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PREFERENTIAL CONFORMATION OF THE CARBON-FLUORINE BOND AND ELECTRONIC INTERACTIONS IN SUBSTITUTED BENZYL FLUORIDES

C. BEGUIN and E. GOUT-MALLARET

C.E.R.M.O., University of Grenoble I, P.O. Box 53, 38041-Grenoble (France)

SUMMARY

CNDO/2 and PCILO calculations have been used to study the preferential conformations and relative stabilities of six para-substituted, three ortho-substituted and two diortho-substituted benzyl fluorides. In non-ortho-substituted compounds, the C—F bond of the CH_2F group lies preferentially in the plane of the phenyl ring. The HOMO energies show that conjugation exists between the substituent and the fluorine atom. Some experimental evidence has been obtained through the use of Raman spectroscopy on the crystalline state. For ortho-substituted compounds the calculations are in agreement with several previous studies which show that steric hindrance can lead to a change in the preferential conformation in the phenyl ring plane as occurs in 2,6-dichlorobenzyl fluoride.

INTRODUCTION

Many studies have appeared recently [1] concerning carbon-fluorine bonds situated near unsaturated systems. Thus the bond between a fluorine atom and an sp^2-hybridized carbon both in olefinic and aromatic systems, the C—F bond in fluorinated methanes and the C—F bond in simple fluorinated substituents on a π system (particularly an aromatic ring) have been examined [1] . Extensive studies have been made on ααα-trifluorotoluenes where the origin of the +R resonance effect has been analyzed in terms of either fluoride ion hyperconjugation and no bond resonance, π inductive effects or fluorine p-π interaction. In the latter case the interaction of the p electrons of the fluorine atom with the π aromatic system was shown to cause a significant reversal of electron density to the ring, which partly counteracted the normal strong inductive withdrawal [2]. No extensive studies have been made on benzyl fluorides, and the aim of this paper is to describe the interaction of the CH_2F group and the aromatic system from different points of view. These studies extend previous work [3, 4].

Two aspects of this subject are discussed. First an attempt has been made to determine via semi-empirical calculations the most stable conformation of the CH_2F group relative to the extent of conjugation between this group and the aromatic system, and the change in conformation which occurs when competition arises between such interactions and steric hindrance around the CH_2F group. The second aspect presents some experimental evidence supporting the first.

SEMI-EMPIRICAL CALCULATIONS FOR PREFERENTIAL CONFORMATION OF THE C–F BOND IN P-SUBSTITUTED AND O-SUBSTITUTED BENZYL FLUORIDES

Two semi-empirical methods have been employed for calculating preferential conformations:

(i) An application of single determinant, self-consistent theory with complete neglect of differential overlap, CNDO/2 [5], on the non-substituted benzyl in three *p*-substituted benzyl fluorides.

(ii) An application of the pertubation method PCILO [6] (especially for *O*-substituted substrates) which is not time consuming and is well adapted for conformational studies when energies for a number of different geometrical values (for example, rotation angles for both CH_2F and Z groups) must be calculated.

Conformation in *p*-substituted benzyl fluorides: Influence of conjugation

The energy value difference ΔE, in kcal mol^{-1} for various values of the dihedral angle between the $C_{aromatic} - C_{benzylic} - F$ plane and the ring plane is listed in Table 1, the value quoted being relative to that for a dihedral angle of zero degrees.

Two main points can be deduced for the four *para*-substituents studied. The more stable conformation (by about 3 kcal mol^{-1}) is that in which the carbon-fluorine bond lies in the plane of the phenyl ring ; the less favored one is that in which the carbon-fluorine bond is perpendicular to the phenyl

TABLE 1

Variation in the energy value difference, ΔE, for various values of the dihedral angle between the C–F bond and the phenyl ring in p-Z-substituted benzyl fluorides as obtained by CNDO/2 calculations

Dihedral angle/	ΔE/kcal mol^{-1}			
degrees	Z = OH_{anti}	Z = F	Z = H	Z = CF_3
0	0	0	0	0
30	0.70	0.75	0.70	0.85
60	1.95	2.15	2.0	2.4
90	2.55	2.95	2.75	3.3

ring. A plane of symmetry can thus be defined containing the phenyl ring, the substituent, the benzylic carbon atom and the fluorine atom. The electron distribution acquires this plane of symmetry, with conjugation from the substituent through the phenyl ring to the fluorine atom being defined.

