The Photoelectron Spectra of Some 1-Halogenobicycloalkanes

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The He photoelectron spectra of the 1-bromo- and 1-iodo-substituted bicyclo[2.2.2]octane, bicyclo[2.2.1]heptane, and bicyclo[2.1.1]hexane have been measured. Comparisons are made with the spectra of the corresponding alkanes, and assignments are derived with the assistance of He$^{\mathrm{II}}$ measurements and *ab initio* molecular orbital calculations based on a valence-electron model-potential method. The low-ionization-energy region of the spectra reveals interesting variations in the competition of spin–orbit coupling and conjugative effects which operate for ionizations involving the halogen lone-pair orbitals.

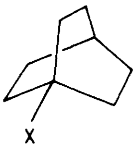
The study of alkyl halides by He$^{\mathrm{I}}$ photoelectron (p.e.) spectroscopy has been confined mainly to the smaller acyclic systems up to and including the isomers of the butyl halides.[1-7] Among the monocyclic alkyl halides, cyclopropyl and cyclobutyl bromides have been included in a study of the competition between spin–orbit coupling and conjugation effects.[1] Among the polycyclic alkyl halides, only 1-bromoadamantane has been investigated.[8]

The He$^{\mathrm{I}}$ p.e. spectra of alkyl halides (excluding alkyl fluorides) are characterised by two main features. First, the low-ionization-energy (I.E.) bands, attributed to the photoejection of electrons from molecular orbitals (MOs) localized on the halogen atom, normally feature an intense doublet caused by spin–orbit (SO) coupling effects in the molecular ions. The magnitude of the splitting and the variation in sharpness of these bands provides a measure of the interaction between halogen and alkane orbitals. The admixture of alkane character in these orbitals can be shown by a He$^{\mathrm{I}}$–He$^{\mathrm{II}}$ relative intensity analysis when He$^{\mathrm{II}}$ p.e. data are available.

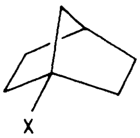
Second, the comparison of the p.e. spectrum of an alkyl halide with that of its parent alkane normally shows the simple stabilizing effect of halogen substitution in increasing the alkane I.E.s, with, for example, bromine producing larger I.E. shifts than iodine due to its higher electronegativity.

This basic description, which is generally accurate for the acyclic bromo- and iodo-alkanes, is varied in the case of many cyclic alkyl halides. In cyclopropyl bromide, the lone pair band at lower I.E. is considerably broadened through conjugative interaction with cyclopropyl orbitals, and its separation from the sharp second band is somewhat greater than that expected by SO coupling effects alone. In 1-bromoadamantane,[8] the characteristic SO doublet is lost, caused by a strong interaction of halogen and alkane orbitals which are proximate in energy. So in large polycyclic alkanes, particularly where ring strain leads to low I.E. bands in the p.e. spectra, such interactions are likely to be common.

The bromo- and iodo-bicycloalkanes included in this study are 1-bromobicyclo[2.2.2]octane (**1b**), 1-iodobicyclo[2.2.2]octane (**1c**), 1-bromobicyclo[2.2.1]heptane (**2b**), 1-iodobicyclo[2.2.1]heptane (**2c**), 1-bromobicyclo[2.1.1]hexane (**3b**), and 1-iodobicyclo[2.1.1]hexane (**3c**). Relevant p.e. studies of the parent alkanes, bicyclo[2.2.2]octane (**1a**)[9,10] bicyclo[2.2.1]heptane (**2a**),[9,10] and bicyclo[2.1.1]hexane (**3a**)[11] have been reported.



(1)



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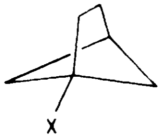

(3)

a; X = H
b; X = Br
c; X = I

Experimental

The six compounds studied were prepared by a variety of techniques, but most commonly by decarboxylative halogenation of the bridgehead carboxylic acids,[12,13] The p.e. spectra were measured on a double-chamber instrument[14] at room temperature with appropriate mixtures of methyl iodide, buta-1,3-diene, acetylene, and nitrogen used for calibration of the I.E. scale. Both He$^{\mathrm{I}}$ and He$^{\mathrm{II}}$ spectra were obtained. The 1 h time-averaged 512 point He$^{\mathrm{I}}$ spectra are shown in Figures 1, 3, and 4 and single-sweep He$^{\mathrm{II}}$ spectra of (**1b**) and (**1c**) are included in Figure 2.

