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Negative Ion States of Cyclopentadiene Derivatives

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Abstract: Gas-phase electron transmission spectra (ETS) have been determined for 1,3-cyclopentadiene (**1**), spiro[4.4]-nona-1,3-diene (**2**), spiro[2.4]hepta-4,6-diene (**3**), and 6,6-dimethylfulvene (**4**). Resonances were observed at 1.19 and 3.3 eV for **1**, at 0.72 and 3.3 eV for **2**, at 0.90 and 3.3 eV for **3**, and at 3.1 eV for **4**. In addition, the observation of a large increase in the ion current at the collision chamber wall for electron energies at and below 0.2 eV for **4** suggests that the attachment energy is ≤ 0.2 eV. The electron affinities of **1** and **3** were determined to be −1.05 and −0.75 eV, respectively. The relationship of these values to the structures of **1–4** and to the influence of the substituents at C_5 is evaluated with reference to minimal and extended basis set ab initio molecular orbital calculations. Evidence is provided that the second negative ion state of **1–3** is destabilized relative to that in 1,3-butadiene due to a destabilizing interaction between C_1 and C_4 in π_4* of **1–3**. Comparison of ETS data for a series of related cyclopentadiene derivatives has indicated that the energies of the first and second negative ion states in thiophene are consistent with stabilization by d orbitals on sulfur.

Introduction

The fundamental concepts of conjugation and hyperconjugation have been extensively investigated by spectroscopic techniques. Photoelectron spectroscopy has provided information concerning the higher occupied molecular orbitals, but little information is available concerning the unoccupied orbitals. In this paper we report the determination of electron attachment energies (AEs) of cyclopentadiene derivatives as determined by electron transmission spectroscopy (ETS). We also show how the analysis of data obtained by this technique is capable of producing new insights into the nature of the wave function in electronic systems and into the magnitudes of the interactions between such systems and adjacent conjugating or hyperconjugating groups.

In electron transmission spectroscopy the transparency of a sample gas to an electron beam is measured as a function of electron energy.[2,3] The transmission is inversely related to the electron scattering cross section. The process of interest here, temporary negative ion formation, occurs with large cross sections only over a narrow energy range. Many negative ions survive for 10^{-12}–10^{-14} s and decay by giving up the trapped electron. The formation and decay process appear as a rapid fluctuation in the electron-scattering cross section. The process as well as the feature in the cross-section curve is referred to as a "resonance". Experimentally the first derivative of the transmitted current as a function of energy is examined since the derivative is sensitive to a rapid change of current. Our instrument follows the design of Sanche and Schulz.[3,4]

Table I. Electron Affinities and Attachment Energies of Cyclopentadiene Derivatives and 1,3-Butadiene

compound	$EA_1{}^{a,b}$	$AE_1{}^{c}$	$AE_2{}^{d}$
1,3-cyclopentadiene (1)	−1.05	1.19^{e}	3.3^{f}
spiro[4.4]nona-1,3-diene (2)		0.72	3.3
spiro[2.4]hepta-4,6-diene (3)	−0.70	0.90	3.3
6,6-dimethylfulvene (4)		<0.2	3.1
furan $(5)^{g}$		1.76	3.14
thiophene $(6)^{g}$		1.17	2.67
pyrrole $(7)^{g}$		2.38	3.44
1,3-butadiene (8)	−0.65	0.75	2.8
	-0.62^{h}	$0.62^{h,i}$	$2.8^{h,j}$

[a] First electron affinity (±0.05 eV). [b] By convention, compounds whose negative ions are unstable with respect to electron detachment have negative electron affinities. [c] First attachment energy (±0.05 eV). [d] Second attachment energy (±0.1 eV). [e] Theory: 0.96 eV; ref 8. [f] Theory: 3.40 eV; ref 8. [g] Reference 9. [h] Reference 10. [i] Theory: 0.50 eV; ref 11. [j] Theory: 3.40 eV; ref 11.

