Organic Magnetic Resonance, 1969, Vol. 1, pp. 375 to 388. Heyden & Son Limited. Printed in Northern Ireland

MULTIPOLAR COMPLEXES—II*

THE SELF ASSOCIATION OF -NO_2 -CN AND -COCN POLAR GROUPS

R. E. USCHOLD and R. W. TAFT
Department of Chemistry, University of California,
Irvine, 92665, USA

(*Received* 3 *June* 1969; *accepted* 4 *June* 1969)

Abstract—Fluorine nuclear magnetic resonance (F-NMR) has been used to determine dissociation constants for multipolar complexes formed by several *p*-substituted fluorobenzenes in CCl_4 and cyclohexane at 25°. Data in CCl_4 were also obtained at $-20°$. The results are interpreted in simplified terms as dipole-dipole interactions which lead to a complex of net zero dipole moment. Although the dissociation constants are not of high accuracy, the values obtained do indicate that both polarity and steric effects are important in the presumed multipolar complexes.

INTRODUCTION

THE HIGH sensitivity of F-NMR shielding in *p*-fluorophenyl derivatives to substituent effects, and to solvent effects upon them, is well established.[1] Because of the sensitivity offered by this method, it has been chosen to study a variety of molecular interactions ranging from strong Lewis acid-base complexes[2] to relatively weak hydrogen bonded complexes.[3] Multipolar complexes are thought to be the result of dipolar interactions which generally fall between hydrogen bonding and van der Waals forces in energy. In spite of this low stability of multipolar complexes, the high sensitivity of F-NMR shielding parameters to minute changes in average molecular magnetic environment makes this method applicable to the study of the self interactions of the -NO_2, -CN and -COCN polar groups.

The historical development and previous experimental investigations of multipolar complexes have been reviewed in the first paper in this series[4] and will not be repeated here.

RESULTS

Table 1 presents dissociation constants and shielding parameters determined for several compounds.† The shift at infinite dilution, i.e. the shift of uncomplexed solute, $\int_0$, was measured experimentally at low concentration (~0·01 M). The limiting shift, or shift of the complex, $\int_{\mathrm{lim}}$, and the dissociation constant, K_d, were obtained by a computer analysis[4] of the F-NMR shielding parameters determined as a function of the concentration of polar solute (0·01 to ~3 M). The data were fitted to equations (1) and (2) with K_d and $\int_{\mathrm{lim}}$ as adjustable parameters. In these equations S_0, S and S_2 represent the total concentration of polar solute, the concentration of

---

* For Part I, see Ref. 4.

† All shifts reported in this paper are given by the delta scale convention adopted by OMR. All shifts are listed as $-\int$ values, however, so that the sign of $-\int$ conforms to that of the $\int$ values given in the initial papers of this series (references 1 to 4).

TABLE 1. DISSOCIATION CONSTANTS AND SHIELDING PARAMETERS FOR MULTIPOLAR COMPLEXES

Compound	Solvent	temp.	$-\int_0$ ‡	$-\int_{\text{lim}}$ ‡	K_d	$\Delta H_d°$*
p-fluorobenzoylcyanide	CCl_4	5	−14·48	−16·1	3·9	+1·3
	CCl_4	−20	−14·70	−16·1	2·5	
	c-C_6H_{12}	25	−14·11	−16·1	5·0	
3,4-difluorobenzoylcyanide	CCl_4	25	−10·67	−12·3	7·0	+1·9
	CCl_4	−20	−10·96	−12·3	3·9	
	c-C_6H_{12}	25	−10·38	−12·3	4·6	
p-fluorobenzonitrile	CCl_4	25	−9·10	−10·6	7·0	+0·8
	CCl_4	−20	−9·31	−10·6	5·5	
	c-C_6H_{12}	25	−8·80	−10·6	7·5	
p-fluoronitrobenzene	CCl_4	25	−9·39	−11·7	5·6	+1·0
	CCl_4	0	−9·48	−11·7	4·6	
	CCl_4	−20	−9·54	−11·7	4·1	
	c-C_6H_{12}	25	−9·01	−11·7	6·1	
3,4-difluoronitrobenzene	CCl_4	25	−5·55	−7·2	7·3	+1·4
	CCl_4	−20	−5·77	−7·2	4·8	
	c-C_6H_{12}	25	−5·24	−7·2	5·8	
p-fluoronitrosobenzene†	CCl_4	25	−11·03	−14·1	12·4	—
2,6-dimethyl-4-fluoronitrobenzene	CCl_4	25	−2·19	−4·6	20·0	—

* In kcal./mole.

