Tetrahedron. Vol. 29, pp. 2129 to 2134. Pergamon Press 1973. Printed in Great Britain

PHOTOELECTRON SPECTRA OF DIAMONDOID MOLECULES

ADAMANTANE, SILAMANTANE AND UROTROPINE*

W. SCHMIDT†
School of Molecular Sciences, The University of Sussex, Brighton BN1 9QJ, U.K.

(*Received in the UK 3 January* 1973; *Accepted for publication 7 February* 1973)

Abstract—The He(1) PE spectra of the title compounds have been measured and bands attributable to CC, SiC, NC and CH ionizations identified. In accordance with recent thermochemical studies, analysis of the spectra in terms of an equivalent orbital (EO) treatment indicates that adamantane is by no means strain-free. Manifestations of its steric discomfort include: (i) a splitting of 2 eV between formally degenerate orbitals localized in the methylene groups, (ii) a similar gap between orbitals correlating with the tertiary CH bonds, and (iii) a CC level ordering strikingly different from that expected on the basis of nearest neighbour CC—CC interactions only. These findings are interpreted in terms of through-space CH···CH and transannular CC···CC interactions. The relevant EO parameters are reported.

Adamantane occupies a special position among saturated carbocyclic hydrocarbons by virtue of its rigidity and high symmetry. Composed of three fused cyclohexane rings in their chair conformation, the molecule exhibits structural features characteristic of the diamond lattice and should therefore be strain-free. This stability is borne out by the fact that many saturated hydrocarbons with at least ten C atoms can be converted to adamantanes upon treatment with suitable catalysts.[1]

Attempts to derive a comprehensive interrelation between the physicochemical properties of adamantane and its structure would undoubtedly benefit from a knowledge of its photoelectron spectrum. It is reported here along with the spectra of the isoelectronic molecules 1,3,5,7-tetrasilamantane and urotropine, all of T_d symmetry. The spectra have been measured on a Perkin-Elmer PS-16 (adamantane, 25°) or PS-18 instrument (silamantane, urotropine, 58°), using He(I) excitation and rare gases as calibrants. Adamantane and urotropine have already been studied by Dewar and Worley[2] at low resolution on a grid-type spectrometer, but no discussion of the spectra was given. Silamantane, whose synthesis has recently been described,[3] was kindly provided by Professor Fritz.

The adamantane spectrum is considered in greater detail, since it is in several respects the simplest, exhibiting six distinct bands that are labelled 1 to 6 in Fig 1. Expanded recordings of the first four bands revealed no regular vibrational structure, suggesting that these bands originate from degenerate MO's, with the resulting complication arising from the Jahn-Teller distortion in the corresponding ions. The fifth band, however, shows fine structure which appears to be dominated by two progressions with frequencies 734 ± 30 and $1175 \pm 40\ cm^{-1}$. Based on force field calculations by Snyder and Schachtschneider,[4] we assign the first progression to a skeletal vibration (calculated 759 cm^{-1} for the molecule), the second tentatively to a CH_2 scissoring mode (calculated 1453 cm^{-1}). Both are totally symmetric and consequently IR-inactive;[5] they have only very recently[6] been identified in the laser raman spectrum of adamantane at 756 and 1436 cm^{-1}.

Neglecting inner shells, the 56 valence electrons of adamantane occupy in the ground state 28 MO's, of which ten are mainly C(2s) in character and will occur largely beyond the range of the He(I) experiment. In the neopentane spectrum the first C(2s) band has been identified[8] at 17·56 eV, so that we expect the corresponding band in adamantane at slightly lower energies. On this bases, bands No. 5 and 6 have a clear correlation with C(2s) levels. After the deconvolution shown in Fig 1, the integrated intensities suggest a ratio of the degeneracy of the first five bands as 3:5:6:3:1. To arrive at these figures, we have assumed that the integrated intensity of a PE band is proportional to the number of ionizable electrons and inversely proportional to the kinetic energy of the ejected electrons. At least the second and third bands have thus to accommodate more than one MO. Little can be said about the degeneracy of the sixth band, for it is too close to the instrumental cut-off at 21 eV. Under He(II) excitation,[7] this band gains considerably in intensity, relative to the fifth band, and appears therefore to be due to ionization from a degenerate level, as is consistent with the lack of any vibrational structure.

