Chem. Ber. **118**, 2927 – 2939 (1985)

Photoelectron Spectra of Symmetrical 1,4-Dihalonorbornanes[1)]

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Received July 23, 1984

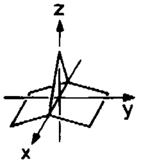
The He(Iα) photoelectron spectra of 1,4-dihalonorbornanes (**2** – **4**) and of 1-bromonorbornane (**5**) have been recorded. Their assignment is based on results derived from recently proposed equivalent bond orbital treatment which has now been adapted to include halogen atoms and to account for spin-orbit coupling.

Photoelektronenspektren symmetrischer 1,4-Dihalonorbornane[1)]

Die He(Iα)-Photoelektronenspektren von 1,4-Dihalonorbornanen (**2** – **4**) und 1-Bromnorbornan (**5**) wurden gemessen. Die Zuordnung basiert auf Ergebnissen eines kürzlich vorgeschlagenen Modells äquivalenter Bindungsorbitale, das auf Halogenatome erweitert wurde und die Spin-Bahn-Kopplung berücksichtigt.

In previous communications we have first presented a “mise au point” of the equivalent bond orbital (EBO) model together with a convenient redefinition in terms of localized molecular orbitals λ_μ (LMO) derived from *ab initio* calculations[1a)] and then its application to the interpretation of the He(Iα) PE spectra of saturated polycyclic hydrocarbons[1b)].

We now use this model to analyze the PE spectra of the symmetrical 1,4-dihalobicyclo[2.2.1]heptanes (= 1,4-dihalonorbornanes) **2**, **3**, and **4**, with halogen = chlorine, bromine, and iodine, respectively.



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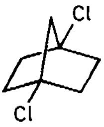

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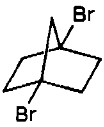

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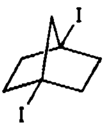

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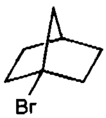

5

These investigations are also of interest within the context of the transmission of substituent effects. 1,4-Disubstituted bicycloalkanes have been used extensively

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to elucidate the nature of polar effects without the concomitant encumbrances of stereochemical and π-conjugated phenomena[2]. Recently a ^{19}F NMR study[3] provided evidence that long-range electronegativity influences contribute significantly to the ^{19}F chemical shifts, and that these effects are decisively dependent upon the kind of the σ-framework. A σ-electron delocalization mechanism has therefore been proposed.

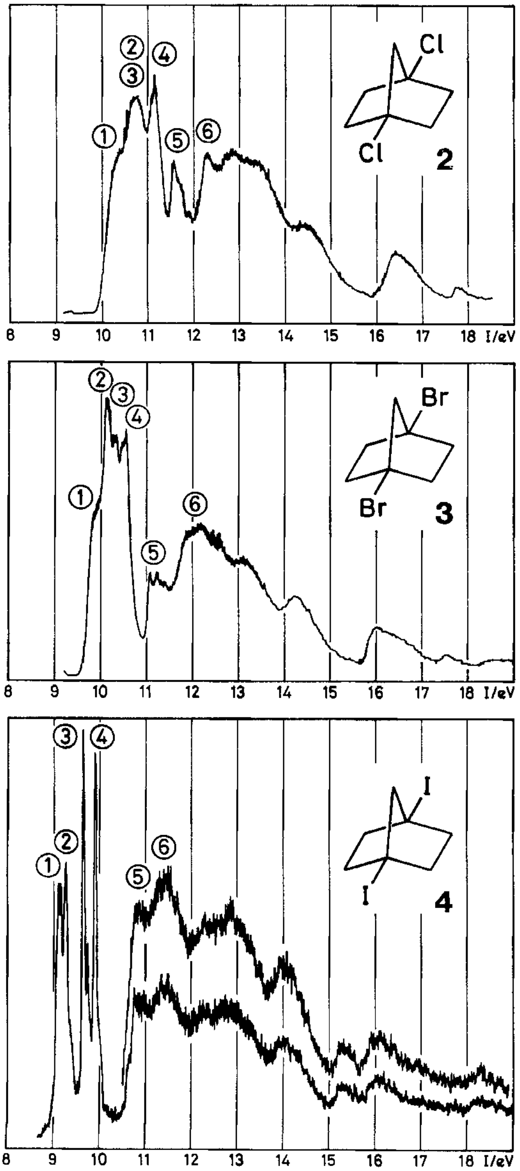


Figure 1. He(Iα) PE spectra of the 1,4-dihalonorbornanes **2**, **3**, and **4**

I. Experimental Results

The He(Iα) PE spectra of **2**, **3**, and **4** are shown in Fig. 1, and, for comparison, the spectrum of 1-bromobicyclo[2.2.1]heptane (**5**) (= 1-bromonorbornane) in Fig. 2. The numbering of the individual band maxima ⓙ (or shoulders) is arbitrary. The positions I_j^m of the corresponding maxima, which are close to the vertical ionization energies I_j^v, are collected in Table 1. (See also Tab. 3, where they are given together with the assignment we wish to propose on the basis of the discussion given below.) The PE spectrum of the parent hydrocarbon bicyclo[2.2.1]heptane (= norbornane) (**1**) has been reported previously[4].