This preferential conformation may be related to the other more stable and less favoured conformations through other data extracted from the CNDO/2 calculations, i.e. (a) the eigenvalue energy of the highest occupied molecular orbital [the E(HOMO) value], and (b) the energy difference between the two extreme positions (the ΔE(//⊥)value).

(a) The energy of the highest occupied molecular orbital

Grable and Kearns have shown [7] that the value of the energy of the HOMO (Table 2) can be used to characterize conjugation in mono-substituted benzenes. The ionization potential, which according to Koopman's theorem provides an experimental measure of $\underline{E}$(HOMO), may be correlated with σ^+ for a family of para-substituted compounds, the slope of the linear plot being greater when conjugation is more extensive. This correlation leads to the following values :

$Z{-}C_6H_4{-}F$; $\underline{E}/V = -0.605\sigma^+ - 0.652 r = 0.962$

$Z{-}C_6H_4CH_2{-}F$; $\underline{E}/V = -0.578\sigma^+ - 0.650 r = 0.969$

$Z{-}C_6H_4{-}CF_3$; $\underline{E}/V = -0.389\sigma^+ - 0.690 r = 0.944$

For para-substituted anilines or toluenes using the same units, the slopes obtained are -0.70 and -0.75, respectively. Conjugation is more extensive in fluorobenzenes than in α-fluorotoluenes, but comparison is still possible and meaningful since in α-fluorotoluenes the C—F bond lies in the nodal plane, and as for trifluorotoluenes the value of E(HOMO) is not very dependent on the conformation of the C—F bonds.

TABLE 2

The energy of the highest occupied molecular orbital, E(HOMO), for p-Z-substituted benzyl fluorides and the energy value difference between the extreme conformation positions of the C—F bond, $\Delta E(//\perp)$, as obtained from CNDO/2 calculations

Z	E(HOMO) /a.u.	$\Delta E(//\perp)$ /kcal mol^{-1}
OH	-0.4421	2.55
OCH_3	-0.4374	2.60
CH_3	-0.4706	2.75
F	-0.4673	2.75
H	-0.4827	2.95
CF_3	-0.5024	3.3
NO_2	-0.4764	3.5

(b) The energy difference $\Delta E(//\perp)$

Values of the energy difference between the rotamer with the C—F bond perpendicular to the phenyl ring plane and that with the C—F bond in the plane were found to increase from 2.5 to 3.5 kcal mol^{-1} as the parameters of the electron-withdrawing substituent increased (Table 2). This may be attributed to the fact that for the rotamer with the C—F bond in the plane conjugation extends from the substituent to the fluorine atom, resulting in an energy stabilization. A higher value of $\Delta E(//\perp)$ (3.5 kcal mol^{-1}) implies more extended conjugation as occurs with a highly electron-withdrawing substituent such as NO_2.

