Through Space Interactions of Double Bonds by Photoelectron Spectroscopy

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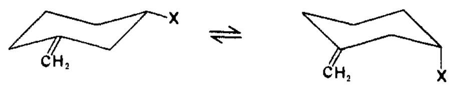
Received May 5, 1986

Abstract: Steric effects between double bonds and remote polar substituents, previously manifested in nuclear magnetic resonance (NMR) spectra, are also evident in the ultraviolet photoelectron spectra (UPS). An ether functionality was introduced at the 3-axial position of *exo*-methylenecyclohexane by means of acetal groups (dimethyl and ethylene). The 3-axial ether group destabilizes the π orbital on the double bond by 0.1–0.2 eV by a through space interaction (the 3-equatorial ether group by itself has little or no effect). This interaction apparently is responsible for the decreased proportion of 3-axial methoxyl observed by NMR spectroscopy. In contrast, 4-axial ether functionalities in cyclohexene show a slight stabilizing of the π orbital by through bond electron withdrawal. These results also agree with the NMR observations, since the endocyclic double bond of cyclohexene permits a much larger proportion of 4-axial methoxyl. Ab initio calculations support the observations by paralleling the observed π-orbital energies and by providing electron densities. Whereas 3-axial methoxyl clearly polarizes the double bond in methylenecyclohexane, 4-axial methoxyl has little or no effect on the electron densities of cyclohexene, even though methoxyl is closer to the endocyclic than to the exocyclic double bond. The NMR, UPS, and ab initio results provide an initial understanding of the three dimensionality of the π-electron steric effects.

Nuclear magnetic resonance studies have shown that the double bond interacts in a complex fashion with remote polar substituents.[2-5] A 3-axial substituent in a six-membered ring is more repulsive with an exocyclic double bond than with a saturated CH_2 group at the same position (eq 1).[2,3] Thus in a nonpolar solvent



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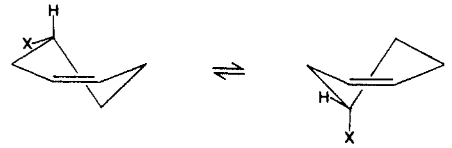
the methoxy group has a free energy difference favoring equatorial of 0.80 kcal/mol for eq 1, compared with an *A* value of 0.55. The NMR studies excluded various through bond interactions and favored a simple through space dipolar electrostatic interaction between the double bond and the polar 3-axial substituent. These conclusions were based on calculations, solvent effects, and examination of the isopropylidene system.[4]

When the *exo*-methylene group ($C{=}CH_2$) was replaced by an isopropylidene group ($C{=}CMe_2$), whose high symmetry conveys a negligible dipole, the free energy preference of 3-methoxyl for equatorial decreased from 0.80 to 0.19 kcal/mol.[4] Thus, in interactions with OCH_3, the $C{=}CH_2$ group is more repulsive and the $C{=}CMe_2$ group is less repulsive than the CH_2 group of cyclohexyl.

For a different perspective on the interactions of double bonds with remote polar substituents, we examined 4-substituted cyclohexenes (eq 2).[5] Here the substituent is about 0.35 Å closer to the double bond than in the exocyclic case (eq 1), and both the angular orientation and the polar properties of the double bond are quite different. We found that the double bond exerted no appreciable repulsive interaction on axial hydroxyl and other groups, the conformational free energy difference being 0.22 kcal/mol for OH. Solvent effects and symmetrization of the double bond through 1,2-dimethyl substitution corroborated the small magnitude of the polar interaction in the cyclohexenes.[5]



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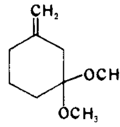
Thus the steric interaction of a double bond with a remote substituent is dependent on the solvent, the substitution pattern of the double bond, and the angular orientation between the double bond and the interacting group.

Ultraviolet photoelectron spectra (UPS) can provide an independent measure of the interaction between a double bond and a remote substituent through direct measurement of orbital energies. The monosubstituted systems of eq 1 and 2 are not useful in this context, because they are in a dynamic equilibrium that prefers the noninteracting equatorial group. Thus the UPS of these systems would in essence provide a control for any through bond interaction, since the through space interaction possible in the axial conformation would contribute in only a minor fashion.

