The Doubly Determined Substitution Structure of 1,2-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 1,2-difluorobenzene. – The experimental work was carried out predominantly by Double Resonance Modulation (DRM) microwave spectroscopy, which allowed the spectra of all ^{13}C-forms to be studied in their natural abundance. The normal and the 4,5-d_2 species were used as parent molecules, and the two sets of structure results are found to agree well with each other. With square brackets indicating consistency limits between the two sets of results, the following bond distances (in Å) and angles (in degrees) have been obtained:

C(1/2) – F(1/2) = 1.3494[4]
C(1) – C(2) = 1.3755[3]
C(2/1) – C(3/6) = 1.3786[3]
C(3/6) – C(4/5) = 1.4004[3]
C(4) – C(5) = 1.3917[6]
C(3/6) – H(3/6) = 1.0829[1]
C(4/5) – H(4/5) = 1.0813[4]

∢ C(1)C(2)F(2) = 119.16[1]
∢ C(1)C(2)C(3) = 121.17[2]
∢ C(2)C(3)C(4) = 118.59[2]
∢ C(3)C(4)C(5) = 120.24[1]
∢ C(2)C(3)H(3) = 119.58[1]
∢ C(3)C(4)H(4) = 119.55[1]

I. Introduction

The lack of a stable isotope of fluorine renders the determination of carbon – fluorine distances in molecules via the isotopic substitution method [1] a more cumbersome task than the determination of other carbon – halogen bond lengths by the same technique. It requires that every isotopically substitutable atom in a fluorine containing compound be placed first, so that the fluorine positions become calculable from the first moment condition and/or from the observed molecular moments of inertia. As a consequence of this, spectroscopic structure studies of fluorinated compounds were carried out preferentially on small molecules such as, for example, the fluoroethylenes [2], and the number of C – F bondlengths which have been determined without the imposition of auxiliary assumptions has remained small. Amongst the many slightly larger aliphatic fluorine compounds, and particularly amongst the many fluorine substituted aromatic rings which have attracted spectroscopic interest, fluorobenzene [3] remained for a long time the only example in which the C – F bondlength had been determined in the fashion outlined above.

Lately, the relative scarcity of experimentally secured C – F bond distances has made itself felt in conjunction with an assessment of the success of structure calculations by *ab initio* methods [4]. This makes it timely to report the results of structure work on 1,2- and 1,3-difluorobenzene (*ortho*- and *meta*-difluorobenzene, abbreviated here as ODFB and MDFB), which was carried out in a style similar to our earlier investigation of 2,6-difluoropyridine [5a] by double resonance modulation (DRM) microwave spectroscopy [5b]. Earlier work on the normal forms of these two compounds had been carried out by Nygaard et al. [6].

The present paper describes our findings on ODFB, and corresponding results for MDFB are reported in the subsequent paper.

II. Experimental

a) Samples

The eleven isotopic species spectra (Table 2), which form the experimental basis of the present study, were obtained from three different samples: Sample 1 was the normal ODFB, supplied by Koch-Light Laboratories, and purified by vacuum distillation. 3/6-d_1-ODFB (sample 2) was prepared by reacting the

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normal compound with excess sodium methoxide and deutero-methanol for 100 hrs at 50 °C [7]. After that period the sample was ~ 30% deuterated in the equivalent 3- and 6-position (~ 60% 3/6-d_1-ODFB). Sample 3 was a mixture of 4/5-d_1- (~ 40%), 4,5-d_2- (~ 50%) and 3,4,5-d_3-ODFB (~ 5–10%). H/D exchange at the meta-positions was accomplished by shaking the normal compound with concentrated D_2SO_4 for about 300 hrs at room temperature. (The enrichments quoted were deduced from the relative intensities of absorption signals under DRM)

All ^{13}C-forms were observed in their natural abundance.

b) *Instrumental*

Transition frequencies of the normal, the 4/5-d_1- and the 4,5-d_2-form were measured largely in a Stark effect modulated (SEM) spectrometer [8] of conventional design, but some 20 transitions were added in each case by DRM spectroscopy. Due to incomplete separation from the methoxide the 3/6-d_1-sample gradually decomposed, and this prevented later verification and extension of the SEM measurements by DRM methods. The 3,4,5-d_3-species and all ^{13}C spectra were measured by DRM spectroscopy alone. A description of the DRM instrument and of our mode of operation has been given previously [5 b]. SEM measurements were made in the range 15–26 GHz which contained the DRM pump transitions for signals in the range 26–40 GHz. All experiments were carried out at room temperature with sample pressures near 20 mTorr. Absorption signals were observed on the oscilloscope.

