was taken to avoid loss of product) and replaced with about 0.2 mL of hexane, and the sample was analyzed by gas chromatography.

For larger samples, a fluidized bed was employed. Quartz tubing fitted with a sintered-glass disk was connected to an oxygen-free nitrogen stream to which chlorine could be added. The zeolite sample (100–700 mg) was added to the bed and fluidized with nitrogen for 5 min. The sample was bathed in UV light from a low-pressure mercury lamp, and chlorine was slowly fed into the nitrogen stream at a controlled rate. After a measured amount of time, the light was turned off and the sample was purged with pure nitrogen. After being weighed, the samples were extracted with methylene chloride overnight and filtered as above. The samples were dried to constant weight to determine mass balances. They were then diluted with 2–5 mL of hexane and analyzed by gas chromatography.

Analysis. Product ratios were determined with a Varian 3700 capillary gas chromatograph fitted with a 12-m SE-30 column and using a Hewlett-Packard 3390A integrator. For the chlorination of dodecane, product identification was made by coinjection of authentic samples. All assignments were confirmed by both NMR (Bruker AF 250) and GC–MS (Hewlett-Packard 5988A) in both EI and CI modes.

Acknowledgment. We thank the Union Carbide Corporation for their generous contribution of zeolite samples, Dr. Jordan Spencer for his helpful comments and advice, and the Air Force Office of Scientific Research, the National Science Foundation, and the Department of Energy for their generous support of this research. A.M.B. thanks the Swiss NSF for a travel grant under project 2.660-0.85.

Registry No. $CH_3(CH_2)_{10}CH_3$, 112-40-3; $CH_3(CH_2)_{11}CH_3$, 629-50-5; $CH_3(CH_2)_{16}CH_3$, 593-45-3; $CH_3(CH_2)_{18}CH_3$, 112-95-8; $CH_3(CH_2)_{11}Cl$, 112-52-7; $CH_3(CH_2)_{11}Br$, 143-15-7; $CH_3(CH_2)_{10}CN$, 2437-25-4; $CH_3(CH_2)_{10}CHO$, 112-54-9; $Cl(CH_{212}Cl$, 3922-28-9; $CH_3(CH_2)_{12}Cl$, 822-13-9; $CH_3(CH_2)_{17}Cl$, 3386-33-2; $CH_3(CH_2)_{19}Cl$, 42217-02-7; 1-bromo-12-chlorododecane, 115141-70-3; 12-chlorododecanenitrile, 115141-71-4; 2-chlorododecanal, 16486-86-5.

The He(I) Photoelectron Spectra of Methylenecyclopropene Derivatives. Correlation with Electrochemical Oxidation

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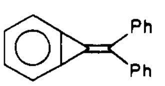
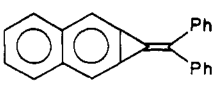
The He(I) photoelectron spectra of benzo and naphtho derivatives of 1,1-diphenylmethylenecyclopropene (DPMC) are presented. A correlation of electrochemical oxidation potentials ($E_{1/2}{}^{\bullet +}$ values) and gas-phase ionization potentials of a series of aromatic hydrocarbons is discussed. This correlation suggests that the difference in $E_{1/2}{}^{\bullet +}$ values for the two DPMC derivatives is due to structure-specific solvation of the radical cations. HAM/3 and HAM/3/CI calculations are compared with a simple structure-derived analysis of the observed photoelectron spectra. It is suggested that the effects of the fused cyclopropene groups are to be found in small ($\sim$−0.2 eV) reductions of the second or higher ionization energies.