In order to obtain measurements on the axial conformer, one may employ either a conformational anchor or geminal disubstitution. We have chosen the latter approach for synthetic reasons and since the single systems provide information on both axial and equatorial groups. We have prepared molecules **1**–**4** for photoelectron studies of the interaction between an axial methoxy



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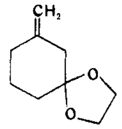

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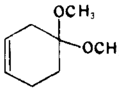

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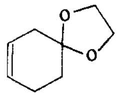

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group and both exo- and endocyclic double bonds. As controls we have also examined the simple alkenes (**5**, **6**), the acetals (**7**, **8**), and the monosubstituted systems of eq 1 (**9**) and eq 2 (**10**).

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[1] (a) Northwestern University; work supported by the Petroleum Research Fund, administered by the American Chemical Society, and by the National Science Foundation (Grant CHE83-12285). (b) The University of Illinois at Chicago; work supported by the American Cancer Society (Grant IN-159) and by the Computer Center of the University of Illinois at Chicago.

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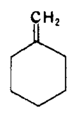

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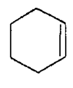

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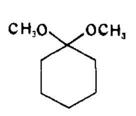

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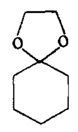

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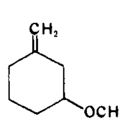
As in other recent studies[6-9] the interpretation of the spectra was aided by results from ab initio and semiempirical calculations, which were carried out on molecules **1–11**. Geometries employed on the calculations were obtained by molecular mechanics methods. The photoelectron results and the calculations provide an excellent molecular orbital view of the steric interactions between double bonds and remote polar substituents.



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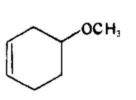

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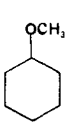

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Results

The preparation of the bifunctional compounds **1–4** of primary interest are shown in Scheme I. The monofunctional compounds **9** and **10** were available from our earlier studies.[2,5]

Preliminary ultraviolet studies were carried out on **1** and **2** and were found to be relatively uninformative. These data are presented only in the Experimental Section. Ultraviolet photoelectron spectra were obtained for compounds **1–9**. Complete spectra are displayed in Figure 1 for the oxygen-containing *exo*-methylene series (**1**, **2**, **9**) and in Figure 2 for the model compounds. Experimental ionization potentials for π and n orbitals are given in Table I as the average of five runs.

Calculations were carried out in order to assign the highest occupied molecular orbitals. Geometries were constructed initially by the program CHEMGRAPH[10] and then refined by the molecular mechanics program MM2.[11] With these geometries ab initio calculations (Gaussian-80 at the STO-3G or higher level)[12] and semiempirical calculations (HAM/3)[13-15] were carried out to obtain theoretical ionization potentials, which are also presented in Table I. The ab initio calculations were corrected by least-squares fitting[16] according to the equation $E(\text{corr}) = 0.555(E(\text{STO-3G})) - 4.87$ (eV). Table I contains only the least-squares corrected values. Ionization potentials were taken as the negative of the orbital energies according to Koopman's theorem.