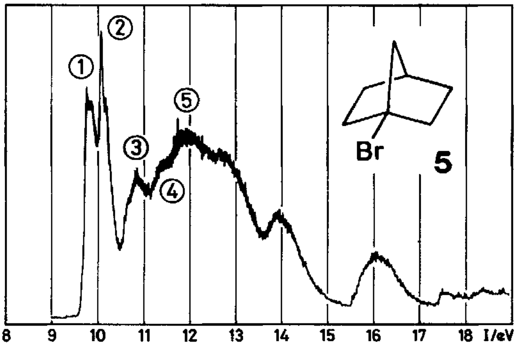


Figure 2. He(Iα) PE spectrum of 1-bromonorbornane (**5**)

Table 1. Ionization energies I_j^m/eV of the 1,4-dihalonorbornanes **2**, **3**, **4**, and of 1-bromonorbornane (**5**). Probable error: ± 0.02 if two decimals given, ± 0.05 if second decimal given as subscript, ± 0.1 if one decimal given. Values in parenthesis = shoulder or overlapped band

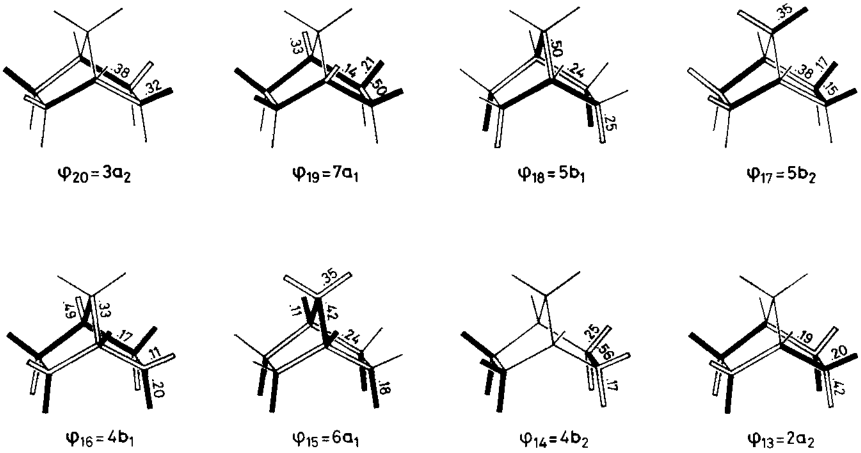
Band	2	3	4	5
①	(10.3_5)	(9.9)	9.11	9.76
②		10.1_5	9.26	10.07
③	10.7_5	(10.3_5)	9.63	10.8_5
④	11.1_0	10.5_5	9.90	(11.4)
⑤	11.5_0	11.1_5[a] (11.5)	10.8	11.9[b]
⑥	12.3	(11.9) to 12.7[b]	11.5[b]	

[a] First vibrational (?) component. — [b] Maximum due to overlapping bands.

II. EBO Model

The EBO model used for **2**, **3**, and **4** is essentially the $A\Delta$ version described previously in lit.[1b], which means that apart from the self-energies A_μ of the LMOs λ_μ, cross-terms $F_{\mu\nu} = \langle \lambda_\mu | \mathcal{F} | \lambda_\nu \rangle$ are included for geminal ($B_{\mu\nu}$) and vicinal ($\Gamma_{\mu\nu}$) LMOs as well as for pairs of LMOs λ_μ, λ_ν separated by two bonds ($\Delta_{\mu\nu}$). All other cross terms are neglected. Obviously this model has to be adapted to account for the presence of the halogen atoms X = Cl, Br, I in positions 1 and 4 of the norbornane skeleton and for spin-orbit coupling.

As a first step the Fock matrix $\mathbb{F}_\lambda(\mathbf{1})$ for the valence shell of norbornane **1** (C_7H_{12}; C_{2v}) is constructed in localized basis according to the rules given in lit.[1b]. Diagonalization of $\mathbb{F}_\lambda(\mathbf{1})$ yields the 20 canonical molecular orbitals (CMO) $\varphi_j = \boldsymbol{\lambda}\mathbf{c}_j$ ($j = 1,2,\ldots 20$), where $\boldsymbol{\lambda} = (\lambda_1 \ldots \lambda_\mu \ldots \lambda_{20})$ is the row vector of the LMOs of **1** and $\mathbf{c}_j = (c_{1j} \ldots c_{\mu j} \ldots c_{20j})^{\mathrm{T}}$ the column vector of the LMO coefficients defining φ_j. The eight highest occupied CMOs φ_j of **1** are displayed in Fig. 3, where open and full bonds refer to LMOs λ_μ with opposite phases. The numbers attached to these bonds are the absolute values $|c_{\mu j}|$ of the LMO coefficients for φ_j (cf.[1a]). Coefficients the absolute values of which satisfy $|c_{\mu j}| < 0.1$, have been disregarded.



$\varphi_{20} = 3a_2$ $\varphi_{19} = 7a_1$ $\varphi_{18} = 5b_1$ $\varphi_{17} = 5b_2$

$\varphi_{16} = 4b_1$ $\varphi_{15} = 6a_1$ $\varphi_{14} = 4b_2$ $\varphi_{13} = 2a_2$

j	ε_j/eV	j	ε_j/eV
20	−10.32	16	−11.47
19	−10.82	15	−11.84
18	−11.16	14	−12.03
17	−11.24	13	−12.36

Figure 3. Representation of the eight highest occupied canonical molecular orbitals (CMO) φ_j of norbornane (**1**), in terms of linear combinations of localized molecular orbitals (LMO) λ_μ (cf. text)

To adapt this EBO model to our compounds **2**, **3**, and **4**, we proceed as follows:

