3. Inverted Hyperconjugation in Symmetrical 1,4-Dihalocubanes1)

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The σ-orbital manifold of cubane **1**, as suggested by its PE spectrum, is divided into two sets separated by a 3 eV gap extending from ~ -10.5 eV to ~ -13.5 eV. Halogen substituents with np AO basis energies falling into this gap (*e.g.* Cl or Br) will, therefore, hyperconjugate appreciably with both sets. Interaction with the lower-lying set will lead to the usual destabilization ('normal' hyperconjugation), whereas interaction with the set above will necessarily lead to a 'stabilization' ('inverted' hyperconjugation). As a result the lone-pair ionization energies of Cl or Br substituted cubanes (derived from PE spectra) are much larger than naively expected for an alkyl halide containing as much as 8 C-atoms. In particular no significant shift of the e_g^{-1} lone-pair bands in the PE spectra of 1,4-dichloro- and 1,4-dibromocubane can be detected with respect to the first ionization energies of the free atoms Cl and Br, or of HCl and HBr.

1. Introduction. – The change $\delta I_{X_j}(R)$ in the jth ionization energy $I_j(XH)$ of the molecule XH (where X could be an atom or a polyatomic moiety), brought about by the replacement of H by an alkyl substituent R to yield XR, *i.e.*

$$\delta I_{X_j}(R) = I_j(XR) - I_j(XH) \tag{1}$$

seems to be a rather straightforward measure of the charge-stabilizing influence of R on X. However, it should be realized that this measure has its limitations, because there is no compelling *a priori* reason that $\delta I_{X_j}(R)$ should parallel closely the traditional substituent parameters of linear free energy relationships (LFER) [2], *i.e.* that linear regressions of the type $\delta I_{X_j}(R) \propto \rho_{X_j}\sigma(R)$ will apply within narrow limits of error if $\sigma(R)$ stands for $\sigma^*(R)$, $\sigma^+(R)$ or any other similar substituent parameter [3]. (Notwithstanding the lack of such a theoretical requirement, rather decent regressions of the above type have been observed in practice [4].) The main reason for this dichotomy between the effects embodied, on the one hand, in $\delta I_{X_j}(R)$ and, on the other, in $\sigma(R)$ is best explained with reference to a naive MO model. Crudely speaking, $\delta I_{X_j}(R)$ refers to a 'one-electron' property, namely the change in the energy needed to remove an electron from a given MO φ_j, whereas the LFER parameters $\sigma(R)$ apply, more often than not, to 'all-electron' properties *i.e.* changes in the total energy of the system. Certainly, this 'explanation' is oversimplified, but it contains more than a grain of truth.

We now use simple *Hückel*-type MO arguments to state our problem. (The reader is advised that the following arguments are by no means intended to play the role of a

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1) Part IV of 'The Equivalent Bond Orbital Model Revisited' (Part III: [1]), and Part 50 of 'Small and Medium Rings' (Part 49: [1]).

'theory', but that they are only part of a convenient language in which we can express ourselves more concisely.) The question to be answered is: what are, within such a simple model, the main electronic mechanisms which lead to a stabilization of a positive charge by an alkyl group R, and hence to an ionization energy reduction $\delta I_{X_j}(R)$, as defined in (*1*).

A) *Inductive Effect.* For a molecule XR, the inductive effect of an alkyl group R is defined to provide an energy shift $\delta A_p(R)$ of the self energy A_p of the basis orbitals ϕ_p of X at the centre p to which R is attached. (If the basis orbitals are localized bond orbitals, they are designated by λ_p [5].) If the ϕ_p participate in a particular (canonical) MO of X according to $\varphi_j = \Sigma_j c_{\mu j}\phi_\mu$, then the first-order inductive perturbation $\delta\varepsilon_j^{ind}$ of the orbital energy ε_j of φ_j is given by

$$\delta\varepsilon_j^{ind} = \Sigma_p c_{pj}^2 \delta A_p(R) \tag{2}$$

Applying *Koopmans'* theorem yields the required shift contribution $\delta I_{X_j}^{ind}(R) = -\delta\varepsilon_j^{ind}$. Another, usually minor effect consists in the introduction of cross-terms $\kappa_{jk} = \Sigma_p c_{pj} c_{pk} \delta A_p(R)$ between pairs of orbitals φ_j, φ_k of X. The resulting second-order shifts due to this interaction can be neglected in a first approximation, except when φ_j, φ_k are (almost) degenerate.

B) *Hyperconjugation.* The term hyperconjugation is usually restricted to designate the conjugative interaction of one or more localized alkyl-group orbitals $\phi_r(R)$ of local p symmetry with π-type orbitals φ_j of the X moiety in a molecule XR. The corresponding interaction matrix element $B_{jr} = \langle\varphi_j|\hat{H}|\phi_r(R)\rangle$ can be expanded with reference to the linear combination $\varphi_j = \Sigma_\mu c_{\mu j}\phi_\mu$, *i.e.*

$$B_{jr} = \sum_p c_{pj}\langle\phi_p|\hat{H}|\phi_r(R)\rangle \tag{3}$$

where the summation is carried out over all basis orbitals ϕ_p of X at the centre of attachement of R. According to second-order perturbation theory, the resulting orbital energy shift $\delta\varepsilon_j^{hyp}$ is given by

$$\delta\varepsilon_j^{hyp} = \sum_r \frac{B_{jr}^2}{\varepsilon_j - \varepsilon_r} \tag{4}$$

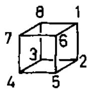
where ε_r is the energy of the pseudo-π-orbital $\phi_r(R)$ of the alkyl group. Using again *Koopmans'* theorem the hyperconjugative shift contribution is $\delta I_{X_j}^{hyp}(R) = -\delta\varepsilon_j^{hyp}$.

Independent of the model-restricted definitions given above, there is a conceptually important difference between the mechanisms *A* and *B*. The inductive mechanism *A* depends on the square of the (real) wave functions φ_j to be perturbed. As φ_j^2 is necessarily totally symmetric the inductive perturbation is always symmetry-allowed, finite (provided $c_{pj} \neq 0$) and of same sign for all orbitals φ_j, independent of their energy ε_j. In contrast, the hyperconjugative mechanism depends on the wave function φ_j itself and on $\phi_r(R)$, which means that it is governed by the relative local symmetries of these orbitals at the centre of junction p. Thus, cases are known where hyperconjugation is symmetry forbidden [6]. A second, from our point of view important difference is that the sign of $\delta\varepsilon_j^{hyp}$, and, therefore, that of δI_j^{hyp} (R) depends on the sign of the denominators $\varepsilon_j - \varepsilon_r$ of the terms in the right-hand sum of (*4*). In those cases usually discussed in the literature, the differences $\varepsilon_j - \varepsilon_r$ are positive because the target orbital φ_j, from which the electron is removed, is either the φ_{HOMO} or a subjacent orbital placed well above the alkyl orbitals $\phi_r(R)$ in energy. Under these conditions hyperconjugation always reduces the ionization energy corresponding to electron ejection from such a target orbital φ_j of X.

