(2 mm); **5d** had bp 65–67° (0.5 mm), lit.[4] 84° (2 mm); **5e** had bp 56–58° (0.3 mm); **5f** had bp 60–63° (0.3 mm), lit.[4] 71° (2 mm); **5g** had bp 74° (0.25 mm.)

Dicyclohexyl-18-crown-6[26] (Aldrich), **6**, was used directly. Reagent grade alcohols were refluxed over and distilled from calcium hydride and then stored under nitrogen.

Solutions of potassium alkoxides in alcohols were prepared by the method of DePuy.[4]

Reaction Procedure. (a) For **6-***t***-BuOK-***t***-BuOH.** Into a glass-stoppered reaction vessel fashioned from 6-mm glass tubing was weighed 0.05 mmol of **3**. After addition of 1.0 ml of *t*-BuOH to dissolve **3**, 1.0 ml of a solution of 0.20 *M* **6** and 0.20 *M* *t*-BuOK in *t*-BuOH was added. After mixing of the contents, the reaction vessel was placed in a 50.0° constant-temperature bath for 3 hr. The vessels were removed and placed in ice. The vessel contents were quickly thawed with warm water, poured into 5 ml of water, and extracted with 5 ml of 40% diethyl ether–60% pentane. The extracts were analyzed by glpc.

(b) For *t*-**BuOK-***t***-BuOH.** Same procedure as above except for the absence of **6** and a 24-hr reaction period.

(c) For **6-***n***-BuOK-***n***-BuOH and 6-***sec***-BuOK-***sec***-BuOH.** Same procedure as with 6-*t*-BuOK–*t*-BuOH except solvent was not added to **3** prior to addition of 2 ml of 0.10 *M* **6** and 0.10 *M* base in solvent.

Glpc Separations and Analysis. Preparative glpc purification of **4a,c,e–g** and **5a,c–g** were conducted using a Varian Aerograph A-90P gas chromatograph with a 4 ft × ³/₈ in. column of 15% Carbowax 20M on Chromosorb W.

Analysis of reaction products was performed on a Varian Aerograph 1700 dual column flame ionization gas chromatograph employing 5 ft × ¹/₈ in. columns of 15% Carbowax 20M on Chromosorb P for reactions conducted in *t*-BuOH and 10-ft columns for reactions carried out in other solvents. Molar responses were determined to be: **4a/5a** = 1.12; **4c/5c** = 0.99; **4d/5d** = 1.09; **4e/5e** = 1.11; **4f/5f** = 1.11; **4g/5g** = 0.98.

Control Experiments. Reaction of **3a** with 0.10 *M* **6** in *n*-BuOH and *t*-BuOH under the conditions of the base-promoted reactions produced negligible amounts of phenylcyclopentenes. Absence of product isomerization was demonstrated by treating **3c** with 0.10 *M* **6**–0.10 *M* *t*-BuOK–*t*-BuOH and 0.10 *M* **6**–0.10 *M* *n*-BuOK–*n*-BuOH at 50.0° for varying reaction periods. Product proportions were invariant with time which demonstrated no isomerization for that product, **5c**, which would be most prone to isomerize.

Calculations. Primary deuterium isotope effects were calculated[27] from the relative proportions of **4a,b** and **5a,b** produced in reactions of **3a,b** with a given base–solvent combination. Hammett ρ values were calculated by computer linear regression least-squares analysis.[28]

(26) A mixture of two isomers: H. K. Frensdorf, *J. Amer. Chem. Soc.*, **93**, 4684 (1971).

(27) M. S. Silver, *J. Amer. Chem. Soc.*, **83**, 3487 (1961).
(28) H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953).

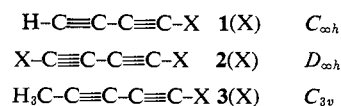# The Photoelectron Spectra of Halodiacetylenes, Dihalodiacetylenes, and Halomethyldiacetylenes

Edgar Heilbronner,* Volker Hornung, John P. Maier, and Else Kloster-Jensen

Contribution from the Physikalisch-Chemisches Institut der Universität Basel, CH-4056 Basel, Switzerland. Received September 25, 1973

Abstract: The photoelectron spectra, excited by HeI radiation, of the halodiacetylenes XC≡CC≡CH, dihalodiacetylenes XC≡CC≡CX, and halomethyldiacetylenes XC≡CC≡CCH₃ with X = Cl, Br, and I are presented. The data afford the determination of the ionization potentials, of spin–orbit coupling (for X = I and Br), and of the discrete vibrational excitation in some of the ionic states. The assignments of the photoelectron bands is discussed in terms of a ZDO LCBO model. It is shown that although the basis orbital parameters as utilized previously in the interpretation of the haloacetylenes XC≡CH and dihaloacetylenes XC≡CY can again reproduce the experimental ionization potentials well, erroneous spin–orbit couplings are predicted. As the magnitude of the spin–orbit coupling is a sensitive probe of the electronic environment and hence of the adequacy of the model, the pitfalls of parametrization to fit ionization potentials alone are illustrated. It is shown that inclusion of antibonding CC π orbitals yields a self-consistent rationalization of the ionization potential and spin–orbit coupling data. The assignment of the bands correlates with the vibrational fine structure observed and the shapes of the Franck–Condon envelopes.

Linear molecules containing heavy atoms, *e.g.*, haloacetylenes, are of special interest in photoelectron (PE) spectroscopy. Not only are their PE spectra of extreme simplicity, but the easily measurable band splits due to spin–orbit coupling yield additional information which makes them an ideal and sensitive probe of the adequacy of simple molecular orbital models.

In Figures 1–3 are shown the HeI PE spectra of the halodiacetylenes **1(X)**, dihalodiacetylenes **2(X)**, and halomethyldiacetylenes **3(X)** with X = Cl, Br, and I.

$$H-C\equiv C-C\equiv C-X \quad \mathbf{1(X)} \quad C_{\infty h}$$
$$X-C\equiv C-C\equiv C-X \quad \mathbf{2(X)} \quad D_{\infty h}$$
$$H_3C-C\equiv C-C\equiv C-X \quad \mathbf{3(X)} \quad C_{3v}$$

The ionization potential and vibrational excitation data are collected in Tables I–VI.

In the range from 8 to 18 eV the PE spectra of **1(X)** or **2(X)** consist of five or six bands, respectively. Bands 1–3 (**1(X)**) or 1–4 (**2(X)**) are twin π bands corresponding to an ionization process

$$M(X) + h\nu \longrightarrow M^+(^2\Psi_j) + e^- \tag{1}$$
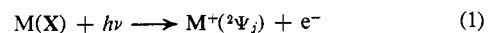
in which the photoelectron e⁻ is ejected from one of the sets of degenerate π orbitals $\psi_j \equiv \pi_\lambda(j)$ of the singlet ground state molecule M(X). (The lower index $\lambda = \pm 1$ of the orbitals $\pi_\lambda(j)$ represents the angular momentum quantum number.) This leaves the radical cation M⁺ in one or the other of the doublet states $^2\Psi_j \equiv$

Table I. Ionization Potentials of the Halodiacetylenes 1(X)[a]

Band	1		2		3		4	5
Ionic state	$\tilde{X}_{3/2}$	$\tilde{X}_{1/2}$	$\tilde{A}_{3/2}$	$\tilde{A}_{1/2}$	$\tilde{B}_{3/2}$	$\tilde{B}_{1/2}$	$\tilde{C}$	$\tilde{D}$
Ionization potential[b]	$I_{3/2}(1)$	$I_{1/2}(1)$	$I_{3/2}(2)$	$I_{1/2}(2)$	$I_{3/2}(3)$	$I_{1/2}(3)$	$I(4)$	$I(5)$
1(Cl)[c]	9.72[d]		12.15[d]		14.07[d]		16.82	17.37
1(Br)	9.59	9.67	11.85	11.96	13.20	13.30	16.10	16.99
1(I)	9.24	9.49	11.05	11.42	12.60[e]	14.90[e]		17.0

[a] In Tables I–III the ionization potentials are the vertical ones; those given in italics correspond to the 0 ← 0 transition. All values in eV. [b] Bands 1–3, values ±0.02 eV; bands 4 and 5, values ±0.05 eV. [c] Spurious peaks at 10.70, 11.74, and 11.85 eV are of an impurity. [d] Spin–orbit coupling not resolved. [e] Estimated vertical ionization potentials, in view of the presence of bands due to traces of water.

Table II. Ionization Potentials of the Dihalodiacetylenes 2(X) (see legend of Table I)

Band	1		2		3		4		5	6
Ionic state	$\tilde{X}_{3/2}$	$\tilde{X}_{1/2}$	$\tilde{A}_{3/2}$	$\tilde{A}_{1/2}$	$\tilde{B}_{3/2}$	$\tilde{B}_{1/2}$	$\tilde{C}_{3/2}$	$\tilde{C}_{1/2}$	$\tilde{D}$	$\tilde{E}$
Ionization potential[a]	$I_{3/2}(1)$	$I_{1/2}(1)$	$I_{3/2}(2)$	$I_{1/2}(2)$	$I_{3/2}(3)$	$I_{1/2}(3)$	$I_{3/2}(4)$	$I_{1/2}(4)$	$I(5)$	$I(6)$
2(Cl)	9.34[b]		11.68[b]		13.75[b]		14.14[b]		16.85	17.28
2(Br)	9.20	9.29	11.22	11.40	12.63	12.85	13.27[c]	13.36	15.85	16.20
2(I)	8.76	9.05	10.25	10.78	11.40	11.79	12.5[c]	12.61	14.60	14.90

[a] Bands 1–4, values ±0.02 eV; bands 5 and 6, values ±0.05 eV. [b] Spin–orbit coupling not resolved. [c] Estimated value from Franck–Condon profile.

Table III. Ionization Potentials of Halomethyldiacetylenes 3(X) (see legend of Table I)

Band	1		2		3	
Ionic state	$\tilde{X}_{3/2}$	$\tilde{X}_{1/2}$	$\tilde{A}_{3/2}$	$\tilde{A}_{1/2}$	$\tilde{B}_{3/2}$	$\tilde{B}_{1/2}$
Ionization potential[a]	$I_{3/2}(1)$	$I_{1/2}(1)$	$I_{3/2}(2)$	$I_{1/2}(2)$	$I_{3/2}(3)$	$I_{1/2}(3)$
3(Cl)	9.15[b]		11.60[b]		13.76[b]	
3(Br)	9.06	9.10[c]	11.31	11.42	12.87[b]	
3(I)	8.82	9.05	10.65	11.02	12.20[b]	

[a] Bands 1–3, values ±0.02 eV. Higher ionization potentials cannot be determined unambiguously (see Figure 3). [b] Spin–orbit coupling not resolved. [c] Value uncertain (range 9.10–9.14 eV) due to complexity of band envelope (see Figure 3).

