Electronic Structure of *exo*-Dimethylenecycloalkanes[1]

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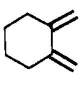
Abstract: The He(I) and He(II) photoelectron spectra of 1,2- and 1,3-dimethylenecyclobutane are presented and discussed on the basis of 4-31G and MINDO/3 orbital energies as well as by means of a simple LCBO model. It is shown that in the 1,3 derivative the through-bond interaction dominates the through-space interaction of the two localized π orbitals, leading to an inverted orbital sequence. The splitting of the π MO's in the 1,2 derivative on the other hand is explained by the fact that the π-π interaction typical for conjugated dienes is effectively reduced by a through-space interaction across the ring between the π and pseudo-π CH_2 orbitals.

Butadiene as the simplest conjugated π system has been the object of a great number of experimental as well as theoretical investigations,[2] but even nowadays it is not yet quite certain whether the second stable conformer, the existence of which was established by thermodynamical arguments in 1946,[3] occurs in the planar cis form[2b] or a nonplanar gauche form.[4] *cis*-Butadiene can be studied only in compounds where the cis conformation is sterically fixed as in the 1,2-dimethylenecycloalkanes. From the fact that the splitting of the first two bands in the photoelectron (PE) spectrum of 1,2-dimethylenecyclohexane (**1**) is about half that observed in the spectrum of 2,3-dimethylenenorbornane (**2**) it was concluded[5] that the exocyclic double bonds in the cyclohexane derivative form a dihedral angle of approximately 60°, indicating that conformational effects of the cyclohexane ring prevail over the conjugative stabilization of the planar cis form. But even in the norbornane derivative (**2**), where the two double bonds are supposed to be coplanar, the splitting of the first two PE bands is considerably smaller than in the unsubstituted *trans*-butadiene.[6] This fact could be due to several reasons, although from theoretical[2] as well as experimental[7] results it is not to be expected that the conjugative interaction is smaller in *cis*-butadiene than in *trans*-butadiene. An investigation of the substituent effect in 2,3-dimethyl-*trans*-butadiene[6] is not conclusive, as the PE spectrum of this compound is dominated by a through-space interaction which cannot occur in the cis conformer.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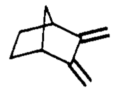
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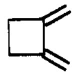
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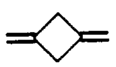
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In order to elucidate the electronic structure of the *exo*-dimethylenecycloalkanes we studied the PE spectra of 1,2- and 1,3-dimethylenecyclobutane (**3** and **4**, respectively). These compounds were chosen as a comparison of their spectra should allow an estimation of the relative importance of conjugative and hyperconjugative interactions. Also ab initio MO calculations using a 4-31G basis set are still quite feasible for these compounds and were carried out.

PE Spectra and MO Calculations

The He(I) and He(II) photoelectron spectra of **3** and **4** are shown in Figure 1; vertical ionization potentials (IP) $I_{v,j} \simeq I_{\max,j}$ are collected in Tables I and II together with negative orbital energy values obtained from ab initio and semiempirical SCF calculations.

From a comparison of the spectra with those of cyclobutene[7] and methylenecyclobutane[8,9] it is seen that σ ionization does not start below 11 eV, so that the first two PE bands certainly correspond to ionization from the π orbitals. This assignment is confirmed by the vibrational fine structure of these bands. For **3** the position of the first two bands as well as the vibrational spacing agree with the values observed for other exocyclic dienes,[5] whereas for **4** the splitting is much smaller and the vibrational spacing of the second band is larger than that of the first band, indicating that through-bond interaction leads to the inverted order of the π orbitals,[10] i.e., $\pi^+ \simeq (\pi + \pi')/2^{1/2}$ above $\pi^- \simeq (\pi - \pi')/2^{1/2}$. No σ orbitals are found above the π orbitals, as predicted from CNDO/2 calculations;[11] these high-lying σ orbitals are obviously just an artefact of the method.

