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THROUGH-BOND INTERACTION IN 1-AZA-ADAMANTANE DERIVATIVES[a]

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Abstract—The photoelectron spectra of 1-aza-adamantane, 1-aza-adamant-4-one and 1-aza-adamant-4-methylene are described and compared with those of the corresponding adamantane analogues. In the 1-aza-adamantane derivatives a through-bond interaction between the nitrogen lone-pair and the 4-substituent is observed. This through-bond interaction is discussed in relation with the sigma-coupled transition observed in the electronic absorption spectrum of 1-aza-adamantane derivatives, and in relation with their relative basicity both in solution and in the gasphase.

INTRODUCTION

Through-bond interaction between nonconjugatively connected π- or n-electron chromophores has been studied extensively[1-6] by photo-electron (PE) spectroscopy.

Most cases described involve interaction between equivalent groups as in the well documented[1,2,7] example of 1,4-diazabicyclo [[2.2.2]octane (DABCO).

For DABCO the first two ionization potentials observed by PE spectroscopy can be attributed to the symmetric (S_n) and antisymmetric (A_n) combinations of nitrogen lone-pair orbitals (*cf* Fig 1). The large gap between S_n and A_n is easily understood (at least qualitatively) from the symmetry allowed mixing of S_n with the symmetric upper σ-orbital (S_{C-C}) a mixing which is symmetry forbidden for A_n.

Examples of through-bond interaction between nonequivalent groups are scarce. PE measurements on some γ,δ-unsaturated ketones have been interpreted[5] to show through-bond interaction between $\pi_{C=C}$ and $\pi_{C=O}$ orbitals and furthermore through-bond interaction between the nitrogen lone-pair and the oxygen lone-pair has been revealed[8] by calculations and PE measurements on some α-aminoketones.

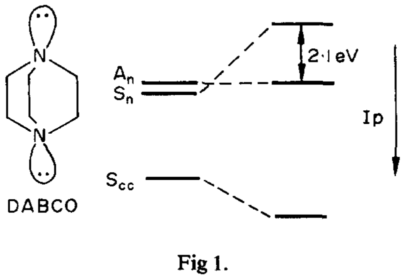
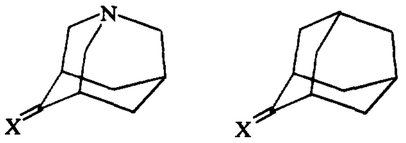


Fig 1.



1: $X = H_2$
3a: $X = CH_2$
3b: $X = O$

2: $X = H_2$
2a: $X = CH_2$
2b: $X = O$

Numbering scheme identical to Ref 10

SCHEME 1

Recently 1-aza-adamantane (**1**)[9] and some of its derivatives (**3a, 3b**)[10] (*cf* Scheme 1) have been synthesized in our laboratory. The bifunctional compounds **3a** and **3b** constitute rigid models for studying through-bond interaction between the N-lone-pair and an ethylene group (**3a**) or a carbonyl-group (**3b**).

A study[10] of the absorption and emission spectra of compounds like **3a** and **3b** in liquid solution revealed the presence of a so called "sigma coupled transition" in the near UV region, which we attributed[10] to an intramolecular charge-transfer

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[a] Part IX in the series 1-Aza-adamantanes; for part VIII see W. N. Speckamp and A. W. J. D. Dekkers, *Tetrahedron Letters* 1857 (1974).

transition resulting from excitation of an N-lone-pair electron to the π^* antibonding level of the ethylene or carbonyl group.

The appearance of this transition suggests a through-bond interaction to exist, since the spatial distance involved seems to preclude any significant direct (through-space) overlap.

In the present paper we describe a study on the PE and gas-phase absorption spectra of **1**, **3a** and **3b** using adamantane (**2**), methyleneadamantane (**2a**) and adamantanone (**2b**) as reference compounds.

RESULTS AND DISCUSSION

The He-I PE spectra of **1**, **2**, **2a**, **2b**, **3a** and **3b** are shown in Figs 2–7.