According to (*4*) one could, however, consider the case that ε_j is embedded in the manifold of the ε_r so that one part of the terms in the summation are positive ($\varepsilon_j > \varepsilon_r$) and another negative ($\varepsilon_j < \varepsilon_r$). In the (assumed) absence of an inductive effect ($\delta I_j^{ind}(R) = 0$) one might then expect that $\delta I_j^{hyp}(R)$ could become zero, or even negative. Unfortunately, it is extremely difficult if not impossible to investigate such a situation experimentally if R is one of the usual alkyl groups. The reason for this failure is the high density of broad, overlapping $\phi_r(R)^{-1}$ bands in the PE spectrum of even a medium-size hydrocarbon RH, and thus (with only small changes) of the R group σ-band system in the PE spectrum of XR [7]. Accordingly, the φ_j^{-1} dominated band, in which we are interested, is usually completely obliterated and beyond deconvolution, if it becomes immersed in the σ-band system, in particular because it tends to be much broadened as a result of the, necessarily extensive, mixing of φ_j with those $\phi_r(R)$ which are close in energy.

Amusingly, there is one particular alkyl group whose rather unique orbital energy manifold provides an ideal opportunity to submit our hypothesis of 'inverted' hyperconjugation, *i.e.* the occurrence of a vanishing or even positive $\delta I_j^{hyp}(R)$ value, to an experimental test. This is the cubyl group ($R = C_8H_7$), derived from cubane (**1**). The σ-band system in the PE spectrum of **1** [8] is subdivided into two subsystems, the first at ~ 8.5 eV to ~ 10.5 eV, corresponding to the $3t_{2g}^{-1}$ and $1t_{2u}^{-1}$ states of $\mathbf{1}^+$, and the second above ~ 13.5 eV, corresponding to the $1e_g^{-1}$, $3t_{1u}^{-1}$, $2a_{2u}^{-1}$ and higher-lying states. These two band systems are separated by a gap of 3 eV completely free of any other feature. This suggests that our problem should be amenable to an experimental test if X is chosen in such a way that the φ_j^{-1} band(s) of this target group come(s) to lie within this gap (10.5 eV to 13.5 eV) where it (they) can be observed easily. Obviously, X = halogen is the target group of choice to be used for such an experiment.

2. Experimental Results. – For practical reasons, it is of advantage to study the PE spectra of the highly symmetrical (D_{3d}) *1,4-dihalo-pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octanes (= 1,4-dihalocubanes)* **2–4**.



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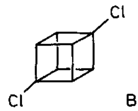

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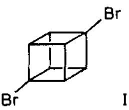

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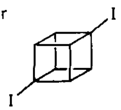

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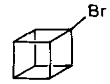

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Their He(Iα) PE spectra including that of 1-bromocubane (**5**), are shown in *Fig. 1*. The positions I_j^m of the individual band maxima, which can be equated, for all practical purposes to the vertical ionization energies ($I_j^m \approx I_j^v$) are collected in *Table 1*. (See also in *Table 2*, where these values are reported together with the assignment based on the theoretical model described below.) The PE spectrum of **1** has been reported previously [7]. (For the sake of comparison schematic representations of this spectrum are given on top of the *Figs. 4–6*, to be discussed below.)

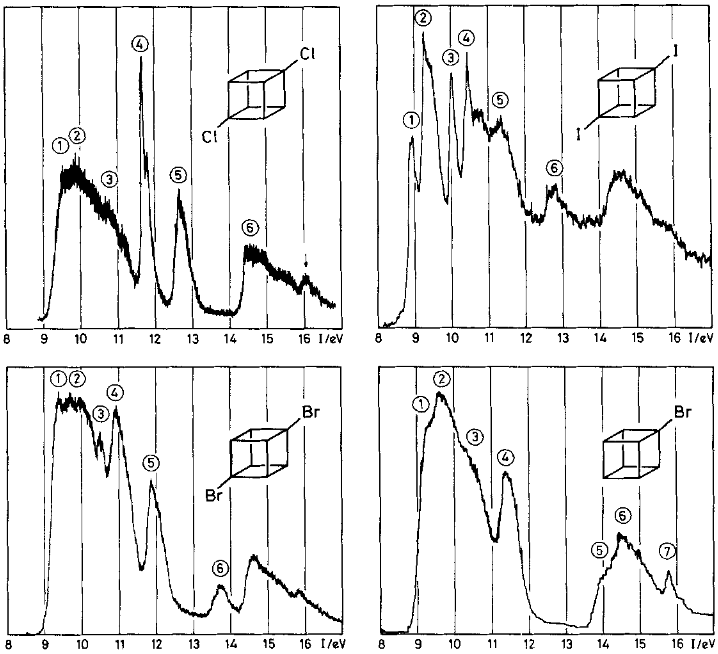

Fig. 1. *He(Iα) PE Spectra of* **2–5**

Table 1. *Ionization Energies* I_j^m/eV *of the 1,4-Dihalocubanes* **2–4** *and of 1-Bromocubane* (**5**). Probable error: ± 0.05 eV if second decimal given as subscript, ± 0.1 eV if one decimal given. Values in parentheses refer to shoulders or overlapped bands.

Band	2	3	4	5
①	(9.5)	9.4_5	8.8_5	(9.3)
②	9.9	(9.7)	9.2_5	9.6_5
③	(10.7)	10.5_0	10.0_0	(10.5)
④	11.6_5	10.9_5	10.4_0	11.3_5
⑤	12.6_5	11.9	(11.2)	(14.0)
⑥	(14.5)	13.7_5	12.7	14.4_5
⑦				15.7_5

3. The Equivalent-Bond-Orbital (EBO) Model. – In [1], we analyzed the PE spectra of the symmetrical 1,4-dihalo-bicyclo[2.2.1]heptanes (= 1,4-dihalonorbornanes) with halogen = Cl, Br, I, using a modified EBO model [5], adapted to account for the presence of halogen atoms and for spin-orbit coupling (*cf.* also [9]).

With respect to the problem at hand, one starts with the *Fock* matrix $\boldsymbol{F}_\lambda(\mathbf{1})$ (order 20 × 20) of cubane, in localized basis [8]. From $\boldsymbol{F}_\lambda(\mathbf{1})$ we remove the matrix elements (diagonal- and cross-terms) which refer to the localized molecular orbitals (LMOs) $\lambda_{CH,1}$, $\lambda_{CH,4}$ of the C–H bonds in positions 1 and 4 of **1**. The remaining 18 × 18 matrix, $\boldsymbol{F}_\lambda(\mathbf{1}^{red})$, is therefore the one of the reduced system $\mathbf{1}^{red}$ *i.e.* the cubane-1,4-diyl moiety of **2–4**. Adding two halogen atoms X to $\mathbf{1}^{red}$ *via* C–X bonds, shifts the self energies A_μ of those LMOs λ_μ of $\mathbf{1}^{red}$ which are geminal or vicinal to λ_1 and λ_4 by small amounts, listed

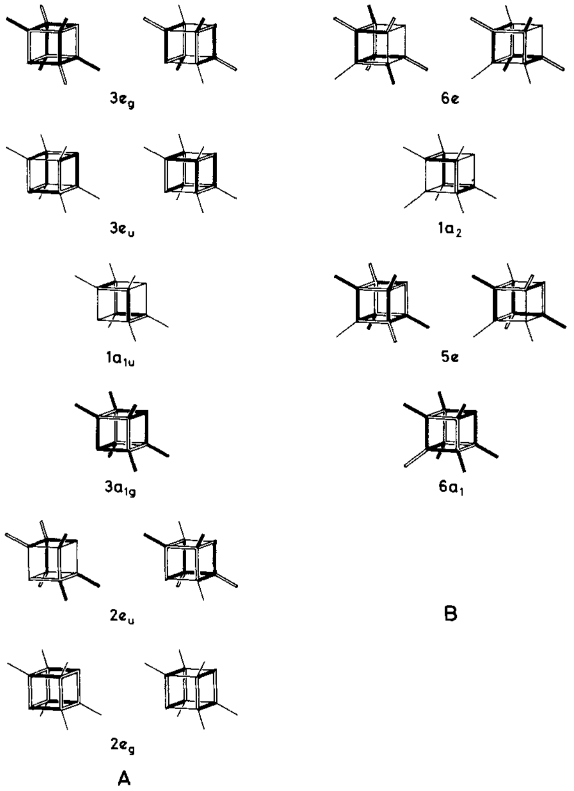

Fig. 2. *Schematic representation* A) *of the 10 highest precanonical orbitals* (PCMO) *of the alkyl moieties of* **2–4**, *which act as 'through-bond' interaction relay orbitals for the halogen lone-pair orbitals np,* and B) *of the 6 highest PCMOs of the cubyl group of* **5**. The sequence shown (from top to bottom) is according to the relative orbital energies.