The band assignments proposed in Fig 1 are

*Photoelectron spectra of σ-bonded molecules, part 4.

†Present address: Institut für Organ. Chemie der Universität, Karlstr. 23, D-8000 München-2.

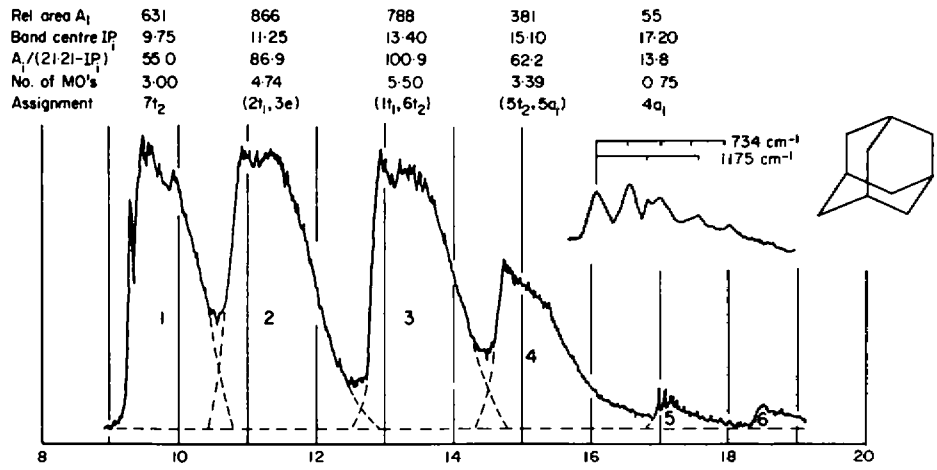

Fig 1. The PE spectrum of adamantane, with interpretation. Overlapping bands have been deconvoluted into their components (see text). The insert shows the 16·96 eV band on an expanded scale. Symmetry species refer to point group T_d and include inner-shell MO's.

based on (i) an equivalent orbital (EO) treatment using parameters deduced in an earlier paper,[9] and (ii) the observed energy level trends across the series of the three molecules. Owing to the high symmetry of adamantane, an EO approach offers an attractive alternative to the conventional LCAO treatment, in that the wave functions of this molecule are largely symmetry-dictated; in consequence their energies can be expressed in terms of only a few independent parameters. Basis orbitals (numbering scheme: Fig 4) are the 16 CH–EO's of energy a and the 12 CC–EO's of energy c. It is convenient to subdivide the former into the 12 secondary and the four tertiary CH–EO's.

These three types of EO's must each be combined to yield semi-localized MO's which span the following irreducible representations:

$$\Gamma_{CC} = a_1 + e + t_1 + 2t_2$$

$$\Gamma_{CH_2} = a_1 + e + t_1 + 2t_2$$

$$\Gamma_{CH} = a_1 + t_2.$$

The resulting CC, CH_2 and CH wave functions along with their orbital energies are collected in Table 1. In the case of degenerate levels only one component is given. Some of these MO's, *e.g.*, the t_2(CC) levels, are not unique in their symmetry species; their energies are therefore only approximate. The σ–π notation in Table 1 follows the usual convention.

If allowance is made for interaction, some of these semi-localized MO's undergo extensive mixing, the extent of which can be gauged from Table 2. Matrix elements involving the parameters b, d, e (nearest neighbour CH—CH, CH—CC and CC—CC interactions) are particularly large,[9] typically of the order of -2 eV. Those containing the parameters w, x (transannular 1–3 and 1–4 CC—CC interactions) and r, s, t, g and v (long range CH—CC and CH—CH interactions) are smaller by a

Table 1. Semi-localized wave functions and orbital energies of adamantane. The basis EO's are defined in Fig 4, the interaction terms in the text and in refs 9 and 10

