

Flash Vacuum Thermolysis of 1-Azabicyclo[1.1.0]butanes. Photoelectron Spectrum of 3-Phenyl-2-azabuta-1,3-diene^[‡]

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The reaction behaviour of 1-azabicyclo[1.1.0]butanes under flash vacuum thermolysis (FVT) conditions was studied. It has been found that the thermal rearrangement of title compounds produces unstable 2-aza-1,3-dienes. The formation of

these products was established by reduction, by Diels–Alder reactions and by UV photoelectron spectroscopy.

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Introduction

Substituted 1-azabicyclo[1.1.0]butanes were first synthesized in the late 1960s.^[2–4] Until recently, however, relatively little interest in synthetic applications of this highly strained and unusual ring system had been shown. Particularly important synthetic applications of 1-azabicyclo[1.1.0]butanes include additions of reagents of the X–Y type across the highly strained N–C(3) σ -bond, a variety of such reagents having thus been treated with 3- and 2,3-disubstituted 1-azabicyclo[1.1.0]butanes to produce corresponding substituted azetidines.^[5,6] The aim of our study was to determine the structures of products formed from 1-azabicyclo[1.1.0]butane under FVT conditions, by chemical trapping and by photoelectron spectroscopy. In analogy with the thermal rearrangement of bicyclo[1.1.0]butane to buta-1,3-diene,^[7,8] the corresponding 2-aza-1,3-dienes would be expected. The formation of similar 2-aza-1,3-dienes was previously observed^[9] during thermolysis of 1-azetidines (structural isomers of 1-azabicyclo[1.1.0]butane).

Results and Discussion

Thermolysis of 3-Phenyl-1-azabicyclo[1.1.0]butane

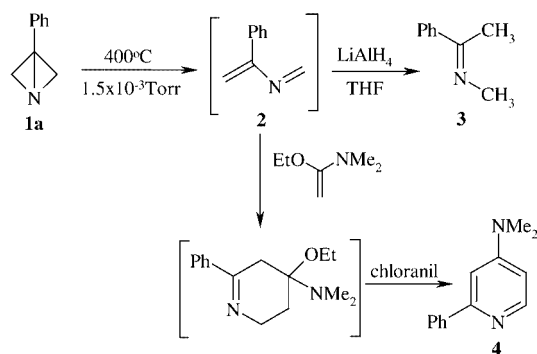
Study of the thermal rearrangement of 1-azabicyclo[1.1.0]butanes was at first performed for 3-phenyl-1-azabicyclo[1.1.0]butane (**1a**). Compound **1a** was thermolysed in the gaseous phase at $1.5 \cdot 10^{-3}$ Torr at 400 °C. (The chosen temperature was the lowest at which the starting material was found not to be present in the reaction mixture after thermolysis.) The product of the thermolysis of **1a** was collected in the cooling trap at –78 °C, then rinsed off with cold CCl₄ and examined by IR and ¹H NMR spectroscopy. This procedure enabled us to record the IR and ¹H NMR spectra of the product, which was identified as 3-phenyl-2-azabuta-1,3-diene (**2**). Warming of the pyrolysate to room temperature each time provoked the polymerisation of products. It is well known that 2-aza-1,3-dienes are too unstable to be isolated and that oligomerisation takes place in solution around 0 °C.^[9,10] In addition to the IR and ¹H NMR spectroscopic data, the formation of 2-azadiene **2** from 1-azabicyclo[1.1.0]butane was also verified chemically. The thermolysis was repeated and followed by chemical trapping of the product at low temperature, the product of the thermolysis of **1a** being rinsed from cold finger with cold THF into a suspension of LiAlH₄ in THF at –20 °C. After workup the acetophenone *N*-methyylimine (**3**) was obtained as the only product. Similarly, trapping of **2** through a Diels–Alder reaction with the electron-rich *N*-(1-ethoxyvinyl)-*N,N*-dimethylamine produced the [4+2] cycloadduct in the reaction mixture. This was aromatised to the 4-(dimethylamino)-2-phenylpyridine (**4**) with chloranil (Scheme 1).

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Scheme 1

The above reactions showed that the thermolysis of 3-phenyl-1-azabicyclo[1.1.0]butane under FVT conditions resulted in the formation of 3-phenyl-2-azabuta-1,3-diene (**2**) as a primary product. Thus, the cleavage of the azabicyclobutane ring proceeds with breaking of two opposite bonds. The 2-azadiene formed is too unstable to be isolated and fully analysed.