in (*12*) of [1]. The resulting matrix $F_\lambda(\mathbf{1}^{\mathrm{red}})$ is diagonalized, yielding 18 'precanonical' orbitals (PCMOs) [10] of the cubane moiety $\mathbf{1}^{\mathrm{red}}$. The LMO phase relationships of the top 10 PCMOs (under D_{3d} symmetry) are shown schematically in *Fig. 2 (A)*. (Removing only the matrix elements referring to the LMO $\lambda_{\mathrm{CH},1}$ from the matrix $F_\lambda(\mathbf{1})$ leads, by the same procedure, to 19 PCMO's of the cubyl moiety of **5**, the top 6 of which are shown in *Fig. 2 (B)*.)

As described in [1] the 18 × 18 PCMO matrix F_λ is now increased to order 24 × 24, to account for the four p-type lone pairs of the two X atoms and the two bond orbitals λ_{CX}. Because the PCMO *Fock* matrix F_Ψ is symmetry-factorized, it is of advantage to add only matrix elements which refer to the symmetry-adapted linear combinations of the additional basis orbitals defined in (*2*) of [1]. The same reference should be consulted for the definition of the cross-terms, including those which are due to spin-orbit coupling [11].

Finally the resulting 24 × 24 hermitian matrices of **2–4** are diagonalized. The orbital energies ε_j and the symmetry labels of the corresponding CMOs φ_j are listed in *Table 2*.

Table 2. *Orbital Energies ε_j/eV and CMO Symmetry Labels Derived from the EBO Model.* The values listed in the columns labeled % X and (% λ_{CX}) are the percentage contributions of the halogen p-type lone-pair orbitals and, of the C–X σ-bond LMOs.

1,4-Dichlorocubane (**2**)

$\left(-\frac{\varepsilon_j}{eV}\right)$	φ_j	% 3p	(% λ_{C-Cl})	I_j^m
9.75	$4e_u$	27	(–)	9.5
9.77		26	(–)	
9.99	$4e_g$	21	(–)	(9.9)
10.01		20	(–)	
10.15	$4a_{1g}$	–	(39)	
10.76	$1a_{1u}$	–	(–)	(10.7)
12.36	$3e_g$	63	(–)	11.6_5
12.40		63	(–)	
13.36	$3e_u$	68	(–)	12.6_5
13.40		69	(–)	
14.13	$3a_{2u}$	–	(87)	
14.95	$2e_u$	5	(–)	Max. 14.5
14.95		5	(–)	
15.68	$2e_u$	15	(–)	
15.69		15	(–)	

1,4-Dibromocubane (**3**)

$\left(-\frac{\varepsilon_j}{eV}\right)$	φ_j	% 4p	(% λ_{C-Br})	I_j^m
9.26	$4e_u$	34	(–)	9.4_5
9.36		30	(–)	
9.58	$4e_g$	31	(–)	9.7
9.67		26	(–)	
9.97	$4a_{1g}$	–	(43)	
10.46	$1a_{1u}$	–	(–)	10.5_0
11.63	$3e_g$	58	(–)	10.9_5
11.82		61	(–)	
12.51	$3e_u$	63	(–)	11.9_0
12.71		67	(–)	
13.33	$3a_{2u}$	–	(94)	13.7_5
14.73	$2e_u$	2	(–)	14.7
14.74		3	(–)	
15.21	$2e_g$	10	(–)	
15.25		12	(–)	

1,4-Diiodocubane (**4**)

$\left(-\frac{\varepsilon_j}{eV}\right)$	φ_j	% 5p	(% λ_{C-I})	I_j^m
8.43	$4e_u$	39	(–)	8.89
8.64		30	(–)	
8.74	$4e_g$	41	(–)	9.2_5
8.96		28	(–)	
9.01	$4a_{1g}$	–	(46)	9.42
9.56	$1a_{1u}$	–	(–)	10.0
10.60	$3e_g$	50	(–)	10.42
10.95		61	(–)	
11.27	$3e_u$	59	(–)	11.2
11.68		68	(–)	
12.20	$3a_{2u}$	–	(95)	12.7
14.17	$2e_u$	1	(–)	(14.80)
14.18		2	(–)	
14.29	$2e_g$	8	(–)	
14.34		11	(–)	

1-Bromocubane (**5**)

$\left(-\frac{\varepsilon_j}{eV}\right)$	φ_j	% 4p	(% λ_{C-Br})	I_j^m
9.30	7e	29	(–)	(9.3)
9.38		25	(–)	
9.75	6e	(0.3)	(–)	Max. 9.6_5
9.75		(0.4)	(–)	
9.83	$7a_1$	–	(20)	
10.01	$1a_2$	–	(–)	10.5
11.90	5e	60	(–)	11.3_5
12.09		62	(–)	
13.40	$6a_1$	–	(57)	(14.0)
14.35	4e	(0.3)	(–)	
14.35		(0.3)		Max. 14.4_5
14.75	3e	10	(–)	
14.79		11	(–)	
15.61	$5a_1$	–	(9)	15.7_5

Attention is drawn to some differences with respect to [1], concerning the calibration of the elements of the *Fock* matrix $F_\lambda(1)$. To construct the *Fock* matrix $F_\lambda(1)$ for cubane **1** an *ab initio* calculation for **1** is carried out, using the bond lengths proposed in [8] (*i.e.* R_{CC} = 156.1 pm, R_{CH} = 108.1 pm), which yields the CMOs φ_j. The occupied manifold of the CMOs is then subjected to the *Foster-Boys* localization procedure [12] to obtain the localized orbitals λ_j. Diagonalization of the corresponding *Fock* matrix $F_\lambda(1)$ yields the original CMOs, which are now expressed in terms of LMOs λ_j.

The regression of the observed band maxima positions I_j^m on the calculated STO-3G orbital energies ε_j (excluding the first few bands, the I_j^m values of which are difficult to assess because of the strong overlap of the *Jahn-Teller*-broadened bands) yields:

$$\left(\frac{I_j^m}{\mathrm{eV}}\right) = (1.905 \pm 1.223) + (0.821 \pm 0.071)\left(\frac{-\varepsilon_j^{\mathrm{STO\text{-}3G}}}{\mathrm{eV}}\right) \qquad (5)$$

with standard error $s(I_j^m) = 0.351$ eV and correlation coefficient $r = 0.989$. This regression was used to calibrate the self energies A_μ and the cross-terms $F_{\mu\nu}$ according to *(20)* in [1].

To estimate the self energy shifts δA_μ caused by halogen substitution in positions 1 and 4 of **1**, sample STO-3G calculations with subsequent localization were carried out for an isobutane and a *t*-BuCl model in both of which the C–C–C bond angles had been fixed at a value of 90°, as in cubane, and where the cubane bond lengths ($R_{CC} = 156.1$ pm, $R_{CH} = 108.1$ pm) had been assumed. Comparison of the self energies A_{CC} and A_{CH} of these model compounds yields $\delta A_{CC} = -1.17$ eV and $\delta A_{CH} = -0.6$ eV.

