Microwave Spectra of Furazan

I. The Doubly Determined Substitution Structure

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Double Resonance Modulation (DRM) microwave spectroscopy has been used to determine the rotational constants of isotopic forms of normal ($C_2H_2N_2O_2$) and perdeuterated furazan ($C_2D_2N_2O$). From these data the complete substitution structures have been derived by Kraitchman methods and by the computer program GEOM. The latter procedure fails to give correct results due to the decrease of the moment of inertia about the C_{2v}-axis and the simultaneous interchange of inertial axes in the ^{18}O-3,4-d_2-form.

The following bondlengths (in Å) and angles (in degrees) are best compatible with the total body of isotopic information:

O−N	= 1.3729 [6]	∢ NON	= 111.15 [8]
N−C	= 1.3032 [13]	∢ ONC	= 105.53 [5]
C−C	= 1.4211 [9]	∢ NCC	= 108.89 [3]
C−H	= 1.0763 [5]	∢ CCH	= 130.16 [3]

Here, the uncertainties cover small differences between normal and d_2-furazan as well as discrepancies resulting from different schemes of structure calculation.

I. Introduction

Furazan, or: 1,2,5-oxadiazole, was first prepared in 1965 [1], and a microwave study of its molecular structure was performed in the same year by Saegebarth and Cox [2]. These investigators also determined the molecular dipole moment ($\mu = \mu_b = 3.38$ D) and they obtained values for the electric field gradients along the inertial axes from an analysis of hyperfine splittings due to the quadrupolar nitrogen nuclei ($\chi_{aa} = -0.69$ MHz, $\chi_{bb} = -0.46$ MHz, $\chi_{cc} = 1.15$ MHz). No further investigation of this substance by microwave spectroscopy has been reported since then.

We undertook the present re-investigation of furazan partly as an addition to the work [3] on the structures and quadrupole coupling constants of related heterocyclics, including oxazole [3i] and isoxazole [3a–c], but primarily in an attempt to clarify an apparent incongruity (details in subsequent paper) between the coupling constants deduced by Saegebarth and Cox, on the one hand, and those obtained by Redshaw, Palmer and Findlay [4] from NQR experiments and from *ab initio* molecular orbital calculations, on the other hand.

Since the evaluation of principal field gradients from microwave data requires precise knowledge of the orientation, with respect to the molecular geometry, of the inertial axes in different isotopic species, we began this work with the determination of the complete substitution structures of normal and 3,4-d_2 furazan by double resonance modulation (DRM) techniques [5]. The results of this section of the work are reported here, and they will be utilized in the subsequent paper, in which the magnitude and orientation of the principal field gradients is obtained from the analysis of hyperfine splittings in the rotation spectrum of monodeuterated furazan.

As an almost inevitable consequence of the use of DRM techniques in the spectroscopic experiments, our work on furazan has also yielded a considerable body of data on the rotation spectra of molecules in vibrationally excited states: For both normal and 3,4-d_2 furazan over 20 satellite spectra with vibrational energies up to 1600 cm^{-1} have been detected, assigned and then correlated via relative intensity measurements [6] with the infrared study by Christensen, Jensen, Nielsen, and Nielsen [7]. These spectra comprise twelve of the fifteen fundamental levels of furazan, and the precise energetic position of two of these was determined by CO_2-laser/microwave double resonance experiments [8]. Details and results of

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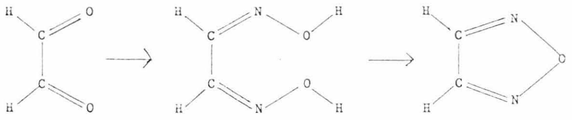
the studies of vibrational properties of furazan will be reported in due course.

