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UPE Studies of Conjugation Involving Group 5A Elements. 2. Substituted *tert*-Butylacetylenes

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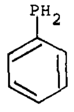
Abstract: UPE spectra are reported and assigned for *tert*-butylacetylene, (*tert*-butylethynyl)phosphine, (*tert*-butylethynyl)-dichlorophosphine, and (*tert*-butylethynyl)bis(diethylamino)phosphine. The usefulness of the *tert*-butylethynyl group as an indicator of conjugative ability is pointed out. The results strongly support the assignment of I_3 in phenylphosphine to the phosphorus lone pair.

The extent to which the lone pair electrons of trivalent group 5A elements can interact conjugatively with adjacent unsaturated systems has been the subject of much discussion. The preceding paper[1] described a new approach to the problem in the case of phosphorus, which led to an apparently unambiguous reassignment of the UPE (ultraviolet photoelectron) spectrum of phenylphosphine (**1**). Here we report another procedure for studying such interactions, which should be readily extendable to other group 5A elements.

In a monosubstituted acetylene, HC≡CX, any field/inductive effect of X will affect the energies of the acetylenic π MOs equally, leaving them degenerate. Any splitting of the two levels can then arise only from conjugative effects of X. Furthermore, such conjugative interactions cannot be avoided by any rotation about the CX bond, a complication which can occur in the case of planar π systems. For example, conjugative interactions between phosphorus and the ring seem to be lacking in phenyldichlorophosphine (**2a**), due to this molecule adopting a bisected geometry where the lone pair AO of phosphorus is orthogonal to the π MOs of the ring.[1] Acetylene has the further advantage of having a very sparse UPE spectrum; so it is easy to identify the ionizations corresponding to its π MOs. The splitting of these should provide a quantitative measure of the conjugative ability of X.



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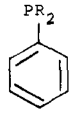


2
a, R=Cl
b, R=NEt$_2$

t-BuC≡CH

3

t-BuC≡CPH$_2$

4

t-BuC≡CPCl$_2$

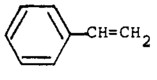
5

t-BuC≡CP(NEt$_2$)$_2$

6

HC≡C-CH=CH$_2$

7



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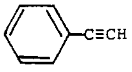

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While extensive studies of derivatives of acetylene by UPE spectroscopy have been reported (see, e.g., ref 2-8), no measurements seem as yet to have been described for ethynylphosphines, arsines, stibines, or bismuthines. In this connection, use of the *tert*-buytlethynyl group as a substrate seems to offer advantages from the point of view of ease of synthesis and stability of the relevant derivatives. The *tert*-butyl group, having in effect axial symmetry, does not remove the degeneracy of the acetylenic π MOs nor do its ionizations occur at low enough energies to interfere with measurement of the acetylenic π ionizations. Here we report such a study of *tert*-butylacetylene (**3**) and three phosphines derived from it, namely (*tert*-butylethynyl)phosphine (**4**), (*tert*-butylethynyl)dichlorophosphine (**5**), and (*tert*-butylethynyl)bis(diethylamino)phosphine (**6**). MNDO[9] calculations were also carried out for **4** and **5** as an aid in assigning their UPE spectra. MNDO has proved very effective[1,9,10] for the calculation of ionization energies of molecules up to ca. 18 eV.[11]

Table I. Ionization Potentials (eV) from UPE Spectra

compd	I_1	I_2	I_3	I_4	I_5
3	10.21				
4	9.05 (10.28)^{a,b}	9.75 (10.81)^{a,b}	11.10 (12.09)^{a,c}		
5	9.58	10.20	10.50		
6	7.62	8.11	8.81	9.43	9.86
7^d	9.58	10.58	12.00		
8^d	8.48	9.28	10.55		
9^d	8.88	9.57	10.38	11.05	

^{a} Values in parentheses calculated by MNDO. ^{b} Assigned by MNDO to acetylenic π ionizations. ^{c} Assigned by MNDO to the lone pair ionization. ^{d} Data from ref 7. ^{e} Maier, J. P.; Turner, D. W. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 196.

Experimental Procedure

The syntheses of **4**–**6** will be reported elsewhere.[12] UPE spectra were acquired on a Perkin-Elmer Model PS-18 photoelectron spectrometer by using a He I source (21.22 eV). Calibration and linearity were maintained by use of argon (15.759 eV) and xenon (12.130 eV) as internal standards. The resolution was consistently 25–35 meV, except for **4** which gave inferior spectra. This problem has arisen in other UPE studies of phosphorus compounds,[13] in particular in our own work on **1**

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(1) Part 1: Cabelli, D. E.; Cowley, A. H.; Dewar, M. J. S. *J. Am. Chem. Soc.*, preceding paper in this issue.