Whereas the self-energy shifts due to Cl substitution can be derived with help of *ab initio* calculations, the shifts δA_{CC} and δA_{CH} due to substitution by Br or I are based on somewhat arbitrary assumptions. Choosing $\delta A_{CC} = -0.8$ eV and $\delta A_{CH} = -0.45$ eV for Br substitution and $\delta A_{CC} = \delta A_{CH} = 0$ for I substitution (as proposed in [1]) leads to a consistent interpretation of the PE spectra of compounds **2**–**4**.

4. Assignment of the PE Spectra.

– Substitution of positions 1 and 4 of **1** by halogen atoms X reduces the symmetry from O_h to D_{3d}. As a result the triply degenerate, irreducible representations of the group O_h decompose as follows: $T_{2g} \rightarrow E_g + A_{1g}$; $T_{1g} \rightarrow E_g + A_{2g}$; $T_{2u} \rightarrow E_u + A_{1u}$; $T_{1u} \rightarrow E_u + A_{2u}$. The PCMOs of the cubane moiety shown in *Fig. 2 (A)* have been labeled accordingly. For reasons of symmetry only the PCMOs of type e_g or e_u are available for hyperconjugative interaction with the symmetry-adapted linear combinations of the halogen lone-pair orbitals of type np, whereas the PCMOs of type a_{1g} or a_{2u} can interact with the in-phase or out-of-phase combination of the LMOs λ_{CX}, respectively. On the other hand, the PCMO $1a_{1u}$ will not interact with any of the above, halogen-centered orbitals. The PCMO sequence depicted in *Fig. 2*

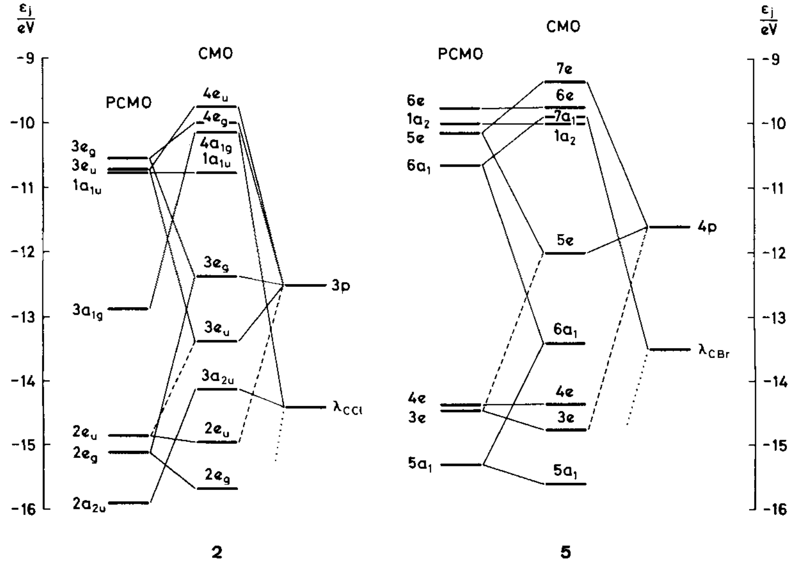

Fig. 3. *Orbital correlation diagrams for* **2** *and* **5**. PCMO = precanonical orbitals of the cubane moieties of **2** and **5**; 3p = lone-pair orbitals of the pair of Cl atoms in **2**; 4p = lone-pair orbitals of the Br-atom in **5**; λ_{CCl} and λ_{CBr} = LMOs of the C–Cl σ-bonds in **2** and of the C–Br σ-bond in **5**.

(A) is valid for all three compounds **2**–**4**, irrespective of small differences in the absolute orbital energies due to the LMO basis shifts discussed above. Furthermore, the qualitative sequence of the CMOs derived from the EBO model is again the same for **2**–**4**, as can be seen from *Table 2*. It is, therefore, sufficient to present only a single example of an interaction diagram, *e.g.* that for 1,4-dichlorocubane **2** in *Fig. 3*, which also shows the analogous diagram for 1-bromocubane (**5**), both of which are selfexplanatory.

With reference to *Table 2* and *Fig. 3* the PE spectra of **2**–**4** are rationalized as follows:

Bands ① and ②, which strongly overlap in the spectra of **2** and **3**, are assigned to the ionization processes $4e_u^{-1}$, $4e_g^{-1}$ and $4a_{1g}^{-1}$. Since these orbitals fall into a narrow energy range of ~ 0.6 eV, the predicted orbital sequence is necessarily uncertain. As indicated in *Table 2* the orbitals $4e_g$ and $4e_u$ exhibit large contributions from the halogen lone-pair orbitals, which increase in the series **2**→**3**→**4** as expected from respective lone-pair basis energies. For the same reasons the orbitals $4a_{1g}$ show increasing contribution from the λ_{CX}-orbitals along the series **2**→**3**→**4**.

Band ③ corresponds to the ejection of an electron from the orbital $1a_{1u}$. The symmetry-conditioned localization of this orbital on six bonds of the CC frame, as shown in *Fig. 2*, leads to a fairly sharp band, clearly visible in the case of **3** and **4**. Due to its localization on six symmetry-equivalent bonds, the orbital energy of $1a_{1u}$ and thus the corresponding ionization energy depend on the self-energy of these bonds, assuming the geminal and vicinal cross-terms to be constant. Therefore, the experimental ionization energy of the $1a_{1u}^{-1}$ band is a good test for the postulated self-energy shifts δA_μ with which the orbitals λ_μ corresponding to these bonds are affected, due to the presence of the halogen atoms.

Bands ④ and ⑤ are due to electron ejection from the orbitals $3e_g$ and $3e_u$, respectively, which are mainly localized at the halogen atoms. Accordingly $3e_g$ and $3e_u$ are those CMOs which can be considered as the 'lone-pair orbitals' of the compounds **2**–**4**. (See comment below.) As is evident from the correlation diagram of *Fig. 3*, the higher of the 'lone-pair' CMOs, $3e_g$, is the resultant of the competitive interaction between the out-of-phase combination of np AOs of the halogen atoms with, on the one hand, the higher lying PCMO $3e_g$ and, on the other, the lower-lying PCMO $2e_g$. The former interaction leads, according to (*4*) to a stabilization ($\delta\varepsilon(3e_g) < 0$) the latter to a destabilization ($\delta\varepsilon(3e_g) > 0$). The same situation prevails with respect to the in-phase linear combination of the halogen np atomic orbitals and the odd PCMOs $3e_u$ and $2e_u$ *(cf. Fig. 3)*. The reason for the resulting CMOs $3e_g$ of **2**–**4** to lie above the respective CMOs $3e_u$ is mainly that the coefficients of the C–C bond LMOs geminal to the C–X bonds (*i.e.* those of importance for hyperconjugation) are rather small in the PCMOs labeled $2e_u$, so that the resulting destabilization of the final CMO $3e_u$ is much smaller than the destabilization of $3e_g$.

Band ⑥, which is well detached in the PE spectra of **3** and **4**, is assigned to the ionization process $3a_{2u}^{-1}$. The vacated orbital is almost completely localized on the C–X bonds, as is evident from the data in *Table 2*.

The ejection of electrons from lower-lying orbitals gives rise to broad overlapping bands, which prevents an accurate correlation between calculated and experimental ionization energies.