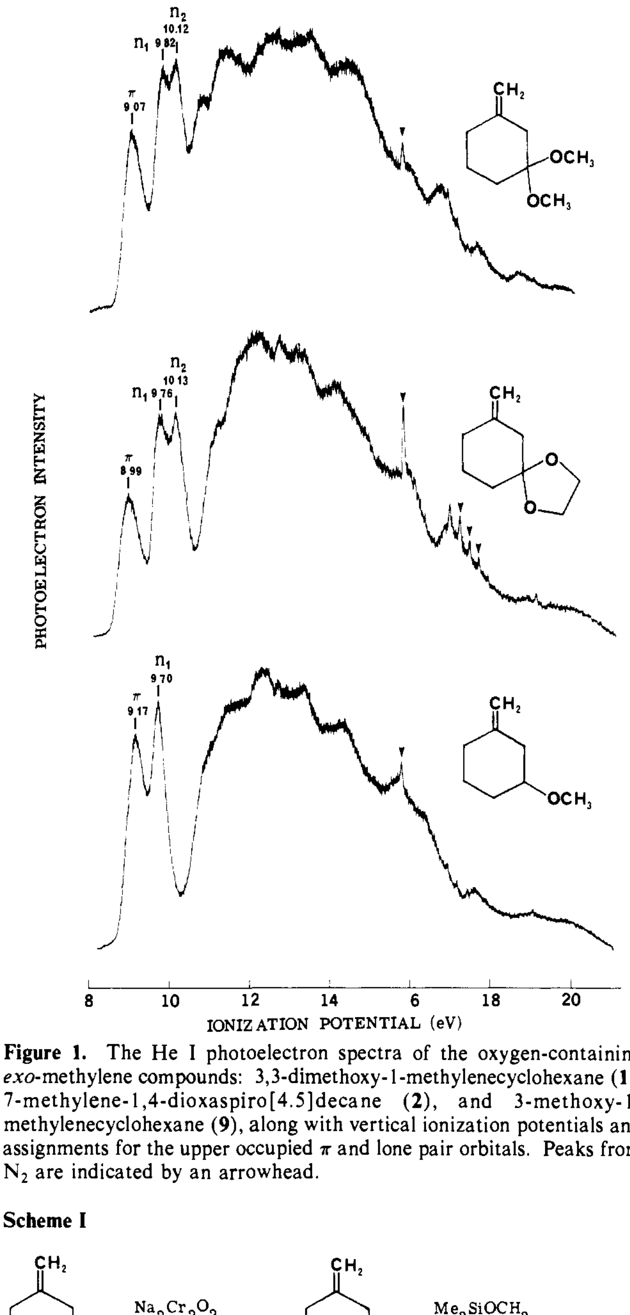

Figure 1. The He I photoelectron spectra of the oxygen-containing *exo*-methylene compounds: 3,3-dimethoxy-1-methylenecyclohexane (**1**), 7-methylene-1,4-dioxaspiro[4.5]decane (**2**), and 3-methoxy-1-methylenecyclohexane (**9**), along with vertical ionization potentials and assignments for the upper occupied π and lone pair orbitals. Peaks from N_2 are indicated by an arrowhead.

Scheme I

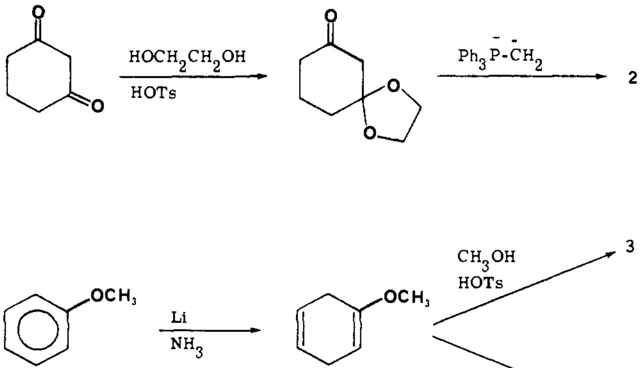

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Table I. Observed and Calculated π and n Electron Ionization Potentials (eV)

	observed			ab initio			HAM/3		
compd	π	n_1	n_2	π	n_1	n_2	π	n_1	n_2
1	9.07	9.82	10.12	9.10	9.77	9.87	8.82	9.90	10.10
2	8.99	9.76	10.13	9.14	9.77	10.15	8.84	9.93	10.08
3	9.31	9.71	10.17	9.18	9.65	9.90	8.64	9.56	9.92
4	9.47	9.47	10.15	9.19	9.67	10.14	8.75	9.87	10.14
5	9.18			9.17			9.22		
6	9.09			9.15			8.93		
7		9.52	10.06		9.84	9.87		9.90	10.12
8		9.30	9.98		9.54	10.12		9.66	10.10
9e[a]	9.17	9.70		9.21	9.74		9.14	9.78	
9a[a]				9.10	9.76		8.86	9.62	
10e[a]				9.21	9.68	10.44	8.92	9.77	10.97
10a[a]				9.12	9.73	10.33	8.64	9.67	10.54
11e[a]					9.66	10.36		9.62	10.71
11a[a]					9.68	10.28		9.70	10.41

[a] It is assumed that the experimental values for **9** derive primarily from the equatorial isomer; calculated values of course could be obtained for both axial and equatorial isomers.