Independently of the chemical trapping reactions, the thermolysis of 3-phenyl-1-azabicyclo[1.1.0]butane (**1a**) was performed in a FVT oven directly coupled to the ultraviolet photoelectron spectrometer (UV-PES).^[1] We first performed studies on conformational favoured structure of 3-phenyl-2-azabuta-1,3-diene (**2**), and then compared the calculated values obtained by Density Functional Theory with the experimentally determined PES ionization potential data.

Photoelectron Spectra

The photoelectron spectrum of 3-phenyl-1-azabicyclo[1.1.0]butane (**1a**, Figure 1, a) displays four broad bands: at 9.0, 9.4, 9.9, and 10.65 eV. The precursor begins to decompose at 500 °C and disappears completely at 630 °C, giving

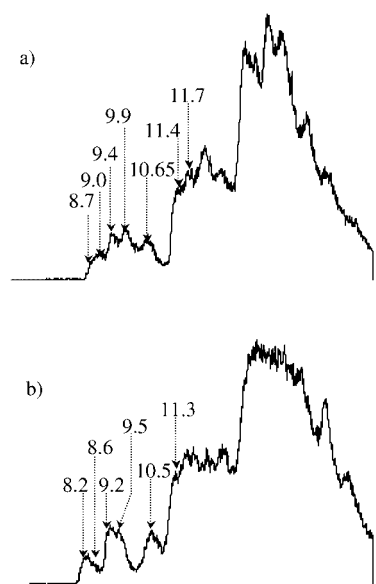


Figure 1. Photoelectron spectra of 3-phenyl-1-azabicyclo[1.1.0]butane, a) at room temp. b) at 630 °C

rise to the spectrum with two new peaks at 8.2–8.4 and 9.2–9.5 eV (Figure 1, b). We observe the disappearance of the intense band belonging to the starting compound at 9.9 eV. The product spectrum has a set of three broad bands around 8.2, 9.2, and 10.5 eV, with marked shoulders at 8.4, 8.6, and 9.5 eV.

The photoelectron spectrum of 2-azabuta-1,3-diene, previously described by Bock,^[11] has the first main band at 9.61 eV with a well resolved vibrational structure (1600 cm⁻¹ $\nu_{C=C}$ stretch), corresponding to the ejection of an electron from the $\pi_{C=C}$ bond and the second one at 10.30 eV associated with the ejection of an electron from the nitrogen lone pair.

In our case, the first broad band could be attributed to the vibrational structure, but for the analysis of the other bands, the co-existence of different conformers has to be taken into account. We consequently decided to perform studies on conformational and electronic structures of 3-phenyl-1-azabicyclo[1.1.0]butane (**1a**) and 3-phenyl-2-azabuta-1,3-diene (**2**).

Theoretical Results and Interpretation of UV Photoelectron Spectra

3-Phenyl-1-azabicyclo[1.1.0]butane (**1a**)

Two minima for the precursor **1** were confirmed by frequency calculations. The favoured conformer **A** (total energy $E_T = -403.1389$ Hartrees) corresponds to the structure with the phenyl ring in the bisector plane of the bicycle. In this case, there is no interaction between the π -system and the nitrogen atom lone pair. The full interaction of these two systems is present in the second conformer **B** (total energy $E_T = -403.1380$ Hartrees), which is less stable than **A** by 0.57 kcal·mol⁻¹. The first ionic state of **A**, calculated at 9.1 eV, corresponds to the b_1 and a_2 ionizations of the phenyl ring. The following ionizations are associated with the σ_{C-C} orbitals of 1-azabicyclo[1.1.0]butane and the nitrogen lone pair. Taking the perpendicular phenyl ring orientation (without any interaction) into account, these experimental bands should be clearly separated. Considering

Table 1. Experimentally determined and estimated values of ionization potentials, Kohn–Shan (K-S) energies (in eV) and the molecular orbital natures for two conformers **A** and **B** of 3-phenyl-1-azabicyclo[1.1.0]butane (**1a**)

