The Doubly Determined Substitution Structure of 1,3-Difluorobenzene

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The carbon – fluorine bond length and the distortion of the benzene ring under fluorination have been determined by the isotopic substitution method for 1,3-difluorobenzene. – The experimental work was carried out predominantly by Double Resonance Modulation (DRM) microwave spectroscopy, which allowed all C^{13}-forms to be studied in their natural abundances. The normal and the 2,4,6,-d_3 species were used as the parent molecules, and the resulting two sets of structure parameters are found to agree well with each other. With square brackets indicating consistency limits between the two sets of results deduced by the Kraitchman method, the following bond distances (in Å) and angles (in degrees) have been found:

$C(1/3) - F(1/3) = 1.3561\,[9]$
$C(2) - C(1/3) = 1.3888\,[1]$
$C(1/3) - C(6/4) = 1.3745\,[7]$
$C(4/6) - C(5) = 1.3956\,[1]$
$C(2) - H(2) = 1.0822\,[3]$
$C(4/6) - H(4/6) = 1.0820\,[2]$
$\sphericalangle\, C(2)\,C(1)\,F(1) = 117.26\,[7]$
$\sphericalangle\, C(1)\,C(2)\,C(3) = 115.74\,[6]$
$\sphericalangle\, C(2)\,C(3)\,C(4) = 123.70\,[5]$
$\sphericalangle\, C(3)\,C(4)\,C(5) = 118.00\,[2]$
$\sphericalangle\, C(4)\,C(5)\,C(6) = 120.86\,[1]$
$\sphericalangle\, C(1)\,C(2)\,H(2) = 122.13\,[3]$
$\sphericalangle\, C(3)\,C(4)\,H(4) = 119.92\,[1]$
$\sphericalangle\, C(4)\,C(5)\,H(5) = 119.57\,[1]$

The bond lenth $C(5) - H(5)$ was assumed as 1.082 ± 0.001 Å.

I. Introduction

The preceding structure study [1] on 1,2-difluorobenzene (orthodifluorobenzene, ODFB) made it desirable to examine also the molecular structure of 1,3-difluorobenzene (meta-difluorobenzene, abbreviated as MDFB) in order to derive experimentally secured information on the carbon – fluorine bond length in this compound and to quantify further the distortion of the benzene ring under fluorination. Ultimately, these data present experimental information needed for gaging the success of existing [2] or future structure calculations on these compounds by *ab initio* methods.

II. Experimental

a) Samples

MDFB was obtained from Koch-light laboratories and purified by vacuum distillation at room temperature. 2-d_1-MDFB ($\sim$ 70% enriched) was prepared [3] by reacting the normal form with sodium methoxide and deutero-methanol at 50 °C for one week. A mixture of 4,6-d_2-MDFB ($\sim$ 20%) and 2,4,6-d_3-MDFB ($\sim$ 60%) was obtained by reacting the normal form with concentrated D_2SO_4 at room temperature for about three weeks. The eight distinct ^{13}C-forms of normal and 2,4,6-d_3-MDFB were studied in their natural abundance of 1.1%.

b) Instrumental

Experimental work on the normal and 2-d_1-form was carried out by conventional Stark Effect Modulation (SEM) [4] microwave spectroscopy. Work on the other isotopic forms was conducted by Double Resonance Modulation (DRM) techniques [5] at room temperature and at sample pressures of $\sim$ 20 mTorr. Frequency ranges for pump- and signal-radiation were as specified in the preceding study [1].

III. Spectroscopic Results

a) Sequence of analysis

At the outset of this study the previous work of Nygaard et al. [6] on the normal form of MDFB was confirmed by DRM spectroscopy, and the assignments were extended by SEM work up to 26 GHz. The spectra of the four distinct ^{13}C-forms of the normal molecule were identified next by DRM tech-

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niques [5]. The highly enriched 2-d$_1$-form was then examined by SEM spectroscopy. This sample deteriorated subsequently, and this prevented the later examination and extension of the assignments by DRM methods. Due to spectral complexity under SEM the 2,4,6-d$_3$ sample was studied by DRM, which also revealed the presence of the 4,5-d$_2$-form in this sample. There was no evidence for the presence of the perdeutero-form in this sample. The spectroscopic work was completed with the study of spectra of the four ^{13}C-forms of the trideutero-species by DRM spectroscopy.

b) Derivation of Rotational Parameters

The twelve spectra of normal and isotopic forms of MDFB were fitted [7] to the Hamiltonian given before [1] with four quartic centrifugal distortion constants. The variation in the number and in the range of J-values of measured transitions for the different isotopic forms required again that a reasonable set of distortion constants be established for use in the final fits of the spectra.