Methylenecyclopropene (**1**), the smallest nonalternant hydrocarbon, has recently been prepared,[1] and spectral observations[2] have confirmed the existence of a significant dipolar (**1a**) contribution to its ground-state electronic structure. Characterization of **1** ↔ **1a** is complicated by its moderately high chemical reactivity, but relatively complete spectral and theoretical determinations for this system are possible and forthcoming.[3] The present work concerns results on the kinetically stable cycloproparenes **2** and **3**, the diarylated benzo and naphtho derivatives of **1**.[4]

1 **1a**



2



3

The stability, imparted by the aryl substitution, allowed some of us to study[5] the electrochemical behavior of **2** and

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[1] Staley, S. W.; Norden, T. D. *J. Am. Chem. Soc.* **1984**, *106*, 3699. Billups, W. E.; Lin, L. J.; Casserly, E. W. *Ibid.* **1984**, *106*, 3698. Maier, G.; Hoppe, M.; Lanz, K.; Reisenauer, P. *Tetrahedron Lett.* **1984**, *25*, 5465.

[2] Norden, Timothy D.; Staley, Stuart W.; Taylor, William, H.; Harmony, Marlin D. *J. Am. Chem. Soc.* **1986**, *108*, 7912–7918. Staley, S. W.; Norden, T. D.; Taylor, W. H.; Harmony, M. D. *J. Am. Chem. Soc.* **1987**, *109*, 7641.

[3] An account of the observed photoelectron spectrum of 1 is currently submitted. S. Staley, private communication.

[4] Halton, Brian; Randall, Clifford, J.; Gainsford, Graeme J.; Stang, Peter J. *J. Am. chem. Soc.* **1986**, *108*, 5949–5956.

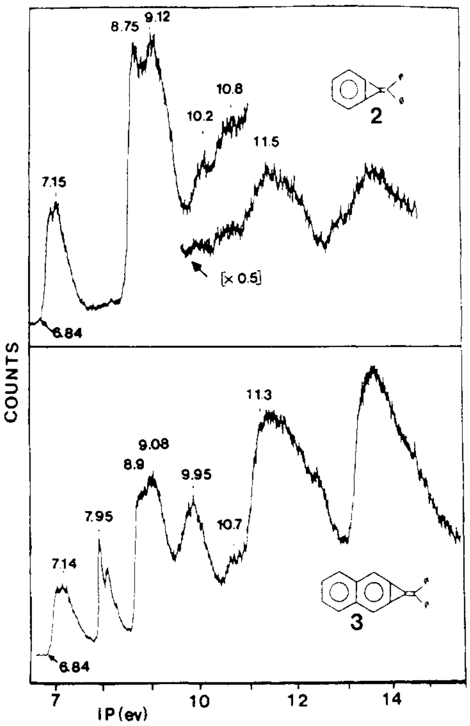

Figure 1. PE spectra of **2** and **3**.

3. A significant result of that work was the fact that the half-wave oxidation potential ($E_{1/2}^{\bullet+}$) for **3** (0.81 eV) was higher than that for **2** (0.68 eV). This ordering goes against the usual idea that the more delocalized system (**3**) should be more easily oxidized. It thus seemed of interest to investigate the photoelectron (PE) spectra of **2** and **3** to see if the $E_{1/2}^{\bullet+}$ difference corresponded to an ionization potential (IP) difference in the gas phase. We now report on our determination of the PE spectra of **2** and **3** and on an analysis of the first several ionic states for these systems. A general correlation between $E_{1/2}^{\bullet+}$ values and PES IPs for aromatic hydrocarbons is presented. This correlation suggests that solvation effects, in the electrochemical oxidation of arenes, increase with increasing IP, due to the smaller molecular size that attends the increased IP within the series. The difference in $E_{1/2}^{\bullet+}$ values for **2** and **3** is rationalized as residual differential solvation effects arising from the difference in hole density distribution.

Experimental Section

The syntheses of **2** and **3** have been published.[4] The half-wave oxidation potentials for **2** and **3** were also as previously described.[5] The photoelectron spectra were obtained from our[6] $\pi/\sqrt{2}$ sector instrument at temperatures between 50 and 100 °C. The spectra were calibrated in duplicate versus Ar,Xe, methyl iodide mixtures. The beginning resolution in each PE determination was less than 30 meV.