A MO's nature	Δ SCF = 9.10		B MO's nature	Δ SCF = 8.35		IP exp.
	K-S	Estimated		K-S	Estimated	
b_1	-6.90	9.0–9.2	b_1-n_N	-6.49	8.6	8.7
a_2	-7.07		a_2	-7.11	9.2	9.0
$n_N-\sigma_{C-C}$	-7.32	9.4	$n_N-\sigma_{C-C}$	-7.44	9.65	9.4
$n_N-\sigma_{C-H}$	-7.83	9.9				9.9
b_1, σ_{C-C}	-9.40	11.5	b_1+n_N	-8.37	10.6	10.65
b_2	-9.57	11.7	b_2	-9.23	11.4	11.4–11.7

Kohn–Shan energies corrected by about 2.1 eV (Table 1) (see Exp. Sect. for calculation of the x shift), the first estimated ionization potential for **A** should be at 9.0–9.2 eV, the second one at 9.4 eV and the third one at about 9.9 eV. The more energetic ionizations have to be above 11.5 eV.

In the case of the **B** conformer, the positions of the first and the fourth bands are modified by the nitrogen lone pair and phenyl ring interactions, so the first ionic state is calculated to be at 8.35 eV and the fourth ionization is estimated at about 10.6 eV.

The interpretation of the photoelectron spectrum of **1** is based on free rotation of the phenyl ring because of the presence of the ionization potentials expected for **A** and also for **B** (8.7 eV shoulder and the large band at 10.65 eV).

3-Phenyl-2-azabuta-1,3-diene (**2**)

Figure 2 displays the stationary points of the potential energy surfaces obtained by varying the C=N–C=C and phenyl–C=C dihedral angles in 3-phenyl-2-azabuta-1,3-diene **2**. The **C** twisted synclinal (+sc) conformer, in which the dihedral angle between C=C and C=N is 55.6° and the phenyl ring is rotated by –30.45°, is favoured. The **T** antiperiplanar (ap) conformer (the dihedral angle between C=C and C=N of –168.0°) with the phenyl ring rotated by 61.3° is less stable than **C** by only 2.19 kcal·mol^{–1}.

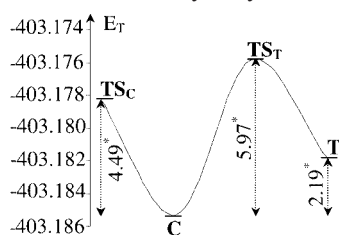


Figure 2. Calculated stationary points of the potential energy surfaces (E_T – total energies in Hartrees) for 3-phenyl-2-azabuta-1,3-diene (**2**). * values in kcal·mol^{–1}

The transition state **TS_C** (synperiplanar sp) lies at 4.49 kcal·mol^{–1} above **C** and has the planar structure (phenyl ring twisted 19.5°). **TS_T** is the highest transition state (5.97 kcal·mol^{–1} above the **C**), with anticlinical conformation (+ac) and coplanar to the C=C bond phenyl ring. The cal-

culated total energy differences are particularly small, so under our experimental conditions ($T = 630\text{ }^{\circ}\text{C}$) we should observe an equilibrium between these two forms and not only the one twisted conformer. This hypothesis may therefore explain the widening of the first three bands. These arguments, though, are based only on the total energy analysis. In order to corroborate these arguments, the first ionic states were calculated for the four conformers. They are presented in Table 2, with the Kohn–Shan energies and the estimated ionization potentials (correcting factor x of about 2 eV).

For the **T** and **TS_C** we expect the first band, corresponding to the $\pi_{C=C}$ orbital interacting with the phenyl ring (b_1 orbital), at 8.2–8.6 eV. The second one, at 9–9.2 eV, is associated with two ionizations: that of the n_N nitrogen lone pair in interaction with phenyl group and that of the a_2 orbital. The third band, at 9.5 eV, is due to the ejection of an electron from the $\pi_{C=N} - \pi_{C=C}$ orbital in interaction with the phenyl ring (b_1). The σ -ionizations would appear beyond 11.3 eV.

For two twisted conformers we would expect the first ionization potential at the lower energies (ca. 8–8.2 eV) corresponding to the ejection of an electron from the $\pi_{C=C}$ orbital interacting with the nitrogen lone pair. The second and third ones, similarly, should be closer (between 9.0 and 9.2 eV) to one another and would be associated with the π -aromatic ring (a_2) and the nitrogen lone pair. The main difference should be seen in the fourth ionization potential, due to the $\pi_{C=N} - \pi_{C=C} + n_N$ orbital, at about 10.3 eV.

