Photoelectron Spectra and Molecular Properties[1] of *trans*-Dihalogenoethylenes: Substituent Effects Spin-orbit Coupling[1,2]

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Summary The photoelectron spectra of *trans*-dihalogenoethylenes are assigned considering spin-orbit coupling and allow unambiguous estimates of inductive, conjugative, and hyperconjugative contributions of the halogen substituent effects.

We report the photoelectron spectra of *trans*-dihalogenoethylenes[3] (Figure 1), from which the lowest five vertical ionization energies are easily determined (Table 1).

Table 1

Vertical ionization energies IE_n (eV)

n	1	2	3	4	5
Cl	9·72	11·79	12·01	12·55	13·79
Br	9·56	11·04	11·04	11·57	12·90
I	8·92	9·86	10·11	10·45	11·85

Our assignment is based on a simple qualitative MO model (Figure 2) in which two "lone pair" orbitals on each halogen and the ethylene π orbital are combined according to their irreducible representations in C_{2h} to yield three π orbitals ($1a_u$, $1b_g$, $2a_u$) and two σ orbitals ($4b_u$, $5a_g$). The latter are destabilized by "through bond" interaction,[4] the antibonding admixture of four a_g orbitals being presumably more effective.

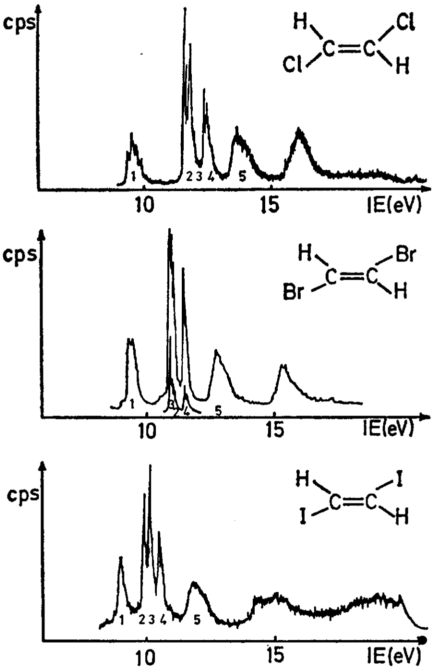

Figure 1. *Photoelectron spectra of* trans-*dihalogenoethylenes.*

From the ionization energies of *trans*-dichloroethylene,[5] (Table 1) various Hueckel parameters may be extracted; the energy of the nonbonding $1b_g$ orbital (12·55 eV) is a good value for the chlorine coulomb integral α_{Cl}.[6] The π-stabilization energy, $\Delta\pi = E(1a_u) - E(1b_g)$, is therefore $(13{\cdot}79 - 12{\cdot}55)$ e.v. which when subtracted from the first ionization potential gives $\alpha_{C=C} = 1{\cdot}24 + 9{\cdot}72 = 10{\cdot}96$ eV. Comparison with the first ionization potential of ethylene[7] itself results in $\Delta\alpha_{C=C} = 10{\cdot}96 - 10{\cdot}51 = 0{\cdot}45$ eV, which represents the inductive substituent effect of chlorine. The secular polynomial $(\alpha_{C=Cl} - IE)(\alpha_{Cl} - IE) - \beta^2_{C-Cl} = 0$, gives a resonance integral β_{C-Cl} 1·9 eV. Finally the "through bond" shifts $\Delta(5a_g) = 12{\cdot}55 - 11{\cdot}79 = 0{\cdot}76$ eV and $\Delta(4b_u) = 12{\cdot}55 - 12{\cdot}01 = 0{\cdot}54$ eV can be read directly from the spectra. These estimates, together with those of the bromo- and iodo-derivatives, approximated in the same way, are shown in Table 2.

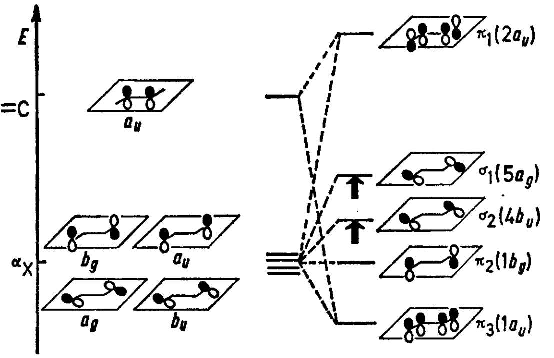

Figure 2. *Qualitative orbital diagram for* trans-*dihalogenoethylenes.*

Table 2

MO parameters (eV) *from photoelectron spectra*

X	α_X	$\Delta\pi$	$\alpha_{C=C}$	$\Delta\alpha_{C=C}$	β_{C-X}	$\Delta(5a_g)$	$\Delta(4b_u)$
Cl	12·55	1·24	10·96	0·45	1·9	0·76	0·54
Br	11·57	1·33	10·89	0·38	1·6	0·53	0·53
I	10·3	1·4	10·5	0·0	1·5	0·2	0·2

For *trans*-dibromoethylene, the photoelectron assignment is analogous, except that the lone pair orbitals $4b_u$ and $5a_g$ are degenerate as shown by the doubled intensity of the second band (Figure 1).