Results and Discussion

The PE spectra of **2** and **3** are shown in Figure 1. They indicate that the observed difference in $E_{1/2}^{\bullet+}$ values has no clear counterpart in the gas phase. The first ionization potential of **2** is essentially the same as that of **3**. This applies to both the first peak maximum (~IP(vertical), 7.145 ± 0.03 eV) and onset (~IP(adiabatic), 6.84 ± 0.03 eV). Figure 2 shows a plot of $E_{1/2}^{\bullet+}$ values [5,7a] against first IP values[7,8] (vertical) for several aromatic systems. The linear correlation predicts an $E_{1/2}^{\bullet+}$ value of 0.73 eV for both **2** and **3**. The observed value for **2** is slightly lower (0.68 eV) while that for **3** is slightly higher (0.81 eV) than the value (0.73 eV) that the linear correlation predicts.

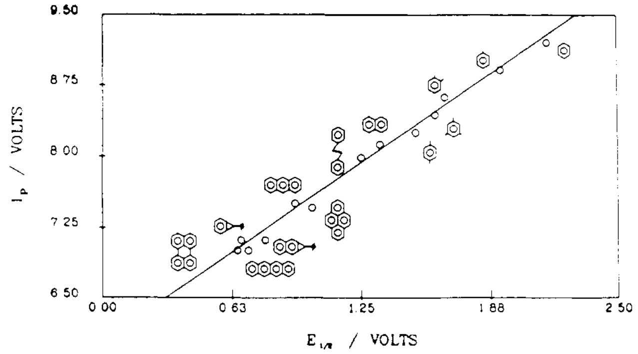

Figure 2. Correlation of $E_{1/2}^{\bullet+}$ with IP.

The regression line (correlation coefficient 0.989) shown in Figure 2 is expressed by eq 1. This can be compared

$$E_{1/2}^{\bullet+} = 0.677\mathrm{IP} - 4.112 \qquad (1)$$

with the simplistic theoretical expression given in eq 2,

$$E_{1/2}^{\bullet+} = \mathrm{IP} + \Delta\Delta G^{\circ}_{\mathrm{sol}} + \text{constant} \qquad (2)$$

where $\Delta\Delta G^{\circ}_{\mathrm{sol}}$ is the difference in solvation of the neutral (reduced) and ionic (oxidized) forms of the hydrocarbon and the constant corrects for the reference electrode potential. The linearity and less than unit slope in eq 1 suggest that $\Delta\Delta G^{\circ}_{\mathrm{sol}}$ contains a term that is proportional to IP. Equation 3 expresses this observation with $-S$ as

$$\Delta\Delta G^{\circ}_{\mathrm{sol}} = -S\cdot\mathrm{IP} + \delta\Delta\Delta G^{\circ}_{\mathrm{sol}} \qquad (3)$$

the proportionality constant and defines the residual solvation, $\delta\Delta\Delta G^{\circ}_{\mathrm{sol}}$. Equation 4 results from these definitions.

$$E_{1/2}^{\bullet+} = (1 - S)\cdot\mathrm{IP} + \delta\Delta\Delta G^{\circ}_{\mathrm{sol}} + \text{constant} \qquad (4)$$

The empirical relationship (eq 1) is obtained by neglecting the $\delta\Delta\Delta G^{\circ}_{\mathrm{sol}}$ term with S equal to 0.323 and the constant equal to −4.112 (eV). The deviations from the value (0.73 eV) predicted for **2** and **3** can be interpreted as residual solvation effects ($\delta\Delta\Delta G^{\circ}_{\mathrm{sol}}$). The values of these deviations (−0.05 eV (−1.2 kcal/mol) for **2** and +0.08 eV (+1.8 kcal/mol) for **3**) are not atypical of the other members of the series shown in Figure 2. Small structure-specific solvation effects are certainly present, and the proposed $\delta\Delta\Delta G^{\circ}_{\mathrm{sol}}$ values are one way to recognize them, at least phenomenologically.

