Conformational Studies of α-Substituted Carbonyl Compounds. Part 1. Conformation and Electronic Interaction in Hetero-substituted Acetones by Infrared and Ultraviolet Spectroscopy

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$\nu_{C=O}$ Frequencies and intensities and $n \longrightarrow \pi^*$ transition energies were measured for some hetero-substituted ketones (XCH_2COMe: X = F, Cl, Br, I, NMe_2, OMe, SMe, or SEt) and compared with the corresponding unsubstituted ketone. The stability of the *gauche*-conformers is discussed in terms of hyperconjugative interactions between σ_{C-X} and $\pi_{C=O}$ orbitals and repulsive interactions between C=O and C–X dipoles. The carbonyl frequency shifts, induced by inductive ($\Delta\nu_I$), field ($\Delta\nu_F$), and hyperconjugative effects ($\Delta\nu_H$), are estimated separately. A close relationship is shown to exist between the $\Delta\nu_H$ values and the energies of the $n \longrightarrow \pi^*$ transition.

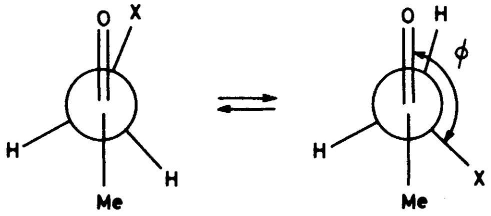
Previous reports from this laboratory[1-3] showed that α-sulphur-substituted ketones exhibit a shift of the carbonyl stretching absorption band to lower frequency, as well as a bathochromic shift and a hyperchromic effect of the $n \longrightarrow \pi^*$ band, in comparison with the corresponding unsubstituted ketones. Recent conformation and u.v. studies on some α-alkylthio-cyclanones[4] have suggested that the hyperconjugative interaction between the C–S bond and carbonyl group in the ground and excited states may be responsible for these changes and have indicated that this interaction is related to the position of the C–S bond to the carbonyl group, described by the dihedral angle ϕ.

In order to investigate the generality of such interactions and the possibility of its occurrence in open-chain systems it became of interest to extend our studies to α-hetero-substituted ketones. It is noteworthy that, although the conformational analysis of α-hetero-substituted acetones by i.r. and u.v. spectroscopy have already been reported,[5-12] no systematic studies have been performed for the whole series.

The aim of the present work is to investigate the relationship between conformation and electronic interactions by i.r. and u.v. studies in some α-substituted acetones, bearing, in the α-substituent, representative elements of the first, second, third, and fourth rows of the Periodic Table, such as fluorine, oxygen, nitrogen, chlorine, sulphur, bromine, and iodine.

Results and Discussion

cis-gauche *Rotational Isomerism.*—The carbonyl stretching frequencies and the corresponding apparent molar absorptivities, measured in n-hexane, carbon tetrachloride, and chloroform, for some α-substituted acetones (2)—(9) and pentan-2-one (1), included for comparison, are shown in Table 1. It may be observed that, except the last compound, which exhibits one carbonyl band and methylthioacetone (7), for which a triplet is observed, the other substituted ketones (2)—(6), (8), and (9) show two superimposed carbonyl bands. As already reported[11,13] the solvent effect on the intensities of these two bands indicates that there is a conformational equilibrium between two rotamers and an absence of Fermi resonance. Thus, as previously,[11,13] it may be assumed that the higher frequency band corresponds to the *cis*- (I) and the lower frequency band to the *gauche*-conformer (II).



(I) (II)

In the case of the methylthioacetone (7), the lower frequency component is intensified as the solvent polarity increases, showing rather similar behaviour to that of 2-methylthiocyclohexanone.[4] This solvent effect seems to suggest that besides the conformational isomerism, Fermi resonance between the carbonyl stretching frequency of one conformer and either a combination band or an overtone of vibrational modes of lower frequencies may occur.

