

Electronic Interactions in 4-Substituted 2,3,5,6-Tetrafluoropyridines

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The mutual electronic interactions between electron-withdrawing and -releasing substituents and the 2,3,5,6-tetrafluoropyridyl system are evaluated from the electric dipole moments of 13 4-substituted 2,3,5,6-tetrafluoropyridines in benzene. The effect of dioxane on some of the solutes is discussed.

A previous paper¹ discussed the extent to which the electric dipole moments of some 16 substituted tetra- and pentafluorobenzenes were modified by the electronic interactions between the fluorine atoms and various electron-withdrawing and -releasing substituents. A natural extension of this work is to investigate how similarly fluorinated derivatives of pyridine are affected by such mutual electronic interactions. It is known that the 2,3,5,6-tetrafluoropyridyl group is more electronegative than the pentafluorophenyl moiety² as expected from the presence of the ring nitrogen atom. Just as pyridine is more susceptible to nucleophilic attack than benzene, so pentafluoropyridine is also considerably more susceptible to attack by nucleophilic reagents than its carbocyclic analogue, hexafluorobenzene, and thus it is possible to produce a whole range of 4-substituted 2,3,5,6-tetrafluoropyridines. We now report a study of the electronic interactions between the 2,3,5,6-tetrafluoropyridyl group and 12 substituents in the 4-position by the method of electric dipole moments.

Experimental

The solutes were prepared and purified by methods reported in the literature³⁻⁸ except for pentafluoropyridine which was obtained commercially. The purified solvents were stored over drying agents, benzene and cyclohexane with sodium, and carbon tetrachloride with calcium chloride. Dioxane when used as solvent was distilled freshly after continuous reflux over sodium. Measurements of dielectric constants, refractive indices and densities were carried out by standard procedures,^{9,10} with results summarised in Table 1.

Discussion

Our electric dipole moment data may be analysed in three ways to give rough estimates of the extent of mutual electronic interactions occurring in the compounds studied.

(a) 2,3,5,6-Tetrafluoropyridine is regarded as a reference compound and evaluating $\Delta\mu_1$, defined as the algebraic

Table 1. Polarisation, refractions, densities, and dipole moments at infinite dilution at 25 °C of substituted 2,3,5,6-tetrafluoropyridines and related compounds.

Substituent	Solvent	Conc. range (10 ⁵ W ₂)	$\alpha\epsilon_1$	β	$-\gamma^1$	P_2/cm^3	$R_{D,\text{av}}/\text{cm}^3$	10 ³⁰ μ^a/cm
X	F	C ₆ H ₆	878—3 199	0.48	0.450	0.143	47.0	20.8
	cC ₆ H ₁₂	827—3 317	0.46	0.447	0.062	49.0	25.7	3.47 ± 0.07
	C ₆ H ₆	552—3 639	2.17	0.427	0.090	111.9	28.5	6.67 ± 0.03 (6.34 ± 0.03) ^c
NH ₂	C ₆ H ₆	894—4 008	11.52	0.461	0.043	390.4	27.0	14.04 ± 0.07
N(CH ₃) ₂	C ₆ H ₆	937—3 838	11.60	0.372	0.056	465.1	36.2	15.24 ± 0.07
NHNH ₂	C ₆ H ₆	866—3 817	9.65	0.509	0.029	359.0	27.6	13.38 ± 0.03
N ₃	C ₆ H ₆	936—5 177	2.11	0.451	0.059	112.0	30.4	6.60 ± 0.03
	C ₄ H ₈ O ₂	1 923—6 261	13.37	0.385	-0.015	396.6	26.2	14.18 ± 0.03
CN	C ₆ H ₆	495—1 329	0.81	0.438	0.137	60.6	22.8	4.44 ± 0.03
H	C ₆ H ₆	958—1 597	3.68	0.354	0.125	137.9	24.6	7.81 ± 0.03
CH ₃	C ₆ H ₆	1 384—3 258	5.24	0.389	0.088	197.3	27.6	9.57 ± 0.07
3-Fluoropyridine	C ₆ H ₆	972—4 067	4.61	0.233	0.042	109.6	23.2	6.80 ± 0.03
2,6-Difluoropyridine	C ₆ H ₆	614—2 079	12.80	0.303	0.089	304.4	22.5	12.34 ± 0.03

^a Calculated on the basis that $P_D = 1.05 R_D$ except for *b* and *c* which are based on the P_D values obtained by adding the apparent moments of hexafluorobenzene³ and chloropentafluorobenzene³ to the R_D values of the compounds concerned. Incremental changes in the relative permittivities, densities, and refractive indices ($\Delta\epsilon$, Δd , and Δn^2 , respectively) were measured for solutions having solute weight fractions w_2 . The coefficients α , β , and γ^1 , were derived from the relations $\alpha\epsilon_1 = \Sigma\Delta\epsilon/\Sigma w_2$, $\beta d_1 = \Sigma\Delta d/\Sigma w_2$, $\gamma^1 n_1^2 = \Sigma\Delta n^2/\Sigma w_3$.

