# Organic Quantum Chemistry. XIII. The Electronic Spectra of the α-Halo Ketones[1,2]

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Abstract: The transition energies and oscillator strengths for the n → π* transition of cyclohexanone, and for the α-halo derivatives in which an axial or equatorial hydrogen is replaced by a halogen (fluorine, chlorine, or bromine) were calculated on the basis of two different models. In the first model, the empty ns orbital of the halogen was allowed to mix with the n orbital on oxygen and the p orbitals on carbon and oxygen. The calculations were made using the Pariser–Parr approximations. These interactions of the halogens were predicted to cause negligible shifts in the n → π* transition energy, while experimentally, shifts are observed of the order of a few tenths of an electron volt. It was concluded this type of interaction is not responsible for the observed shifts. The second model considered the p and n orbitals on carbon and oxygen as previously, together with the σ bond from carbon to halogen (sp³ on carbon, np on halogen). In this case small or negligible blue shifts were predicted for all the equatorial halogens, as observed, and a large red shift was predicted for axial fluorine, and even larger shifts were predicted for axial chlorine and bromine, in reasonable agreement with experiment.

Compounds containing a halogen attached to the α carbon of a carbonyl group, and particularly the α-halo ketones, have been very useful in conformational analysis.[3] Among the interesting properties of these molecules are two with which the present paper is specifically concerned, the ultraviolet spectra and the conformational equilibria. To summarize briefly,[3] the substitution of a halogen for an α-hydrogen atom in cyclohexanone will have an effect upon the absorption band in the ultraviolet which is attributed to the n → π* transition of the ketone, depending on whether the halogen is axial or equatorial, and depending on which halogen is involved. In cyclohexanone itself, this band occurs at about 280 mμ (depending on the solvent), and it has an extinction coefficient of about 20. The substitution of a fluorine, chlorine, or bromine into the equatorial position at the α carbon leads to a small or negligible blue shift, with little or no change in the extinction coefficient of this absorption band. If the halogen is substituted into an axial position on the α carbon, there is a shift of the absorption to longer wavelength by an amount which increases from about 12 mμ for the fluorine to about 24 mμ for bromine, and there is a corresponding increase in the intensity of the band from an extinction coefficient of about 20 for fluorine to about 120 for bromine. These facts were first noted by Jones[4] in the case of steroidal systems and were subsequently extended to simple cyclohexanones by Corey.[5] Corey made a suggestion that the red shift of the n → π* absorption might be attributed to a resonance form I, which would correspond to the σ bonding electrons of the C–X bond being donated into the π* orbital.[6]

I
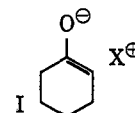
Subsequently, an alternative explanation in molecular orbital terms was offered.[7] The interaction suggested was between s*, the lowest lying empty orbital on halogen (3s on fluorine, 4s on chlorine, etc.), and the π* orbital of the carbonyl group. The interaction would lower the π* energy and raise the s* energy, with the consequent red shift in the n → π* absorption band. This is an interaction which affects predominantly the excited state, and it cannot be written with the aid of any conventional valence-bond pictures or resonance forms. If the halogen were equatorial, the overlap between the s* orbital on halogen and the π system would be negligible, but overlap would occur between the s* orbital on the halogen and the n orbital on oxygen. Because of the wide disparity in the energies of these orbitals, the n orbital on oxygen would be pushed down, but slightly, yielding a small blue shift.

Qualitatively, this explanation appears attractive. The present paper considers a quantitative treatment of these ideas, which turn out to be inadequate to explain the experimental facts.

The other point of interest concerns the equilibria between the equatorial and axial halogen conformers, as illustrated.

These equilibria are influenced by the solvent. Since the equatorial isomer has a higher dipole moment, it is stabilized more by solvation, and hence the equilibria tend to shift more toward the equatorial form as the polarity of the solvent is increased. The equilibrium constants have been determined in a nonpolar solvent (heptane) at high dilution, and the absolute values of

(1) Paper XII: J. C. Tai and N. L. Allinger, *J. Am. Chem. Soc.*, **88**, 2179 (1966).

(2) This research was supported by Grant DA-ARO-D-31-124-G494 from the Army Research Office.

(3) For reviews see E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Division of John Wiley and Sons, New York, N. Y., 1965, p 460; C. Djerassi, "Optical Rotatory Dispersion," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p 115.