III. Spectroscopic Results

a) *Method and Sequence of Spectral Analysis*

The study of isotopic forms of ODFB was preceded by an extension of the earlier investigation of Nygaard et al. [6], which had been carried out by SEM spectroscopy in the frequency range from 12–20 GHz. To cover our DRM pump range the spectrum of the normal species was studied up to 26 GHz, and Q-band (26–40 GHz) transitions were then observed as DRM signals. From guessed molecular models the rotation spectra associated with the three distinct ^{13}C-forms were then predicted and subsequently identified without difficulty by DRM double-search experiments [5 b].Observation of these spectra by SEM spectroscopy was prevented by the lack of sensitivity. The 3/6-d_1- and 4/5-d_1-forms were studied next, and this completed the establishment of a first set of isotopic data for the determination of the molecular geometry.

Examination by DRM techniques of the ~ 50% enriched 4,5-d_2-species yielded not only the three different ^{13}C-forms of this species, but also the spectrum of the 3,4,5-d_3-form. In conjunction with the 4/5-d_1-species (above) there resulted therefore a second set of isotopic data from which the structure could be calculated, but now with the 4,5-d_2-form as the parent molecule.

b) *Derivation of Rotational Parameters*

The observed spectra of ODFB and its isotopic forms were fitted [9] to the Hamiltonian

$$\begin{aligned} H = {} & A P_a^2 + B P_b^2 + C P_c^2 \\ & + (1/4)(\tau_{aaaa} P_a^4 + \tau_{bbbb} P_b^4 + \tau_{aabb} P_a^2 P_b^2 \\ & + \tau_{abab} P_a P_b P_a P_b) \qquad (1) \end{aligned}$$

which has proven adequate in a number of previous studies of planar molecules [10]. Of course, it could not be expected that all seven molecular parameters in (1) would be determinable in the case of rare isotopic forms with only ~ 30 measured transitions (see Table 2, row 4). This made it desirable to establish a reasonable set of distortion constants τ prior to the final fit of such spectra.

b-1) *Distortion Treatment*

The determination of distortion constants was based on the observed spectra of the normal, the 4/5-d_1- and the 4,5-d_2-form, for which over 90 transitions have been measured in each case. The approach taken is best followed with the help of Table 1. To begin with, each of the three spectra was fitted to four distortion constants. The results (rows 1–3) show good consistency between the three species, and accuracies of 15–30% (3 σ errors) are indicated for all but the constant τ_{aabb}, which is seen to carry an error of 100%–200%. Obviously, that constant cannot be determined reliably from the transitions available, and we therefore adopted the average value of τ_{aabb} = 0.274 kHz as a fixed value in the subsequent refit of the spectra to six variable parameters. As a

Table 1. Determination of centrifugal distortion constants in 1,2-difluorobenzene (ODFB).