Table 2. Comparison of moments (in benzene at 25 °C) of 4-derivatives of 2,3,5,6-tetrafluoropyridines with (a) 2,3,5,6-tetrafluoropyridine and (b) those of corresponding 4-substituted pyridines

Substituent X	4- $\text{XC}_5\text{F}_4\text{N}$ $\mu(\text{C}_5\text{NF}_4\text{X})^a$	$\Delta\mu_1^b$	4- $\text{XC}_5\text{H}_4\text{X}$ $\mu(\text{C}_5\text{H}_4\text{NX})^c$	$\Delta\mu_2^d$	μ_{calc}^e for $\text{C}_5\text{H}_4\text{NX}$	$\Delta\mu_3^f$
F	3.70	-4.11	3.54	+0.16	2.57	+1.13
Cl	6.67	-1.14	2.80	+3.87	2.03	+4.64
NH ₂	14.04	+6.23	13.11	+0.93	12.01*	+2.03
N(CH ₃) ₂	15.24	+7.43	14.44	+0.80	12.98*	+2.26
NHNH ₂	13.38	+5.57			12.61*	+0.77
N ₃	6.60	-1.21			3.87*	+2.73
OH	12.04	+4.23	17.68	-5.64	9.07	+2.97
OCH ₃	11.51	+3.70	10.34	+1.17	9.24	+2.27
CN	4.44	-3.37	5.44	-1.00	6.17	-1.73
NO ₂	4.17	-3.64			5.90	-1.73
H	7.81	0.00	7.44	+0.37	7.44	+0.37
C ₆ H ₅	10.61	+2.80	8.57	+2.04	7.34	+3.27
CH ₃	9.57	+1.76	8.61	+0.96	8.57	+1.00

^a Observed dipole moments in benzene at 25 °C (this work). ^b $\Delta\mu_1 = \mu(\text{C}_5\text{NF}_4\text{X}) - \mu(\text{C}_5\text{HNF}_4)$. ^c Observed dipole moments in benzene at 25 °C selected from A. L. McClellan 'Tables of Experimental Dipole Moments, Volume 2' Rahrara Enterprises, California, 1974. ^d $\Delta\mu_2 = \mu(\text{C}_5\text{NF}_4\text{X}) - \mu(\text{C}_5\text{H}_4\text{NX})$. ^e Calculated dipole moments for $\text{C}_5\text{H}_4\text{NX}$ *. ^f $\Delta\mu_3 = \mu(\text{C}_5\text{NF}_4\text{X}) - \mu(\text{C}_5\text{H}_4\text{NX})_{\text{calc}}$.

difference between the moment of the 4-substituted 2,3,5,6-tetrafluoropyridine, $\mu(\text{C}_5\text{NF}_4\text{X})$, and the moment of 2,3,5,6-tetrafluoropyridine, $\mu(\text{C}_5\text{HNF}_4)$, is evaluated. Thus $\Delta\mu_1$ provides a quantitative measure of the effect of the substituent X on the electronic charge distribution in the 2,3,5,6-tetrafluoropyridyl system.

(b) $\Delta\mu_2$, defined as the algebraic difference between the moment of the 4-substituted 2,3,5,6-tetrafluoropyridine, $\mu(\text{C}_5\text{NF}_4\text{X})$ and the moment of the corresponding 4-substituted pyridine, $\mu(\text{C}_5\text{H}_4\text{NX})$ is evaluated. Thus $\Delta\mu_2$ should reveal the polarisation effect of the four fluorines on the 4-substituted pyridines. If mutual interactions between the 2,3,5,6-fluorines and the ring substituents are absent, the moments of the 4-substituted 2,3,5,6-tetrafluoropyridines should be equal to those of the corresponding 4-substituted pyridine derivatives, i.e. $\Delta\mu_2$ should be effectively zero because the moments of the four C-F bonds should mutually cancel one another.

