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PREFACE

The widespread application of the NMR spectroscopy of "other nuclei" is clearly reflected in the contributions to these volumes. As with some earlier members of this series of reports, the present volume is split into two parts.

Volume 10B is the more specific one, dealing with the ^{19}F NMR parameters of various series of compounds. It comprises extensive tabulations of ^{19}F NMR data and serves to update reports in earlier volumes of this series.

The range of topics covered in volume 10A indicates some of the numerous areas of science which are dependent upon NMR as a primary investigative tool. The areas covered include transition metal NMR, ^{13}C NMR applications to synthetic polymers, and some uses of ^{31}P NMR in biochemistry.

All the authors writing for volume 10 are new to Annual Reports and, in welcoming their contributions, I wish to thank all of them for their efforts and patience both in the preparation of their manuscripts and of this volume.

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December 1979

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Fluorine-19 Nuclear Magnetic Resonance Spectroscopy (1976–1978)

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I. INTRODUCTION

As in previous years the major objective has been to collect the scattered information on F-19 NMR parameters in a form that can readily be retrieved and used. The large volume of data has necessitated a change in policy regarding the presentation of this information. The present reviewer hopes that the use of tables classified according to the type of molecule and internal ordering according to molecular formula will ease the retrieval and comparison of data. Such an approach supplements previous data collections and will hopefully ease computation of such data in the future. The data have been compiled from the author's own records and from the literature abstracts of Current Contents (Physical Sciences), Nuclear Magnetic Resonance Literature (Preston Publications, Illinois), and CA Selects: Nuclear Magnetic Resonance (Chemical Aspects).

All chemical shifts have been converted to the δ scale, with $CFCl_3$ as reference and positive shifts to high frequency of the reference, using the conversion factors shown in Table I. The original reference has been indicated if it was not $CFCl_3$, since several authors persist in not indicating their sign convention or change their convention from paper to paper; some errors may be present in the tables as a consequence. It would be preferable if all journals insisted on the sign convention recommended by IUPAC* and used here.

TABLE I

Reference compound shifts

Index	Compound	Shift from $CFCl_3$ (ppm)	Index	Compound	Shift from $CFCl_3$ (ppm)
(a)	$CF_3 \cdot CO_2H$	−78·5(0)	(j)	$\overline{CF_2 \cdot CF_2 \cdot CF_2 \cdot CF_2}$	−136·0(0)
(b)	C_6F_6	−162·9(0)	(k)	$pF \cdot C_6H_4 \cdot F$	−120·0(0)
(c)	$C_6H_5 \cdot CF_3$	−63·9(0)	(l)	$CF_3 \cdot CO_2CH_3$	−74·2(1)
(d)	C_6H_5F	−113·15	(m)	$CF_3 \cdot C(OH)_2 \cdot CF_3$	−92·7(7)
(e)	$\underline{CFCl_2 \cdot CFCl_2}$	−67·3(0)	(n)	$CF_3 \cdot CCl_3$	−82·2(0)
(f)	$CF_2 \cdot CF_2 \cdot CCl_2 \cdot CCl_2$	−114·1(0)	(o)	$C_6H_5 \cdot SO_2F$	+65·5(0)
(g)	CF_2Cl_2	−6·9(0)	(p)	1-fluoronaphthalene	−123·0(0)
(h)	F_2	+422·9(0)	(q)	2-fluoronaphthalene	−117·0(0)
(i)	$CF_3 \cdot CO \cdot CF_3$	−84·6(0)			

The major part of this work consists of tables containing chemical shift and spin–spin coupling constant information for compounds in the liquid state or in solution. The remainder covers studies in solids and liquid crystals, together with biological applications and theoretical studies involving F-19 NMR. To keep this presentation manageable these latter sections either only give the relevant literature references (solids, polymers,

* "Recommendations for the presentation of NMR data for publication in chemical journals. B. Conventions relating to spectra from other nuclei", *Pure Appl. Chem.*, 1976, **45**, 217.

and liquid crystal tables) or brief descriptions with literature references (biological applications and theoretical studies). Finally a bibliography of review articles containing F-19 NMR information is presented.