† Data from reference 4.

‡ Shifts in units of delta scale; see previous footnote, p. 375.

uncomplexed solute and the concentration of the dimer complex, respectively.

$$K_d = \frac{S^2}{S_2} \tag{1}$$

$$\int_{\text{obs}} = \frac{S}{S_0}\int_0 + \frac{S_2}{S_0}\int_{\text{lim}} \tag{2}$$

The details of the program have been previously described.[4] Figure 1 illustrates typical data obtained for *p*-fluoronitrobenzene in CCl_4 at three temperatures. For convenience of illustration, the ordinate for the data at 0° and −20° has been *arbitrarily adjusted* so that $\int_0$'s coincide for all cases. The shielding parameters at any concentration are known to ±0·02 ppm and the fits to eqn (2) hold to this same precision over the entire concentration range. Figure 1 clearly demonstrates the effects expected from an increase in association as the temperature is lowered, i.e. by the increased slopes of the curves at lower temperatures. Similar temperature studies could not be carried out in cyclohexane because of its high freezing point.

Internal fluorobenzene was used as a reference for measurement of the shielding parameters for all mono-fluoro compounds listed in Table 1. In order to provide an independent check on these results, 3,4-difluoronitrobenzene and 3,4-difluorobenzoylcyanide were studied. In these cases the *m*-fluorine was used as the reference signal. Values of K_d have large uncertainties due to the relatively large uncertainties (±0·3 ppm) associated with the limiting shift values. This error arises from the long