The location of a resonance is defined by an electron attachment energy (AE) which corresponds nominally to the maximum in the scattering cross section in the vicinity of the resonance. As explained previously,[5] we define the attachment energy in the derivative spectrum as the energy at the point vertically midway between the minimum and maximum that characterizes the sudden decrease in transmitted current at the resonance. If a temporary negative ion survives for a time comparable to a vibrational period, sharp structure indicating progressions of vibrational levels in the negative ion may appear in the resonance (see for example, Figure 1, top trace). In this event an adiabatic electron affinity (EA) corresponding to the lowest vibration level (vertically midway between the first minimum and the first maximum) can be obtained.

Of particular importance is the fact that the relative energies of the various negative ion states approximates the negative of the relative energies of the unoccupied SCF orbitals of the molecule *if* one assumes the validity of Koopmans' theorem.[6] Thus electron transmission spectroscopy complements photoelectron spectroscopy which provides the energies of the radical cation states which, in most cases, closely approximate the negative

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(1) (a) University of Nebraska-Lincoln; (b) University of Maryland.

(2) Review: K. D. Jordan and P. D. Burrow, *Acc. Chem. Res.*, **11**, 341 (1978).

(3) L. Sanche and G. J. Schulz, *Phys. Rev. A*, **5**, 1672 (1972); A. Stamatovic and G. J. Schulz, *Rev. Sci. Instrum.*, **41**, 423 (1970).

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(6) T. Koopmans, *Physica*, **1**, 104 (1934).

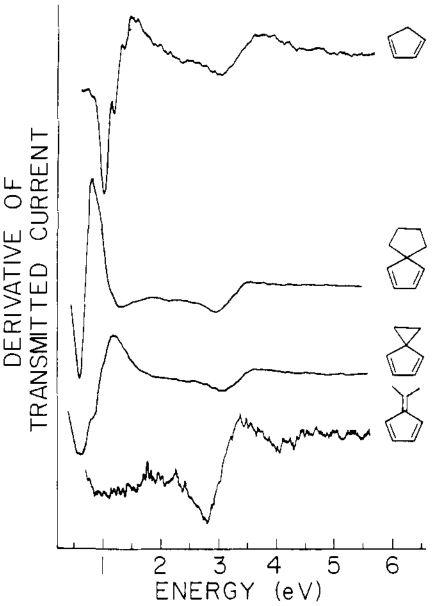
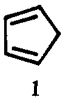


Figure 1. Spectra of **1–4** presented as the derivative of the transmitted current vs. electron energy. The 1.98-eV feature in the spectrum of nitrogen was used to calibrate these spectra.

of the relative energies of the occupied orbitals.

Results and Discussion

The electron transmission spectra of cyclopentadiene derivatives **1–4**[7] are displayed in Figure 1, and the value of the EAs and AEs



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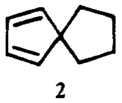

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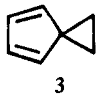

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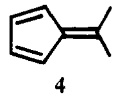

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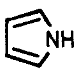

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of these and related compounds (**5–8**) are listed in Table I. The results are also presented as an orbital correlation diagram in Figure 2. As seen in Figure 1, the spectra for dienes **1–3** each display two resonances which arise from temporary capture of an electron in antibonding orbitals predominantly consisting of π_3* and π_4* of the diene moiety (AE_1 and AE_2, respectively). The

