

Multi-Conformational Compounds with Two Absorbing Groups

IV. 2-Fluoroacetaldehyde and 2-Fluorocarbonyl Compounds*

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The series of rotational isomers obtainable from 2-fluoroacetaldehyde has been studied by the CNDO/2 method and by an SCF-CI technique. Correlations concerning relative stabilities within the series, dipole moments, spectra and the transmission of electronic effects, are presented.

Die Reihe von Rotationsisomeren, die man vom 2-Fluoroacetaldehyd gewinnen kann, wurde mit Hilfe der CNDO/2-Methode und einer SCF-CI-Technik untersucht. Zusammenhänge, welche die relativen Stabilitäten innerhalb der Reihe sowie die Dipolmomente, Spektren und die Leitung elektronischer Effekte betreffen, werden dargelegt.

On étudie la série des isomères rotationnels concevables pour le fluoro-2 acétaldehyde, par la méthode CNDO/2 et par une technique SCF-CI. Les calculs permettent d'établir des corrélations entre les stabilités relatives, les moments dipolaires, les spectres et la transmission des effets électroniques dans cette série.

1. Introduction

Jones and his co-workers showed in 1952 [2] that introduction of an equatorial bromine atom next to the keto-group of chair-form cyclohexanone (Fig. 1, $x = \text{Br}$) produces a substantial shift, to higher frequency, of the carbonyl stretching vibration; only little displacement was observed on axial substitution (Fig. 2, $x = \text{Br}$). It has been shown since that the magnitude of the effect depends on the dihedral angle between the $\text{O}=\text{C}-\text{C}$ and $\text{C}-\text{C}-\text{X}$ planes, and that it is not limited to six-membered rings [3, 4] or to the bromine atom, but is general for

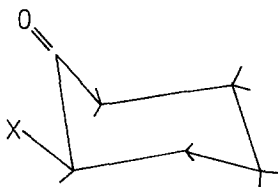


Fig. 1

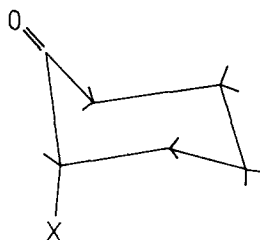


Fig. 2

* For part III, see Ref. [1].

α -halogeno-carbonyl groups [5–7]. Another property of α -bromoketones, reported in 1954 [8], is that their carbonyl $n \rightarrow \pi^*$ absorption band shifts to longer wavelengths when the substitution is axial, but is almost unaffected when it is equatorial. Again, the effect is produced, though to a varying degree, by all halogens [9] and also by some other groups which carry lone-pair electrons [10, 11]. A third peculiarity of haloketones is the unusually large interaction of their C–X and C=O dipoles [12, 13].

Jones discounted “electromeric” interaction (transmitted from C–X to C=O through C–C) as reason for the IR equatorial shifts, and proposed a Coulombic field effect of the C–X dipole on the C=O bond; this remains the current opinion [14]. The consequences of such an interaction were studied, by classical methods, by Cantacuzène [15, 16]; subsequently, a quantumchemical comparison of acetaldehyde and chloroacetaldehyde has been carried out [17]. The red $n \rightarrow \pi^*$ shift, observed in axial substitution, was first interpreted [5] as the outcome of electron-donation from the C–X bond into the π^* orbital; later publications [18, 19] suggested that π^* interacted with either the lowest empty halogen orbital or the virtual σ^* orbital related to the C–X bond. The phenomenon has also been approached in terms of perturbation theory [20]. None of these studies, however, considered the complete series of rotational isomers, the discussions being limited to the axial and equatorial conformations. The electronic structure and expected physical properties of other possible conformations remain unstudied.

The aim of the present paper is to investigate how far one can interpret the properties of α -halocarbonyl compounds by application of those LCAO schemes most used now in such studies, namely the CNDO/2 all-valence-electron method [21, 22], and the SCF–CI π -electronic approach. We limit ourselves here to fluoro-ketones. Some experimental data are summarized in Table 1, where the dissimilarity in properties of axial and equatorial structures is very clear. We note, in anticipation of the ensuing discussion, that it is not easy to envisage molecules in which the C=O and C–F bonds lie in an unambiguous *anti*-conformation.

For the CNDO/2 studies we consider as model the molecule of fluoro-acetaldehyde, for which the following geometrical parameters are assumed: $r_{\text{CO}} = 1.215$, $r_{\text{CC}} = 1.507$, $r_{\text{CF}} = 1.36$, $r_{\text{CH}} = 1.08$, $\sphericalangle \text{OCC} = 120^\circ$, other angles 109.5° . In Fig. 3 bold-face lines indicate an initial *anti*-situation, $\Theta = 0^\circ$, with coplanar C=O and C–F bonds. Next, the $-\text{CH}_2\text{F}$ group is gradually rotated around C_2C_3 , the degree of rotation being defined by the angle Θ between the plane xy and the projection of C_3F_4 on a plane, passing through C_3 and perpendicular to xy and to C_2C_3 ; the dihedral angle is $(180^\circ - \Theta)$. Thus one proceeds, through the perpendicular rotamer of $\Theta = 90^\circ$, where F attains its highest z -value, to the *syn*-situation, $\Theta = 180^\circ$, depicted in Fig. 3 by dashed lines. The series of *rotamers*, defined by Θ , defines in turn a series of *conformers*, of which the equatorial (Fig. 1, $\Theta = 164^\circ$), axial (Fig. 2, $\Theta = 77^\circ$) and *anti* ($\Theta \sim 0$ – 10°) conformations are particularly relevant to the subsequent discussion. The CNDO/2 procedure was applied to the complete rotamer series, at steps of 10° . For the SCF-CI treatment of these rotamers, we consider the bare structure $\text{F} \dots \text{C}=\text{O}$, disregarding C_3 and all hydrogen atoms, as well as orbitals of σ and s symmetry.