Due to the impossibility of determining the apparent molar absorptivities of the pure *cis*- and *gauche*-rotamers, their relative concentrations in the equilibrium mixture were estimated from the ratio of the apparent molar absorptivities at the absorption maxima of the two components of the carbonyl band ($\varepsilon_c/\varepsilon_g$), assuming as an approximation equality of the molar absorptivity of the two rotamers (see Table 1). The values of $\varepsilon_c/\varepsilon_g$ obtained in chloroform follow the order: $F \sim O > N > Cl \sim Br > S > I$. This order is similar to that reported for the 2-halogenocyclohexanones,[14] in which the equatorial/axial ratio was a maximum for the fluoro- and a minimum for the iodo-substituted compounds. By analogy with those compounds, the *cis*/*gauche* ratios for the α-hetero-acetones, in chloroform, were compared with the corresponding C–X bond polarizabilities listed in Table 2. It may be observed that the progressive decrease of the *cis*/*gauche* ratio, going from fluoro- (2) to iodo-acetone (9), is followed by an increase of the C–X bond polarizability. Actually, a correlation between $\log \varepsilon_c/\varepsilon_g$† and C–X bond polarizability yielded equation (1) (Figure 1A).

$$\log \varepsilon_c/\varepsilon_g = -0.23\,\bar{\alpha} + 0.39 \qquad (1)$$
$$(n\ 6;\ r\ 0.988;\ s\ 0.08)$$

This result is analogous to that for the 2-halogenocyclohexanones, for which a dipolar hyperconjugative structure has been proposed[14] to account for the stability of the axial

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† $\log \varepsilon_c/\varepsilon_g$ is roughly proportional to ΔG of the two rotamers, for $\Delta G = -RT\ln C_c/C_g$ and $\varepsilon_c/\varepsilon_g \sim C_c/C_g$.

Table 1. Frequencies and intensities [a] of the carbonyl stretching bands in the i.r. spectra of α-monosubstituted acetones XCH_2COMe

		$n-C_6H_{14}$			CCl_4			$CHCl_3$		
Compd.	X	ν/cm^{-1}	ε/l mol^{-1} cm^{-1}	$\varepsilon_c/\varepsilon_g$ [b]	ν/cm^{-1}	ε/l mol^{-1} cm^{-1}	$\varepsilon_c/\varepsilon_g$	ν/cm^{-1}	ε/l mol^{-1} cm^{-1}	$\varepsilon_c/\varepsilon_g$
(1)	Et [c]	1 726	360		1 720	421		1 711	370	
(2)	F	1 751	20	0.07 [e]	1 748	30	0.14 [e]	1 738	207	1.81 [e]
		1 737	270		1 732	216		1 722	115	
(3)	MeO	1 742	47	0.19	1 738	77	0.29	1 731	274	1.86
		1 729	240		1 724	265		1 716	146	
(4)	Me_2N	1 737	80	0.29	1 732	104	0.36	1 725	263	1.57
		1 722	273		1 717	285		1 710	167	
(5)	Cl	1 755	43	0.22	1 751	65	0.28	1 745	100	0.53
		1 729	195		1 723	235		1 719	189	
(6)	Br	1 748	47	0.18	1 743	70	0.23	1 737	121	0.47
		1 723	260		1 719	305		1 714	260	
(7)	MeS [d]	1 736	56		1 730	56		1 732	40	
		1 717	240		1 714	245		1 712	168	
		1 706	124		1 709	172		1 703	296	
(8)	EtS	1 735	22	0.07	1 730	32	0.09	1 725	74	0.23
		1 714	304		1 709	360		1 701	322	
(9)	I	1 740	24	0.07	1 734	40	0.09	1 727	48	0.12
		1 718	350		1 713	443		1 707	387	

[a] Expressed by ε, the apparent molar absorptivity. [b] Subscripts c and g indicate *cis*- and *gauche*-rotamers, respectively. [c] Parent compound. [d] The triplet was not graphically separate, and the apparent molar absorptivities were estimated from the absorption maxima of the triplet's components. [e] ε *trans* Instead of ε_g.

Table 2. Taft's inductive (σ_I) parameters,[a] mean polarizabilities ($\bar{\alpha}$),[b] and bond and group moments (μ_b, μ_g) [c]

Group	σ_I	$\bar{\alpha}$/Å^3	$10\mu_b$ (e.s.u.)	$10\mu_g$ (e.s.u.)
F	0.51	0.67	1.41	1.92
OMe	0.26	0.60	0.74	1.22
NMe_2	0.05	0.65	0.22	
Cl	0.47	2.53	1.46	2.05
Br	0.45	3.61	1.38	1.9
SEt	0.19		0.9	
I	0.39	5.40	1.19	1.87

[a] J. March, ' Advanced Organic Chemistry,' McGraw-Hill, Kogashuga, Tokyo, 1977, 2nd. edn., p. 256; [b] $\bar{\alpha}$ refers to the carbon–heteroatom bonds and were taken from R. J. W. Le Fèvre, *Adv. Phys. Org. Chem.*, 1965, 3, p. 50; [c] C. P. Smyth, ' Dielectric Behaviour and Structure,' McGraw-Hill, New York, 1965, pp. 243 and 244.