Calculations

In order to assess the effect of halogen substitution on the electronic structure of the parent alkanes, molecular orbital (MO) calculations were performed on each alkane and its bromo- and iodo-derivative. All-electron *ab initio* MO programs do not routinely accommodate molecules containing bromine or iodine, so the valence-electron-only model-potential (VEOMP) MO method[15,16] was used. This *ab initio* method, which is specially designed for calculations on molecules containing heavy atoms, is based on the all-electron GAUSSIAN 70 program[17] and uses a minimum-valence STO-3G basis. The method is non-empirical and involves a valence-electron Hamiltonian including a core-pseudopotential and screening function. It is able to produce orbital energies and equilibrium geometries in good agreement with the corresponding all-electron calculations, in particular for small molecules of first-,[15] second-,[16] and third-row[18] atoms. The minimum basis

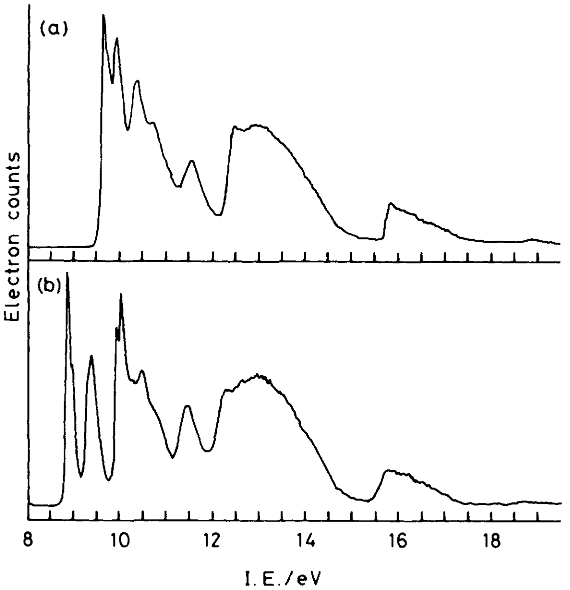

Figure 1. Time-averaged He^{I} photoelectron spectra of (a) 1-bromobicyclo[2.2.2]octane and (b) 1-iodobicyclo[2.2.2]octane

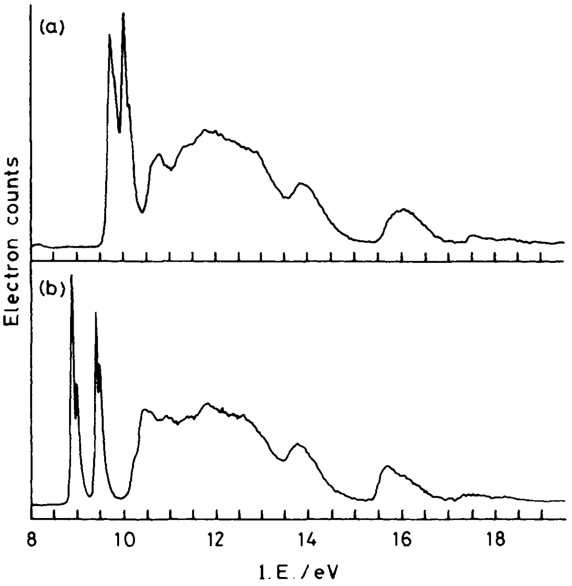

Figure 3. Time-averaged He^{I} photoelectron spectra of (a) 1-bromobicyclo[2.2.1]heptane and (b) 1-iodobicyclo[2.2.1]heptane