(2) (a) Haink, H. J.; Heilbronner, E.; Hornung, V.; Kloster-Jensen, E. *Helv. Chim. Acta* **1970**, *53*, 1073. (b) Heilbronner, E.; Hornung, V.; Kloster-Jensen, E. *Helv. Chim. Acta* **1970**, *53*, 331.

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(11) MNDO estimates of the higher ionizations of organic molecules, corresponding to loss of electrons from MOs derived largely from 2s AOs, are too large, due to the neglect in MNDO of 1s–2s interactions.[9] The ionization energies of MOs derived largely from AOs of third period elements (Al–Cl) are also overestimated, again because of the neglect of interactions between inner shell (1s,2s,2p) electrons and electrons in the valence shell (3s,3p).[7]

(12) Kyba, E. P.; Huemuller, H., to be published.

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and its derivatives.[1] However, the resolution in the case of **4** remained 30–60 meV over the region of interest in its UPE spectrum.

Theoretical Procedure

The MNDO calculations were carried out by using the standard MNDO procedures and parameters.[9,14] All geometries were optimized by the DFP (Davidon–Fletcher–Powell) algorithm used in our standard MNDO program,[9] no assumptions of any kind being made.

Results and Discussion

The UPE spectra of **3**–**6** are available as supplementary material. The relevant ionization energies derived from them are shown in Table I. As previously,[1] we will discuss them on the assumption that the observed ionization energies can be equated to the corresponding *minus* orbital energies (Koopmans' theorem). For convenience, we will refer to the energies of orbitals in terms of the corresponding ionization energies, i.e., as positive, to avoid continual use of the qualifier *minus*.

The UPE spectrum of **3** contained a single broad band without vibrational fine structure, centered at 10.12 eV, which must correspond to the degenerate π MOs. The shift of 1.28 eV from acetylene (11.40 eV) can of course be attributed to hyperconjugation and/or to field/inductive effects of the *tert*-butyl group.

The UPE spectrum of **4** showed three distinct bands in the low energy region, centered at 9.05, 9.75, aand 11.10 eV. These must be derived from the two acetylene π MOs (ϕ_1,ϕ_2) and the lone pair AO (p) of phosphorus. As noted above, the latter can interact with only one of the π MOs, the other remaining unaffected by conjugative interactions with phosphorus. The splitting of the π ionizations in **4** should therefore correspond to the lone pair π interaction. According to simple LCMO PMO theory,[15] the interaction should lead to an equal and opposite shift in the energy of the lone pair AO(p). Since the interaction cannot lead to crossing of the interacting orbitals and since $I_3 - I_2 > I_2 - I_1$, I_1 must correspond to the perturbed π MO and I_3 to the perturbed lone pair.

This argument could fail only if other effects (field/inductive effects or interactions with other MOs) altered the relationship between the $I_3 - I_2$ and $I_2 - I_1$ separations, which seems out of the question. The orbital densities in both π MOs of **4** at the methine carbon are identical, so inductive/field effects would alter their energies to equal extents. Any secondary resonance interactions would involve orbitals of much higher, or much lower, energy than the phosphorus lone pair. The differential effects of such interactions must therefore be small in relation to the primary splitting of the π level by the lone pair interaction. If then I_2 and I_3 corresponded to the π ionizations, the splitting due to interaction with the lone pair could not be much less than $I_3 - I_2$ and would therefore be significantly greater than $I_2 - I_1$. The energy of the unperturbed lone pair would then have to be greater than I_2, in which case I_1 could correspond to the perturbed lone pair only if the interaction led to a crossing of the p and π MOs, which is not allowed. Numerous studies of the UPE spectra of acetylenes and polyacetylenes by Heilbronner and his group (see, e.g., ref 4, 6–8) have moreover shown how well they can be explained in terms of simple PMO theory, and hence by implication how little the orbital splittings, etc., are affected by factors other than the interactions between the lower energy π-type MOs.