Microwave data[12] indicate that **3** is planar, but no structural data are available for **4**. We therefore carried out SCF calculations for these two molecules on two different levels of sophistication. MINDO/3 calculations[13] with complete geometry optimization based on the Fletcher-Powell search procedure[14] indicate a planar structure with very similar bond lengths and bond angles for both molecules. This result is not unexpected, as it is well known that the puckering of small hydrocarbon rings is generally underestimated by MINDO/3 calculations.[15] Therefore ab initio SCF calculations were performed using a STO-3G basis set[16] with partial geometry optimization; i.e., some bond lengths and bond angles were taken from experimental data for related compounds[17] and only the remaining structural parameters were optimized. Table III shows that again similar bond lengths and bond angles are obtained for both molecules, but that for **3** in agreement with the microwave data bond lengths may be much less uniform than predicted by the MINDO/3 results. The four-membered ring is again calculated to be planar for both molecules, so that in the following we assume that **3** is of C_{2v} symmetry and **4** of D_{2h} symmetry. Thus in Tables I and II the MINDO/3 as well as the ab initio orbital energies, which were calculated using the optimized geometries of Table III and a 4-31G basis set,[18] are therefore classified according to these symmetries. The order of the MINDO/3 and the ab initio MO energies agrees except for the well-known weakness of the MINDO method[15,19] to produce high-lying σ orbitals which are found not only above the π orbital near 10 eV but also above the pseudo-π CH_2 orbital in the region near 15 eV, where three MO's are energetically close to each other. On the basis of Koopmans' approximation[20] Wiberg et al.[9] gave a least-squares fit between experimental IP's and MO energies calculated using 4-31G basis set for cycloalkenes and methylenecycloalkanes: $-\mathrm{IP}_i = 0.772\epsilon_i - 2.22$ [eV]. Using the same relation we obtained the scaled IP values of Tables I and II, which are in fair agreement with the experimentally observed PE spectra. This establishes the sequence of the π MO's, i.e., natural order in **3** (b_2 below a_2) and the inverted order in **4** (b_{1u} above b_{3g}), and also suggests an assignment of IP = 13.5 eV in **4**, which in agreement with the calculated orbital energies is separated by approximately 1 eV from the higher as well as from the lower IP's, to the π_{CH_2} combination of b_{2g} symmetry. This result will be needed in the following section.

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Table I. Vertical Ionization Potentials ($I_{v,i}$) and Negative Orbital Energies ($-\epsilon_i$) of 1,2-Dimethylenecyclobutane (**3**)[a]

symmetry	MINDO/3	4-31G calcd	4-31G scaled	exptl He(I)	exptl He(II)
$2a_2$	9.06	8.61	8.86	8.66 (1400)	8.67
$2b_2$	10.93	11.41	11.02	10.62 (1150)	10.62
$7a_1$	10.05	12.31	11.72	11.2	11.2
$5b_1$	10.18	12.52	11.88	11.7	11.7
$6a_1$	11.06	12.89	12.17	12.1	12.1
$1a_2$	12.13	13.92	12.97	12.9	12.8
$4b_1$	13.44	15.65	14.30	13.9	13.8_5
$5a_1$	14.54	17.07	15.39	~15.0	~15.0
$1b_2$	15.50	17.09	15.41	~15.3	~15.3
$4a_1$	15.02	17.45	15.70	~15.6	~15.6
$3b_1$	16.34	18.14	16.21	~16.1	~16.2
$3a_1$	21.17	22.09	19.30	~19.1	~19.0
$2b_1$	22.34	22.96	19.89	~19.7	~19.9

[a] Energies in eV; vibrational fine structure (cm^{-1}) in parentheses. Only valence orbitals are considered in labeling the MO's.

Table II. Vertical Ionization Potentials ($I_{v,i}$) and Negative Orbital Energies ($-\epsilon_i$) of 1,3-Dimethylenecyclobutane (**4**)[a]

symmetry	MINDO/3	4-31G calcd	4-31G scaled	exptl He(I)	exptl He(II)
$2b_{1u}$	9.43	9.26	9.36	9.08 (1450)	9.11
$1b_{3g}$	10.12	10.11	10.02	9.94 (1570)	9.92
$3b_{3u}$	9.90	12.05	11.50	11.0	11.0_5
$2b_{1g}$	10.73	12.21	11.65	11.4_5	11.4
$3b_{2u}$	10.56	13.52	12.66	12.4_5	12.4
$1b_{2g}$	12.79	14.89	13.70	13.5	13.5_5
$2b_{3u}$	13.70	15.87	14.50	14.2	14.2_5
$1b_{1u}$	15.33	16.74	15.12	~15.1	~15.1
$1b_{1g}$	14.90	16.80	15.21	~15.5	~15.5
$4a_g$	14.36	17.28	15.56		
$3a_g$	17.37	19.14	17.01	~17.1	~17.0
$2b_{2u}$	18.84	19.67	17.42	~17.4	~17.4
$1b_{3u}$	25.24	24.98	21.50		~21.5
$2a_g$	26.43	25.70	22.06		~22.0