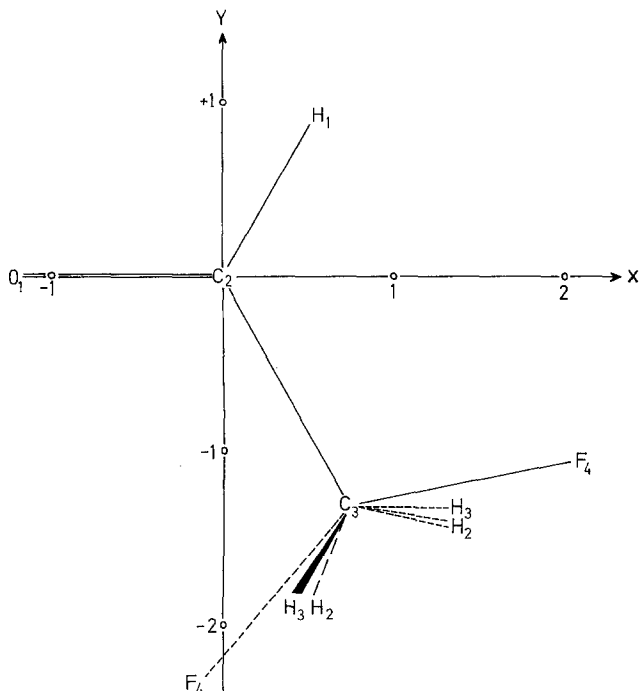


Fig. 3

Table 1

Compound	ν_{CO} (cm^{-1})	$\lambda(\text{nm})$ and ϵ	Ref
<i>trans</i> -1-Decalone	1713 (CCl_4)	290 (26, CHCl_3)	[23]
2-Fluoro (equatorial)	1737 (CCl_4)	288 (30, CHCl_3)	
2-Fluoro (axial)	1729 (CCl_4)	300 (48, EtOH)	
<i>trans</i> -2-Decalone	1713 (CCl_4)	280 (20, EtOH)	[24]
3-Fluoro (equatorial)	1740 (CCl_4)	283 (21, EtOH)	
3-Fluoro (axial)	1735 (CCl_4)	299 (19, EtOH)	
4- <i>tert</i> -Butylcyclohexanone		283 (20, EtOH)	[25]
		292 (16, C_7H_{16})	
2-Fluoro (equatorial)		284 (16, EtOH)	
		291 (15, C_7H_{16})	
2-Fluoro (axial)		299 (17, EtOH)	
		302 (19, C_7H_{16})	
Acetone	1718 (neat)		[26]
Fluoro (less polar form)	1742		[6]
Fluoro (more polar form)	1720, 1725		
Alkanals	1720–1740 (sol.)	280–310 (14–21, <i>i</i> - C_8H_{18})	[27, 28]
2-Fluoro	1735–1740 (neat)	~296, 307 (~35, C_6H_{12})	[29]

For the all-valence-electron treatment we used an appropriately modified version of the CNDO/2 program, authored by Clark and Ragle [30] and kindly supplied by the Quantum Chemistry Program Exchange. The π -electronic computation was performed by three consecutive programs evaluating, in turn, geometrical parameters, SCF-CI wave functions, then [31] dipole and transitionmoment integrals.

2. The π -Electronic Scheme

The π -electronic computation has been carried out by an extended version of our conventional scheme [1, 32]. Each rotamer was built up from three atoms, C, O, and F, of electronic configurations C (trtrtr π), O ($s^2\sigma\pi n^2$) and F ($s^2\sigma^2 n^2 n^2$), furnishing altogether five atomic orbitals of π -type symmetry: $\chi_g(2p\pi, C)$, $\chi_h(2p\pi, O)$, $\chi_H(2pn, O)$, $\chi_f(2pn, F)$ and $\chi_F(2pn, F)$. In our coordinate system (Fig. 3), χ_g , $\chi_h\epsilon z$, $\chi_H\epsilon y$ and, by choice, $\chi_F \perp z$, which also fixes χ_f . The atomic parameters, carried over from other work [32, 33], are given in Table 2. These are the bielectronic monocentric integrals, $(\mu\mu, \nu\nu)$, $(\mu\mu, \mu\mu)$ and $(\mu\nu, \nu\mu)$, where μ and ν belong to the same atom, the one-electron parameter W_μ , considered as the neutral atom VSIP [34], and the orbital exponents Z_s and Z_{eff} used, respectively, for the evaluation of overlap and Coulomb repulsion integrals [1].