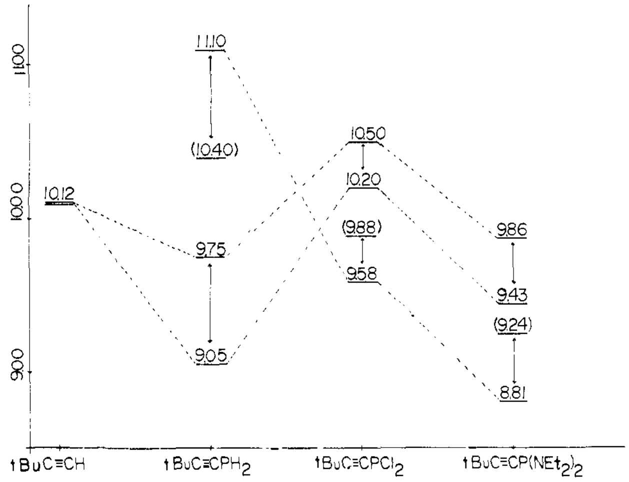

Figure 1. Orbital correlation diagram for **3**–**6**. The unperturbed phosphorus lone pair energies are indicated in parentheses.

This assignment could also be made almost unequivocally on the basis of the MNDO calculations for **3** and **4** (Table I). While MNDO systematically overestimates the energies of MOs composed largely of phosphorus lone pairs,[11] the errors in the case of such compounds, and for very many ionizations of organic molecules of all kinds, have never exceeded 1.5 eV. It therefore seems virtually certain that I_3 must correspond to the phosphorus lone pair, as MNDO predicts.

On this basis the unperturbed phosphorus lone pair energy in **4** is equal to $I_3 - (I_2 - I_1) = 10.40$ eV. This is greater by 0.75 eV than the corresponding value for **1** (9.65 eV[1]), a difference readily attributed to the greater +F/+I field/inductive effect of ethynyl relative to phenyl.

The UPE spectrum of (*tert*-butylethynyl)dichlorophosphine (**5**) also showed three bands in the low energy region (Table I), the second of which must again correspond to the unperturbed π ionization. This, as expected, appears at higher energy (10.20 eV) than in **4** (9.75 eV), reflecting the greater +F/+I field/inductive effect of PCl_2 compared with PH_2. Since the $I_2 - I_3$ separation (0.30 eV) is less than $I_1 - I_2$ (0.62 eV), I_3 must correspond to the other π ionization and I_1 to the phosphorus lone pair. The unperturbed phosphorus lone pair energy is then equal to $I_1 + (I_3 - I_2) = 9.88$ eV.

The UPE spectrum of the last compound in our series, (*tert*-butylethynyl)bis(diethylamino)phosphine (**6**), showed five distinct ionizations in the relevant region (Table I). These must derive from the two nitrogen lone pairs, the phosphorus lone pair, and the two acetylenic π MOs. The first two, at 7.62 and 8.06 eV, are almost the same as I_1 (7.51 eV) and I_2 (8.11 eV) for the analogous benzene derivative (**2b**) which were assigned[1] unambiguously to the nitrogen lone pairs. The same assignment must hold for **6**. The remaining three ionizations must then correspond to the acetylene π MOs and the phosphorus lone pair. The same reasoning as before leads to the conclusion that the two higher, at 9.43 and 9.86 eV, correspond to the π ionizations and I_3 (8.81 eV) to the lone pair. The unperturbed phosphorus lone pair energy is then 8.81 + (9.86 − 9.43) = 9.24 eV.

Figure 1 shows an orbital correlation diagram for **3**–**6**. The results reported here also provide further confirmation of the reassignment of the UPE spectrum of **1**, given in the preceding paper. The assignments given here for **4**–**6** are unequivocal and lead to unequivocal estimates of the phosphorus lone pair orbital energies. As we have pointed out, these correspond nicely to the values estimated[1] for **1** and **2**, assuming the new assignment. Any attempt to identify I_1 in **1** with the lone pair would lead to an unreasonably large difference between the unperturbed lone pair energies in **1** and **4**.

The conjugative interaction between the lone pair and the triple bond in **4** is equal to the splitting of the π MOs. In the previous paper, the corresponding interaction in benzene was shown to be equal to the splitting of the degenerate π HOMO of benzene by the substituent. The ratio of these splittings (1.4) should then be a measure of the relative conjugative abilities of ethynyl and phenyl. A further check on our analysis and assignments can then

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be obtained by comparing the splittings with those in another pair of compounds, HC≡CX and PhX. Table I shows data for the case where X is vinyl, derived from the UPE spectra of vinylacetylene (**7**) and styrene (**8**). In each case I_2 and I_3 are known to correspond to the π MOs of acetylene or benzene. The ratio of the splittings is 1.4, the same as for **4** and **1**.