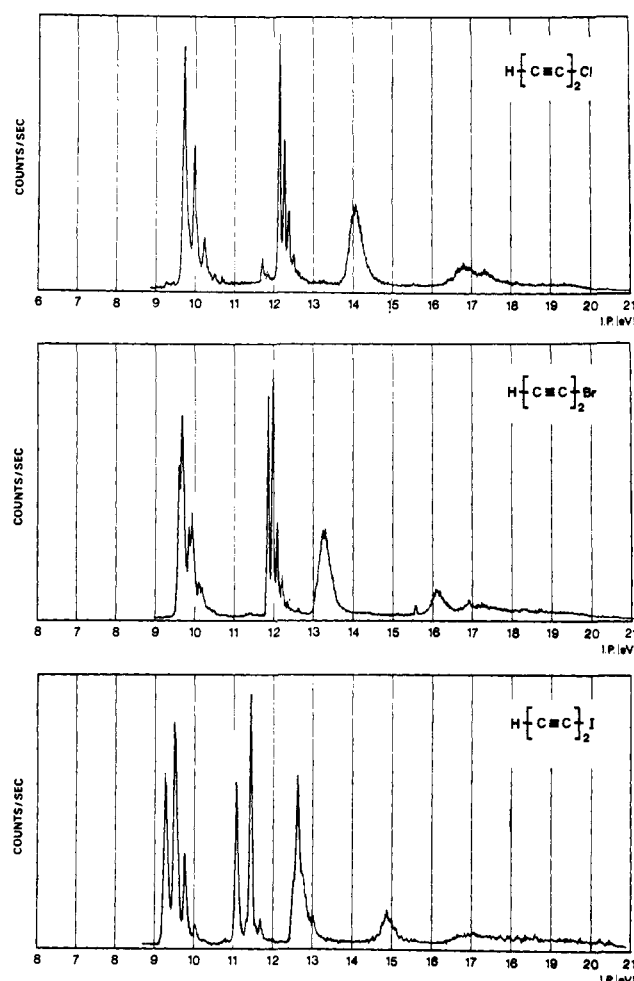**Table IV.** Vibrational Frequencies Excited in the Ionic States of the Halodiacetylenes 1(X)[a]

Electronic state Band (Figure 2)	$\tilde{X}_{\Omega}$[b] 1	$\tilde{A}_{\Omega}$[b] 2	—X[c]—				
			ν_1	ν_2	ν_3	ν_4	ν_5
1(Cl)	2180, 320	1050	3327	2252	2071	1093	525
1(Br)	2180	1050	3335	2237	2095	1046	425
1(I)	2100	1050	3332	2211	2060	1025	362

[a] All values in cm⁻¹, frequencies from PE spectra ±80 cm⁻¹. [b] $\Omega = {}^3/_2, {}^1/_2$. [c] Ground molecular state values from D. H. Christensen, I. Johnsen, P. Klaboe, and E. Kloster-Jensen, *Spectrochim Acta, Part A*, **25**, 1569 (1964); M. K. Phibbs, *ibid.*, **29**, 599 (1973); Approximate description of the Σ^+ normal modes: ν_1 (C–H str.), ν_2 (C≡C sym. str.), ν_3 (C≡C asym. str.), ν_4 (C–C str.), ν_5 (C–X str.).

Table V. Vibrational Frequencies Excited in the Ionic States of the Dihalodiacetylenes 2(X)[a]

Electronic state Band (Figure 1)	$\tilde{X}_{\Omega}$[b] 1	$\tilde{A}_{\Omega}$[b] 2	—X[c]—		
			ν_1	ν_2	ν_3
2(Cl)	2180	1290 (970)[d]	2245	1202	330
2(Br)	2100	1050	2205	1127	250
2(I)	2100	970	2227	1145	185

[a] All values in cm⁻¹, frequencies from PE spectra ±80 cm⁻¹. [b] $\Omega = {}^3/_2, {}^1/_2$. [c] Ground molecular state values from E. Kloster-Jensen, unpublished results. Approximate description of the Σ_g^+ normal modes: ν_1 (C≡C str.), ν_2 (C–C str.), ν_3 (C–X str.). [d] Vibrational intervals corresponding to the difference between $v' = 1$ and $v' = 0$ or the $v' = 2$ and $v' = 1$ levels, respectively.

Figure 1. PE spectra of the halodiacetylenes 1 (X) with X = Cl, Br, and I.

$^2\Pi_{3/2}$ or $^2\Pi_{1/2}$. Band(s) 4 or 5, 6 are classified as σ bands under the assumption that the photoelectron stems from σ orbitals $\psi_j \equiv \sigma(j)$ which are centered essentially on the axially symmetrical lone-pair orbital n(X) of the halogen

Table VI. Vibrational Frequencies Excited in the Ionic States of the Halomethyldiacetylenes 3(X)^a

Electronic state Band (Figure 3)	$\tilde{X}_\Omega{}^b$ 1	$\tilde{A}_\Omega{}^b$ 2	X^c ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7
3(Cl)	2260, 400	1290 (970)^d	2935	2272	2179	1385	1231	862	470
3(Br)	2020	1050	2933	2259	2162	1385	1212	815	365
3(I)	2020	1050	2933	2246	2158	1385	1197	815	315

^{a} All values in cm^{-1}; frequencies from PE spectra ±80 cm^{-1}. ^{b} $\Omega = {}^3/_2, {}^1/_2$. ^{c} Ground molecular state values from D. W. Turner, *Proc. Roy. Soc., Ser. A*, **307**, 15 (1968). Approximate description of the Σ^+ normal modes listed: ν_1 (CH$_3$ sym. str.), ν_2 (C≡C sym. str.), ν_3 (C≡C asym. str.), ν_4 (CH$_3$ sym. def.), (C–C asym. str.), ν_6 (C–C sym. str.), ν_7 (C–X str.). ^{d} Vibrational intervals corresponding to the difference between the $v' = 1$ and $v' = 0$ or the $v' = 2$ and $v' = 1$ levels, respectively.
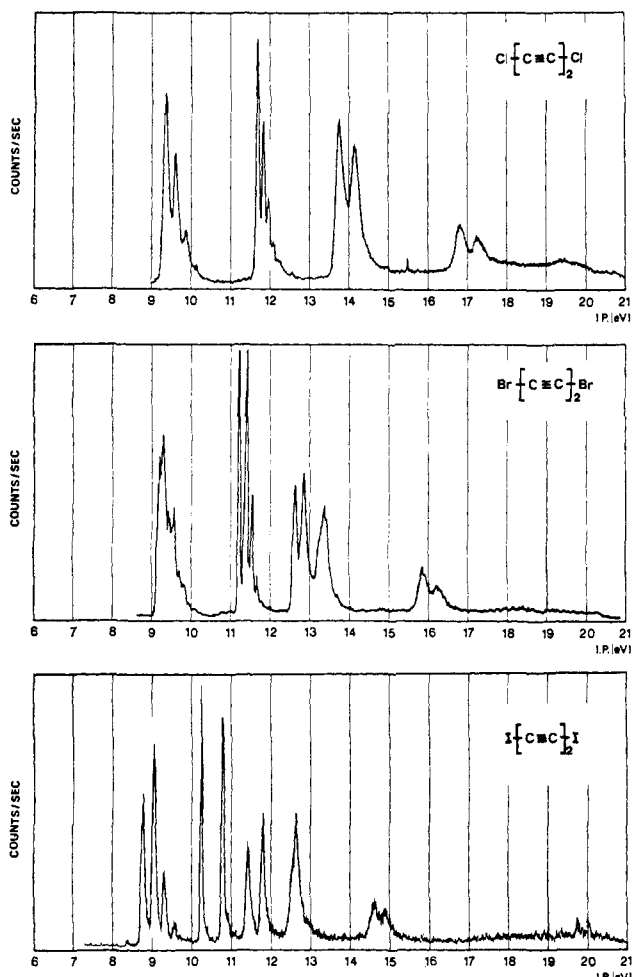

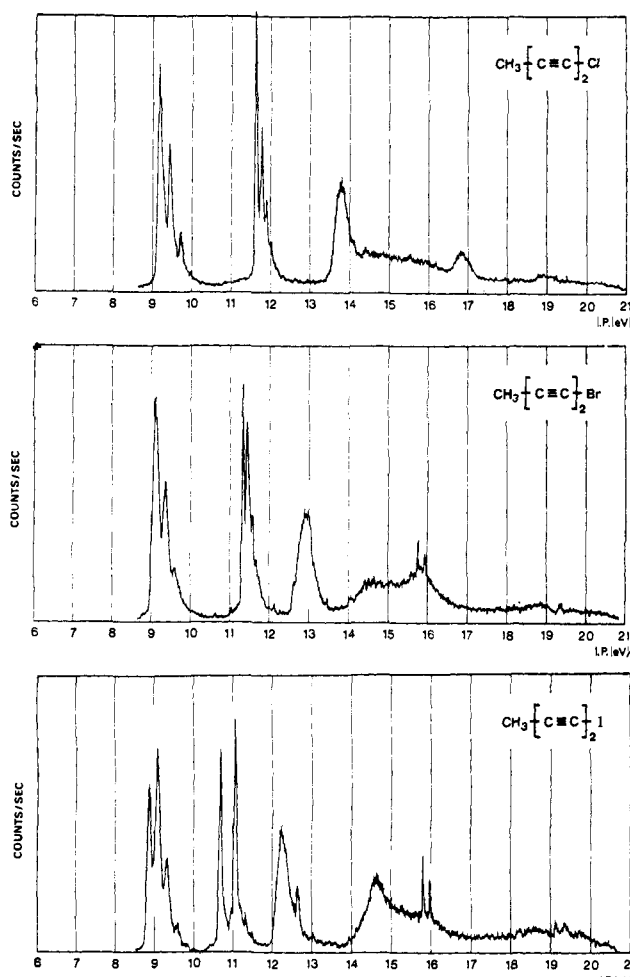**Figure 2.** PE spectra of the dihalodiacetylenes **2**(X) with X = Cl, Br, and I.

Figure 3. PE spectra of the halomethyldiacetylenes **3**(X) with X = Cl, Br, and I.

atom X in **1**(X) or on the symmetry adapted linear combinations

$$n_+(X) = (n(X_1) + n(X_2))/\sqrt{2}$$
$$n_-(X) = (n(X_1) - n(X_2))/\sqrt{2} \tag{2}$$

in **2**(X), leaving M$^+$ in the doublet states $^2\Sigma$ (**1**(X)) or $^2\Sigma_g{}^+$, $^2\Sigma_u{}^+$ (**2**(X)), respectively.