conformers with a C–X bond of increasing polarizability. It seems reasonable to suggest that in the case of the heteroacetones the enhancement of C–X bond polarizability can be correlated with an increasing contribution of the dipolar hyperconjugative structure (III). Thus, the hyperconjugative interaction between σ_{C-X} and π_{CO} may be responsible for the increased stabilization of the *gauche*-rotamers of the heteroacetones in chloroform, on going from fluoro- (2) to iodoacetone (9) (Table 1). It is noteworthy that a hyperconjugative interaction has been also proposed,[15] from photoelectron spectroscopy studies, as being responsible for the predominance of the *gauche*-conformers in some hetero-substituted allylic systems.

Some additional information is obtained from literature data of the microwave spectroscopy [16] and dipole moment [17] measurements which show that there is a progressive decrease in the dihedral angle of the *gauche*-rotamer on going from fluoro- to chloro- and bromo-acetone. Thus, it is 180° for fluoroacetone in the vapour state, and 130° and 120° for chloro- and bromo-acetone, respectively, in carbon tetrachloride. It is well known [18] that the decrease of the dihedral angle (ϕ) between the carbonyl group and the C–X bond (Figure 2) leads to a larger overlap between π_{CO} and σ_{C-X} orbitals.

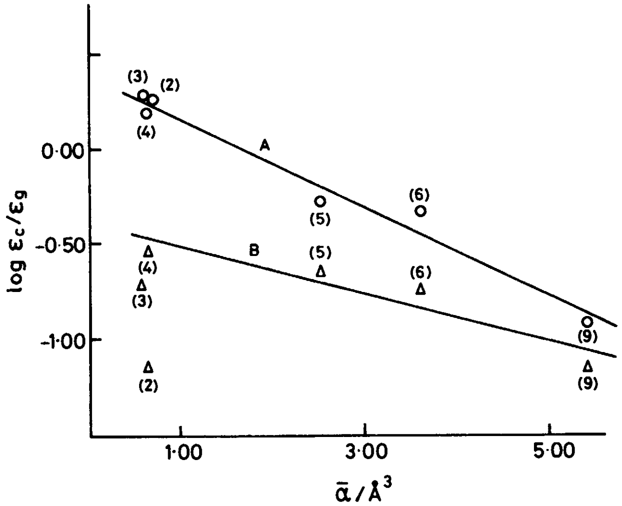
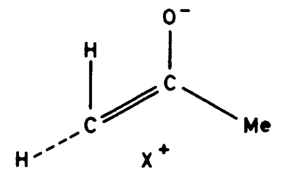


Figure 1. Plot of the log of the *cis*/*gauche* ratio, estimated from i.r. data in chloroform, A, and in n-hexane, B, against the C–X bond polarizability, for the α-monosubstituted acetones (2)—(6) and (9) (A, *r* 0.988), (B, *r* 0.942)

However, it may be observed (Table 1) that in less polar solvents, such as n-hexane and carbon tetrachloride, a decrease of the *cis*/*gauche* ratio occurs on going from dimethylaminoacetone (4) not only down to iodoacetone (9), but also up to fluoroacetone (2). This is an unexpected result since owing to the low values of the C–X polarizabilities for compounds (2)—(4) an increase of the *cis*/*gauche* ratio should occur. The correlation between log $\varepsilon_c/\varepsilon_g$ in n-hexane against the C–X bond polarizability (Figure 1B) clearly illustrates this abnormal behaviour as, while for compounds (4)—(9) the data fall on a straight line, those for (2) and (3) depart progressively from



(III)