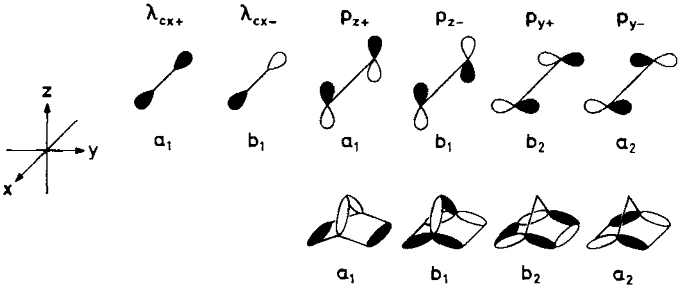
a) We first remove the two LMOs $\lambda_{\mathrm{CH},1}$ and $\lambda_{\mathrm{CH},4}$, which correspond to the two CH-bonds in position 1 and 4 of **1**, to yield the reduced system $\mathbf{1}^{\mathrm{red}}$. With respect to $\mathbb{F}_\lambda(\mathbf{1})$ this means that we strike out the diagonal matrix elements in question, as well as all cross terms linking them to the remaining 18 LMOs λ_μ. Diagonalization of this reduced Fock matrix $\mathbb{F}_\lambda(\mathbf{1}^{\mathrm{red}})$ yields the 18 so-called "precanonical" molecular orbitals (PCMO) ψ_j ($j = 1$ to 18) of the alkyl moiety $\mathbf{1}^{\mathrm{red}}$ present in the dihalides **2**, **3**, **4**. (For more details of this approach, cf. lit.[5].) For symmetry reasons the PCMOs ψ_j of $\mathbf{1}^{\mathrm{red}}$ belonging to the irreducible representations A_2 and B_2 are identical to the CMOs φ_j of **1**, both in shape and energy, whereas those of A_1 and B_1 symmetry obtained for $\mathbf{1}^{\mathrm{red}}$ differ from the corresponding CMOs of **1**. However, the latter PCMO energies E_j are always close to the parent CMO energies ε_j. Note that the PCMO Fock matrix $\mathbb{F}_\psi$ of $\mathbf{1}^{\mathrm{red}}$ is diagonal, i.e. $\mathbb{F}_\psi = \mathrm{diag}(E_1 \ldots E_j \ldots E_{18})$.

b) The reduced system $\mathbf{1}^{\mathrm{red}}$ has now to be augmented by the inclusion of the LMOs $\lambda_{\mathrm{CX},1}$ and $\lambda_{\mathrm{CX},4}$ of the carbon-halogen σ-bonds in positions 1 and 4 of **2**, **3**, **4**, and by the degenerate set of lone pair orbitals $p_{z,1}$, $p_{y,1}$, $p_{z,4}$ and $p_{y,4}$ at the two halogen centres X. [Depending on the nature of the latter (X = Cl, Br or I), these AOs are 3p, 4p, or 5p orbitals]. Accordingly, the resultant Fock matrices $\mathbb{F}(\mathbf{2})$, $\mathbb{F}(\mathbf{3})$, $\mathbb{F}(\mathbf{4})$ will now be of order 24 × 24.

Because the PCMO Fock matrix $\mathbb{F}_\psi$ of $\mathbf{1}^{\mathrm{red}}$ is symmetry factorized, it is of course of advantage to add only matrix elements which refer to the symmetry adapted linear combinations of the new basis orbitals mentioned above. These are:

$$\begin{array}{lll} & & \text{Symmetry} \\ \lambda_{\mathrm{CX}+} &= (\lambda_{\mathrm{CX},1} + \lambda_{\mathrm{CX},4})/\sqrt{2} & A_1 \\ \lambda_{\mathrm{CX}-} &= (\lambda_{\mathrm{CX},1} - \lambda_{\mathrm{CX},4})/\sqrt{2} & B_1 \\ p_{z+} &= (p_{z,1} + p_{z,4})/\sqrt{2} & A_1 \\ p_{z-} &= (p_{z,1} - p_{z,4})/\sqrt{2} & B_1 \\ p_{y+} &= (p_{y,1} + p_{y,4})/\sqrt{2} & B_2 \\ p_{y-} &= (p_{y,1} - p_{y,4})/\sqrt{2} & A_2 \end{array} \qquad (1)$$

Qualitative representations of these linear combinations are shown in the following diagrams together with schematic sample PCMOs of $\mathbf{1}^{\mathrm{red}}$ with which interaction would be symmetry allowed.



(2)

The self energies A_μ (= diagonal matrix elements) of these linear combinations (1), (2) are the same as those of their basis orbitals (at least within the approximation used!) because of the large spatial separation of the latter, so that:

$$\begin{array}{l} A_{\mathrm{CX},+} = A_{\mathrm{CX},-} = A_{\mathrm{CX}} \equiv \langle \lambda_{\mathrm{CX},\mu} | \mathcal{F} | \lambda_{\mathrm{CX},\mu} \rangle \\ A_{p_{z,\pm}} = A_{p_{y,\pm}} = A_p \equiv \langle p_{z,\mu} | \mathcal{F} | p_{z,\mu} \rangle \equiv \langle p_{y,\mu} | \mathcal{F} | p_{y,\mu} \rangle \end{array} \qquad (3)$$

The cross-terms linking the individual linear combinations (1), (2) to the PCMOs ψ_j of appropriate symmetry have to be evaluated according to (4).

$$\begin{aligned} F_{j,CX+} &= \langle\psi_j|\mathcal{F}|\lambda_{CX+}\rangle \\ F_{j,CX-} &= \langle\psi_j|\mathcal{F}|\lambda_{CX-}\rangle \\ F_{j},p_r &= \langle\psi_j|\mathcal{F}|p_r\rangle; (r = z+, z-, y+, y-) \end{aligned} \tag{4}$$

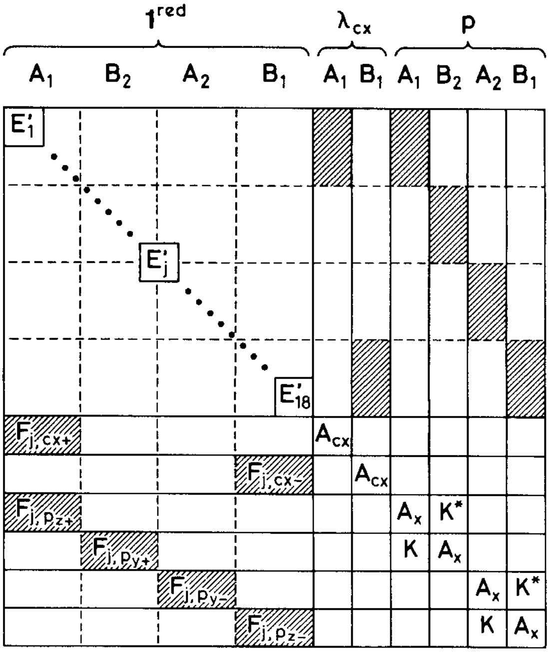
i.e. in terms of the matrix elements $\langle\lambda_\mu|\mathcal{F}|\lambda_{CX}\rangle$ or $\langle\lambda_\mu|\mathcal{F}|p_r\rangle$ between the basis LMOs λ_μ of $\mathbf{1}^{red}$ and the basis orbitals of the linear combinations (1), and of the coefficients $\mathbf{c}_j$ defining the PCMOs ψ_j.