Spin-orbit coupling in bromine (Br_2^+ 0·33 eV) is large compared to that in chlorine (Cl_2^+ 0·07 eV), but in *trans*-dibromoethylene σ- and π-interactions (Table 2) still prevail. In the iodo-derivative however spin-orbit interactions (I_2^+ 0·63 eV) can no longer be neglected. This local coupling mixes σ- and π-type electron pairs on each iodine and prohibits any classification of the corresponding molecular orbitals with respect to the lost mirror plane σ_h. With respect to the centre of inversion retained, mixing is only allowed within even (g) or odd (u) functions (Figure 3).

Spin-orbit coupling can be incorporated into the elegant one-electron-MO model used by Brogli and Heilbronner.[8] Clearly, the two $(\sigma_1 + \pi_2)_g$ orbitals do not imply any degeneracy but rather complete σ–π mixing (C_{2h} double group: $e_{1/2g}$). The latter can be neglected among the odd orbitals because of strong π interaction (β_{C-J} = 1·5eV, Table 2).

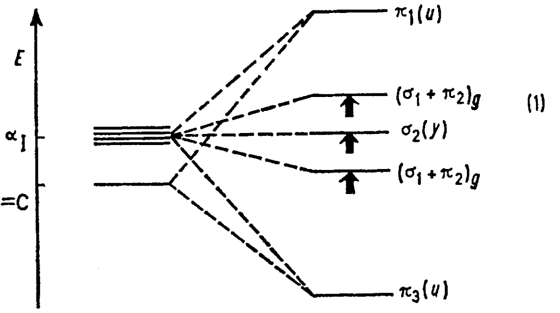

FIGURE 3. *Qualitative orbital diagram for spin orbit coupling in* trans-*di-iodoethylene.*

All three electron pair orbitals are "through bond" destabilized. Calculations[2,8] restrict $\Delta(\sigma_1 + \pi_2)_g \geqslant 0{\cdot}6$ eV, the experimental value (Table 1:0·59 eV) being in excellent agreement. The $(\sigma_1 + \pi_2)_g$ assignment of bands 2 and 4 in the photoelectron spectrum is further confirmed by their similar vibrational fine structure ($\Delta\nu = 560 \pm 100\ \text{cm}^{-1}$).

The MO parameters† (Table 2) obtained from the photoelectron spectra of the *trans*-dihalogenoethylenes deserve further comment.

Usually a distinction is made between inductive and conjugative parts of substituent effects, hyperconjugation contributing to both of them. Normally neither effect can be measured separately.

Within our model compounds the parameter α_X—taken from the only occupied b_g orbital—represents the unperturbed halogen lone pair ($IE_{Cl} > IE_{Br} > IE_I$). Combination of the observed five lowest ionization potentials yields $\Delta\alpha_{C=C}$, which can be considered a fair estimate of the separated inductive effect σ_X due to partial electron transfer among low lying orbitals ($\sigma_{Cl} > \sigma_{Br} \gg \sigma_I \sim 0$).

The resonance term β_{C-X} reflects diminishing overlap (Cl > Br > I). This is opposed by a decreasing energy gap between the interacting orbitals $\Delta\alpha = \alpha_X - \alpha_{C=C}$ (Cl > Br > $J \approx 0$), resulting in an almost constant π donor strength as shown by the $\Delta\pi$ values.

In addition the rather large influence of hyperconjugation—that is "through bond" shifts between σ orbitals of the same irreducible representation—is demonstrated by the parameters $\Delta(5a_g)$ and $\Delta(4b_u)$.

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† When transferred to other compounds, the MO parameters in Table 2 are hardly more reliable than 0·1–0·2 eV.

[1] For previous paper in this series see H. Bock and H. Stafast, *Chem. Ber.*, 1972, **105**, 1158.

[2] Taken in part from the thesis of K. Wittel.

[3] *Cf.*, H. Bock and G. Wagner, *Angew. Chem.*, 1972, **84**, 119; *Angew. Chem. Internat. Edn.*, 1972, **11**, 150, or ref. 1.

[4] R. Hoffmann, A. Imamura, and W. J. Hehre, *J. Amer. Chem. Soc.*, 1968, **90**, 1499.

[5] *Cf.* N. Jonathan, K. Ross, and V. Tomlinson, *Internat. J. Mass. Spectrometry Ion Phys.*, 1970, **4**, 51; R. F. Lake and H. Thompson, *Proc. Roy. Soc.*, 1970, **A315**, 323. Careful re-examination of the spectrum shows that the peak at 11·93 eV is more likely due to vibrational fine structure ($\nu = 560 \pm 80\ \text{cm}^{-1}$), since a third component can be located.

[6] A. Streitwieser, jun., "Molecular Orbital Theory for Organic Chemists", Wiley & Sons, London 1961, p. 23, 117.

[7] D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy", Wiley-Interscience, London, 1970.

[8] F. Brogli and E. Heilbronner, *Helv. Chim. Acta*, 1971, **54**, 1423.