II. Experimental

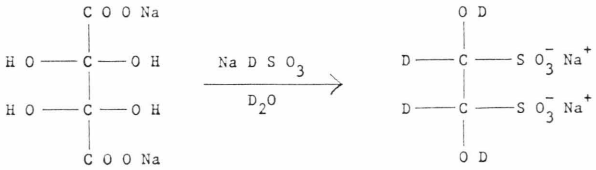
a) Sample Preparations

A first sample of furazan (I) was kindly provided by Dr. M. H. Palmer of the University of Edinburgh. Further samples were prepared from glyoxal (III) according to the method of Olofson and Michelman [1]:



(III) (II) (I)

For the preparation of 3,4-d_2 furazan, carefully washed ($\sim$ 40 l of H_2O per 50 g) sodium-tetrahydroxy-succinate [9] (V) (34 g $\simeq$ 0.15 mol) was decarboxylated with sodium metabisulphite (40 g $\simeq$ 0.2 mol) in D_2O (100 g, 99.9%) to yield perdeutero-glyoxal-sodium-bisulphite (IV) (30–35 g, $\sim$ 85% yield):



(V) (IV)

As the yield of this latter reaction was about four times higher than expected [1], two preparations (involving a total of only 200 g of D_2O) provided sufficient material (IV) ($\sim$ 65 g) for the preparation of perdeuteroglyoxal (III) and its conversion, via the glyoxime (II), to 3,4-d_2 furazan ($\sim$ 80% d_2- and $\sim$ 15% d_1-furazan).

The exothermic cyclisation of glyoxime (II) to furazan was always carried out on a small scale (5–8 g) to avoid overheating [1] of the reaction mixture. To obtain pure furazan we found it advantageous to extract first the volatile components (furazan and water) from the crude product (containing succinic acid and anhydride) by vacuum distillation ($p \sim 10$ mTorr) at room temperature. The supernatant water was then separated from the immiscable component and the remaining furazan (3–5 g, $\sim$ 60% yield) was dried with anhydrous sodium sulphate.

^{13}C-, ^{15}N- and ^{18}O-species of the normal and of 3,4-d_2-furazan were studied in their natural abundances.

b) Instrumental

The spectra of furazan and its isotopic forms were observed in the DRM spectrometer described previously [5]. Signal frequencies ranged from 21–40 GHz, pump frequencies from 15–26 GHz. After their identification by DRM methods, the transitions between 12–28 GHz were re-measured in a Stark effect modulated (SEM) spectrometer [10] of conventional design. Both instruments were operated with free-running, frequency-swept signal klystrons. Absorptions were observed on the oscilloscope. All measurements were carried out at toom temperature with sample pressures ranging from 1–10 mTorr.

III. Spectroscopic Results

a) Assignments

DRM methods made the identification of the spectra of the ^{18}O-species of the normal form of furazan, and of the ^{13}C-, ^{15}N- and ^{18}O-species of 3,4-d_2-furazan as straightforward as the extension of measurements on the isotopic forms previously detected by Saegebarth and Cox [2]. There remains only one feature which may be worth noting here: The near-oblate character of furazan ($\varkappa = 0.715$) is enhanced in the 3,4-d_2 species ($\varkappa = 0.871$), and when the oxygen atom of the latter form is replaced by the ^{18}O isotope there occurs an interchange of the *a* and *b* axes. As a result, the spectrum of ^{18}O-3,4-d_2 furazan ($\varkappa = 0.954$) shows only *a*-type transitions, while all other spectra consist entirely or predominantly of *b*-type lines. The 3-d_1 form shows *a*- and *b*-type transitions of comparable intensity ($\mu_b^2/\mu_a^2 \simeq 3$) due to the large swing (30.1°) of the inertial axes.