c) Replacing the two CH-bonds in position 1 and 4 of **1** by CX-bonds has of course repercussions on the self energies A_μ of the remaining LMOs λ_μ of the alkyl moiety $\mathbf{1}^{red}$ in **2**, **3**, and **4**. The basis energy shifts δA_μ are due to the fact that our LMOs λ_μ are not strictly localized on a particular bond μ, but exhibit little tails in other regions of the molecule to ensure orthogonality with the remaining LMOs λ_ν, $\nu \neq \mu$, of the set. As a consequence, changing the nature of a particular bond ν will not only change A_ν but also influence the A_μ values of LMOs λ_μ localized on some other bond μ. The resultant shifts δA_μ are the larger, the closer the bonds ν and μ. In practice, only shifts δA_μ of LMOs λ_μ geminal and vicinal to λ_ν need to be taken into consideration.

The necessary corrections of the PCMO energies E_j of $\mathbf{1}^{red}$ are obtained either by a first order perturbation calculation according to (5)

$$E_j' = E_j + \delta E_j \qquad \delta E_j = \sum_\mu c_{\mu j}\delta A_\mu \tag{5}$$

or, if necessary, by diagonalization of the matrix $\mathbb{F}_\lambda'(\mathbf{1}^{red})$ in which the diagonal elements A_μ have been shifted by δA_μ.



(7)

d) Finally we have to account for the effect of spin-orbit coupling by introducing cross terms (6)

$$\begin{aligned} \langle p_{z+} | H_{SOC} | p_{y+} \rangle &= \langle p_{z-} | H_{SOC} | p_{y-} \rangle = \kappa \equiv \frac{i}{2}\zeta(X) \\ \langle p_{y+} | H_{SOC} | p_{z+} \rangle &= \langle p_{y-} | H_{SOC} | p_{z-} \rangle = \kappa^* \equiv -\frac{i}{2}\zeta(X) \end{aligned} \tag{6}$$

where H_{SOC} is the spin-orbit coupling hamiltonian and $\zeta(X)$ the spin-orbit coupling constant typical for the free halogen atom X, namely $\zeta(Cl) = -0.073$ eV, $\zeta(Br) = -0.305$ eV, and $\zeta(I) = -0.628$ eV, i.e. $\zeta(X) = (2/3)\ [E(^2P_{3/2}) - E(^2P_{1/2})]$[6-8].

The complete $\mathbb{F}'$ matrix for the dihalonorbornanes **2**, **3**, **4** is shown in the schematic representation (7). Note that $\mathbb{F}'$ is hermitian because of the presence of the spin-orbit coupling terms K and their complex conjugates K*.

III. Calibration of the Halogen Parameters

Localization of the CMOs φ_j of an alkyl halide RX (e.g. by the method of *Foster* and *Boys*[9]) yields three (almost) equivalent lone-pair LMOs $\lambda_{n\mu}$ of essentially sp^2 character at the halogen centre X. From the $\lambda_{n\mu}$, the basis atomic orbitals p_z and p_y needed for the linear combinations (1), (2) are obtained according to (8).

$$\begin{aligned} p_z &= (2\lambda_{n1} - \lambda_{n2} - \lambda_{n3})/\sqrt{6} \\ p_y &= (\lambda_{n2} - \lambda_{n3})/\sqrt{2} \\ s &= (\lambda_{n1} + \lambda_{n2} + \lambda_{n3})/\sqrt{3}. \end{aligned} \tag{8}$$

If the local symmetry at the X atom were exactly C_{3v}, the p(s) orbital would span the $E(A)$ representation. Whereas the basis energies A_p of the p_z, p_y orbitals are -12.97, -11.85, and -10.45 eV for the free atoms X = Cl, Br, I, respectively[7,10], and are thus close to the frontier orbital energies of norbornane **1** (cf. Fig. 3), the basis energies A_s of the s orbitals are more than 10 eV lower, i.e. -25.54, -23.80, and -20.61 eV for the atoms X = Cl, Br, I[10]. It is obvious that the latter AOs can be safely neglected for our purposes. A further consequence of the low energy of the halogen s AOs is that the CX-bond σ orbitals $\lambda_{CX,1}$ and $\lambda_{CX,4}$ (cf. (1), (2)) are essentially linear combinations of a carbon sp^3 AO and an almost pure halogen p_x AO.

To calibrate the self energies A_p and A_{CX} of the LMOs p_z, p_y and λ_{CX}, as well as the interaction matrix elements F_{j,p_r} (cf. definition (4)) of the former with PCMOs ψ_j of appropriate symmetry, we make use of the PE spectroscopic data of methyl chloride, bromide, and iodide[11] (see (9)).

	$\overline{I_1^m}$/eV	I_2^m/eV	I_3^m/eV	
CH_3Cl	11.29	14.42	15.47	
CH_3Br	10.69	13.52	15.14	(9)
CH_3I	9.85	12.30	14.80	

The value $\overline{I_1^m} = (I_1^m(^2E_{3/2}) + I_1^m(^2E_{1/2}))/2$ is the mean of the ionization energies of the two lone-pair bands, which are split by spin-orbit coupling.