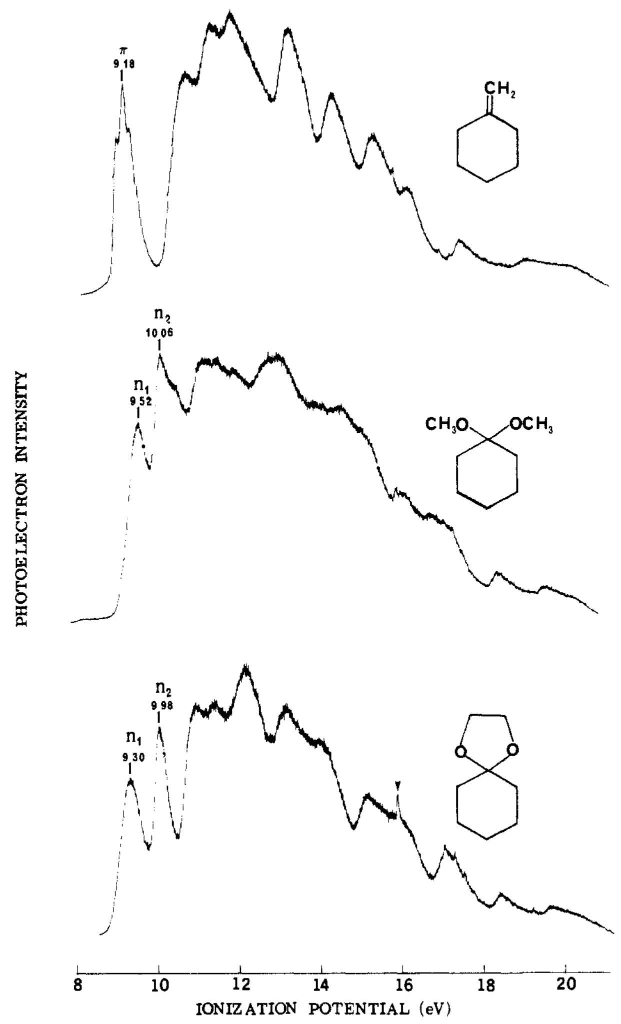


Figure 2. The He I photoelectron spectra of the model compounds methylenecyclohexane (**5**), 1,1-dimethoxycyclohexane (**7**), and 1,4-dioxaspiro[4.5]decane (**8**). For further details, see Figure 1.

The ionization potentials predicted by HAM/3 in Table I were obtained directly from the calculations without least-squares fitting. All of the ab initio and semiempirical results were in agreement with regard to the energetic ordering of upper occupied π and lone pair orbitals. As in earlier studies of heterocycles,[6,7] it was found that, before least-squares fitting of the STO-3G results, the HAM/3 calculations provided a more accurate measure of the absolute ionization potentials of the molecules studied.

The σ and π electron densities of the double bond may be perturbed by the presence of the substituents at the 3 position in the *exo*-methylene series and at the 4 position in the endocyclic system. Electron densities were calculated from the ab initio results and are listed in Table II.

Discussion

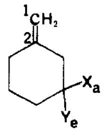
The alkenes **5** and **6** provide models for the ionization potentials of the π electrons of unperturbed exocyclic and endocyclic double bonds, 9.18 and 9.09 eV, respectively. Similarly, the acetals **7** and **8** provide models for the ionization potentials of the n electrons of unperturbed acetals. There are two nondegenerate n orbitals in each case, since the geminal methoxy groups interact. The values are given in Table I as n_1 and n_2. Our calculations demonstrate that in all cases the π orbitals are of higher energy than the n orbitals in the difunctional compounds. Any interaction between the double bond and the 3-axial ether group would result in a change in the π orbital energy. The perturbations can be sufficient to differentiate four different n orbitals, since each geminal oxygen has two lone pairs. The energies of n_3 and of n_4 are not of interest and are not listed in Table I. Our analysis is directed primarily at determining how the π orbital is influenced by the introduction of the methoxy groups.

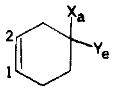
In the absence of a through space effect or of direct conjugation, the methoxy group should exert a modest through bond electron-withdrawing effect in both exo- and endocyclic systems, resulting in a lowering of the orbital energy. The monomethoxy exocyclic case **9** illustrates this effect. Its observed π electron ionization potential (9.17 eV) is unchanged from that of **5** (9.18 eV).