b) Quadrupole Effects

The largest hyperfine splittings occur in the spectrum of 3-d_1 furazan. After the quadrupole analysis (Part II), low-*J* transitions of this species were corrected for these effects before being used in the determination of rotational constants. – While we had no difficulty in observing the two $J = 2 \rightarrow 3$ (signal) transitions of the ^{13}C-3,4-d$_2$-species under DRM, we were not able to detect under SEM more than a broad 'ripple' at the position of the $J = 1 \rightarrow 2$ (pump) transitions. This, at first disconcerting, feature is explained by the fact that the ^{13}C-3,4-d$_2$-form has the second largest quadrupole coupling constants along its inertial axes. As a result, the intensity of the $J = 1 \rightarrow 2$ transitions is distributed over a range of ~ 5 MHz, as illustrated in Figure 1a. The signal transitions (Fig. 1b), which were used in the fit of this spectrum, are seen to be unsplit, and the accuracy of the rotational constants cannot be impaired therefore by quadrupole effects. Similar, though smaller quadrupole features were also noted in the spectrum of the ^{13}C-form of normal furazan, where many Q-branch transitions showed a triplet structure of the type depicted in Figure 1c. No hyperfine splittings were observed on transitions of the ^{15}N- and ^{18}O-forms of furazan. This was a consequence of the small values of the coupling constants (see II, Table 3) and of the weakness of the low-J transitions of these isotopic forms.

c) Rotational and Distortion Constants

The spectra of the nine isotopic species of furazan were fitted to a Hamiltonian with four quartic distortion constants [11]. Unfortunately, there occur only six R-branch transitions of reasonable intensity ($\Delta\tau = 0, 2$) below 40 GHz, reaching no higher than $J = 2 \rightarrow 3$. It was therefore not possible to obtain distortion constants of more than qualitative significance (Table 1, set I). Only for the normal species could this problem be remedied through the DRM identification of a further six weak R-branch lines ($\Delta\tau = 4, 6$) reaching up to $J = 7 \rightarrow 8$. As set II of Table 1 shows, these few additional transitions suffice to fix three of the distortion constants of the normal form to $\sim 10\%$ or better, while τ_{aabb} still carries a 3σ-uncertainty of $\sim 45\%$. – The identification of R-branch lines with $\Delta\tau = 4, 6$ was not possible for isotopic species. Their spectra were therefore fitted to only six parameters, τ_{aabb} being fixed at the value of the normal form. However, this approach resulted in unrealistically accurate values of the other three distortion constants. We therefore repeated the fitting procedure with τ_{aabb}-values adjusted to the lower (-2.4 kHz) and the upper (-6.4 kHz) limit of the 3σ-range, thus obtaining the uncertainties quoted in Table 2. Variations in the rotational constants and moments of inertia in dependence of the assumed values of τ_{aabb} are very small and well within the quoted 3σ-limits for all isotopic forms. For the parent species they just reach these limits, and for that reason the quoted uncertainties for that species were increased to 4σ. These uncertainties also encompass the values of rotational constants which are obtained if all four distortion constants are left variable in the fits of the spectra.

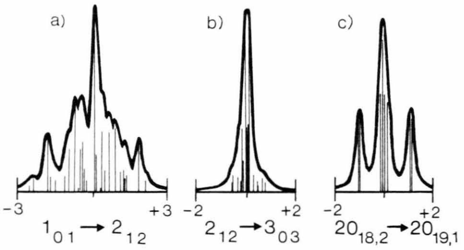


Fig. 1. Hyperfine splitting patterns in the spectrum of ^{13}C-3,4-d$_2$ furazan (intensities not drawn to scale).

Table 1. Distortion constants (in kHz) of furazan, as deduced from a least squares fit with six R-branch lines up to $J = 2 \rightarrow 3$ (set I), and with twelve R-branch lines up to $J = 7 \rightarrow 8$ (Set II).

Distortion constants	Set I	Set II
$\tau_{aaaa} \pm 3\sigma$	-22.0 ± 4.7 (21%)	-17.10 ± 0.67 (4%)
$\tau_{bbbb} \pm 3\sigma$	-25.1 ± 4.4 (17%)	-20.47 ± 0.61 (3%)
$\tau_{aabb} \pm 3\sigma$	-19.2 ± 14.0 (73%)	-4.41 ± 2.01 (45%)
$\tau_{abab} \pm 3\sigma$	-2.9 ± 4.7 (160%)	-7.81 ± 0.69 (9%)

The rotational parameters of furazan and its isotopic species are collected in Table 2, which in its upper part gives some statistics of the spectroscopic work. Listings of measured transition frequencies (661 in total) have been deposited with the 'Sektion für Strukturdokumentation' of the University of Ulm, FRG.