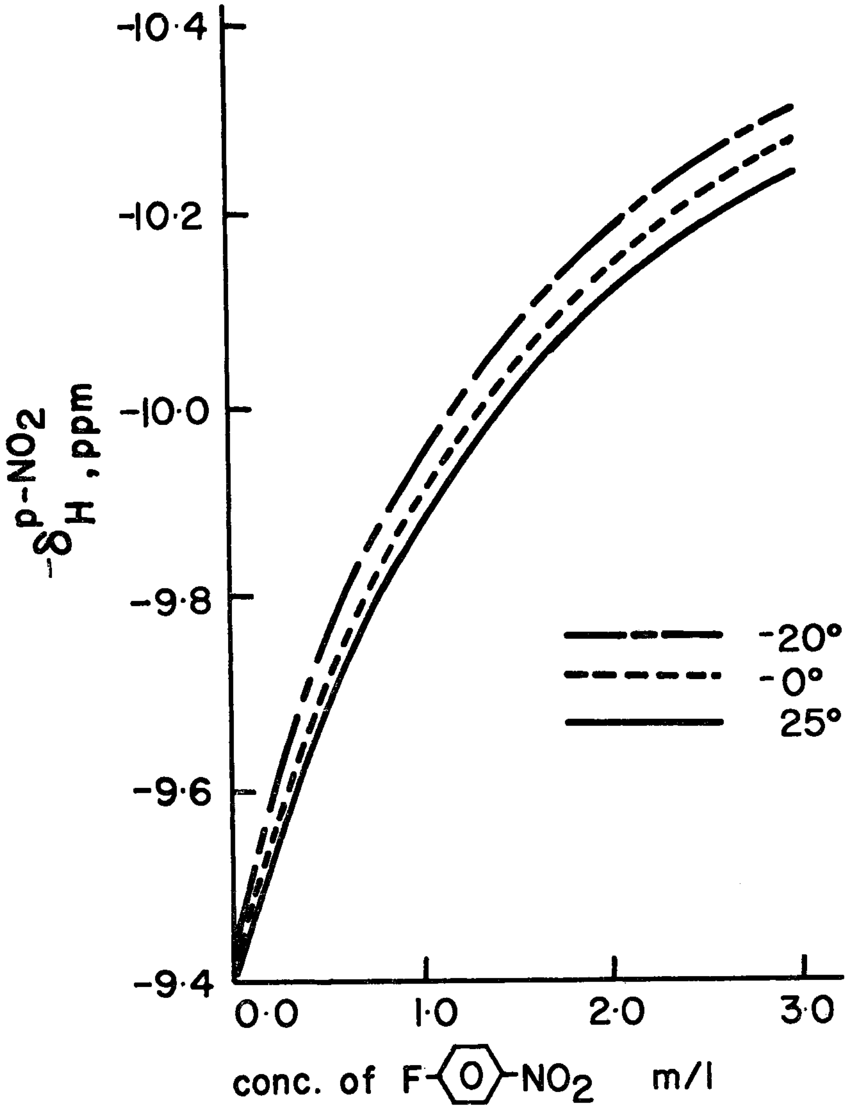


Fig. 1. Shielding parameters for *p*-fluoronitrobenzene at 3 temperatures. Ordinate is adjusted for data at 0° and −20° so that δ_0 coincides for all temperatures.

extrapolations to 100% complex formation. Within these uncertainty limits, the dissociation constants are the same for the pairs: 3,4-difluoronitrobenzene and *p*-fluoronitrobenzene; 3,4-difluorobenzoylcyanide and *p*-fluorobenzoylcyanide. Further, within a similar uncertainty limit, the dissociation constants in CCl_4 and cyclohexane are the same. Thus, the mean value of K_d at 25° for the COCN function is 5·1 ± 0·9; for the NO_2 function, is 6·1 ± 0·5; and for the CN function, is 7·3 ± 0·3. This same order of increasing K values is also observed at −20° (COCN, 3·2 ± 0·7; NO_2, 4·5 ± 0·4; CN, 5·5). Mean values of $\Delta H_d{}^\circ$ also appear to indicate the same stability order: COCN, 1·6 ± 0·3 > NO_2, 1·2 ± 0·2 > CN, 0·8.

Improvements in the measurement of the shielding parameters since the first paper in this series has led to a revision of the calculated parameters for the complexes studied in that paper. For example, K_d, $-\int_0$ and $-\int_{\mathrm{lim}}$ for *p*-fluoronitrobenzene were calculated to be 4·0, —9·43 and —11·2, respectively.[4] These values compare with 5·6, —9·39 and —11·7 for K_d, $-\int_0$ and $-\int_{\mathrm{lim}}$, respectively, in the present study. Similar differences arise for the calculated parameters for 3,4-difluoronitrobenzene. Since we have measured $\int_0$ directly, it is no longer treated as an adjustable parameter.

Recent cryoscopic studies[5] of dilute CCl_4 solutions of benzonitrile, nitrobenzene and 2-nitro-*m*-xylene are consistent with K_d values of 1·9, 2·0 and >250, respectively. These values are only in fair agreement with our results at —20° but are probably within combined experimental errors since the author* feels his results are correct to within a factor of two.

DISCUSSION

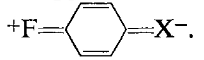
The $\int_0$ values in Table 1 show a definite order with respect to temperature and solvent. In every case $\int_0$ is at lower field strength at —20° than at 25° and in CCl_4 than cyclohexane. Previous work[1] on pure solvent effects has shown that the latter result is indeed general for +R polar substituents. The previous work[4] also suggests that an increase in association is expected with increased dipole-dipole interaction. The mean values of K_d and ΔH_d appear to support the stability order expected, i.e. COCN > NO_2 > CN > NO. It is of interest to note that with —R *p*-substituted fluorobenzenes no appreciable temperature effect is observed (cf. Table 2).

TABLE 2. TEMPERATURE EFFECT ON F-NMR SHIELDING PARAMETERS* FOR SOME —R *p*-SUBSTITUTED FLUOROBENZENES.

p-X	$-\int_H$ †(CCl_4 25°)	$-\int_H$ †(CCl_4 −20°)
$-CH_3$	5·45	5·44
–F	6·80	6·79
$-OCH_3$	11·65	11·72

* Solute concentration is 0·01 M. Shielding parameters are relative to internal 0·1 M fluorobenzene.