	Species	Quartic distortion constants (in kHz)			
		τ_{aaaa}	τ_{bbbb}	τ_{aabb}	τ_{abab}
		1) All four distortion constants variable			
1	Normal	-2.944 ± 0.627 *	-0.584 ± 0.060	0.352 ± 0.372	-0.487 ± 0.093
2	4/5-d_1	-2.826 ± 0.348	-0.572 ± 0.102	0.173 ± 0.441	-0.436 ± 0.144
3	4,5-d_2	-2.754 ± 0.429	-0.506 ± 0.087	0.298 ± 0.411	-0.485 ± 0.126
				0.274 ± 0.225	
		2) τ_{aabb} fixed to average value			
4	Normal	-2.844 ± 0.402	-0.591 ± 0.048	0.274 (fixed)	-0.472 ± 0.060
5	4/5-d_1	-2.853 ± 0.327	-0.550 ± 0.036		-0.467 ± 0.048
6	4,5-d_2	-2.741 ± 0.363	-0.510 ± 0.033		-0.479 ± 0.063
					-0.473 ± 0.015
		3) τ_{aabb} and τ_{abab} fixed to average values			
7	Normal	-2.840 ± 0.207	-0.591 ± 0.036	0.274 (fixed)	-0.473 (fixed)
8	4/5-d_1	-2.820 ± 0.159	-0.547 ± 0.024		
9	4,5-d_2	-2.775 ± 0.147	-0.513 ± 0.021		
		-2.812 ± 0.082			
		4) τ_{aaaa}, τ_{abab} and τ_{aabb} fixed to average values			
10	Normal	-2.812 (fixed)	-0.586 ± 0.004	0.274 (fixed)	-0.473 (fixed)
11	4/5-d_1		-0.546 ± 0.004		
12	4,5-d_2		-0.518 ± 0.004		

* Uncertainties are three times the standard error.

consequence of this, the results for τ_{abab} are now seen (rows 4–6) to coincide so closely that the adoption of the average value $\tau_{abab} = -0.473$ kHz for all three species appears justified. Refitting of the spectra with both τ_{aabb} and τ_{abab} fixed produces an analogous result for the constant τ_{aaaa} (rows 7–9), which in the final fits of the three species was also held constant at $\tau_{aaaa} = -2.812$ kHz. The standard deviations of the fits were not influenced by the described fixing of the distortion constants.

The approach contains, of course, an element of uncertainty which arises from the adoption of the average τ_{aabb}-value in the first step. We have therefore repeated the calculations with larger and smaller values of this constant. This showed that variations of ± 0.05 kHz in the adopted τ_{aabb} entail changes by ± 0.04 kHz in τ_{aaaa}, of ± 0.01 kHz in the three τ_{bbbb}-values, and of less than ± 0.02 kHz in τ_{abab}.

b-2) Rotational Constants

On the basis of the described results, the spectra of 3/6-d_1-ODFB and of the ^{13}C-species associated with the normal molecule were fitted with the distortion constants of row 10 of Table 1, while the spectra of the 3,4,5-d_3-species and of the ^{13}C-forms associated with the 4,5-d_2-species were fitted with the constants of row 12. Variations of the deduced rotational constants as a consequence of the described determination of the distortion constants are negligible and well inside the 3σ-limits quoted.

The rotational constants of the eleven species studied are collected in Table 2. The publication of the 534 measured transition frequencies does not appear justified to us. Instead we include at the top of Table 2 a summary of the spectra, giving for each species the number of measured R- and Q-branch transitions, the

1	Species		Normal	^{13}C(1/2)	^{13}C(3/6)	^{13}C(4/5)	3/6-d_1	4/5-d_1
2	Fitted transitions		40 R & 53 Q	17 R & 14 Q	19 R & 14 Q	21 R & 13 Q	23 R & 14 Q	48 R & 43 Q
3	Range of J-values		3-16 & 7-38	6-12 & 15-23	6-12 & 15-24	6-12 & 14-25	4-9 & 11-23	5-13 & 12-39
4	Measured by SEM/DRM		75[a] / 18	- / 31	- / 33	- / 34	37 / -	68 / 23
5	Std. deviation (in MHz)		0.072	0.072	0.063	0.077	0.084	0.067
6	*A*	in MHz	3263.527 (3)[b]	3253.668 (4)	3223.200 (5)	3253.918 (4)	3139.704 (8)	3234.821 (3)
7	*B*		2227.885 (2)	2226.005 (3)	2222.368 (3)	2191.049 (3)	2222.451 (4)	2147.680 (2)
8	*C*		1323.856 (2)	1321.566 (3)	1315.238 (2)	1309.204 (3)	1301.159 (4)	1290.581 (2)
9	τ_{aabb} [c]	in kHz	-0.586 (4)	-0.586 [d]	-0.586	-0.586	-0.586	-0.546 (4)
10	I_a	in uÅ^2	154.85577(16)	155.32498(21)	156.79327(23)	155.31309(20)	160.96294(39)	156.22999(16)
11	I_b		226.84120(30)	227.03276(32)	227.40425(29)	230.65482(32)	227.39581(45)	235.31253(19)
12	I_c		381.74557(56)	382.40693(78)	384.24686(67)	386.01779(79)	388.40451(123)	391.58787(48)
13	$I.D.=I_c-I_a-I_b$		0.04861(63)	0.04918(87)	0.04934(77)	0.04988(88)	0.04576(144)	0.04535(54)