The spectrum of **2** has been discussed in detail in

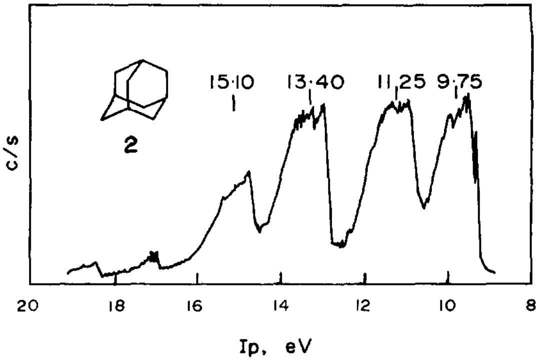

Fig 2.

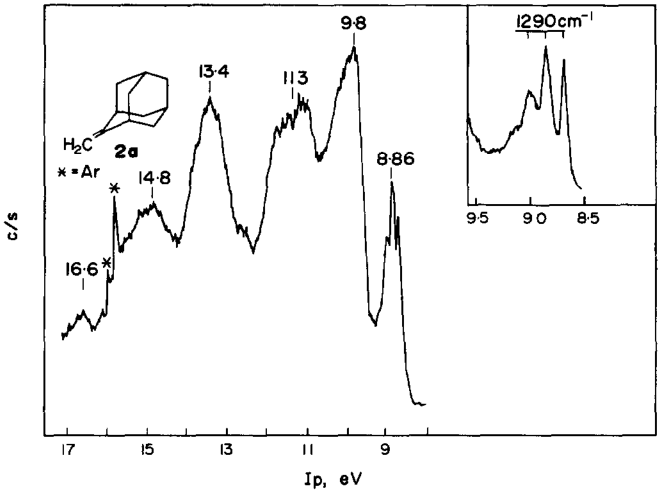

Fig 3.

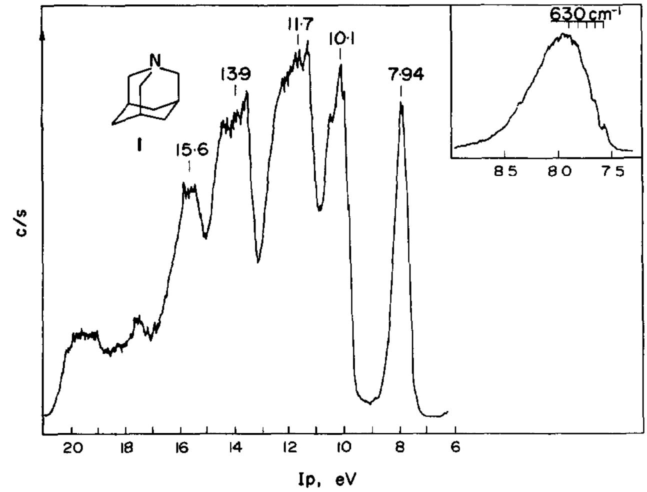

Fig 4.

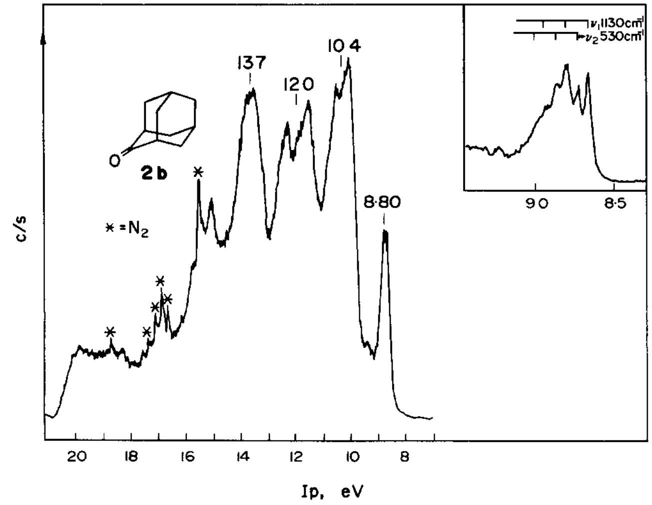

Fig 5.