The absolute value for $E(//\perp)$ obtained for benzyl fluoride (2.95 kcal mol^{-1}) by the CNDO/2 method differs considerably from that obtained from the

STO-3G ab initio method described by Pople [8] (0.25 kcal mol^{-1}). Pople's value, which was obtained from values for other compounds, depends on the number of atomic orbitals in the base and on the chosen geometry. Nevertheless, the more stable conformation is still that in which the C–F bond is coplanar with the phenyl ring. This form "is possibly more stable than the orthogonal forms due partially to hyperconjugation effects" [8] . These $\Delta E(//\perp)$ values permit a comparison of the $\Delta E(//\perp)$ values for benzal fluoride and benzyl fluoride. In benzal fluoride the C–H) bond lies in the phenyl ring plane whilst in benzyl fluoride it is the C–F bond which lies in this plane. We would therefore expect more extensive conjugation in the second case and thus a higher value of $\Delta E(//\perp)$ for benzyl fluoride. Pople's results (0.18 kcal mol^{-1} for benzal fluoride and 0.25 kcal mol^{-1} for benzyl fluoride) are consistent with this expectation, and as experimental results from ^{1}H NMR spectroscopie studies of benzal fluoride lead to a value of ca 0.5 kcal mol^{-1} for the rotational barrier [9] , our value of 3 kcal mol^{-1} is reasonable.

The total energy values versus the dihedral angle obtained from PCILO calculations on the same substrates are shown in Table 3. At first glance it appears that two minimum values occur at $\Theta = 0^{o}$ and $\Theta = 180^{o}$.

TABLE 3

The total energy of benzyl fluoride as a function of the dihedral angle, as obtained from PCOLO calculations

Dihedral angle/ degrees	Total energy, E/ a.u.
0	-52 044.323
30	-52 043.068
60	-52 040.779
90	-52 040.210
120	-52 041.545
150	-52 042.785
180	-52 043.143

This artifact results from the use of localized bonds in the PCILO method, and to recover the symmetry the two Kekule formulae must be used for the phenyl ring. It then appears as if the localized form of 3-fluoropropene with the C—F bond in the syn form is more stable than that in the anti form by 1.7 kcal mol^{-1} (with these two configurations being more stable that the orthogonal one).

The conformation in which the carbon-fluorine bond lies in the plane of the phenyl ring is also shown to be the most stable to the extent of ca. 3.5 kcal mol^{-1}. The application of this method leads to no significant variation among the energies of the conformations considered in the series.

Conformation in o-substituted benzyl fluorides: Competition between conjugation and steric hindrance

The PCILO method has also been employed to study the energies of different conformations in ortho-substituted benzyl fluorides (Z = OH, CH_3, F, CF_3) and diortho-substituted benzyl fluorides (Z_1 = Z_2 = CH_3, F), the geometries chosen being the same as above. In the following the terms syn, orthogonal and anti are used respectively for $\Theta = 0^{\circ}$, 90° and 180° when the arrangement of the four atoms is non-linear, i.e. aromatic carbon bonded to the substituent in the ortho position, aromatic carbon-atom bonded to the CH_2F group, benzylic carbon and fluorine atom, respectively.

In ortho-substituted compounds the anti conformation has been found to be the most stable. The energy differences between the orthogonal and anti conformation and between the syn and anti conformation as calculated for one localized position are shown in Table 4. Thus the difference between the orthogonal and anti conformation is 4.2 ± 0.3 kcal mol^{-1} with no significant variation as the nature of the substituent is varied. On the other hand, the energy difference between the syn and anti conformations exhibits a general tendency to decrease when the steric hindrance decreases. However, for a more general discussion of this phenomenon more examples need to be studied. Two substituents demonstrate a special behaviour, i.e. the F substituent (in which electron repulsion from lone pairs on the fluorine atom may be visualized in the conventional manner in the PCILO method) and the CF_3 substituent (where a type of "gear effect" may be imagined between the rotation of the CH_2F and CF_3 group [10]).