(4) R. N. Jones, D. A. Ramsay, F. Herling, and K. Dobriner, *J. Am. Chem. Soc.*, **74**, 2828 (1952).

(5) E. J. Corey, *ibid.*, **75**, 2301 (1953).

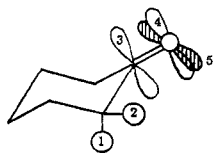(6) E. J. Corey and H. J. Burke, *ibid.*, **77**, 5418 (1955).

(7) (a) Reference 3, p 151, footnote 79; (b) E. M. Kosower, G. Wu, and T. S. Sorensen, *J. Am. Chem. Soc.*, **83**, 3147 (1961).

these numbers are of interest, and of further interest is the variation with the change in halogen. The per cent axial conformer was found to be as follows: fluorine, 48; chlorine, 76; bromine, 85. It can be seen that the energy difference under vacuum would be nearly zero for chlorine, whereas the fluorine would be more stable in the equatorial form by about 0.6 kcal/mole, while the bromine would be more stable in the axial form by about 0.4 kcal/mole. Earlier, a calculation was carried out to try to determine the effect of the interaction between the dipoles in these molecules on the equilibrium, and it was found that the approximate numbers could be predicted adequately, but it was not possible to predict the observed difference. The difficulty might be due to effects which could not properly be treated by classical methods, but might come out of the quantum mechanical treatment which would be required for the ultraviolet spectral calculations.

The α-halo ketones are, of course, very complicated molecules to try to treat by quantum mechanical methods. However, since we wished only to predict the changes which would occur when a halogen was substituted for a hydrogen in the molecule, it might be reasonably expected that even fairly crude calculations would give reasonably good predictions. From the general nature of the experimental facts, namely, a red shift from an axial halogen, and little or no shift from an equatorial one, it seemed clear that whatever the interaction between the halogen and the rest of the system was, it must push down the π^* orbital in the axial case and have very little effect on the difference between the n and π^* orbitals in the equatorial case. There would appear to be only two orbitals which lie above the π^*, and might conceivably push it down. These are the lowest lying empty s orbital on the halogen and the σ^* orbital connecting the halogen and the α carbon. Calculations were carried out for both types of interaction. The general method employed was that of Pariser and Parr,[8] which may be characterized for present purposes by the neglect of multicentered integrals and the empirical evaluation of resonance and repulsion integrals. The details of the calculations are given below.

Details of the Calculations

A. **Using the Empty s (s*) Orbital.** Five orbitals were considered in this case, as numbered and shown in the figure.

Orbitals 1 and 2 can be the hydrogen 2s orbitals, or one

of these can be the fluorine 3s, chlorine 4s, or bromine 5s orbital. Orbital 3 is the carbon 2pπ, and orbitals 4 and 5 are the oxygen 2pπ and 2pn orbitals, respectively.

The empirical one-center repulsion integrals of C_π and O_π were obtained in the usual way.[8,9] We used the values $\gamma_{C_\pi C_\pi} = 11.08$ ev, $\gamma_{O_\pi O_\pi} = 14.52$ ev, $\gamma_{O_\pi O_\pi} = 12.82422$ ev, and $(O_\pi O_\pi / O_\pi O_\pi) = 0.84789$ ev, obtained from spectroscopic data.[10] The orbital exponents of all the orbitals were obtained according to Slater's rules, and no inductive effect within the σ system was considered. Orbitals 1 and 2 are so diffuse that the scaling down of the one- or two-center repulsion integrals which are involved to account for electron correlation appeared unnecessary; hence theoretical values were used for all of these integrals.

Overlap integrals involving 2s, 3s, 5s, and 2p orbitals are calculated from equations given by Mulliken, et al.[11] Those involving 4s orbitals were taken from tables.[12] The resonance integrals β_{ij} were calculated by the equation

$$\beta_{ij} = -A_\pi (I_i + I_j) \frac{S_{ij}}{1 + S_{ij}}$$

for $\pi\pi$-type overlap, and

$$\beta_{ij} = -A_\sigma (I_i + I_j) \frac{S_{ij}}{1 + S_{ij}}$$

for sσ-type overlap. A_π was given the value 0.720, which allowed the calculated value for the n $\rightarrow$ π^* transition in cyclohexanone to agree with experiment. A_π was set to equal $0.773A_\pi$ as suggested by Mulliken.[13]