(c) A third approach is to calculate the dipole moments of the 4-substituted pyridines by vectorial addition of the appropriate group moments and then take the algebraic difference between the moments of the 4-substituted pyridines, $\mu(\text{C}_5\text{H}_4\text{NX})$, and the calculated moments of the corresponding 4-substituted pyridines, $\mu(\text{C}_5\text{H}_4\text{NX})_{\text{calc}}$. This gives $\Delta\mu_3$. This method is particularly useful in cases where the moment of the appropriate 4-substituted pyridine is not known but it suffers from the disadvantage that interactions between the nitrogen ring atom and the 4-substituent are not allowed for.

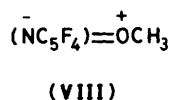
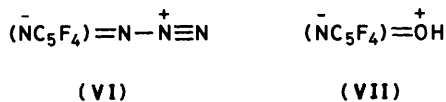
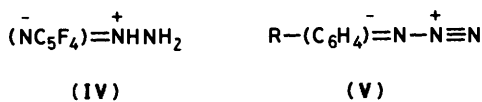
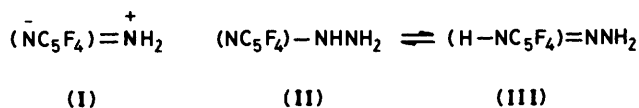
The results of these calculations are summarised in Table 2. The $\Delta\mu$ values are found to be either positive or negative. In the case of $\Delta\mu_1$, negative values imply group substituent moments acting in opposition to the moment of the 2,3,5,6-tetrafluoropyridyl group so as to lower the overall moment of the 4-substituted 2,3,5,6-tetrafluoropyridine. The substituents CN, NO₂, F, Cl, and N₃ fall into this category. Positive $\Delta\mu_1$ values are shown by the substituents NH₂, NMe₂, NHNH₂, OMe, OH, Ph, and Me; these are groups which raise the moment of 2,3,5,6-tetrafluoropyridine. In the case of $\Delta\mu_2$ and $\Delta\mu_3$, there is a closer correlation between the signs of the values and the inductive and mesomeric properties of the substituent. We find that negative values are associated with the powerful electron withdrawing (-I, -M) substituents such as CN and NO₂; whereas positive values are associated with electron-releasing (-I, +M) substituents such as NH₂, NMe₂, NHNH₂, OMe, Ph, Me, F, and Cl. The position of OH is complicated by

intramolecular hydrogen bonding and the existence of the 4-hydroxy compound as tautomeric mixtures.

2,3,5,6-Tetrafluoropyridine.—In the absence of interaction between the four fluorines and the ring nitrogen, 2,3,5,6-tetrafluoropyridine should have a dipole moment of 7.34×10^{-30} C m, i.e. that of pyridine itself. Our observed value of 7.81×10^{-30} C m for 2,3,5,6-tetrafluoropyridine shows that some interaction does exist. The dipole moment of pyridine is derived from a π -electron contribution, a σ -electron contribution, and a moment arising from hybridization of the lone-pair electrons of the N atom.¹¹ The N atom in pyridine is a σ -acceptor and only very slightly a π -acceptor.¹² Since the effect of replacing the hydrogens by fluorines is to cause the σ -orbitals to be more tightly bound but leaving the π -orbitals relatively unaffected,¹³ we may expect the σ - and π -acceptor strength of N to be modified, but it is not clear what the final pattern of charge density distribution will be without resorting to an *ab initio* MO calculation. In any case, since mutual inductive effects from the two *ortho*-fluorines would lower the resultant moment of the molecule, we conclude that any *ortho*-inductive effects¹⁴ that may exist are outweighed by other effects accompanying the insertion of the F atoms.

(i) **Electron-attracting (-I, -M) Substituents:** CN, NO₂.—The negative $\Delta\mu_1$ values indicate that the CN and NO₂ group moments act vectorially to reduce the overall moment of the corresponding 4-substituted 2,3,5,6-tetrafluoropyridine. The negative $\Delta\mu_2$ and $\Delta\mu_3$ values imply that the presence of four fluorines reduces the effective moments of these two substituents, as in the case of the penta- and 2,3,5,6-tetrafluorobenzene derivatives.¹ The lower moment of 4-nitrotetrafluoropyridine compared with 4-cyanotetrafluoropyridine may largely be attributed to a reduced -M effect of the NO₂ group caused by steric inhibition of resonance.