TABLE 4

Energy differences between various conformations in O-Z-substituted benzyl fluorides, as obtained from PCILO calculations for one localized position

Z	$\Delta E_{\text{ortho-anti}}$ /kcal mol^{-1}	$\Delta E_{\text{syn-anti}}$ /kcal mol^{-1}
OH	4.4	4.4
CH_3	3.9	3.2
CF_3	4.0	0.0
H	3.9	1.2
F	4.3	3.6

With diortho-substituted compounds the influence of steric is less ambiguous. In these molecules the bond lengths, the bond angles and the conformations of the substituents were always chosen symmetrically with respect to the plane perpendicular to the phenyl ring, and in these instances as the steric hindrance of the ortho substituents increases ($H < F < CH_3$), the energy difference $\Delta E(//\perp)$ decreases (from 3.5 to 2 and finally to -2.5 kcal mol^{-1}). When H and F substituents are present conjugation from the phenyl ring to the C–F bond is more important than steric hindrance, but with methyl substituents steric hindrance is more important than the conjugative effect.

EXPERIMENTAL EVIDENCE FOR A PREFERENTIAL CONFORMATION AND COMPETITION BETWEEN CONJUGATION AND STERIC HINDRANCE

Some experimental evidence for a preferential conformation may be found from a detailed analysis of the Raman spectra of benzyl fluoride at low temperature. An attempt to obtain more direct evidence by complete ^1H NMR analysis of the product formed in a nematic solvent is at present in progress. Experimental evidence for competition between conjugation and steric hindrance may be obtained from an analysis of different NMR results, although more direct evidence has now been achieved by an NMR analysis of diortho-chlorobenzyl fluoride in a nematic solvent [11] .

Experimental information from Raman spectroscopy

Since, as far as we are aware, no experimental data on the preferential conformation of the C—F bond have as yet been determined, we have studied the behaviour observed at very low temperatures (77 k) in the solid state where almost all the conformations are blocked. The Raman spectrum of benzyl fluoride at liquid nitrogen temperature is shown in Figure 1(a) and (b), and although a detailed study was not undertaken two major features are worthy of comment.

(1) The existence of a transition at 129 cm^{-1} is easily been from Figure 1(b), the intensity being too strong to be attributable to rotation of the whole molecule [12, 13] and the frequency being too low to be related' to an aromatic interaction [14] . Compounds of almost the same moment of inertia (benzoïc aldehyde and anisole) exhibit torsional frequencies (135 and 113 cm^{-1}, respectively) [15] , this libration being pure or partially coupled with the molecular libration or with torsional cycle 16a, which has the same symmetry. According to Pauling [16] , the potential barrier, which may be related to the frequency by the equation $W = 2V_o^{0.5}I^{-0.5}$, has a value of 8.6 kcal mol^{-1}, the relatively high value of this vibration in the crystal being much greater than that given by Dupeyre [17] whose used an indirect method and studied the liquid state. However, it is not unreasonable for values for partially hindered rotations in the liquid state and for the corresponding vibrations in trapped molecules in the crystalline state to differ by this extent [18] .

(2) The complete Raman spectrum appears to correspond to the superposition of two identical halogenobenzene spectra [13] of different intensity displaced relative to other. This is particularly obvious in the spectral region 1150 to 1250 cm^{-1}, corresponding to vibrations A1 (9a, 7a) and B1 (9b) in the Mulliken nomenclature [19] , and also in the 16a region (315 and 352 cm^{-1}). A more exhaustive study is at present in progress [20] , but nevertheless some assertions can be made. Thus a Davidov split is excluded (maximum from 5 to 15 cm^{-1}), but two crystalline phases could be present with one stable at low temperature and the other at high temperature [21]; a study of the UV spectrum at 4 k is in progress in an attempt to elucidate this latter point. The existence of two spectral systems may be associated with the observations of Broude and Klimuskeva [22] on the UV spectra of monoalkylbenzenes where a series of polarised lines was related to the existence