Wave functions	Energies
$a_1(\sigma CH) = 1/2\,(\phi_{13}+\phi_{14}+\phi_{15}+\phi_{16})$	$a+3v$
$a_1(CC) = 1/\sqrt{12}\,(\phi_{17}+\phi_{18}+\phi_{19}+\phi_{20}+\phi_{21}+\phi_{22}+\phi_{23}+\phi_{24}+\phi_{25}+\phi_{26}+\phi_{27}+\phi_{28})$	$c+3e+4w+2x$
$a_1(\sigma CH_2) = 1/\sqrt{12}\,(\phi_1+\phi_2+\phi_3+\phi_4+\phi_5+\phi_6+\phi_7+\phi_8+\phi_9+\phi_{10}+\phi_{11}+\phi_{12})$	$a+b+2t$
$e(CC) = 1/\sqrt{8}\,(\phi_{17}-\phi_{18}+\phi_{20}-\phi_{21}+\phi_{25}+\phi_{26}-\phi_{27}-\phi_{28})$	$c-2w-x$
$e(\sigma CH_2) = 1/\sqrt{8}\,(\phi_1+\phi_2-\phi_3-\phi_4+\phi_9+\phi_{10}-\phi_{11}-\phi_{12})$	$a+b-t$
$t_1(CC) = 1/\sqrt{8}\,(\phi_{17}-\phi_{18}-\phi_{20}+\phi_{21}-\phi_{25}+\phi_{26}-\phi_{27}+\phi_{28})$	$c-2e+2w-x$
$t_1(\pi CH_2) = 1/\sqrt{6}\,(\phi_1-\phi_2+\phi_3-\phi_4+\phi_5-\phi_6)$	$a-b-t$
$t_2(\sigma CC) \sim 1/\sqrt{6}\,(\phi_{17}-\phi_{18}-\phi_{23}+\phi_{24}-\phi_{26}+\phi_{27})$	$c-e-3/2w+2x$
$t_2(\pi CH_2) = 1/4\,(\phi_1-\phi_2+\phi_3-\phi_4-2\phi_5+2\phi_6-\phi_9+\phi_{10}+\phi_{11}-\phi_{12})$	$a-b+t$
$t_2(\sigma CH) = 1/\sqrt{2}\,(\phi_{14}-\phi_{15})$	$a-v$
$t_2(\sigma CH_2) = 1/\sqrt{8}\,(\phi_1+\phi_2-\phi_3-\phi_4-\phi_9-\phi_{10}+\phi_{11}+\phi_{12})$	$a+b$
$t_2(\pi CC) \sim 1/\sqrt{22}\,(\phi_{17}-\phi_{18}+2\phi_{20}-2\phi_{21}+\phi_{23}-\phi_{24}-2\phi_{25}-\phi_{26}+\phi_{27}+2\phi_{28})$	$c+2e-1/2w-x$

Table 2. Matrix elements between the semi-localized CC, CH and CH_2 orbitals of adamantane defined in Table 1

	a_1(CC)	a_1(CH)	$a_1(\sigma CH_2)$
a_1(CC)	$c+3e+4w+2x$		
a_1(CH)	$\sqrt{3}(d+r)$	$a+3v$	
$a_1(\sigma CH_2)$	$2(d+r+s)$	$2\sqrt{3}g$	$a+b+2t$

	e(CC)	$e(\sigma CH_2)$
e(CC)	$c-2w-x$	
$e(\sigma CH_2)$	$2d-r-s$	$a+b-t$

	t_1(CC)	$t_1(\pi CH_2)$
t_1(CC)	$c-2e+2w-x$	
$t_1(\pi CH_2)$	$1/\sqrt{3}(r-s)$	$a-b-t$

	$t_2(\sigma$CC)	$t_2(\pi CH_2)$	$t_2(\sigma$CH)	$t_2(\sigma CH_2)$	$t_2(\pi$CC)
$t_2(\sigma$CC)	$c-e-3/2w+2x$				
$t_2(\pi CH_2)$	$4/\sqrt{6}(s-r)$	$a-b+t$			
$t_2(\sigma$CH)	$1/\sqrt{3}(d-3r)$	0	$a-v$		
$t_2(\sigma CH_2)$	$2/\sqrt{3}(d-r-s)$	$\sqrt{2}t$	$2g$	$a+b$	
$t_2(\pi$CC)	$2/\sqrt{6}w$	$1/2(r-s)$	$1/\sqrt{11}(5d+r)$	$1/\sqrt{3}(2d+r+s)$	$c+2e-1/2w-x$

factor of two or three. Some matrix elements vanish totally or involve differences in parameters which are of the same sign and of similar size.