It is further assumed that the electronic ground state X of M is well represented by a single determinantal wave function

$$\Gamma = \|\ldots\psi_j\bar{\psi}_j\ldots\psi_2\bar{\psi}_2\psi_1\bar{\psi}_1\| \tag{3}$$

based on the canonical Hartree–Fock SCF orbitals ψ_j, i.e., which correspond to the configurations

1(X): $\ldots\sigma(4)^2\pi_\lambda(3)^4\pi_\lambda(2)^4\pi_\lambda(1)^4$

2(X): $\ldots\sigma_u(6)^2\sigma_g(5)^2\pi_{\lambda g}(4)^4\pi_{\lambda u}(3)^4\pi_{\lambda g}(2)^4\pi_{\lambda u}(1)^4$ $\tag{4}$

A qualitative representation of the molecular orbitals $\psi_j \equiv \pi_{\lambda(g,u)}(j)$, $\sigma_{(g,u)}(j)$ used in (3) and (4) is given in the schematic diagrams of Figure 4.

Ejecting an electron from an orbital ψ_j of M will lead in Koopmans' approximation[1] to configurations

$$^2\Psi_j = \begin{cases} \|\ldots\psi_j\ldots\psi_1\bar{\psi}_1\| \\ \|\ldots\bar{\psi}_j\ldots\psi_1\bar{\psi}_1\| \end{cases} \tag{5}$$

of M$^+$, e.g., for the molecules **1**(X) to

$$^2\Pi_{3/2}(j) = \begin{cases} \|\ldots\pi_1(j)\bar{\pi}_1(j)\pi_{-1}(j)\ldots\| \\ \|\ldots\bar{\pi}_1(j)\pi_{-1}(j)\bar{\pi}_{-1}(j)\ldots\| \end{cases}$$

$$^2\Pi_{1/2}(j) = \begin{cases} \|\ldots\pi_1(j)\pi_{-1}(j)\bar{\pi}_{-1}(j)\ldots\| \\ \|\ldots\pi_1(j)\bar{\pi}_1(j)\bar{\pi}_{-1}(j)\ldots\| \end{cases} \tag{6}$$

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

which are representative for the following states of M^+, where the indices in brackets correspond to the number j of the vacated orbital. The symbols $\tilde{X}$, $\tilde{A}$, $\tilde{B}$, ... are conventionally used for the electronic ground state and successive electronically excited states of the radical cation M^+, whereas X is reserved for the neutral mole-

$$1(X): \quad \tilde{X}_{3/2} \equiv {}^2\Pi_{3/2}(1); \quad \tilde{X}_{1/2} \equiv {}^2\Pi_{1/2}(1)$$

$$\tilde{A}_{3/2} \equiv {}^2\Pi_{3/2}(2); \quad \tilde{A}_{1/2} \equiv {}^2\Pi_{1/2}(2)$$

$$\tilde{B}_{3/2} \equiv {}^2\Pi_{3/2}(3); \quad \tilde{B}_{1/2} \equiv {}^2\Pi_{1/2}(3)$$

$$\tilde{C} \equiv {}^2\Sigma(4)$$

$$2(X): \quad \tilde{X}_{3/2} \equiv {}^2\Pi_{3/2u}(1); \quad \tilde{X}_{1/2} \equiv {}^2\Pi_{1/2u}(1)$$

$$\tilde{A}_{3/2} \equiv {}^2\Pi_{3/2g}(2); \quad \tilde{A}_{1/2} \equiv {}^2\Pi_{1/2g}(2) \qquad (7)$$

$$\tilde{B}_{3/2} \equiv {}^2\Pi_{3/2u}(3); \quad \tilde{B}_{1/2} \equiv {}^2\Pi_{1/2u}(3)$$

$$\tilde{C}_{3/2} \equiv {}^2\Pi_{3/2g}(4); \quad \tilde{C}_{1/2} \equiv {}^2\Pi_{1/2g}(4)$$

$$\tilde{D} \equiv {}^2\Sigma_g^+(5)$$

$$\tilde{E} \equiv {}^2\Sigma_u^+(6)$$
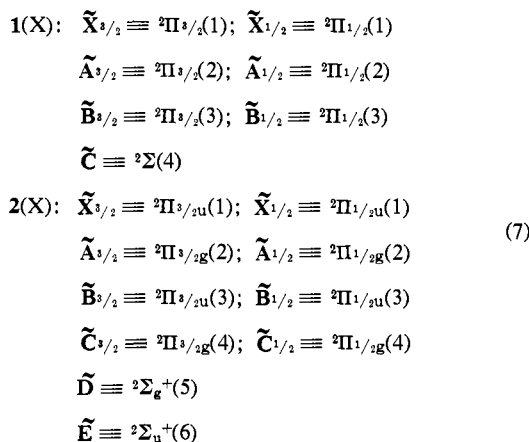
cule M.[2] This notation is used in Tables I–VI.

The lower index Ω in the designation of the π states, *e.g.*, $\tilde{X}_\Omega \equiv {}^2\Pi_\Omega(1)$, is the total angular momentum quantum number $\Omega = \Lambda + \Sigma$ (Λ, Σ = total orbital and spin angular momentum quantum numbers, respectively) which can take the values $\Omega = 1 + {}^1/_2 = {}^3/_2$ and $\Omega = 1 - {}^1/_2 = {}^1/_2$. States with $\Omega = {}^3/_2$ and ${}^1/_2$ have different energies due to spin–orbit coupling, the state with $\Omega = {}^3/_2$ lying below that with $\Omega = {}^1/_2$ (inversion). Consequently the state energy split

$$\Delta(j) = \mathcal{E}({}^2\Pi_{3/2}(j)) - \mathcal{E}({}^2\Pi_{1/2}(j)) = I_{3/2}(j) - I_{1/2}(j) \qquad (8)$$

due to spin–orbit coupling is defined as a negative quantity by convention.

For M^+ in a state ${}^2\Pi_\Omega(j)$ the split $\Delta(j)$ can be written in a first approximation as the sum of contributions from the individual atoms r in the system. Each of these contributions is proportional (a) to a characteristic constant $\zeta(\text{atom r})$ which increases roughly as the square Z_r^2 of the nuclear charge of the atom, and (b) to the probability of presence of the unpaired electron at the center r.[3,4]

Individual π bands are characterized by the ionization potentials $I_\Omega(j)$, the σ bands by $I(j)$. For a given π band the $I_\Omega(j)$ are defined as the positions of the fine-structure peaks of highest intensity (*e.g.*, the $0 \leftarrow 0$ components of bands 1 and 2) or as the position $I_m(j)$ of the maximum of the Franck–Condon envelope if the vibrational structure is unresolved. Thus for bands 1 and 2 we have $I_\Omega(j) = I_{\Omega,a}(j) \approx I_{\Omega,v}(j)$, *i.e.*, $I_\Omega(j)$ is equal to the adiabatic and close to the vertical ionization potentials. For unresolved bands we assume in a first approximation $I_\Omega(j) = I_m(j) \approx I_{\Omega,v}(j)$.

In the framework of the Koopmans' approximation,[1] the energies of the states ${}^2\Pi_{3/2}(j)$ and ${}^2\Pi_{1/2}(j)$ are split symmetrically relative to $\epsilon(\pi_\lambda(j)) - \mathcal{E}(X)$ so that

$$\epsilon(\pi_\lambda(j)) = -\bar{I}(j) = -(I_{3/2}(j) + I_{1/2}(j))/2 \qquad (9)$$

Figure 4. Qualitative representations of the molecular orbitals of of $1(X)$ and $2(X)$.

where $\epsilon(\pi_\lambda(j))$ is the orbital energy associated with the canonical molecular π orbital $\pi_\lambda(j)$ singly occupied in the configurations (6) of M^+. This approximation assumes that spin–orbit coupling can be treated formally as a first-order perturbation. Second-order interactions, *e.g.*, between the states ${}^2\Pi_{1/2}$ and ${}^2\Sigma_{1/2}$ are small because of the large difference in energy. This conclusion is supported by the observation that a "sum-rule" for spin–orbit splittings is obeyed within the limits of experimental error[5,6] in the case of the halo- and dihaloacetylenes $4(X)$ and $5(X,Y)$.

In previous communications of this series we have discussed the PE spectra of the four haloacetylenes $4(X)$ with $X = F$, Cl, Br, and I[5] and of the six dihaloacetylenes $5(X,Y)$ with X, $Y = Cl$, Br, and I.[6] The π-band

$$\begin{array}{cc} H-C\equiv C-X & X-C\equiv C-Y \\ 4(X) & 5(X,Y) \end{array}$$

positions $I(j)$ were interpreted in terms of a simple ZDO LCBO (linear combination of bond orbitals) model[7] using only the lone-pair orbitals $p_\lambda(X)$ of the halogen atoms and the π orbitals $\pi_\lambda(C\equiv C)$ of the triple bonds as a basis, *i.e.*, yielding molecular orbitals which correspond to those sketched in Figure 4, except for the varying basis orbital coefficients. It was shown that such a model reproduces the π-ionization potentials of all the ten compounds within ± 0.05 eV. However, in the case of $5(X,Y)$ the model did not yield the correct spin–orbit splittings $\Delta(j)$.[6]

It is therefore evident that even perfect agreement of calculated and "observed" orbital energies (assuming Koopmans' approximation) is not a sufficient criterion for the quality of a chosen orbital model, *i.e.*, it does not

(2) (a) C. Baker and D. W. Turner, *Proc. Roy. Soc., Ser. A*, **308**, 19 (1968); (b) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy," Wiley-Interscience, London, 1970.
(3) *Cf.* J. N. Murrell, S. F. A. Kettle, and J. M. Tedder, "Valence Theory," Wiley, London, 1965.
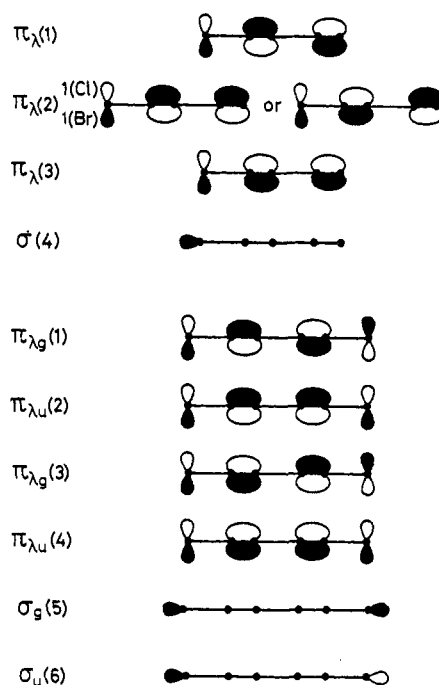(4) E. Ishiguro and M. Kobori, *J. Phys. Soc. Jap.*, **22**, 263 (1967).