The proposed assignment of the PE spectrum of **5** follows from the right-hand diagram of *Fig. 3* and the last entries in *Table 2*. The highest CMO 7e of **5** results from a destabilization of the PCMO 5e the Br 4p-orbitals, the contribution of the latter being ~27%. The CMO 6e is essentially the PCMO 6e, almost entirely located in the cubane moiety, because of the very small values of the LMO coefficients of the C–C bonds emanating from position 1. The PCMO $1a_2$ which corresponds to the PCMO $1a_{1u}$ of the cubane moiety of the 1,4-dihalocubanes, can not interact with any of the Br orbitals. The CMO $7a_1$ of **5** is due to interaction between the PCMO $6a_1$ and the two λ_{CX}, the percentage contribution of the latter being ~20%. Ejection of electrons from these orbitals leads to the broad-band system containing the strongly overlapping bands ①, ② and ③. It is obvious that the relative order of these bands which range, from 9.3 eV to 10.5 eV, could well be different, depending on small changes in the parameters. This leads to the conservative statement that the band system in this region is due to the ionization processes $7e^{-1}$, $6e^{-1}$, $7a_1^{-1}$ and $1a_2^{-1}$, not necessarily in this order.

Band ④ is due to $5e^{-1}$, *i.e.* to ejection from an orbital which is mainly located at the Br- atom, the contribution from its 4p orbital being ~61%.

Band ⑤ is assigned to $6a_1^{-1}$, this orbital showing considerable contribution (57%) from λ_{CX}.

Bands ⑥ and ⑦ with $I_6^m = 14.4$ eV and $I_7^m = 15.75$ eV are due to electron ejection from 4e, 3e, and $5a_1$, respectively, all of which are mainly localized in the cubane moiety.

5. Discussion. – The discussion relies on the data summarized in the *Figs. 4–6*, which contain the following information:

a) The top diagram is a schematic representation of the PE spectrum of cubane (**1**) [8] and of its assignment. Note that the orbital sequence $3t_{2g}$, $1t_{2u}$ is uncertain.

b) In the schematic representations of the PE spectra of the derivatives **2**–**4** *(cf. Fig. 1)*, the positions of those bands which are the (dominantly) lone-pair bands are indicated by vertical bars at positions I_j^m corresponding to the band maxima. For the remaining bands only the outline of their *Franck-Condon* envelopes is indicated, except for **4** where this envelope encompasses also the lone-pair bands, which are overlapped and partly obliterated by the bands due to electron ejection from the orbitals centered on the cubane moiety.

c) This part of the diagram shows the position I_j^m of the lone-pair bands of the halides RX (R = H, Me, Et, i-Pr, *t*-Bu; X = Cl, Br, I [13]). These values are corrected for spin-orbit coupling, being the mean of the two band positions corresponding to the states $^2E_{3/2}$ and $^2E_{1/2}$ of the radical cation RX^+, *i.e.* $I_j^m = (I_1^m(^2E_{3/2}) + I_1^m(^2E_{1/2}))/2$. Strictly speaking this formula implies that R = H (where the states should be labeled $^2\Pi_{3/2}$, $^2\Pi_{1/2}$), Me or *t*-Bu, but it can also be used without significant error if RX does not possess an axis of order 3, *e.g.* for R = Et or i-Pr [11]. For R = H and Me the band positions marked σ are those of the bands due to electron ejection from the highest occupied axially symmetric orbital of RX.

d) The energies of the basis orbitals np of X = Cl (n = 3), Br (n = 4) and I (n = 5) have been derived from the ionization energies of the free atoms X [14]: I(Cl) = 13.01 eV, I(Br) = 11.84 eV, I(I) = 10.45 eV (for $X(^2P_{3/2}) \rightarrow X^+(^3P_2) + e^-$). These are the values used in *Figs. 4–6*. (Another set of basis energies would have been the ones corresponding to the valence state ionization energies $I_{v.st} = (3/4)E(^3P) + (1/4)E(^1D)$ with spin-orbit coupling averaged to zero [15]. These values are ~0.4 eV larger than those given above.)

e) For comparison the positions of the π bands in the PE spectra of the dihaloacetylenes XC≡CX [16] and the haloacetylenes XC≡CH [17] are given, together with the basis orbital energies of the triple bond π orbitals and of the halogen np orbitals derived from them [18].

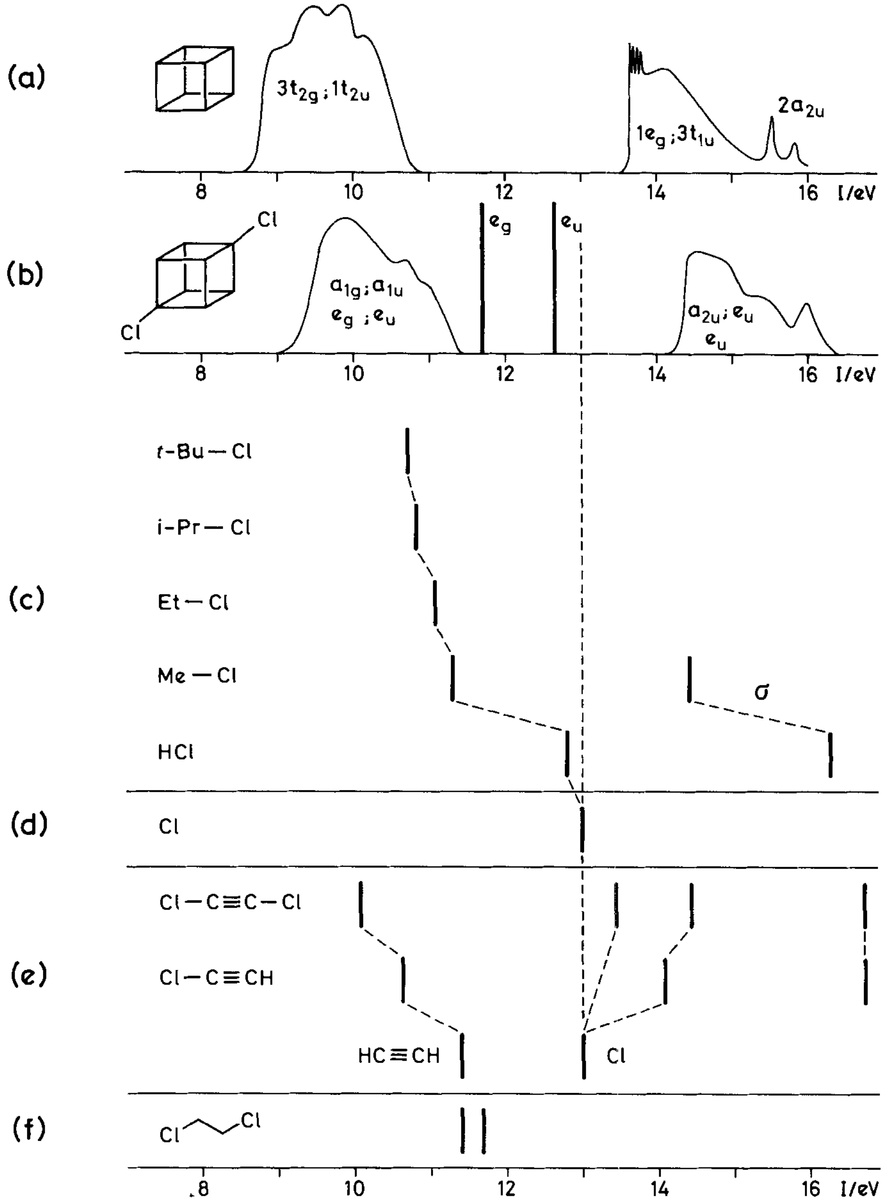

Fig. 4. *Cl lone-pair band-correlation diagram.* For comments on (*a*) to (*f*), see text.

f) Finally the positions of the lone-pair bands in the PE spectra of the 1,2-dihaloethanes $XH_2C{-}CH_2X$ with X = Cl and Br are presented [13].