The observed photoelectron spectrum corresponds well to the twisted synclinal and antiperiplanar conformer equilibrium of 3-phenyl-2-azabuta-1,3-diene.

The first intense band (at 8.2–8.4 eV) and that at 10.4–10.6 eV originate from favoured twisted **C** and **TS_T** conformers. The existence of planar **T** and **TS_C** conformers is confirmed through 8.6 and 9.5 eV ionization fingerprints.

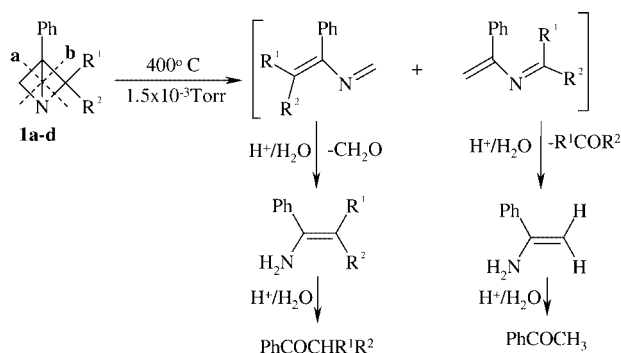
The calculated energy values for these two conformers, and the inter-conversion barriers and the good correlation between the observed and calculated ionization potentials, allowed us to infer, without ambiguity, the formation of 3-phenyl-2-azabuta-1,3-diene from 3-phenyl-1-azabicyclo[1.1.0]butane.

Table 2. Experimentally determined and estimated values of ionization potentials, Kohn–Shan (K-S) energies (in eV) and the molecular orbital natures for four stationary points of 3-phenyl-2-azabuta-1,3-diene (**2**) and corresponding total energies (E_T in Hartrees).

MO's nature	TWISTED CONFORMERS				MO's nature	PLANAR CONFORMERS				IP exp.
	C		TS _T			T		TS _C		
	<i>E</i> _T = −403.1853		<i>E</i> _T = −403.1758			<i>E</i> _T = −403.1818		<i>E</i> _T = −403.1782		
	ΔSCF = 8.06		ΔSCF = 7.88			ΔSCF = 8.47		ΔSCF = 8.09		
	K-S	Estim.	K-S	Estim.		K-S	Estim.	K-S	Estim.	
π _{C=C} -n ^σ _N -b ₁	−6.23	8.2	−6.05	8.0	π _{C=C} -b ₁			−6.27	8.2	8.2
a ₂	−6.98	9.0	−7.13	9.1	π _{C=C} -π _{C=N} - b ₁ n _N -(φ)	−6.61 −6.97	8.6 9.0	−7.20	9.1	8.6 9.0−9.2
n _N +b ₁	−7.18	9.2	−7.25	9.3	a ₂	−7.19	9.2	−6.89	8.8	
π _{C=C} -π _{C=N} +n _N	−8.24	10.3	−8.26	10.3	π _{C=C} -π _{C=N} + b ₁	−7.54	9.55	−7.72	9.65	9.5
					σb ₂	−9.58	11.59	−9.35	11.3	10.5
										11.3

Thermolysis of **1b–d** Precursors with Chemical Trapping Experiments

Let us now consider 2-substituted precursors. We showed above that, when the ring opening of 1-aza-bicyclo[1.1.0]butane **1a** to 1,3-azadiene **2** is carried out thermally, the central bond remains intact while two opposite lateral C–C and C–N bonds break with formation of the product. It is not possible to consider the regiochemistry of this reaction in the case of the symmetrical 3-phenyl-1-aza-bicyclo[1.1.0]butane molecule. However, compounds **1b–d**, substituted in the 2-position, should allow us to determine the regiochemistry of this reaction. In an unsymmetrically substituted molecule the cleavage of a pair of bonds [N–C(2) and C(3)–C(4) (path **a**) or C(2)–C(3) and C(4)–N (path **b**)] should produce two isomeric substituted 2-aza-1,3-dienes. These unstable products were trapped by acid-promoted hydrolysis at low temperature, giving the corresponding ketones (Scheme 2). The ratios of ketones formed were determined (see Exp. Sect.) from the ^1H NMR spectra (Table 3). We presumed that the relative ratios of ketones formed correspond to the ratio of primary 2-azadienes.