[a] See footnote *a* for Table I.

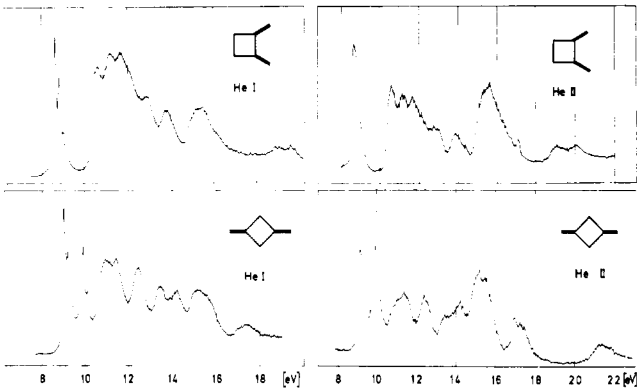


Figure 1. He(I) and He(II) photoelectron spectra of 1,2- and 1,3-dimethylenecyclobutane.

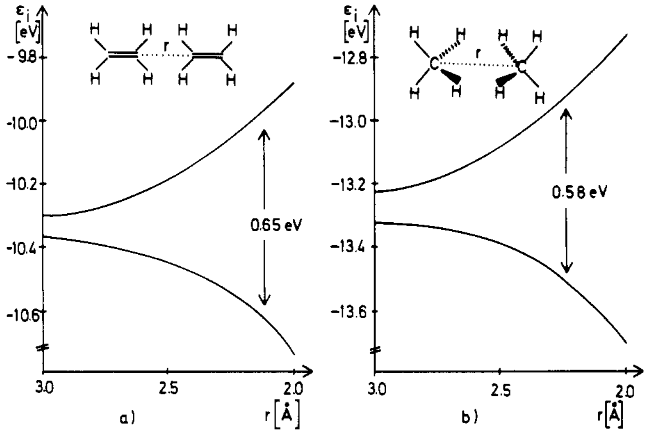
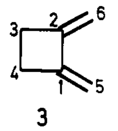


Figure 2. MINDO/3 results for π and π_{CH_2} orbital splitting as a function of the intermolecular distance (a) for two interacting ethylene molecules and (b) for two interacting methane molecules.

Table III. Bond Lengths (in Å) and Bond Angles of 1,2- (**3**) and 1,3-Dimethylenecyclobutane (**4**)



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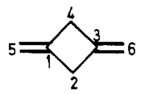

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	3 MINDO/3[a]	3 STO-3G[b]	3 exptl[c]	4 MINDO/3	4 STO-3G
C=C	1.332	1.310	1.342	1.330	1.308
$C_1—C_2$	1.518	1.471	1.485		
$C_2—C_3$	1.522	1.537	1.522	1.521	1.538
$C_3—C_4$	1.523	1.559	1.551		
$\angle C_2C_1C_4$	90.1	91.66		89.3	92.88
$\angle C_2C_1C_5$	135.6	134.6	134.0		
$\angle HC_4H$	104.0	109.1	109.3	104.0	108.8
$\angle HC_5H$	110.5	118.0	120	110.6	118.0
$C_4—H$	1.114	1.092	1.09	1.115	1.092
$C_5—H$	1.100	1.093	1.08	1.100	1.093

[a] Fully optimized geometry. [b] Partially optimized geometry (see text). [c] Structural proposal based on the microwave spectrum.[12]

Through-Space and Through-Bond Interactions

The inverted order of the π MO's indicates that in **4** through-bond or hyperconjugative interactions dominate. This system seems therefore to be particularly suited to determine the relative importance of through-space and through-bond interactions[10] and to get a semiquantitative estimate of the latter, particularly as apart from the IP's corresponding to the π MO's the IP corresponding to a π_{CH_2} combination could be identified in the PE spectrum of **4**.