α) Distortion Treatment

Initial fits of the spectra of the normal and the three deuterated species showed 3σ-uncertainties of up to 200% in the widely differing distortion constants τ_{aabb} and τ_{abab} (see Table 1) of these four species. Guided by the previous results on ODFB, a weighted average of $\tau_{aabb} = 0.325$ kHz was inserted as a fixed parameter into the re-fits, and this resulted in close agreement between the initially different values of τ_{abab}, leading to an average value of $\tau_{abab} = (-0.385 \pm 0.007)$ kHz for the four isotopic species. With this constant fixed in the described manner, $\tau_{aabb} = (0.323 \pm 0.009)$ kHz was redetermined, and these two values were subsequently used in the final fitting of all the spectra. For fitting the ^{13}C-spectra the constants τ_{aaaa} and τ_{bbbb} were also held fixed at the values of the parent forms (normal and 2,4,6-d$_3$-species, Table 1, rows 5 and 8). Minute variations of the rotational constants as a result of the described disposition over the distortion constants are covered by the 3σ-limits quoted.

β) Rotational Constants

These are collected in Table 2 together with the resulting moments of inertia of the 12 isotopic forms. The top of this table gives the usual statistics of the fitted spectra. The 564 measured transition frequencies have been deposited with the "Sektion für Spektren und Strukturdokumentation" of the University of Ulm. They are also available from the author.

IV. Structure Calculation

Table 2 contains sufficients isotopic data for independent determinations [8] of the ring geometry of MDFB in the reference frame of the normal species and in the inertial axis system of the 2,4,6-d$_3$-species. The two axis systems are interconnected simply by a shift of the origin (centre of gravity) along the C$_{2v}$-axis (b-axis). For placing the peripheral hydrogen or deuterium atoms, the same experimental data have to be used twice: the hydrogen positions of H(2) and H(4/6)

Table 1. Determination of centrifugal distortion constants in 1,3-difluorobenzene (MDFB).

	Species	Quartic distortion constants (in kHz)			
		τ_{aaaa}	τ_{bbbb}	τ_{aabb}	τ_{abab}
		All four distortion constants variable			
1	Normal	-2.673 ± 0.171*	-0.445 ± 0.022	$+0.413 \pm 0.086$	-0.443 ± 0.050
2	2-d$_1$	-3.189 ± 0.815	-0.539 ± 0.093	$+0.141 \pm 0.247$	-0.266 ± 0.153
3	4,6-d$_2$	-2.605 ± 0.315	-0.334 ± 0.082	$+0.650 \pm 0.363$	-0.523 ± 0.159
4	2,4,6-d$_3$	-2.231 ± 0.057	-0.408 ± 0.009	$+0.303 \pm 0.024$	-0.368 ± 0.017
		τ_{aabb} *and* τ_{abab} *fixed to average values*			
5	Normal	-2.816 ± 0.108	-0.459 ± 0.018	$+0.323$ (fixed)	-0.385 (fixed)
6	2-d$_1$	-2.590 ± 0.110	-0.472 ± 0.032		
7	4,6-d$_2$	-2.504 ± 0.123	-0.407 ± 0.009		
8	2,4,6-d$_3$	-2.212 ± 0.050	-0.406 ± 0.009		

* Uncertainties are three times the standard error.

Table 2. Rotational constants and moments of inertia of 1,3-difluorobenzene (MDFB) and its isotopic species.

1	Species		Normal	^{13}C(2)	^{13}C(1/3)	^{13}C(4/6)	^{13}C(5)	2-d_1
2	Fitted transitions		26 R & 63 Q	9 R & 21 Q	10 R & 23 Q	10 R & 23 Q	8 R & 21 Q	14 R & 29 Q
3	Range of *J*-values		2–39 & 6–30	11–14 & 11–30	11–14 & 11–29	11–14 & 11–30	11–14 & 14–30	3–25 & 9–30
4	Measured by SEM/DRM		86/13	–/30	–/33	–/33	–/29	63/–
5	Std. deviation (in MHz)		0.079	0.047	0.064	0.059	0.070	0.076
6	A	in MHz	3744.224 (5)[a]	3717.796 (3)	3742.618 (4)	3709.627 (3)	3655.115 (4)	3629.899 (7)
7	B		1760.529 (3)	1760.626 (2)	1752.133 (3)	1751.513 (2)	1760.555 (3)	1760.627 (4)
8	C		1197.344 (2)	1194.675 (2)	1193.291 (2)	1189.630 (2)	1188.088 (3)	1185.459 (3)
9	τ_{aaaa}[c]	in kHz	-2.816 (108)	-2.816[b]	-2.816	-2.816	-2.816	-2.590 (110)
10	τ_{bbbb}		-0.459 (20)	-0.459	-0.459	-0.459	-0.459	-0.472 (32)
11	I_a	in μÅ^2	134.97483 (17)[d]	135.93431 (11)	135.03276 (15)	136.23363 (13)	138.26541 (17)	139.22593 (27)
12	I_b		287.05924 (50)	287.04344 (30)	288.43466 (39)	288.53675 (36)	287.05489 (47)	287.04313 (64)
13	I_c		422.08073 (70)	423.02392 (63)	423.51451 (82)	424.81772 (76)	425.36924 (99)	426.31263 (120)
14	I.D. $= I_c - I_a - I_b$		0.04665 (87)	0.04617 (70)	0.04709 (93)	0.04734 (87)	0.04894 (112)	0.04358 (138)