Scheme 2

Table 3. The ratios of ketones obtained after hydrolyses of products formed in FVT of **1a–d**

Azabicyclobutane	Path a	Path b
1a $\text{R}^1 = \text{R}^2 = \text{H}$	PhCOCH_3 100%	
1b $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{H}$	$\text{PhCOCH}_2\text{CH}_3$ 93%	PhCOCH_3 7%
1c $\text{R}^1 = \text{R}^2 = \text{Me}$	$\text{PhCOCH}(\text{CH}_3)_2$ 76%	PhCOCH_3 24%
1d $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{H}$	PhCOCH_2Ph 87%	PhCOCH_3 13%

Table 3 shows that the regiochemistry of the reaction depends greatly on the presence of the substituents in the 2-position. The thermal fragmentation of **1b–d** occurred mainly through the cleavage of the N–C(2) and C(3)–C(4) bonds (pathway **a**).

For the ring opening of bicyclobutanes to butadienes, Shevlin and McKee^[8] predicted two-step mechanisms with intermediate 3-butenylidene (especially for photolytic reaction) or cyclopropylcarbinyl biradicals for this substituent-containing system. The biradical mechanism was proposed earlier by Dewar.^[12] However, the azabicyclobutane system

is different and more complicated, because of the presence of the nitrogen atom. It is possible that the intermediate carbene (or nitrene) is not involved in the reaction. In our opinion, thermal opening of the azabicyclobutane ring proceeds as a biradical stepwise process. It seems possible that the cleavage of the N–C(2) bond produces the more stable biradical which, in a further step, is rearranged to 2-aza-1,3-diene through cleavage of the C(3)–C(4) bond. The inverse order of bond cleavage is less probable. The cleavage of the C(2)–C(3) bond affords a diradical, the stability of which changes with variation of substituents at C(2). If we presume that the C(2)–C(3) bond reacted at the first step we can explain the changes of the regiochemistry caused by a substituent at C(2).

Conclusion

Thermal degradation of unsubstituted or 2-substituted 3-phenyl-1-azabicyclo[1.1.0]butanes under FVT conditions favours the formation of the corresponding 3-phenyl-2-azabuta-1,3-dienes. The experimentally ascertained UV-PES studies and the Density Functional Theory calculations also highlight the great thermodynamic instability of the 2-azabuta-1,3-diene system and the predominance of the twisted synclinal conformer. The ring opening of azabicyclobutanes to 2-azadienes proceeds as biradical process with cleavage of the two opposite bonds, the cleavage of the C–N bond in the first step being strongly favoured.

Experimental Section

General Remarks: Melting points were determined in a Boëtius apparatus and were uncorrected. The ^1H NMR spectra were recorded on a VARIAN GEMINI 200 spectrometer with TMS as an internal standard. IR spectra were recorded on a Specord 75 IR instrument.

Starting Materials: All starting 1-azabicyclo[1.1.0]butanes were prepared by described procedures: 3-phenyl-1-azabicyclo[1.1.0]butane,^[4] 2-methyl-3-phenyl-1-azabicyclo[1.1.0]butane,^[4] 2,2-dimethyl-3-phenyl-1-azabicyclo[1.1.0]butane,^[4] and *cis*-2,3-diphenyl-1-azabicyclo[1.1.0]butane.^[6]

FVT: The flash vacuum thermolyses were carried out in a 30×2 cm horizontal quartz tube packed with quartz rings, electrically heated to 400 °C at 1.5×10^{-3} Torr. Compounds **1a–d** were slowly distilled into the thermolysis tube. The products were collected in a CO_2 /acetone trap.

Thermolysis of **1a**

3-Phenyl-2-azabuta-1,3-diene (2): IR (CCl_4 , 25 °C): $\nu_{\text{C}=\text{N}}$ 1640 cm^{-1} . ^1H NMR (200 MHz, CCl_4 , 25 °C): δ = 4.55 (br. s, 1 H), 4.85 (br. s, 1 H), 7.30–7.80 (m, 7 H) ppm.