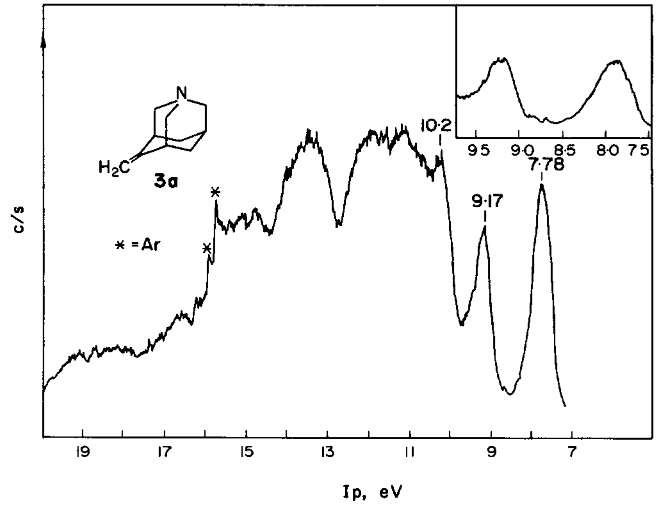

Fig 6.

several recent publications[11–14] and for **2a** and **2b** the position and nature of the first PE band have been reported.[12]

The spectra **1**, **3a** and **3b** are reported here for the first time.

The adamantane (**2**) PE spectrum shows four broad bands in the 9–16 eV region (Fig 2). Various calculations[11–14] indicate that these originate from ionizations involving the seven highest occupied MO levels, which are of t_2, t_1, e, t_2, t_1, t_2, and a_1 symmetry respectively (under T_d pointgroup) in order of increasing ionization potential (I_p).

Some uncertainty exists regarding the composition of the four broad PE bands. From the apparent splitting of the first band, this has been concluded to contain the first t_2 and t_1 levels.[11,12] At the other hand the relative intensities of the first and second band (3 : 5) have been argued[13,14] as evidence for the first band to contain only t_2 and the second t_1 plus e. The splitting of the first band can than be attributed to a Jahn-Teller distorsion of the adamantane kation radical in its first $^2T_2$ state.

The spectra of the monofunctionalized adamantanes **1**, **2a** and **2b** show a remarkable correspondence with that of adamantane in the 9–16 eV region. In addition a new band appears below 9 eV which is attributed to the N-lone-pair (**1**), ethylene π-level (**2a**) and oxygen lone-pair (**2b**) respectively. The lowered symmetry (C_{3v} for **1** and C_{2v} for **2a** and **2b**) apparently does not lead · to extensive mixing

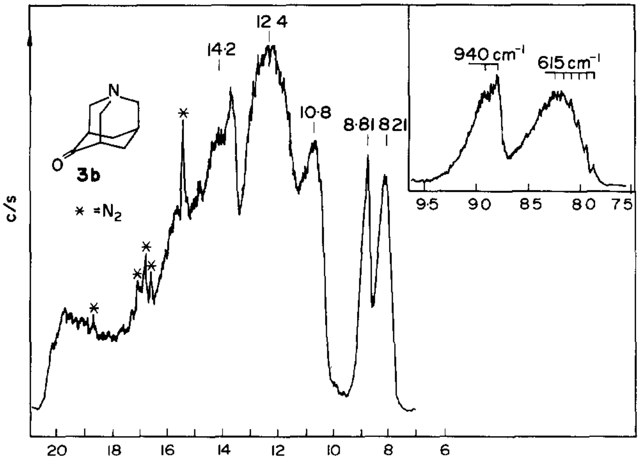

Fig 7.

between levels for which this is forbidden under T_d (i.e. adamantane) symmetry.

For **2a** (*cf* Fig 3) the four bands in the 9–16 eV region remain at the same position (within 0·05 eV) and have about the same intensity ratio as in **2**. The expected splitting of the first adamantane level under the lowered symmetry of **2a** (C_{2v}) is only evident from the shallow minimum between the 9·8 eV and the 11·3 eV bands in **2a** (*cf* Fig 3) as compared with **2** (*cf* Fig 2). In the correlation diagram (Fig 8) it is tentatively assumed that this originates from mixing between the ethylene π-level (b_1) and the b_1 component of the first adamantane level ($t_2(T_d) \rightarrow a_1 + b_1 + b_2$ (C_{2v})) shifting the latter to the 10·5 eV region.