Keeping this in mind, the orbital energies listed in Table 1 form an intelligible pattern from which the following band assignments can be deduced.

The semi-localized levels $t_2(\pi CH_2)$ and $t_1(\pi CH_2)$ are seen to be symmetrically displaced from the reference $(a-b) = -14{\cdot}1$ eV by an amount $|t|$ which represents the through-space interaction between the individual methylene groups. These two orbitals correlate directly with the neopentane πCH_2 levels $3t_2$ and $1t_1$ (band centres in neopentane 15·4 and 12·7 eV), and on ionization give rise to the fourth band and one component (we cannot say which) of the third band. These orbitals have been labelled $5t_2$ and $1t_1$ in Fig 1. That their observed splitting (roughly 2 eV) is smaller than in neopentane (2·7 eV), appears to be associated with the matrix element $1/\sqrt{3}(r-s)$ which mixes $t_1(\pi CH_2)$ with the equal-energy MO t_1(CC). This interaction is absent in the neopentane case.

From Table 2 we expect that the semi-localized CH levels (t_2 and a_1 components) interact strongly with lower-lying CC orbitals through the matrix elements $1/\sqrt{11}(5d+r)$ and $\sqrt{3}(d+r)$, respectively. Neglecting the parameter v for the moment, this interaction raises their energies from a to $(\frac{3}{4}a+\frac{1}{4}c-\frac{3}{2}d+\frac{1}{2}e)$ which can be shown to be very close to $(a-b)$. Through-space interaction via the negative parameter v places the t_2 above the a_1 component. Neglecting contributions from πCH_2 levels and the higher-lying t_2(CC) orbital (the matrix elements in question are small), the centroid of the two nominally CH bonding MO's, which have been termed $6t_2$ and $5a_1$ in Fig 1, is predicted to be close to that of the two πCH_2 levels already identified in the spectrum. Since the C(2s) levels in adamantane are expected to spread more than in neopentane, the assignment of the 16·96 eV band to the highest C(2s) level $4a_1$ is beyond reasonable doubt. This is further supported by the observed excitation of a skeletal and CH_2 scissoring mode, and the dominance of the 0–0 vibrational component: from Table 1 it is seen that $4a_1$ is essentially the *minus* linear combination of a_1(CC) and $a_1(\sigma CH_2)$, so that this MO classifies as only weakly bonding. The CH level $5a_1$ has consequently to be correlated with the fourth band, which gives $v \approx -0{\cdot}4$ eV, so that $6t_2$ is predicted to have an energy of *ca.* $-13{\cdot}7$ eV. It appears therefore reasonable to assign this MO to the second component of the third band, with vertical IP of *ca.* 13·4 eV.

Since all high-energy CH_2 and CH levels have already been accounted for in the spectrum, the first and second bands can only arise from CC MO's. This is confirmed by the fact that the CC level $4t_2$ in neopentane ionizes in the same spectral region, *i.e.*, at 11·3 eV. According to Table 1 the only possible candidates are the t_1, the e and one component of the t_2 CC levels. From the spectrum it appears that the e level coincides with one of the t MO's. This suggests that the CC level ordering in adamantane is not that dictated by the nearest neighbour CC—CC interaction only as this would give rise to three equidistant levels of order $t_1 > t_2 > e$. We therefore conclude that the transannular (through-space) interaction between the individual CC bonds has to be included into the bonding scheme. In order to extract the hitherto unknown parameters w and x from the spectrum, we diagonalized the EO matrices for the t_1, t_2 and e levels, taking into account all matrix elements and using trial values for w and x. As expected, both parameters turned out to be negative ($w \approx -1{\cdot}1$ eV; $x \approx -0{\cdot}1$ eV), and the resulting orbital sequence was $t_2 > t_1 \approx e$, that is, different from that dictated

by the parameter e alone. This level reversal is clearly associated with the fact that the nearest neighbour and transannular CC interactions oppose each other in t_1, whereas they work in the same direction in t_2.