(5) H. J. Haink, E. Heilbronner, V. Hornung, and E. Kloster-Jensen, *Helv. Chim. Acta*, **53**, 1073 (1970).
(6) E. Heilbronner, V. Hornung, and E. Kloster-Jensen, *Helv. Chim. Acta*, **53**, 331 (1970).
(7) G. G. Hall, *Proc. Roy. Soc., Ser. A*, **205**, 541 (1951); D. F. Brailsford and B. Ford, *Mol. Phys.*, **18**, 621 (1970); J. N. Murrell and W. Schmidt, *J. Chem. Soc., Faraday Trans. 2*, **68**, 1709 (1972), and references given therein.

imply that it will also be adequate for the rationalization or prediction of other PE spectroscopic quantities (which refer to the radical cation M^+), let alone of properties of the neutral parent molecule M. This is of course well known.[1,8] Nevertheless, as this is a point of some importance in view of the widespread endeavors to parametrize simple molecular orbital models only on the basis of PE ionization potentials, we shall demonstrate the shortcomings of the simple LCBO model using 2(X) as an example. Relative to the basis the

$$X-C\equiv C-C\equiv C-X$$
$$p_{\lambda,1}(X) \quad \pi_{\lambda,1} \quad \pi_{\lambda,2} \quad p_{\lambda,2}(X) \tag{10}$$
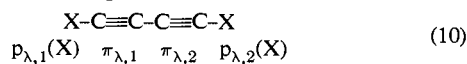
following matrix elements are defined, where $\mathfrak{IC}$ stands for the hamiltonian of the π system

$$A_X = \langle p_{\lambda,r}(X)|\mathfrak{IC}|p_{\lambda,r}(X)\rangle$$
$$A_{CC} = \langle \pi_{\lambda,r}|\mathfrak{IC}|\pi_{\lambda,r}\rangle$$
$$B_{CX} = \langle p_{\lambda,r}(X)|\mathfrak{IC}|\pi_{\lambda,r}\rangle \tag{11}$$
$$B_{XX} = \langle \pi_{\lambda,1}|\mathfrak{IC}|\pi_{\lambda,2}\rangle$$

Solving the secular determinant defined by (10) and (11), and using Koopmans' approximation in the form (9) yields

$$A_{CC} + A_X = -\frac{1}{2}(\bar{I}(\bar{1}) + \bar{I}(\bar{2}) + \bar{I}(\bar{3}) + \bar{I}(\bar{4}))$$

$$A_{CC} - A_X = \frac{1}{2}\frac{(\bar{I}(\bar{4}) - \bar{I}(\bar{2}))^2 - (\bar{I}(\bar{3}) - \bar{I}(\bar{1}))^2}{\bar{I}(\bar{1}) - \bar{I}(\bar{2}) + \bar{I}(\bar{3}) - \bar{I}(\bar{4})} \tag{12}$$

$$B_{CC} = \frac{1}{2}(\bar{I}(\bar{1}) - \bar{I}(\bar{2}) + \bar{I}(\bar{3}) - \bar{I}(\bar{4}))$$

$$B_{CX} = -\left[A_X A_{CC} - \frac{1}{2}(\bar{I}(\bar{1})\bar{I}(\bar{3}) + \bar{I}(\bar{2})\bar{I}(\bar{4}))\right]^{1/2}$$

The parameters A_X, A_{CC}, B_{CX}, B_{CC} calculated from (12) (in eV), i.e.,

	A_{CC}	A_X	B_{CX}	B_{CC}	
X = Cl	-11.00	-13.4	-1.10	-1.37	
X = Br	-10.87	-12.43	-1.00	-1.32	(13)
X = I	-10.59	-11.19	-0.96	-1.29	

necessarily reproduce the observed $I(j)$ values exactly and they compare favorably to those derived previously from the PE spectra of 4(X)[5] and 5(X,Y)[6] (in eV).

	A_X				A_{CC}		B_{CX}			
	Cl	Br	I	Cl	Br	I	Cl	Br	I	
4(X)	-13.3	-11.9	-10.6	-11.4	-11.4	-11.4	-1.4	-1.3	-1.0	
5(X, Y)	-13.4	-12.3	-10.9	-11.1	-10.9	-10.6	-1.3	-1.2	-1.1	(14)

However, it is easy to show that the linear combinations

$$\pi_\lambda(j) = a_j(p_{\lambda,1}(X) + p_{\lambda,2}(X)) + b_j(\pi_{\lambda,1} + \pi_{\lambda,2}) \tag{15}$$

corresponding to the LCBO model orbital energies $\epsilon(\pi_\lambda(j)) = -\bar{I}(j)$ are rather poor, by making use of the information contained in the splittings due to spin–orbit coupling. As discussed previously,[4,5,6,9] these quantities can be calculated according to

$$\Delta(j) = 2a_j^2\zeta(X) \tag{16}$$

where $\zeta(X)$ is the spin–orbit coupling constant for the halogen atom X and a_j the atomic orbital coefficient

of the halogen p_λ orbitals in the linear combinations $\pi_\lambda(j)$ given in (15). The implication of eq 16 and of the normalizing condition $\Sigma a_j^2 = 1$, is the existence of a "sum-rule" for spin–orbit splittings, as mentioned above. This rule has been stated and discussed previously[5,6] and is found to hold for the molecules presented in this communication, as well as for the systems halomethylacetylenes, halotrifluoromethylacetylenes, and cyanohaloacetylenes to be discussed in a future publication.

The constants $\zeta(X)$ can be derived from the electronic spectra of the free halogen atoms $X(\zeta(X) = (2/3)\cdot[\mathcal{E}(^2P_{3/2}) - \mathcal{E}(^2P_{1/2})]$; $\zeta(Cl) = -0.073$ eV; $\zeta(Br) = -0.305$ eV; $\zeta(I) = -0.628$ eV),[10] or from the PE spectra of the halogens $X_2\mathcal{E}(\zeta(X) = \mathcal{E}(^2\Pi_{3/2u}) - \mathcal{E}(^2\Pi_{1/2u})$; $\zeta(Cl) = -0.08_0$ eV;[11,12] $\zeta(Br) = -0.35_0$ eV[11,12], -0.36 eV;[13] $\zeta(I) = -0.63_5$ eV,[11] -0.65 eV,[12] -0.64 eV[13]), or of axially symmetrial halides, e.g., the hydrogen halides HX $(\zeta(X) = \mathcal{E}(^2\Pi_{3/2}) - \mathcal{E}(^2\Pi_{1/2})$; $\zeta(Cl) = -0.10$ eV,[14] -0.08 eV;[15] $\zeta(Br) = -0.32$ eV,[14] -0.33 eV,[15] -0.335 eV;[16] $\zeta(I) = -0.66$ eV[14]). The splits $\zeta(X)$ observed for the lone-pair bands in the (PE) spectra of alkyl halides RX (e.g., methyl halides MeX: $\Delta(Cl) = -0.08$ eV;[17,18] $\Delta(Br) = -0.030$ eV,[17] -0.032 eV;[18-20] $\Delta(I) = -0.64$ eV,[17] -0.63 eV,[18] -0.62 eV[19,20]) are identical within the limits of error with $\zeta(X)$, notwithstanding the conjugation of the halogen p_λ orbitals with the pseudo-π-orbitals of the alkyl moiety. Finally the splits $\Delta(2)$ observed for the central π band in the PE spectra of 5(X,-X) $(\Delta(2) = -0.29$ eV for X = Br, $\Delta(2) = -0.60$ eV for X = I)[6] yield only lower limits for $\zeta(X)$ because of the mixing of $(p_{\lambda,1} - p_{\lambda,2})/\sqrt{2}$ with the antibonding π orbital π_λ^* of the central triple bond. Using the results to be developed later in this communication, one obtains from the $\Delta(2)$ values quoted above for 5(Br,Br) and 5(I,I) the constants $\zeta(Br) = -0.32$ eV and $\zeta(I) = -0.65$ eV. For the present work we have chosen $\zeta(Cl) = -0.10$ eV, $\zeta(Br) = -0.33$ eV, and $\zeta(I) = -0.65$ eV as representative values.

For 2(Br) and 2(I) one obtains according to (16) the following predictions for $\Delta(j)$ which are quite at variance with the observed values (17). This comparison clearly indicates that the parameters in (13) and (14) must be seriously in error, i.e., even qualitatively.

(10) C. E. Moore(-Sitterley), "Atomic Energy Levels," U. S. Bureau of Standards Circular 467, Vol. 1-3, 1949, 1952, 1958; T. M. Dunn, Trans. Faraday Soc., 51, 1441 (1961).

(11) A. B. Cornford, D. C. Frost, C. A. McDowell, J. L. Ragle, and I. A. Stenhouse, J. Chem. Phys., 54, 2651 (1971).

(12) A. W. Potts and W. C. Price, Trans. Faraday Soc., 67, 1242 (1971).

(13) S. Evans and A. F. Orchard, Inorg. Chim. Acta, 5, 81 (1971).

(14) D. C. Frost, C. A. McDowell, and D. A. Vroom, J. Chem. Phys., 46, 4255 (1967).

(15) H. J. Lempka, T. R. Passmore, and W. C. Price, Proc. Roy. Soc., Ser. A, 304, 53 (1968).

(16) J. Delwiche, P. Natalis, J. Momigny, and J. E. Collin, J. Electron Spectrosc., 1, 219 (1972/73).

(17) W. C. Price, J. Chem. Phys., 4, 539, 547 (1936).

(18) J. L. Ragle, I. A. Stenhouse, D. C. Frost, and C. A. McDowell, J. Chem. Phys., 53, 178 (1970).

(19) F. Brogli and E. Heilbronner, Helv. Chim. Acta, 54, 1423 (1971).

(20) A. W. Potts, H. J. Lempka, D. G. Streets, and W. C. Price, Phil. Trans. Roy. Soc. London, Ser. A, 268, 59 (1970).

(8) W. G. Richards, J. Mass. Spectrom. Ion Phys., 2, 419 (1969), and references given therein.

