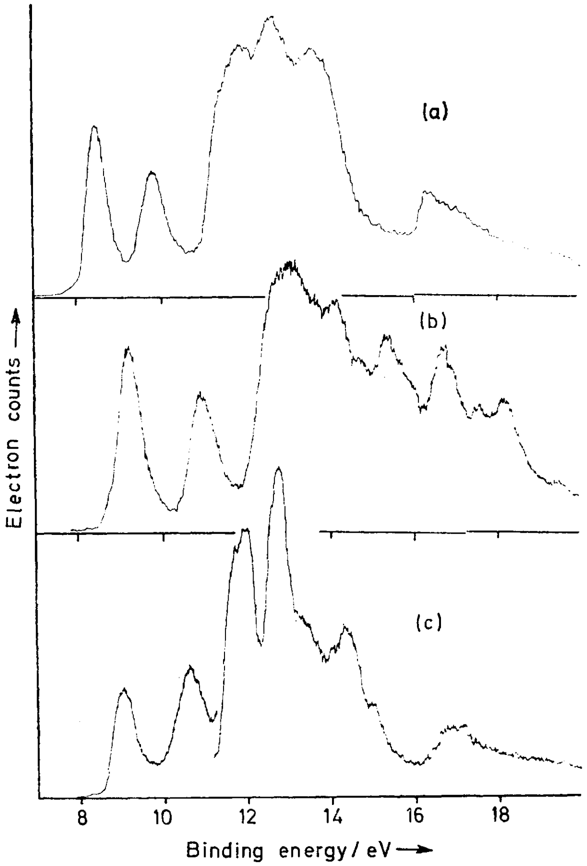
DISCUSSION

The p.e. spectra are shown in the Figure as well as in Figure 1 of ref. 4 and Figure 2 of ref. 6; the vertical ionisation potentials are listed in the Table. The spectra may be divided into three major regions on the basis of the earlier analysis[4] of those of cyclopentadiene, methylcyclopentadiene, and silylcyclopentadiene. These regions, indicated, in the Table are as follows. (i) Beyond *ca.* 15·5 eV weak bands appear in all cases due to C_5H_5 ring σ-bonding levels derived mainly from C 2*s* orbitals. In the spectra of the fluoro-compounds there will also be bands due to F $2p_\pi$ ' lone pairs ' and to Si–F or P–F bonding orbitals in this region. The weakness of the observed bands is at least partly due to the relative insensitivity of our analyser/detector system to low-energy electrons.

Observed vertical ionisation potentials for RC_5H_5/eV

R Regions	H	1-CH_3	2-CH_3	5-SiH_3	5-GeH_3	5-PF_2	5-SiF_3	5-$SiCl_3$
iii	8·6	8·4	8·4	8·7	8·5	9·2	9·1	9·0
Ring π	10·7	10·6	10·4	10·2	9·8	9·9	10·9	10·6
						11·4		
	12·2	11·7	11·8	12·0	11·9		10·9	11·9
		12·2	12·2					
ii	12·6	12·8	12·6	12·8	12·7	12·8	13·0	12·9
Ring *p*	13·2	13·4	13·4					13·4
	13·8	13·9	13·9	13·9	13·6	14·1	14·0	14·4
				14·1				
	15·0	14·9	14·7			15·2	15·2	15·1
i	16·5	15·9	15·9	16·5	16·4	16·5	16·7	16·7
Ring *s*	17·5	16·9	16·6	17·0	17·0	17·2	17·5	
	18·4	17·7	17·8				18·2	

(ii) Between *ca.* 11 and 15·5 eV all the spectra contain a broad band due to C_5H_5 ring σ-bonding levels derived mainly from C 2*p* orbitals. There should also be a band due to the R–C bonding orbital, though it cannot be distinguished from the stronger ring bands. Similarly, CH, SiH, and GeH bonding levels should give broad bands in this region but are not distinguishable. The spectrum of $SiCl_3C_5H_5$ contains strong bands near 12 eV due to the Cl $3p_\pi$ ' lone pairs ' and a weaker band near 14 eV due to the Si–Cl bonding levels.



P.e. spectra of (a) $GeH_3C_5H_5$, (b) $SiF_3C_5H_5$, and (c) $SiCl_3C_5H_5$

(iii) Below 11 eV binding energy all spectra contain two bands of comparable intensity due to the two occupied π-bonding orbitals of the C_5H_5 ring. (The spectrum of $PF_2C_5H_5$, as reported earlier,[6] also contains a third band in this region due to the P $3p_z$ ' lone pair '.)

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[6] S. Cradock and D. W. H. Rankin, *J.C.S. Faraday II*, 1972, 940.