To derive the needed parameters from the data (9) we assign to the methyl group of the methyl halides MeX a pair of pseudo π group orbitals $\psi_{\mathrm{Me},z}$, $\psi_{\mathrm{Me},y}$ of basis energy $A_{\mathrm{Me}} = -14.2$ eV[12]. Assuming the validity of *Koopmans*' theorem and a simple MO model one finds in a first approximation the relationships (10), where the cross-terms Γ_X is defined as $\Gamma_X = \langle p_z | \mathcal{F} | \psi_{\mathrm{Me},z} \rangle = \langle p_y | \mathcal{F} | \psi_{\mathrm{Me},y} \rangle$.

$$\begin{aligned} A_{CX} &\approx -I_2^m \\ A_X &\approx -(\overline{I_1^m} + I_3^m + A_{\mathrm{Me}}) \\ \Gamma_X^2 &\approx [(\overline{I_1^m} - I_3^m)^2 - (A_X - A_{\mathrm{Me}})^2]/4 \end{aligned} \qquad (10)$$

From (9) and (10) one obtains the following set of parameters, which are used for the construction of the matrices (6) of **2**, **3**, and **4**, together with the spin-orbit coupling constants $\zeta(X)$ (also included in (11)).

X	A_{CX}/eV	A_X/eV	Γ_X/eV	ζ(X)/eV
Cl	−14.4	−12.5	−1.9	−0.07
Br	−13.5	−11.6	−1.8	−0.31
I	−12.3	−10.5	−1.7	−0.63

(11)

Whereas methyl halides have been used, in conjunction with the somewhat arbitrary assumption $A_{\mathrm{Me}} = -14.2$ eV, to derive the parameters (11), we now use the observed ionization energies of *tert*-butyl halides to estimate the perturbations δA_μ needed for calculating δE_j and thus E'_j according to (5). From the literature values for *tert*-butyl chloride ($\overline{I_1^m} = 10.69$ eV, $I_2^m = 12.05$ eV), *tert*-butyl bromide ($\overline{I_1^m} = 10.10$ eV, $I_2^m = 11.56$ eV) and *tert*-butyl iodide ($\overline{I_1^m} = 9.37$ eV, $I_2^m = 10.87$ eV)[11] we obtain (12),

X	δA_{CC}(geminal)	δA_{CH}(vicinal)
Cl	−1.3 eV	−0.4 eV
Br	−0.7 eV	−0.2 eV
I	0.0 eV	0.0 eV

(12)

where geminal, vicinal refer, of course, to the CX bond. A sample STO-3G calculation of *tert*-butyl chloride with subsequent localization yielded $\delta A_{CC} = -1.3$ eV, $\delta A_{CH} \approx -0.6$ eV (± 0.1 eV depending on conformation), i.e. values consistent with the empirical results. It should be noted that the above corrections, although reflecting the trend expected on the basis of the electronegativity of the halogen atoms, can only be considered as very crude first approximations.

The resulting diagonal elements E'_j (according to (5)) are presented in Tab. 2.

Table 2. Shifted PCMO energies E_j'/eV of the norbornane moiety 1^{red} contained in the 1,4-dihalonorbornanes **2**, **3**, and **4** and in 1-bromonorbornane (**5**)

2		**3**		**4**		**5**	
E_j'	Symm.	E_j'	Symm.	E_j'	Symm.	E_j'	Symm.
−11.20	a_2	−10.80	a_2	−10.32	a_2	−10.51	a″
−12.25	b_2	−11.78	b_1	−11.17	b_1	−11.11	a′
−12.27	b_1	−11.79	b_2	−11.24	b_2	−11.42	a′
−12.67	a_1	−12.19	a_1	−11.64	a_1	−11.55	a″
−12.93	a_2	−12.55	b_2	−12.03	b_2	−12.18	a′
−13.01	b_2	−12.65	a_2	−12.36	a_2	−12.19	a″
−13.67	a_1	−13.13	a_1	−12.50	a_1	−12.50	a″
−13.76	b_1	−13.45	b_1	−13.16	b_1	−13.20	a′
−14.27	b_2	−13.98	b_2	−13.68	b_2	−13.38	a″

IV. Calculation of Molecular Orbital Energies

After insertion of the matrix elements presented in previous section, the resulting hermitian matrices (7) of **2**, **3**, and **4** are diagonalized, using a routine developped by *A. Schmelzer* (Institut für Physikalische Chemie, Universität Basel).

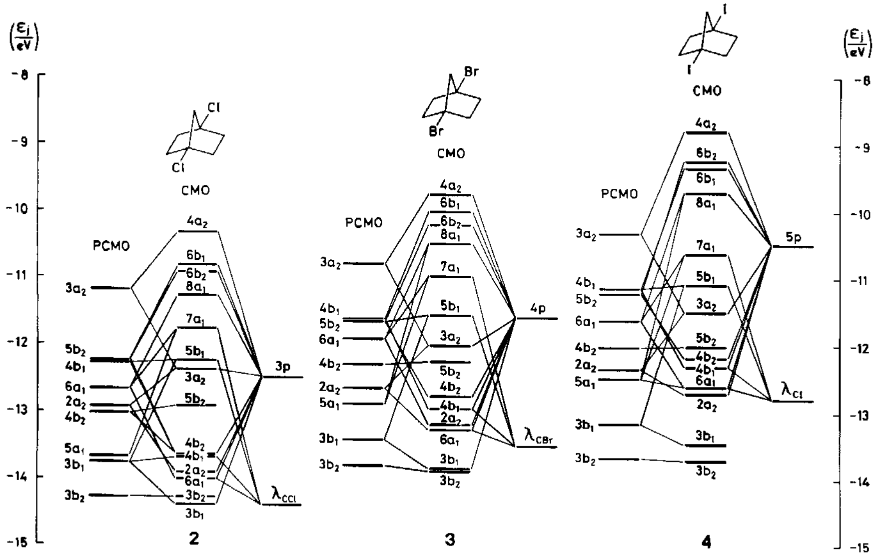


Figure 4. Schematical representation of the interaction between the PCMOs ψ_j of the norbornane moiety of the dihalonorbornanes **2**, **3**, **4** with the respective halogen np lone-pair orbitals and the localized λ_{CX} bond orbitals

The orbital energies ε_j so obtained and the symmetry labels of the corresponding orbitals φ_j are given in Tab. 3 and in Fig. 4. The symmetry labels of the φ_j are numbered, starting for each irreducible representation with 1 for the lowest of the valence shell orbitals only, i.e. disregarding the orbitals of carbon 1 s parentage and the inner orbitals of the respective halogen atom X. This allows a meaningful cross referencing of the orbitals of **2**, **3**, and **4**.