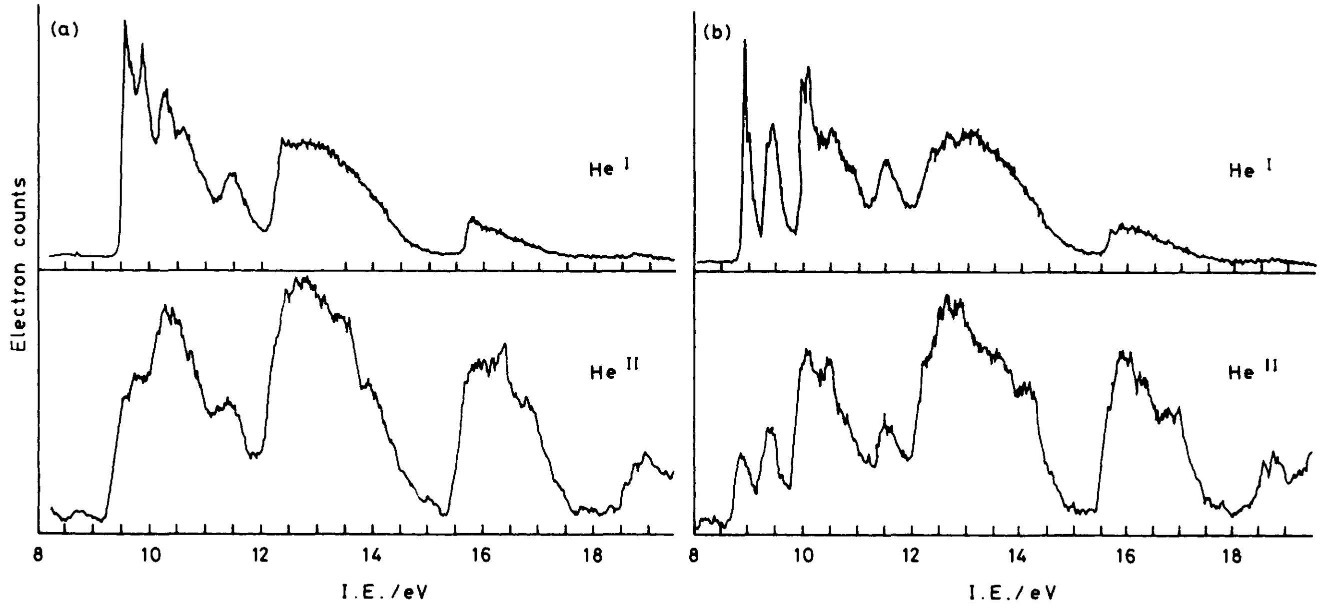

Figure 2. Comparisons of single-sweep He^{I} and He^{II} photoelectron spectra of (a) 1-bromobicyclo[2.2.2]octane and (b) 1-iodobicyclo[2.2.2]octane

sets for Br and I were extended to bring the relative energies of alkane and halogen orbitals into better correspondence when the Koopmans' approximation is used with experimental I.E.s. The minimum STO-3G basis performs less adequately for halogen atoms than for hydrocarbons, but additional valence *ns* and *np* functions, each of exponent 1.0, are sufficient to provide an acceptable stabilization of the halogen valence orbitals.

While a MO calculation of each ground-state molecule is able to represent the conjugative interaction between halogen and alkane orbitals, the effects of spin–orbit coupling can be approximated by performing a semi-empirical calculation using the relevant atomic splitting parameters with the self-consistent closed-shell wavefunction. This procedure,[19] where the molecular Hamiltonian is amended with a one-electron spin–orbit interaction operator, simulates the relevant ion states *via* the Koopmans' approximation. Because it includes both first- and second-order contributions, it is useful in deriving SO shifts for the I.E.s of molecules of lower than three-fold symmetry. So while the 1-halogenobicyclo[2.2.2]octanes (of C_{3v} symmetry) are expected to show splitting in their halogen bands based mainly on spin–orbit effects, the splittings in the 1-halogenobicyclo[2.2.1]heptanes and 1-halogenobicyclo-[2.1.1]hexanes (of C_s symmetry) are expected additionally to include some conjugative effects.

Of the molecules studied only bicyclo[2.2.1]heptane has a reliable experimental geometry,[20] and this was used in the MO calculations. For bicyclo[2.2.2]octane, an unstrained geometry of D_{3h} symmetry, based on standard bond lengths and