For each separate conformer, we construct a Coulomb repulsion matrix Γ and the core matrix H , both of order 5. Diagonal elements $H_{\mu\mu}$ are computed from

$$H_{\mu\mu} = W_\mu - \sum_{\substack{\nu=1 \\ \nu \neq \mu}}^5 [n_\nu(\mu\mu, \nu\nu) - \frac{1}{2}(\mu\nu, \nu\mu)]$$

(subject to the ZDO assumption, unless μ and ν occur on the same atom), and the non-diagonal ones by

$$H_{\mu\nu} = -S_{\mu\nu}\beta_{\mu\nu}^0,$$

$$\beta_{\mu\nu}^0 = \frac{1}{2}(\beta_\mu^0 + \beta_\nu^0).$$

Our usual parametrization [32] yields

$$\beta_C^0 = 10.092,$$

$$\beta_O^0 = (2H_{gh}/S_{gh}) - 10.092$$

Table 2

	C	O	F
W_μ (eV)	-11.54	-17.21 (π) -14.75 (n)	-18.06
Z_s	3.25	4.55	5.20
Z_{eff}	1.854	2.346	2.786
$(\mu\mu, \mu\mu)$ (eV)	9.87	12.49	14.83
$(\mu\mu, \nu\nu)$ (eV)	-	11.14	13.23
$(\mu\nu, \nu\mu)$ (eV)	-	0.6733	0.7997

and β_F^0 is chosen so that $\beta_C^0 : \beta_O^0 : \beta_F^0$ be proportional to the corresponding CNDO triad [22], namely,

$$\beta_F^0 = 1.8 \beta_O^0 - 8.0736.$$

From Γ and trial molecular orbitals we form the bielectronic matrix G , under the aforementioned limitations on $(\mu\nu, \nu\mu)$, then the Hartree-Fock matrix, $F = H + G$. Repeated diagonalization and reconstruction of F leads to SCF molecular orbitals φ_i , which permit a CI treatment, based upon the ground electronic configuration $\Psi_1(\varphi_2^2\varphi_3^2\varphi_4^2\varphi_5^2)$ and the mono-excited

$$\Psi_2(n \rightarrow \pi^*, \varphi_1\varphi_2\varphi_3^2\varphi_4^2\varphi_5^2), \Psi_3(\pi \rightarrow \pi^*, \varphi_1\varphi_2^2\varphi_3\varphi_4^2\varphi_5^2), \\ \Psi_4(f \rightarrow \pi^*, \varphi_1\varphi_2^2\varphi_3\varphi_4\varphi_5^2) \text{ and } \Psi_5(F \rightarrow \pi^*, \varphi_1\varphi_2^2\varphi_3^2\varphi_4\varphi_5).$$

To simplify the programming, (fF, Ff) was neglected when preceded by a small numerical coefficient; this caused a minor deviation from Brillouin's condition and a slight ground-state depression (not exceeding 10^{-4} eV), which were disregarded.

Preliminary calculations revealed at this point that the scheme was not sensitive to the rotation angle Θ . This led us to adopt the "variable- $H_{\mu\mu}$ " technique, which can be viewed as a second-order correction [35] or as a means to compensate for neglect of penetration integrals [36]; we prefer to consider it as the outcome of the π -inductive effect exerted by the fluorine atom. The effect was first studied by Murrell and his school [37, 38], applied by Clark and Elmsley [39] and also used in qualitative discussions of organic-chemical phenomena [40]. By this approach, a substituent carrying lone-pair electrons affects the π -system not only through its mesomeric interaction, but also by two additional factors: a field effect, probably of minor importance in the fluorine case, and a short-range overlap-dependent mechanism, which is a consequence of the Pauli exclusion principle. Following the application to the fluorobenzene molecule [39], we have to consider the influence of σ -polarization upon the π -system, and to assign positive increments (π -inductive parameter) to $H_{\mu\mu}$.

In our fluoroketone studies, σ -bonds, and therefore, σ -effects, are excluded, except for the C—O pair, where we assume all factors as implicitly included in the parametrization. As for the π -inductive parameter, it is certainly negligibly small for the F...O pair, and nil for $\chi_g \dots \chi_F$, which are orthogonal by construction. This leaves us with $\chi_g \dots \chi_f$, equidistant in all rotamers, but of varying overlap, maximal at $\omega = 0^\circ$, minimal at $\omega = 90^\circ$, where ω is the angle between χ_f and $\chi_g \varepsilon Z$. Thus, for $\mu = g, f$, $H_{\mu\mu}$ is replaced by

$$H' = H + A \cos \omega$$

where A was taken equal to 0.5 eV.