Table 2 continued

1	Species		4,5-d_2	d_2-^{13}C(1/2)	d_2-^{13}C(3/6)	d_2-^{13}C(4/5)	3,4,5-d_3
2	Fitted transitions		45 R & 50 Q	13 R & 15 Q	14 R & 14 Q	16 R & 12 Q	19 R & 17 Q
3	Range of J-values		5-14 & 12-39	7-13 & 14-30	7-13 & 14-26	7-13 & 14-26	7-13 & 13-31
4	Measured by SEM/DRM		71 / 24	- / 28	- / 28	- / 28	- / 36
5	Std. deviation (in MHz)		0.065	0.053	0.066	0.053	0.089
6	*A*	in MHz	3199.540 (3)	3190.067 (3)	3160.683 (4)	3190.218 (3)	3080.172 (5)
7	*B*		2077.012 (2)	2074.983 (2)	2072.866 (3)	2046.594 (2)	2073.000 (3)
8	*C*		1259.303 (2)	1257.089 (2)	1251.726 (2)	1246.634 (2)	1238.960 (3)
9	τ_{aabb}	in kHz	-0.518 (4)	-0.518	-0.518	-0.518	-0.518
10	I_a	in uÅ^2	157.95271(15)	158.42175(15)	159.89454(18)	158.41426(18)	164.07394(28)
11	I_b		243.38176(19)	243.55669(26)	243.80546(31)	246.93510(26)	243.78972(39)
12	I_c		401.31418(47)	402.02101(64)	403.74317(80)	405.39253(62)	407.90339(97)
13	$I.D.=I_c-I_a-I_b$		0.04271(53)	0.04257(70)	0.04317(88)	0.04317(70)	0.03973(108)

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

respective ranges of J-values, and a breakdown into measurements by SEM and DRM spectroscopy (rows 2–5). Listings of the observed transitions have been deposited with the "Sektion für Spektren und Strukturdokumentation" of the University of Ulm. They may also be obtained from the author.

IV. Structure Calculations

The procedure for the determination of molecular structures from observed changes Δ in the moments of inertia under isotopic substitution was formulated by Kraitchman [1]. It is limited by the assumptions that the molecular structure is rigid (vibrationless) and unchanged by the isotopic substitutions. Following the trend of times, the Kraitchman procedure, which is simple enough for hand-calculation, has been superceded during the past 15 years by the emergence of computer schemes which either perform this very simple calculation or match molecular structures to the observed moments of isotopic forms by least squares methods. One of the earliest programs of the latter type, GEOM, was developed by the research group at the ETH Zürich [11]. The most recent programs in this family, RU 110 and RU 238, are due to H. D. Rudolph [12] of the University of Ulm.