IV. Structure Calculations

The abundance of isotopic data in Table 2 permits independent determinations of the ring structure of furazan in the inertial axis system of the normal form (from isotopic species in column I–VI) and of the 3,4-d$_2$ form (from isotopic species in columns VI–IX, V and I). The two axis systems are interconnected simply by a shift of the origin along the C_{2v} axis of the

Table 2. Rotational constants and moments of inertia of furazan and its isotopic forms.

		I	II	III	IV	V
Species		Normal	^{13}C	^{15}N	^{18}O	3 - d_1
Observed transitions in fit		12 R & 82 Q	5 R & 55 Q	5 R & 44 Q	3 R & 79 Q	10 R & 89 Q
Range of J-values		0 - 8 & 2 - 24	0 - 3 & 2 - 15	0 - 3 & 2 - 13	1 - 3 & 4 - 24	0 - 3 & 2 - 39
SEM measurements a)		48 (23)	38 (10)	31 (5)	47 (-)	55 (2)
Standard deviation (in MHz)		0.055	0.054	0.052	0.058	0.046
A	in MHz	10457.210 (12) b)	10300.374 (17)	10442.809 (17)	9986.724 (19)	10117.008 (10)
B		9681.647 (12)	9568.622 (17)	9449.126 (17)	9683.083 (19)	9093.894 (10)
C		5023.703 (12)	4957.020 (16)	4957.088 (15)	4912.802 (19)	4785.873 (10)
τ_{aaaa}	in kHz	-17.1 (7) c)	-16.7 (7)	-16.7 (7)	-15.9 (7)	-18.0 (7)
τ_{bbbb}		-20.5 (7)	-19.9 (7)	-19.4 (7)	-20.4 (7)	-17.0 (7)
τ_{aabb}		- 4.4 (20) c)	- 4.4 (20)	- 4.4 (20)	- 4.4 (20)	- 4.4 (20)
τ_{abab}		- 7.8 (7)	- 7.3 (7)	- 7.4 (7)	- 7.5 (7)	- 5.9 (7)
I_a	in uÅ^2	48.32800 (6)	49.06385 (8)	48.39464 (8)	50.60478 (10)	49.95311 (5)
I_b		52.19938 (7)	52.81597 (9)	53.48389 (9)	52.19164 (10)	55.57311 (6)
I_c		100.59831 (25)	101.95158 (33)	101.95017 (30)	102.86920 (39)	105.59747 (21)
$I.D. = I_c - I_a - I_b$		0.07093 (27)	0.07176 (35)	0.07163 (33)	0.07278 (42)	0.07124 (23)

		VI	VII	VIII	IX
Species		3,4 - d_2	^{13}C - 3,4 - d_2	^{15}N - 3,4 - d_2	^{18}O - 3,4 - d_2
Observed transitions in fit		5 R & 94 Q	2 R & 63 Q	5 R & 53 Q	3 R & 52 Q
Range of J-values		0 - 3 & 2 - 24	2 - 3 & 4 - 23	1 - 3 & 4 - 19	1 - 3 & 6 - 32
SEM measurements a)		60 (13)	27 (-)	27 (-)	22 (-)
Standard deviation (in MHz)		0.044	0.050	0.040	0.055
A	in MHz	9302.623 (13)	9209.190 (18)	9290.769 (11)	8998.455 (18)
B		8997.267 (13)	8884.521 (18)	8791.644 (11)	8895.090 (18)
C		4570.732 (13)	4519.048 (18)	4514.249 (11)	4470.334 (18)
τ_{aaaa}	in kHz	-13.5 (7)	-13.8 (7)	-13.5 (7)	-16.4 (7)
τ_{bbbb}		-17.3 (7)	-16.6 (7)	-16.5 (7)	-13.7 (7)
τ_{aabb}		- 4.4 (20)	- 4.4 (20)	- 4.4 (20)	- 4.4 (20)
τ_{abab}		- 5.6 (7)	- 5.3 (7)	- 5.4 (7)	- 5.5 (7)
I_a	in uÅ^2	54.32618 (8)	54.87735 (11)	54.39550 (6)	56.16253 (11)
I_b		56.16995 (8)	56.88275 (12)	57.48367 (7)	56.81516 (12)
I_c		110.56786 (31)	111.83240 (44)	111.95128 (25)	113.05105 (45)
$I.D. = I_c - I_a - I_b$		0.07172 (33)	0.07230 (47)	0.07211 (27)	0.07336 (48)