3. All-Valence-Electron Results

Let us denote occupied MO's by φ_{+1} (HOMO), φ_{+2} , etc., and the LVMO by φ_{-1} . For formaldehyde, CNDO/2 indicates the established symmetries for $\varphi_{-1} \varepsilon B_1(\pi^*)$, $\varphi_{+1} \varepsilon B_2(n)$ and $\varphi_{+2} \varepsilon B_1(\pi)$, while for the next two orbitals it yields

$\varphi_{+3}\varepsilon A_1$, $\varphi_{+4}\varepsilon B_2$, which is controversial, some authors [40] advocating the inverse ordering. In fluoroacetaldehyde one finds that φ_{-1} and φ_{+1} retain the local symmetry (B_1 and B_2) at the C=O group, so that the first electronic transition is certainly $n \rightarrow \pi^*$. On the other hand, the structure of φ_{+2} and φ_{+3} is angle-dependent: at $\Theta = 0^\circ$ and $\Theta = 180^\circ$, φ_{+2} is predominantly of π -, φ_{+3} of σ -symmetry, the opposite being true at around 90° . This suggests that the second transition $\varphi_{+2} \rightarrow \varphi_{-1}$ (unstudied as yet) is $A_1(\pi \rightarrow \pi^*)$ for the equatorial, $B_1(\sigma \rightarrow \pi^*)$ for the axial conformer. It does not follow that the transition "disappears" in the non-planar rotamers: not only is $\varphi_{+2} \rightarrow \varphi_{-1}$ allowed throughout, but it may also be overtaken, at $\Theta \sim 90^\circ$, by $\varphi_{+3} \rightarrow \varphi_{-1}$. Let us remark, though, that there is nothing in our π -electronic results to substantiate such an eventuality.

Calculated $n \rightarrow \pi^*$ transition energies are too high (~ 5.5 eV instead of ~ 4.5 eV), which is not unexpected [42]. The important result, however, is that the highest values occur at $\Theta = 0^\circ$ and $\Theta = 180^\circ$, and a minimal value at 100° . This is not only in line with the bathochromic shift attending axial substitution, but also indicates that *anti*-rotamers, which have not been studied, should be similar, in this respect, to the equatorial conformer. This also follows from our π -electron calculations.

The *ionization potentials* of formaldehyde, approximated as the appropriate eigenvalues (at an energy-zero of -4 eV [43]), are $I_1 = 10.63$ eV, $I_2 = 14.45$ eV, $I_3 = 16.37$ eV, in line with experiment [41]. These potentials are predicted to diverge with Θ in fluoroacetaldehyde, having values 10.11, 12.19, 14.18 eV ($\Theta = 160^\circ$, equatorial), 10.23, 12.89, 13.61 eV ($\Theta = 80^\circ$, axial), and 10.13, 12.16, 14.46 eV ($\Theta = 10^\circ$). Again, the two extreme conformations are similar to each other, and different from the perpendicular one.

Population Analysis. The CNDO/2 program provides for the construction of the charge and bond-order matrix, and also for a Mulliken population analysis [44], based on overlap-renormalized CNDO wave functions. In our case it is found that the angle-dependence of the net atomic charges is very small; oxygen, for example has $q = -0.277$ at 0° , $q = -0.256$ at 110° and $q = -0.258$ at 180° . Values for the other atoms are:

$$q(\text{C}_2) = 0.242 \pm 0.001, q(\text{C}_3) = 0.145 \pm 0.006, q(\text{F}) = -0.236 \pm 0.008,$$

$$q(\text{H}_1) = 0.020 \pm 0.009, q(\text{H}_2) = 0.053 \pm 0.005, q(\text{H}_3) = 0.044 \pm 0.013.$$

Comparing with the formaldehyde values, $q(\text{O}) = -0.255$, $q(\text{C}) = 0.225$ and $q(\text{H}) = 0.015$, we note that the CNDO method does reveal at least *some* of the changes undergone by the carbonyl group under the influence of the fluorine atom (*vide infra*).

The cited data bring to light two additional points of interest. One is that the enantiomeric protons H_2 and H_3 are actually diastereoisomeric, except at 0° , 180° and (accidentally) 30° , and should be distinguishable. The second, that the most decisive changes occur at H_3 , so that substituents on C_3 are expected to manifest long-range influences upon C=O. This is readily illustrated by comparison of ν_{CO} of the two $\text{CH}_3\text{COCH}_2\text{Cl}$ rotamers, 1726 and 1752 cm^{-1} ($\Delta = 26$) with those of $\text{CH}_3\text{COCHClCH}_3$, 1715 and 1728 cm^{-1} ($\Delta = 13$) [45], or of $(\text{CH}_3)_2\text{CHCOCH}_2\text{Cl}$, 1720 and 1740 cm^{-1} ($\Delta = 20$), with

Table 3

	μ_x	μ_y	μ_z
Equatorial			
μ_T	-3.418	-0.494	+0.254
μ_π	-3.688	+0.003	0.
μ_σ	+0.270	-0.497	+0.254
Axial			
μ_T	-1.444	-0.188	+1.313
μ_π	-3.553	+0.002	0.
μ_σ	+2.109	-0.190	+1.313
$\Theta = 10^\circ$			
μ_T	-0.594	+0.456	+0.232
μ_π	-3.692	+0.001	0.
μ_σ	+3.098	+0.455	+0.232

$(\text{CH}_3)_2\text{CHCOCHClCH}(\text{CH}_3)_2$, 1717 and 1728 cm^{-1} ($\Delta = 11$) [46]. Thus, although an alkyl at position α to the carbonyl is known to have but a slight effect on ν_{CO} , it does influence it noticeably, if there also is a halogen atom at the same position.