If we use symmetry adapted combinations of the two localized π orbitals π and π'

$$\pi^+ = (\pi + \pi')/2^{1/2} \quad (b_{1u})$$
$$\pi^- = (\pi - \pi')/2^{1/2} \quad (b_{3g})$$

and of the pseudo-π CH_2 group orbitals ϕ and ϕ'

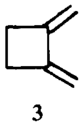
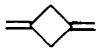
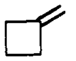
$$\phi^+ = (\phi + \phi')/2^{1/2} \quad (b_{1u})$$
$$\phi^- = (\phi - \phi')/2^{1/2} \quad (b_{2g})$$

to describe the π system by a simple LCBO model[21] within the framework of the HMO approximation, we need the following self-energies and cross terms:

$$A_{\pi\pi} = \langle\pi|\mathcal{H}|\pi\rangle,\ A_{\phi\phi} = \langle\phi|\mathcal{H}|\phi\rangle,$$
$$B^*_{\pi\pi'} = \langle\pi|\mathcal{H}|\pi'\rangle,\ B^*_{\phi\phi'} = \langle\phi|\mathcal{H}|\phi'\rangle,\ B_{\pi\phi} = \langle\pi|\mathcal{H}|\phi\rangle^{22}$$

i.e., a total of five parameters are needed out of which $B_{\pi\phi}$ describes the through-bond interaction which we are looking for. Three parameters can be determined from the PE spectrum, as three bands have been assigned to MO's of π symmetry. To get the remaining two values we decided to take for the relatively small through-space interactions $B^*_{\pi\pi'}$ and $B^*_{\phi\phi'}$ theoretical values. Figure 2 shows the splitting of the π MO's of two ethylene molecules and of the pseudo-π CH_2 MO's of two methane molecules for C···C distances between 2.0 and 3.0 Å, obtained from MINDO/3 calculations. This splitting should be equal to $2B^*_{\pi\pi'}$ or $2B^*_{\phi\phi'}$, respectively, and it is seen that for the distances of interest $|B^*_{\pi\pi'}| > |B^*_{\phi\phi'}|$. Choosing

Table IV. Comparison of π Orbital Energies Calculated by Means of the LCBO Model with Experimental Ionization Potentials (Energies in eV)

 3			 4					
symmetry	$-\epsilon_\pi$	IP	symmetry	$-\epsilon_\pi$	IP	symmetry	$-\epsilon_\pi$	IP
$2a_2$	8.77	8.66	$2b_{1u}$	9.09	9.08	$3b_2$	9.39	9.35
$2b_2$	10.84	10.62	$1b_{3g}$	9.95	9.94	$2b_2$	12.40	12.72
$1a_2$	12.74	12.9	$1b_{2g}$	13.50	13.5	$1a_2$	13.50	13.53
$1b_2$	15.86	15.41 (4-31G)	$1b_{1u}$	15.66	15.12 (4-31G)	$1b_2$	16.41	15.72

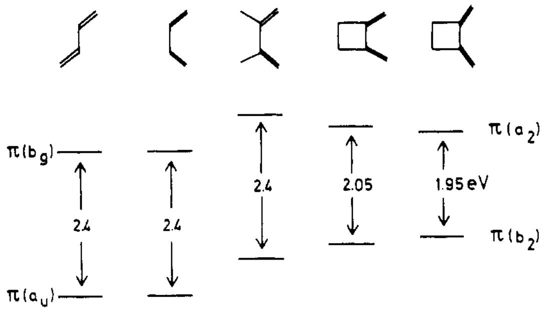


Figure 3. The influence of different structural features on the splitting of the π orbital energies in 1,2-dimethylenecyclobutane.