π_3*

π_4*

resonances at higher energy are broader in each case, probably

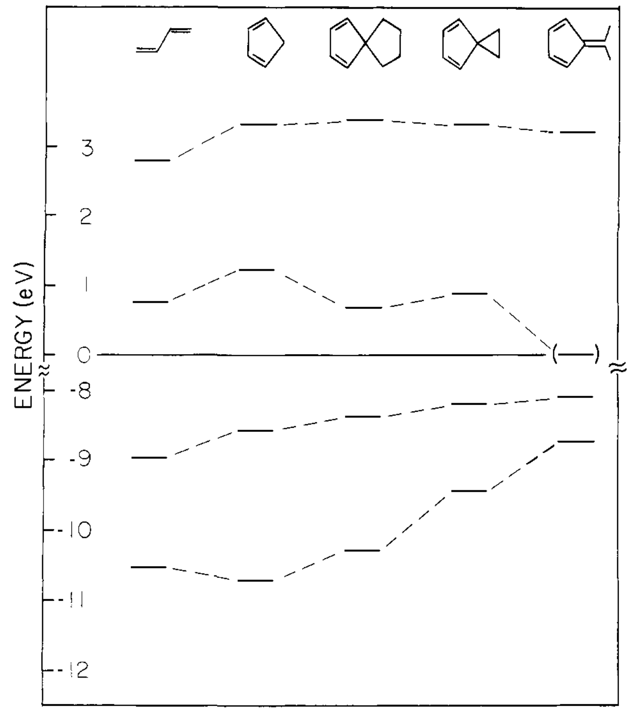

Figure 2. Correlation diagram for the π and π* orbitals of **1–4** and **8**. The energies of the bonding orbitals are based upon photoelectron spectroscopic data (ref 12).

owing largely to the shorter lifetimes of the corresponding negative ion states. A resonance below 2 eV in **4** (corresponding to AE_1 in **1–3**) could not be detected, possibly because the first negative ion state is a bound state. However, a large increase in the ion current measured at the collision chamber wall for incident electron energies at and below 0.2 eV indicates that AE_1 is near 0.0 eV.

Second Negative Ion States. In order to understand the values of AE_1 and AE_2 in **1–4**, one must consider interactions both within the π system as well as between the π system and the substituent at C_5. The interpretation of the AE_2 values will be considered first since the relevant orbital (π_4*) has a nodal plane normal to the plane of the diene carbon atoms and passing through position 5. For this reason, π interactions between π_4* of the diene unit and most substituents at position 5 will be zero or very small.

We initially consider the energy of π_4* of **1** (3.3 eV) with respect to π_4* of *s-trans*-1,3-butadiene (**8**), which has been determined to occur at 2.8 eV (Table I). Changes in C–C bond lengths do not contribute to this 0.5-eV destabilization of π_4* on going from **8** to **1** since the bond lengths of the diene unit of **1**[13] are essentially identical with those of the corresponding bonds in **8**.[14] However,

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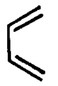

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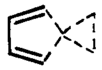

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several factors can be considered to influence the observed energy change. In order to convert the geometry of the π system of **8** into that of **1** (represented by *s-cis*-1,3-butadiene (**10**)), there must be a rotation of 180° around the C_2–C_3 bond to form **9** followed by a decrease in $\angle C_1C_2C_3 = \angle C_2C_3C_4$ from 123[13] to 109°.[14] The resultant increased C_1–C_4 π interaction in both steps will destabilize π_4*, whereas the increased C_1–C_3 and C_2–C_4 interactions which occur in the latter step will stabilize π_4*.[5]

Since the net effect is clearly one of destabilization (by 0.5 eV), this suggests that C_1–C_4 π destabilization is the dominant factor. This point was investigated by performing ab initio SCF calcu-

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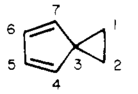
(7) Diene **3** is numbered as shown in order to be consistent with that for the corresponding carbons in **1**, **2**, and **4**. The IUPAC numbering is



(8) L. Åsbrink, C. Fridh, and E. Lindholm, *J. Electron Spectrosc. Relat. Phenom.*, **16**, 65 (1979).

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(13) D. Damiani, L. Ferretti, and E. Gallinella, *Chem. Phys. Lett.*, **37**, 265 (1976).

(14) K. Kuchitsu, T. Fukuyama, and Y. Morino, *J. Mol. Struct.*, **1**, 463 (1968); **4**, 41 (1969).

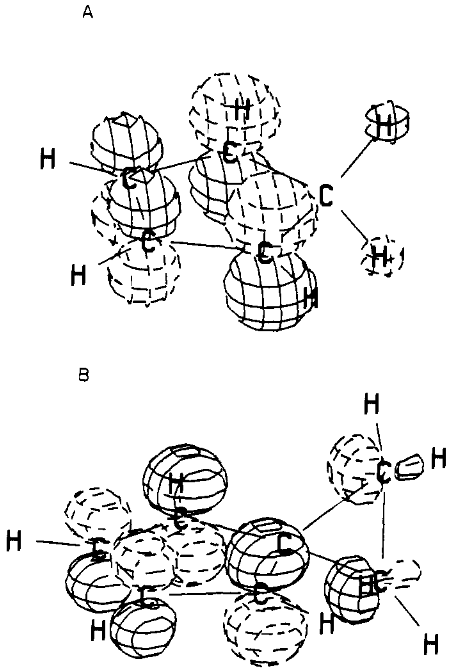

Figure 3. Three-dimensional plots of STO-3G wave functions calculated with the PSI/77 program (ref 25): (A) π_3^* of 1,3-cyclopentadiene (**1**); (B) π_3^* of spiro[2.4]hepta-4,6-diene (**3**).