Overlap populations, bond orders, π -populations and π bond-orders (as given by CNDO/2), are almost independent of Θ , e. g. the C=O population is confined to the range 1.70 ± 0.01 , and likewise C-F to 0.92 ± 0.02 . This finding is therefore not in line with the suggestion [17] that C=O stretching frequencies, in substituted ketones, are population-dependent, but we cannot propose an alternative correlation: a rough calculation in which the total energy of fluoroacetaldehyde was computed as function of the C=O distance, then best-fitted by a Hooke-type potential curve, yielded force constants $3.24 \cdot 10^6$ (equatorial) and $3.26 \cdot 10^6$ dyn/cm (axial), which are obviously in the wrong order. Thus, some of the influence exerted by the fluorine on the carbonyl group is *not* accounted for by the CNDO technique.

Dipole Moments. The dipole moments of equatorial and axial 2-fluoro-4-*tert*-butylcyclohexanone are, respectively, 4.35 and 2.95 *D* [25]; the calculated values are 3.46 and 1.96 *D*, thus low by about 1 *D*. While summation of "group moments" remains the method of choice for reliable predictions, the quantumchemical results are helpful in detecting the various components of the moment. Some computed data are assembled in Table 3, where μ_T refers to the total (σ and π) moment, computed by CNDO/2, μ_π to the π -moment (Section 4), and μ_σ to the difference between these two; the coordinate system is the one given in Fig. 3.

The directional components of μ_T reveal that its main contributors are the non-symmetric bond populations at C^+O^- and C^+F^- . The non-symmetric charge distribution about O and F may be inferred from an additional datum, namely, that the primary moment accounts in all cases for only about 50% of the total moment; for example, the polarization components in the equatorial case are $\mu_x = -1.931$, $\mu_y = -0.372$ and $\mu_z = +0.088$. Comparing now μ_π with μ_σ , we see that the localization of the non-bonding electrons on F causes μ_π to be almost constant and directed as C=O, while the inductive property of the halogen, acting in the opposite direction, creates μ_σ which counteracts μ_π and lowers the

total. The resultant diminishes therefore with Θ , so that $\mu(\text{axial}) < \mu(\text{equatorial})$, and the very small value of $0.78 D$ is predicted for $\Theta = 10^\circ$ (group moment summation leads to $1.1 D$).

Relative Stabilities. As the reliability of energetic predictions, based on CNDO procedures, has been questioned [47], it is of interest to find out that computed *total* energies are lower at rotational extremes (-1702.87 eV and -1702.88 eV at $\Theta = 0^\circ$ and $\Theta = 180^\circ$, respectively) than at intermediate situations (-1702.71 eV at $90-100^\circ$). In contrast, *electronic* energies diminish monotonously on passing from $\Theta = 0^\circ$ (-3439.24 eV) to $\Theta = 180^\circ$ (-3484.01 eV), and the same trend is followed by the π -electronic energies.

It follows immediately from the total-energy results that the equatorial conformation ($\Theta = 164^\circ$) is somewhat preferred to the axial one ($\Theta = 77^\circ$). This conclusion is in agreement with another study [16], based on a classical model, and with the experimental finding [19, 25] that 2-fluorocyclohexanone, unlike other halo-derivatives, is more stable in the equatorial conformation. On the other hand, the *anti*-rotamer is predicted to be as stable as the equatorial, and expected to occur wherever the molecular structure permits. A recent IR study of fluoroacetone [6] revealed, however, only a "less polar" (i. e. $\Theta \sim 90^\circ$ [3]) and a "more polar" ($\Theta \sim 180^\circ$) form, with nothing to indicate the existence of *anti*-structures.

It is possible that fluoroacetone does contain an *anti*-rotamer, un-detected in IR studies because of its similarity to the "more polar" form, and hardly detectable in dipole moment studies [3] because of its low moment. However, it is even more probable [47] that CNDO treatments, as carried out at present, do not weigh correctly energy terms: we note that the *electronic* contribution did have the correct trend, and that the discrepancy arose only at the stage of adding it to the *nuclear* contribution to form the *total* energy. It is not precluded, therefore, that the particular parametrization of the CNDO/2 scheme necessitates some calibration of the nuclear terms, and that these would improve not only energetical, but also force-constant relationships.

4. π -Electron Results

In Table 4 we present SCF wavefunctions, eigenvalues (ϵ , eV) and absorption wavelengths (λ , nm) for the three rotation angles 10° , 80° , and 160° , corresponding roughly to the *anti*, axial and equatorial conformations. CI statefunctions are not given, as these are constituted, in all cases, by almost pure (>0.998) configurations and have no effect upon λ .

The main point to notice is that there is only slight mixing of the carbonyl and fluorine orbitals, so that the particularities of the UV spectrum do not depend, in our model, on charge-transfer phenomena. The decisive factor is the *population* of atomic orbitals, which is seen to depend more on symmetry, than on interatomic distances; thus, the molecular orbitals of extreme conformations are similar, and different from those of the perpendicular rotamer.