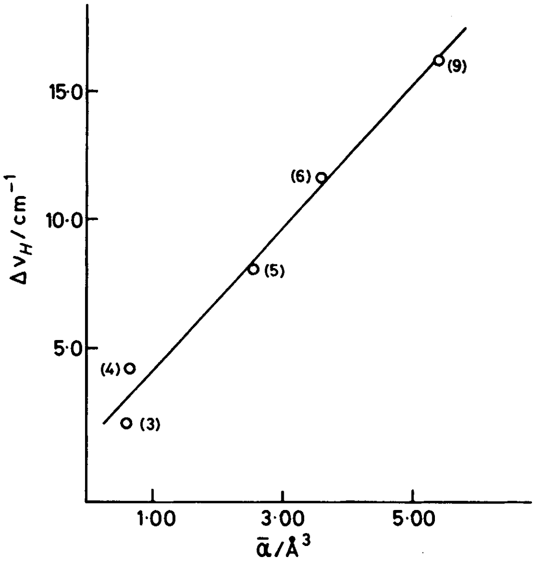


Figure 2. Plot of the computed carbonyl frequency shifts for the α-monosubstituted acetones (3)—(6) and (9), induced by the hyperconjugative effect, against the mean polarizability values of the carbon–heteroatom bonds (*r* 0.992)

this line. The low values for the latter compounds may be explained considering the corresponding C–X bond moments (or the group moments) (μ_b and μ_g, Table 2). In fact, they progressively increase from the C–N to C–F bond and, therefore, may lead to an electrostatic repulsive interaction between C=O and C–X dipoles (field effect), destabilizing the *cis*-conformation. This effect, though still present, should be weaker in chloroform due to the solvation effect and, consequently, the polarizability of the C–X bond would become the predominant factor responsible for the order of the *cis*/*gauche* ratio.

Carbonyl Stretching Frequency Shifts.—Table 3 shows the frequency shifts (Δν) for the *cis*- and *gauche*-rotamers of the hetero-ketones (2)—(6), (8), and (9), in comparison with those of pentan-2-one (1), in carbon tetrachloride. It may be observed that the Δν values for the *cis*-conformers are positive. It is noteworthy that Bellamy and Williams[6] appointed, without excluding the possibility of the inductive effect, the field effect as the major factor responsible for the positive $\Delta\nu_{CO}$ values in the *cis*-conformers of the halogeno-acetones. The shifts of the *cis*-conformer carbonyl stretching bands to higher frequencies for compounds (2)—(9) (Table 3) roughly follow the σ_I inductive parameter of the substituents (*r* 0.818), in close analogy to what has been observed for the ω-hetero-substituted acetophenones.[19] This indicates that the inductive effect is not the only one responsible for the increase of the carbonyl group frequency and that the field effect should be also operating. Therefore, the inductive (I_σ) and the field (*F*) effects are of greatest significance for the *cis*-conformers. It seems reasonable to suggest that the larger the combined effect of the substituents' polar effects ($I_\sigma + F$), the larger the carbonyl double bond character will be, and this will result in a larger force constant and in a corresponding higher stretching frequency.

Table 3. Frequency shifts for the *cis* ($\Delta\nu_c$) and *gauche* ($\Delta\nu_g$) rotamers of α-monosubstituted acetones[a] in CCl_4; computed carbonyl frequency shifts[b] induced by the inductive ($\Delta\nu_I$), field ($\Delta\nu_F$), and hyperconjugative ($\Delta\nu_H$) effects of the substituents

Compd.	$\Delta\nu_c$/cm^{-1}	$\Delta\nu_g$/cm^{-1}	$\Delta\nu_I$/cm^{-1}	$\Delta\nu_F$/cm^{-1}	$\Delta\nu_H$/cm^{-1}
(2)	+28	+12	12.0	16.0	0
(3)	+18	+4	6.1	11.9	−2.1
(4)	+12	−3	1.2	10.8	−4.2
(5)	+31	+3	11.1	19.9	−8.1
(6)	+23	−1	10.6	12.4	−11.6
(8)	+10	−11	4.5	5.5	−15.5
(9)	+14	−7	9.2	4.8	−16.2

[a] $\Delta\nu_c$ and $\Delta\nu_g$ refer to the difference: ν(substituted acetone) − ν(parent compound), for the *cis*- and *gauche*-rotamers, respectively. [b] See text.

The shifts of the carbonyl stretching band of the *gauche*-conformers ($\Delta\nu_g$) for compounds (2)—(6), (8), and (9) in relation to the parent unsubstituted ketone (1), in carbon tetrachloride, are within a +12 to −11 cm^{-1} range (Table 3). These shifts cannot be due to the inductive effect alone as it should lead to the positive values only. However, the frequency shifts correlates well with the substituents' inductive parameters (σ_I) and the polarizability of the C–X bonds ($\bar{\alpha}$), as shown in equation (2).