The $-S\cdot$IP term of eq 4 may be related to recent observations[9] of the $E_{1/2}^{\bullet+}$ values of a series of molecules of high IP. In those studies it was found that the correlation

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[5] Ashley, Kevin; Foley, John K.; Mei, Qui; Ghoroghchian, Jamal; Sarfarazi, Fereshteh; Cassidy, John; Halton, Brian; Stang, Peter; Pons, Stanely *J. Org. Chem.* **1986**, *51*, 2089. Ashley, K.; Sarfarazi, F.; Buckland, S. J.; Foley, J. K.; Mei, Q.; Halton, B.; Stang, P. J.; Pons, S. *Can. J. Chem.*, in press.

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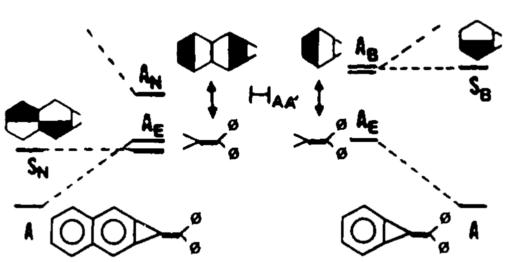
[7] Koenig, T.; Tuttle, M.; Wielesek, R. A. *Tetrahedron Lett.* **1974**, 2537–2540. Koenig, T.; Tuttle, M. *J. Org. Chem.* **1974**, *39*, 1308. (a) Ross, S. D.; Finkelstein, M.; Rudd, E. F. "Anodic Oxidation" In *Organic Chemistry, A Series of Monographs*; Academic: New York, 1975; Vol. 32, Chapter 5. Eberson, E.; Utley, J. H. P. In *Organic Electrochemistry*, 2nd ed.; Baiser, M. M., Lund, H. Eds.; Marcel Dekker: New York, Chapter 13. Yoshida, K. *Electrooxidation in Organic Chemistry. The Role of Cation Radicals as Synthetic Intermediates*; Wiley: New York, 1984. Phelps, J.; Santhanam, K. S. V.; Bard, A. J. *J. Am. Chem. Soc.* **1967**, *89*, 1752.

[8] Heilbronner, Edgar; Maier, J. P. In *Electron Spectroscopy, Theory Techniques and Applications*; Brundle, C. R., Baker, A. D., Eds.; Academic: New York, 1977; Vol. 1, pp 205–287.

[9] Dibble, T.; Bandyopadhyay, S.; Ghoroghchian, J.; Smith, J. J.; Sorfarazi, F.; Fleischmann, M.; Pons, J. *J. Phys. Chem.* **1986**, *90*, 5275.

Scheme I



between $E_{1/2}{}^{\bullet+}$ and IP changed from one that was linear and of unit slope (saturated hydrocarbons) to one of less than unit slope at the high IP–small molecular size end. The assistance to oxidation by the solvent is of greater magnitude in the high IP–small molecular size range. Reduced molecular size accompanies increased IP in the aromatic hydrocarbon series of Figure 2, and the $-S\cdot\mathrm{IP}$ term of eq 4 may be explained by the higher vacancy density per unit volume in the ions of high IP and smaller π-orbital size. The difference in $E_{1/2}{}^{\bullet+}$ for 2 and 3 is well within expectations for structure-specific solvation energy differences, which we describe by the $\delta\Delta\Delta G°_{\mathrm{sol}}$ term.