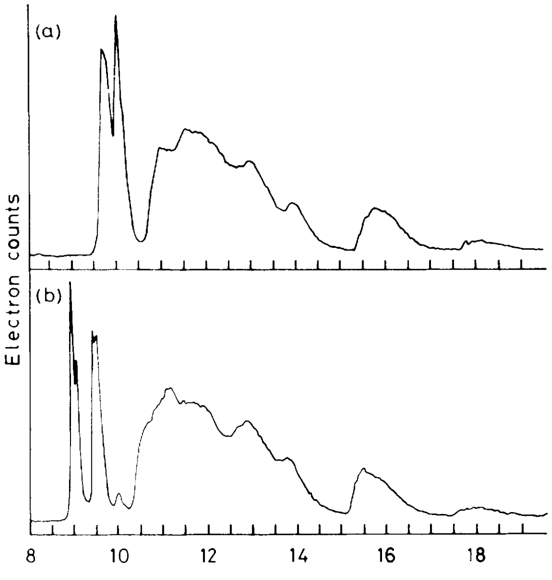

Figure 4. Time-averaged He^I photoelectron spectra of (a) 1-bromobicyclo[2.1.1]hexane and (b) 1-iodobicyclo[2.1.1]hexane

tetrahedral angles, was used. However, while bicyclo[2.1.1]hexane has an experimental geometry,[21] there is doubt concerning its accuracy,[22] as this differs considerably from the theoretical geometry. We have recently shown[11] that the theoretical geometry produces an eigenvalue distribution which is more consistent with the valence photoelectron spectrum. Consequently, the optimized geometry (STO-3G basis) was used in calculations. For the bromo- and iodo-cycloalkanes standard bond lengths were used for C–Br (1.94 Å) and C–I (2.14 Å) bonds.

Discussion

The assignment of each He^I photoelectron spectrum is illustrated by reference to the calculated molecular orbitals and their eigenvalues.

1-*Bromo- and* 1-*Iodo-bicyclo*[2.2.2]*octane*.—The experimental I.E.s of the halogenobicyclo[2.2.2]octanes (**1b** and **c**) obtained from the time-averaged He^I spectra shown in Figure 1 are listed in Table 1, where they are compared with those of bicyclo[2.2.2]octane (**1a**).[9,10] Table 1 also includes the theoretical Koopmans' I.E.s based on the VEOMP calculations for the three molecules.

Because the first I.E. of (**1a**), at 9.7 eV, is close to that of its bromo-derivative (**1b**), at 9.67 eV, it is not surprising that the bromine lone-pair orbitals, n_{Br}, in (**1b**) are associated with bands which are broadened due to conjugative effects. By comparison the iodo-derivative (**1c**), with a first I.E. of 8.87 eV, has more obviously localized iodine lone-pair orbitals, n_I, involved in its first two bands. Of the bicycloalkanes considered here, (**1a**) has the lowest first I.E., so that (**1b** and **c**) show the greatest variation in their first and second bands from the common pattern observed for the acyclic alkyl halides. So the comparison of the single-sweep He^I and He^{II} spectra shown in Figure 2 offers a useful confirmation that in (**1b** and **c**) the first and second bands, which show the largest relative intensity decrease with decreased wavelength, are indeed mainly associated with halogen character.

However, it is also the case that the third band in each molecule also shows diminution under He^{II} conditions, suggesting its assignment to the carbon–halogen bonding orbital in each case.

The observed SO splitting in (**1b**) of 0.28 eV is similar to that of t-butyl bromide[1] (0.29 eV) and marginally reduced from the atomic SO coupling parameter of 0.31 eV,[23] while the value obtained by the VEOMP SO procedure is 0.22 eV. This theoretical value is mainly a reflection of the conjugative mixing calculated as resulting in 80% bromine character in the outermost MOs, 8e. However, it also shows a contribution of −0.02 eV arising from a second-order SO interaction with the $8a_1$ orbital since the first-order SO splitting of the 8e orbitals is calculated as 0.24 eV. A comparison of experimental and calculated splittings suggests that the calculation is overestimating the conjugative mixing of alkane orbitals in 8e, though it is possible that Jahn–Teller effects are also operating to result in the greater splitting observed.

The observed SO splitting in (**1c**) of 0.54 eV is likewise similar to that of t-butyl iodide[1] (0.56 eV), both being considerably reduced from the atomic value of 0.63 eV.[23] In this case the VEOMP-calculated splitting is 0.49 eV, being composed of a first-order contribution of 0.60 eV based on the 8e orbitals of 92% iodine character, and a second-order contribution of −0.11 eV arising from interaction with the $8a_1$ orbital of σ_{CI} character. While this second-order contribution is relatively large, the observed broadening of the second band in the spectrum of (**1c**) suggests that the $e_{\frac{1}{2}}$ component is showing interaction with the $e_{\frac{1}{2}}$ ion state arising from the $8a_1$ MO.