(ii) **Halogen (-I, +M) Substituents:** F, Cl.—Measurements of the dipole moment of pentafluoropyridine in three different solvents (benzene, carbon tetrachloride, and cyclohexane) indicate the absence of any solute-solvent interaction of the type found to occur when pyridine and substituted pyridines are mixed with carbon tetrachloride.¹⁵ This is consistent with the fact that pentafluoropyridine unlike pyridine, is not sufficiently basic to yield either a co-ordination compound with boron trifluoride, or a salt with hydrogen chloride. The negative $\Delta\mu_1$



(NC₅F₄) = 2,3,5,6-tetrafluoro-4-pyridyl

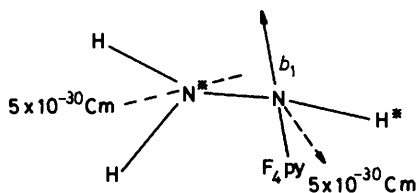


Figure 1.

values for both F- and Cl-substituted tetrafluoropyridines (even after correcting for the maximum possible atomic polarisation) show that replacement of the hydrogen atom by these halogens results in an overall lowering of moment, caused essentially by the $-I$ effect. However, the relatively large difference in $\Delta\mu_1$ values for the two substituents is surprising and needs to be explained. The different behaviour of these halogens when attached to C₆H₅ or C₆F₅ appears to be related to the polarity of the ring-halogen σ -bond.¹⁶ In the halobenzenes, this bond will be rather highly polar with the halogen atom at the negative end of the dipole. This polarity will favour the back donation of halogen lone-pair electrons to the benzene ring so that the halogens will appear as π -donors in the order I < Br < Cl < F. In the pentafluorophenyl system, however, the relatively high electronegativity of the C₆F₅ group will reduce the polarity of the ring-substituent σ -bond, and the tendency of the halogen to donate its lone-pairs to the ring will be correspondingly reduced¹⁶ although the donor strength is still in the order I < Br < Cl < F. Accordingly if we assume that the reduction in polarity of the C-Cl σ -bond is disproportionately greater than that of the C-F σ -bond and that the corresponding changes in π -bonding are much less significant as far as dipole moment values are concerned, the strikingly different values of $\Delta\mu_1$ for Cl and F can be explained.

(iii) *Electron-releasing* ($-I$, $+M$) *Substituents*: NH₂, N(CH₃)₂, NHNH₂, N₃, OH, OCH₃.—4-Amino- and 4-dimethylamino-tetrafluoropyridine. Just as the dipole moment of 4-aminopyridine (13.11×10^{-30} C m) is appreciably higher than that of aniline (5.10×10^{-30} C m), so too is the moment of 4-amino-tetrafluoropyridine (14.04×10^{-30} C m) greater than that of 2,3,5,6-tetrafluoroaniline¹ (6.10×10^{-30} C m) by about the

same magnitude. This suggests that the presence of the four fluorines affects 4-aminopyridine to the same extent as aniline. Our result that the moment of 4-aminotetrafluoropyridine is greater than that of 4-aminopyridine, shows that the four C-F bonds, which may be expected to mutually cancel out in the first approximation, may have in fact through the $-I$ effects of the four fluorines, enhanced the importance of the double-bonded structure (I) thus leading to an exaltation of moment.

Thus we may conclude that the ability of NH₂ to donate π -electrons appears to be further stimulated by the strongly electron-withdrawing tetrafluoropyridine group even though the NH₂ group may not be quite coplanar with the pyridine ring. A similar mechanism would explain why the moment of 4-dimethylaminotetrafluoropyridine is greater than that of 4-dimethylaminopyridine (*cf.* Table 2).

It was also observed in this work that the dipole moment of 4-dimethylaminotetrafluoropyridine in benzene is appreciably higher than that of 4-aminotetrafluoropyridine. This is consistent with the demonstration,¹⁷⁻²⁰ confirmed by our own calculations of mesomeric moments,²¹ that the mesomeric interaction and presumably the p character of the nitrogen atom's lone pair orbital increases upon N-methylation of the amino group and with the introduction of electronegative substituents into the phenyl ring.

4-Hydrazinotetrafluoropyridine. Like 4-hydrazinopyridine which exists predominantly in the hydrazine form^{22,23} 4-hydrazinotetrafluoropyridine is a potentially tautomeric compound (II) \rightleftharpoons (III).