In the following two subsections we present the structure of ODFB which emerges from the experimental data of Table 2 by use of the simple Kraitchman formalism (IV-a) and by use of the computer program GEOM (IV-b).

a) Kraitchman Calculations

The determination of coordinates of substituted atoms with Kraitchman's equations for planar molecules was carried out in the same style as in previous structure studies on planar ring compounds [10]. That is, the a- and b-coordinates of substituted atoms were calculated not only from ΔI_a and ΔI_b, as is possible in planar molecules, but also from the combination of ΔI_a with $\Delta I_b^* = \Delta I_c - \Delta I_a$ and from the combination of $\Delta I_a^* = \Delta I_c - \Delta I_b$ with ΔI_b. Clearly, if the inertia defect, I.D., of an isotopic form is the same as in the parent molecule (as Kraitchman assumes), the three sets of coordinate values obtained by this process are identical. For $\Delta\,(\mathrm{I.D.}) \neq 0$, as is usually the case due to changes in zero-point vibration under substitution, the three pairs of coordinate values will differ. The numbers given in rows 1–6 of Table 3 are the averages obtained by the described method of calculation, and the quantities in square brackets behind the coordinates reflect the incompatibility of individual values with the quoted average. In our experience, these 'incompatibilities' are usually larger than the uncertainties associated with the limited accuracy of rotational constants, and they reach particularly large magnitudes when a coordinate is determined from an isotopic form which has an I.D. noticeably different from that of the parent species (e.g. the a-coordinate in row 4 of Table 3). While we would not wish this approach to be mis-interpreted as a means for surmounting the inherent limitation of the Kraitchman formalism (neglect of vibrations), we consider it to have the merit of bringing this limitation to the surface, rather than ignoring or concealing it.

Rows 5a and 5b of Table 3 reflect the fact that the substitution coordinates of H (4/5) can be determined from the inertial differences between either the 4/5-d_1-species and the parent form (row 5a) or the 4,5-d_2-species and the parent form. The a-coordinates of the unsubstitutable fluorine atoms (row 6)) were determined from the first moment condition. Calculation of the b_F-coordinates from this condition is prevented by the C_{2v} symmetry of ODFB, and the observed moment of inertia, $I_a^{\mathrm{obs.}}$, had to be utilized instead. However, since substitution structures generally under-produce the effective moments by a few tenths of a percent, a corresponding amount, δI_a (row 9), was first extracted from the observed moment. This amount was estimated to be 0.05 – 0.10% larger than the corresponding deficiency δI_b (row 12), which could be worked out from the known a-coordinates. From the resulting moment, $I_a^{\mathrm{calc.}}$ (row 8), the contributions from C- and H-atoms were then extracted to yield $2\,m_F\,b_F^2$ which, in turn, gave the b-coordinates of row 6. The large uncertainty in b_F comprises an estimated uncertainty of 0.05% in δI_a and the accumulated contributions from carbon- and hydrogen-atoms.

The abundance of isotopic data, – which is an almost natural consequence of the use of DRM techniques in the spectroscopic analysis –, allowed analogous calculations to be carried out with the 4,5-d_2-species as the parent molecule. The results of this calculation are given in column II of Table 3.

In column III of this table, the a-coordinates of atoms in the normal reference frame are compared with those in the 4,5-d_2 frame. Ideally, their differ-

Table 3. Summary of structure calculations on 1,2-difluorobenzene (ODFB) by the Kraitchman method.