a) The figures in brackets give the number of transitions taken over from the work of Saegebarth and Cox [2].

b) Uncertainties are 4σ limits for the parent form, 3σ limits for all other forms, and they are given in units of the last quoted decimal.

c) See text for determination of distortion constants and for significance of the quoted uncertainties.

molecule (inertial axis b). The position of the hydrogen or deuterium atoms may be deduced in either axis frame in three different ways (see below). The results in the normal and the 3,4-d_2 frame may be compared and combined to yield the structure best compatible with all the isotopic information.

The following two subsections give details and results of these calculations, which were carried out first by the Kraitchman method [12] and which were then repeated by use of the computer program GEOM [13].

a) *Kraitchman Calculations*

For a rigid planar molecule, Kraitchman's method for locating an atom in the inertial axis frame of a 'parent' form requires the changes (Δ), under isotopic substitution of that atom, of the two in-plane moments (ΔI_a, ΔI_b) only. The spectroscopic experiment, however, yields changes of all three moments, and their values reveal the limitation of the Kraitchman method: Due to zero-point vibration and its small variation under isotopic substitution, small changes occur in the inertia defect, I.D., and small negative ΔI-values are frequently observed when an atom on an inertial axis is replaced by a heavier isotope.

In order to take these facts into account, we have calculated the atomic coordinates in furazan not only from the observed values of ΔI_a and ΔI_b, but also from the combinations of ΔI_a with $\Delta I_b^* = \Delta I_c - \Delta I_a$ and of $\Delta I_a^* = \Delta I_c - \Delta I_b$ with ΔI_b. Coordinate values deducible from the combination of ΔI_a^* with ΔI_b^* were also considered following the view of Rudolph [14] that these should be included in the derivation of a 'balanced' structure. The averaged coordinate values, which were obtained under omission or inclusion of the combination of ΔI_a^* with ΔI_b^*, are collected in Table 3 a-1, where rows giving values according to the latter scheme are indexed with the letter 'R'. The quantities in square brackets in this table express the maximum deviation of individual coordinate values from the quoted average. Details of the calculation of coordinates are given in the appendix.

The calculation of bondlengths and angles followed in the usual, trivial way from the coordinates of Table 3 a-1, and the results are presented in Table 3 a-2. Structure parameters deduced from rows indexed 'R' in Table 3 a-1 are given in Table 3 a-2, R of the appendix. In both these tables the selected coordinate sets are repeated for convenience. To obtain the furazan structure best compatible with all the isotopic data according to one or the other scheme of calculation (column IV), straight averages were taken over corresponding a-coordinates. The b-coordinates in the 3,4-d_2 frame were transformed to the normal axis system and then averaged with their counterparts.

Table 3 a-1. Substitution coordinates (in Å) of atoms in furazan.