If the CMOs of acetylenes, *e.g.* of dihaloacetylenes or haloacetylenes are subjected to a localization procedure, one obtains for each triple bond three banana LMOs which are symmetry-equivalent with respect to a C_3 axis through the C-atoms. Consequently, the local situation with respect to a halogen atom attached to the triple bond

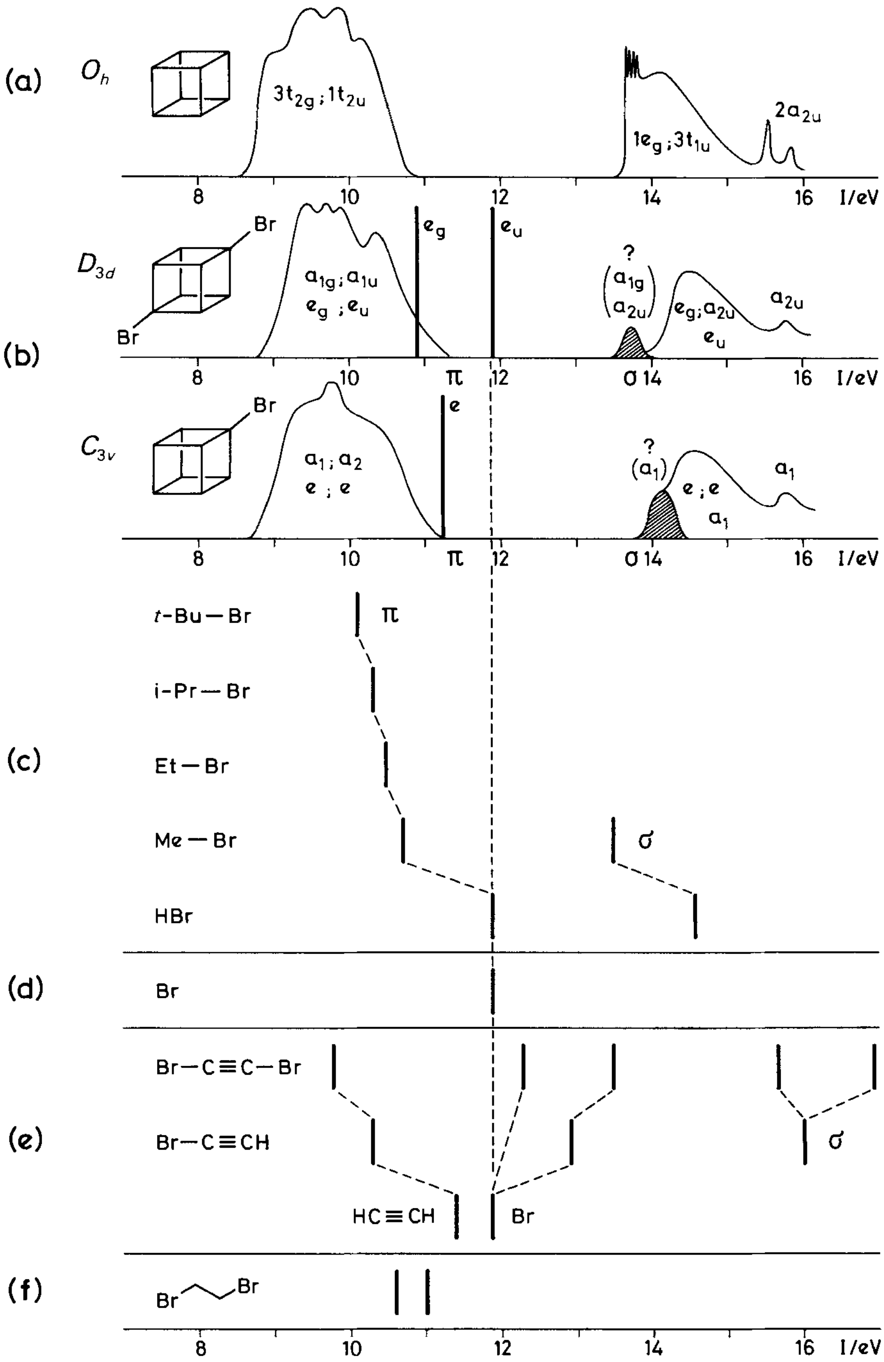

Fig. 5. *Br lone-pair band-correlation diagram.* For comments on (*a*) to (*f*), see text.

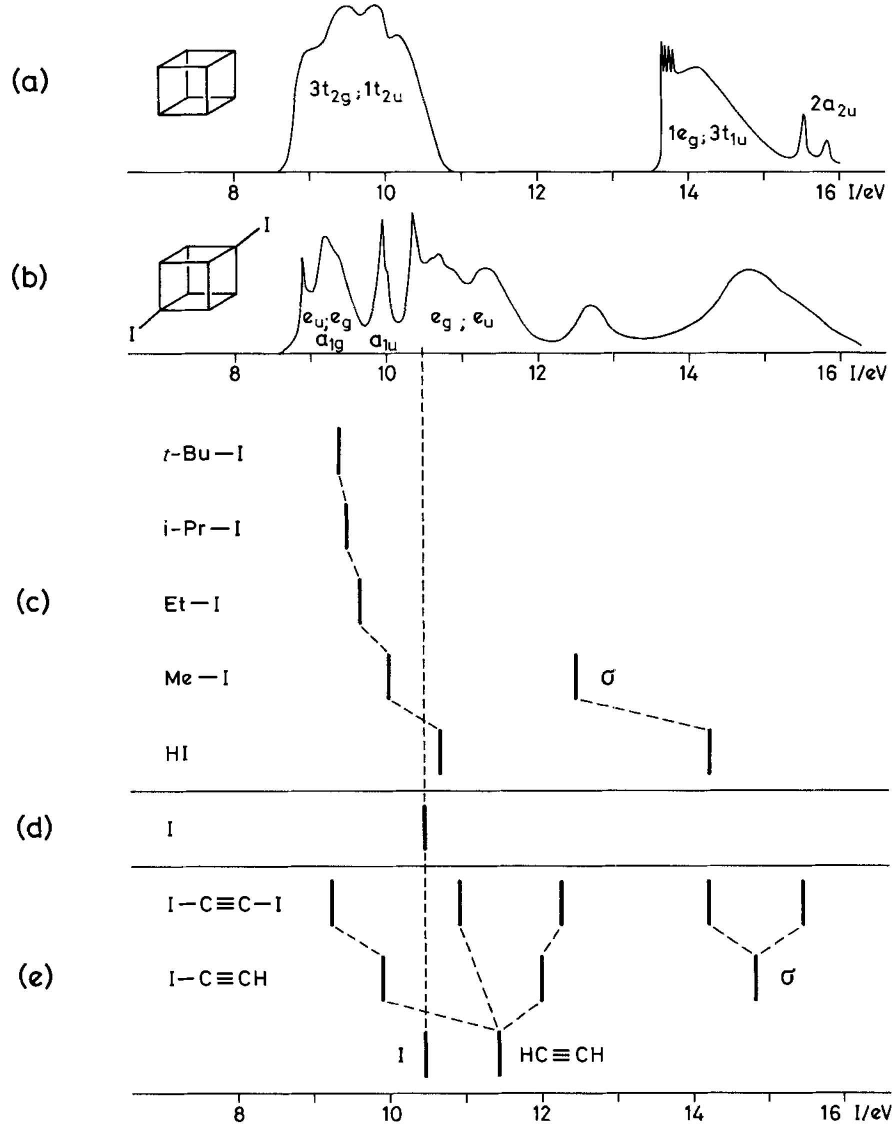

Fig. 6. *I lone-pair band-correlation diagram.* For comments on (*a*) to (*e*), see text.

is not very different from that prevailing in an alkyl halide RX and it is therefore not surprising that the np basis orbital energies are not much different. In fact they are almost the same as those obtained for the free atoms *(cf. c, d, e)* of *Figs. 4–6*. From this we tend to conclude that the same np basis energies are still valid for the compounds **2–5**, so that the positions of the (dominantly) lone-pair bands in their PE spectra have to be compared to these values, indicated in *Figs. 4–6* by a vertical dashed line.