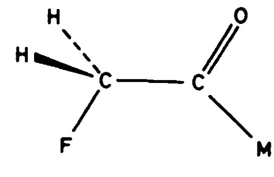
$$\Delta\nu_g = -3.3\bar{\alpha} + 30.7\sigma_I - 2.3 \qquad (2)$$
$$(n\ 6;\ r\ 0.993;\ s\ 1.0\ \text{cm}^{-1})$$

This indicates that the frequency shifts of the *gauche*-conformers depend upon both substituent parameters, the inductive one, which has an increasing effect and the polarizability of the C–X bond parameter, which has a decreasing effect.

As in the case of the *cis*/*gauche* ratio (see above) the increase of the polarizability of the C–X bond favours a hyperconjugative effect. It seems reasonable to admit, now, that the decreasing effect on the carbonyl frequency of the *gauche*-conformer by the increase in polarizability of the C–X bond may be due to the hyperconjugative interaction which, as shown by structure (III), would lead to a decrease of the force constant of the carbonyl group.

It may be argued that the shift of ν_{CO} to lower frequencies could be due to some vibrational effect. In fact, on going from C–F to C–I bonds there is a decrease in the C–X oscillator stretching frequency (ν_{C-F} *ca.* 1 100 cm^{-1} to ν_{C-I} *ca.* 500 cm^{-1}).[20] However, it seems reasonable to admit that the frequency shifts range of *ca.* 23 cm^{-1} from fluoro- (2) to iodo-acetone (9) cannot be explained, or only to a minimal extent, by the C=O and C–X oscillators' mechanical coupling changes, for they are insulated by a carbon–carbon single bond and their frequencies are far apart (*ca.* 1 730 and 1 100—500 cm^{-1}).

Therefore, it is reasonable to suggest that two effects, hyperconjugative and inductive, are the most important influence on the *gauche*-conformers of the hetero-acetones, decreasing and increasing ν_{CO}, respectively. Thus, the sign of $\Delta\nu_g$ would depend on the predominance of one of these effects. However, in the case of fluoroacetone, whose geometry in the vapour phase is *trans* (φ 180°)[16] [structure (IV)], the hyperconjugative interaction should probably be neg-



(IV)

ligible. Therefore, it can be assumed that the carbonyl frequency increase for this compound ($\Delta\nu_g$ +12 cm^{-1}; Table 3), in the *trans*-form, is due only to the inductive effect of fluorine (σ_I 0.51) (Table 2).

Consequently, the carbonyl frequency shifts of the α-substituted acetones (3)—(9), induced by the inductive effect alone ($\Delta\nu_I$; Table 3), may be computed from the substituents' inductive parameters (Table 2) by assuming that there is a simple proportionality between them. On the other hand, as the frequency shifts of the *cis*- ($\Delta\nu_c$) and *gauche*- ($\Delta\nu_g$) rotamers result from the sum of the inductive and field effects ($\Delta\nu_I + \Delta\nu_F$) and of the inductive and hyperconjugative effects ($\Delta\nu_I + \Delta\nu_H$), respectively, $\Delta\nu_F$ and $\Delta\nu_H$ may be determined once the $\Delta\nu_I$ values are known. Table 3 shows that the carbonyl frequency shifts, induced by the hyperconjugative effect ($\Delta\nu_H$), for compounds (3)—(9) are negative and that their absolute values increase with the increase in the C−X bond polarizability. Actually, both variables are well correlated, as shown by equation (3) and Figure 2.

$$\Delta\nu_H = 2.75\bar{\alpha} + 1.39 \qquad (3)$$

$$(n\ 5;\ r\ 0.992;\ s\ 0.8\ \text{cm}^{-1})$$

Inspection of the data in Table 3 indicates that the positive carbonyl frequency shifts of the *gauche*-conformers of compounds (3) and (5) are due to the predominance of the inductive over the hyperconjugative effect, while the negative frequency shifts of compounds (4), (6), (8), and (9) result from the predominance of the hyperconjugative over the inductive effect.

The data in Table 3 also show that the carbonyl frequency shifts due to the field effect ($\Delta\nu_F$) are positive in sign and that they follow approximately the C−X bond moments (or group moments) (μ_b and μ_g; Table 2). It is also possible to observe that the frequency shifts, induced by the field effect ($\Delta\nu_F$), predominate over the inductive effect ($\Delta\nu_I$) for the *cis*-conformers of the hetero-acetones (2)—(8), iodoacetone (9) being an exception.