1	Species		4,6-d_2	2,4,6-d_3	d_3-^{13}C(2)	d_3-^{13}C(1/3)	d_3-^{13}C(4/6)	d_3-^{13}C(5)
2	Fitted transitions		13 R & 32 Q	49 R & 50 Q	12 R & 21 Q	12 R & 21 Q	13 R & 21 Q	13 R & 20 Q
3	Range of *J*-values		11–15 & 10–31	5–35 & 6–32	11–15 & 18–32	11–15 & 16–32	11–15 & 18–33	11–15 & 17–32
4	Measured by SEM/DRM		–/45	4/95	–/33	–/33	–/34	–/33
5	Std. deviation (in MHz)		0.038	0.051	0.052	0.069	0.062	0.060
6	A	in MHz	3601.478 (5)	3492.670 (3)	3469.670 (3)	3491.131 (4)	3463.099 (3)	3415.859 (3)
7	B		1704.444 (2)	1704.537 (2)	1704.622 (2)	1696.656 (2)	1696.085 (2)	1704.560 (2)
8	C		1156.814 (2)	1145.403 (1)	1142.905 (2)	1141.675 (2)	1138.402 (2)	1137.025 (2)
9	τ_{aaaa}	in kHz	-2.504 (123)	-2.212 (51)	-2.212	-2.212	-2.212	-2.212
10	τ_{bbbb}		-0.407 (9)	-0.406 (9)	-0.406	-0.406	-0.406	-0.406
11	I_a	in μÅ^2	140.32462 (19)	144.69617 (11)	145.67629 (12)	144.75995 (15)	145.93171 (15)	147.94991 (14)
12	I_b		296.50483 (30)	296.48880 (28)	296.47396 (30)	297.86587 (40)	297.96627 (35)	296.48465 (34)
13	I_c		463.86890 (46)	441.22097 (30)	442.18565 (65)	442.66198 (87)	443.93443 (75)	444.47222 (75)
14	I.D. $= I_c - I_a - I_b$		0.03946 (58)	0.03599 (43)	0.03540 (74)	0.03617 (97)	0.03645 (84)	0.03766 (81)

[a] Uncertainties are three times the standard deviation, and given in units of the last quoted decimal. [b] Distortion constants without uncertainties were held fixed in the fit. [c] $\tau_{aabb} = 0.323$ kHz, $\tau_{abab} = -0.385$ kHz throughout. [d] Conversion factor: 505376 MHz μÅ^2.

(see figure 1) are determinable in the normal axis frame from the moments of the 2-d_1- and 4,6-d_2-species, while the positions of D(2) and D(4/6) in the 2,4,6-d_3-species can be calculated from the moments of the 4,6-d_2-form (better called '2-h_1-form' in this context) and from those of the 2-d_1-form (better called '4,6-h_2-form'). The position of H(5), which could not be exchanged for deuterium, has to be assumed in both reference frames. The location of the unsubstitutable fluorine atoms can then be determined from the first moment condition and from the observed moments about the *b*-axis of the two parent molecules (normal and 2,4,6-d_3-MDFB). As in the previous case of ODFB [1] the structure calculation was carried out first on the basis of Kraitchman's equations for planar molecules [8] and then repeated with the program GEOM [9].