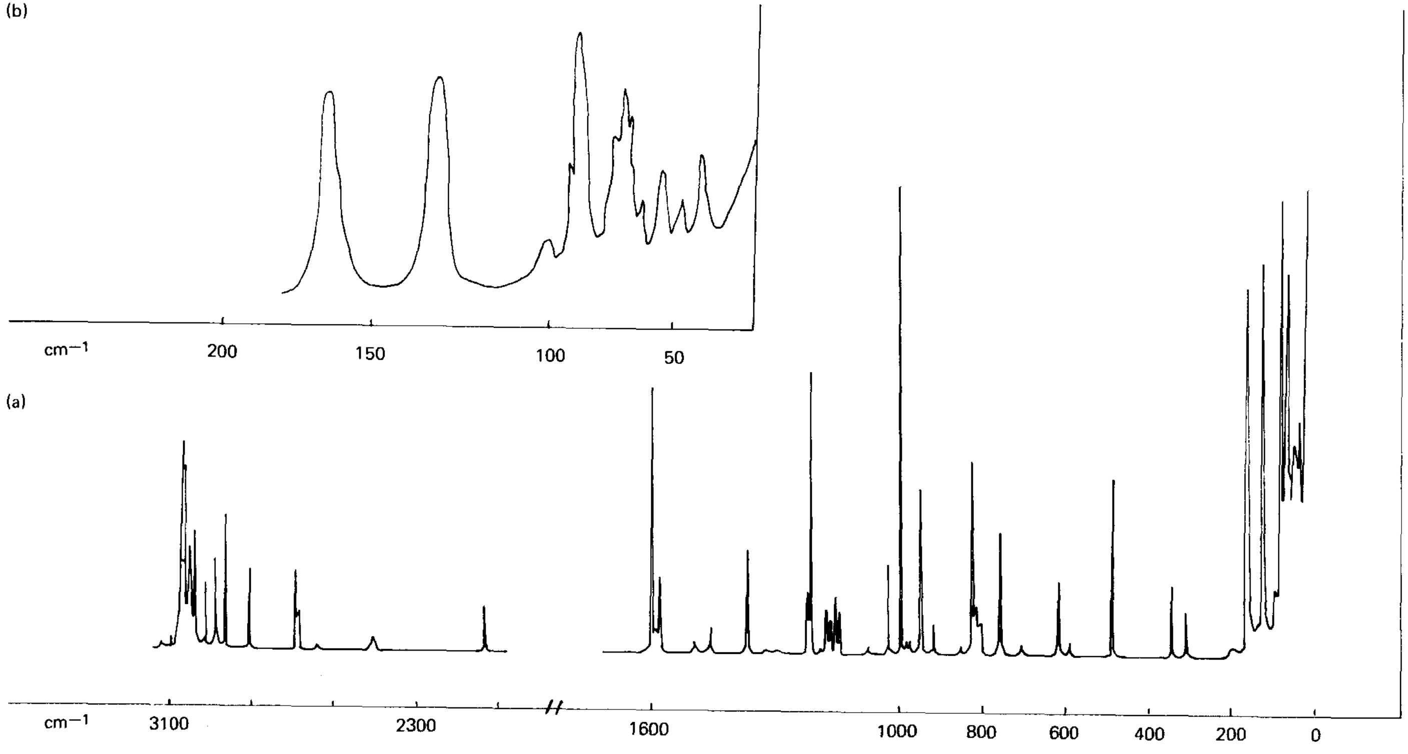


Fig. 1. Raman spectrum of benzyl fluoride at liquid nitrogen temperature. (a) Complete spectrum and (b) enlarged spectrum over the range 0 - 200 cm^{-1}.

of two C_s symmetries (C_{s_1} and C_{s_2}, with the plane of symmetry perpendicular to the phenyl ring). In the present case, the two spectral systems could be related to two rotamers of C_{s_1} and C_{s_2} symmetry trapped in the crystal. The low-frequency spectral system with the low intensity is similar to that of chlorobenzene [12] and could be attributed to the C_{s_2} rotamer (the mass numbers of CH_2F and Cl being almost equal with interaction of the CH_2F group with the phenyl ring being small in the C_{s_2} symmetry). The more intense spectral system would then belong to the C_{s_1} rotamer. However, the intensity ratio of the two spectral systems is not related simply to the molar ratio of the rotamer in the liquid state trapped in the crystal lattice.