lations at both minimal basis set (STO-3G) and extended basis set (4-31G and 6-31G) levels.[15] At the STO-3G level π_4^* of **8** is 0.05 eV less stable than π_4^* of **1**, whereas the latter orbital is 0.13 and 0.19 eV less stable[16-19] than the corresponding orbital in **8** at the 4-31G and 6-31G levels, respectively (Table II). This reversal of relative π_4^* levels (by over 0.2 eV) is consistent with expectations based on a significant $C_1(\pi)$–$C_4(\pi)$ destabilization since the carbon (and hydrogen) valence orbitals are more diffuse at the extended basis set level. Further support for this view is provided by the fact that π_4^* is destabilized by 0.44 eV at the 6-31G level on rotating **8** to **9** due to a $C_1(\pi)$–$C_4(\pi)$ destabilization and is then stabilized to a lesser extent (0.18 eV) on going to **10** owing to dominant stabilizing $C_1(\pi)$–$C_3(\pi)$ and $C_2(\pi)$–$C_4(\pi)$ interactions resulting from a decrease in $\angle C_1C_2C_3 = \angle C_2C_3C_4$. Our view is that temporary negative ion states are much more diffuse than is indicated on the basis of the orbitals produced by minimal basis set calculations and that "through-space" interactions may often be more significant than indicated by such calculations.

It is of considerable interest that AE_2 in **1**–**3** and the related dienes **5** and **7** has a relatively constant value of 3.3 ± 0.2 eV. What makes this series so interesting is the fact that high-quality microwave structures are available for all of these compounds (Table II) and that significant structural changes occur, from the highly localized structure of cyclopentadiene (**1**) ($r_{C_1C_2}$ = 1.344 Å, $r_{C_2C_3}$ = 1.468 Å) to the relatively delocalized structure of pyrrole (**7**) ($r_{C_1C_2}$ = 1.382 Å, $r_{C_2C_3}$ = 1.417 Å). Since there is a node between each pair of carbon atoms in π_4^* in this series, a stabilizing effect of lengthening $C_1{=}C_2$ and $C_3{=}C_4$ is apparently more or less balanced by a destabilizing effect due to shortening C_2–C_3. The lower value of AE_2 for thiophene (**6**) (2.67 eV)[9] is particularly interesting in this context and is fully consistent with the stabilization of this orbital through interaction with a $3d_{xy}$ orbital (where the z axis is coincident with the molecular axis) on the sulfur atom.[20] This point is discussed further below.