Thus the whole of the adamantane spectrum is qualitatively understood, except that the relative order of the closely spaced levels $(2t_1, 3e)$, $(1t_1, 6t_2)$ and $(5t_2, 5a_1)$ is still open to dispute. It is hoped that an *ab-initio* calculation, which is in progress in our laboratory, will shed some light on this problem.

The strongest evidence for the correctness of our bonding scheme comes from the silamantane spectrum (Fig 2), the essential features of which are readily understood on the basis of the larger SiC distance and the smaller electronegativity of Si.

In analogy with adamantane the shoulder at 9·7 eV is assigned to a t_2(SiC) ionization, the broad feature extending from 10 to 11·6 eV to unresolved t_1(SiC) and e(SiC) ionization. The reduction in splitting and the trend to lower IP's are due to diminished nearest neighbour and transannular SiC—SiC interactions and the higher self-energy of the SiC bond. As was the case in adamantane, the band due to t_1 and e ionization has the same IP as the t_2 band in the corresponding reference molecule, tetramethylsilane.[11]

From its position (*cf*[12] SiH_4) and intensity, the next band at 12 eV can only arise from the t_2 component of the principally SiH bonding orbitals. Since the t_2/a_1 splitting is expected to be smaller than in adamantane, ionization from the a_1 component should occur somewhere between 14 and 15 eV. The weak band at 15·5 eV would then be analogous to the 16·96 eV band in adamantane.

Similarly the assignment of the remaining bands at 13·1 and 14·4 eV to the πCH_2 levels t_1 and t_2 is straightforward. The reduced separation of these bands reflects again the diminished through-space interactions between the methylene groups. It is remarkable, however, that the centre of these bands is found at 13·7$_5$ eV rather than at *ca* 14·1 eV as in adamantane. This shift to lower IP's could be due to an inductive effect or to weaker interaction between the semi-localized MO's t_1(CC) and $t_1(\pi CH_2)$. The former explanation is preferred as a similar shift has been observed on passing from neopentane to tetramethylsilane.

To summarize, there exists a close one-to-one correspondence between the bands of the two molecules, except that the two components of the third adamantane band are well resolved in the silamantane spectrum, due to the different self-energies of the CH and SiH bonds. The band assignments set out in Fig 2 receive further support from a study[13] of the PE spectra of silamantanes bearing fluoro, chloro and methyl substituents in positions 1, 3, 5 and 7.

An assignment of the urotropine spectrum shown in Fig 3 may be advanced along similar lines. The unique feature of this molecule is of course the presence of four tetrahedrally arranged nitrogen lone-pairs which replace the tertiary CH bonds in adamantane. The first PE band is readily identified as the t_2 lone-pair combination on account of its position (*cf* first vertical IP of NMe_3: 8·5 eV), relative intensity, lack of vibrational structure and symmetrical Franck-Condon envelope. There is then a large gap between this band and the broad, unresolved feature commencing at 11·8 eV, indicating that the t_2/a_1 lone-pair splitting amounts to at least 3·6 eV. This suggests that the through-space interaction via the parameter v is enhanced by coupling with the CN bonds through the matrix element $1/\sqrt{3}(d-3r)$.

Owing to the higher electronegativity of N compared to C, the CN bonds ionize at similar energies as $t_1(\pi CH_2)$. Thus, whereas the assignment of the shoulder at 16·4 eV to $t_2(\pi CH_2)$ is beyond reasonable doubt, the true nature of the peak at 15·6 eV is uncertain. This could arise either from $t_1(\pi CH_2)$, in which case the through-space effect between the