Ground State. In the ground state there is almost no delocalization of non-bonding electrons, and π -dipole moments depend on charge separation within

Table 4

ε	λ	SCF Wavefunctions
$\Theta = 10^\circ; H_{gg} = -57.100, H_{ff} = -66.423$		
-0.540	-	$\varphi_1 = 0.261 \chi_g - 0.507 \chi_h - 0.013 \chi_f - 0.003 \chi_F$
-13.261	278	$\varphi_2 = \chi_H$
-15.890	151	$\varphi_3 = 0.506 \chi_g + 0.861 \chi_h - 0.045 \chi_f - 0.009 \chi_F$
-18.319	98	$\varphi_4 = 0.034 \chi_g + 0.032 \chi_h + 0.998 \chi_f - 0.002 \chi_F$
-18.823	95	$\varphi_5 = 0.007 \chi_g + 0.006 \chi_h + 0.002 \chi_f + 0.999 \chi_F$
$\Theta = 80^\circ; H_{gg} = -57.765, H_{ff} = -68.655$		
-0.769	-	$\varphi_1 = 0.854 \chi_g - 0.519 \chi_h - 0.011 \chi_f - 0.009 \chi_F$
-13.341	290	$\varphi_2 = 0.999 \chi_H - 0.003 \chi_f$
-16.006	152	$\varphi_3 = 0.518 \chi_g + 0.853 \chi_h - 0.043 \chi_f - 0.028 \chi_F$
-18.418	101	$\varphi_4 = 0.032 \chi_g + 0.030 \chi_h + 0.003 \chi_H + 0.998 \chi_f - 0.019 \chi_F$
-18.615	99	$\varphi_5 = 0.023 \chi_g + 0.020 \chi_h + 0.017 \chi_f + 0.999 \chi_F$
$\Theta = 160^\circ; H_{gg} = -57.153, H_{ff} = -70.551$		
-0.556	-	$\varphi_1 = 0.861 \chi_g - 0.508 \chi_h - 0.011 \chi_f - 0.005 \chi_F$
-13.260	279	$\varphi_2 = 0.001 \chi_h + 0.999 \chi_H - 0.036 \chi_F$
-15.893	151	$\varphi_3 = 0.506 \chi_g + 0.859 \chi_h - 0.002 \chi_H - 0.062 \chi_f - 0.033 \chi_F$
-17.763	106	$\varphi_4 = 0.041 \chi_g + 0.047 \chi_h + 0.997 \chi_f - 0.013 \chi_F$
-18.133	103	$\varphi_5 = 0.022 \chi_g + 0.026 \chi_h + 0.036 \chi_H + 0.011 \chi_f + 0.998 \chi_F$

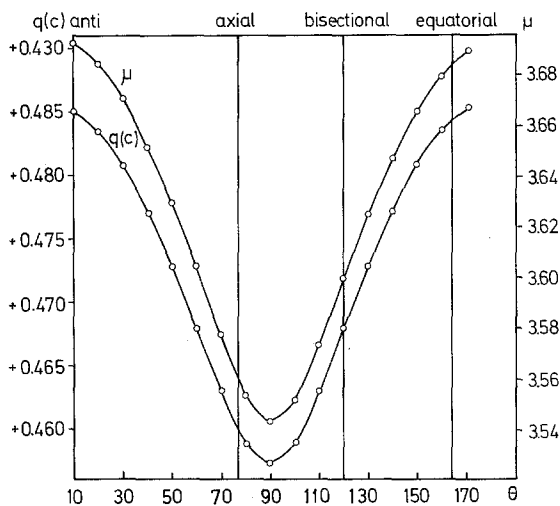


Fig. 4

the C=O π -bond. This is illustrated in Fig. 4, where both dipole moment and carbon charge $q(C)$ [$q(O) = 2 - q(C)$] are plotted against Θ . One finds that charge separation is highest at conformational extremes, lowest at $\Theta = 90^\circ$, which reflects both the similarity of the equatorial and *anti* conformers, and their difference from the axial one. As we saw in Sect. 3, the total charge at C_2 is maintained almost constant, independently of angle, which means that π -charge distribution is compensated by a σ -drift in the opposite direction. In other words, the σ - π separability condition does not apply strictly.

n→ π^* Transition. In a sense, the *n*→ π^* transition serves as the pivotal point of the present study, as its peculiarities provided the criterion which led to the adoption of the π -inductive model. Fig. 5 then confirms that the equatorial conformer absorbs at a shorter wavelength than the axial, and that an eventual