Since tables for two-center Coulomb repulsion integrals are available only for orbitals up to $n = 2$, simulated orbitals with $n = 2$ are used in place of the 3s, 4s, and 5s orbitals for the purpose of calculating the corresponding repulsion integrals. The construction of the simulated orbitals consisted of substituting for the orbital exponent $\delta_{X_{ns}}$ of the ns orbitals of X a new exponent $\delta_{X_{2s}}$ of a 2s orbital. The value of $\delta_{X_{2s}}$ was selected such that the new orbital would have the same effective "size" as the ns orbital in question, where the "size" of the orbital was taken to be measured by the expectation value or average value of r. The relation between $\delta_{X_{ns}}$ and $\delta_{X_{2s}}$ was obtained as follows.

$$\psi_{nlm} = \left[\frac{(2\xi)^{2n+1}}{(2n)!} \right]^{1/2} r^{n-1} e^{-\xi r} Y_{lm} (\theta, \phi)$$

$$\langle r \rangle = \int \psi_{nlm}{}^* r \psi_{nlm} \, d\tau$$

$$= \int_0^\infty \int_0^{2\pi} \int_0^{\pi/2} \psi_{nlm}{}^* r \psi_{nlm} r^2 \sin\phi \, d\phi \, d\theta \, dr$$

$$= \frac{(2\xi)^{2n+1}}{(2n)!} \int_0^\infty r^{2n+1} e^{-2\xi r} \, dr$$

$$= \frac{(2\xi)^{2n+1}}{(2n)!} \frac{(2n+1)!}{(2\xi)^{2n+2}} = \frac{2n+1}{2\xi}$$

(8) (a) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 711 (1953); **23**, 711 (1955). (b) Extensions of the Hückel and SCF MO methods to other than planar conjugated π systems have been made frequently during the last few years. See, for example, R. F. Hoffman, *J. Chem. Phys.*, **39**, 1397 (1963); G. Klopman, *J. Am. Chem. Soc.*, **86**, 4550 (1964); J. A. Pople, D. P. Santry, G. A. Segal, *J. Chem. Phys.*, **43**, S129, S136 (1965); N. L. Allinger and J. C. Tai, *J. Am. Chem. Soc.*, **87**, 1227 (1965). While the (Pariser-Parr-Pople) approximations used in π systems are clearly less soundly based in cases such as the present one, it can reasonably be expected that most of the error introduced by such approximations will cancel when a series of related molecules is considered.

(9) T. Anno, *J. Chem. Phys.*, **29**, 1161 (1958).
(10) H. A. Skinner and H. O. Pritchard, *Trans. Faraday Soc.*, **49**, 1254 (1953).
(11) R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).
(12) ADI Document No. 5481.
(13) R. S. Mulliken, *J. Phys. Chem.*, **56**, 295 (1952).

Let

$$\frac{2n + 1}{2\xi_{ns}} = \frac{2 \times 2 + 1}{2\xi_{2s}'} = \langle r \rangle$$

then

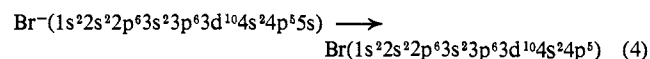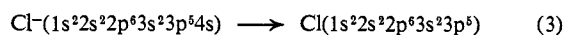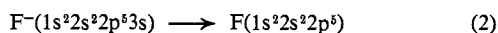$$\xi_{2s}' = \frac{5\xi_{ns}}{2n + 1}$$
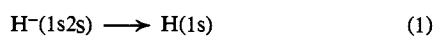
for example, when $n = 3$

$$\xi_{2s}' = {}^{5}/_{7}\xi_{3s}$$

The orbital exponents of the ns and their simulated 2s orbitals of H, F, Cl, and Br are given in Table I.