	Atom	I Normal axis system		II 3,4-d_2 axis system		III Shift of C.o.G.
		$\pm a$	b	$\pm a$	b	$\lvert b^{II} - b^{I}\rvert$
1	0(1)	–	1.08119 [22]	–	1.12997 [19]	0.04878
1 R		–	1.08065 [108]	–	1.12947 [100]	0.04882
2 a	N(2/5)	1.13329 [24]	0.30101 [106]	1.13388 [15]	0.34776 [63]	(0.04675)
2 a R		1.13332 [21]	0.30128 [81]	1.13388 [15]	0.34792 [53]	(0.04664)
2 b		1.13246 [11]	← 0.30452 [40][a]	1.13239 [11]	← 0.35274 [34][a]	0.04822
2 b R		1.13235 [25]	← 0.30491 [88][a]	1.13228 [25]	← 0.35311 [80][a]	0.04820
3	C(3/4)	0.71066 [35]	−0.92885 [32]	0.71066 [25]	−0.87899 [27]	0.04986
3 R		0.71072 [29]	−0.92895 [30]	0.71069 [22]	−0.87909 [25]	0.04986
4 a	H/D	1.40472 [9]	−1.75101 [10]	1.40446 [36]	−1.70227 [26]	0.04874
4 a R		1.40471 [8]	−1.75104 [11]	1.40457 [32]	−1.70223 [21]	0.04881
5 a	H_2/D_2	1.40467 [7]	−1.75107 [6]	1.40467 [7]	−1.70215 [6]	0.04892
5 b		1.40471 [6]	−1.78107 [4][b]	1.40471 [6]	−1.73265 [5][b]	(0.04842)
						average shift: 0.04891

[a] From first-moment condition.
[b] These b-coordinates refer to the ^{18}O-forms as the parent species.

Table 3a-2. Structure results for furazan from averaged Kraitchman coordinates.

		I		II		III	IV	
		Normal axis system		3,4-d_2 axis system		Shift of C. o. G.	Combined data (Normal axis system)	
	a) Selected coordinates (in Å)							
		±a	b	±a	b	$\lvert b^{II} - b^{I}\rvert$	±a	b
1	O(1)	--	+1.08119 [22]	--	+1.12997 [19]	0.04878	--	+1.08112 [8] a)
2	N(2/5)	*1.13246 [11]*	*+0.30452 [40]*	*1.13239 [11]*	*+0.35274 [34]*	*0.04822*	*1.13243 [4]*	*+0.30417 [35]*
3	C(3/4)	0.71066 [35]	-0.92885 [32]	0.71066 [25]	-0.87899 [27]	0.04986	0.71066 [-]	-0.92839 [46]
4	H/D	1.40470 [5]	-1.75104 [5]	1.40460 [14]	-1.70222 [7]	0.04882	1.40465 [5]	-1.75110 [6]
					average shift:	0.04892		
					expected shift:	0.04893		
	b) Observed and calculated moments of parent forms (in uÅ^2)							
5	I_a(obs.)	48.32800		54.32618			48.32800	
6	I_a(calc.)	48.18125		54.12240			48.15278	
7	δI_a	0.14675 = 0.30%		0.20378 = 0.38%			0.17522 = 0.36%	
8	I_b(obs.)	52.19938		56.16995			52.19938	
9	I_b(calc.)	52.01507		55.98064			52.01289	
10	δI_b	0.18431 = 0.35%		0.18931 = 0.34%			0.18649 = 0.36%	
	c) Deduced bond lengths (in Å)					$\lvert$Difference$\rvert$		
11	O - N	1.3732 [5]		1.3735 [4]		0.0003	1.3733 [2] a)	
12	N - C	1.3035 [8]		1.3019 [7]		0.0016	1.3027 [8]	
13	C - C	1.4213 [7]		1.4213 [5]		--	1.4213 [-]	
14	C - H/D	1.0760 [5]		1.0767 [5]		0.0007	1.0763 [4]	
	d) Deduced bond angles (in degrees)							
15	∠ N O N	111.11 [5]		111.07 [4]		0.04	111.09 [2]	
16	∠ O N C	105.56 [5]		105.56 [5]		--	105.56 [-]	
17	∠ N C C	108.88 [3]		108.90 [2]		0.02	108.89 [1]	
18	∠ C C H/D	130.17 [3]		130.13 [3]		0.04	130.15 [2]	
	∠ N C H/D	120.95 [6]		120.97 [5]		0.02	120.96 [1]	

a) The square brackets in column IV express the compatibility of the combined data with their counterparts in column I and II.

b) Computer Fits of the Structure of Furazan

For comparison with the results of the preceding subsection, the isotopic data of Table 2 were inserted into the structure fitting program GEOM [13]. This numerical routine matches bondlengths and angles by the least-squares method to reproduce the observed changes in all three moments for every isotopic form. In analogy to the Kraitchman calculations, GEOM-fits were run separately in the reference frame of normal furazan and in the inertial axis frame of 3,4-d_2 furazan. Finally, all isotopic data were matched simultaneously. The results are presented in Table 3b-1. Differences between these results and their counterparts in Table 3a-2 are given in the columns headed 'D'.