In the case of the compounds **2**, **3** and **5** where the 3p or 4p basis energies fall into the wide gap between the two σ-orbital energy manifolds of the cubane moiety, it is immediately obvious that the shifts $\delta I_{\mathrm{X},4}$ and $\delta I_{\mathrm{X},5}$ (as defined in *(1)*) are much smaller than those observed for the usual alkyl halides RX notwithstanding the fact that the alkyl moiety is now twice as big (C_8H_6 or C_8H_7) as a *t*-Bu group:

	Me	Et	i-Pr	*t*-Bu	
$-\delta I_{\mathrm{Cl},1}(\mathrm{R})/\mathrm{eV}$	1.51	1.74	1.99	2.11	
$-\delta I_{\mathrm{Br},1}(\mathrm{R})/\mathrm{eV}$	1.18	1.42	1.60	1.77	(6)

2 $-\delta I_{\mathrm{Cl},4} = 1.1_5$ eV; $-\delta I_{\mathrm{Cl},5} = 0.1_5$ eV

3 $-\delta I_{\mathrm{Br},4} = 0.9_0$ eV; $-\delta I_{\mathrm{Br},5} = 0.0$ eV

The reason is rather obvious. The symmetry adapted linear combinations e_g(np), and e_u(np) of the lone-pair basis orbitals of the halogen atoms in **2** and **3** interact mainly with the PCMOs of the cubane moiety which are situated above the np in energy ($\varepsilon(3e_g)$, $\varepsilon(3e_u) > \varepsilon(\mathrm{np})$) and those which are immediately below ($\varepsilon(2e_g)$, $\varepsilon(2e_u) < \varepsilon(\mathrm{np})$) *(Fig. 3)*. Consequently, the leading terms of the right-hand sum of *(4)* are of opposite sign with the consequence that *e.g.* $\delta\varepsilon_5^{\mathrm{hyp}}$ becomes almost zero. In other words, hyperconjugation with the higher-lying σ-orbitals ('inverted hyperconjugation') leads to a depression of the resultant orbital energy and thus to a very small shift $\delta I_{\mathrm{X},j}$, as compared to the naive extrapolation based on the traditional shifts observed for the usual alkyl halides RX.

Of course, this result is neither unexpected nor novel. It occurs in all cases where the lone-pair basis energies are embedded into the energy manifold of the alkyl group to which X is attached. What is new is that the effect can be easily observed in the PE spectra of the compounds presented in this contribution because of the particular structure of the cubane σ-manifold with its large, orbital-free energy gap extending from ~ -10.5 eV to ~ -13.5 eV. Because of this, the lone-pair bands can be recognized and located, which is by no means the case if they are part of a densly populated σ-band system, as is usually the case for other, large alkyl moieties.

This particular difficulty is nicely illustrated by the PE spectroscopic results for **4**, summarized in *Fig. 6*. Here the 5p basis energy of the I atom lone-pairs is -10.45 eV and matches, therefore, closely the orbital energies of the cubane $3t_{2g}$ and $1t_{2u}$ orbitals. As a consequence it becomes much more difficult to recognize those bands in the PE spectrum which should correspond to electron ejection from the lone-pair dominated MOs. In this respect, the computed results given in *Table 2* for **4** are rather instructive. They draw attention to the complicated orbital structure underlying a band system *(cf. Fig. 1)* which at first sight seemed to be easy to deconvolute. Notwithstanding the fact that the assignment looks reasonable, a closer examination raises some doubts about its validity. The low intensity of band ① suggests strongly that it can correspond only to the $^24E_{u,3/2}$ state of $\mathbf{4}^+$, whereas the $^24E_{u,1/2}$ band must be part of ②. This means that our model underestimates the size of the split, due to spin-orbit coupling, affecting the ^24E_u state. On the other hand, the split of the ^24E_g state may well be a bit smaller than computed. Furthermore, the relatively sharp structure of bands ① and ② suggests a higher 5p character of the corresponding CMOs than that derived from our model. In contrast, the broadened appearance of bands following ④ and terminating with ⑤ points to a considerable mixing of the iodine 5p basis orbitals with the PCMOs of the cubane moiety. In principle both observations could be accounted for by a negative shift of the 5p basis orbital energies, but this seems rather unlikely in view of previous experience. For these reasons the proposed assignment is, at best, tentative.

6. Conclusions. – *Fig. 7* summarizes our conclusions, which are based on the results obtained for **2**, **3** and **5**, the molecule **4** being obviously a special case, as discussed above. We add the following remarks:

1) Due to the unique orbital structure of the cubane system and thus of the PE spectrum of **1**, it is possible to observe the positions I_j^m of the 'uncontaminated' lone pair bands of **2**, **3** and **5**. As was to be expected, they deviate much less (or even not significantly) fom the ionization energies of the free atoms Cl or Br, or of the molecules HCl or HBr, than in the case of the usual alkyl halides RCl or RBr, due to the fact that the 3p or 4p AOs of the halogen atoms hyperconjugate with σ-orbitals (PCMOs) of the cubane moiety which lie above as well as below in energy.

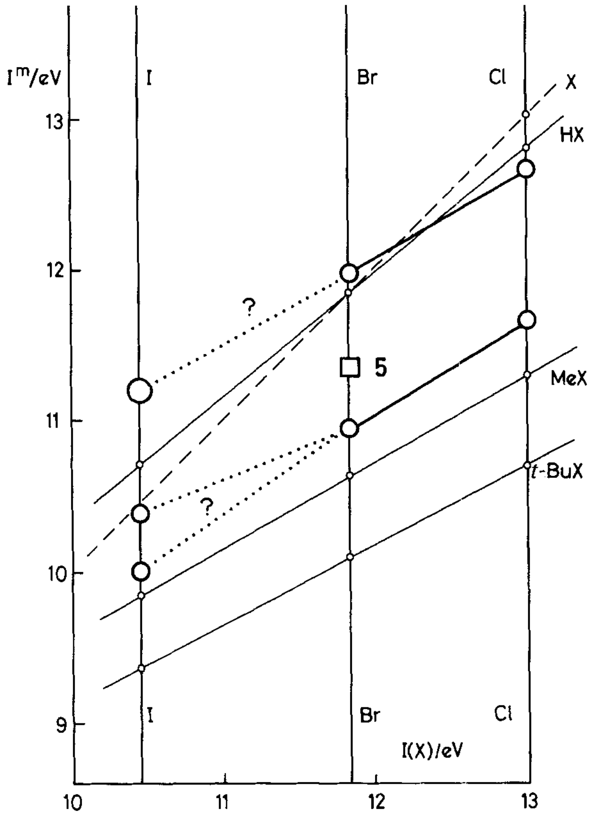

Fig. 7. *Regression of observed halogen lone-pair band positions* I^m *on the ionization energies* I(X) *of the free halogen atoms.* The thin broken line labeled X has slope unity. The thin regression lines refer to the hydrogen halides (HX), methyl halides (MeX) and *t*-butyl halides (*t*-BuX). The open circles correspond to the lone-pair band positions in the PE spectra of **2**–**4**. In the latter case, these positions are open to question (*cf.* text). The square dot labeled **5** corresponds to the Br lone-pair band position in the PE spectrum of **5**.