Table 3. Computed orbital energies ε_j/eV and assignment of the observed bands (I_j^m) in the PE spectra of the compounds **2** to **5**. The symmetry labels ("Orb.") refer to C_{2v} in the case of **2**, **3**, **4**, and to C_s in the case of **5**. The percentage contribution of the np or λ_{CX} orbitals corresponds to the square of the corresponding coefficient(s) in the expansion of φ_j. Two values I_j^m tied by a bracket labeled S.O. correspond to spin-orbit split components

1,4-Dichloronorbornane (**2**)					1,4-Dibromonorbornane (**3**)					
$\left(-\frac{\varepsilon_j}{\mathrm{eV}}\right)$	φ_j	% 3p	(λ_{C-Cl})	I_J^m	$\left(-\frac{\varepsilon_j}{\mathrm{eV}}\right)$	φ_j	% 4p	(λ_{C-Br})	I_J^m	
10.33	$4a_2$	31	(–)	10.3_5	9.76	$4a_2$	39	(–)	9.9	S.O.
10.83	$6b_1$	50	(1)	10.7_5	10.14	$6b_1$	54	(1)	10.1_5	
10.93	$6b_2$	49	(–)		10.25	$6b_2$	58	(–)	10.3_5	S.O.
11.29	$8a_1$	57	(5)	11.1_0	10.58	$8a_1$	60	(5)	10.5_5	
11.78	$7a_1$	2	(29)	11.5_0	11.15	$7a_1$	3	(34)	11.1_5	
12.25	$5b_1$	2	(46)	12.3 to	11.58	$5b_1$	–	(59)	(11.5)	
12.39	$3a_2$	20	(–)	12.6	12.02	$3a_2$	28	(–)	(11.9) to	
12.92	$5b_2$	4	(–)	Max: 12.8_5	12.49	$5b_2$	4	(–)	12.7	
13.64	$4b_2$	39	(–)	13.4	12.96	$4b_2$	34	(–)		
13.68	$4b_1$	16	(27)		13.03	$4b_1$	29	(13)		
13.91	$2a_2$	49	(–)		13.26	$2a_2$	35	(1)		
14.02	$6a_1$	38	(9)		13.32	$5a_1$	33	(8)		
14.29	$3b_2$	2	(–)	14.4	13.87	$3b_1$	14	(1)		
14.40	$3b_1$	30	(–)		14.01	$3b_2$	2	(–)		

1,4-Diiodonorbornane (**4**)						1-Bromonorbornane (**5**)					
$\left(-\frac{\varepsilon_j}{\mathrm{eV}}\right)$	φ_j	% 5p	(λ_{C-I})	I_J^m		$\left(-\frac{\varepsilon_j}{\mathrm{eV}}\right)$	φ_j	% 4p	(λ_{C-Br})	I_J^m	
8.80	$4a_2$	56	(–)	9.11		9.89	9a″	38	(–)	9.76	S.O.
9.25	$6b_2$	70	(1)	9.26	S.O.	10.27	13a′	53	(–)	10.07	
9.26	$6b_1$	52	(1)	9.36	S.O.	10.89	8a″	14	(–)	10.8_5	
9.71	$8a_1$	63	(3)	9.90		10.95	12a′	–	(17)	(11.4) to	
10.45	$7a_1$	3	(42)	10.8		11.46	11a′	1	(26)	12.8	
10.79	$5b_1$	1	(70)	11.5		11.66	10a′	4	(10)	Max: 11.9	
11.50	$3a_2$	33	(–)			12.17	7a″	4	(–)	12.7_5	
12.02	$5b_2$	1	(–)			12.25	6a″	8	(–)		
12.19	$4b_2$	29	(–)	12.2 to 13.3		13.01	5a″	27	(–)		
12.30	$4b_1$	31	(4)			13.14	9a′	30	(1)		
12.58	$6a_1$	28	(8)			13.65	8a′	11	(4)	13.9	
12.71	$2a_2$	20	(–)			13.85	4a″	2	(–)		
13.44	$3b_1$	6	(2)	13.9		15.55	7a′	1	(5)	Max: 16.0_5	
13.71	$3b_2$	1	(–)	(14.3_5)		15.77	6a′	–	(28)		

V. Discussion of the Results

As shown in Fig. 4 the orbital interaction-pattern and consequently the overall CMO sequence is predicted to be the same for **2**, **3**, and **4**. This can be rationalized as follows: Due to the basis energy shifts δA_μ (cf. (12)) the PCMOs of **2** and **3** are shifted towards lower energies, but exhibit the same sequence (with marginal differences) as the unshifted PCMOs of **4**. In addition the basis energies of the np and λ_{CX} orbitals show the same trend towards higher energies, going from **2** to **3** to **4** as the corresponding PCMOs, so that the energy difference between the np and λ_{CX} basis energies remains about the same (i.e. 1.9 eV for **2** and **3**; 1.8 eV for **4**). Finally the cross-terms Γ_X are all of the same magnitude.

The orbital schemes of Fig. 4 allow therefore a general and rather straightforward rationalization of the PE spectra for **2** to **4**: The top four orbitals belong to the four different irreducible representations of C_{2v} ($4a_2$, $6b_1$, $6b_2$, $8a_1$) and give rise to the bands ① to ④, which are nicely separated in the PE spectrum of **4** due to the large effect of spin-orbit coupling. As indicated in Table 3 these orbitals exhibit high contributions from the halogen np orbitals, the percentage increasing from **2** to **3** to **4**, as would be expected from the relative positions of their basis energies. Bands ⑤ and ⑥ are due to the ejection of electrons from the orbitals ($7a_1$, $5b_1$) which show considerable contributions from the λ_{CX} bond orbitals. Electron ejection from the lower lying orbitals gives rise to overlapping bands, which prevents an accurate correlation between calculated and experimental ionization energies.