Carbonyl n $\longrightarrow$ π* *Transition Energies and Intensities*.—Table 4 shows the $n \longrightarrow \pi^*$ transition energies, as well as the corresponding band intensities for compounds (1)—(9), in n-hexane. The $n \longrightarrow \pi^*$ transition band displays a bathochromic shift and hyperchromic effect, which progressively increase, on going from fluoro- (2) to iodo-acetone (9).

Allinger *et al.*[21] have found by MO calculations that the red shift, induced in the cyclohexanone $n \longrightarrow \pi^*$ transition by axial halogen substituents, is due to an interaction between the carbonyl π^*_{CO} level and relatively low-lying σ^*_{C-X} orbital. The mixing of these two orbitals should move the π^*_{CO} level to lower energy, thus producing the observed red-shift. It has been suggested by Yates[12] that there is a conformational similarity between the *cis*- and *gauche*-rotamers of the α-hetero-substituted acetones and the equatorial and axial conformers of the α-hetero-substituted cyclohexanones, respectively. It has also been reported[18] that EH and *ab initio* calculations for α-aminoacetone indicated that the antibonding σ^*_{C-N} orbital mixes into the lower lying π^*_{CO} in a bonding mode for ϕ *ca.* 90° for the amino-group and that the $n \longrightarrow \pi^*$ transition is extremely sensitive to the angle of rotation about the C−N bond. These reports, added to our evidence for the hyperconjugative interaction in the ground-state of the hetero-acetones, suggest that the bathochromic shift and hyperchromic effect of the $n \longrightarrow \pi^*$ transition is due to the hyperconjugative interaction between the π^*_{CO} and σ^*_{C-X} orbitals, which operates in the *gauche*-rotamers, whereas the *cis*-rotamers do not exhibit any significant effect. As a consequence, the observed modification of the $n \longrightarrow \pi^*$ bands on going from fluoro- (2) to iodo-acetone (9) would be due to the progressive increase of the stabilization of the π^*_{CO} orbital, taking into consideration the fact that in n-hexane solutions the *gauche*-form is dominant in all cases (see Table 1).

Table 4. U.v. data for the carbonyl $n \longrightarrow \pi^*$ transition of the α-monosubstituted acetones (1)—(9); [a] and σ_{C-X} vertical ionization potentials (IP)

Compd.	$\lambda_{max.}$/nm	$\bar{\nu}_{max.}$ [b]/cm^{-1}	log ε	IP/eV
(1)	279	(35 842)	1.20	−12.6 [d]
(2)	280	(35 714)	1.10	−16.2 [e]
(3)	283	(35 335)	1.23	−15.1 [f]
(4)	291	(34 364)	1.45	−14.4 [g]
(5)	291	(34 364)	1.56	−14.4 [e]
(6)	300	(33 333)	2.05	−13.5 [e]
(7)	302	(33 112)	2.33	−13.7 [f]
(8)	301	(33 222)	2.35	
(9)	306	(32 679) [c]	2.50	−12.5 [e]

[a] In n-hexane. [b] Computed values from $1/\lambda_{max.}$. [c] Shoulder. [d] Refers to π_{CO} orbital (W. C. Tam, D. Yee, and C. E. Brion, *J. Electron Spectrosc. Relat. Phenom.*, 1974, **4**, 77). [e] Ref. 15. [f] H. Ozata, H. Onizuka, Y. Nikei, and H. Yamada, *Bull. Chem. Soc. Jpn.*, 1973, **46**, 3036. [g] K. Kimura and K. Osafune, *Mol. Phys.*, 1975, **29**, 1073.

Some additional evidence, which reinforces this hypothesis, may be added. Thus, the $n \longrightarrow \pi^*$ transition energies do not correlate with the substituents' σ inductive parameter although it is well known that σ_I affects both the energy level of the carbonyl oxygen lone pair ($n_{O(CO)}$) and the carbonyl antibonding π orbital (π^*_{CO}). However, it may be seen from the data in Table 4 that the decrease of the $n \longrightarrow \pi^*$ transition energy, going from fluoro- (2) to iodo-acetone (9), is accompanied by a decrease of the vertical ionization potential of the σ_{C-X} molecular orbital of the corresponding hetero-substituted methane (r 0.965). This correlationship is in accord with the rules of the molecular orbital simple perturbation theory,[22] which indicates that the lower ionization potential of the σ_{C-X} molecular orbital, the closer will be the energy levels of the unperturbed σ_{C-X} and $\pi_{C=O}$ bonding molecular orbitals. Therefore, larger interactions between these orbitals will occur, resulting in a progressive destabilization (δE) of the π_{CO} orbital energy level. It is well known[18] that the smaller the bonding character of the σ_{C-X} orbital, the smaller will be the antibonding character of the σ^*_{C-X} orbital and, therefore, the closer also will be the energy levels of the σ^*_{C-X} and π^*_{C-O}. This should result in a larger interaction between the energy levels of both orbitals, leading to a stabilization of the π^*_{C-O} orbital (δE^*) and, thus, to bathochromic shift of the $n \longrightarrow \pi^*$ transition (Figure 3).