Introduction of the second oxygen atom requires that there be an axial oxygen at all times, thereby providing a molecule in which the interaction between the double bond and the axial group must exist. The π orbital ionization potentials decrease, from the unperturbed value of 9.18 eV in **5** to 9.07 for the exocyclic dimethoxy compound **1** and to 8.99 for the ethylene acetal **2**, indicating a raising of the energy of the bonding π orbital. This effect may also be seen by calculation in the monomethoxy case **9** (Table I). Experimental measurements are not possible for the axial form **9a**, since it is in an unfavorable equilibrium that favors the equatorial form **9e**. The ab initio and semiempirical calculations indicate that the ionization potential decreases (π-orbital energy increases) on going from the noninteracting equatorial form to the therefore repulsively interacting axial form, from 9.21 (**9e**) to 9.10 (**9a**) eV by STO-3G and from 9.14 to 8.86 eV by HAM/3. Thus both experiment and calculation show that the introduction of an axial oxygen atom has a destabilizing effect on the energy of the π orbital. These results are in accord with the NMR observation that in nonpolar solvents the interaction between the exocyclic double bond and the axial methoxy group is repulsive.[2]

The endocyclic systems provide a contrasting situation. Introduction of the axial oxygen atom via geminal substitution in **3** and **4** raises the ionization potential (lowers the π orbital energy) from the unperturbed value of 9.09 eV in **6** to 9.31 in **3** and to

Table II. Electron Densities





compd	$d_1(\pi)$	$\Delta d_1/d_1^{0\,a}$	$d_1(\sigma)$	$\Delta d_1/d_1^{0\,a}$	$d_2(\pi)$	$\Delta d_2/d_2^{0\,a}$	$d_2(\sigma)$	$\Delta d_2/d_2^{0\,a}$
5 (X, Y = H)	1.053	0	5.087	0	0.961	0	5.025	0
9e (X = H; Y = MeO)	1.046	−0.7	5.092	0.1	0.969	0.8	5.019	−0.1
9a (X = MeO; Y = H)	1.047	−0.7	5.088	0.0	0.966	0.5	5.016	−0.2
1 (X, Y = MeO)	1.046	−0.7	5.088	0.0	0.967	0.6	5.015	−0.2
2 (X, Y = OCH_2CH_2O)	1.043	−1.0	5.091	0.1	0.970	0.9	5.013	−0.2
6 (X, Y = H)	1.009	0	5.056	0	1.009	0	5.056	0
10e (X = H, Y = MeO)	1.009	0.0	5.056	0.0	1.009	0.0	5.055	0.0
10a (X = MeO, Y = H)	1.008	0.0	5.053	−0.1	1.009	0.0	5.052	−0.1
3 (X, Y = MeO)	1.011	0.2	5.051	−0.1	1.006	−0.3	5.053	−0.1
4 (X, Y = OCH_2CH_2O)	1.005	−0.4	5.055	0.0	1.012	0.3	5.049	−0.1

[a] Difference from hydrocarbon **5** or **6**, divided by the hydrocarbon value, times 100, as a percentage change; a positive $\Delta d/d$ indicates a higher electron density.

9.47 in **4**. In the NMR experiments, only a small interaction was evident between an axial methoxy group and the endocyclic double bond.[5] The photoelectron results corroborate these observations, since the repulsive interaction in the exocyclic case results in a lowering of the ionization potential. In the absence of the through space repulsive interaction, the through bond stabilizing effect of introducing a second oxygen atom results in the raising of the ionization potential (lowering of the π-orbital energy).

Examination of electron densities (Table II) leads to similar conclusions. Effects on σ electron densities are small in all cases (changes of 0.2% or less). Differential effects of π electron densities ($\Delta d_2/d_2^0 - \Delta d_1/d_1^0$) in the exocyclic system are as high as 2%. The π-electron densities of the two double bond carbons in the exocyclic system move in opposite directions, as the introduction of the axial oxygen atom polarizes the double bond in an apparently repulsive interaction. On the other hand changes in π-electron densities in the endocyclic case are negligible, in agreement with the NMR and UPS results. These electron densities were recalculated at the 4-31G level and found to follow the same pattern.