$B^*_{\pi\pi'} = -0.35$ eV and $B^*_{\phi\phi'} = -0.30$ eV, we obtain from the assignment of the PE bands at 9.94 and 13.5 eV to the b_{3g} and b_{2g} MO respectively

$$\langle \pi^- | \mathcal{H} | \pi^- \rangle = A_{\pi\pi} - B^*_{\pi\pi'} \text{ or}$$
$$A_{\pi\pi} = -9.94 - 0.35 \simeq -10.3 \text{ eV}$$

and

$$\langle \phi^- | \mathcal{H} | \phi^- \rangle = A_{\phi\phi} - B^*_{\phi\phi'} \text{ or}$$
$$A_{\phi\phi} = -13.5 - 0.30 = -13.8 \text{ eV}$$

in agreement with the value given by Heilbronner et al.[23] for $A_{\pi\pi'}$ and from the 2 × 2 secular problem for the b_{1u} MO's one obtains

$$9.08 = (A_{\pi\pi} + B^*_{\pi\pi'} + A_{\phi\phi} + B^*_{\phi\phi'})/2 - [4B^2_{\pi\phi} + (A_{\pi\pi} + B^*_{\pi\pi'} - A_{\phi\phi} - B^*_{\phi\phi'})^2/4]^{1/2} \text{ or}$$
$$B_{\pi\phi} = -1.40 \text{ eV}$$

For this value of $B_{\pi\phi}$ the second root of the b_{1u} secular problem is calculated to be at −15.7 eV, in fair agreement with the value of −15.12 eV obtained for this orbital energy from the 4-31G calculation (Table II). These values fall just into that part of the PE spectrum where three ionizations are so close together that an unequivocal assignment is not possible.

In 1,2-dimethylenecyclobutane the symmetry adapted orbitals π^+ and ϕ^+ are of b_2 symmetry and π^- and ϕ^- of a_2 symmetry. Choosing for the conjugated π bonds the butadiene value $B_{\pi\pi'} = -1.2$ eV[6] and setting as a first approximation $B_{\phi\phi'} = B_{\pi\phi} = -1.40$ eV and $B^*_{\pi\phi'} = B^*_{\phi\phi'} = -0.30$ eV, we obtain the results given in Table IV.

The experimental values for the first two IP's, which correspond to π ionization, are reproduced fairly well. The good agreement of the other two values with the orbital energies obtained from the 4-31G calculation for the pseudo-π CH_2 orbitals of a_2 and b_2 symmetry respectively confirms the consistency of our parameter set.

Our value $B_{\pi\phi} = -1.40$ eV for the through-bond interaction is slightly more negative than the value −1.20 eV found for the conjugative interaction of two neighboring CC double bonds[6] and somewhat smaller in absolute value than the value of −1.70 eV derived by Heilbronner et al.[23] from the PE spectrum of 1,4-cyclohexadiene. This discrepancy is partly due to the assignment of the PE band at 14.7 eV to the pseudo-π CH_2 orbital by Heilbronner; using the value 13.8 eV instead, which appears to be equally consistent with the spectrum of 1,4-cyclohexadiene, leads to a value of $B_{\pi\phi} = -1.5$ eV, much closer to our value. Symmetry arguments show that for methylenecyclobutane a combination of π_{CH_2} orbitals is the only occupied MO of a_2 symmetry. Therefore this orbital should have the same energy as the combination ϕ^- in **4** (cf. the LCBO results in Table IV). The fact that the corresponding PE band is indeed found at 13.53 eV[9] is taken as confirmation of the assignment of the pseudo-π CH_2 orbital, which forms the basis of the parametrization of our LCBO model.

Discussion

The analysis of the PE spectra of **3** and **4** showed that the through-bond as well as the trough-space interactions of π orbitals with the pseudo-π CH_2 orbitals determine the electronic structure for the *exo*-methylene derivatives of cyclobutane. For 1,3-dimethylenecyclobutane (**4**), the splitting of the π MO's is governed by the fact that through-bond interaction dominates the through-space interaction of the two π bonds across the ring and thus leads to the inverted order of the delocalized orbitals. For the 1,2-dimethylene derivative **3**, on the other hand, it is mainly the through-space interaction across the ring between the π orbitals and the pseudo-π CH_2 orbitals which is responsible for the small splitting of the π MO's compared with other butadienes.[6] The effect of this interaction is quite obvious from the off-diagonal element H_{12} for the 2 × 2 secular problem, which is given by