In 1-aza-adamantane (**1**) (*cf* Fig 4) the four bands in the 9–16 eV region are all moved towards higher I_p by $0{\cdot}5 \pm 0{\cdot}05$ eV. This phenomenon has been observed before[1] in comparable compounds and can be attributed to the higher electronegativity of N as compared with C. Upon closer examination it is found that the intensity ratio† of the first two "adamantane" bands is changed from 3:5 in **2** to 2:6

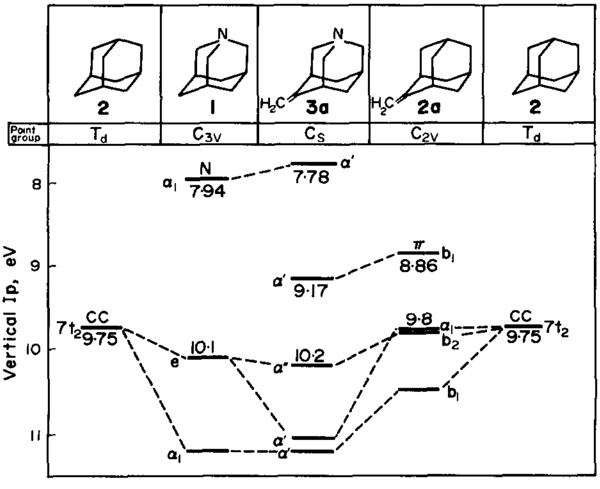

Fig 8. Correlation of upper occupied levels in **1**, **2**, **2a** and **3a** as determined by PE spectroscopy. The identification of levels at $I_p > 10{\cdot}5$ eV should be regarded as tentative. Symmetry species indicated refer to the irreducible representations of the appropriate molecular pointgroups.

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†Intensity ratio's calculated by assuming that the area under the band is proportional to the number of ionizable electrons and inversely proportional to the kinetic energy of the ejected electrons.[13]

in **1**. In the correlation diagram it is tentatively assumed that this stems from extensive mixing between the a_1 component of the first band ($t_2(T_d) \rightarrow a_1 + e$ (C_{3v})) and the a_1 N-lone-pair orbital. Such extensive mixing is evident from the broad shape of the PE band attributed to ionization of the N-lone-pair (I_p (vertical) = 7·94 eV; I_p (adiabatic) = 7·57 eV). The present interpretation lends support to the assignment[13,14] of the first broad band in the adamantane spectrum containing only one MO level (i.e. the highest t_2 level)!

In adamantanone (**2b**) (*cf* Fig 5) the inductive effect of the carbonyl group apparently shifts all bands in the 9–16 eV region towards higher I_p (0·6 ± 0·1 eV), relative to their position in adamantane. The vertical I_p of the oxygen lone-pair is found at 8·80 eV in reasonable agreement with the literature[12] value of 8·88 eV. The vibrational envelope of the corresponding PE band (Fig 5 insert) is very irregular in contrast with the more gaussian envelope reported[12] in literature. Furthermore at least two vibrational progressions (1130 cm^{-1} and 530 cm^{-1}) are observed, while the spectrum reported earlier[12] shows only one (1210 cm^{-1}). The reasons for this discrepancy are not clear at the moment.

In the bifunctionalized adamantane derivatives **3a** and **3b** (Fig 6 resp. Fig 7) symmetry is lowered to C_s. The more extensive mixing and resulting increased delocalization allowed by this low symmetry is apparent from several observations. In the < 9 eV region the PE bands loose their vibrational structure (in **3a** this is extremely dramatic for the band assigned to π-ionization) and in the 9–16 eV region the characteristic adamantane pattern is lost almost completely for **3a**.

In **3a** the N-lone-pair and the ethylene orbital are of a′ symmetry and can in principle be coupled through-bond via skeletal orbitals of a′ symmetry. The occurrence of this through-bond coupling is supported by the increased difference in I_p between the bands attributed to lone-pair and π-ionization as compared with these processes in **1** and **2a** respectively (*cf* Fig 8).

The extent of splitting ($\Delta I_p = 0{\cdot}47$ eV) is much smaller than in the case of DABCO (*cf* Fig 1). It should be stressed, however, that in DABCO this large splitting is mainly dictated by the high (D_{3h}) molecular symmetry. It thus seems that in such "asymmetric" cases of through-bond coupling its extent would more reliably be measured from the resulting delocalization than from the level splitting observed. Delocalization of the N-lone-pair in **3a** is not only indicated by the loss of vibrational structure of the corresponding PE band, but also by the low basicity of **3a** (*vide infra*).