It is instructive to calculate the dipole moment of 4-hydrazinotetrafluoropyridine assuming the basic conformation that has been deduced for phenylhydrazine^{24,25} (Figure 1). To provide for maximum orbital overlap, the plane of the tetrafluoropyridyl ring is maintained parallel to a line joining N* and H*. The amino group (N*H₂) produces a component of 5×10^{-30} C m acting at 55° to the N-N longitudinal axis whereas the unit N*-N(H)NC₅F₄ contributes a component of 5×10^{-30} C m acting at *ca.* 43° to the C-N direction and in the plane containing the b_1 and b_3 semi-axes of the molecule. It is further assumed that the plane of N*-N and the bisector of the angle H-N*-H is at right angles to the plane of N*-N and the bisector of the angle H-N-C and in which the free electron pair of the NH₂ group is *trans* to the pyridyl ring. The vectorial resultant of the moments of pyridine and phenylhydrazine gives 12.61×10^{-30} C m neglecting the presence of the four fluorine atoms. This is smaller than our observed value of 13.38×10^{-30} C m in benzene. The difference suggests that the hydrazino group interacts with the ring possibly *via* the electromer (IV).

4-Azidotetrafluoropyridine. The azide group itself has a negative σ -inductive ($-I$) effect and a positive π -mesomeric ($+M$) effect comparable to that of fluorine. The electromeric influence of the azide group on a benzene ring^{13,26-28} must be strongly electron donating to account for its *ortho-para* orienting character and its marked activating influence on electrophilic substitution, and as a result the structure (V) is of considerable importance in describing the influence of the p -azido group.

A value of *ca.* 150° for the valence angle of the azide group is consistent with the dipole moment values of some *para*-substituted phenyl azides.²¹ We have calculated the dipole moment of 4-azidotetrafluoropyridine from the equation $\mu^2_{\text{calc}} = \mu^2_{\text{py}} + \mu^2_{\text{PhN}} + 2\mu_{\text{py}}\mu_{\text{PhN}} \cos 150^\circ$. The calculated value of 3.87×10^{-30} C m is considerably lower than the observed value of 6.60×10^{-30} C m. This difference could be largely due to the presence of the four fluorine atoms in the pyridyl ring, which enhances the mesomeric ($+M$) effect of the azide group giving extra stability to structure (VI) which in turn enhances the magnitude of the dipole moment of 4-azido-tetrafluoropyridine.

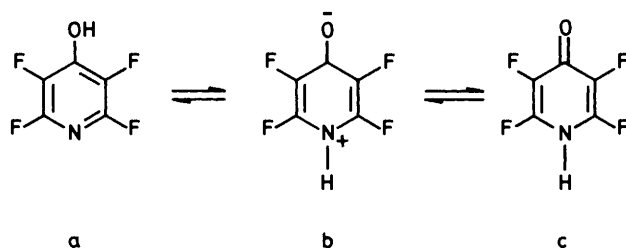


Figure 2.

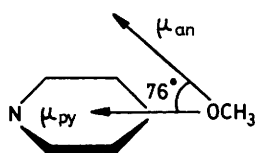


Figure 3.

4-Hydroxytetrafluoropyridine.—Unlike 4-hydroxypyridine,^{12,29–33} 4-hydroxytetrafluoropyridine exists principally in the pyridine (Figure 2a) and not in the pyridone form (Figure 2c) in carbon tetrachloride in the absence of added acid or base.³⁴ The predominance of the pyridine form can be attributed to the reduced electron availability on nitrogen. The presence of *ortho*-fluorines would also result in intramolecular hydrogen bonding thus stabilising the coplanar phenol structure through increased mesomeric interaction. The smaller moment of 4-hydroxytetrafluoropyridine compared with 4-hydroxypyridine is thus explained.

The dipole moment of 4-hydroxytetrafluoropyridine can be calculated by the vectorial addition of the moments of pyridine (or tetrafluoropyridine) and phenol taking the angle at which they intersect to be 88°. This gives a moment of 9.07×10^{-30} if pyridine is used as a component or 9.47×10^{-30} C m if tetrafluoropyridine is used. The disparity between observed and calculated values indicates a possible contribution from resonance structure (VII).