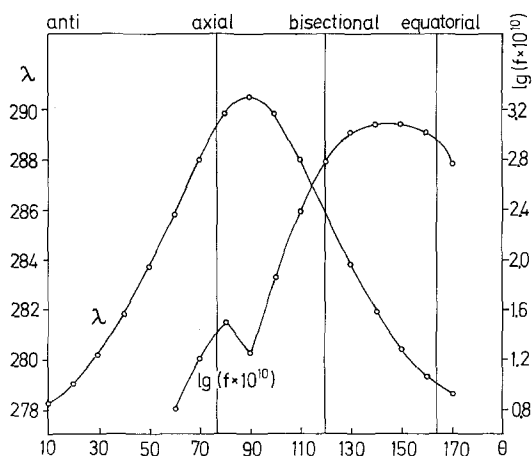


Fig. 5

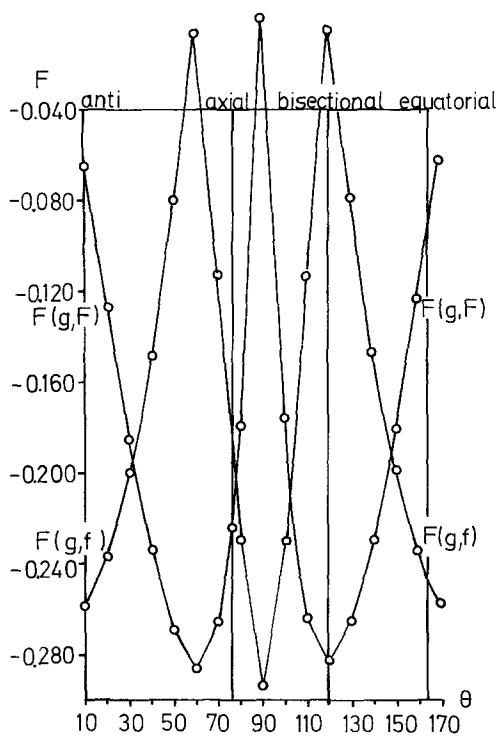


Fig. 6

anti-conformer should be similar, in this respect, to the equatorial one. We also note that, electronically, the transition is forbidden throughout. We would like to stress that Fig. 5 is merely meant to depict the trend of change, which is independent of calibration. Adjustment of the parameters A and H_{gh} (within reasonable limits) would provide other values for absorption wavelengths and axial-equatorial separation, *keeping always* to the same regularity.

In contrast with the ground state π -dipole moment, highest in the conformational extremes ($3.69 D$) and minimal at $\Theta = 90^\circ$ ($3.54 D$), the dipole moment of the $n \rightarrow \pi^*$ configuration is low at the extremes ($1.07 D$) and maximal at $\Theta = 90^\circ$ ($1.14 D$). This relationship sets up a conformation-dependent difference, and should be reflected by solvent shifts of the transition band. The prediction that equatorial and *anti*-conformations manifest a larger shift than the axial one, provides the rationale for the behaviour of 2-fluoro-4-*tert*-butylcyclohexanone [25], cited in Table 1.

As the phenomenon is detectable even prior to the CI treatment, one may well search in the matrix F for a possible explanation. Fig. 6 shows $F(g, f)$ and $F(g, F)$ as function of Θ ; other inter-chromophore interactions are relatively small. It is immediately seen that at the axial disposition ($\Theta = 77^\circ$), $F(g, f)$ equals $F(g, F)$ and both are large; at the *anti* and equatorial conformations, the first is large, the other small. While this relationship depends upon the particular construction, its outcome does not: at 77° , the total interaction $C \dots F$ is much higher than at the equatorial case. However, the same situation occurs three more times ($32^\circ, 102^\circ, 148^\circ$), while the $n \rightarrow \pi^*$ curve (Fig. 5) shows only one extremum (90°). Thus, the fine interplay of interactions selects 90° as extremal, for reasons which are not apparent in F .

Second Electronic Transition. The $\pi \rightarrow \pi^*$ transition has not been studied experimentally. It is expected to be very strong ($f = 0.346$ at $\Theta = 80^\circ$, $f = 0.332$ at $\Theta = 170^\circ$) and almost independent of angle, being confined to 151–152 nm, by our present choice of H_{gh} . The dipole moment of this excited configuration never exceeds $0.02 D$, and solvent effects — determined by the ground state dipole moment — can be expected.

5. Recapitulation

Two conformers of 2-fluoroketones, equatorial and axial, have been studied experimentally and extensively discussed in the literature. Of the two, the equatorial structure is more stable, has ν_{CO} at higher frequency and the $n \rightarrow \pi^*$ transition at longer wavelength. In an attempt to gain insight into the electronic nature of the two conformers, and to trace the properties of other possible structures, we undertook a study of the complete rotameric series defined by 2-fluoroacetaldehyde. An SCF-CI treatment, extended to include the π -inductive effect, permitted the reproduction of the $n \rightarrow \pi^*$ absorption trend. Other π -electronic regularities, comprising energy, charge distribution, transition energies and oscillator strengths, could then be considered. A concurrent CNDO/2 treatment was found helpful in many respects, except, notably, its failure to account for the IR trends. Possible reasons are that the various terms which enter the energy expression are not

given realistic weights, and that field effects (even when overlap-dependent) are not properly accounted for.

The *anti*-conformer, unstudied as yet, is predicted to be similar to the equatorial one in many respects, including electronic energy, UV spectrum and ionization potentials; this is tantamount to stating that the cited properties depend more on symmetry than on distance. Another generalization concerns substituents geminal to the 2-fluorine atom, which are shown to transmit to the carbonyl group the environmental modifications which they undergo.