a) Kraitchman calculations

The *a*- and *b*-coordinates of the carbon atoms C(1/3) and C(4/6) were caluclated from all three possible combinations of ΔI_g-values and the different results were averaged, as in the case of ODFB. This same procedure, which in the case of ODFB could be applied for *all* atoms, could not be used for placing C(2), C(5) and H(2) in MDFB, because their *a*-coordinates are zero by symmetry while $\Delta I_b < 0$ for all three substitutions. The *b*-coordinates of these three atoms could be calculated for a rigid molecule either from ΔI_a alone or from ΔI_c alone, which should be equal in that case. In reality, the change in zero-point vibration under substitution leads to a relatively large discrepancy between ΔI_a and ΔI_c, while ΔI_a and $\Delta I_a^* = \Delta I_c - \Delta I_b$ (with $\Delta I_b < 0$) are fairly close and give therefore reasonably consistent *b*-coordinates. On this ground we *chose* to adopt the average *b*-coordinates resulting from the use of ΔI_a and ΔI_a^* for the Kraitchman calculation (compare Table 5 for details). The *b*-coordinate of the pair H(4/6) was determined in the same way, while its *a*-coordinate was deduced from $a^2 = \Delta I_b / 2(m_D - m_H)$ once by the use of the observed ΔI_b-value and once from $\Delta I_b^* = \Delta I_c - \Delta I_a$. The hydrogen atom H(5) on the symmetry axis was *assumed* as 1.082 ± 0.001 Å from C(5). – The substitution coordinates obtained by that approach are given in rows 1–7 of Table 3, where the square brackets have the same significance as before [1].

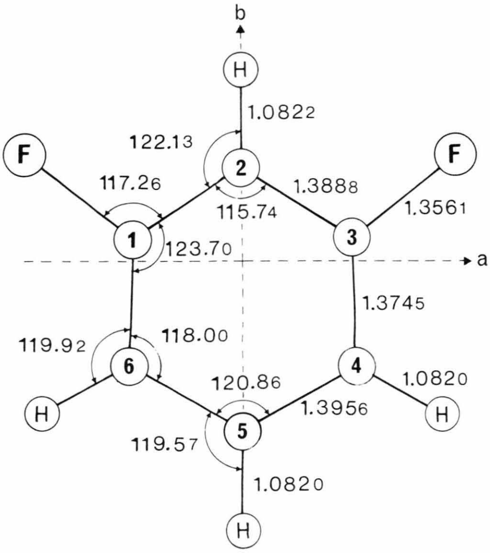

Fig. 1. The doubly determined substitution structure of *meta*-difluorobenzene (MDFB) according to Kraitchman's method.

The coordinates of the unsubstitutable fluorine atoms, finally, were obtained as follows: Calculation of b_F from the first moment condition completed the set of *b*-coordinates, which allowed the calculation of the moment about the *a*-axis for comparision with the observed value. This revealed (row 9–11 of Table 3) a deficiency of 0.14% in the moment deduced from the substitution coordinates. The same percentage deficiency was subtracted from the observed moment $I_b^{\text{obs.}}$, and the resulting, adjusted moment about the *b*-axis was then used together with the known *a*-coordinates of C(1/3), C(4/6) and H(4/6) to yield a_F.

The same procedure was followed in the determination of coordinates in the inertial axis system of 2,4,6-d_3-MDFB (column II of Table 3), in which *b*-coordinates should differ from those in the normal system by a constant amount, namely the shift of the centre of gravity under deuteration (column III of Table 3).

To obtain the coordinate set of column IV, the *b*-coordinates of atoms in the 2,4,6-d_3-frame were transformed to the normal axis system and averaged with their counterparts in that system. The *a*-coordinates, which, ideally, should be equal in the two systems, were taken as the straight averages, except for the small *a*-coordinate of C(1/3), which was weighted by

Table 3. Summary of structure calculations on 1,3-difluorobenzene (MDFB) by the Kraitchman method.