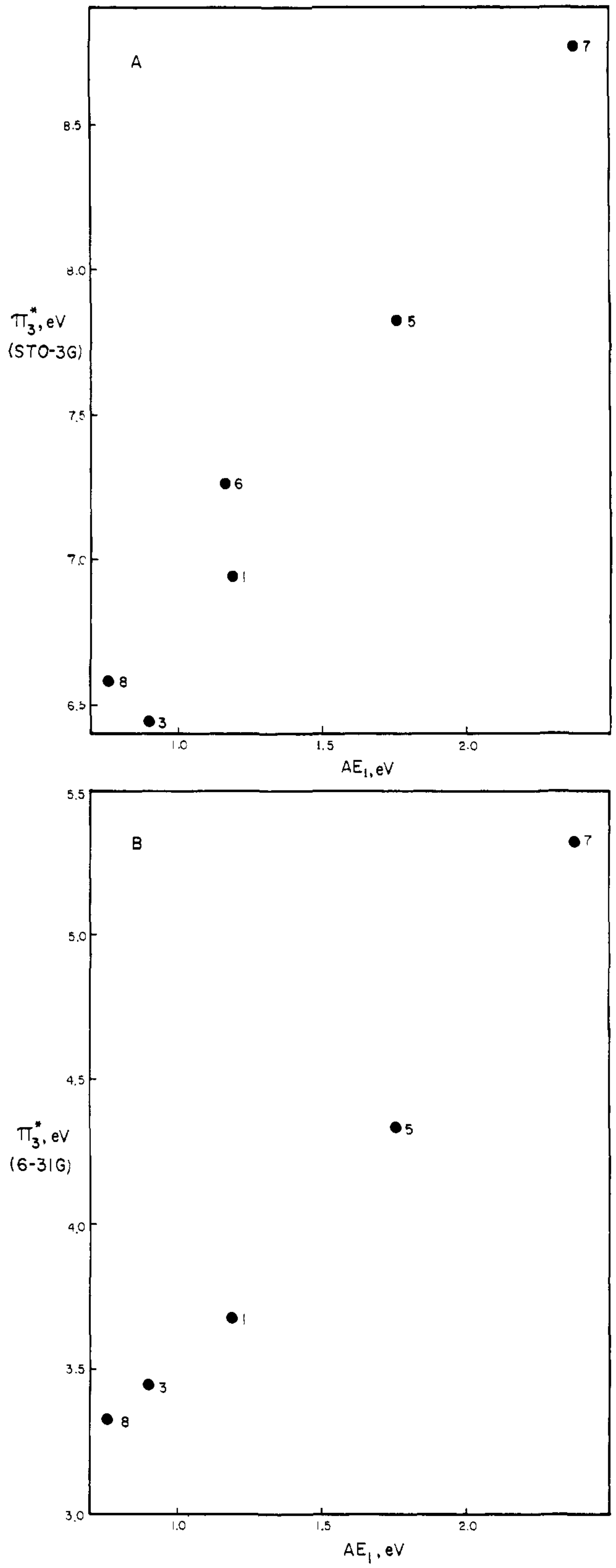

Figure 4. Plot of AE_1 vs. the π_3^* ab initio orbital energy for various dienes: (A) STO-3G basis set; (B) 6-31G basis set. The calculation for **6** failed to converge.

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(15) W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, *QCPE*, **11**, 236 (1973).

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(20) For recent ab initio calculations on thiophene, see M. H. Palmer and R. H. Findlay, *J. Chem. Soc., Perkin Trans. 2*, 974, 1223 (1975), and references cited.

Table II. Microwave (r_s) Bond Lengths and ab Initio Orbital Energies for Various Dienes

compound	bond length (Å)		orbital energy (eV)			
			π_3^*		π_4^*	
	$r_{C_1=C_2}$	$r_{C_2-C_3}$	STO-3G	6-31G	STO-3G	6-31G
1,3-cyclopentadiene (1)[a]	1.344	1.468	6.94	3.67	11.20	7.06
spiro[2.4]hepta-4,6-diene (3)[b]	1.361	1.467	6.44	3.44	11.12	7.10
furan (5)[c]	1.361	1.430	7.82	4.33	10.54	6.49
thiophene (6)[d]	1.370	1.423	7.26	*e*	10.99	*e*
pyrrole (7)[f]	1.382	1.417	8.76	5.32	11.14	7.03
1,3-butadiene (8)[g]	1.345	1.465	6.58	3.32	11.25	6.87

[a] Structure: ref 13. [b] Structure: ref 16. [c] Structure: ref 17. [d] Structure: ref 18. [e] Calculation failed to converge. [f] Structure: ref 19. [g] Electron diffraction (r_g) structure: ref 14.

Finally, we note that STO-3G calculations place two π^* orbitals (π_4^* and π_5^*) at nearly the same energy in **4**[21] (11.42 and 12.04 eV). It is most probable that the single observed resonance at 3.1 eV is actually a composite of two resonances corresponding to π_4^* and π_5^*.