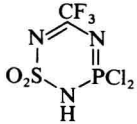
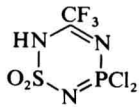
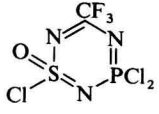
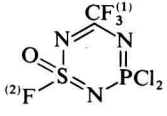
The tables are arranged according to the type of carbon (or element) to which the fluorine nucleus is bound. The appearance of a compound, with more than one type of fluorine-bonded carbon, in a particular table is according to which fluorine has its chemical shift reported and/or comes higher in the list of tables found above. Thus a molecule with a trifluoromethyl group and a fluoroaromatic residue will appear in Section II provided that the shift of the trifluoromethyl group is reported, but in the fluoroaromatic table (Section V) if only the shift of the fluorine bound to the aromatic residue is reported. Similarly where only coupling constant information is reported the same priority exists. Chemical shift information takes priority over coupling constant information. The only exception to the above is Section VII where an attempt has been made to include all the data for carbonium ions and carbanions irrespective of whether fluorine is directly attached to the charged carbon or not.

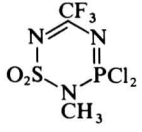
Each table, apart from those in Sections IX to XI consists of (1) the molecular formula of the compound, (2) the structure of the compound, (3) the F-19 chemical shift data, (4) the F-19 spin–spin coupling constant data, and (5) the literature reference number with the reference compound index (from Table I) given in parentheses, where applicable. In Sections IX to XI only columns (1), (2), and (5) are included. Each table is arranged according to the index of the molecular formulae, and the convention adopted for priority of the elements is C, F, H, and then the other elements in alphabetical order. Only the relevant nuclei in the molecule are numbered [column (2)]. In cases where only one number is given but the system shows two chemical shifts, for example the AB spectra from CF_2 groups, these are distinguished by letters following the number.

In all cases fluorine–fluorine and fluorine–hydrogen coupling constants are indicated in column (4) by two numbers separated by a hyphen [e.g. (1–2) indicates a J(F–F) or J(F–H) between nuclei numbered (1) and (2) in the structural formula in column (2)], or by numbers followed by letters for AB systems [e.g. (2A–2B) indicates a J(F–F) between fluorine nuclei of an AB system numbered (2) in the structural formula in column (2)]. Other couplings are represented by a number for the fluorine (or F) and an element symbol separated by a hyphen, with the higher atomic number nucleus having priority. The element involved in the coupling may be numbered, but the coupled nuclei, other than fluorine, are always denoted by the element symbol followed by the number [e.g. a coupling between phosphorus and fluorine may appear in column (4) as (P–z), (P–F), (Px–z), (Px–F), ^{y}J(P–z), ^{y}J(P–F), ^{y}J(Px–z), or ^{y}J(Px–F), where x, y, and z are integers]. The above should be self-evident from the tables.

II. FLUORINE BONDED TO A CARBON OF A SATURATED ALIPHATIC HYDROCARBON

A. Fluorine nuclei in a CF_3 group

Molecular formula	Structure of compounds	Chemical shifts (ppm)	Coupling constants (Hz)	Ref.
1. CF_3 group bonded to carbon				
$C_2F_3HBr_2$	$CF_3^{(1)}\cdot CH^{(2)}Br_2$	−75·1	(1-2) 6	23(a)
$C_2F_3HCl_2N_3O_2PS$	 and 	−73·6	(P-F) 6	30
$C_2F_3H_2NO$	$CF_3^{(1)}\cdot CH^{(2)}{=}NOH$	−67·5	(1-2) 5	32(a)
$C_2F_3H_3O$	$CF_3^{(1)}\cdot CH_2^{(2)}OH$ (neat)		(1-2) 8·94 (variation with solvent studied)	35
$C_2F_3BrCl_2$	$CF_3\cdot CBrCl_2$	−80·3		23(a)
$C_2F_3Br_2Cl$	$CF_3\cdot CBr_2Cl$	−79·1		23(a)
$C_2F_3Br_3$	$CF_3\cdot CBr_3$	−78		23(a)
$C_2F_3Cl_3$	$CF_3\cdot CCl_3$	−81·5		23(a)
$C_2F_3Cl_3N_3OPS$		−75.8	(P-F) 7·3	30
C_2F_4BrCl	$CF_3^{(1)}\cdot CF^{(2)}BrCl$	(1) −83·7 (2) −76·9	(1-2) 8	23(a)
$C_2F_4Br_2$	$CF_3^{(1)}\cdot CF^{(2)}Br_2$	(1) −81·8 (2) −77·2	(1-2) 10	23(a)
$C_2F_4Cl_2N_3OPS$		(1) −75·97 (2) +77·2	(P-1) 8·5 (P-2) 6·8	30