Considerable halogen contribution to the MO responsible for the third band in each spectrum is indicated by its intensity enhancement relative to the corresponding region of the p.e. spectrum of (**1a**).[9] These bands also undergo significant reduction in intensity with He^{II} radiation thereby confirming their halogen character. A vibrational spacing of 690 ± 70 cm^{-1} is observed on the (**1c**) band, in precise agreement with that measured for the first band and similar to the typical C–I stretching frequency.[24] On the basis of these observations the third band can reasonably be assigned to the C–X bonding orbital as predicted by the VEOMP results. The halogen contributions as calculated by VEOMP are 37% for (**1b**) and 53% for (**1c**). The (**1a**) MO involved in the C–X bond is the second uppermost occupied MO, $4a_1'$, which also contributes substantially to the bonding of the carbon bridges.

Substitution of a halogen atom at the bridgehead of (**1a**) has a fairly uniform electrostatic influence on the I.E.s of the alkane MOs. The higher electronegativity of bromine compared with iodine is demonstrated by the more significant inductive shifts it effects. This feature is clearly illustrated by the bands at 11.6 and 11.45 eV respectively in the (**1b** and **c**) spectra. The MO which is responsible for the related band in the (**1a**) spectrum is of a_1'' symmetry and possesses a node at each bridgehead site. Any shifts must then be attributed to the inductive effect of halogen substitution. The stabilizations exhibited by the (**1b** and **c**) spectra are 0.4 and 0.25 eV, respectively.

Those MOs of (**1a**) belonging to the a_1' and a_2'' symmetry species of the D_{3h} point group have the appropriate symmetry to interact with the halogen p orbital directed along the C–X bond. With the reduction of symmetry brought about by substitution these symmetry species transform to a_1 in the C_{3v} point group. It would be anticipated that resonance electron donation by the bromine and iodine atoms to these MOs would compete with their inductive stabilization. Of note is the σ_{CBr} MO derived from the symmetric bridgehead σ_{CH} MO of (**1a**). The I.E. of this MO is only slightly increased from the alkane value of 10.2 eV while the σ_{CI} MO is shifted to lower I.E. by 0.2 eV.

The VEOMP results predict a similar effect on the remaining a_1 MOs. Consequently the antisymmetric combination of

Table 1. Comparison of experimental and calculated vertical ionization energies (in eV) and molecular orbital assignments of bicyclo[2.2.2]octane (**1a**) (D_{3h}), 1-bromobicyclo[2.2.2]octane (**1b**) (C_{3v}), and 1-iodobicyclo[2.2.2]octane (**1c**) (C_{3v})

(**1a**)			(**1b**)			(**1c**)		
Experimental I.E.[a]	Assignment MO[b]	VEOMP $-\varepsilon$	Experimental I.E.[c]	Assignment MO[d]	VEOMP $-\varepsilon$	Experimental I.E.[c]	Assignment MO[d]	VEOMP $-\varepsilon$
9.7	$3e''$	9.64	9.67	$(n_{Br})8e$	9.95	8.87	$(n_I)8e$	8.32
10.2	$4a_1'$	9.74	9.95		10.17	9.41		8.81
11.2	$1a_1''$	11.53	10.39	$(\sigma_{CBr})8a_1$	10.70	10.02	$(\sigma_{CI})8a_1$	9.80
12.0	$4e'$	11.99	10.7	7e	11.00	10.5	7e	10.87
12.6	$3e'$	12.65	11.6	$2a_2$	12.50	11.45	$2a_2$	12.51
13.0	$3a_2''$	12.85	12.5	$7a_1$	12.84	12.3	$7a_1$	12.42
13.2	$2e''$	13.34	12.9	6e	13.36	12.6	6e	13.24
14.2	$1a_2'$	14.47	13.2	5e	13.80	13.0	5e	13.79
15.8	$2e'$	16.52	13.6	4e	14.48	13.4	4e	14.44
16.4	$3a_1'$	17.07	14.1	$1a_2$	15.49	14.0	$1a_2$	15.49
18.8	$2a_2''$	17.60	15.85	$6a_1$	16.83	15.75	$6a_1$	16.61
			16.2	3e	17.65	16.1	3e	17.63
			18.8	$5a_1$	18.50	18.6	$5a_1$	19.71

[a] From the spectrum in ref. 9. [b] Orbital numbering within valence shell for D_{3h} point group. [c] Accuracies vary between ±0.01 and ±0.1 eV. [d] Orbital numbering within valence shell for C_{3v} point group.