First Negative Ion States. The energies of the first negative ion states in **1**–**4** as well as in **5**–**7** will be strongly influenced by the substituent at position 5 since π_3^* of the diene unit is symmetric with respect to a plane normal to the molecular plane and passing through position 5. The energy change of π_3^* of the diene unit resulting from interaction of the latter with an appropriate bonding (or antibonding) orbital of the substituent, Φ (or Φ^*), is given by

$$\Delta E = \frac{\langle \pi_3^* | H' | \Phi \rangle^2}{E_{\pi_3^*} - E_\Phi} \qquad (1)$$

where $E_{\pi_3^*}$ and E_Φ are the unperturbed energies of π_3^* and Φ, respectively, and H' is the interaction Hamiltonian. It is readily seen that ΔE is largest when π_3^* and Φ (or Φ^*) overlap strongly (large numerator) and are close in energy (small denominator). π_3^* will be destabilized by Φ of the substituent and stabilized by Φ^* of the substituent.

In order to fully analyze the interactions between π_3^* and Φ or Φ^*, it is necessary to define an unperturbed energy for π_3^* in diene units with the geometries of **1**–**7**. These values are not available experimentally, but significant conclusions can be drawn from certain trends in the data in Table I. For example, two dienes (**5** and **7**) with unshared pairs of 2p electrons at position 5 show a marked destabilization of π_3^*, whereas a stabilization is predicted by the $C_1{=}C_2$ and $C_3{=}C_4$ bond length changes which occur in these compounds relative to **1**. Furthermore, this destabilization is greater in the case of the nitrogen derivative (**7**, 2.38 eV)[9] compared with the more electronegative oxygen derivative (**5**, 1.76 eV).[9] The value of π_3^* for the carbon derivatives (**1**–**3**) is in every case much lower (1.19–0.75 eV), not only because destabilization by Φ is less than by the corresponding lone-pair orbital in **5** and **7**, but also because stabilization occurs through interaction with one or more antibonding orbitals (Φ^*) which are not present in **10** or the s-cis diene corresponding to **3** (**11**).

Note that the relatively low value of π_3^* in thiophene (**6**) (1.17 eV)[9] is consistent with a stabilization of this orbital through interaction with the sulfur $3d_{yz}$ orbital. This interpretation is further supported by the findings that (a) the inclusion of d orbitals in the basis sets produced a stabilization of the calculated singlet π^* excited states of thiophene,[22] and (b) the relative energies of the Hartree–Fock virtual orbitals (π_3^* and π_4^*) for **5**–**7** correlate well with the values for AE_1 and AE_2 when a large basis set of double ζ quality (with inclusion of d orbitals) is employed.[23]

The role of hyperconjugation or conjugation by the CH_2 and cyclopropyl groups in **1** or **3**, respectively, in determining the energy of π_3^* is of considerable interest. Experimentally, AE_1 of **1** (1.19 eV) is 0.4 eV greater than AE_1 of butadiene (**8**, 0.75 eV). This effect is similar to that of the two methyl groups in *trans,trans*-2,4-hexadiene, where AE_1 is 1.13 eV.[24] However, the calculations in Table II indicate that π_3^* in *s-cis*-butadiene (**10**) is 0.4 eV lower than that in **8** at the 6-31G level, so that π_3^* in **1** is actually destabilized by 0.75 eV by hyperconjugation with the CH_2 group. Since the corresponding destabilization is only 0.22 eV at the STO-3G level with less diffuse π_3^* and H 1s orbitals, we conclude that this destabilization arises primarily from an antibonding interaction between the CH_2 H 1s orbitals and the p(π) orbitals at C_1 and C_4 (see Figure 3A).

The orbital plot of π_3^* of **1** in Figure 3A provides an interesting insight. The large coefficient for the C_5 hydrogen 1s orbitals and the small coefficient for the C_5 p(π) orbital give π_3^* the character of a distorted D_{5h} orbital. This high pseudo-symmetry is consistent with the relatively long lifetime of the first negative ion state of **1** compared with the corresponding states for **2** and **3** (which are at lower energy), as evidenced by the much more pronounced vibrational structure in the spectrum of **1**.