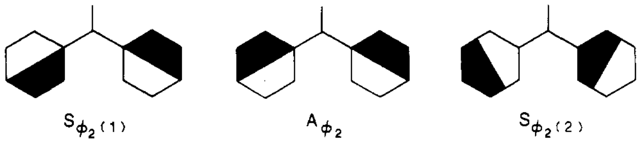
The observed (Figure 1) near equality in the first IPs of 2 and 3 can be understood by considering their π-electron systems as perturbed[10] 1,1-diphenylethenes.[11] The energetic positions and symmetries of the perturbing benzynic (2) and naphthynic (3) π-electron groups, with respect to that of the lowest ionic state of 1,1-diphenylethene[11] (4), are shown in Scheme I. The conrotation of the two phenyl groups with respect to coplanarity, shown by the X-ray structure for 2, leaves an approximate[12] C_2 axis along the exo methylene group. The labeling in Scheme I designates the basis structures as symmetric ($\mathrm{S_B}$, 2; $\mathrm{S_N}$, 3) or antisymmetric ($\mathrm{A_B}$, 2; $\mathrm{A_N}$, 3; $\mathrm{A_E}$, 4) with respect to this symmetry element. The first IPs of 2 and 3 are then describable as combinations from the appropriate $\mathrm{A_i}$ manifold.

The first naphtho ($\mathrm{A_N}$, Scheme I) hole structure in 3, which will perturb the first one derived from 4 ($\mathrm{A_E}$, 8.25 eV,[11] Scheme I), corresponds to the *second* ionic state of naphthalene ($^2\mathrm{B_{1u}}$, 8.88 eV).[8] The corresponding hole structure for 2 ($\mathrm{A_B}$, Scheme I) is one of the $\mathrm{e_g}$ pair of benzene (9.3 eV). The difference in energy between $\mathrm{A_N}$ and $\mathrm{A_E}$ is 0.6 eV (3) while that for $\mathrm{A_B}$ and $\mathrm{A_E}$ is 1.02 eV (2). The smaller difference for 3 compared to 2 leads one to expect a lower first IP for 3 as is the usual case. On the other hand, the interaction constant (H_{AA}, Scheme I) for mixing $\mathrm{A_N}$ and $\mathrm{A_E}$ (3) will be smaller than that for $\mathrm{A_B}$ and $\mathrm{A_E}$ (2). The lowered interaction constant for 3 would lead to a higher first IP in 3 compared to 2. The net result of the smaller energy gap *and* smaller interaction constant for 3 is the fortuitous equality in the first IP of 3 with that of 2.

In this very simple analysis, the ionic ground states of 2 and 3 would both be completely (π) delocalized. However, the fortuitous equality in first IPs of 2 and 3 implies that essentially the *same* (~70%) fraction of the vacancy should reside on the 1,1-diphenylethene grouping in the two ionic ground states. The fraction of the hole distributed on the benzo and naphtho grouping would also be the same (30%). The vacancy density, on a per-atom basis, would be lower in the naphtho substructure. This would be expected to lead to a lowered differential solvation energy ($\delta\Delta\Delta G°_{\mathrm{sol}}$) and hence an increased $E_{1/2}{}^{\bullet+}$ for 3 compared to 2. This explanation of the difference in the $E_{1/2}{}^{+}$ values of 2 compared to 3 is at least internally consistent since it is derived from the same physical source as suggested for the larger $-S\cdot\mathrm{IP}$ term in eq 4.

Scheme I also predicts that the second PE band for 3 should correspond to the first ionic state of naphthalene (8.15 eV, $^2\mathrm{Au}$).[8] The symmetry of this basis representation ($\mathrm{S_N}$) is such that it will not be overlap-sensitive to the attached 1,1-diphenylethene unit. The second ionic state of 3 should thus be describable as one localized on the naphtho unit with bond distance changes that correspond to those for the lowest ionic state of naphthalene itself. Indeed, the position (7.95 eV) and vibrational shape of the second PE band of 3 (Figure 1) strongly support this assignment.

Analysis of the PE spectra of 2 and 3 in terms of perturbed diphenylethene (4) ionic states can also be extended to the 9-eV region. The experimental spectrum of 4[11] shows that two ionic states are located (both) at 9.05 eV with a third state at 9.2 eV. This set is describable in terms of combinations of hole structures localized on the two phenyl groups with little or no ethene (π) cationic character. Two of the three are of S symmetry ($\mathrm{S}_{\phi2(1)}$, $\mathrm{S}_{\phi2(2)}$). The one of A symmetry ($\mathrm{A}_{\phi2}$) has low coefficients at the phenyl carbons that are joined to the ethene group, giving negligible ethene–phenyl mixing.