† Shifts in units of delta scale; see previous footnote, p. 375.

Since each of the polar monomers have shifts ($\int_0$ values) which are increasingly shifted to lower field in the order: cyclohexane (25°), CCl_4(25°), CCl_4(—20°), this order corresponds to the apparent ability of the solvents to increasingly support charge separation, e.g.  In contrast, the shifts for the dimers of each compound ($\int_{\mathrm{lim}}$ values) were found to be identical within the probable experimental error in both solvents and at both temperatures in CCl_4. The averaged values of $\int_{\mathrm{lim}}$ listed in Table 1 were used in the final evaluation of K_d values. The apparent insensitivity of $\int_{\mathrm{lim}}$ values to solvent and temperature is consistent with the concept that the multipolar complex results from an antiparallel alignment of dipoles of the two polar molecules to give a dimer of essentially zero dipole moment. Such an orientation would presumably yield a substituted fluorobenzene, which like the —R *p*-substituted fluorobenzenes of Table 2, would tend to be insensitive to solvent and temperature change.

---

* G. A. Chappel, private communication.

Although the errors in K_d values require extreme caution in the interpretation of $\Delta H_d{}^\circ$ values, these latter values are in each case greater than RT, as required for the concept of a definite complex. However, since the largest $\Delta H_d{}^\circ$ value obtained is only 1·9 kcal., it appears appropriate to regard multipolar complexes as little more than encounter complexes. It is evident that it would be desirable to study even more highly polar functional groups than those of Table 1 in order to obtain $\int_{\text{lim}}$, K_d, and $\Delta H_d{}^\circ$ values of greater accuracy. However, in this connection it is to be noted in Table 1 that the dissociation constant for 2,6-dimethyl-4-fluoronitrobenzene is about 4 times greater than that for *p*-fluoronitrobenzene. This result indicates that steric factors adversely effect the stability of multipolar complexes. Thus steric factors must be minimized to achieve greatest complex stability.

We have also noted that the shift of *p*-fluoro-*N*,*N*-dimethyl benzamide relative to internal fluorobenzene is essentially the same in 0·01 M solution in CCl_4 at 35° ($-\int_H = -1{\cdot}61$ ppm) as in the pure amide to which a small amount of CCl_4 has been added to depress the melting point to 35° ($-\int_H = -1{\cdot}68$ ppm). This result indicates that there is little tendency for dimerization to occur with the benzamide in accord with the polarity and steric considerations noted above.[6]

EXPERIMENTAL

Materials: *p*-fluoronitrobenzene, *p*-fluorobenzonitrile, fluorobenzene and *o*-difluorobenzene were purchased from Pierce Chemical Co. and were purified by distillation. The 1,1,2,2-tetrachloro-3,3,4,4-tetrafluorocyclobutane (TCTFCB) was used as obtained from J. T. Baker Co. Professor

TABLE 3. F-NMR SHIFT DATA

(1) F^{19}-NMR Shift Data for *p*-FC_6H_4COCN in CCl_4 at 25°

(FC_6H_4COCN), M	$-\int_{H}^{p\text{-COCN}}$, ppm
0·0202	−14·50
0·0606	−14·52
0·101	−14·56
0·202	−14·61
0·404	−14·72
0·583	−14·80
0·800	−14·89
1·00	−14·94
1·17	−14·98
2·00	−15·12
2·33	−15·13
3·00	−15·19

Free fit parameters for dimerization:

$$K_d = 2{\cdot}95 \pm 0{\cdot}32;$$

$$-\int_0 = -14{\cdot}47 \pm 0{\cdot}01;$$

$$-\int_{\text{lim}} = -15{\cdot}93 \pm 0{\cdot}12$$

Note: A similar series of experiments for the same concentration range with *m*-FC_6H_4COCN gave no measurable effects of concentration.