(9) E. Heilbronner, V. Hornung, and E. Kloster-Jensen, Helv. Chim. Acta, 53, 331 (1970).

	2(Br)		2(I)		
	Calcd	Obsd	Calcd	Obsd	
$-\Delta(1)$	0.03	0.09	0.10	0.29	
$-\Delta(2)$	0.13	0.18	0.42	0.53	(17)
$-\Delta(3)$	0.27	0.22	0.54	0.39	
$-\Delta(4)$	0.17	0.09	0.21	0.11	

Indeed, the sequence $-\Delta(2) > -\Delta(3) > -\Delta(1) > -\Delta(4)$ observed for 2(I) can only arise if the basis orbital energy A_I lies *above* A_{CC}, *i.e.*, if $|A_I| < |A_{CC}|$, as can be seen by inspection from the qualitative orbital correlation diagram of Figure 5,[21] which is almost self-explanatory. The split between the linear combinations

$$p_{\lambda+} = (p_{\lambda,1} + p_{\lambda,2})/\sqrt{2}$$
$$p_{\lambda-} = (p_{\lambda,1} - p_{\lambda,2})/\sqrt{2} \tag{18}$$

of the basis p orbitals of the iodine atoms must be practically zero (for clarity it has been exaggerated in Figure 5), whereas the linear combinations

$$\pi_{\lambda,+} = (\pi_{\lambda,1} + \pi_{\lambda,2})/\sqrt{2}$$
$$\pi_{\lambda,-} = (\pi_{\lambda,1} - \pi_{\lambda,2})/\sqrt{2} \tag{19}$$

are split by 2.45 eV, as indicated by the results for diacetylene[2a,22,23] and triacetylene.[23] They must therefore bracket the orbitals given in (18). The observation that $\Delta(2)$ is the largest and $\Delta(4)$ the smallest of the spin–orbit coupling splits is only compatible with the conclusion stated above, *i.e.*, that the basis orbitals $p_{\lambda,s}$ lie above $\pi_{\lambda,r}$. Thus the splits $\Delta(j)$ due to spin–orbit coupling indicate that the set of parameters in (13) cannot be even *qualitatively* correct notwithstanding the fact that they reproduce the observed ionization potential exactly.

This result shows dramatically that simple LCBO models with a basis consisting of bonding orbitals only can be parametrized in such a way as to reproduce observed ionization potentials exactly under the assumption of Koopmans' approximation, but that the corresponding linear combinations will be inadequate; *i.e.*, they will yield erroneous charge distributions and/or spin–orbit couplings for the radical cation M^+. Obviously, for molecular systems of the type under discussion the observed splittings $\Delta(j)$ represent a much more sensitive tool for the parametrization of an LCBO or any other orbital model, because they yield information about the size of atomic orbital coefficients at selected centers in the radical cation M^+.

We shall now show how a parametrization can be obtained that allows a self-consistent rationalization of all the PE spectroscopic data (*i.e.*, $I(j)$ and $\Delta(j)$ of the compounds 1(X), 2(X), 4(X), and 5(X,Y) studied so far. To derive such a model in the framework of an LCBO approximation it is obviously necessary to enlarge the basis and this is achieved most easily by including the antibonding π orbitals $\pi_{\lambda,r}^*$ of the triple bonds. This is indicated in the following diagram (20) for 2(X), which also shows the convention used for the relative phases of the basis orbitals. As a consequence the
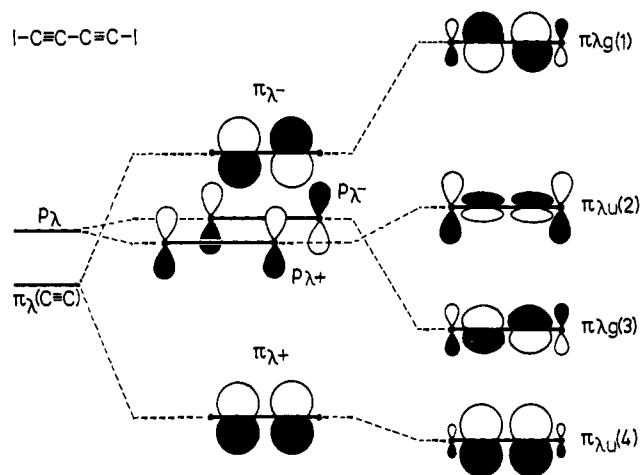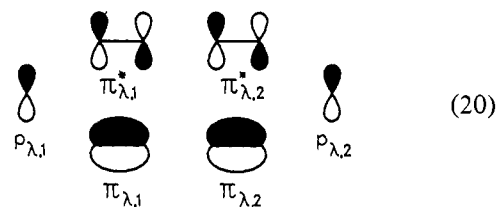

Figure 5. Orbital correlation diagram for diiododiacetylene 2(I).

$$\tag{20}$$

set of parameters in (11) has to be increased by the inclusion of

$$A_{CC}^* = \langle \pi_{\lambda,r}^* | \mathcal{H} | \pi_{\lambda,r}^* \rangle$$
$$B_{CX}^* = \langle p_{\lambda,1} | \mathcal{H} | \pi_{\lambda,1}^* \rangle$$
$$B_{CC}^* = \langle \pi_{\lambda,1} | \mathcal{H} | \pi^*_{\lambda,2} \rangle \tag{21}$$
$$B_{CC}^{**} = \langle \pi_{\lambda,1}^* | \mathcal{H} | \pi_{\lambda,2}^* \rangle$$

Note the changes in sign for other pairs of orbitals, *e.g.*, $\langle p_{\lambda,2} | \mathcal{H} | \pi_{\lambda,2}^* \rangle = -B_{CX}^*$ etc. To simplify our treatment we postulate that

$$B_{CX}^* = B_{CX}$$
$$B_{CC}^* = B_{CC}^{**} = B_{CC} \tag{22}$$

To calibrate the parameters in (11) and (21) under the restriction (22), we use the data for diiodoacetylene 5(I,I) as a start. The choice of this particular molecule is motivated by the fact that the presence of two iodine centers with large $\zeta(I)$ leads to large and easily measurable splits $\Delta(j)$. A few numerical experiments yield the following set of starting parameters (in eV)

$$A_{CC} = -11.10$$
$$A_{CC}^* = -6.00$$
$$A_I = -10.43 \tag{23}$$
$$B_{CI} = -1.04_5$$

which reproduce the observed data of 5(I,I) rather well.

	Obsd	Calcd		Obsd	Calcd	
$I(1)$	9.25	9.29	$-\Delta(1)$	0.44	0.40	
$I(2)$	10.93	10.82	$-\Delta(2)$	0.60	0.60	(24)
$I(3)$	12.28	12.28	$-\Delta(3)$	0.21	0.25	

The $\Delta(j)$ have been calculated according to (16) from the atomic orbital coefficient a_j of

$$\pi_\lambda(j) = a_j(p_{\lambda,1} + p_{\lambda,2}) + b_j\pi_{\lambda,1} + c_j\pi_{\lambda,1}^* \tag{25}$$

using $\zeta(I) = -0.65$ eV.

(21) E. Heilbronner, *Proc. Int. Congr. Pure Appl. Chem. 23rd*, 7, 9 (1971).
(22) C. Baker and D. W. Turner, *Chem. Commun.*, 797 (1967).
(23) F. Brogli, E. Heilbronner, V. Hornung, and E. Kloster-Jensen, *Helv. Chim. Acta*, 56, 2171 (1973).
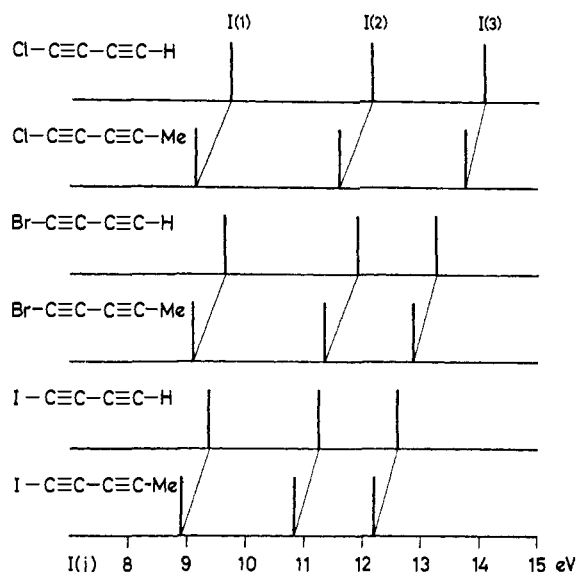
Figure 6. Methyl group induced shifts in the π-band positions of halomethyldiacetylenes **3**(X) relative to those of the halodiacetylenes **1**(X) with X = Cl, Br, and I.

A similar treatment of **5**(Br,Br) and **5**(Cl,Cl), keeping the basis orbital energy of the antibonding π orbitals $\pi_{\lambda,r}^*$ at the fixed value $A^* = -6.00$ eV, yields $A_{Br} = -11.79$ eV, $A_{Cl} = -12.96$ eV, $B_{CBr} = -1.27$ eV, and $B_{CCl} = -1.46$ eV.

It has been observed, e.g., in the case of the halogen hydrides HX,[15] the halogens X_2,[11,12] the methyl halides CH_3X,[24] the haloacetylenes **4**(X),[5] or the trimethyl-silylhaloacetylenes,[25] that the basis orbital energies A_X of the heteroatoms are linear functions with slope unity of the ionization potentials $I(X)$ of the free atoms X[9] (process $X(^2P_{3/2}^0) \rightarrow X^+(^3P_2) + e^-$; $I(F) = 17.42$ eV, $I(Cl) = 13.01$ eV, $I(Br) = 11.84$ eV, $I(I) = 10.45$ eV).

$$A_X = -(k + I(X)) \tag{26}$$

It is noteworthy that the same relationship holds for the p atomic orbital energies A_X with X = N, P, As, and Sb in the series of heterocyclic compounds pyridine, phospha-, arsa-, and stibabenzene.[26] From the values A_X and $I(X)$ given above we find that the constant in (26) is $k = -0.04$ eV, i.e., practically zero. (Note that for other molecules, e.g., $XC\equiv N$, k differs significantly from zero.)

In a previous communication[23] we have shown that the inclusion of $\pi_{\lambda,r}^*$ in the basis set of π orbitals used in a LCBO model for the calculation of the ionization potentials of acetylene ($I(1) = 11.40$ eV),[2,27] diacetylene ($I(1) = 10.17$ eV; $I(2) = 12.62$ eV),[2,23] and triacetylene,[28] ($I(1) = 9.50$ eV; $I(2) = 11.55$ eV; $I(3) = 12.89$ eV) leads to $B_{CC} = -1.225$ eV, and to basis energies A_{CC} and A_{CC}^* which differ from -11.4 and -6.00 eV (assumed) by $+0.27$ eV for each $-C\equiv CH$ substit-

(24) R. N. Dixon, J. N. Murrell, and B. Narayan, *Mol. Phys.*, **20**, 611 (1971).