Table I. Data for the ns orbitals

X	n	ns	2s	I_{ns}, ev
H	2	0.075	0.075	0.18675
F	3	0.35	0.250	0.9075
Cl	4	0.28378	0.15766	0.9450
Br	5	0.2625	0.11932	0.975

The valence-state ionization potentials of H 2s, F 3s, Cl 4s, and Br 5s electrons correspond, respectively, to the energy changes accompanying the following reactions

$$H^-(1s2s) \longrightarrow H(1s) \tag{1}$$

$$F^-(1s^22s^22p^53s) \longrightarrow F(1s^22s^22p^5) \tag{2}$$

$$Cl^-(1s^22s^22p^63s^23p^54s) \longrightarrow Cl(1s^22s^22p^63s^23p^5) \tag{3}$$

$$Br^-(1s^22s^22p^63s^23p^63d^{10}4s^24p^55s) \longrightarrow$$
$$Br(1s^22s^22p^63s^23p^63d^{10}4s^24p^5) \tag{4}$$

The energy change accompanying reaction 1, E_1, can be looked upon as the sum of the energy changes E_5 and E_6 of the following two reactions.

$$H^-(1s^2) \longrightarrow H(1s) \tag{5}$$

$$H^-(1s2s) \longrightarrow H^-(1s^2) \tag{6}$$
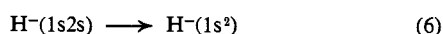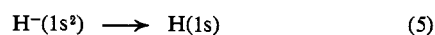
Now E_5 is just the electron affinity of the hydrogen atom, and E_6 is the energy of the state $H^-(1s2s)$ with respect to $H^-(1s^2)$ as the ground state. The value of E_6 was deduced from the fact that for He, the corresponding value of E_6 is about 75% of that of E_5.[14] The same factor was used for the s orbitals under consideration so E_1 equals 25% of E_5. Since E_6 is quite small anyway, the error introduced by this approximation is insignificant. The estimated ionization potentials of the negative ions of the hydrogen and the halogens which result from the addition of an s electron outside the valence shell are listed in Table I. The electron affinities of the hydrogen, fluorine, and chlorine atoms are 0.747, 3.63, and 3.78, respectively,[7] and that of the bromine is (by extrapolation) approximately 3.90 ev.

The geometry of the cyclohexanone molecule adopted here is the same as described earlier.[1] The coordinates of the X atom were calculated by the equations in Table VI of ref 1 using the following C–X bond lengths (A): $R_{CH} = 1.10$, $R_{C-F} = 1.39$, $R_{C-Cl} = 1.78$, and $R_{C-Br} = 1.94$.

An LCAO MO CI treatment including all the singly and doubly excited configurations was used as de-

(14) National Bureau of Standards, Circular No. 467, U. S. Government Printing Office, Washington, D. C.

scribed previously.[15] The original MO's were obtained by diagonalizing a Hückel-type matrix which was constructed in such a way that the resultant MO's were as close as possible to SCF MO's (as shown by the very small interaction elements between the ground configuration and the singly excited configurations). This was done by setting $\alpha_H = 0$, $\alpha_X = (I_H - I_X)/A$, with the off diagonal elements (β's) having the same values as the resonance integrals in the core matrix. A is a constant that was determined so as to give the MO's with the desired property. After a number of trials it was found that $A = 2.2$ was satisfactory.

(B) **Using C–X σ^* Orbital.** The orbitals considered for cyclohexanone are shown and numbered in the figure.
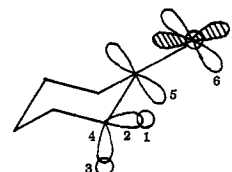
Orbitals 1 and 3 were taken to be a H_{1s}, F_{2p}, Cl_{3p}, or Br_{4p} orbital, as appropriate for the description of the particular compound. Orbitals 2 and 4 are carbon sp^3 orbitals.

The one-center repulsion integrals involving C_{sp^3} were obtained as linear combinations of the following integrals, whose empirical values were determined from spectroscopic data by Anno.[9]

$$(\pi_C\pi_C|\pi_C\pi_C) = (\sigma_C\sigma_C|\sigma_C\sigma_C) = 11.08 \text{ ev}$$

$$(S_CS_C|S_CS_C) = 12.23 \text{ ev} = (S_CS_C|\sigma_C\sigma_C)$$

$$(\pi_C\bar{\pi}_C|\pi_C\bar{\pi}_C) = 0.619 \text{ ev}$$

$$(S_C\sigma_C|S_C\sigma_C) = -(S_C\pi_C|S_C\pi_C) =$$

$$-\frac{925}{243}(\pi_C\bar{\pi}_C|\pi_C\bar{\pi}_C) = -2.35628 \text{ ev}$$

$$(\sigma_C\sigma_C|\pi_C\pi_C) = 9.841 \text{ ev}$$

thus

$$\gamma_{22} = \gamma_{44} = \frac{1}{16}[(SS|SS)_C + 12(S\pi|S\pi)_C +$$

$$9(\sigma\sigma|\sigma\sigma)_C + 6(SS|\sigma\sigma)_C]$$

$$= \frac{1}{16}(7 \times 12.33 + 12 \times$$

$$2.35628 + 9 \times 11.08) = 13.35034 \text{ ev}$$

and

$$\gamma_{24} = \frac{1}{16}[7 \times (SS|SS)_C + 12 \cos \theta \ (S\pi|S\pi)_C +$$