		I Normal axis system		II 2,4,6-d_3 axis system		III Shift of centre of gravity	IV Combined data (Normal axis system)	
	a) Coordinates (in Å)							
		$\pm a$	b	$\pm a$	b	$\lvert b^{I} - b^{II} \rvert$	$\pm a$	b
1	C(2)	0	+0.98206 [13][a]	0	+0.99243 [15]	0.01037	0	+0.98198 [8][b]
2	C(1/3)	1.17580 [12]	+0.24273 [60]	1.17632 [7]	+0.25435 [32]	(0.01162)	1.17614 [34][c]	+0.24346 [70][c]
3	C(4/6)	1.21386 [19]	−1.13056 [20]	1.21376 [12]	−1.11991 [14]	0.01065	1.21381 [5]	−1.13050 [6]
4	C(5)	0	−1.81923 [32]	0	−1.80873 [23]	0.01050	0	−1.81925 [2]
5	H(2)	0	+2.06405 [38]	0	+2.07491 [41]	0.01086	0	+2.06422 [17]
6	H(4/6)	2.16600 [41]	−1.64417 [56]	2.16599 [43]	−1.63385 [57]	0.01032	2.166600 [1]	−1.64428 [11]
7	H(5)	0	−2.90123 [132][d]	0	−2.89073 [123][d]	(0.01050)	0	−2.90125 [2]
8	F(1/3)	2.34322 [93][e]	+0.93460 [72][f]	2.34294 [93][e]	+0.94442 [52][f]	0.00982	2.34313 [19]	+0.93413 [47]
					average shift:	0.01054		
					expected shift:	0.01053		
	b) Observed and calculated moments of parent forms (in $\mu Å^2$)							
9	$I_a^{obs.}$	134.97483		144.69617			134.97483	
10	$I_a^{calc.}$	134.79337		144.64702			134.76580	
11	δI_a	0.18146 = 0.14%		0.22915 = 0.16%			0.20903 = 0.15%	
12	$I_b^{obs.}$	287.05924		296.48880			287.05924	
13	$I_b^{calc.}$	286.62865		296.04410			286.62819	
14	δI_b	0.43059 = 0.15% [g]		0.44470 = 0.15% [g]			0.43105 = 0.15% [g]	
	c) Deduced bondlengths (in Å)							
15	C(2) – C(1/3)	1.3889 [5]		1.3887 [3]			1.3888 [1][b]	
16	C(1/3) – C(6/4)	1.3738 [9]		1.3748 [9]			1.3745 [7]	
17	C(4/6) – C(5)	1.3956 [4]		1.3956 [3]			1.3956 [0]	
18	C(2) – H(2)	1.0820 [5]		1.0825 [6]			1.0822 [3]	
19	C(4/6) – H(4/6)	1.0818 [8]		1.0821 [8]			1.0820 [2]	
20	C(5) – H(5)	1.0820 ass'd		1.0820 ass'd			1.0820 ass'd	
21	C(1/3) – F(1/3)	1.3570 [16]		1.3554 [13]			1.3561 [9]	
22	C(2) ... C(5)	2.8013 [5]		2.8012 [4]			2.8012 [1]	
	d) Deduced bond angles (in degrees)							
23	C(1) C(2) C(3)	115.68 [6]		115.79 [4]			115.74 [6]	
24	C(2) C(3) C(4)	123.75 [5]		123.67 [3]			123.70 [5]	
25	C(3) C(4) C(5)	117.98 [5]		118.01 [4]			118.00 [2]	
26	C(4) C(5) C(6)	120.86 [6]		120.85 [5]			120.86 [1]	
27	C(1) C(2) H(2)	122.16 [3]		122.11 [2]			122.13 [3]	
28	C(3) C(4) H(4)	119.93 [7]		119.92 [7]			119.92 [1]	
29	C(4) C(5) H(5)	119.57 [3]		119.57 [3]			119.57 [0]	
30	C(2) C(3) F(3)	117.19 [10]		117.29 [8]			117.26 [7]	

[a] See text for significance of square brackets. [b] Compatibility of normal and 2,4,6-d_3 values. [c] The data in the d_3-frame were given twice the weight in the combination. [d] Uncertainty in assumed C – H distance is included. [e] Most of this uncertainty arises from an estimated error of 33% in the assumed value of $\delta I_a = I_a^{obs.} - I_a^{calc.}$. [f] Coordinate derived from first moment condition. Uncertainty assumes maximum error in the other b-coordinates. [g] Assumed as 0.15% ± 0.05%.

a factor 2 in favour of the apparently more accurate value in the 2,4,6-d_3 system. The fluorine coordinates of the combined set were re-derived as outlined above.

Bond distances and angles following in the usual way from the three coordinate sets are given in the lower half of Table 3. The square brackets in column IV of this table give the compatibility of the combined data with their counterparts in the normal and the 2,4,6-d_3 axis system. The molecular structure which emerges from the Kraitchman method is shown in Figure 1.

b) Structure Calculation with the Program GEOM

The results of computer fits of the structure of MDFB to the isotopic data of Table 2 are summerised in Table 4. In analogy to the calculations of the preceding section and to those of the previous study of ODFB, the structure of MDFB was determined separately in the normal and the 2,4,6-d_3 axis system by matching the input parameters (Kraitchman results) to the ΔI_g-values of appropriate isotopic forms. Finally, all isotopic data were used together (column IV of Table 4).

Table 4. Summary of structure results on MDFB from the program GEOM.