Conclusions

Ultraviolet photoelectron spectra of molecules containing a double bond and a remote ether oxygen demonstrate the angular dependence of steric effects on π electrons. Molecules **1**–**4** have been synthesized to position a nonadjacent ether oxygen close to the double bond in the ground-state conformation. In the endocyclic cases (**3**, **4**), the π orbitals are stabilized by the axial oxygen, presumably as the result of through bond electron withdrawal. In the exocyclic cases (**1**, **2**), the π orbitals are destabilized, presumably by a through space repulsive interaction that exceeds the through bond stabilizing effect. These results are in agreement with the NMR experiments, in which the axial/equatorial equilibria in eq 1 (**9**) and eq 2 (**10**), the solvent effects, and the effect of dimethylation of the double bonds all indicated that a 3-axial oxygen atom has a repulsive interaction with the exocyclic double bond. These same experiments indicate that the 4-axial oxygen atom has little or no interaction with the endocyclic double bond, even through the distance is smaller in the endocyclic case. Ab initio calculations of electron densities show the same distinctions between the exo- and endocyclic systems.

These results illustrate the spatial complexity of the π-electron steric effect, which arises from differences not only in the dipolar properties of the endocyclic and exocyclic doubler bonds but also in the angular orientation between the double bond and the ether oxygen in the two systems.

Experimental Section

Photoelectron Spectra. Gas-phase photoelectron spectra were measured with a Perkin-Elmer PS-18 spectrometer. The spectrometer has an energy resolution of 0.018 eV for ionization potentials in the range 9.0–11.0 eV. All spectra were measured at 23 ± 2 °C. Ionization potentials were calibrated by using the $^2p_{3/2}$ and $^2p_{1/2}$ bands of Xe and Ar.

3,3-Dimethoxy-1-methylenecyclohexane (1). A solution of 1.68 g of 3-hydroxy-1-methylenecyclohexane[2] (0.015 mol) and 400 mL of acetone was placed in a 3-necked 1-L flask equipped with an addition funnel and a bubbler. The solution was deoxygenated by bubbling N_2 through for 1 h, after which time the solution was cooled to 0 °C. To the reaction mixture was added 41 mL of Jones reagent (13.36 g of $Na_2Cr_2O_7$ and 11.5 mL of concentrated H_2SO_4, diluted to 50.0 mL with H_2O). The solution was stirred 5 min, and 400 mL of H_2O was added. The solution was extracted 5 times with 150 mL of pentane. The organic material was washed twice with 50 mL of saturated $NaHCO_3$ and twice with 50 mL of brine. The solution was dried with $MgSO_4$, filtered, and concentrated by rotary evaporation.

A solution of 3 drops of trimethylsilyl triflate, 2 mL of CH_2Cl_2, and 3.15 g (0.030 mol) of trimethylmethoxysilane was prepared and cooled to −78 °C under N_2. To this solution was added the product from the Jones oxidation in 1 mL of CH_2Cl_2. The reaction temperature was maintained at −78 °C for 3 h, and the reaction was warmed to −20 °C for 12 min. The reaction was quenched by the addition of 5 drops of pyridine. The solution was poured into 50 mL of saturated $NaHCO_3$ solution and extracted three times with 50 mL of ether. The ether solution was washed twice with 20 mL of saturated $CuSO_4$ solution, dried with a 1/1 mixture of Na_2SO_4 and Na_2CO_3, filtered, and concentrated. The resulting 1.35 g of solution contained approximately 20% of the desired product. The compound was isolated via preparative GC on a 6 ft × $^1/_4$ in. 25% DEGS column at 100 °C with a flow rate of 86 cm^3/min. A yield of 0.170 g (7%) was obtained: ^1H NMR ($CDCl_3$) δ 4.72 (br s, 2, $=CH_2$), 3.19 (s, 6, OCH_3), 2.37 (br s, 2), 2.13 (t, 2), 1.85–1.45 (m, 4); UV (pentane) λ_{max} 241 nm (ϵ 1100). Anal. Calcd for $C_9H_{16}O_2$: C, 69.20; H, 10.32. Found: C, 69.80; H, 10.43.

6-Oxo-1,4-dioxaspiro[4.5]decane was prepared by the procedure of Cronyn and Goodrich[17] in 48% yield: bp 69–73 °C (0.02 mmHg) (lit.[17] bp 84–85 °C (1 mmHg)).