Table 2. Comparison of experimental and calculated vertical ionization energies (in eV) and molecular orbital assignments of bicyclo[2.2.1]heptane (**2a**) (C_{2v}), 1-bromobicyclo[2.2.1]heptane (**2b**) (C_s), and 1-iodobicyclo[2.2.1]heptane (**2c**) (C_s)

(**2a**)			(**2b**)			(**2c**)		
Experimental I.E.[a]	Assignment MO[b]	VEOMP $-\varepsilon$	Experimental I.E.[c]	Assignment MO[d]	VEOMP $-\varepsilon$	Experimental I.E.[c]	Assignment MO[d]	VEOMP $-\varepsilon$
10.2	$5b_2$	9.87	9.71	(n_{Br}) $14a'$	9.84	8.96	(n_I) $14a'$	8.36
10.4	$3a_2$	9.90	10.02	$9a''$	10.21	9.45	$9a''$	8.88
10.7	$7a_1$	10.70	10.75	$(\sigma_{CBr})13a'$	11.35	10.55	$(\sigma_{CI})13a'$	10.24
11.1	$6a_1$	11.06	11.4	$8a''$	11.20	11.0	$8a''$	11.11
11.4	$5b_1$	11.13	11.8	$12a'$	11.80	11.5	$12a'$	11.45
12.1	$4b_2$	11.57	12.0	$11a'$	12.28	11.9	$11a'$	12.15
12.3	$2a_2$	12.01	12.25	$7a''$	12.48	12.1	$7a''$	12.38
12.7	$4b_1$	12.18	12.5	$10a'$	12.56	12.4	$10a'$	12.40
13.4	$3b_2$	13.52	12.75	$6a''$	13.26	12.6	$6a''$	13.17
13.7	$3b_1$	13.56	13.0	$5a''$	13.34	12.9	$5a''$	13.28
15.5	$5a_1$	15.82	13.8	$9a'$	14.55	13.8	$9a'$	14.46
15.9	$2b_1$	15.83	14.0	$4a''$	14.64	14.0	$4a''$	14.62
16.4	$4a_1$	16.84	15.8	$8a'$	16.46	15.7	$8a'$	16.22
17.5	$2b_2$	18.52	16.0	$7a'$	16.97	15.9	$7a'$	16.93
18.2	$3a_1$	19.13	16.3	$3a''$	17.06	16.2	$3a''$	17.02
			17.5	$6a'$	19.17	17.5	$6a'$	18.99
			18.3	$5a'$	20.09	18.3	$5a'$	19.96

[a] From the spectrum in ref. 9. [b] Orbital numbering within the valence shell for C_{2v} point group. [c] Accuracies vary between ±0.01 and ±0.1 eV. [d] Orbital numbering within the valence shell for C_s point group.

bridgehead σ_{CH} and σ_{CI} entities, $7a_1$, is calculated to lie at lower I.E. than the $2a_2$ MO of (**1c**). A reversal of these two MOs from bromo- to iodo-substitution seems unlikely in view of the remarkable similarity between the p.e. spectra in the 11—15 eV region. Assignment of the halogen-containing MOs to the structure at 12.4 eV is consistent with its diminution when He^{II} radiation is employed. It may also be observed that application of the Koopmans' approximation to the $1a_1''$ MO of (**1a**) overestimates its IE in relation to adjacent MOs, a deficiency which could also apply to the $2a_2$ MOs of (**1b** and **c**).