$$H_{12} = 1/2\langle \pi \pm \pi' | \mathcal{H} | \phi \pm \phi' \rangle = B_{\pi\phi} \pm B^*_{\pi\phi'}$$

with the + and − sign for the orbitals of b_2 and a_2 symmetry, respectively. Thus due to $B^*_{\pi\phi'}$ the splitting of the two π MO's is effectively reduced from the value $B_{\pi\pi}$ of the unsubstituted butadiene to a value which for the present choice of orbital energies $\epsilon(\pi)$ and $\epsilon(\phi)$ is close to $B_{\pi\pi} - B^*_{\pi\phi'}$; i.e., the through-space interaction is responsible for a reduction of the splitting ΔI_π of the IP's of the π levels from 2.40 eV to approximately 2.05 eV. The difference between this value and the experimental value of 1.96 eV may be explained either by an increased length of the formal CC single bond or by an increased angle of the exocyclic butadiene system as compared with a sterically unhindered butadiene. Whereas the MINDO/3 results indicate a considerable lengthening of the CC single bond, the STO-3G calculations do not support this result (Table III). On the other hand, both methods lead to CCC angles close to 135°, which again according to both methods should reduce the splitting ΔI_π by $\simeq$0.1 eV as compared to a CCC angle of 120°. We therefore explain the π ionization potentials of **3** as indicated in Figure 3.

Experimental Section

Photoelectron Spectra. The PE spectra were measured on a modified PS 16 spectrometer from Perkin-Elmer Ltd (Beaconsfield, England); the accuracy is ±0.03 eV for bands with vibrational fine structure and ±0.05 eV for unresolved bands.

Compounds. The compounds were prepared using literature methods and purified by preparative gas chromatography. Identity and purity was confirmed by IR and NMR spectroscopy: 1,2-dimethylenecyclobutane (**3**) was obtained from *trans*-1,2-cyclobutanedicarboxylic acid by Cope elimination as reported by Doering and Dolbier;[24] 1,3-dimethylenecyclobutane (**4**) was obtained as described by Caserio and Roberts[25] from 3-methylenecyclobutanecarbonitrile[26] prepared from allene and acrylonitrile.

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On the Assignment of the Photoelectron Spectrum of *trans*-Oxalyl Fluoride

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Abstract: The ionization potentials of *trans*-oxalyl fluoride are computed by a many-body Green's function method. The ordering of the ionization potentials is according to the calculations: $7a_g(n_+)$, $6b_u(n_-)$, $2b_g(\pi)$, $2a_u(\pi)$, $6a_g$, $5b_u$, $5a_g$, $1b_g(\pi)$, $4b_u$, $1a_u(\pi)$. The computed splitting between the n_+ and n_- ionization potentials is 2.1 eV and between the first two π ionization potentials 0.5 eV.

I. Introduction

In a recent publication Frost et al.[2a] presented the photoelectron spectra (PES) of the oxalyl halides $(COX)_2$ with X = F, Cl, and Br. The spectra were interpreted based on the assumption that the trans form of these molecules predominates in the gas phase. In fact the molecules can exist in trans, cis, and gauche forms and little is known at present about the equilibrium in the gas phase (see ref 2a for a summary and appropriate references). The PES in conjunction with variable temperature spectroscopy led to the conclusion that one form (probably the trans form) predominates in the gas phase, but other conformational isomers are present too. Based on calculations it was expected that two of the possible isomers have similar values of the ionization potentials (IPs) and that the third one differs in the IPs. Semiempirical calculations and the known PES of related oxalyl compounds were taken as an aid in assigning the spectra. The assignment proved, however, to be a difficult task—in particular for oxalyl fluoride—because of the closely spaced bands and the complex and sometimes diffuse vibrational structure in the spectra. Thus only a tentative assignment was given for oxalyl fluoride and only certain bands were identified. Since this molecule is still small enough so that reasonably accurate calculations can be performed on it a theoretical assignment of the PES of this molecule will be given here. The IPs are calculated by an ab initio many-body Green's function method which includes the effect of electron correlation and reorganization.[2b] This method has been successfully applied to a fairly large number of molecules and high accuracy can be achieved (see ref 3 and references cited therein). The results of these calculations are presented in the following section.

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