7-Methylene-1,4-dioxaspiro[4.5]decane (2). Into a 500 mL, 3-necked, round-bottomed flash equipped with a condenser and an addition funnel were added 6.79 g of Ph_3PCH_3Br (0.019 mol) and 100 mL of ether. The system was placed under N_2, and 8.2 mL of PhLi in 70/30 cyclohexane/ether was added over 10 min. The solution was stirred for 30 min, and 3.12 g of 7-oxo-1,4-dioxaspiro[4.5]decane (0.020 mol) in 10 mL of ether was added over 30 s. The solution was stirred for 2 h, and 1 mL of acetone was added. The solution was stirred an additional 15 min and then filtered. The solid was washed with 10 mL of ether. The organic layers were combined and washed three times with 30 mL of brine. The solution was dried with $MgSO_4$, filtered, and concentrated. To the resulting liquid was added 20 mL of hexane. A reddish oil settled out of the solution and was removed. The remaining liquid was concentrated, and 1.40 g of material was obtained. The solution was found to contain 70% of starting material and 30% of the desired product. Preparative GC was used to isolate the compound with a 6 ft × $^1/_4$ in. 25% DEGS column at 120 °C with a flow rate of 100 cm^3/min. A 3% yield of the desired material was obtained: ^1H NMR ($CDCl_3$) δ 4.75 (d, 2, $=CH_2$), 3.95 (s, 6, OCH_3), 2.34 (s, 2), 2.13 (t, 2), 1.80–1.50 (m, 4); UV (pentane)

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(17) Cronyn, M. W.; Goodrich, S. E. *J. Am. Chem. Soc.* **1952**, *74*, 3331–3333.

234 nm (ϵ 1080). Anal. Calcd for $C_9H_{14}O_2$: C, 70.01; H, 9.15. Found: C, 70.00; H, 8.79.

1-Methoxy-1,4-cyclohexadiene was prepared by the Birch reduction of anisole.

4,4-Dimethoxycyclohexene (3). 1-Methoxy-1,4-cyclohexadiene (2.0 g, 0.018 mol) was dissolved in 50 mL of anhydrous ether (distilled from Na/benzophenone) and placed in a 100-mL round-bottomed flask. Methanol (6 mL, 0.148 mol) was added along with several crystals of *p*-toluenesulfonic acid. The mixture was stirred overnight under N_2. The mixture was neutralized with NaOMe and washed once with 50 mL of H_2O. The ether solution was dried (Na_2CO_3), filtered, and distilled. The product was a colorless liquid: bp 48-50 °C (10 mmHg); ^1H NMR ($CDCl_3$) δ 5.62 (q, 2, alkene), 3.24 (s, 6, OCH_3), 2.27 (br s, 2, allylic CH_2), 2.10 (br s, 2, allylic CH_2), 1.81 (t, 2, CH_2).

1,4-Dioxaspiro[4.5]dec-7-ene (4).[18] 1-Methoxy-1,4-cyclohexadiene (3.0 g, 0.0272 mol) was dissolved in 50 mL of anhydrous toluene (distilled from Na/benzophenone) and placed in a 100-mL round-bottomed flask fitted with a Dean-Stark trap. Ethylene glycol (1.70 g, 0.0272 mol) was then added along with several crystals of *p*-toluenesulfonic acid. The solution was heated to 110 °C, and H_2O was taken off via the trap. The organic solution was washed twice with 50 mL of saturated $NaHCO_3$ and 30 mL of H_2O, dried ($MgSO_4$ and K_2CO_3), filtered, and concentrated. The resulting solution was distilled: bp 62-64 °C (7 mmHg); ^1H NMR ($CDCl_3$) δ 5.64 (m, 2, alkene), 3.93 (s, 4, OCH_2CH_2O), 1.5-2.3 (m, 6, CH_2).

Methylenecyclohexane (5) was prepared by a standard Wittig reaction of cyclohexanone.

1,1-Dimethoxycyclohexane (7) was prepared by the reaction of cyclohexanone with trimethylsilyl trifluoromethanesulfonate and trimethylmethoxysilane.

1,4-Dioxaspiro[4.5]decane (8) was prepared by the reaction of cyclohexanone with ethylene glycol.

3-Methoxy-1-methylenecyclohexane (9) was prepared by the method of Clikeman:[2] UV(pentane) λ_{max} 229 nm (ϵ 1410).

4-Methoxycyclohexene (10) was prepared by the method of Marko.[5]

Calculations. Semiempirical and ab initio calculations were carried out on an IBM 2700 computer at the University of Illinois at Chicago. CHEMGRAPH and MM2 calculations were carried out on a Harris H1000 computer, Department of Chemistry, Northwestern University.