Experimental evidence for competition between conjugation and steric hindrance

As far as we are aware, hindered rotation in substituted benzyl halides was first described experimentally by Cupas et al. [23], Reuvers et al. [24] and by Schaefer et al. [25]. Only Schaefer, however, was able to reach any conclusions regarding substituted benzyl fluorides (see below).

(a) Activation entropy for molecular re-orientation in solution

The measurement of the quadrupolar relaxation time of the deuterium atom introduced in the benzylic position has been made by line-shape analysis of the NMR signals of the proton or fluorine atom spin-spin coupled with this deuterium atom [4, 17]. By studying the correlation time determining this relaxation time as a function of the temperature it was possible to obtain the corresponding activation parameters. The correlation time describes the molecular re-orientation around the deuterium atom which is most likely related to the rotation of the CHDF group around the C_1-C_7 bond. Studies of the change in the solvent system 2-nitropropane + 1 mol ℓ^{-1} HMPT to 2-nitropropane + 3 mol ℓ^{-1} phenol have shown that the entropy of activation increases from 4 to 16 cal K^{-1} mol^{-1} when the hydrogen bonding character of the solvent increases. A fluorine atom can be solvated by a hydrogen-bond-donating molecule [26 - 28], and this means that with a highly H-bond-donating solvent, the highly solvated CH_2F group becomes more bulky so that the preferential conformation of the C—F bond may no longer be in the phenyl ring plane but perpendicular to that plane. When rotation occurs the solvated C—F bond will be hindered by the ortho-hydrogen atom of the phenyl ring and desolvation will occur. The more important desolvation involving rotation of the transition state leads to a higher entropy of activation. Thus steric hindrance in the compounds studied here can arise either from bulky ortho substituents or from the behaviour of the highly solvated CH_2F group in strong H bond donor solvents.

(b) Compounds with predominant steric hindrance

Schaefer has studied 2,6-dichlorobenzyl fluoride and has discussed the values of the two spin-spin coupling constants $^6J[H(p)F]$ [25] . He has assumed that in this compound the conformation of the C—F bond is perpendicular to the aromatic ring, this conformation being favored by a least 3 kcal mol^{-1} over one in which the C—F bond eclipses a C—Cl bond. The coupling constants were measured from an analysis of the results of double resonance experiments involving the ^1H NMR spectrum at 60 MHz in benzene-d_6. This spectrum has been re-investigated in carbon tetrachloride at 250 MHz and a LAOCOON analysis made of the AB_2X_2 part of the AB_2X_2R spectrum. All the values of the coupling constants listed in Table 5 are very close to those of Schaefer, the chemical shifts being solvent-dependent.

(c) Determination of the most stable conformation of the C—F bond in 2,6-dichlorobenzyl fluoride

The most stable conformation of the C—F bond in 2,6-dichlorobenzyl fluoride has been clearly established in this laboratory through a complete ^1H NMR spectral analysis of this compound using a "Merk IV" nematic solvent [11].

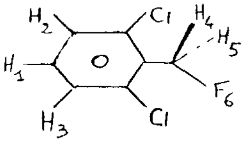
CONCLUSION

The various experimental results obtained exhibit good correlations with semi-empirical calculations on substituted benzyl fluorides.