Inspection of Table 3b-1 prompts the following comments: – Negative ΔI-values for the case that an atom is substituted by a heavier isotope are outside the scope of the GEOM routing. Hence, in the case of the ^{18}O-form of normal furazan, the routine fits ΔI_a and ΔI_c, but cannot approach the observed negative ΔI_b-value beyond the limit $\Delta I_b = 0$. As a consequence, the observed $\Delta I_b < 0$ contributes in full to the deviations which remain at the end of the fit, and $\Sigma(\delta I^2)$ (row ii) is therefore comparatively large in the normal axis frame. More than three quarters of its value are due to the unfittable ΔI_b of the ^{18}O-species.

It seems almost like a 'freak' that GEOM-fits of 3,4-d_2-furazan seemingly do not suffer from the equal decrease of the moment about the C_{2v}-axis when ^{16}O is replaced by ^{18}O. $\Sigma(\delta I^2)$ now turns out five times smaller than for the normal form. The reason for this surprising result is the interchange of the a- and b axes between the 'parent' 3,4-d_2-form and its ^{18}O-species

Table 3b-1. Structure results for furazan from the computer program GEOM.

		I Normal axis system		II 3,4-d_2 axis system		III	IV Combined data (Normal axis system)	
i	Species fitted	6		6			9	
ii	$\Sigma\ (\delta I^2)$	8.3×10^{-5}		1.5×10^{-5}			1.0×10^{-4}	
	a) Fitted bond lengths (in Å)							
			D[a]		D	II - I		D
11	O - N	1.3726 (7)[b]	- 6	1.3718 (4)	-17	-0.0008	1.3724 (5)	- 9
12	N - C	1.3039 (15)	+ 4	1.3040 (7)	+21	+0.0001	1.3043 (9)	+16
13	C - C	1.4213 (22)	-	1.4199 (19)	-14	-0.0014	1.4208 (13)	- 5
14	C - H/D	1.0760 (11)	-	1.0766 (5)	- 1	+0.0006	1.0759 (7)	- 4
	b) Fitted angles (in degrees)							
15	∠ N O N	111.21 (9)	+10	111.27 (4)	+20	+0.06	111.24 (5)	+15
16	∠ O N C	105.51 (9)	- 5	105.46 (4)	-10	-0.05	105.49 (5)	- 7
17	∠ N C C	108.88 (7)	--	108.90 (3)	--	+0.02	108.89 (4)	--
18	∠ C C H/D	130.16 (5)	- 1	130.19 (4)	+ 6	+0.03	130.18 (3)	+ 3
	∠ N C H/D	120.96 (12)	+ 1	120.91 (6)	- 6	-0.05	120.93 (6)	- 3
	c) Deduced coordinates (in Å)							
		±a	b	±a	b	$\lvert b^{II} - b^{I} \rvert$	±a	b
1	O(1)	--	+1.08030	--	+1.12844	0.04814	--	+1.08007
2	N(2/5)	1.13260	+0.30494	1.13236	+0.35412	0.04918	1.13267	+0.30517
3	C(3/4)	0.71066	-0.92875	0.70996	-0.87959	0.04916	0.71041	-0.92888
4	H/D	1.40465[c]	-1.75106	1.40465[c]	-1.70208	0.04898	1.40465[c]	-1.75086
				Average shift of C.o.G.:		0.04887		
	d) Observed and calculated moments of parent forms (in uÅ^2)							
5	I_a(obs.)	48.32800		54.32618			48.32800	
6	I_a(calc.)	48.15333		54.11785			48.15370	
7	δI_a	0.17467 = 0.36%		0.20833 = 0.38%			0.17430 = 0.36%	
8	I_b(obs.)	52.19938		56.16995			52.19938	
9	I_b(calc.)	52.02367		55.95543			52.01958	
10	δI_b	0.17571 = 0.34%		0.21452 = 0.38%			0.17980 = 0.34%	

a) Difference between GEOM results and the Kraitchman parameters of Table 3a-2 in units of the last quoted digit.

b) Uncertainties of all parameters are obtained from fits of different input structures. c) In the final GEOM fits this coordinate was held fixed, leaving four lengths and one angle to be fitted.