1-Bromonorbornane (**5**): This molecule belongs to the symmetry group C_s, and the orbital interaction pattern is therefore less determined by symmetry, than was the case of the dihalonorbornanes **2** to **4**. However, our model leads again to a straightforward rationalization of its PE spectrum: Bands ① and ② are due to the ejection of electrons from the orbitals 9a″and 13a′which are separated by 0.31 eV, mainly due to spin-orbit coupling. Both bands show a vibrational fine structure (①: $\Delta\tilde{\nu} = 645\ \mathrm{cm}^{-1}$; ②: $\Delta\tilde{\nu} = 807\ \mathrm{cm}^{-1}$). As in the case of the molecules **2** to **4** the corresponding top orbitals exhibit the highest contribution from the bromine 4p orbitals. Band ③ with $I_3^m = 10.8_5$ eV is due to the ejection of an electron from the orbital 8a″which is mainly located in the norbornane moiety. According to our calculation it should still possess about 14% bromine 4p orbital character. Removal of an electron from the orbitals 12a′and 11a′gives rise to band ④ ($I_4^m \approx 11.4$ eV). These orbitals show high contribution from λ_{CBr}. The double band labeled ⑤ is due to overlapping bands which, however, can not be correlated with accuracy with the calculated data.

This work was supported by the *Fonds der Chemischen Industrie*, by the *Dr. Jost-Henkel-Stiftung*, by the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung*, by *Ciba-Geigy SA*, by *Sandoz SA*, and by *F. Hoffmann-La Roche & Cie SA*, Basel.

Experimental Part

Melting points: Büchi 510 melting point apparatus, uncorrected. – 80 MHz ^{1}H NMR spectra: Bruker WP 80. – All samples were stored under nitrogen and to the exclusion of light. Their purity was checked by VPC on several columns. Preparative VPC was performed on a 4 m column of 10% Carbowax 20 M on Chromosorb R-NAW (60/80 mesh). Starting Materials: Norcamphor: Aldrich – Europe, Hexachlorocyclopentadiene: Merck AG. Solvents: 1,2-Dibromoethane and diiodomethane were distilled over calcium oxide directly before use. The halogen exchange and the modified Hunsdiecker reactions were carried out under nitrogen.

1,4-Dichlorobicyclo[2.2.1]heptane (**2**): Prepared according to *Wilcox* and *Zajacek*[13] via addition of ethylene to hexachlorocyclopentadiene. The four chlorines were removed in two steps: the two bridge chlorines by treatment with zinc in acetic acid, those in olefinic position by hydrogenation with Raney nickel in the presence of excess potassium hydroxide. Sublimation of a small amount of **2** provided white crystals, m.p. 79–80.5°C (lit.[13] 78–79°C). – IR ($CHCl_3$): 2975 m-sh, 2960 m, 2925 m, 2880 m, 1455 m, 1315 s, 1280 m, 1012 s, 865 cm^{-1} vs. – ^1H NMR ($CDCl_3$): δ = 1.96, 2.15 (q, 8H, J = 8 Hz); 2.17 (s, 2H). – For the conversion of **2** into the corresponding dibromo and diiodo derivatives (according to *Wiberg* et al.[14]) a bridgehead halogen exchange method developped by *Pincock*[15] was used with slight modifications:

1,4-Dibromobicyclo[2.2.1]heptane (**3**): Small strips of aluminium foil (0.70 g, 25 mmol) in 100 ml of 1,2-dibromoethane were heated with bromine (0.60 g, 3.8 mmol) to 80°C. After 15 min the temperature was raised to 100°C and **2** (1.0 g, 6.1 mmol) in 20 ml of CH_2Br_2 was added dropwise. The mixture was kept at 100°C for 1 h. After cooling and removal of the solvent under reduced pressure the dark residue was carefully washed with cold water, solved in ether and decolourized with activated charcoal. After evaporation of the solvent the remaining solid was sublimed at 30°C/0.3 Torr to give 0.50 g (2.3 mmol, 38%) of white needles of **3**, m.p. 73–73.5°C (lit. 73.5–74°C[14], 73°C[15]). – IR ($CHCl_3$): 2980 w-sh, 2955 m, 2930 w, 2870 w, 1450 m, 1310 s, 1270 s, 1008 vs, 845 cm^{-1} vs. – ^1H NMR ($CDCl_3$): δ = 2.03, 2.23 (q, 8H, J = 8 Hz); 2.31 (s, 2H).

1,4-Diiodobicyclo[2.2.1]heptane (**4**): In analogy to the procedure described above bromine (0.40 g, 25 mmol) was added to aluminium foil (0.35 g, 13.0 mmol) in 15 ml of diiodomethane at 70°C. The reaction mixture was heated to 95°C, and after 25 min **2** (1.0 g, 6.1 mmol) in 10 ml of CH_2I_2 was added dropwise. After 60 min the suspension was cooled and poured into cold water. The organic layer was separated, treated with activated charcoal and dried over $MgSO_4$. The solvent was removed under reduced pressure (0.3 Torr, 60°C). The residue had to be sublimed twice to provide 0.50 g (1.4 mmol, 27%) of slightly yellow needles of **4**, m.p. 103°C (lit. 102–103°C[14], 101°C[15]). – IR ($CHCl_3$): 2985 w, 2950 m, 2915 w, 2870 w, 1445 s, 1310 s, 1265 s, 995 vs, 832 cm^{-1} s. – ^1H NMR ($CDCl_3$): δ = 2.04, 2.27 (q, 8H, J = 8 Hz); 2.43 (s, 2H).