Registry No. 1, 104598-80-3; **2**, 104598-81-4; **3**, 16831-48-4; **4**, 7092-24-2; **5**, 1192-37-6; **6**, 110-83-8; **7**, 933-40-4; **8**, 177-10-6; **9**, 59627-58-6; **10**, 15766-93-5; **11**, 931-56-6; Ph_3PCH_3Br, 27200-84-6; 3-hydroxy-1-methylenecyclohexane, 6749-63-9; 7-oxo-1,4-dioxaspiro[4.5]decane, 4969-01-1; 1-methoxy-1,4-cyclohexadiene, 2886-59-1; cyclohexanone, 108-94-1; anisole, 100-66-3.

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(18) Tsunoda, T.; Suzuki, M.; Noyori, R. *Tetrahedron Lett.* **1980**, *21*, 1357-1358.

Theoretical Studies of Diphosphene and Diphosphinylidene in Their Closed-Shell States, Low-Lying Open-Shell Singlet and Triplet States, and Transition States. Search for a Stable Bridged Structure[†]

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Abstract: We have undertaken a systematic study of the various low-lying electronic states of the H_2P_2 system, about which little is known experimentally, using the methods of ab initio molecular electronic structure theory. For each state we have predicted its molecular geometry, energy, dipole moment, vibrational frequencies, and their associated normal modes. The ground state is *trans*-HP=PH, 3.5 kcal/mol below *cis*-HP=PH. The $H_2P{=}P$ isomer lies at a relative energy of 28 kcal/mol above the ground state. For the ground state the highest occupied molecular orbital (HOMO) is n_+, a symmetric lone-pair combination; the second HOMO is the P-P π bond. In $H_2P{=}P$ a lone pair n_y is the HOMO, and the P-P π bond is the second HOMO. For both isomers the lowest unoccupied molecular orbital (LUMO) is the antibonding P-P π^* orbital. A variety of states involving n-π^* and π-π^* excitations have been studied for various molecular geometries. The lowest energy open-shell singlet is a pyramidal H_2PP $^1A''$ state (out-of-plane angle 77°) at a relative energy of 46 kcal/mol. A skewed HPPH ^1B state (torsion angle 109°) is at 64 kcal/mol. Highly distorted geometries are also characteristic of the triplet states. A pyramidal H_2PP $^3A''$ state (out-of-plane angle 79°) has a relative energy of only 21 kcal/mol, and thus it is predicted to lie below the closed-shell planar H_2PP state. A skewed HPPH ^3B state (torsion angle 90°) is at 29 kcal/mol. An unsuccessful search has been made for a stable doubly bridged PH_2P structure, analogous to SiH_2Si. Studies of transition states between the various structures show the following. (1) Closed-shell cis-trans isomerization occurs more readily by internal rotation (barrier 34 kcal/mol) than by inversion (barrier 66 kcal/mol). From this calculated rotation barrier and experimental data in the literature, it is estimated that the cis isomer of bis(2,4,6-tri-*tert*-butylphenyl)diphosphene lies approximately 14 kcal/mol above the trans isomer. (2) Between closed-shell *trans*-HPPH and H_2PP, both planar, the transition state is nonplanar (torsion angle 112°) at 53 kcal/mol. Evidence is presented showing that the unusual structure of this transition state is caused by attraction of the transiting proton to the P-P π bond. (3) Between triplet skewed HPPH and pyramidal H_2PP, both nonplanar, the transition state is also nonplanar (torsion angle 87°) at 49 kcal/mol. (4) Other internal rotation barriers in the HPPH system, and inversion barriers in the H_2PP system, are also examined. Finally, it is shown that in many cases polarization functions (phosphorus d orbitals and hydrogen p orbitals) play an important role in predicting the chemistry of the H_2P_2 system.

The double-bonded nitrogen structure, -N=N-, has been well known for many years in the form of diazene (also called diimide or diimine), HN=NH, and substituted diazenes (also called azo compounds), RN=NR. However, it was long thought that if phosphorus, the next member of group 15, did form the analogous diphosphene configuration, -P=P-, then it was of only fleeting significance. The only experimental evidence for its existence was the observation of H_2P_2, by means of its mass spectrum, in the thermal decomposition products of diphosphine, H_4P_2.[1-3] The

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[†] Presented in part by T.L.A. at the 5th International Congress on Quantum Chemistry, Montreal, Aug. 18-24, 1985. Abstract No. 14-C.

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