Solvent Effect on Compounds with Substituents NH₂, N(CH₃)₂, NHH₂, and OH.—The increase in the dipole moment of an amine in dioxane solution has been attributed to hydrogen bonding between the amino hydrogen atoms and the oxygen atoms of dioxane.^{35,36} It has also been inferred that an appreciable increase in molecular polarisation, and consequently in apparent moment accompanies the hydrogen bonding only when an increase in the mesomeric effect can occur, *i.e.* when it results in an increased donation of electron density from the hydrazino, amino nitrogen atom, or the oxygen atom of the OH group to the ring. These conclusions should also apply to the relevant compounds in Table 1 which shows that relative to benzene, dioxane raises the dipole moment of 4-aminotetrafluoropyridine by 2.13×10^{-30} C m but for 4-dimethylaminotetrafluoropyridine the increase is only 0.6×10^{-30} C m presumably because in the latter compound there are no amino hydrogens to form hydrogen bonds.

4-Methoxytetrafluoropyridine. The $\Delta\mu_1$ observed in this work suggests that in spite of the lack of coplanarity,^{37–41} the mesomeric (+M) effect of the methoxy group is enhanced when the four 2,3,5,6-hydrogens in 4-methoxypyridine are replaced by fluorines. Vectorial analysis⁴² based on the moments of pyridine²² and anisole⁴³ yields a moment of 9.24×10^{-30} C m for 4-methoxypyridine assuming the absence of resonance interaction between the methoxy group and the ring nitrogen (see Figure 3). This would also be the moment of 4-methoxytetrafluoropyridine in the absence of interaction of the

nitrogen atom and the methoxy group with the four fluoro substituents.

The observed moment of 4-methoxypyridine (10.34×10^{-30} C m) suggests that there is interaction between the methoxy group and the ring nitrogen probably arising from the existence of resonance hybrids such as (VIII).

Comparison of the observed moment difference ($\Delta\mu_2$) between 4-methoxytetrafluoropyridine and 4-methoxypyridine (1.17×10^{-30} C m) and that between pentafluoroanisole and *p*-fluoroanisole (0.40×10^{-30} C m) is consistent with chemical evidence that the 2,3,5,6-tetrafluoropyridyl group is more electronegative than the pentafluorophenyl moiety.³

The vectorial resultant of the dipole moment of 2,3,5,6-tetrafluoropyridine and of *p*-HC₆F₄OCH₃¹ is 10.27×10^{-30} which is closer to the experimentally observed value of 11.51×10^{-30} C m for 4-methoxytetrafluoropyridine. However, the residual difference is consistent with an enhancement of the (+M) effect of the methoxy group when it is placed in the 4-position as in 4-methoxytetrafluoropyridine.

(iv) **C₆H₅ and CH₃ Substituents.**—Replacement of a hydrogen atom in a heterocyclic ring by a phenyl group should not introduce a second primary moment into the molecule.⁴⁴ The apparent phenyl group moment of 4-phenyltetrafluoropyridine may be explained essentially in terms of induction of the highly polarisable phenyl group by the primary dipole located near the nitrogen atom.⁴⁵ However, the presence of the four fluorine atoms would affect the net charges on the carbon atoms of the pyridyl ring, causing greater displacement of the electrons of the phenyl group. Greater π -electron conjugation between the ring systems could arise due to the increase in the positive charge on the substituted carbon atom in the pyridine ring.

In the absence of steric effects and of induction between *ortho*-fluorine atoms and between methyl and fluorine, the dipole moment of 4-methyl-2,3,5,6-tetrafluoropyridine should be equal to that of γ -picoline²⁶ (2.57 D; 8.57×10^{-30} C m). Alternatively, the moment may be expected to be equal to the sum of the moments of toluene²⁷ (0.37 D; 1.23×10^{-30} C m) and 2,3,5,6-tetrafluoropyridine (2.34 D; 7.81×10^{-30} C m) *i.e.* 2.71 D or 8.94×10^{-30} C m. The observed moment of 4-methyl-2,3,5,6-tetrafluoropyridine is however, 0.2–0.3 D or *ca.* 0.6 – 1.0×10^{-30} C m higher than the expected values, much as in the case of 2,3,5,6-tetrafluorotoluene and pentafluorotoluene.

Induction between *ortho*-fluorine atoms and the ring nitrogen atom slightly raises the moment of 2,6-difluoropyridine (this compound has a moment of 3.70 D or 12.34×10^{-30} C m instead of the value of 3.65 D or 12.18×10^{-30} C m expected from vectorial addition). Induction between fluorine and methyl is expected to be negligible¹ and induction between *ortho*-fluorine atoms decreases the value of the moment.¹ Thus the discrepancies between the expected values and the observed moment of 4-methyl-2,3,5,6-tetrafluoropyridine seem best attributed to hyperconjugation between the methyl group and the aromatic 2,3,5,6-tetrafluoropyridyl system.

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