		I Normal axis system		II 4,5-d_2 axis system		III Shift of centre of gravity	IV Combined data (Normal axis system)	
	a) Coordinates (in Å)							
		a	± *b*	*a*	± *b*	$\lvert a^{II} - a^{I}\rvert$	*a*	± *b*
1	C (1/2)	+0.43765 [45][a]	0.68790 [29]	+0.48767 [10]	0.68759 [7]	0.05002	+0.43763 [3][b]	0.68755 [15]
2	C (3/6)	−0.74237 [33]	1.40125 [18]	−0.69158 [22]	1.40120 [11]	0.05079	−0.74201 [36]	1.40122 [3]
3	C (4/5)	−1.95201 [22]	0.69614 [65]	−1.90155 [8]	0.69556 [23]	0.05046	−1.95181 [20]	0.69585 [25]
4	H (3/6)	−0.71273 [122]	2.48370 [37]	−0.66129 [140]	2.48366 [39]	(0.05144)	−0.71204 [75]	2.48368 [3]
5a	H (4/5)	−2.88612 [39]	1.24040 [97]	−2.83646 [30]	1.23984 [64]	0.04966	−2.88628 [16]	1.23995 [20]
5b	H (4,5)	−2.88624 [26]	1.23990 [59]	−2.83619 [25]	1.23990 [59]	0.05005		
6	F (1/2)	+1.61634 [15][c]	1.34554 [127][d]	+1.66565 [15][c]	1.34505 [108][d]	0.04931	+1.61597 [37][c]	1.34530 [25][d]
					average shift:	0.05005		
					expected shift:	0.05006		
	b) Observed and calculated moments of parent forms (in uÅ²)							
7	$I_a^{obs.}$	154.85577		157.95721			154.85577	
8	$I_a^{calc.}$	154.43812		157.44711			154.39572	
9	δI_a	0.41765 = 0.27% [e]		0.50560 = 0.32% [e]			0.46005 = 0.30% [e]	
10	$I_b^{obs.}$	226.84120		243.31876			226.84120	
11	$I_b^{calc.}$	226.35498		242.67035			226.27676	
12	δI_b	0.48622 = 0.21%		0.64841 = 0.27%			0.56444 = 0.25%	
	c) Deduced bondlengths (in Å)							
13	C (1) − C (2)	1.3758 [6]		1.3752 [2]			1.3755 [3][b]	
14	C (2/1) − C (3/6)	1.3789 [9]		1.3784 [4]			1.3786 [3]	
15	C (3/6) − C (4/5)	1.4001 [9]		1.4007 [4]			1.4004 [3]	
16	C (4) − C (5)	1.3923 [13]		1.3911 [5]			1.3917 [6]	
17	C (3/6) − H (3/6)	1.0828 [6]		1.0829 [6]			1.0829 [1]	
18	C (4/5) − H (4/5)	1.0810 [12]		1.0817 [7]			1.0813 [4]	
19	C (1/2) − F (1/2)	1.3497 [13]		1.3490 [8]			1.3494 [4]	
	d) Deduced bond angles (in degrees)							
20	C (1) C (2) C (3)	121.15 [4]		121.18 [2]			121.17 [2]	
21	C (2) C (3) C (4)	118.61 [8]		118.57 [4]			118.59 [2]	
22	C (3) C (4) C (5)	120.24 [4]		120.25 [2]			120.24 [1]	
23	C (2) C (3) H (3)	119.58 [12]		119.58 [10]			119.58 [1]	
24	C (3) C (4) H (4)	119.55 [4]		119.54 [3]			119.55 [1]	
25	C (1) C (2) F (2)	119.16 [7]		119.17 [4]			119.16 [1]	

[a] See text for significance of square brackets. [b] Compatibility of normal and 4,5-d_2 values. [c] Derived from first moment condition. [d] Most of this uncertainty arises from the estimated uncertainty in the assumed value of δI_a. [e] Assumed as 0.05% larger than δI_b.

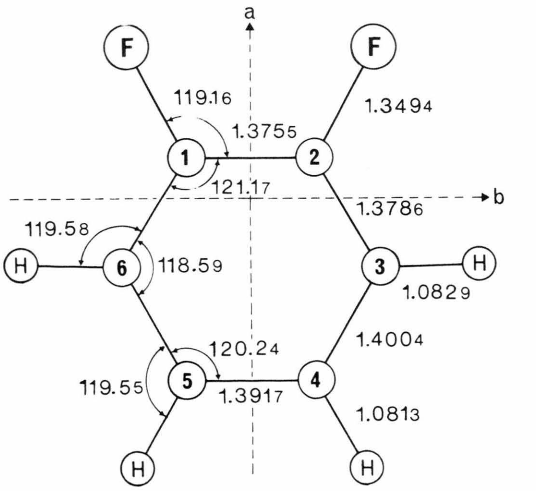

Fig. 1. The doubly determined substitution structure of *ortho*-difluorobenzene (ODFB).

ences, a^{II}-a^{I}, should be the same for all atoms and equal to the shift of the centre of gravity when the hydrogens H (4,5) are replaced by deuterium. Inspection shows that all but one value (which arises from the poorly determined *a*-coordinates of H (3/6), (row 4) agree to better than ± 0.001 Å with this expectation. The average shift, which is obtained from the experimentally determined *a*-coordinates of atoms, agrees very well indeed with the value expected from the position of the two substituted hydrogen atoms H (4/5).