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References

1. Meyer, A. Y.: *Theoret. chim. Acta (Berl.)* **9**, 401 (1968).
2. Jones, R. N., Ramsay, D. A., Herling, F., Dobriner, K.: *J. Amer. chem. Soc.* **74**, 2828 (1952).
3. Mizushima, S.: *J. chem. Physics* **21**, 815 (1953).
4. Leonard, N. J., Owens, F. H.: *J. Amer. chem. Soc.* **80**, 6039 (1958).
5. Corey, E. J., Burke, H. J.: *J. Amer. chem. Soc.* **77**, 5418 (1955).
6. Crowder, G. A., Cook, B. R.: *J. chem. Physics* **47**, 367 (1967).
7. Cook, B. R., Crowder, G. A.: *J. chem. Physics* **47**, 1700 (1967).
8. Cookson, R. C.: *J. chem. Soc. (London)* **1954**, 282.
9. Djerassi, C.: *Optical rotatory dispersion*. New York: McGraw-Hill 1960.
10. Cookson, R. C., Dandegaonker, S. H.: *J. chem. Soc. (London)*, **1955**, 352.
11. Tsubomura, H.: *Bull. chem. Soc. Japan* **37**, 417 (1961).
12. Kumler, W. D., Huitric, A. C.: *J. Amer. chem. Soc.* **78**, 3369 (1956).
13. Allinger, J., Allinger, N. L.: *Tetrahedron* **2**, 64 (1958).
14. Bellamy, L. J.: *Advances in infrared frequencies*. London: Methuen 1968.
15. Cantacuzène, J.: *J. Chim. physique* **59**, 186 (1962).
16. — C. R. Acad. Sci. (Paris) **256**, 3066 (1963).
17. Bratož, S., Besnaïnou, S.: *J. chem. Physics* **34**, 1142 (1961).
18. Kosower, E. M., Wu, G., Sorensen, T. S.: *J. Amer. chem. Soc.* **83**, 3147 (1961).
19. Allinger, N. L., Tai, J. C., Miller, M. A.: *J. Amer. chem. Soc.* **88**, 4495 (1966).
20. Julg, A.: *J. Chim. physique* **53**, 453 (1956).
21. Pople, J. A., Santry, D. P., Segal, G. A.: *J. chem. Physics* **43 S**, 129 (1965).
22. —, Segal, G. A.: *J. chem. Physics* **43 S**, 135 (1965).
23. Casadevall, A., Casadevall, E., Mion, M.: *Bull. Soc. chim. France* **1968**, 4498.
24. Mion, L., Casadevall, A., Casadevall, E.: *Bull. Soc. chim. France* **1968**, 2950.
25. Allinger, N. L., Blatter, H. B.: *J. org. Chem.* **27**, 1523 (1962).
26. Hartwell, E. J., Richards, R. E., Thompson, H. W.: *J. chem. Soc. (London)* **1948**, 1436.
27. Bellamy, L. J.: *The infra-red spectra of complex molecules*, 2nd ed. London: Methuen 1958.
28. Propanal value, quoted in: Kamlet, M. J., Ed.: *Organic electronic spectral data*, Vol. 1. New York: Interscience 1960.
29. Elkkik, E.: *Bull. Soc. chim. France*, **1964**, 2254.
30. Clark, P. A., Ragle, J. A.: CNDOTWO-SCF-LCAO-MO. QCPE 100.
31. Meyer, A. Y.: *J. Chim. physique* **65**, 837 (1968).
32. —, Serre, J.: *Theoret. chim. Acta (Berl.)* **8**, 117 (1967).
33. Moreau, C., Serre, J.: *Theoret. chim. Acta (Berl.)* **2**, 40 (1964).
34. Parr, R. G., Mulliken, R. S.: *J. chem. Physics* **18**, 1338 (1950).
35. Fischer-Hjalmars, I.: *J. chem. Physics* **42**, 1962 (1965).
36. Edwards, T. G., Grinter, R.: *Molecular Physics* **15**, 349 (1968).
37. Murrell, J. N., Kettle, S. F. A., Tedder, J. M.: *Valence theory*. London: Wiley 1965.
38. —, Williams, D. R.: *Proc. Roy. Soc. (London)* **291**, A224 (1966).

39. Clark, D. T., Elmsley, J. W.: *Molecular Physics* **12**, 365 (1967).
40. Chambers, R. D., Musgrave, W. K. R., Chadwick, L.: *Tetrahedron* **24**, 877 (1968).
41. Baker, A. D., Baker, C., Brundle, C. R., Turner, D. W.: *Internat. J. Mass Spectrometry* **1**, 285 (1968).
42. Giessner-Prettre, C., Pullman, A.: *Theoret. chim. Acta (Berl.)* **9**, 279 (1968).
43. Davies, D. W.: *Chem. Physics Letters* **2**, 173 (1968).
44. Mulliken, R. S.: *J. chem. Physics* **23**, 1833 (1955).
45. Caristan, A., Bodot, H.: *Bull. Soc. chim. France* **1967**, 3227.
46. Bellamy, L. I., Williams, R. L.: *J. chem. Soc. (London)* **1951**, 4294.
47. Herndon, W. C., Feuer, J.: *Tetrahedron Letters (London)* **1968**, 2625.

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