1-Bromobicyclo[2.2.1]heptane (**5**): 1-Chlorobicyclo[2.2.1]heptane was prepared according to *Wiberg* et al.[16]. The bridgehead halogen exchange method – as described above – proved to be unsuccessful for the conversion into **5**. Thus, crude 1-chlorobicyclo[2.2.1]heptane was treated with lithium and carbon dioxide to provide bicyclo[2.2.1]heptane-1-carboxylic acid according to *Bixler* and *Niemann*[17]. The acid, purified by sublimation, was converted into the corresponding bromide by means of a modified *Cristol-Firth-Hunsdiecker* reaction[18]. The carboxylic acid (1.0 g, 7.1 mmol) was heated with anhydrous $MgSO_4$ (1.0 g, 8.1 mmol) and red mercuric oxide (1.3 g, 6.0 mmol) in 40 ml of dibromomethane to 80°C. Bromine (1.4 g, 8.7 mmol) was added dropwise, and the reaction mixture was stirred for 8 h. After cooling and filtration the solution was washed with diluted aqueous $NaHSO_3$, NaOH, and brine. After drying ($MgSO_4$/K_2CO_3) the solvent was removed under reduced pressure (25 Torr, 30°C). The remainder was distilled to give 0.49 g (2.80 mmol, 39.4%) of **5** as a colourless liquid, b.p. 63–65°C/20 Torr (lit.[18] 62–64°C/23 Torr). A sample of **5** was stored over K_2CO_3 and purified by preparative VPC. – IR (liq.): 2965 s, 2920 m, 2865 m, 1442 m, 1295 m, 1242 m, 1208 m, 1180 w, 1150 m, 1137 m, 1093 w, 1010 w, 970 s, 928 m, 885 m, 820 m, 750 cm^{-1} m. – ^{1}H NMR ($CDCl_3$): δ = 1.90 (m).

Note added in proof (20.5.1985): A recent paper (*E. W. Della, R. S. Abeywickrema, M. K. Livett,* and *J. B. Peel,* J. Chem. Soc., Perkin Trans. **II, 1984**, 1653) reports on the photoelectron spectra of some 1-halogenobicycloalkanes. The assignment of the PE spectrum of **5** proposed therein differs slightly from that given in this work.

1) Part III of The Equivalent Bond Orbital Model Revisited. – 1a) Part I: *E. Honegger, Z.-z. Yang,* and *E. Heilbronner,* Croat. Chim. Acta, in press. – 1b) Part II: *E. Heilbronner, E. Honegger, P. Schmitt, H. Günther,* and *W. Zambach,* Helv. Chim. Acta **67**, 1681 (1984). – Part 49 of Small and Medium Rings. – Part 48: *H.-D. Martin, B. Mayer, R. W. Hoffmann, A. Riemann,* and *P. Rademacher,* Chem. Ber. **118**, 2514 (1985).

2) *R. B. Davidson* and *C. R. Williams,* J. Am. Chem. Soc. **100**, 2017 (1978); *C. A. Grob, A. Kaiser,* and *T. Schweizer,* Helv. Chim. Acta **60**, 391 (1977); *W. F. Reynolds,* J. Chem. Soc., Perkin Trans. 2 **1980**, 985; *O. Exner* and *P. Fiedler,* Collect. Czech. Chem. Commun. **45**, 1251 (1980).

3) *W. Adcock, A. N. Abeywickrema,* and *G. B. Kok,* J. Org. Chem. **49**, 1387 (1984).

4) *P. Bischof, J. A. Hashmall, E. Heilbronner,* and *V. Hornung,* Helv. Chim. Acta **52**, 1745 (1969); *G. Bieri, F. Burger, E. Heilbronner,* and *J. P. Maier,* ibid. **60**, 2213 (1977).

5) *E. Heilbronner* and *A. Schmelzer,* Helv. Chim. Acta **58**, 936 (1975).

6) *F. Brogli* and *E. Heilbronner,* Helv. Chim. Acta **54**, 1423 (1971); *F. T. Chau* and *C. A. McDowell,* J. Phys. Chem. **80**, 2923 (1976).

7) *C. E. Moore,* U.S. Natl. Bureau Standards, Circ. No. 467, Atomic Energy Levels, I–III, 1948, 1952, 1958 [Chem. Abstr. **42**, 6654e (1948), **47**, 4191h (1953), **52**, 11558c (1958)], *T. M. Dunn,* Trans. Faraday Soc. **57**, 1441 (1961).

8) *W. C. Price,* J. Chem. Phys. **4**, 539, 547 (1936); *J. L. Ragle, I. A. Stenhouse, D. C. Frost,* and *C. A. McDowell,* ibid. **53**, 178 (1970); *F. Brogli* and *E. Heilbronner,* Helv. Chim. Acta **54**, 1423 (1971).

9) *J. M. Foster* and *S. F. Boys,* Rev. Mod. Phys. **32**, 300 (1960).

10) *T. A. Carlson,* Photoelectron and Auger Spectroscopy, p. 337, Plenum Press, New York 1976.

11) *K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki,* and *S. Iwata,* Handbook of the HeI Photoelectron Spectra of Fundamental Organic Molecules, Japan Scientific Societies Press, Tokyo, 1981.

12) *E. Honegger,* Thesis, University of Basel 1983.

13) *C. R. Wilcox jr.,* and *J. G. Zajacek,* J. Org. Chem. **29**, 2209 (1964).

14) *K. B. Wiberg, W. F. Bailey,* and *M. E. Jason,* J. Org. Chem. **41**, 2711 (1976).

15) *J. W. McKinley, R. E. Pincock,* and *W. B. Scott,* J. Am. Chem. Soc. **95**, 2030 (1973).

16) *K. B. Wiberg, B. R. Lowry,* and *T. H. Colby,* J. Am. Chem. Soc. **83**, 3998 (1961).

17) *R. L. Bixler* and *C. Niemann,* J. Org. Chem. **23**, 743 (1958).

18) 18a) *G. S. Poindexter* and *P. J. Kropp,* J. Org. Chem. **41**, 1215 (1976). – 18b) *F. W. Baker, H. D. Holtz,* and *L. M. Stock,* J. Org. Chem. **28**, 514 (1963). – 18c) *S. J. Cristol* and *W. C. Firth,* J. Org. Chem. **26**, 280 (1961).

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