The less-tightly bound of the ring π orbitals correlates with $1a_2$ of cyclopentadiene, and has a nodal plane perpendicular to the ring through the 5-position. The more-tightly bound orbital correlates with $2b_1$ of cyclopentadiene, and has no nodal plane in this position. An important consequence of this difference is that, in a 5-substituted cyclopentadiene, the first band in the photoelectron spectrum corresponds to a level that cannot interact with the substituent except by a long-range π-effect. The second band can be affected by the substituent, mixing with any level that is symmetric to the plane bisecting the ring through C_5 being permitted. An obvious example is afforded by $PF_2C_5H_5$ where mixing of the second ring π level with the P $3p_z$ lone-pair level increases the separation between the corresponding bands, the second and third in the spectrum. It is also possible [4] for the R–C_5 σ-bonding level to interact with the second (symmetric) ring π level.

The position of the first band, then, may be taken as affected mainly by the inductive effect of the substituent, which causes a variation in the net charge on the ring. The vertical ionisation potentials for the first bands in the spectra show the expected variation with R, the halogen-containing substituents giving ionisation potentials around 9·0 eV and the hydrides having first ionisation potentials around 8·5 eV.

Similar inductive effects should operate on the second band; if these were the only effects the separation of the first two bands would not change in the series of molecules. This is clearly not so; among the hydrides, for instance, the separation is about 1·4 eV in the silyl and germyl compounds but *ca.* 2·1 eV in the methyl compounds and in cyclopentadiene itself. (The calculations reported earlier [4] show that the separation to be expected for the 5-methyl isomer is very similar to that for the 1-methyl.) The variations in the separation thus correlate well with the differences in fluxional behaviour, for the silyl and germyl compounds show fast fluxional behaviour whereas the methyl compounds and cyclopentadiene itself do not.

For $SiF_3C_5H_5$, which shows intermediate, slow fluxional, behaviour, the observed separation is 1·8 eV, intermediate between the separations found for compounds in the fast and very slow groups. For $PF_2C_5H_5$ the interaction with the P $3p_z$ level makes it difficult to define the separation; taking the mean of the positions of the second and third bands as representing the unperturbed second ring level gives a separation of 1·5 eV. This is quite consistent with the observed fluxional behaviour.

The most difficult observation to reconcile with the overall pattern is the low separation of 1·6 eV for $SiCl_3C_5H_5$, which does not exhibit fluxional behaviour. We suggest that this may be due to an additional interaction of the second ring level with Cl $3p_\pi$ lone-pair levels. These seem to be responsible for two distinct bands in the spectrum, at 11·9 and 12·7 eV. If even part of this 0·8 eV splitting is due to an interaction of one component with the second ring π level the unperturbed separation of ring levels could rise above 2 eV.

There is then a variation in the relative positions of the first and second bands in the photoelectron spectra that correlates with the variation in fluxional behaviour. A small separation (1·4 eV) is characteristic of molecules with fast fluxional behaviour, if interactions with neighbouring groups are allowed for.

At this stage it is worth noting that there is no comparable variation in the separation of the highest occupied and lowest unoccupied orbitals of the ring. The transition between these gives rise to a band in the u.v. spectrum that is essentially unchanged in position (240 ± 5 nm; $5{\cdot}2_5 \pm 0{\cdot}1$ eV) throughout the series. The variation in fluxional behaviour is thus not controlled by the variation in excitation energy to the first electronically excited state.

The most satisfactory explanation for the correlation between fluxional behaviour and the separation of the two occupied ring π-bonding levels is that suggested earlier.[4] The separation is directly related to the degree of interaction of the more tightly-bound ring π level with the R–C_5 σ-bonding level. For the hydrides, the energy difference between the interacting levels will be considerably greater for $R = CH_3$ than for $R = SiH_3$ or GeH_3, so that the degree of interaction will be reduced. Within the set of silyl derivatives ($R = SiH_3$, SiF_3, or $SiCl_3$) the more electronegative substituents on silicon will tend to increase the binding energy of other bonding levels associated with that atom, increasing the energy mis-match with the ring π level and thus decreasing the degree of interaction.

The observed decrease in separation between the ring π levels in molecules that exhibit fluxional behaviour is then a symptom of interaction of the symmetric π level with the R–C_5 bonding level. Such an interaction, leading to a mixing of the wavefunctions associated with the two canonical ' group orbitals ' (ring π-bonding and R–C_5 σ-bonding) must provide the mechanism for the relative rotation of the ring and the group R. The physical details of the rotation are still unclear, but it seems possible that a ' π-allyl ' (h^3) intermediate is involved.

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