$$9 \cos^2 \theta \ (\sigma\sigma|\sigma\sigma)_C + 9 \sin^2 \theta \ (\sigma\sigma|\pi\pi)_C]$$

$$= \frac{1}{16}[7 \times 12.23 - 12 \times 0.33333 \times 2.35628 +$$

$$9 \times 0.11111 \times 11.08 + 9 \times 0.88889 \times$$

$$9.841] = 10.37456 \text{ ev}$$

The one-center repulsion integrals of the H_{1s}, F_{2p}, Cl_{3p}, and Br_{4p} orbitals were obtained as the difference

(15) N. L. Allinger and J. C. Tai, *J. Am. Chem. Soc.*, 87, 2081 (1965).

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between the valence-state ionization potentials and electron affinities which are listed in Table II. Also in Table II are the orbital exponents of these orbitals and those of their simulated 2p orbitals in cases where $n > 2$, and these were calculated in the same way as described for the simulated 2s orbitals. The valence state ionization potentials and electron affinities of Br in Table II were estimated by comparing the change of atomic state ionization potentials for the series F, Cl, and Br.[16] It is seen that the difference between the atomic-state ionization potentials of F and Cl is about four times as big as that between those of Cl and Br. It was assumed that the corresponding difference in the valence-state ionization potentials and in the valence-state electron affinities would have the same 4:1 ratio, which led to values of 13.63 and 3.86 for the valence-state ionization potential and electron affinity of Br.

Table II. Data for the σ Orbitals

					I_X		
					Atomic[a]	Valence	
X	n	ξ_n	$\xi_{3'}$	$\xi_{2'}$	state	state	A
H	1	1	...	...	13.595	13.595[b]	0.747
F	2	2.6	...	...	17.422	20.88[b]	3.65
Cl	3	2.03333	...	1.45238	12.959	15.08[b]	3.82
Br	4	1.72973	1.34533	0.96096	11.844	13.63[c]	3.86[c]

[a] See ref 16. [b] See ref 10. [c] Estimated value (see text).

Two-center theoretical repulsion integrals and overlap integrals were taken from the NASA tables[17] for orbitals with $n \leq 2$. For Cl and Br, simulated 2p orbitals were used. The integrals are then scaled down according to the formula $\gamma_{12}(\text{emp}) = \gamma_{12}(\text{theo}) - (S_{12}/2)[\gamma_{11}(\text{theo}) - \gamma_{11}(\text{emp}) + \gamma_{22}(\text{theo}) - \gamma_{22}(\text{emp})]$. However, S_{12} is not always the true overlap integral between orbitals 1 and 2. When one of the two centers carries an s-type orbital, S_{12} is taken to be S_{ss}; when one of them carries an C_{sp^3} orbital and the other a halogen $p\sigma$ orbital, S_{12} is taken to be $S_{\sigma\sigma}$; when any other p-p- or p-sp^3-type integrals are considered, S_{12} is taken to be $S_{\pi\pi}$. This was done so that the scaling factor would be a function of distance and independent of small variations in the relative orientation of the two orbitals concerned.

The resonance integrals β_{ij} were calculated by the same formulas given under section A, except here A_π was set equal to 0.688. The first or second equation in section A was used according to the type of binding between i and j. For simplicity, whenever there are both π- and σ-type contributions, the bond was treated as of the type which contributes more. Thus β_{25}, β_{26}, β_{45}, β_{46}, and β_{56} are of the $\pi\pi$ type and β_{27} and β_{47} are of the $\sigma-\sigma$ type. The resonance integrals between hydrogen 1s or halogen p and any other orbitals were calculated as of the $\sigma-\sigma$ type. It should be noted that in order to fit the n $\rightarrow$ π^* transition of the standard compound cyclohexanone, a different value of A_π from that used in calculations described under section A was used. The overlap integrals required in those