Reduction of **2 with LiAlH_4 :** The product of the thermolysis of **1a** (655 mg, 5 mmol) was rinsed from the cold finger with cold THF (5 mL) at 0 °C into a suspension of LiAlH_4 (114 mg, 3 mmol) in THF (10 mL). The mixture was heated to room temperature and stirred for 1 hour, and was then hydrolysed with 20% NaOH. The organic phase was separated and the water layer was extracted with

Et₂O. The combined organic phases were dried (MgSO₄) and concentrated to give a pale yellow liquid methylimine of acetophenone (**3**, 598 mg, 90%). The IR and ¹H NMR spectra of **3** were identical with the spectroscopic data of an authentic sample of acetophenone methylimine.^[13]

Diels Alder Reaction between 3-Phenyl-2-azabuta-1,3-diene (2) and N-(1-Ethoxyvinyl)-N,N-dimethylamine: The product of the thermolysis of **1a** (655 mg, 5 mmol) was rinsed from the cold finger with cold Et₂O (5 mL) into a solution of N-(1-ethoxyvinyl)-N,N-dimethylamine (585 mg, 5 mmol) in Et₂O (10 mL) at -10 °C. The mixture was stirred at -8 °C for 24 hours and concentrated. A solution of chloranil (1.148 g, 4.8 mmol) in benzene (50 mL) was added to the residue, and the reaction mixture was stirred for 30 min. The solvent was removed under reduced pressure to give a crystalline solid. Recrystallization from a pentane/ethyl ether mixture gave pure 4-dimethylamino-2-phenylpyridine (**4**, 230 mg, 23%), identical with an authentic sample.^[14]

Acid Hydrolysis of 2-Aza-1,3-dienes 2a–d: The products of the thermolyses of **1a–d** (5 mmol) were rinsed from the cold finger with methanol (5 mL) into mixtures of 4% HCl (5 mL) and methanol (10 mL), cooled to -50 °C. After warming to room temperature, the mixture was concentrated under reduced pressure and extracted with Et₂O. The extract was dried (MgSO₄) and the solvents were evaporated, yielding mixtures of the corresponding ketones. The ratios of ketones were determined from the ¹H NMR spectra by comparison of the integrals of the singlet of the acetophenone methyl group (δ = 2.59 ppm) with the triplet of the propiophenone methyl group (δ = 1.19 ppm), the doublets of the two isobutyrophenone methyl groups (δ = 1.20 ppm) and the singlet of the deoxybenzoin methylene group (δ = 4.21 ppm), respectively.

UV-Photoelectron Spectra: The photoelectron spectra were recorded on a home-made spectrometer—three part assembly: main body spectrometer (Meca2000), equipped with a spherical analyser (Omicron), and a photon source (Focus) using HeI 21.21 eV radiation. The spectrometer was monitored by use of a microcomputer supplemented with a digital analogue converter. The spectra were calibrated on the basis of the known auto-ionization of xenon at 12.13 and 13.45 eV, and of the nitrogen at 15.59 eV and 16.98 eV. Thermolyses were carried out in a short path internal oven included in the apparatus with 2 cm distance between oven exit and ionisation head.

Computational Methods: Quantum calculations were performed with Gaussian 98.^[15] The optimization of all geometry parameters and vibrational analysis were carried out by Density Functional Theory^[16] by use of the B3LYP^[17–19] functional with a conjunction of 6-311G(d,p) basis set. Total energies of molecules (E_T in Hartrees) were uncorrected. Δ SCF – first vertical ionization potential $IP_{1v}^{calcd.}$ was calculated as the difference E_T (cation) – E_T (neutral molecule). Recent works^[20–25] have shown that ϵ_i^{KS} could be associated with experimentally determined vertical ionization potentials (IP_v) by uniform shift $x = |-\epsilon_i^{KS}(\text{HOMO}) - IP_v^{exp}|$. This approach gives a remarkable agreement with experimentally ascertained values and is justified by the fact that the first calculated vertical ionization potential $IP_v^{calcd.}$ [as the difference $E_T(\text{cation}) - E_T(\text{neutral molecule})$] lies very close to the experimentally determined values. Stowasser and Hoffman^[26] have recently shown that the localizations of KS orbitals are very similar to those obtained after HF calculations, so it is possible to determine the nature of the first ionizations and to interpret the photoelectron spectra unambiguously.

Acknowledgments

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