(25) G. Bieri, F. Brogli, E. Heilbronner, and E. Kloster-Jensen, *J. Electron Spectrosc.*, **1**, 67 (1972/73).

(26) C. Batich, E. Heilbronner, V. Hornung, A. J. Ashe III, D. T. Clark, U. T. Cobley, D. Kilcast, and I. Scanlan, *J. Amer. Chem. Soc.*, **95**, 928 (1973).

(27) D. C. Frost, F. G. Herring, C. A. McDowell, and I. A. Stenhouse, *Chem. Phys. Lett.*, **4**, 533 (1970).

(28) E. Koster-Jensen, *Angew. Chem.*, **84**, 483 (1972); *Angew. Chem., Int. Ed. Engl.*, **11**, 438 (1972).

uent. Together with the additional parameters derived from the data available for **5**(I,I), **5**(Br,Br), and **5**(Cl,-Cl), the parametrization in (28) is obtained, where $\delta A(R)$ is the change in basis energy $A_{CC}^0 = -11.40$ eV due to the replacement of H by a group R in acetylene.

$$A_{CC} = -11.40 + \delta A(R_1) + \delta A(R_2) \tag{27}$$

(It is not necessary to provide for similar changes in $A_{CC}^* = -6.00$ eV. The interactions of $\pi_{\lambda,r}^*$ with $\pi_{\lambda,s}$ or $p_{\lambda,s}$ are essentially second order and the calculated results are only marginally changed if A_{CC}^* is varied within the limits -6.3 to -5.7 eV.)

	H	C≡CH	Cl	Br	I	
$\delta A(R)$	0	+0.27	−0.09	+0.02	+0.15	
A_X			−12.96	−11.79	−10.43	(28)
B_{CR} $_{CX}$		−1.22$_5$	−1.46	−1.27	−0.97$_5$	

The ionization potentials $\bar{I}(j)$ and the splittings $\Delta(j)$ calculated for **1**(X), **2**(X), **4**(X), and **5**(X,Y) on the basis of the parameters in (28) are listed in Tables VII-X and compared to the experimental values. The

Table VII. Calculated vs. Observed Values of Mean Ionization Potentials $I(j)$ and of Spin-Orbit Coupling Splits $\Delta(j)$ for Halodiacetylenes **1**(X) (eV)

	1(Cl)		1(Br)		1(I)	
	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd
$I(1)$	9.81	9.72	9.70	9.63	9.50	9.63
$I(2)$	12.31	12.15	12.00	11.91	11.12	11.18
$I(3)$	14.08	14.07	13.20	13.25	12.69	12.60
$-\Delta(1)$			0.05	0.08	0.21	0.25
$-\Delta(2)$			0.13	0.11	0.34	0.37
$-\Delta(3)$			0.13	0.1	0.04	

Table VIII. Calculated vs. Observed Values of Mean Ionization Potentials $I(j)$ and of Spin-Orbit Coupling Splits $\Delta(j)$ for Dihalodiacetylenes **2**(X) (eV)

	2(Cl)		2(Br)		2(I)	
	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd
$I(1)$	9.46	9.34	9.30	9.25	0.07	8.91
$I(2)$	11.96	11.68	11.49	11.31	10.48	10.52
$I(3)$	13.92	13.75	12.78	12.74	11.47	11.62
$I(4)$	14.21	14.14	13.37	13.32	12.77	12.63
$-\Delta(1)$		0.02	0.08	0.09	0.26	0.28
$-\Delta(2)$		0.03	0.17	0.18	0.52	0.54
$-\Delta(3)$		0.08	0.23	0.22	0.38	0.39
$-\Delta(4)$		0.06	0.12	0.09	0.07	0

agreement is as good as can reasonably be expected both for $I(j)$ and for $\Delta(j)$.

The influence of a terminal methyl group on the π-ionization potentials $I(j)$ of **1**(X), i.e., the difference

$$\Delta I(j) = I(j)_{3(X)} - I(j)_{1(X)} \tag{29}$$

is displayed graphically in Figure 6. It is noteworthy that the shifts $\Delta I(j)$ do not correlate with the changes $\Delta\epsilon(\pi_\lambda(j))$ which are calculated from the linear combinations

$$\pi_\lambda(j) = c_j \times p(X) + c_{j,1}\pi_{\lambda,1} +$$
$$c_{j,2}\pi_{\lambda,2} + c_{j,1}^*\pi_{\lambda,1}^* + c_{j,2}^*\pi_{\lambda,2}^* \tag{30}$$

of **1**(X) by an inductive and/or conjugative MO model. In an inductive model one would assume that the methyl

Table IX. Calculated *vs.* Observed Values of Mean Ionization Potentials $I(j)$ and of Spin-Orbit Couplings Splits $\Delta(j)$ for Haloacetylenes 4(X) (eV)

	4(F) Calcd	4(F) Obsd	4(Cl) Calcd	4(Cl) Obsd	4(Br) Calcd	4(Br) Obsd	4(I) Calcd	4(I) Obsd
$I(1)$	11.22	11.26	10.70	10.63	10.44	10.31	9.91	9.94
$I(2)$	17.99	17.8(?)	14.06	14.08	13.02	13.00	11.97	12.08
$-\Delta(1)$			0.02		0.11	0.14	0.41	0.41
$-\Delta(2)$			0.07	0.08	0.20	0.14	0.22	0.22

Table X. Calculated *vs.* Observed Values of Mean Ionization Potentials $I(j)$ and of Spin-Orbit Coupling Splits $\Delta(j)$ for Dihaloacetylenes 5(X,Y) (eV)

	5(Cl,Cl) Calcd	5(Cl,Cl) Obsd	5(Br,Br) Calcd	5(Br,Br) Obsd	5(I,I) Calcd	5(I,I) Obsd	5(Cl,Br) Calcd	5(Cl,Br) Obsd	5(Cl,I) Calcd	5(Cl,I) Obsd	5(Br,I) Calcd	5(Br,I) Obsd
$I(1)$	10.09	10.09	9.77	9.77	9.29	9.25	9.91	9.98	9.59	9.60	9.50	9.51
$I(2)$	13.53	13.40	12.31	12.26	10.82	10.93	12.69	12.64	11.54	11.66	11.34	11.46
$I(3)$	14.45	14.45	13.39	13.39	12.28	12.28	14.16	14.06	14.05	13.87	13.04	13.03
$-\Delta(1)$			0.14	0.20	0.40	0.44	0.10		0.33	0.31	0.34	0.34
$-\Delta(2)$			0.31	0.29	0.60	0.60	0.23	0.19	0.34	0.36	0.41	0.43
$-\Delta(3)$			0.18	0.13	0.25	0.21	0.08		0.08		0.21	

group in 3(X) destabilizes the Coulomb term $A_{CC,2}$ of the terminal triple bond by δA whereas the conjugative model postulates an interaction describable by a resonance integral β' between $\pi_{\lambda,2}$ and the pseudo-π-orbitals of the methyl groups. Limiting the treatment to the bonding basis orbital $\pi_{\lambda,2}$ of 1(X), a combined first-order (inductive effect) and second-order (conjugative effect) treatment would lead to expect an orbital shift

$$\Delta\epsilon(\pi_\lambda(j)) = c_{j,2}{}^2[\delta A + \beta'^2/(\epsilon(\pi_\lambda(j)) - \epsilon(\text{pseudo } \pi))] \quad (31)$$

As the difference $\epsilon(\pi_\lambda(j)) - \epsilon(\text{pseudo } \pi)$ is roughly constant, one should observe a reasonably good correlation between the calculated $c_{j,2}{}^2$ and the observed displacements $I(j)$. This, however, is not at all the case. Inclu-

1(X)/ 3(X)	$-\Delta I(\bar{1})$	$c_{1,2}{}^2$	$-\Delta I(\bar{2})$	$c_{2,2}{}^2$	$-\Delta I(\bar{3})$	$c_{3,2}{}^2$
X = Cl	0.57	0.39	0.55	0.55	0.31	0.03
Br	0.55	0.35	0.54	0.48	0.38	0.14
I	0.43	0.25	0.40	0.31	0.40	0.40

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (32)$

sion of the perturbations δA^* experienced by the antibonding π orbital $\pi_{\lambda,2}^*$ on methyl substitution or of the conjugation of $\pi_{\lambda,2}$ with antibonding pseudo-π-orbitals of the terminal methyl group does not lead to a significant improvement of the results.

The reason for this failure of the simple inductive/conjugative perturbation treatment will be discussed in greater detail in connection with an investigation of halomethylacetylenes, halotrifluoromethylacetylenes, and cyanohaloacetylenes.[29] It is mainly due to the neglect of the electron rearrangement which accompanies the ionization process (eq 1); *i.e.*, to a break down of the Koopmans' approximation as has been demonstrated recently for alkyl- and dialkylfulvenes.[30]

As has been shown by Turner and his coworkers,[2] the PE spectra of acetylenes yield a good deal of information about their ionic states from the usually abundant vibrational fine structure discernible (see also ref 5 and 6).

In the PE spectra reproduced in Figures 1–3, the wealth of fine detail is evident. Thus, it is of some interest to examine how the Franck–Condon envelopes, and the vibrational modes excited, bear out the orbital scheme presented in Figure 4.

In Tables IV–VI the vibrational frequencies from the peaks of the vibrationally excited states of the radical ions are listed. The vibrational frequencies listed are the interval $v_i' = 0$ to $v_i' = 1$ for the vibrational mode v_i excited; when feasible, obtained from the bands corresponding to both spin-orbit states $^2\Pi_{3/2}(j)$, $^2\Pi_{1/2}(j)$. A certain degree of anharmonicity is reflected in successive intervals, *e.g.*, Table IV, footnote *c*. However, the diminishing Franck–Condon factors, and often the complexity of the overlapping bands due to $^2\Pi_{3/2}(j)$ and $^2\Pi_{1/2}(j)$ preclude a reliable estimate of the anharmonicity constants.