1-Bromo- and 1-Iodo-bicyclo[2.2.1]*heptane*.—The procedures applied to assignment of 1-bromobicyclo[2.2.1]heptane (**2b**) and 1-iodobicyclo[2.2.1]heptane (**2c**) are very similar to those employed for (**1b** and **c**). VEOMP calculations produce eigenvalues which simulate the band groupings observed in the p.e. spectra. Comparison of the experimental and theoretical Koopman's I.E.s is provided in Table 2. Experimental I.E.s for (**2a**) were obtained from the spectrum measured by Bischof et al.[9]

Spin–orbit interactions are exhibited by p.e. bands emanating from the non-bonding halogen *p* orbitals perpendicular to the C–X bond. The very similar bandwidths of the two SO components of the first band of the (**2c**) spectrum indicate that minimal interaction occurs with the alkane group. This view is supported by the VEOMP calculations which attribute a mean iodine contribution of 92% to the 8e MOs, and where the calculated SO splitting of 0.52 eV, which includes a contribution of 0.12 eV due to conjugative effects, agrees well with the observed value of 0.49 eV. The significant intensity reduction with He^{II} radiation, which was the largest measured in this study, also corroborates the non-bonding character assigned to these MOs. A vibrational spacing of 700 ± 70 cm^{-1} is measured and assigned to a C–I stretching vibration. A more substantial

Table 3. Comparison of experimental and calculated vertical ionization energies (in eV) and molecular orbital assignments of bicyclo[2.1.1]hexane (**3a**) (C_{2v}), 1-bromobicyclo[2.1.1]hexane (**3b**) (C_s), and 1-iodobicyclo[2.1.1]hexane (**3c**) (C_s)

(**3a**)			(**3b**)			(**3c**)		
Experimental I.E.[a]	Assignment MO[b]	VEOMP $-\varepsilon$	Experimental I.E.[c]	Assignment MO[d]	VEOMP $-\varepsilon$	Experimental I.E.[c]	Assignment MO[d]	VEOMP $-\varepsilon$
10.5	$4b_1$	10.15	9.72	(n_{Br}) 13a′	10.05	8.98	(n_{I}) 13a′	8.47
10.8	$2a_2$	10.35	10.06	7a″	10.27	9.46	7a″	8.98
11.1	$4b_2$	10.52	11.0	(σ_{CBr})12a′	11.39	10.7	(σ_{CI})12a′	10.29
11.4	$7a_1$	10.76	11.5	6a″	11.73	10.9	6a″	11.64
12.1	$3b_1$	11.71	11.8	5a″	12.34	11.1	5a″	12.06
12.5	$6a_1$	12.12	12.1	11a′	12.35	11.6	11a′	12.08
13.2	$3b_2$	12.96	12.4	10a′	12.56	11.9	10a′	12.22
13.4	$1a_2$	13.31	12.8	9a′	13.35	12.7	9a′	13.31
15.2	$2b_2$	15.86	13.1	4a″	14.13	13.0	4a″	14.10
15.7	$5a_1$	15.86	13.9	3a″	14.71	13.8	3a″	14.58
16.5	$4a_1$	17.23	15.5	8a′	16.46	15.4	8a′	16.15
17.6	$3a_1$	19.03	15.8	2a″	17.03	15.6	2a″	16.99
			16.1	7a′	17.24	15.9	7a′	17.17
			18.1	6a′	19.84	17.9	6a′	19.54

[a] From ref. 11. [b] Orbital numbering within valence shell for C_{2v} point group. [c] Accuracies vary between ±0.01 and ±0.1 eV. [d] Orbital numbering within valence shell for C_s point group.

interaction, however, is indicated by the band contours of the low I.E. bands of (**2b**). Conjugation between the bromine and alkane orbitals is enhanced by their energy proximity. The bromine *p* orbital in the plane of the single C bridge is calculated to undergo the greater destabilization due to its antibonding combination with the parallel bridgehead carbon *p* orbital. Its bromine content is calculated to be 70% compared with 84% for the other component MO. The relative compositions are supported by the bandshapes observed experimentally, where the broader component corresponding to more significant conjugative interaction occurs at lower I.E. This is further shown by the theoretical SO analysis where the calculated splitting of 0.37 eV is dominated by a conjugative contribution of 0.30 eV. The fact that this latter value agrees well with the observed splitting of 0.31 eV suggests that the SO contribution of 0.07 eV may be an overestimate.