The $\mathrm{S_B}$ structure (9.3 eV) for 2, shown in Scheme I, is likewise isolated by symmetry from the ethene unit. Thus, for 2, at least four ionic states should reside in the 9-eV region. The observed intensity pattern in the spectrum of 2 supports this analysis since the relative area of the 8.7–9.9-eV section is 4.5 times that of the resolved 7.14-eV band. These arguments also apply to 3 (except for the $\mathrm{S_B}$ structure), and the gross appearance of the 9-eV region of the PE spectrum of 3 is expected to be similar to that for 2.

While the major features of the low-energy region of the PE spectra of 2 and 3 are simply understandable, the above analysis has ignored possible effects due to dipolar contributions analogous to **1a** in the neutral hydrocarbons and effects due to distortions of the fused benzo and naphtho groups. The X-ray data for 2[4] show a significant reduction in the bond distance between the two carbons in the fused cyclopropene ring. Table I shows results of HAM/3[13] and HAM/3/CI[14] calculations for 2 and 3. The X-ray structure was used for 2 and the additional C–H groups of 3 were simply added at naphthalene positions. These calculations predict essentially equal first ionization potentials for 2 and 3 although the calculated values are appreciably higher than observed. The high values are not too surprising since the HAM/3 transition-state method overestimates the first IP of benzene by a similar (~0.4 eV) amount. The HAM/3 method has not been previously tested on such large systems, and the results of Table I suggest that the existing parameterization may not yet be optimal for such systems.

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[10] Koenig, T.; Imre, Daniel; Hoobler, James A. *J. Am. Chem. Soc.* **1979**, *101*, 6446. Koenig, T.; Longmaid, H. *J. Org. Chem.* **1974**, *39*, 560.

[11] Maier, J. P.; Turner, D. W. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 196–206.

[12] The X-ray structures of 2 indicates nonplanarity and distortion of the cyclopropene ring. In spite of the absence of any real symmetry elements, the approximate C_2 axis along the ethene bond is useful.

[13] Lindholm, L.; Asbrink, L. *Molecular Orbitals and Their Energies by the Semiempirical HAM Method*; Springer-Verlag: Berlin, 1985.

Table I. Calculated and Observed Outer Valence PE Spectra of 2 and 3

	2			**3**		
Γ^a	obsd, eV	HAM/3	HAM/3/CI^b	obsd	HAM/3	HAM/3/CI^b
A	7.15	7.67	7.53	7.14	7.66	7.59
S_N				7.95	8.21	8.14
$S_{\phi_2(1)}{}^c$	8.75	8.97	9.02	8.91	8.88	9.09
$A_{\phi_2}{}^c$	*d*	9.00	9.10	*d*	8.92	9.17
$S_{\phi_2(2)}{}^c$	9.12	9.08	9.11	9.08	9.00	9.19
S_B	*d*	9.52	9.83			
A_B or A_N	*d*	9.67	9.79	*d*	9.40	9.33
						9.99*
A_E'	10.2	10.64	10.80*	9.95	10.02	10.55*
			11.06*			10.67*
S_N'				*d*	10.05	10.37
σ	10.8	10.79		(10.7)	10.67	

[a] Approximate symmetry. [b] An asterisk designates a state with appreciable shakeup character.[14] [c] State with vacancy localized on the diphenyl substituent. [d] Peak unresolved but present.

The position of the S_N state of **3** (7.95 eV) is shifted downward compared to the corresponding band in the spectrum of naphthalene (8.15 eV).[8] This decrease is in the direction expected for the shortened (1.355 Å) C–C distance between the two carbon atoms common to the cyclopropene and naphthalene rings. The HAM/3 calculations give a calculated shift of –0.19 eV in the S_N band for **3** compared to naphthalene at its experimental geometry. A similar shift is calculated for the S_B position in **2** compared to benzene but the S_B band is not resolved from the other four states seen in the 8.75–9.7-eV group for **2**. The lowering of the energetic position of the S_N band in the spectrum of **3**, compared to its correspondent state of naphthalene, may be taken as a measure of the net shift attributable to the shortened bond length in the ring fusing carbon atoms in **3**.