The analysis of the vibrational modes excited is facilitated in linear molecules by their high symmetry. As only totally symmetric modes can be excited in any number of quanta (in the absence of vibronic perturbations), the choice of assignment is limited and reasonably clear from consideration of the magnitudes of the frequencies and of the Franck–Condon factors.[2,31]

In 1(Cl)$^+$ (*i.e.*, the radical cation of 1(Cl)) the spin-orbit coupling is sufficiently small, within the experimental resolution limit of $E/\Delta E \approx 250$, (*cf.* ζ(Cl) ≈ 0.1 eV) only to contribute to the vibrational peak width. For example, the peak widths at half-height (ΔE) of the second bands of the dihalodiacetylenes, 2(X), are for X = Br and I $\Delta E \approx 50$ meV for electrons of ≈ 10 eV kinetic energy, while for X = Cl $\Delta E \approx 80$ meV, albeit the energy of the photoelectrons is ≈ 9 eV.[32] The same trend is evident on comparison of the PE spectra of the other diacetylenes. In 1(I)$^+$, 2(I)$^+$, and 3(I)$^+$ the spin-orbit coupling in the states $\tilde{X}_\Omega$ and $\tilde{A}_\Omega$ is large enough to allow the identification of the vibrational progressions on both components characterized by $\Omega = 3/2$ and $1/2$. In contrast, the magnitude of the spin–orbit coupling is intermediate in the ionic states of the bromo derivatives

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(ζ(Br) $\approx$ 0.3 eV) and consequently often results in a complex band structure (e.g., band 1 in the PE spectra of 1(Br), 2(Br), and 3(Br)).

In the PE spectra of the centrosymmetrical molecules 2(X), vibrational fine structure is resolved on the first two bands (see Figure 2). In these molecules there are three totally symmetric vibrational modes (Σ_g^+ in $D_{\infty h}$). The frequencies of these modes in the neutral molecules 2(X) in their electronic ground state X and an indication of their nature are shown in Table V. A progression in ν_1 (C$\equiv$C stretch) appears to be excited in the ground ionic states $\widetilde{X}_\Omega$ of the radical cations 2(X)$^+$ with but a slight reduction of the frequency relative to the X values. In 2(I) the analysis reveals that the vibrational quantum coincides (under the experimental resolution) with the magnitude of the spin–orbit coupling split $-\Delta(1)$ = 0.28 eV $\approx$ 2250 cm^{-1} (cf. Table VIII). In the ground ionic state X of diacetylene, a corresponding C$\equiv$C stretching mode (ν_2) is excited[2] and the Franck–Condon profile is similar. This is in accord with the nodal characteristics of the highest occupied molecular orbital $\pi_{\lambda g}(1)$ of diacetylene,[2,23] which is essentially the out-of-plane linear combination of two triple bond basis orbitals $\pi_{\lambda,r}$.

The Franck–Condon envelopes of the second bands (Figure 2) are particularly suited for comparison with the molecular orbital scheme proposed in Figure 5. In this second band, of all three molecules 2(X), the 0 $\leftarrow$ 0 transition is most intense and a progression corresponding to the excitation of the ν_2 (C–C stretch) mode is observed. The latter frequencies are reduced somewhat relative to the neutral molecule excitations (see Table V). In case of 2(Cl) and 2(Br) several members ($v' \geqslant$ 5) of the progression are discernible. However, for 2(I) the 0 $\leftarrow$ 0 transition dominates and the next two components show very rapid fall-off in intensity due to a decrease in the Franck–Condon factors. The difference is in harmony with the conclusion derived from the observed spin–orbit coupling split $-\Delta(2)$ = 0.54 eV (see Table VIII) that the orbital $\pi_{\lambda,u}(2)$ is centered strongly on the two terminal p_λ atomic orbitals as shown in Figure 5. From this it must be deduced that in the case of 2(I) the change in electron density on ionization is localized predominantly on the iodine atoms and indeed the Franck–Condon band shape is that usually observed in PE spectroscopy for "lone-pair" ionization (e.g., the $^2B_1$ state in H_2O^+)[2] while for 2(Cl) and 2(Br) more delocalization is suggested. In the spectra of the latter two compounds the band profile is similar to that of the second band in the PE spectrum of diacetylene[2,32] (associated with photoelectrons ejected from the in-phase combination of the basis $\pi_{\lambda,r}$ orbitals) where the corresponding C–C stretching mode (ν_3) is excited. This agrees with the greater contribution of $\pi_{\lambda,1}$ and $\pi_{\lambda,2}$ to the molecular orbitals $\pi_{\lambda,u}(2)$ of 2(Cl) and 2(Br).

The two remaining π bands 3 and 4 in the PE spectra of 2(X) do not show distinct vibrational peaks, though there is some evidence of a low frequency, i.e., possible ν_3 (C–X stretch), mode excitation. Both bands have a broad Franck–Condon profile, the third to a lesser extent. This is consistent with the nodal properties of the molecular orbitals $\pi_{\lambda,g}(3)$ and $\pi_{\lambda,u}(4)$ with which the bands are associated (see Figures 4 and 5).

The first three bands in the PE spectra of the monohalodiacetylenes 1(X) (Figure 1) and halomethyl-

diacetylenes 3(X) (Figure 3) correlated with the three π-symmetry ionic states $\widetilde{X}_\Omega$, $\widetilde{A}_\Omega$, and $\widetilde{B}_\Omega$ display a similar pattern. The vibrational frequencies discernible are given in Tables IV and VI, respectively. Although the reduced symmetry $C_{\infty v}$ of 1(X) and C_{3v} of 3(X) results in a increase of the number of totally symmetric modes (five Σ^+ modes and seven A_1 modes, respectively), it is found that the modes corresponding most closely to those observed in the PE spectra of 2(X) are excited. Band 1 in the spectra of Figures 1 and 3 reveal that several C$\equiv$C stretching modes are excited which correspond presumably to ν_2 in diacetylene,[2] or perhaps to ν_3, the antisymmetric stretching mode of the latter molecule. The observed frequencies are only little reduced in magnitude relative to those in the neutral molecule and the Franck–Condon profile resembles that of band 1 in the PE spectra of 2(X). In the spectra of 1(I) and 3(I) the vibrational quantum matches again the spin–orbit coupling split: $-\Delta(1)$ = 0.25 eV $\approx$ 2000 cm^{-1} for 1(I), $-\Delta(1)$ = 0.23 eV $\approx$ 1900 cm^{-1} for 3(I) (see Tables VII and III, respectively).

The second bands in the PE spectra of 1(X) and 3(X) are again similar to the second bands in those of 2(X). The excitation of the C–C stretching mode ν_4 (in 1(X)) and of ν_5 (in 3(X)) is resolved. As before the location of the corresponding molecular orbitals $\pi_\lambda(2)$ on the halogen center (see Figure 4) manifests itself not only by the magnitude of the spin–orbit coupling but by the dominance of the 0 $\leftarrow$ 0 transition.

The third bands in the PE spectra of 1(X) and 3(X) are broad and there is some indication of a low frequency mode (C–X stretch). These bands may be compared to the fourth bands in the PE spectra of 2(X), i.e., associated with ejection of electrons from bonding orbital $\pi_\lambda(3)$.

Bands 4 and 5 of 1(X) (cf. Table I) and bands 5 and 6 of 2(X) correspond to the ionic states $\widetilde{C},\widetilde{D}$ or $\widetilde{D},\widetilde{E}$ of Σ symmetry. Within the scheme presented in Figure 4, these states are associated with ejection of the photoelectron from the σ orbitals $\sigma(4)$ and $\sigma(5)$ (not shown in Figure 4) or $\sigma_g(5)$ and $\sigma_u(6)$, respectively. In the case of 3(X), ionization potentials higher than those corresponding to the third band (state $\widetilde{B}_\Omega$; cf. Table III) cannot be determined unambigously due to the complexity arising from the bands associated with ionization from the pseudo-π-orbitals of the methyl groups.

Comparison of the ionization potentials observed for the third band (state $^2\Sigma^+$ (3)) in the PE spectra of the haloacetylenes 4(X)[5] ($I(3)$ = 16.76, 15.99, and 14.86 eV for X = Cl, Br, and I) and for the fourth band (state $\widetilde{C} \equiv {}^2\Sigma^+(4)$) in the PE spectra of 1(X) ($I(4)$ = 16.82, 16.10, and 14.90 for X = Cl, Br, and I) indicates almost no change. These ionization potentials are associated with ionization from orbitals predominantly centered on the axially symmetrical lone-pair basis orbital n(X). The fifth band in the PE spectra of 1(X) (state $\widetilde{D} \equiv {}^2\Sigma^+$ (5)) corresponds to the ejection from an orbital best described as of C–H character. These bands are shifted by roughly -0.5 eV toward lower ionization potentials with respect to the corresponding fourth band in the PE spectra of 4(X),[5] presumably due to increased mixing of the C–H basis orbital with the lower lying σ levels of 1(X).

In the PE spectra of the symmetrical dihalodiacety-

Table XI. Correlation of the Lone-Pair Ionization Potentials of 1(X), 2(X), 4(X), and 5(X,X) *vs.* the Ionization Potentials I(X) of the Free Halogen Atoms[a]

X	I(X)	1(X) I(4)	2(X) I(5)	2(X) I(6)	4(X) I(3)	5(X,X) I(4)	5(X,X) I(5)
Cl	13.01	16.81	16.85	17.28	16.76	16.76	17.81
Br	11.84	16.10	15.85	16.20	15.99	15.64	16.90
I	10.45	14.90	14.60	14.90	14.86	14.22	15.48
Slope[b]		0.750 ± 0.073	0.880 ± 0.013	0.930 ± 0.003	0.744 ± 0.044	0.993 ± 0.018	0.914 ± 0.070
r[c]		0.995	1.000	1.000	0.998	1.000	0.997

[a] All values in eV. [b] The slopes are given with their standard error. [c] r = correlation coefficient, rounded to 0.001.

lenes 2(X) the bands 5 and 6 (states $\tilde{D} \equiv {}^2\Sigma_g^+(5)$, $\tilde{E} \equiv {}^2\Sigma_u^+(6)$; see (7)) stem from the orbitals $\sigma_g(5)$ and $\sigma_u(6)$ which are centered essentially on the linear combinations $n_+(X)$ $n_-(X)$ given in (2). As in the symmetrical dihaloacetylenes 5(X,X) the observed splittings are

		Cl	B	I	
2X	I(5) − I(4)	0.43	0.35	0.30 eV	(33)
5(X,X)	I(4) − I(3)	1.05	1.26	1.26 eV	

due to the interaction with deeper lying (*i.e.*, below ~ -19 eV) σ CC orbitals. In both cases the even linear combination σ_g (containing $n_+(X)$) is expected to lie above σ_u (containing $n_-(X)$). However, as shown in (33), the splittings I(5) − I(4) of 2(X) are much smaller than those observed for 5(X,X). This was to be expected, because in contrast to 5(X,X) there are deeper lying σ CC orbitals in 2(X) of odd symmetry behavior relative to inversion, which can therefore interact with (and thus destabilize) the $n_-(X)$ linear combination. (For comparison: the split of the nitrogen lone-pair orbitals in cyanogen has been found to be 0.37 eV.[2])

As shown in Table XI there is again a linear relationship between the ionization potential I(4) of 1(X), I(5), I(6) of 2(X), and the ionization potentials I(X) of the free halogen atoms as observed previously[5,6] for 4(X) and 5(X,X). Note that the slope is practically unity in the symmetrically substituted compounds 2(X) and 5(X,X) but only 3/4 in the monosubstituted 1(X) and 4(X). The reason for this smaller slope has been discussed previously (*cf.* Figure 3 of ref 5): it is due to the mixing of n(X) with the σ CH orbital, the basis orbital energy of which is similar to that of n(X).