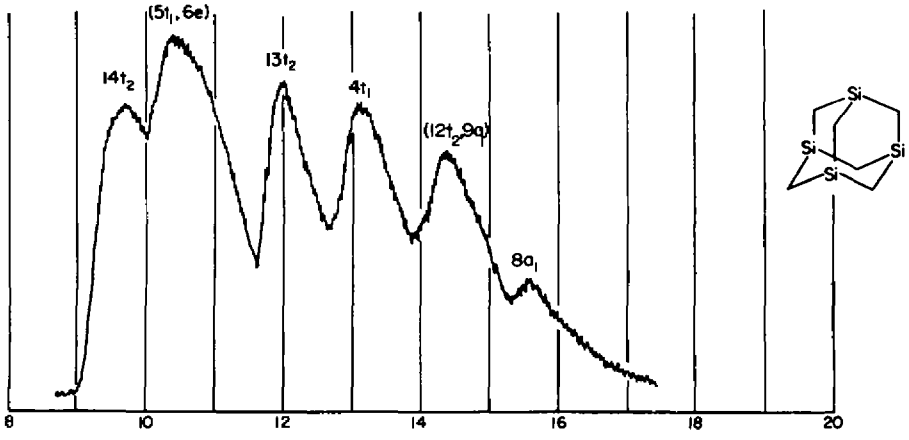

Fig 2. The PE spectrum of silamantane, with interpretation.

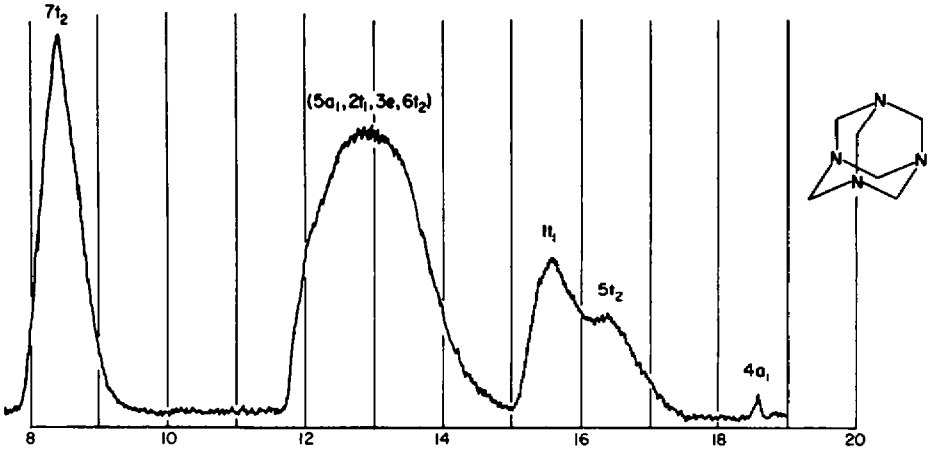

Fig 3. The PE spectrum of urotropine, with interpretation.

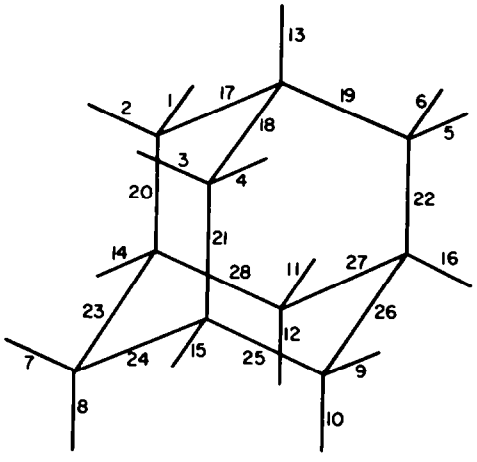

Fig 4. Molecular topography and numbering scheme for the basis EO's in adamantane.

methylene groups would be grossly reduced relative to the adamantane case, or from t_1(CN). Both alternatives imply substantial interaction between the semi-localized t_1 MO's. The ordering of the levels relating to the second band is even more doubtful.

Despite these reservations some noteworthy features were brought up in the present study which deserve comment.

First, the experimental finding that the through-space and transannular parameters t, v, w and x are sizable and negative in adamantane and urotropine, is a clear manifestation of their steric discomfort and leads us to conclude that they are by no means strain-free, despite the fact that they are devoid of eclipsed conformations, short H···H contacts and angles deviating from 109·5°. In terms of a one-electron scheme which includes overlap, interaction between formally degenerate, fully occupied orbitals should increase the total energy of the system ("closed-shell repulsion"; *cf* the case of two approaching He atoms). In an SCF theory, such a generalization is of course not possible because the total energy is not identical with the sum of the one-electron orbital energies. Experience shows, however, that these two quantities exhibit a high degree of proportionality within a series of closely related molecules, *e.g.*, the paraffins. It is therefore interesting that a recent and highly refined determination of the heat of combustion of adamantane has been interpreted in terms of a strain energy of 6·5 kcal/mole;[14] this figure exceeds previous estimates by a factor of three or four. In addition, the latest and probably most accurate electron diffraction study[15] indicated that the CC bond length in adamantane comes quite close to that found in diamond (1·5445 Å); it is thus significantly longer than that observed in ethane or propane.