It may be seen in the Table 4 that the $n \longrightarrow \pi^*$ transition energy for fluoroacetone (2) is almost the same as for the unsubstituted ketone (1) and a small hypsochromic effect is observed. This is not in accord with the i.r. data for the same compound in n-hexane (Table 1), which indicate that the carbon–fluorine bond remains *ca.* 93% in the form of the *gauche*-rotamer. By analogy with the axial conformer of 4-t-

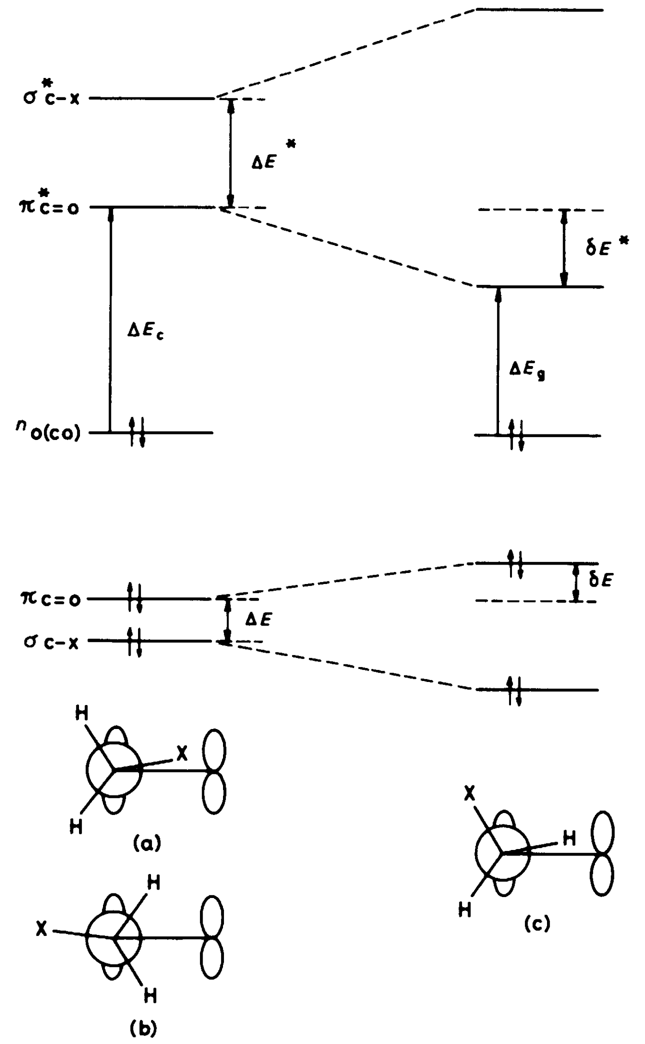


Figure 3. Qualitative energy level diagram, for the σ_{C-X} and $\pi_{C=O}$ orbitals of the *cis*- (a), *trans*- (b), and *gauche*- (c) rotamers of the α-monosubstituted acetones. It shows the hyperconjugative interactions between these orbitals in the *gauche*-rotamers, in the ground and excited states, and the origin of the corresponding $n \longrightarrow \pi^*$ red-shift

butyl-2-fluorocyclohexanone[23] a slight bathochromic shift and hyperchromic effect of the $n \longrightarrow \pi^*$ transition should have been observed. However, the u.v. results for fluoroacetone are in accord with $\Delta\nu_H = 0$ for this compound and, thus, reinforce the hypothesis that the dihedral angle between the C=O and C–F bonds is nearly 180° (*trans*-conformation), in n-hexane solution, preventing hyperconjugative interactions from occurring.

The dependence of the hyperconjugative interaction in the ground and excited states on the *cis*- or *trans*- and *gauche*-conformations are also shown in Figure 3. The energy diagram clearly indicates that the hyperconjugative interaction occurs in the *gauche*-rotamer, where ϕ is *ca.* 120° (*i.e.* close to 90°) and it is negligible for the *cis*- or *trans*-rotamer, where ϕ is *ca.* 0 or 180°, respectively.