While in **3a** the I_p for the N-lone-pair is lowered as compared to **1**, it is found to be raised in **3b**. This cannot be explained from interaction with the oxygen lone-pair which is of different (a″) symmetry nor from through-bond interaction with the carbonyl π-level (which is expected to be in the 14 eV region,[24] rather far removed from the N-lone-pair in energy). We propose the increased I_p of **3b** to result mainly from the inductive effect of the carbonyl group. Using a field model[15] with the parameters given in Fig 9, the presence of a C═O dipole of 2·8 Debye[16] is calculated to increase the I_p of an electron located on the N Atom with $\Delta I_p = 0{\cdot}33$ eV, in reasonable agreement with the observed increase of 0·27 eV.

Basicity

In connection with the PE data discussed above it is interesting to note that no simple relation[17] exists

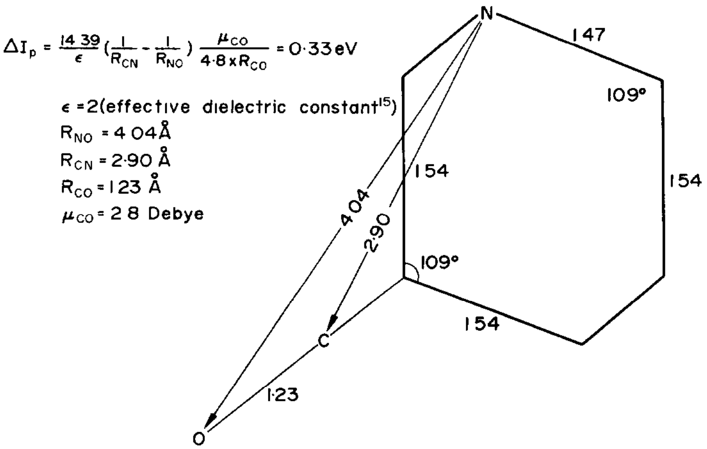

Fig 9. Projection of the 1-aza-adamant-4-one (**3b**) molecule in the mirror plane defined by the nitrogen atom and the carbonyl group, assuming standard bondlengths and angles.[23] The increase (ΔI_p) of the nitrogen lone-pair ionization potential as a result of the carbonyl dipole is calculated from a point-charge model with μ_{CO} = 2·8 Debye.

between the I_p of the N-lone-pair in **1**, **3a** and **3b** and their relative basicities. We have shown earlier[10] that the relative basicities in aqueous solution are **1** > **3a** > **3b** (pK_b values of 2·96; 4·16 and 5·43 at 22° resp.). Recently ioncyclotron measurements[18] have revealed that the same order holds in the gasphase as well. The I_p values, however, increase in the order **3a** < **1** < **3b**. We attribute the lowered basicity of **3a** to the large delocalization of the N-lone-pair in this compound, resulting from through-bond interaction with the ethylene group.

Electronic absorption spectra

The liquid (n-hexane) and gasphase absorption spectra of **1**, **2a** and **3a** are shown in Figs 10, 11.

The first absorption band in **2a** is identified as a $\pi \rightarrow \pi^*$ transition from its intensity and position and from the vibrational progression ($1430\,cm^{-1}$) it shows in the gasphase. This vibrational progression can be compared with that observed in the first PE band of **2a** ($1290\,cm^{-1}$ *cf* Fig 3).

1-Aza-adamantane (**1**) shows a gasphase spectrum which is typical[19,20] for such rigid cage amines. The first strong absorption is found at ca. $45{,}000\,cm^{-1}$ with a principal vibrational progression of $623\,cm^{-1}$. This may be compared with the progression of $630\,cm^{-1}$ observed (*cf* Fig 4) for its first PE band.

This absorption band has been attributed[20] to a $2p \rightarrow 3p$ Rydberg type of transition of the N-lone-pair. The Rydberg nature of this transition is supported[19] by its large shift from gasphase to liquid phase (*cf* Figs 10 and 11). The spectrum of **3a** shows a strong new absorption band† at *ca* $45{,}000\,cm^{-1}$. This band shows only weak vibrational structure even in gasphase and its position is found to be almost unchanged on going from gas to liquidphase.

The $2p \rightarrow 3p$ transition is not detected in **3a** possibly because it is obscured by this new absorption band. In fact the minor vibrational structure observed for the latter might stem from the underlying $2p \rightarrow 3p$ transition.