TABLE 3 (*cont.*)

(2) F^{19}-NMR Shift Data for *p*-FC_6H_4COCN in C_6H_{12} at 25°

(FC_6H_4COCN), M	$-\int_{H}^{p\text{-COCN}}$, ppm
0·0200	−14·14
0·0600	−14·16
0·100	−14·18
0·200	−14·22
0·400	−14·39
0·600	−14·43
0·800	−14·50
1·00	−14·55
1·20	−14·63
1·50	−14·70
2·00	−14·80
2·40	−14·86
3·00	−14·94

Free fit parameters for dimerization:

$K_d = 5{\cdot}90 \pm 0{\cdot}84$;

$-\int_{0} = -14{\cdot}12 \pm 0{\cdot}01$;

$-\int_{\text{lim}} = -16{\cdot}26 \pm 0{\cdot}30$

(3) F^{19}-NMR Shift Data for *p*-FC_6H_4COCN in CCl_4 at −20°

(FC_6H_4COCN), M	$-\int_{H}^{p\text{-COCN}}$, ppm
0·0105	−14·71
0·0210	−14·73
0·0612	−14·75
0·105	−14·80
0·210	−14·87
0·420	−14·98
0·612	−15·04
0·840	−15·12
1·01	−15·20
1·23	−15·24
2·10	−15·34

Free fit parameters for dimerization:

$K_d = 2{\cdot}80 \pm 0{\cdot}46$;

$-\int_{0} = -14{\cdot}70 \pm 0{\cdot}01$;

$-\int_{\text{lim}} = -16{\cdot}15 \pm 0{\cdot}2$

TABLE 3 (*cont.*)

(4) F^{19}-NMR Shift Data for *p*-FC_6H_4CN in CCl_4 at 25°

(FC_6H_4CN), M	$-\int_{H}^{p\text{-CN}}$, ppm
0·0200	−9·11
0·0605	−9·13
0·100	−9·15
0·200	−9·19
0·400	−9·26
0·605	−9·31
0·800	−9·34
1·00	−9·40
1·21	−9·43
1·42	−9·46
1·60	−9·50
2·00	−9·56
2·40	−9·61
3·13	−9·66

Free fit parameters for dimerization:

$$K_d = 7{\cdot}75 \pm 0{\cdot}98;$$

$$-\int_{0} = -9{\cdot}11 \pm 0{\cdot}01;$$

$$-\int_{\text{lim}} = -10{\cdot}72 \pm 0{\cdot}20$$

(5) F^{19}-NMR Shift Data for *p*-FC_6H_4CN in C_6H_{12} at 25°

(FC_6H_4CN), M	$-\int_{H}^{p\text{-CN}}$, ppm
0·0195	−8·81
0·0585	−8·83
0·0975	−8·85
0·195	−8·90
0·390	−8·97
0·585	−9·03
0·780	−9·11
0·975	−9·12
1·17	−9·17
1·47	−9·22
1·95	−9·32
2·34	−9·37
2·93	−9·42

Free fit parameters for dimerization:

$$K_d = 6{\cdot}53 \pm 0{\cdot}81;$$

$$-\int_{0} = -8{\cdot}80 \pm 0{\cdot}01;$$

$$-\int_{\text{lim}} = -10{\cdot}52 \pm 0{\cdot}22$$

Table 3 (*cont.*)

(6) F^{19}-NMR Shift Data for p-FC_6H_4CN in CCl_4 at −20°

(FC_6H_4CN), M	$-\int_{H}^{p\text{-CN}}$, ppm
0·0211	−9·33
0·0638	−9·34
0·106	−9·36
0·211	−9·41
0·422	−9·49
0·638	−9·54
0·844	−9·57
1·06	−9·59
1·28	−9·66
1·58	−9·72

Free fit parameters for dimerization:

$K_d = 6{\cdot}07 \pm 2{\cdot}28$;

$-\int_{0} = -9{\cdot}32 \pm 0{\cdot}01$;

$-\int_{\lim} = -10{\cdot}73 \pm 0{\cdot}63$

(7) F^{19}-NMR Shift Data for p-$FC_6H_4NO_2$ in CCl_4 at 25°

(p-$FC_6H_4NO_2$), M	$-\int_{H}^{p\text{-}NO_2}$, ppm
0·0100	−9·40
0·0600	−9·41
0·100	−9·44
0·200	−9·50
0·400	−9·61
0·600	−9·72
0·800	−9·80
1·000	−9·88
1·20	−9·92
1·50	−10·00
2·00	−10·12