(16) G. Herzberg, "Atomic Spectra and Atomic Structure," Dover Publications, New York, N. Y., 1944, p 200.
(17) R. C. Sahni and J. W. Cooley, National Aeronautics and Space Administration, Technical Notes D-146-I, D-146-II, Washington, D. C., 1960.

formulas were calculated between the orbitals considered whenever numerical tables were available. This was found to be possible for integrals between most orbital pairs, except $\text{Cl}_{3p}-\text{O}_{2p}$, $\text{Br}_{4p}-\text{O}_{2p}$, $\text{Br}_{4p}-\text{C}_{2p}$, and $\text{Br}_{4p}-\text{H}_{1s}$. In the first two cases, simulated 2p orbitals of Cl and Br were used. In the case of the $\text{Br}_{4p}-\text{C}_{2p}$ pair, since $S_{4p\sigma 2p\sigma}$, $S_{3p\sigma 2p\sigma}$, and $S_{3p\pi'2p\pi}$ are known, $S_{4p\pi 2p\pi}$ was approximated by $S_{3p\pi'2p\pi}(S_{4p\sigma 2p\sigma}/S_{3p\sigma'2p\sigma})$, where $3p\sigma'$ and $3p\pi'$ are simulated 3p orbitals of Br. In the case of the $\text{Br}_{4p}-\text{H}_{1s}$ pair, overlap integrals over $\text{Br}_{3p'}-\text{H}_{1s}$ and $\text{Br}_{2p'}-\text{H}_{1s}$ were calculated, and $S_{\text{Br}_{4p}-\text{H}_{1s}}$ was then set equal to $S_{3p'1s}(S_{3p'1s}/S_{2p'1s})$.

The geometry of the molecules, the construction of the Hückel matrices, and the extent of configuration interaction were all the same as described above. It is interesting to note that while the total number of configurations is 28 when five orbitals are considered, the number jumps up to 91 when seven orbitals are considered. The computation time (which is spent mostly on the diagonalization of the CI matrix, on the IBM 7074 computer) was less than 5 min for the former case, while for the latter case it was about 1 hr.

Results and Discussion

The calculated energies of the n $\rightarrow$ π^* transitions of the cyclohexanone (calculation B) and the α-halocyclohexanones are compared with the experimental values in Table III.

Table III. Transition Energies (ev)

	Calculation B[a]		Obsd[c]	
Molecule	ΔE	$\delta\Delta E$[b]	ΔE	$\delta\Delta E$
Cyclohexanone	4.24	—	4.25	
α-ax F	4.18	−0.07	4.11	−0.14
α-ax Cl	4.03	−0.22	4.05	−0.20
α-ax Br	4.07	−0.18	3.94	−0.31
α-eq F	4.26	+0.01	4.28	+0.03
α-eq Cl	4.29	+0.04	4.34	+0.09
α-eq Br	4.25	+0.00	4.26	+0.01

[a] The $C_{sp^3}-X\sigma$ orbitals are taken to be the perturbing orbital. The calculation is described in section B of the text. [b] $\delta\Delta E$ is the shift in the n $\rightarrow$ π^* transition from cyclohexanone. [c] See ref 3.

It was found that by using the empty halogen orbitals, following the earlier suggestions, no shifts were predicted. The results are therefore not tabulated. The C–X σ^* orbitals do, on the other hand, account for very substantial shifts for the axial halogens. The calculated values are within about 5 mμ of the experimental values, almost to within experimental error of the measurement (considering the ambiguity in the definition of the experimental transition energy), except for axial bromine, where the calculated shift is only 13 mμ, which is definitely smaller than the experimental value of 24 mμ. This may be due, at least in part, to the use of approximations resulting from the simulated 2p orbital, which are clearly worse here than for chlorine.

Attempts have been made to obtain different results by treating some parameters differently from the ways described above. We have tried to scale down the two-center repulsion integrals differently, to treat the overlap between a certain orbital pair i,j as of a different type so that β_{ij} would be different. It is found that as long as all the corresponding quantities in all the

molecules were treated the same way, the calculated shifts of the n → π* transition remain virtually unchanged.

The conclusions drawn are that interactions between the σ* orbitals of the C–X and C–H bonds with the π* orbitals offers a reasonable explanation of the observed trends in the spectra, while similar interactions involving the unfilled higher s orbitals on the halogens do not, and this conclusion is not affected by any reasonable variation of the empirical quantities.