Intensification of the low I.E. edge of the bulk of the p.e. spectrum of each halogenobicyclo[2.2.1]heptane relative to that of the unsubstituted alkane can be detected. This intensity enhancement is diminished in the He^{II} spectra, consistent with the assignment of these bands to the σ_{CX} bonding orbital as predicted by the VEOMP calculations.

The electrostatic influence of halogen substitution on the I.E.s of (**2a**) replicates that already noted for (**1a**). The inductive effect of the bromine atom exceeds the iodine electron-withdrawing effect as shown by a comparison of I.E.s in Table 2. The electronegativity difference between bromine and iodine is also evident in the location of bands of significant halogen character.

1-Bromo- and 1-Iodo-bicyclo[2.1.1]*hexane*.—As the two-carbon bridges are contracted to methylene bridges in the transition from (**1a**) to bicyclo[2.1.1]hexane (**3a**) the molecule is expected to become progressively more strained. However, since the first I.E. of (**3a**) at 10.50 eV is greater than those of both (**1a**) (9.71 eV) and (**2a**) (10.17 eV), this strain is not producing sufficient antibonding character in the outer MOs to oppose the reducing hyperconjugative effect which is the dominant influence.

Consequently the n_{X} bands, which display simple spin–orbit splittings, demonstrate that minimal interaction with the alkane electronic structure has allowed a retention of cylindrical symmetry in the electron distribution of the C–X bond. The bandshapes of the SO components indicate the extent of conjugative contribution to this loss of degeneracy.

In the p.e. spectrum of (**3b**) a broader peak at the lower I.E. of the 9.72—10.06 eV doublet confirms the difference between bromine contributions to the calculated MOs of 76 and 81%, respectively. The VEOMP calculation obtains a splitting of 0.22 eV including a small conjugative contribution of 0.06 eV. Since the experimental splitting is surprisingly large at 0.34 eV it seems that both conjugative and spin–orbit contributions are larger than indicated by the calculation. By contrast the broader component of the first band of the spectrum of (**3c**) lies at higher I.E. However, each of the associated MOs is calculated to possess 93% iodine character and the splitting observed is largely due to SO coupling calculated at 0.49 eV in good agreement with the experimental value of 0.48 eV. Minimal interaction with the alkane structure enhances this localized mechanism for lifting the pseudo-degeneracy of the two ionic states. A vibrational spacing of 700 ± 70 cm^{-1} is measured for the first n_{I} band and is assigned to the C–I stretching vibration. The small peak at 10.0 eV is an unidentified impurity band.

As in the p.e. spectra of the higher halogenobicycloalkanes the σ_{CX} MO is responsible for the low energy edge of the alkane-based spectrum. Comparison of the He^{I} and He^{II} spectra confirms the assignment of this MO to the first p.e. band in this region, substantiating a Koopmans' ordering of I.E.s.

Contraction of the 15.5—16.5 eV region of the (**3a**) p.e. spectrum on halogen substitution is predicted by the VEOMP calculation as due to halogen contribution in the MO responsible for the 16.5 eV band. This interaction is borne out by a comparison of the p.e. spectrum of (**3a**) with those of its 1-bromo- and 1-iodo-derivative.

Conclusions.—The bromo- and iodo-derivatives of the bicycloalkanes considered in this study are each substituted at a tertiary carbon atom. Consequently their He^{I} photoelectron spectra show similarities to those of t-butyl bromide and t-butyl iodide. However, the competition between conjugative and spin–orbit coupling effects which influence the ionization energies and the splittings observed for the first two bands in each spectrum show interesting variations which are difficult to simulate by molecular orbital calculations. An indication of the complexities involved is that the observed splittings for the bromobicycloalkanes increase in going from (**1b**) to (**2b**) to (**3b**), but for the iodobicycloalkanes decrease from (**1c**) to (**2c**) to (**3c**). The quality of calculations required to explain these observations in detail is beyond present capabilities for molecules of the size represented here. Electro-oxidation studies on these iodobicycloalkanes[25] give $E_{\frac{1}{2}}$ values which show good correlation with the first I.E.s measured here. The $E_{\frac{1}{2}}$ values obtained (and compared with the I.E.s) are 1.80 V for (**1c**) (8.87 eV), 1.88 V for (**2c**) (8.96 eV), and 1.87 V for (**3c**) (8.98 eV), with uncertainties of ± 0.03 V.

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