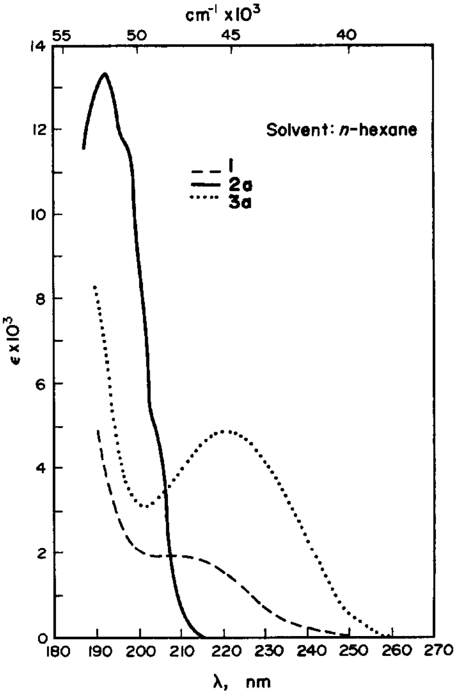

Fig 10. Liquidphase absorption spectra of **1**, **2a** and **3a**.

The $\pi \rightarrow \pi^*$ transition for **3a** is identified at *ca* $55{,}200\,cm^{-1}$ hypsochromically shifted by $3000\,cm^{-1} = 0{\cdot}37\,eV$ from its position in **2a**. This hypsochromic shift correlates remarkably well with the increased I_p for the π-level in **3a** as compared with **2a** ($\Delta I_p = 0{\cdot}31\,eV$; *cf* Fig 8). Furthermore the gap between the $\pi \rightarrow \pi^*$ transition and the "new" absorption band in **3a** ($10{,}000\,cm^{-1} = 1{\cdot}26\,eV$) correlates with the difference in I_p for the first two levels of **3a** (1·39 eV; *cf* Fig 8). Although such correlations should be treated carefully[21] the present data nevertheless support our earlier[10] conclusions that

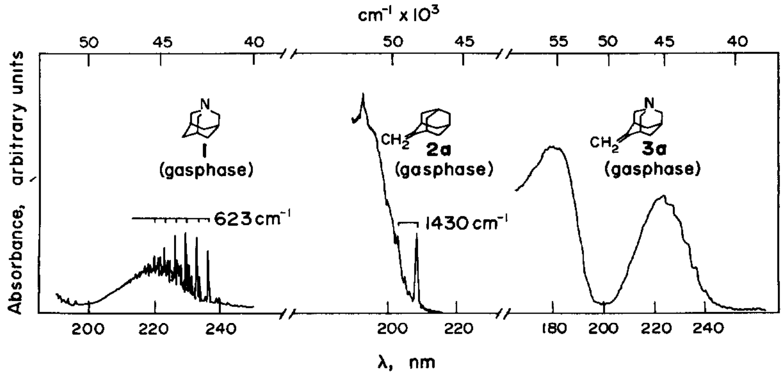

Fig 11. Gasphase absorption spectra of **1**, **2a** and **3a**.

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†This band was reported erroneously at 210 nm ($47{,}600\,cm^{-1}$) in an earlier paper.[10]

the "new" absorption in **3a** can be described as an internal charge-transfer transition in which an electron is excited from a level being mainly N-lone-pair in character to a level mainly ethylene-π^* in character.

EXPERIMENTAL

The syntheses of 1-aza-adamantane (**1**) and its derivatives **3a**, **3b** have been described elsewhere.[9,10]

Adamantanone (**2b**) was obtained commercially and was purified before use by vacuum sublimation and preparative GLC. Its structure and purity were ascertained by IR, ^{13}C-NMR[10], elemental analysis and TLC.

Methyleneadamantane (**2a**) was obtained from **2b** as described previously[22] and was purified by vacuum sublimation.

PE spectra were run on a Vacuum Generators type ESCA-2 spectrometer employing He-I emission (21·21 eV) as the ionizing radiation,[24] resolution 0·015 eV accuracy 0·02 eV. Calibration was achieved by the use of N_2 or Ar as internal references. The spectrum of adamantane (**2**) was taken from ref 13.

Electronic absorption spectra were run on a N_2 flushed Cary-14 recording spectrophotometer in the region above 187 nm and on a McPherson 125 double beam spectrometer below 187 nm. For all liquid-phase spectra n-hexane was used as the solvent with a 2 mm pathlength. Gasphase spectra were run at or slightly above room temperature employing pathlengths of 1–10 cm to obtain sufficient absorption.

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The vacuum UV spectrum of **3a** was measured by Drs. P. van de Coolwijk.

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