2) In the case of **5** the observed 'lone-pair' ionization energy $I_4^m = 11.3_5$ eV (square dot in *Fig. 7*) is the largest one observed in alkyl bromides RBr, *e.g.* I_1^m(MeBr) $= 10.7_0$ eV, I_1^m(*t*-BuBr) $= 10.1_0$ eV, I_1^m(cyclohexylbromide) $= 10.0_0$ eV, (1-bromobicyclo[2.2.2]-octane) $= 9.9_5$ eV (all corrected for spin-orbit coupling).

3) For **2** and **3** (open circles in *Fig. 7*) the size of the hyperconjugation induced shift (*cf.* (*4*)) depends critically on the symmetry of the linear combination of the lone-pair AOs, which exemplifies what has been said in the introduction. Thus the shift incured by the e_u combination is roughly zero whereas the e_g combination is shifted by $\sim$ 1 eV (*cf.* (*6*)). In the former case, the shift contributions (*4*) due to 'inverted hyperconjugation' with σ-orbitals higher in energy than the halogen np basis orbital combination cancel almost exactly those due to 'normal' hyperconjugation with the orbitals below. In the second case, 'normal' hyperconjugation dominates, but its effect is drastically reduced by the interaction with the σ-orbitals lying above the lone-pair basis orbitals. Let us mention again that this result is in no way surprising or unexpected, and that the only novelty is the ease with which it can be observed in the PE spectra of the compounds **2**, **3** and **5**.

4) Finally, a word of caution seems to be in order. All theoretical calculations for alkyl halides RX, whether they have been carried out using an EBO model or more sophisticated models, suggest that the mixing between the halogen lone-pair AOs np and the alkyl group orbitals $\Phi_r(R)$ of proper symmetry is considerable. In fact, it is larger than one would expect on the basis of the observed *Franck-Condon* envelopes of the lone-pair bands in the PE spectra of RX (*cf.* [13]), and also of the observed splittings due to spin-orbit coupling. This strongly suggests that the above treatment of the alkyl group induced shifts $\delta I_{X_J}(R)$ (*cf.* (*1*)) is incomplete and in need of improvement.

Experimental. – *General.* Melting points were measured on a *Büchi 510* instrument and are uncorrected. IR spectra were measured on a *Perkin Elmer 297*. Characteristic absorption maxima are given in cm^{-1}. 60-MHz ^{1}H-NMR spectra ($CDCl_3$) were recorded on a *Varian EM 360 A* instrument; chemical shifts are given in ppm downfield from TMS (= 0 ppm) as an internal standard. Mass spectra (MS) were performed on a *Varian MAT-CH5* instrument at 70 eV ionization electron energy, source temperature 250°, inlet temp. r.t.; the most important ions are listed as *m/z* values with relative intensities (% of basepeak) in parenthesis. Elementary analyses were measured at the facilities of the *Department of Pharmacy, University of Düsseldorf, Düsseldorf.*

1-Bromocubane (**5**) and *1,4-dibromocubane* (**3**) were prepared according to methods previously described by *Eaton* and *Cole* [19], *Chapman et al.* [20] and *Della* and *Patney* [21] with essential modifications to obtain higher yields. *1,4-Dichlorocubane* (**2**) and *1,4-diiodocubane* (**4**) were obtained from **3** by a halogen exchange reaction in analogy to a method described in [22].

1,4-Dichloropentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane (1,4-dichlorocubane; **2**). Alumina foil (160 mg, 5.9 mmol) and Br_2 (320 mg, 2.0 mmol) in 20 ml $CHCl_3$ were refluxed for 10 min. Then, 200 mg (0.8 mmol) **3** in 20 ml $CHCl_3$ were added in one portion and stirred for another 10 min. After cooling to r.t., the mixture was washed with aq. $NaHCO_3$ and H_2O. The $CHCl_3$-phase was dried ($MgSO_4$), evaporated to dryness, and the crude product purified by sublimation (60°/15 mm) and recrystallization from hexane to give 86 mg (65%) of **2**. M.p. 157–158°. IR (KBr): 3010*w*, 3000*m*, 1311*w*, 1270*s*, 1265*s*, 1252*s*, 1238*s*, 1224*s*, 1192*s*, 1085*w*, 1052*s*, 994*s*, 900*s*, 835*s*, 824*s*. ^{1}H-NMR: 4.15 (*s*, 6H). ^{13}C-NMR: 52.3 (*d*, ^1J(C,H) = 164.9, C(2), C(3), C(5), C(6), C(7), C(8)); 72.8 (*s*, C(1), C(4)). MS: 173 (1) 171 (3), 148 (7), 146 (13), 139 (15), 138 (16), 137 (45), 136 (38), 114 (27), 113 (13), 112 (57),111 (22), 103 (35), 102 (100), 101 (65), 99 (12), 86 (12), 85 (11), 77 (56), 76 (33), 75 (59), 74 (42), 73 (38), 63 (28), 62 (23), 61 (14), 60 (13), 52 (15), 51 (63), 50 (59), 49 (15). Anal. calc. for $C_8H_6Cl_2$ (173.04): C 55.53, H 3.50; found: C 55.18, H 3.44.

1,4-Dibromopentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane (1,4-dibromocubane; **3**). ^{13}C-NMR: 54.4 (*d*, ^1J(C,H) = 165.8, C(2), C(3), C(5), C(6), C(7), C(8)); 63.5 (*s*, C(1), C(4)).

1,4-Diiodopentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane (1,4-diiodocubane; **4***).* Compound **4** was prepared in analogy to **2**. Conditions were changed to CH_2Cl_2 as a solvent and a reaction time of 30 min at 80°. Sublimation (100°/0.01 mm) and recrystallization from hexane gave 120 mg (44%) of **4**. M.p. 226–227° (dec.). IR (KBr): 3000*w*, 2990*w*, 1228*s*, 1195*w*, 1190*s*, 1090*w*, 1085*m*, 1045*m*, 1035*m*, 1018*s*, 970*w*, 880*m*, 862*w*, 845*w*, 832*w*, 825*w*. ^{1}H-NMR: 4.45 (*s*, 6H). ^{13}C-NMR: 57.3 (*d*, ^1J(C,H) = 165.4, C(2), C(3), C(5), C(6), C(7), C(8)); 35.6 (*s*, C(1), C(4)). MS: 355(1), 228 (3), 204 (34), 103 (45), 102 (100), 101 (18), 77 (48), 52 (34), 51 (45), 50 (52). Anal. calc. for $C_8H_6I_2$ (355.95): C 26.97, H 1.69; found: C 26.87, H 1.69.

1-Bromopentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane (1-bromocubane; **5***).* ^{13}C-NMR: 45.8 (*d*, ^1J(C,H) = 161.0, C(3), C(5), C(7)); 48.0 (*d*, ^1J(C,H) = 160.0, C(4)); 57.5 (*d*, ^1J(C,H) = 161.0, C(2), C(6), C(8)); 64.4 (*s*, C(1)).

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