Column IV of Table 3, finally, gives the coordinate set which results from the combination of the data in columns I and II. The *b*-coordinates of this set are straight averages between I and II, and the *a*-coordinates were obtained by transformation of those of column II and subsequent averaging with their counterparts in column I. The square brackets in this com-

Table 4. Results of structure calculations on 1,2-difluorobenzene (ODFB) with the computer program GEOM.

		I Normal axis system		II 4,5-d_2 axis system		III Shift of centre of gravity	IV Combined data		Δ[a]
i	Species fitted	7		7			11		
ii	$\sum(\delta I^2)$	0.28×10^{-4}		0.26×10^{-4}			0.82×10^{-4}		
	a) Fitted bond lengths (in Å)								
13	C(1) – C(2)	1.3759(9)[b]		1.3751(9)			1.3756(7)		+0.0001
14	C(2/1) – C(3/6)	1.3788(8)		1.3784(8)			1.3789(4)		+0.0003
15	C(3/6) – C(4/5)	1.4000(5)		1.4006(5)			1.4004(6)		–
16	C(4) – C(5)	1.3921[c]		1.3910[c]			1.3915[c]		–0.0002
17	C(3/6) – H(3/6)	1.0829(3)		1.0829(3)			1.0828(4)		–0.0001
18	C(4/5) – H(4/5)	1.0811(2)		1.0818(2)			1.0813(4)		–
19	C(1/2) – F(1/2)	1.3500(7)		1.3493(7)			1.3495(5)		+0.0001
	b) Fitted bond angles (in degrees)								
20	C(1) C(2) C(3)	121.15(2)		121.18(2)			121.16(2)		–0.01
21	C(2) C(3) C(4)	118.61(3)		118.56(3)			118.59(3)		–
22	C(3) C(4) C(5)	120.24[c]		120.26[c]			120.25[c]		+0.01
23	C(2) C(3) H(3)	119.58(4)		119.57(5)			119.58(4)		–
24	C(3) C(4) H(4)	119.54(4)		119.53(4)			119.52(7)		–0.03
25	C(1) C(2) F(2)	119.14(5)		119.15(5)			119.15(6)		–0.01
	c) Deduced coordinates (in Å)								
		a	$\pm b$	*a*	$\pm b$	$\lvert a^{II} - a^{I}\rvert$	*a*	$\pm b$	
1	C(1/2)	+0.43746	0.68793	+0.48749	0.68754	0.05003	+0.43756	0.68781	
2	C(3/6)	–0.74256	1.40120	–0.69178	1.40119	0.05078	–0.74227	1.40128	
3	C(4/5)	–1.95206	0.69607	–1.90159	0.69550	0.05047	–1.95198	0.69573	
4	H(3/6)	–0.71277	2.48370	–0.66128	2.48368	(0.05159)	–0.71242	2.48370	
5	H(4/5)	–2.88628	1.24018	–2.83634	1.23996	0.04994	–2.88626	1.24008	
6	F(1/2)	+1.61662	1.34525	+1.66591	1.34478	0.04929	+1.61625	1.34519	
	d) Observed and calculated moments of parent forms (in $\mu Å^2$)								
7	$I_a^{obs.}$	154.85577		157.95721			154.85577		
8	I_a^{GEOM}	154.40391		157.41629			154.38734		
9	$\delta I_a = I_a^{obs.} - I_a^{GEOM}$	0.45186 = 0.29%		0.54092 = 0.34%			0.46843 = 0.30%		
10	$I_b^{obs.}$	226.84120		243.31876			226.84120		
11	I_b^{GEOM}	226.16620		242.71252			226.33757		
12	$\delta I_b = I_b^{obs.} - I_b^{GEOM}$	0.67500 = 0.30%		0.60624 = 0.25%			0.50363 = 0.22%		

[a] Difference between 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.

bined data set reflect the compatibility limits of set I and II with the combined set IV.