Free fit parameters for dimerization:

$K_d = 6{\cdot}64 \pm 0{\cdot}90$;

$-\int_{0} = -9{\cdot}37 \pm 0{\cdot}01$;

$-\int_{\lim} = -11{\cdot}87 \pm 0{\cdot}39$

TABLE 3 (*cont.*)

(8) F^{19}-NMR Shift Data for *p*-$FC_6H_4NO_2$ in C_6H_{12} at 25°

$(FC_6H_4NO_2)$, M	$-\int_{H}^{p\text{-}NO_2}$, ppm
0·0101	−9·01
0·0201	−9·02
0·0600	−9·04
0·101	−9·10
0·201	−9·18
0·402	−9·32
0·600	−9·40
0·804	−9·49
1·01	−9·54
1·20	−9·59
1·50	−9·70
2·01	−9·80
2·40	−9·90
3·00	−9·99

Free fit parameters for dimerization:

$$K_d = 5{\cdot}2 \pm 0{\cdot}6;$$

$$-\int_0 = -9{\cdot}01 \pm 0{\cdot}01;$$

$$-\int_{\text{lim}} = -11{\cdot}4 \pm 0{\cdot}31$$

(9) F^{19}-NMR Shift Data for *p*-$FC_6H_4NO_2$ in CCl_4 at −20°

$(FC_6H_4NO_2)$, M	$-\int_{H}^{p\text{-}NO_2}$, ppm
0·0105	−9·54
0·0210	−9·56
0·0630	−9·59
0·105	−9·65
0·210	−9·73
0·420	−9·84
0·630	−9·94
0·840	−10·02
1·05	−10·10
1·26	−10·16
1·57	−10·24
2·10	−10·35
2·52	−10·39
3·15	−10·46

Free fit parameters for dimerization:

$$K_d = 3{\cdot}9 \pm 0{\cdot}3;$$

$$-\int_0 = -9{\cdot}53 \pm 0{\cdot}01;$$

$$-\int_{\text{lim}} = -11{\cdot}6 \pm 0{\cdot}12$$

TABLE 3 (*cont.*)

(10) F^{19}-NMR Shift Data for 3,4-$F_2C_6H_3NO_2$ in CCl_4 at 25°

$(F_2C_6H_3NO_2)$, M	$-\int_{3\text{-F}}^{4\text{-F}}$, ppm
0·0201	−5·58
0·100	−5·59
0·201	−5·62
0·404	−5·70
0·604	−5·77
0·621	−5·73
0·776	−5·84
1·00	−5·86
1·55	−5·97
2·01	−6·03

Free fit parameters for dimerization:

$K_d = 9{\cdot}08 \pm 3{\cdot}5;$

$-\int_0 = -5{\cdot}56 \pm 0{\cdot}02;$

$-\int_{\text{lim}} = -7{\cdot}49 \pm 0{\cdot}94$

(11) F^{19}-NMR Shift Data for 3,4-$F_2C_6H_3NO_2$ in C_6H_{12} at 25°

$(F_2C_6H_3NO_2)$, M	$-\int_{3\text{-F}}^{4\text{-F}}$, ppm
0·0200	−5·25
0·0600	−5·28
0·200	−5·35
0·400	−5·46
0·600	−5·54
0·800	−5·62
1·00	−5·67
1·20	−5·73
1·50	−5·78
2·00	−5·89
2·40	−5·94
3·00	−6·01

Free fit parameters for dimerization:

$K_d = 5{\cdot}3 \pm 0{\cdot}3;$

$-\int_0 = -5{\cdot}23 \pm 0{\cdot}01;$

$-\int_{\text{lim}} = -7{\cdot}15 \pm 0{\cdot}10$

TABLE 3 (*cont.*)