		I Normal axis system		II 2,4,6-d_3 axis system		III Shift of centre of gravity	IV Combined data		Δ[a]
i	Species fitted	7		7			12		
ii	$\sum(\delta I^2)$	0.87×10^{-3}		0.83×10^{-3}			0.19×10^{-2}		
	a) Fitted bond lengths (in Å)								
15	C(2) – C(1/3)	1.3875(17)[b]		1.3874(17)			1.3873(27)		−0.0015
16	C(1/3) – C(6/4)	1.3726(20)		1.3736(19)			1.3734(22)		−0.0011
17	C(4/6) – C(5)	1.3953[c]		1.3953[c]			1.3953[c]		−0.0003
18	C(2) – H(2)	1.0841(30)		1.0844(28)			1.0843(27)		+0.0021
19	C(4/6) – H(4/6)	1.0820(15)		1.0823(14)			1.0810(18)		−0.0010
20	C(5) – H(5)	1.0820 ass'd		1.0820 ass'd			1.0820 ass'd		–
21	C(1/3) – F(1/3)	1.3573 (5)		1.3577 (5)			1.3563 (6)		+0.0002
22	C(2) ... C(5)	2.7966(30)		2.7967(29)			2.7966(28)		−0.0046
	b) Fitted bond angles (in degrees)								
23	C(1) C(2) C(3)	115.88[c]		115.98[c]			115.94[c]		+0.20
24	C(2) C(3) C(4)	123.64(13)		123.57(13)			123.60(15)		−0.10
25	C(3) C(4) C(5)	117.96[c]		117.99[c]			117.98[c]		−0.02
26	C(4) C(5) C(6)	120.92[c]		120.90[c]			120.90[c]		+0.04
27	C(1) C(2) H(2)	122.06 (7)		122.01 (7)			122.02 (7)		−0.11
28	C(3) C(4) H(4)	119.93(20)		119.92(20)			120.04(24)		+0.12
29	C(4) C(5) H(5)	119.54[c]		119.55[c]			119.55[c]		−0.02
30	C(2) C(3) F(3)	117.14 (7)		117.24 (7)			117.22(10)		−0.04
	c) Deduced coordinates (in Å)								
		$\pm a$	b	$\pm a$	b	$\|b^{II} - b^{I}\|$	$\pm a$	b	
1	C(2)	0	+0.97797	0	+0.98861	0.01064	0	+0.97798	
2	C(1/3)	1.17591	+0.24149	1.17642	+0.25317	(0.01168)	1.17617	+0.24235	
3	C(4/6)	1.21388	−1.13054	1.21375	−1.11992	0.01062	1.21386	−1.13049	
4	C(5)	0	−1.81860	0	−1.80813	0.01047	0	−1.81864	
5	H(2)	0	+2.06206	0	+2.07303	0.01097	0	+2.06227	
6	H(4/6)	2.16614	−1.64434	2.16614	−1.63403	0.01031	2.16414	−1.64581	
7	H(5)	0	−2.90060	0	−2.89013	0.01047	0	−2.90064	
8	F(1/3)	2.34178	−0.93651	2.34155	+0.94629	0.00978	2.34164	+0.93601	
	d) Observed and calculated moments of parent forms (in μÅ²)								
9	$I_a^{obs.}$	134.97483		144.69617			134.97483		
10	I_a^{GEOM}	134.77914		144.45384			134.76367		
11	δI_a	0.19567 = 0.14%		0.24233 = 0.17%			0.21116 = 0.16%		
12	$I_b^{obs.}$	287.05924		296.48880			287.05924		
13	I_b^{GEOM}	286.38089		295.80371			286.35133		
14	δI_b	0.67835 = 0.24%		0.68509 = 0.23%			0.70791 = 0.25%		

[a] Difference between the GEOM results and the Kraitchman results of Table 3. [b] Uncertainties in units of the last quoted digit. [c] Parameter was not fitted, but deduced from the coordinates.

In Table 4 it will be noticed that the sum, $\sum(\delta I^2)$ in row i, of the squared differences between the observed ΔI_g-values and those calculated by the program is about 30 times larger than in the case of ODFB, which has no atoms on its symmetry axis. Examination shows that ~ 95% of the $\sum$-values in the present case arise from the atoms H(2) and C(2) which lie on the C_{2v} axis of MDFB and which give rise to negative ΔI_b-values upon substitution. These values can, of course, not be matched by the computer scheme (nor by the Kraitchman formalism). It is equally impossible to match simultaneously the noticeably different values of ΔI_a and ΔI_c for substitution of H(2) and C(2). This, in turn, leads to the relatively pronounced discrepancies (column headed Δ in Table 4) in the distances from the C(2) atom, i.e. in the bond lengths C(2) – H(2) and C(2) – C(1/3) and in the ring diameter C(2) ... C(5). As is shown in Table 5, these incongruities between Kraitchman and GEOM results arise ultimately from the occurrence of negative ΔI_b-values

Table 5. The *b*-coordinates of, and distances between (in Å), atoms on the C_{2v} axis of MDFB, calculated from different combinations of ΔI_g-values.