Rows 13–25 of Table 3 give bond lengths and angles deduced from the coordinates in each case. The resulting structure of ODFB is shown in Figure 1.

b) Structure Calculation with the Computer Program GEOM

The GEOM program is designed to adjust an initial set of structure parameters (bond lengths and angles) iteratively to give an optimal fit to the observed changes in the moments of inertia under isotopic substitution. Atomic coordinates are then deduced for the optimized structure. As in Kraitchman's original work [1], the molecular structure is assumed to be rigid and unchanged by isotopic substitutions. The computational approach of fitting lengths and angles is the reverse of the Kraitchman scheme, in which atomic coordinates are the prime information from which lengths and angles are deduced by trivial arithmetic. This aspect is reflected in the arrangement of results in Table 4.

The GEOM fits were carried out in analogy to the calculations in Sect. IV-a, and the results of the Kraitchman calculations were used as input data in the separate fits of the normal species, the 4,5-d_2-species and of the combined isotopic data. The computer results are presented in Table 4. The last column of this table (headed: Δ) gives the differences between the results obtained by GEOM and their counterparts in Table 3 ($\Delta = r_{\text{GEOM}} - r_{\text{Kraitchman}}$). Inspection of this column shows that all bond lengths agree to better than 0.0003 Å and angles coincide to within 0.03° with the Kraitchman results. This perhaps surprisingly close coincidence between the two methods of structure calculation finds its explanation in the fact that GEOM fits ΔI_a, ΔI_b and ΔI_c simultaneously, which is of course equivalent to our approach in Sect. IV-a, where we have derived average coordinate values from all three changes $\Delta I_{a,b,c}$ (see above). Moreover, since ODFB does not have any atoms on its C_{2v} symmetry axis nor particularly close to the b-axis, and since $\Delta I > 0$ for all substitutions, close coincidence between GEOM and Kraitchman results is to be expected.

V. Discussion

a) Experimental Technique

The abundance of isotopic data (Table 2) demonstrates once more the power of the DRM technique for the detection and the analysis of isotopic species spectra. The presence of low-lying vibration states in ODFB, – and of course in all other molecules of comparable size –, required of course some care in the identification of the spectra of isotopic forms. In our experience this problem is best solved by the complete rotational assignment of all detectable spectra of a molecule and subsequent distinction between isotopic species spectra and vibrational satellite spectra on account of relative intensities, inertial defects and, of course, model calculations of the isotopic spectra. While this simple approach may appear a rather 'tall order' if it were to be tackled by SEM spectroscopy, the molecular selectivity of the DRM technique allows this task to be completed quite quickly. The simultaneous sensitivity of the technique ensures considerable economy in structure studies by making the chemical preparation of expensive isotopic forms (^{13}C-species in the present case) superfluous. We have first pointed out, and experimentally demonstrated these aspects of DRM spectroscopy more than a decade ago [10a] and they should not need re-emphasis.

b) Structure Calculation

The results presented in section IV indicate a very high degree of consistency between the structure parameters obtained in the 4,5-d_2 reference frame of ODFB and their counterparts in the axis system of the normal form, irrespective of the method by which these results are derived (GEOM or Kraitchman). This supports the basic assumption that structure parameters are not changed significantly by isotopic substitutions. – The individual values for the shift of the centre of gravity under deuteration (column III of Table 3 and 4), which are probably the most objective indicators for the reliability of coordinate values, suggest an accuracy in the range of 0.001 Å and the same degree of precision is indicated for all bond lengths. Bond angles appear trustworthy to 0.05°. This gratifying consistency within the doubly determined structure of ODFB is, however, to some extent due to the fact that no ambiguities occur in the structure calculation and, in the light of the results of the subsequent determination of the structure of MDFB, it seems advisable to double the uncertainties to 0.002 Å and 0.1°.

c) Comparison with Related Compounds

This will be deferred to the end of the subsequent paper on MDFB.

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