(12) F^{19}-NMR Shift Data for *p*-$FC_6H_4NO_2$ in CCl_4 at 0°

$(FC_6H_4NO_2)$, M	$-\int_{H}^{p\text{-}NO_2}$, ppm
0·0206	−9·51
0·0615	−9·54
0·103	−9·56
0·206	−9·63
0·412	−9·75
0·615	−9·87
0·824	−9·94
1·03	−10·01
1·55	−10·14
2·06	−10·25
2·46	−10·32
3·10	−10·39

Free fit parameters for dimerization:

$K_d = 4\cdot87 \pm 0\cdot30;$

$-\int_{0} = -9\cdot48 \pm 0\cdot01;$

$-\int_{\text{lim}} = -11\cdot65 \pm 0\cdot12$

(13) F^{19}-NMR Shift Data for 3,4-$F_2C_6H_3NO_2$ in CCl_4 at −20°

$(F_2C_6H_3NO_2)$, M	$-\int_{3\text{-}F}^{4\text{-}F}$, ppm
0·0210	−5·78
0·0630	−5·84
0·105	−5·87
0·210	−5·90
0·420	−5·96
0·630	−6·04
0·840	−6·09
1·05	−6·15
1·26	−6·16
1·57	−6·21
2·10	−6·32
3·15	−6·42

Free fit parameters for dimerization:

$K_d = 5\cdot1 \pm 0\cdot5;$

$-\int_{0} = -5\cdot77 \pm 0\cdot01;$

$-\int_{\text{lim}} = -7\cdot30 \pm 0\cdot12$

TABLE 3 (*cont.*)

(14) F^{19}-NMR Shift Data for 3,4-$F_2C_6H_3COCN$ in CCl_4 at 25°

($F_2C_6H_3COCN$), M	$-\int_{3\text{-F}}^{4\text{-F}}$, ppm
0·0199	−10·66
0·0593	−10·69
0·0994	−10·72
0·199	−10·75
0·398	−10·83
0·593	−10·88
0·795	−10·93
0·994	−10·97
1·19	−11·01
1·49	−11·07
1·99	−11·13
2·37	−11·17
2·99	−11·24

Free fit parameters for dimerization:

$K_d = 5{\cdot}73 \pm 0{\cdot}49$;

$-\int_{0} = -10{\cdot}66 \pm 0{\cdot}01$;

$-\int_{\text{lim}} = -12{\cdot}13 \pm 0{\cdot}10$

(15) F^{19}-NMR Shift Data for 3,4-$F_2C_6H_3COCN$ in C_6H_{12} at 25°

($F_2C_6H_3COCN$), M	$-\int_{3\text{-F}}^{4\text{-F}}$, ppm
0·0200	−10·40
0·0603	−10·43
0·100	−10·45
0·200	−10·52
0·400	−10·62
0·603	−10·71
0·800	−10·79
1·00	−10·85
1·21	−10·90
1·50	−10·98
2·00	−11·05
2·41	−11·11
3·00	−11·23

Free fit parameters for dimerization:

$K_d = 5{\cdot}37 \pm 0{\cdot}50$;

$-\int_{0} = -10{\cdot}38 \pm 0{\cdot}01$;

$-\int_{\text{lim}} = -12{\cdot}44 \pm 0{\cdot}10$

TABLE 3 (*cont.*)

(16) F^{19}-NMR Shift Data for 3,4-$F_2C_6H_3COCN$ in CCl_4 at −20°

($F_2C_6H_3COCN$), M	$-\int_{3\text{-F}}^{4\text{-F}}$, ppm
0·0209	−10·95
0·0623	−11·02
0·105	−11·04
0·209	−11·08
0·418	−11·19
0·623	−11·24
0·836	−11·29
1·05	−11·32
1·25	−11·37
1·57	−11·42
2·09	−11·47
2·49	−11·50
3·14	−11·63

Free fit parameters for dimerization:

$K_d = 4{\cdot}16 \pm 0{\cdot}99;$

$-\int_{0} = -10{\cdot}97 \pm 0{\cdot}02;$

$-\int_{\text{lim}} = -12{\cdot}33 \pm 0{\cdot}21$

(17) F^{19}-NMR Shift Data for 2,6-dimethyl-4-fluoronitrobenzene in CCl_4 at 25°

($FC_6H_2(CH_3)_2NO_2$), M	$-\int_{H}^{NO_3}$, ppm
0·0200	−2·18
0·0600	−2·20
0·200	−2·25
0·400	−2·27
0·600	−2·32
0·800	−2·34
1·00	−2·39
1·20	−2·43
1·50	−2·46
2·40	−2·59
3·00	−2·68

Free fit parameters for dimerization:

$K_d = 20{\cdot}2 \pm 6{\cdot}9;$

$-\int_{0} = -2{\cdot}19 \pm 0{\cdot}01;$

$-\int_{\text{lim}} = -4{\cdot}62 \pm 1{\cdot}2$

G. Illuminati kindly supplied a sample of 2,6-dimethyl-4-fluoronitrobenzene and 3,4-difluoronitrobenzene was prepared as described in the literature.[4]

3,4-*Difluoroacetophenone* 25 g of *o*-difluorobenzene and 75 g of $AlCl_3$ were added to 100 ml CS_2. The mixture was refluxed and 17·2 g acetyl chloride was added. Refluxing was continued for 24 hrs. Then the mixture was poured onto ice and dilute HCl was added. The product was extracted with ether and distilled. b.p. 93 to 95°/8·6 mm. Yield 76%.

3,4-*Difluorobenzoic acid* 33 g of NaOH was dissolved in 280 ml water and cooled to 0°. 48 g of bromine were added maintaining the temperature between 0 to 5°. The hypobromite solution was warmed to room temp. and 9·5 g 3,4-difluoroacetophenone were added. The mixture was stirred for 36 hrs., after which a precipitate of CBr_4 was removed and the product was precipitated with HCl. m.p. 118 to 120°. Yield 70%.

3,4-*Difluorobenzoylcyanide* 5 g of 3,4-difluorobenzoic acid and 20 ml of thionyl chloride were refluxed for 3 hrs. The excess thionyl chloride was removed by distillation and 4 g of dry cuprous cyanide were added to the reaction flask. The flask was heated at 200 to 210° for 1½ hrs. The mixture was vigourously shaken every 15 mins. The mixture was cooled and the product was extracted from the copper salts with ether and then distilled. b.p. 58 to 61°/1·6 mm. Yield 42%. The *p*-fluorobenzoylcyanide was prepared from *p*-fluorobenzoic acid according to the directions given above for the preparation of 3,4-difluorobenzoylcyanide.

Shift measurements: Samples were prepared by diluting appropriate volumes of stock solutions and contained 0·1 M fluorobenzene as an internal reference. A capillary of TCTFCB in CCl_4 was used as frequency lock reference for use with a Varian Associates model HA-60 spectrometer. Fluorine signals were decoupled from proton by means of an SD-60B Heteronuclear Spin Decoupler from NMR Specialties Co. A time averaging computer was employed to obtain shift data for solutions containing $<0{\cdot}05$ M fluorine and the temperature was controlled to $\pm 1°$. Shift measurements were reproducible on independently prepared samples of equivalent concentration to $\pm 0{\cdot}02$ ppm. The individual shift data in ppm on the delta scale are listed in Table 3.

Acknowledgement—This work was supported in part by the National Science Foundation. Grateful acknowledgement is also made to NSF for support which made available the NMR spectrometer.

REFERENCES

1. R. W. Taft, *et al.*, *J. Am. Chem. Soc.* **85**, 709, 3146 (1963).
2. R. G. Pews, Y. Tsuno and R. W. Taft, *J. Am. Chem. Soc.* **89**, 2391 (1967).
3. D. Gurka *et al.*, *J. Am. Chem. Soc.* **89**, 5957 (1967).
4. R. W. Taft, G. B. Klingensmith and S. Ehrenson, *J. Am. Chem. Soc.* **87**, 3620 (1965).
5. G. A. Chappel, PhD Thesis, State University of New York at Buffalo, February, 1968.
6. Compare, for example, M. Rabinowitz and A. Pines, *J. Am. Chem. Soc.* **91**, 1585 (1969).