The energies of the axial and equatorial pairs of the halo ketones were available from the calculations and were examined with the hope that the relative values might prove to be significant. The absolute values were on the order of −300 ev, and the differences between isomers were very small indeed, less than 0.01 ev from the σ*-orbital interactions, and less than 0.0001 ev from the s*-orbital interactions. It was calculated that these interactions would stabilize the equatorial fluorine relative to the axial by 0.22 kcal/mole and the chlorine by 0.06 kcal/mole, while for the bromine, the axial would be stabilized relative to the equatorial by 0.12 kcal/mole. Qualitatively, these are the differences observed, but the experimental values are about three times larger than calculated. Since the calculated differences in the total energies amount to less than one part in 30,000, we will not dwell on these numerical values.

The oscillator strengths of the n → π* transitions of the compounds were also calculated. In a molecule such as formaldehyde, the oscillator strength would be identically zero for the isolated nonvibrating molecule, but actually a very small value is observed, due to the destruction of the symmetry by vibration. For the cyclohexanone calculation described herein which employs the σ orbitals, the calculated oscillator strength is 0.00009, the difference from zero being due mainly to our not considering symmetrical parts of the molecule. Introduction of an axial halogen leads to an increase in the calculated oscillator strengths, to 0.00023, 0.00046, and 0.00035 for fluorine, chlorine, and bromine, respectively. Thus the value is increased upon substitution of fluorine for hydrogen, and increased further upon substitution of chlorine. Experimentally, this is qualitatively what is observed, although the experimental values are always larger (by a factor of about 10) than calculated. Since the slight asymmetry resulting from the presence of the hydrogen leads to a substantial increase in oscillator strength when the molecule vibrates, the larger asymmetry resulting from the halogen might reasonably be expected to yield a proportionately larger oscillator strength. The real conflict with experiment comes

with axial bromine, for which the calculated oscillator strength is smaller than for chlorine, while the experimental value is considerably larger. Here again, the results for bromine are expected to be less accurate than for the other halogens because of the additional approximations needed.

A physical picture of a model which has the characteristics of the calculations described was considered desirable, for often the emerging concepts can be carried over to cases where calculations may be unavailable or impractical. The physical model of the empty halogen orbital interacting with the π* orbital and depressing the energy of the latter is easy to visualize, and tracing through the calculations shows that this happens as would be expected, but the halogen orbital has such a high energy that the effect is too small to explain the experimental results.

The same type of concept is in principle applicable to the σ*–π* interactions. However, the form of the orbitals is so complicated that we cannot trace the changes brought about by halogen substitution through the intermediate stages of the calculations and retain any clear-cut physical picture of the situation. Nevertheless, it would seem that a generalization can be made from these calculations, which is that if an empty orbital is situated so as to overlap with the π* orbital of the carbonyl, and if it is sufficiently low in energy, a red shift and intensification will occur in the n → π* absorption, while any new interaction with the n orbital will lead to only very minor changes. "Sufficiently low in energy" here means lower than the C–H σ* orbital. Any σ* orbital from a C–X bond should show these properties if either X is electronegative, or if the bond is weak (so that σ and σ* are not widely separated). A properly oriented carbon–carbon π bond is weak enough to get involved under the latter category, but the corresponding σ bond is not. Thus it is known that for X = –OH, or –OCH₃, or vinyl or phenyl, spectral behavior analogous to that observed with the halogens has already been reported.[18,19] Similar behavior can be predicted for other electronegative groups (amines, mercaptans, and their oxygenated derivatives such as nitro, sulfone, etc.) and unsaturated groups (cyano, acetylene, azo, etc.).

(18) (a) H. Labhart and G. Wagniere, Helv. Chim. Acta, 42, 2219 (1959); (b) S. MacKenzie, S. F. Marsocci, and H. C. Lampe, J. Org. Chem., 30, 3328 (1965); (c) R. C. Cookson and J. Hudec, J. Chem. Soc., 429 (1962).

(19) The authors are grateful to the referee for pointing out that the ultraviolet transitions observed in saturated organic compounds with nonbonding electrons as in bromo- and iodomethanes (J. R. Majer and J. P. Simons, Advan. Photochem., 2, 137 (1964)), and in alcohols and ethers (H. Tsubomura, K. Kimura, K. Kaya, J. Tanaka, and S. Nagakura, Bull. Chem. Soc. Japan, 37, 417 (1961)), are believed to be of the n → σ* rather than n → s* type.