The direction of the dipole (**1a**) of **1** suggests that the ionic states that are localized on the two phenyl substituents in **2** and **3** might be stabilized so that they would appear at lower IP in **2** and **3** than in **4**. The observed spectra could be viewed as being in agreement with this expectation in that the maxima in the second PE bands of **2** (8.7 eV) and the third band in **3** (8.8 eV) are lower than that corresponding in **4** (9.05 eV) by 0.2–0.3 eV. The HAM/3-calculated shifts for these (S_{ϕ_2}, A_{ϕ_2}, Table I) states, in **2** and **3** compared to **4**, are between –0.24 and –0.34 eV. The small reduction in the positions of the second and third bands in the spectra of **2** and **3** could thus be a reflection of the increased polarization or polarizability of the ethene group in **2** and **3** compared to **4** and thus reflect the nonalternacy of the system.

The calculations at detailed geometries confirm the simple analysis given above in terms of band assignments up to the ~9.5-eV point of the observed spectra. However, the simple analysis ignored some of the basis functions in the A_i manifold which are included in the HAM/3 calculations. These include the basis function associated with the 10.6-eV band in the spectrum of **4**,[11] which we label A_E' in Table I. Also, the naphtho compound (**3**) should show a second symmetry-factored (S) state that corresponds to the third ($^2B_{2g}$) ionic state in naphthalene (10.08 eV). This state for **3** is labeled S_N' in Table I. The calculated position of the first member of the σ manifold is also included in Table I. The HAM/3 calculations and assignments seem to be in acceptable agreement with the experimental spectra.

The HAM/3/CI[14] results (Table I) suggest that non-Koopmans' effects are appreciable in the ionic states of **2** and **3** beginning in the 10–11-eV region. Such shaken-up phenomena give an increased number of bands that are broader than single-excitation counterparts. The observed spectra of **2** and **3**, between 10 and 11 eV, mildly suggest that these effects may be present but the number of states is too high to show shake-up effects very clearly. As has been discussed[15] in the case of stilbene, the rotational angle of the phenyl groups with respect to the ethene group in **2**, **3**, and **4** may not be the same in the gas phase as given by crystal structures. Additional calculations on these relative large systems at variable geometries would be required before their PE spectra can be analyzed to the non-Koopmans (configuration interaction) level. Other derivatives such as the fluorenylidene analogues of **2** and **3** would be better candidates for revealing the non-Koopmans effects.

Conclusions

The present work shows that there is little or no difference in the first ionization potentials of **2** and **3**. An apparently linear correlation between $E_{1/2}{}^{\bullet+}$ values and gas-phase IPs of a series of aromatic hydrocarbons indicates that the difference in $E_{1/2}{}^{\bullet+}$ values of **2** and **3** is due to structure-specific solvation effects. The HAM/3 method gives acceptable agreement with the experimental spectra in terms of order of states but appears to overestimate all of the IPs to a fairly significant extent. The HAM/3/CI method indicates that shake-up phenomena are expected in this series above the 9.5-eV level. Studies of other members of this series could serve to test the $E_{1/2}{}^{\bullet+}$–IP correlation and might show the non-Koopmans effects more clearly.

Acknowledgment. S.P. and K.A. thank the Office of Naval Research for support of this work. P.S. and T.K. thank the NSF (Grants CHE 84-19099 and CHE 84-19950) for support.

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(14) Koenig, T.; Winter, R.; Rudolf, K. *J. Am. Chem. Soc.* **1987**, *109*, 2515.

(15) Bigelow, Richard W. *Chem. Phys. Lett.* **1985**, *117* (1), 22–8.