The C—F bond in non-substituted and para-substituted fluorides has a preferential conformation lying in the plane of the phenyl ring. The energy difference values between the more and the less favorable conformations could not be determined unambiguously since the values obtained are dependent on the method of calculation (CNDO/2, PCILO, STO-3G) and on the nature of the experimental medium (the crystal line state at very low temperature

TABLE 5

Coupling constant values (in Hz) obtained from a LAOCOON analysis of the ^{1}H NMR spectrum of 2,6-dichlorobenzyl fluoride in carbon tetrachloride at 250 MHz and from double resonance studies of the ^{1}N NMR spectrum of the same compound in benzene-d_6 at 60 MHz

Coupling constant	LAOCOON at 250 MHz	Schaefer [25] at 60 MHz
		
δ_1	404.339 ± 0.06	77.88
$\delta_2 = \delta_3$	427.273 ± 0.06	92.10
$\delta_4 = \delta_5$	0.016 ± 0.033	0.0
J(1,2)	7.939 ± 0.056	8.14 ± 0.05
J(1,4)	-0.056 ± 0.056	-0.16 ± 0.02
J(1,6)	-2.357 ± 0.09	-2.43 ± 0.04
J(2,4)	+0.114 ± 0.04	0.34 ± 0.04
J(2,6)	1.564 ± 0.12	1.25 ± 0.04
J(4,6)	47.802 ± 0.06	47.5 ± 0.10

and the liquid state at room temperature resulting in solvating conditions). This preferential conformation gives rise to a plane of symmetry through the phenyl ring plane which includes conjugation, and hence to a nodal plane for the π-electron distribution from the substituent to the fluorine atom through the phenyl ring and the aromatic benzylic bond.

Competition between conjugation and steric hindrance leads to changes in all the energy difference values. Steric hindrance is observed with bulky ortho substituents or when extensive solvation of the CH_2F group occurs. With two ortho substituents, the most stable conformation is perpendicular to the plane of the phenyl ring.

EXPERIMENTAL

Computing conditions

Standard programs (CNDO/2, PCILO, LAOCOON) were used and calculations made using the IBM 360/67 at Grenoble University or the IBM 370/165 of the Centre National de la Recherche Scientifique (CIRCE).

As geometrical data from crystallographic or microwave studies are not known for $ArCH_2F$ compounds, bond lengths and bond angles were chosen using following criteria (Fig. 2):

(i) The bond lengths in the substituted benzyl rings were those chosen by Taft [29] .

(ii) The C_1–C_7 sp^2-sp^3 aromatic-benzylic bond length was chosen by comparison with those in toluene [30] , propene [31, 32] , 3-fluoropropene [33] and ethyl fluoride [34] . This value is in agreement with that given by MacBee [35] .

(iii) The C_7–F bond between an sp^3 carbon atom and a fluorine atom was chosen by comparison with those of ethyl fluoride [34] and 3-fluoropropene [33] . This value is somewhat higher than that reported by MacBee ; however, this author reports that such values are not particularly sensitive to reasonable variations in the bond lengths and angles [35] .

(iv) The bond angles have been taken from Ref. [29] except for the angles in the CH_2F group which were from Refs. [33] and [34] . All previously unknown geometrical parameters are shown in Table 6. The total energy

TABLE 6

Previously unrecorded geometrical parameters for $ArCH_2F$ compounds (see Fig. 2 for numbering of atoms)

Bond angles /degrees	Bond lengths /Å
$C_1 - C_2 - C_3 = 120^\circ$	$C_1 - C_2 = 1.397$
$C_1 - C_2 - H_1 = 120^\circ$	$C_1 - H_1 = 1.084$
$C_1 - C_7 - F = 111^\circ\ 40'$	$C_7 - F = 1.382$
$H_6 - C_7 - H_7 = 108^\circ\ 05'$	$C_1 - C_7 = 1.497$
$H_6 - C_7 - F = 107^\circ\ 22'$	