Molecular formula	Structure of compounds	Chemical shifts (ppm)	Coupling constants (Hz)	Ref.
C_2F_7NOS	$CF_3^{(1)}\cdot CF_2^{(2)}\cdot NSOF_2^{(3)}$	(1) −87·6 (2) −86·8 (3) −50·4	(1-3) 1·25 (2-3) 9·4	42
C_2F_7P	$CF_3^{(1)}\cdot CF_2^{(2)}\cdot PF_2^{(3)}$	(1) −83·4 (2) −139.4 (3) −106·4	(1-2) 2·0 (1-3) 6·4 (2-3) 9·0 (P-1) 7·4 (P-2) 101·0 (P-3) 1259·3	50
$C_2F_8H_2S$	$CF_3^{(1)}\cdot CH_2^{(4)}\cdot SF_4^{(2)}F^{(3)}$	(1) −65·4 (2) +68·2 (3) +75·5	(1-2) 10·1 (1-4) 8·8 (2-3) 138 (2-4) 7·3	52
$C_2F_8O_3S$	$CF_3^{(1)}\cdot C(O)\cdot OO\cdot SF_4^{(2)}F^{(3)}$	(1) −171·8 (2) +56·7 (3) +57·9	(2-3) 154·8	18
C_2F_8Si	$CF_3^{(1)}\cdot CF_2^{(2)}\cdot SiF_3^{(3)}$	(1) −86·5 (2) −134.4 (3) −150·2	(1-2)−3·59 (1-3) −2·81 (2-3)+4·92 (Si-3) +275·3	21
C_2F_9HS	$CF_3^{(1)}\cdot CH^{(5)}F^{(2)}\cdot SF_4^{(3)}F^{(4)}$	(1) −76·3 (2) −172·1 (3) +51·6 (4) +68·2	(1-2) 11·0 (1-3) 11·0 (1-5) 5·4 (2-3) 2·5 (2-4) 2·5 (2-5) 43·5 (3-4) 144·0 (3-5) 5·0	52
C_2F_9BrS	$CF_3^{(1)}\cdot CF^{(2)}Br\cdot SF_4^{(3)}F^{(4)}$	(1) −80·0 (2) −100·3 (3) +50·2 (4) +63·8	(3-4) 146·6	53
$C_2F_{10}O_3S$	$CF_3^{(1)}\cdot CF^{(2)}(OSO_2F^{(3)})\cdot SF_4^{(4)}F^{(5)}$	(1) −79·9 (2) −110·3 (3) +51·2 (4) +45·3 (5) +62·3	(1-2) 12·0 (1-3) 2·8 (2-3) 2·8 (2-4) 12·0 (2-5) 4·2 (3-4) 9·5 (4-5) 142	52
C_3F_3HBrN	$CF_3^{(1)}\cdot CH^{(2)}Br\cdot CN$	−71·5	(1–2) 7·0	62
$C_3F_3H_2N$	$CF_3^{(1)}\cdot CH_2^{(2)}\cdot CN$	−66·8	(1-2) 9·2	62
$C_3F_3H_3Cl_2N_3O_2PS$		−74·2	(P-F) 6·3	30