Method of calculation	I Normal axis system				II 2,4,6-d_3 axis system			
	Kraitchman (IV-a) (compare Table 3)			GEOM (IV-b) (see Table 4)	Kraitchman (IV-a) (compare Table 3)			GEOM (IV-b) (see Table 4)
Coordinate derived from:	$\Delta I_a^* = \Delta I_c - \Delta I_b$	ΔI_a alone	ΔI_c alone	$\Delta I_a, (\Delta I_b), \Delta I_c$	$\Delta I_a^* = \Delta I_c - \Delta I_b$	ΔI_a alone	ΔI_c alone	$\Delta I_a, (\Delta I_b), \Delta I_c$
$b_{H(2)}$	2.06367	2.06443	2.05967		2.07450	2.07532	2.07069	
Average from ΔI_a^* and ΔI_a (used in IV-a)	2.06405 [38]				2.07491 [41]			
Average from ΔI_a and ΔI_c		2.06210 [233]		↔ 2.06206		2.07300 [232]		↔ 2.07303
$b_{C(2)}$	0.98139	0.98218	0.97381		0.99228	0.99258	0.98473	
Average from ΔI_a^* and ΔI_a (used in IV-a)	0.98206 [13]				0.99243 [15]			
Average from ΔI_a and ΔI_c		0.97800 [419]		↔ 0.97797		0.98866 [407]		↔ 0.98861
$b_{C(5)}$	1.81954	1.81891	1.81834		1.80896	1.80850	1.80780	
Average from ΔI_a^* and ΔI_a (used in IV-a)	1.81922 [32]				1.80873 [23]			
Average from ΔI_a and ΔI_c		1.81862 [29]		↔ 1.81860		1.80815 [35]		↔ 1.80813
Distances deduced: C(2)–H(2)	1.08174	1.08225	1.08596		1.08222	1.08274	1.08596	
Average from ΔI_a^* and ΔI_a (used in IV-a)	1.08199 [26]				1.08248 [26]			
Average from ΔI_a and ΔI_c		1.08410 [176]		↔ 1.08410		1.08435 [161]		↔ 1.08442
C(2)...C(5)	2.80147	2.80109	2.79215		2.80124	2.80116	2.79253	
Average from ΔI_a^* and ΔI_a (used in IV-a)	2.80128 [19]				2.80120 [4]			
Average from ΔI_a and ΔI_c		2.79662 [447]		↔ 2.79657		2.79681 [428]		↔ 2.79674

on the one hand, and our particular selection of ΔI_g-values for use in the Kraitchman calculation on the other hand: in Section IV-a the b-coordinates of atoms on the C_{2v} axis are heavily weighted towards the use of ΔI_a alone, and b-values deduced from ΔI_c alone are neglected completely. The GEOM routine, in contrast, matches the different values of ΔI_a and ΔI_c simultaneously, and therefore necessarily poorly, to arrive at the average between two substantially different coordinates (and bond lengths). This shows that the discrepancies between the GEOM and Kraitchman calculations are a consequence of the choice of experimental data used in either case. They are not due to the finite accuracy of the data nor to numerical errors in the Kraitchman calculations.

An extensive discussion of the physical merit of one or the other, or of further schemes [10, 11] of structure calculation would exceed the frame-work of the present study and is therefore omitted. This can also be justified by the fact that the discrepancies, which arise from the different weighting of particular ΔI_g-values in Sect. IV-a and IV-b, do not exceed 0.002 Å for the bond lengths in MDFB. Moreover, the sought-after C–F distance turns out virtually identical in the two schemes of calculation as 1.356_2 Å.

V. Discussion

a) Centrifugal Distortion Treatments

In the previous study [6] of the normal forms of the difluorobenzenes only the distortion constants τ_{bbbb} and τ_{cccc} could be determined experimentally after τ_{aaaa} and τ_{abab} had been fixed to values derived from the force-field of these two compounds. The larger number of transitions observed for several isotopic forms in the present studies (compare Tables 2 of this and the preceding paper) does not require the imposition of such additional assumptions, and therefore affords a comparison between the constants previously estimated from the force-field and those deduced from the analyses of the rotational spectra alone. This comparison is presented in Table 6, and indicates a high degree of correlation for both ODFB and MDFB. This justifies the approach taken here and in the earlier work [6].

b) Structure Calculations

The possibility of calculating a molecular structure from two different, and largely independent sets of isotopic data naturally enhances confidence in the correctness and accuracy of the spectroscopic work and in the reliability of the deduced structure parameters. The latter results depend however on the method of structure calculation adopted. This is illustrated in the present case of MDFB in Table 4 and Table 5. There exist, in addition to the Kraitchman [8] and GEOM [9] procedures, which we have employed and contrasted above, procedures recommended by Chutjian [10] and by Rudolph [11]. While the first two of these methods ignore the possible occurrance of changing inertia defects through the assumption of an absolutely rigid structure, Chutjian's method equally suppresses such effects, but now on the basis of symmetry considerations. The 'averaged Kraitchman' procedure, which we have used here as well as in previous structure determinations, is very close to the method advocated by Rudolph [11], who however recommends the inclusion of a fourth coordinate value (derived from the combination of $\Delta I_b^* = \Delta I_c - \Delta I_a$ with $\Delta I_a^* = \Delta I_c - \Delta I_b$) in the averaging process described in Sect. IV-a, above.