In our studies[1] of **1** and **2**, we assumed that any field/inductive effect of a substituent in benzene will alter the energies of the benzene π MOs (a_1 and b_2) to equal extents. Support for this assumption, and for the use of PMO theory in this and the preceding[1] paper, is provided by the UPE spectrum of phenylacetylene (**9**) (Table I). Here I_3 and I_4 are known to correspond to the acetylenic π MOs. The π interaction between ethynyl and phenyl is then equal to their separation, i.e., 0.67 eV. I_1 corresponds to the perturbed (b_1) benzene π MO, the unperturbed energy of which should be greater by the π interaction i.e., equal to I_1 + 0.67 = 9.55 eV. This is essentially the same as the value for the (unperturbed) a_2 π MO (9.57 eV), showing that the field/inductive effect of ethynyl raised both by the same amount (0.35 eV).

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Supplementary Material Available: Photoelectron spectra for **3**–**6** (4 pages). Ordering information is given on any current masthead page.

Slow Multiphoton Excitation as a Probe of Bimolecular and Unimolecular Reaction Energetics. Multiphoton Dissociation of Proton Bound Alcohol Dimers

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Abstract: Many bimolecular reactions proceed through a long-lived intermediate. In some cases an alternate reaction can be used to prepare the intermediate as a stable molecule or complex. A study of the unimolecular dissociation of this species helps elucidate the energetics of the corresponding bimolecular process. Following preparation of the stable intermediate, low-power continuous-wave laser-radiation effects slow multiphoton excitation and decomposition along the lowest energy pathway. In this manner, infrared activation can be used to identify the lowest energy reaction in a complicated, bimolecular process. This technique is demonstrated in the present work. Proton bound dimers of simple aliphatic alcohols ($(R_1OH)H^+(R_2OH)$ where $R_1 = R_2 = CH_3$, C_2H_5, i-C_3H_7, n-C_3H_7, s-C_4H_9, t-C_4H_9, and t-C_5H_{11} are intermediates formed in gas phase reactions of the corresponding protonated alcohols with neutral alcohols. Products from the decomposition of these chemically activated species are compared with those obtained by slow multiphoton excitation. In addition, it is shown that isomeric ions are distinguished by formation of different sets of decomposition products. Also, we report the first observation of multiple sets of products arising from low-power infrared activation. This result is due to an exothermic isomerization in the transition state which makes accessible more than one reaction pathway. Use of infrared multiphoton excitation as a complementary technique to collisional activation of ions in mass spectrometric analysis of mixtures is discussed. For this study, ions are formed, stored, and detected by using techniques of ion cyclotron resonance (ICR) spectroscopy.

In complex chemical systems where multiple sets of products result from a bimolecular encounter, reaction coordinate diagrams have proven extremely useful for visualizing reaction energetics. Consider, for example, the hypothetical ion–molecule reaction between A^+ and B which has two exothermic reaction channels, reactions 1 and 2. Figure 1 depicts three possible sets of reaction coordinates for this system. Although this example is an ion–molecule reaction, the considerations are general and apply to reactions of neutral species as well. Typically, ΔH_1 and ΔH_2 are well known. AB^+ may represent a cluster or another stable species whose thermochemistry is well characterized. For most ion–molecule systems the values of activation energies E_{a1} and E_{a2} are not known. When reaction of A^+ with B yields both C^+ and F^+ all that can be inferred is that no point along paths followed on the potential energy surface from reactants to products exceeds the energy E^* available to the reactive intermediate AB^+. No information is available to distinguish among cases I, II, and III in Figure 1.

$$A^+ + B \rightarrow [AB^+]^* \rightarrow C^+ + D \qquad \Delta H_1 < 0 \qquad (1)$$

$$A^+ + B \rightarrow [AB^+]^* \rightarrow F^+ + G \qquad \Delta H_2 < 0 \qquad (2)$$

Several experimental techniques have been developed to probe details of a reaction potential energy surface.[1] These typically involve measuring branching ratios as a function of E^*.[1] One commonly used method is to form AB^+ from different sets of reactants (such as A + B^+).[2] Varying reactant translational energy also changes the value of E^*.[3] Formation of stable (i.e., vibrationally "cold") AB^+ followed by collisional excitation provides information on activation energies and the nature of the reaction coordinate in the exit channel.[4]

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