An interaction similar to that discussed above for **1** is evident in spiro[2.4]hepta-4,6-diene (**3**) when the ETS data for AE_1 in **1**, **3**, and **5**–**8** are plotted against π_3^* calculated at both the STO-3G (Figure 4A) and 6-31G (Figure 4B) levels. It can be seen that the point for **3** lies below the STO-3G line of points but coincides with the 6-31G line. The conclusion that the destabilizing through-space $C_1(C_2)$–$C_4(C_7)$ interactions in π_3^* of **3** (Figure 3B) are not adequately represented at the STO-3G level is supported by the fact that π_3^* is stabilized by 0.13 eV at this level on going from **11** to **3** but is destabilized by 0.64 eV at the 6-31G level. We also suggest that the lower value of AE_1 in **2** compared to **3** might arise, at least in part, from a stabilizing interaction on π_3^* by the proximate C–H σ^* orbitals on the cyclopentane ring of **2**.

Note that the point for thiophene (**6**) lies 0.3 eV above the line of points in Figure 4A. Since d orbitals on sulfur were not included in this calculation, this either provides further support for the stabilization of π_3^* by the sulfur d_{yz} orbital or indicates that the s and p exponents in the STO-3G basis for sulfur are not balanced with respect to those for oxygen, nitrogen, and carbon.[20]

Interaction of the unperturbed diene π_3^* orbital in **4** with the low-lying π^* orbital of the exocyclic double bond lowers AE_1 to $\leq$0.2 eV. It is therefore possible that the negative ion state corresponding to capture of an electron by the lowest unoccupied molecular orbital (LUMO) of **4** is a bound state.

Summary

The value of AE_1 in **1**–**4** is primarily determined by competing interactions between Φ, the highest molecular orbital (HOMO) of the substituent, and Φ^*, the LUMO of the substituent, with π_3^* of an *s-cis*-1,3-butadiene (such as **10** or **11**). Evidence for a substantial hyperconjugative destabilization of π_3^* in cyclopentadiene (**1**) is presented. The energy of π_4^* in s-cis dienes **1**–**3** is greater than that in *s-trans*-1,3-butadiene (**8**) primarily because

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(21) Structure: J. F. Chiang and S. H. Bauer, *J. Am. Chem. Soc.*, **92**, 261 (1970).

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J. Am. Chem. Soc. **1981**, *103*, 7061–7064

of destabilizing $C_1(\pi)$–$C_4(\pi)$ interactions in the former compounds. The value of AE_1 and AE_2 in thiophene (**6**) is consistent with stabilizing interactions between the C_1 and C_4 $p(\pi)$ orbitals and the d_{yz} and d_{xy} orbitals on sulfur in π_3^* and π_4^*, respectively.

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Electronic Spectroscopy of a Diplatinum(II) Octaphosphite Complex

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Abstract: Fluorescence and phosphorescence have been observed at room temperature and at 77 K from a P–O–P bridged Pt(II) dimer. The terms assigned to these emissions, $^1A_{2u}$ and $^3A_{2u}$, respectively, were also observed in the absorption and excitation spectra. The low-temperature (~77 K) phosphorescence spectrum of the solid exhibited vibrational fine structure, which we have subjected to a Franck–Condon analysis. The prominent 118-cm^{-1} progression corresponds to the symmetrical stretching vibration of the Pt centers. We conclude that the electronic transition is $\sigma^*(5d_z) \rightarrow \sigma(6p_z)$. Low-temperature results indicate a weak spin–orbit splitting of the $^3A_{2u}$ term into E_u ($\tau = 1.58$ μs) and A_{1u} ($\tau = 880$ μs) components separated by 49.6 cm^{-1}.

In 1977 Sperline et al.[1] reported the preparation of a Pt complex isolated from a K_2PtCl_4–H_3PO_3 melt that exhibited an intense luminescence in aqueous solution. Subsequently Sadler et al.[2] characterized the complex by X-ray crystallography as an octaphosphite Pt(II) dimer bridged by four $(HO)OP$–O–$PO(OH)^{2-}$ linkages in an eclipsed configuration with a Pt–Pt distance of 2.925 Å.