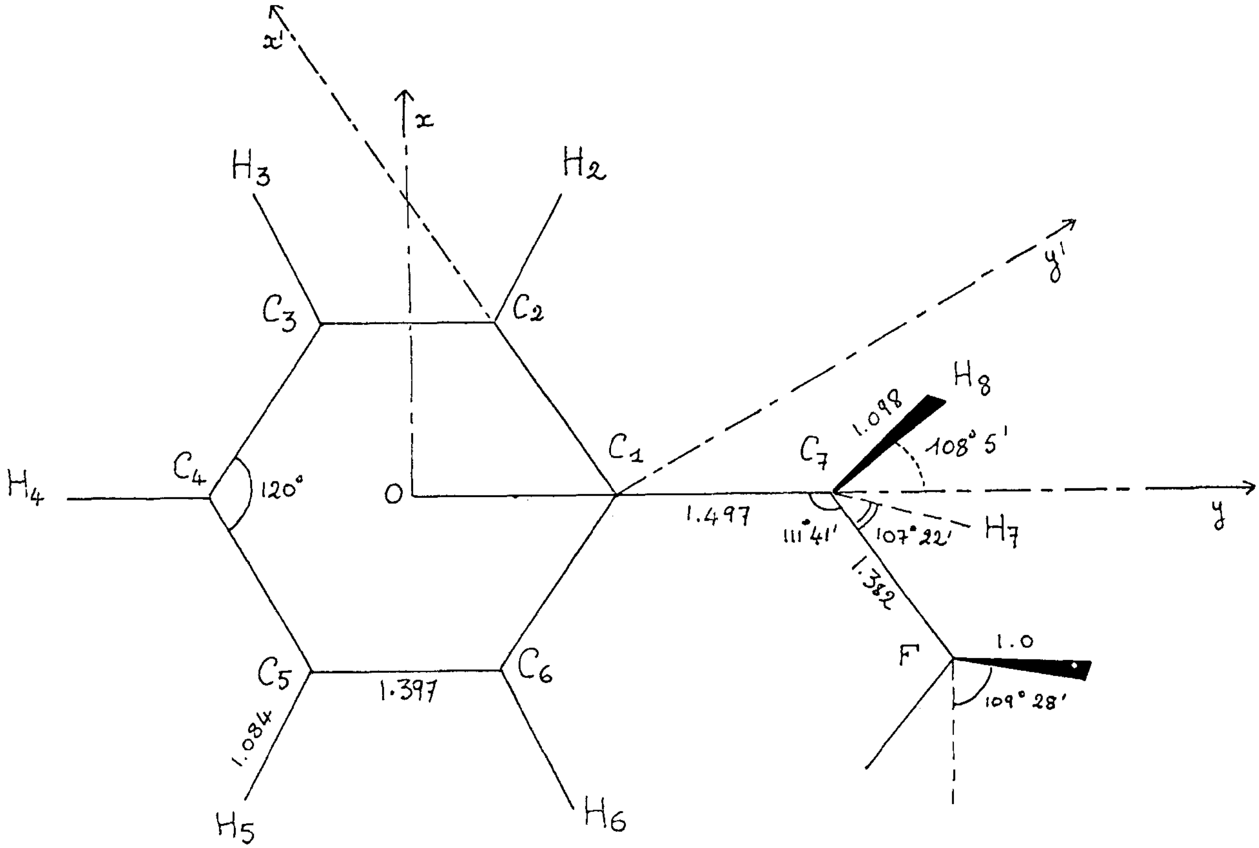


Fig. 2. Geometrical arrangement of $ArCH_2F$ compounds as compiled from various data.

values were calculated as a function of the dihedral angle Θ between the phenyl ring plane and the plane defined by the C_1—C_7 and C_7—F bonds, from 0° to 180° in increments of 30°, the zero value corresponding to the C—F bond in the phenyl ring plane.

Spectral measurements

Raman spectra were recorded at the Centre Universitaire Scientifique de Chambery on a CODERG P.H. I instrument fitted with a Spectra Physics Laser 164. ^{1}H NMR spectra at 250 MHz were recorded on a Cameca 250 instrument of the Laboratoire Grenoblois de RMN Haute Résolution.

Materials

Benzyl fluoride and 2,6-dichlorobenzyl fluoride were prepared from the corresponding bromides (Schuchardt) by exchange with anhydrous potassium fluoride in N-methylpyrrolidone [36].

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