c) Comparison with Related Compounds

Figure 2 brings together the structures of ODFB and MDFB, as determined in the preceding paper [1] and in this study. Fluorobenzene [13] is included in

Table 6. Centrifugal distortion constants (in kHz) in difluorobenzenes as derived from the force-field (F.F.) and from the rotational spectra (R.S.)

Compound	C.D.C.'s derived from	τ_{aaaa}	τ_{bbbb}	τ_{cccc} *	τ_{abab}
ODFB	F.F.	−3.053	−0.592	−0.100	−0.583
	R.S.	−2.812 (82)	−0.586 (4)	−0.117(24)	−0.473(15)
MDFB	F.F.	−2.981	−0.439	−0.080	−0.474
	R.S.	−2.816(108)	−0.459(18)	−0.097(12)	−0.385(50)

* τ_{cccc} was calculated [12] from the data of Tables 1 and 2.

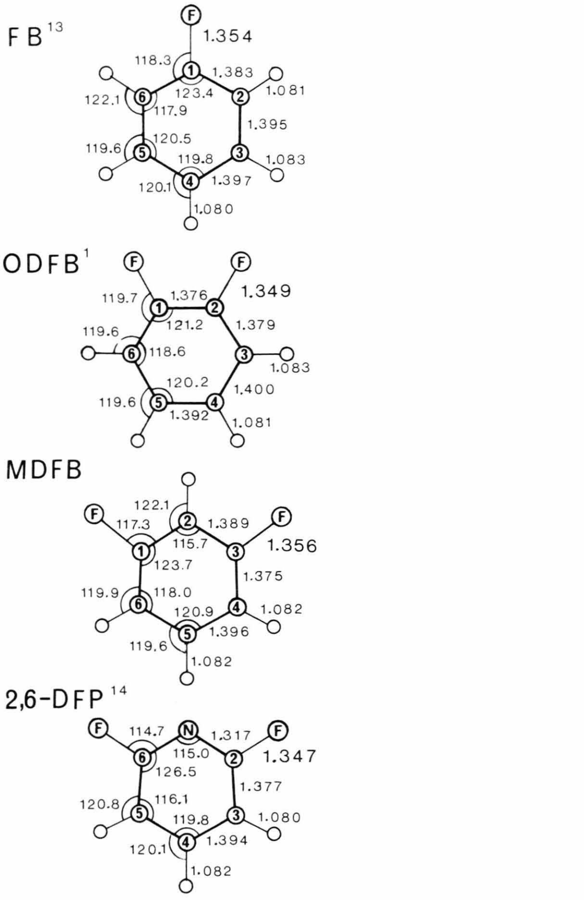

Fig. 2. The substitution structures of fluorinated benzenes and pyridine.

this figure, and the structure of 2,6-difluoropyridine [14] is added for comparison with MDFB. – A glance indicates that the effective C – F bondlengths in these four cyclic compounds deviate by less than 0.01 Å from each other, and they give an average value of 1.352 ± 0.005 Å. Earlier values [6], as short as 1.30 Å for the C – F lengths in the two difluorobenzenes were derived from the moments of the parent forms alone with the assumption that the benzene ring remained unaffected by fluorine substitution. All four structures of Fig. 2 show this assumption to have been incorrect, and the earlier, short C – F distances must therefore be dismissed. When taken collectively, the experimental C – F lengths of the four compounds suggest that the 'off-set' value (additive correction) of – 0.026 Å, which was adopted by Boggs et al. [2] to convert the results of their *ab initio* calculations into C – F bond lengths as determined by substitution (mixed r_0/r_s type) should perhaps be reduced towards – 0.017 Å. Distortion of the benzene ring upon fluorine substitution is seen to be characterized by a contraction of the two ring bonds adjacent to the site of fluorination by 0.03 – 0.04 Å in total, and a simultaneous opening of the ring angle between these bonds by ~ 3.5° in the case of fluorobenzene and MDFB. In ODFB this angle increases only by ~ 1°. Ring bond lenths removed by one or two bonds from the site of substitution deviate little from the benzene value of 1.396 Å, with distortion taken up by appropriate changes in the angles. *Ab initio* structure calculations, available [2b] for MDFB, are qualitatively in keeping with the results obtained here, though differences of 0.02 Å and 1.5° between experimental and theoretical structure parameters remain.

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