Final evidence for the occurrence of a hyperconjugative interaction in the excited state of the hetero-acetones is given by the fact that the $n \longrightarrow \pi^*$ transitions are correlated reasonably well with the carbonyl stretching frequency shifts induced by the hyperconjugative interaction ($\Delta\nu_H$), as shown by equation (4) and Figure 4.

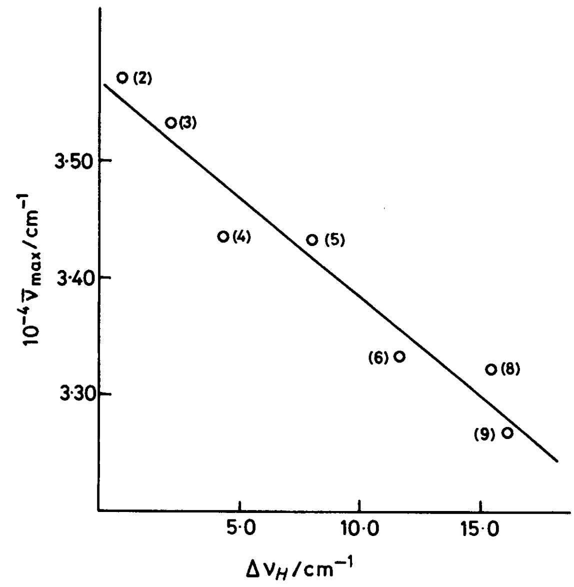


Figure 4. Plot of the u.v. frequencies for the $n \longrightarrow \pi^*$ carbonyl transition, in n-hexane, against the i.r. carbonyl frequency shifts induced by the hyperconjugative effect, for the α-monosubstituted acetones (2)—(6), (8), and (9) (*r* 0.968)

$$\nu_{max.} = -169\ \Delta\nu_H + 36\,541 \qquad (4)$$

$$(n\ 7;\ r\ 0.968;\ s\ 307\ \text{cm}^{-1})$$

The estimation of $\Delta\nu_H$ showed that a hyperconjugative interaction occurs not only in the *gauche*-conformers of compounds such as the sulphur- and iodo-substituted acetones with negative $\Delta\nu_g$ values (Table 3), but also, quite strongly, in bromo- and chloro-substituted acetones, in which it is masked by a strong inductive effect. This is now confirmed by the u.v. data.

Experimental

Materials.—All solvents for spectrometric measurements were spectrograde and were used without further purification. Commercial pentan-2-one and chloroacetone were purified as described elsewhere.[24] Commercial fluoroacetone was used without further purification. The following compounds were prepared by literature procedures: methoxy-,[25] dimethylamino-,[26] bromo-,[27] methylthio-,[28] ethylthio-,[29] and iodoacetone.[30] All compounds were analysed by g.l.c. to assess their purity.

I.r. Measurements.—I.r. spectra were recorded on a Perkin-Elmer model 283 grating spectrometer at room temperature. The spectral slit width was 2.0 cm^{-1} in the carbonyl region. The carbonyl stretching frequencies were measured, in the transmittance scale mode, for 1.0—2.0 × 10^{-2}M solutions in n-hexane, carbon tetrachloride, and chloroform, using a pair of 1.00 mm sodium chloride matched cells. Further dilution did not affect the spectra markedly. The spectra were calibrated with polystyrene at 1601.4 cm^{-1} and the carbonyl frequencies, for the more and less intense components of the doublet, are accurate to ± 0.5 and ± 1 cm^{-1}, respectively. The *cis*/*gauche* ratios of the separate bands[31] were obtained from spectra recorded in the 1 800—1 600 cm^{-1} region, in the absorbance scale mode. The estimated errors of the relative apparent molar absorptivities are within 10%.

U.v. Measurements.—U.v. spectra were recorded on a Beckman model DK-2A spectrophometer. Quartz matched cells of 1.00 cm pathway and spectrograde n-hexane were employed. For each substance, the spectra of three solutions of different concentrations (10^{-4}—10^{-2}M) were recorded, and $\varepsilon_{max.}$ for the bands assigned to the $n \longrightarrow \pi^*$ transition was estimated by linear regression of the absorbance against concentration. All spectra were run at room temperature (25 ± 1 °C).

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