Experimental Section[33]

Preparation of Dihalodiacetylenes, General Procedure. The reactions were carried out on a 10–30-mmol scale in absolute ether under an atmosphere of nitrogen and with exclusion of light. All glass equipment was fitted with high vacuum cocks and silicon high vacuum grease was used. All samples of dihalodiacetylenes so obtained were mass spectrometrically pure.

Freshly prepared and redistilled diacetylene[34] in absolute ether was added from a cooled dropping funnel into an ethereal solution of phenyllithium at −50° under vigorous stirring over a period of 20 min. While stirring for another 20 min the temperature was allowed to rise to −20°. Molecular halogen (chlorine in trichlorofluoromethane (Freon-11) distilled over phosphorus pentoxide), bromine undissolved, or iodine in ether solution) was added dropwise under stirring at −55° during *ca.* 20 min, whereby a strongly exothermal reaction took place. The addition of halogen was discontinued when samples of the reaction mixture were no longer alkaline after addition of water. Almost equivalent amounts of halogen were then consumed. Fractional distillation of the

reaction mixture was undertaken at −45° (9 Torr). Fractions of 10–15 ml were trapped at −80° and subjected to glc. The dihalodiacetylene collected mainly in the last fraction, which was distilled at room temperature. After further concentration at −45° (9 Torr) the products were isolated as specified below.

Dichlorodiacetylene. Diacetylene (500 mg, 10 mmol) in 10 ml of ether was added to 2 equiv of phenyllithium (from chlorobenzene and metallic lithium) in 80 ml of ether. A *ca.* 15% solution of chlorine in Freon-11 was added from a dropping funnel cooled at −80° until the reaction mixture became neutral. After fractional distillation the last fraction was gas chromatographed[35] at 70° (retention time 32 min). This yields 360 mg (30.3%) of snow-white dichlorodiacetylene of 98–99% purity. (Large amounts of chlorobenzene were also found, due no doubt to an incomplete reaction with metallic lithium (*ca.* 50%).) A second purification by glc yielded 205 mg of mass spectrometrically pure product, mp 11.0–11.2°; vapor pressure 4.5 Torr/0°.

Dibromodiacetylene. Diacetylene (1.6 g, 32 mmol) in 10 ml of ether was added to 2 equiv of phenyllithium (from bromobenzene and metallic lithium) in 80 ml of ether; 10.25 g (64 mmol) of bromine was added subsequently and the reaction mixture was neutral when 97% of the bromine was consumed. By fractional distillation at −41° (9 Torr) the last fraction (−24 to −20°, 20 ml, trapped in liquid nitrogen) contained *ca.* 300 mg of crystalline material, exhibiting a characteristic odor of the product. Dibromodiacetylene was not eluted by glc at 90°. From the residue were isolated another 4 ml of distillate which yielded 1.26 g of solids. By further evaporation from the residue were isolated additional 1.7 and 0.5 g of crystalline product, yield 52%. Resublimation of the 500-mg portion in the second fraction gave 263 mg of MS pure dibromodiacetylene, mp 51.5–52.0° dec.

Diiododiacetylene. Diacetylene (1.5 g, 30 mmol) was introduced into 2 equiv of phenyllithium (from bromobenzene and methyllithium) in 60 ml of ether; 15.25 g (60 mmol) of iodine in 100 ml of ether was added at −30°. The yellowish-brown reaction mixture was left overnight at −80°; 50 ml of the solution was shaken with water (2 × 20 ml), dried with calcium chloride, and concentrated under vacuum. The partly crystalline residue was extracted with light petroleum (bp 40–60°) in portions of 10–20 ml. Removal of the solvent from the second and later colorless extracts left crystalline needles (*ca.* 2.9 g) of mp *ca.* 85°. Portions of about 300 mg were recrystallized three times from petroleum ether quickly and with exclusion of light. MS pure diiododiacetylene melts at 94–95° under explosion and illumination.

The halodiacetylenes were prepared as described previously[36] and the halomethyldiacetylenes according to modified procedures.[37]

The PE spectra were obtained with a modified Perkin-Elmer photoelectron spectrometer (PS-15) based on the design of Turner.[38] This incorporated a $\pi/\sqrt{2}$ electrostatic sector analyzer (5 cm radius) and a dc capillary discharge generating the HeI resonance line (21.22 eV). The working resolution was usually 20–30 meV full width at half-height for 5 eV electrons. The ordinate scale of the spectra is in arbitrary units (counts sec^{-1}). The abscissa scale is in electron volts obtained *via* internal calibration using the pure gases and the 0←0 vibrational peak of the ${}^2B_1$ state of water, which is sometimes present in minute amounts in the sample or the spectrometer. The intensity of the bands falls off in such an analyzer toward low kinetic energy of the electrons, especially in the $\sim$0–3 eV range.

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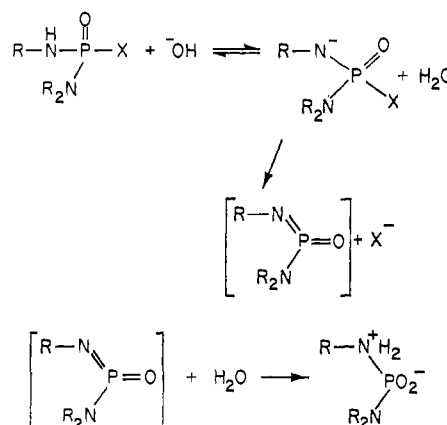(38) D. W. Turner, *Proc Roy. Soc., Ser. A*, **307**, 15 (1968).

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Photolysis of 1-Azido-2,2,3,4,4-pentamethylphosphetane 1-Oxide: Monomeric Metaphosphonimidate[1-3]

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Abstract: Monomeric metaphosphorimidates, $O=P(OR)=NR'$, have been postulated as reactive intermediates in phosphorus chemistry. Stereochemical evidence for such intermediates has now been obtained by photolysis, in methanol, of cis- and trans-1-azido-2,2,3,4,4-pentamethylphosphetane 1-oxide to yield the cis- and trans-2-methoxy-3,3,4,5,5-pentamethyl-1,2-azaphospholidene 2-oxides and eight other products. The starting materials and products have been separated and purified by high-pressure liquid chromatography, and their stereochemistry was established through their nmr spectra. The formation of the principal products has been rationalized on the assumption that photolysis of the azides leads to ring expansion with insertion of a nitrogen atom into the ring to yield a monomeric metaphosphonimidate, or with insertion of an oxygen atom into the ring to yield a new type of chemical intermediate. Consistent with this explanation, the ratio of cis- to trans-methyl phostamates, obtained as products of photolysis, is essentially independent of whether cis or trans azide is used as starting material. The chemistry and stereochemistry of monomeric metaphosphorimidates are discussed on the basis of these findings. The other products have also been accounted for, in most cases by assuming that a nitrene, or incipient nitrene, is formed in the photolysis.

The mechanisms of hydrolysis of phosphoramidates, like those of other phosphates, are of biochemical interest. Phosphoramidates where one or more hydrogen atoms are attached to nitrogen are particularly sensitive to alkaline hydrolysis,[4] and in 1957 a metaphosphorimidate mechanism was advanced to account for this fact.[5] Kinetic and stereochemical investigations have supported this hypothesis and have placed limits upon its range of applicability.[6] In particular, Gerrard and Hamer[7] showed that the alkaline hydrolysis of methyl N-cyclohexylthiophosphorochlo-

ridate occurs with racemization, presumably through a metaphosphorimidate intermediate; but when p-nitrophenolate ion rather than chloride is the leaving group, chirality is preserved; this fact suggests that a metaphosphorimidate, if it participates in the hydrolytic process, is not entirely free, or that it reacts with solvent in a time short compared with that needed to pass through a planar configuration.

Recently Harger[8] has carried out the photolytic ring enlargement of 1-azido-2,2,3,4,4-pentamethylphosphetane 1-oxide (I) to yield 2-methoxy-3,3,4,5,5-pentamethyl-1,2-azaphospholidene 2-oxide (II).

By taking advantage of high-pressure liquid chromatography, we have now separated the cis and trans isomers of both starting material and products. Photolysis of either the cis or trans azide in methanol leads to the same ratio of cis and trans phostamic esters; this

(1) Preliminary communications: Remsen Lecture, John Hopkins University, May 1973; *Pure Appl. Chem.*, in press.

(2) In this paper, species with the structure $O=P(OR)=NR$ are called metaphosphorimidates and those with the structure $O=P(R)=NR'$ are called metaphosphonimidates. The arguments in this paper apply to the members of both classes.

(3) Abbreviations used are: Azide, I, 1-azido-2,2,3,4,4-pentamethylphosphetane 1-oxide; methyl phostamate, II, 2-methoxy-3,3,4,5,5-pentamethyl-1,2-azaphospholidene 2-oxide; unsaturated amino ester, III, O-methyl (1,1,2,3-tetramethyl-3-butenyl)phosphoramidate; phosphetane ester, IV, 1-methoxy-2,2,3,4,4-pentamethylphosphetane 1-oxide; methyl phostonate, V, 2-methoxy-3,3,4,5,5-pentamethyl-1,2-oxaphospholane 2-oxide; phosphetane hydroxamate, VI, 1-methoxyamino-2,2,3,4,4-pentamethylphosphetane 1-oxide; phostonate amide, VII, 2-amino-3,3,4,5,5-pentamethyl-1,2-oxaphospholane 2-oxide; anhydride, VIII, anhydride of 1-hydroxy-2,2,3,4,4-pentamethylphosphetane 1-oxide; phosphetane chloride, IX, 1-chloro-2,2,3,4,4-pentamethylphosphetane 1-oxide.

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