Secondly, comparison of Figs 1 and 2 demonstrates that replacing the CC bonds in a given hydrocarbon by SiC bonds in such a way that the molecular symmetry is retained, results in a strikingly simplified PE spectrum: bands correlating with SiC orbitals suffer an indiscriminate shift to lower IP's, whereas CH ionizations are hardly perturbed. Furthermore, owing to the larger SiC bond length compared to CC, through-space and transannular interactions, which frequently obscure the spectra of hydrocarbons, are diminished by a factor of two or three. The overall effect of silicon substitution is thus to separate CC and CH levels without introducing additional orbitals as is the case with fluorine. This feature has been successfully utilized at several occasions by us (*e.g.*,[16,17]), and it may prove useful in other situations too.

Thirdly, the present work which unequivocally identifies the first band in the adamantane spectrum as arising from a CC level, adduces further evi-

dence that this holds also in linear, branched and cyclic aliphatic hydrocarbons, including ethane.

Acknowledgements—The author wishes to thank Professor J. N. Murrell for helpful discussions and the firm but friendly criticism of the present approach, to Professor G. Fritz (University of Karlsruhe) for a generous gift of silamantane, to Dr. J. N. A. Ridyard (Perkin-Elmer Ltd., Beaconsfield) for his hospitality and help with the PS-18 spectrometer, and to Dr. R. Boschi and Mr. B. T. Wilkins for their cooperation in the early stages of this work.

REFERENCES

[1]R. C. Fort and P. von R. Schleyer, *Chem. Rev.* **64**, 277 (1964); H. Stetter, *Angew. Chem.* Int. Ed. **1**, 286 (1962)
[2]M. J. S. Dewar and S. D. Worley, *J. Chem. Phys.* **50**, 654 (1969)
[3]G. Fritz, W. König and H. Scheer, *Z. anorg. allg. Chem.* 377, 240 (1970)
[4]R. G. Snyder and J. H. Schachtschneider, *Spectrochim. Acta* **21**, 169 (1965)
[5]R. Mecke and H. Spiesecke, *Chem. Ber.* **88**, 1997 (1955)
[6]R. T. Bailey, *Spectrochim. Acta* **27A**, 1447 (1971)
[7]R. Boschi and H. J. Lempka, unpublished results
[8]W. Schmidt and B. T. Wilkins, *Angew. Chem.* Int. Ed. **11**, 221 (1972)
[9]J. N. Murrell and W. Schmidt, *J.C.S. Faraday Trans. II* **68**, 1709 (1972)
[10]G. G. Hall, *Proc. Roy. Soc.* **205A**, 541 (1951); D. F. Brailsford and B. Ford, *Mol. Phys.* **18**, 621 (1970)
[11]M. C. Green, M. F. Lappert, J. B. Pedley, W. Schmidt and B. T. Wilkins, *J. Organomet. Chem.* **31**, C55 (1971)
[12]A. W. Potts and W. C. Price, *Proc. Roy. Soc. London* **326A**, 165 (1972)
[13]W. Schmidt, B. T. Wilkins, G. Fritz and R. Huber, *J. Organomet. Chem.*, in press
[14]M. Manson, N. Rapport and E. F. Westrum, *J. Am. Chem. Soc.* **92**, 7296 (1970); P. von R. Schleyer, J. E. Williams and K. R. Blanchard, *Ibid.* **92**, 2377 (1970)
[15]I. Hargittai and K. Hedberg, *Chem. Commun.* 1499 (1971)
[16]R. Boschi, M. F. Lappert, J. B. Pedley, W. Schmidt and B. T. Wilkins, *J. Organomet. Chem.* **50**, 69 (1973)
[17]C. S. Cundy, M. F. Lappert, J. B. Pedley, W. Schmidt and B. T. Wilkins, *Ibid.* in press.