Our interest in this species was sparked by the similarity of the face-to-face square planes of the dimer with the columnar structure of $[Pt(CN)_4]^{2-}$ complexes in the solid state[3] and the existence of intense luminescence from both systems. These similarities suggested to us that the dimer may model the Pt–Pt interactions in solids containing the $[Pt(CN)_4]^{2-}$ ion. In addition the Pt(II) dimer complex is isostructural and isoelectronic in the d shell with $[Rh_2(bridge)_4]^{2+}$ (bridge = 1,3-diisocyanopropane), a substance that has been extensively studied by Gray and co-workers.[4] Thus, we hoped that a study of the electronic character of the Pt(II) complex would also provide insight into the electronic structure of the Rh(I) complex and those of the less extensively investigated diphosphine-bridged isocyanide Rh(I) dimers.[5]

We report here the observation of both a fluorescence and a phosphorescence from the Pt dimer $[Pt_2(pop)_4]^{4-}$. The terms responsible for these emissions have also been observed in the absorption and excitation spectra. Moreover, the low-temperature (<77 K) phosphorescence spectrum of the solid exhibits a pronounced vibrational fine structure that has yielded geometrical information via a Franck–Condon analysis (FCA). Finally the spin–orbit splitting of the manifold responsible for the phosphorescence has been determined from the results of low-temperature lifetime measurements and related to the orbital character of the term.

Experimental Section

The complex $K_4[Pt_2H_8P_8O_{20}]\cdot 2H_2O$ ($[Pt_2(pop)_4]^{4-}$) was prepared as dark green crystals by the method of Sadler et al.[2] All computations and spectral data acquisition were accomplished with a Digital 11/34 system. Spectra were plotted with a Tektronix 4662 digital plotter. Absorption spectra were recorded on a Cary 14 spectrophotometer, and room temperature emission and excitation spectra were obtained on a Hitachi MPF-2A spectrofluorimeter. At 77 K in a Nujol mull the phosphorescence excitation spectrum of $[Pt_2(pop)_4]^{4-}$ was measured by exciting the sample with the output from a 1000-W tungsten–iodide lamp passed through a Spex Doublemate monochromator (0.5-nm resolution). The variation in phosphorescence intensity was monitored by a detection system consisting of a Spex Minimate monochromator and a thermoelectrically cooled RCA C31034A photomultiplier.

For the Franck–Condon studies low-temperature phosphorescence spectra were obtained by exciting solid samples with light from a 150-W Hg lamp filtered through 5 cm of an aqueous $CuSO_4$ solution (100 g/L) and a Corning 7-60 glass filter. Scattered exciting light was blocked by a Corning 3-73 glass cut-off filter located before the entrance slit of a 0.5-m Jarrell-Ash monochromator. Resolution was sample limited. The signal from a thermoelectrically cooled RCA C31034A photomultiplier was amplified with a Keithley picoammeter. The sample temperature was controlled in an Andonian Model 0-24/7 M-H dewar described previously.[6] All emission spectra were corrected for monochromator and photomultiplier efficiency. Excitation spectra were also corrected for monochromator efficiency and variations of lamp intensity.

Lifetimes of the phosphorescence were obtained as a function of temperature by exciting the sample in a 2:1 ethylene glycol/water glass with a Molectron UV-22 nitrogen laser. The emitted light was filtered through a KNO_2 solution, detected with an EMI 9558B photomultiplier wired for fast response,[7] and displayed on a Tektronix 549 oscilloscope. Lifetimes were determined by a linear least-squares fit of ln intensity vs. time. The sample temperature was controlled as indicated above.

Results

Absorption, Emission, and Excitation Spectra. The absorption spectrum of $[Pt_2(pop)_4]^{4-}$ in water at room temperature is shown in Figure 1. The spectrum is characterized by four maxima at 22 100 cm^{-1} ($\epsilon = 120$ M^{-1} cm^{-1}), 27 200 cm^{-1} (33 500), 33 000 cm^{-1} (849), and 37 000 cm^{-1} (1360). The extinction coefficient and position of the maximum at 27 200 cm^{-1} is in general agreement with the spectrum reported by Sadler et al.[2] The positions of the two highest energy maxima agree with those previously reported, but the extinction coefficients we report are substantially lower; the discrepancy may be due to the fact that we recorded the absorption spectrum of a crystallized sample. The relatively weak lowest energy absorption maximum has not been

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