(section III-a, above): The GEOM routing now fits the observed difference $\Delta I_a > 0$ and $\Delta I_b > 0$, and ignores the interchange of axes. The reduction of the moment about the parent b-axis under ^{18}O-substitution does not contribute therefore to the remaining deviations as in the normal axis frame. Instead, it produces a reduction of the b-coordinate of the oxygen atom. Naturally, this leads to a noticeably shorter O–N distance and to a larger NON angle than in the normal form. This spurious reduction of the b_{O}-coordinate is also borne out by the value of $b_{\mathrm{O}}^{II} - b_{\mathrm{O}}^{\mathrm{I}} = 0.0481$ Å, which is smaller than it ought to be.

Structure parameters deduced by a simultaneous fit of the moments of all isotopic forms contain, of course, this spurious effect from the ^{18}O-3,4-d_2-species, and must therefore be considered with suspicion. We thus arrive at the overall conclusion that parameters derived for the 3,4-d_2-species and those obtained from a simultaneous fit of all the experimental data by the GEOM program are incorrect, particularly if they involve the oxygen atom, notwithstanding the fact that they are obtained from a computer program which has worked satisfactorily numerous times before.

The failure of the GEOM routine in the present case can be circumvented in two ways, both of which are however incongruous with the intentions of the authors of the program. The most obvious way is simply to omit the measured rotational constants of the ^{18}O-3,4-d$_2$-form from the input data. The remaining eight isotopic species then lead to structure parameters very similar those of column I of Table 3 b-1. A fit of the 3,4-d$_2$ structure to only five isotopic forms (^{18}O-species omitted) fails to give acceptable results. – The second way of by-passing the difficulty caused by the negative ΔI-values and the interchange of axes in the ^{18}O-3,4-d$_2$ form, in particular, is the adjustment of the rotational constant A of the latter form so as to equal the B-constant of its parent 3,4-d$_2$ species. The B constant of ^{18}O-furazan may then also be equated to the B value of its parent form (removal of both negative ΔI-values). The results of fits of such adjusted data are given in Table 3 b-2 of the appendix. They are seen to approach the results of the Kraitchman calculations more closely than those of the fits (Table 3 b-1) of the true rotational constants.

V. Discussion

The ease with which DRM-techniques [5] provide the experimental data (Table 2) needed for structure determinations by microwave spectroscopy is contrasted in the present case by the ambiguities which arise in the calculation of structure parameters from these isotopic data. While most of the early structure work on planar molecules was based on the use of in-plane moments (ΔI_a, ΔI_b) only, we have preferred for some time [3 d, g, h, i, j] to derive coordinate values also from the combinations of ΔI_a with ΔI_b^* and of ΔI_a^* with ΔI_b, and then to average over the three values thus obtained (Table 3 a-2). This method of calculation, which takes observed values of ΔI_c into consideration, rather than discarding these completely, lies three quarters of the way towards the scheme advocated by Rudolph [14] (Table 3 a-2, R), which takes the averaging process one step further by including coordinate values derived from the combination of ΔI_a^* with ΔI_b^*. Both these quantities are, of course, constructed from observed ΔI_c-values, rather than being observed quantities themselves, and the Rudolph-scheme is recognized from this as putting still more emphasis on the ΔI_c-values than the scheme which we have used here and previously. This increasing emphasis on the observed, though usually with ΔI_a and ΔI_b inconsistent, values of ΔI_c reaches an extreme in the GEOM routine, which considers observed ΔI-values only (Tables 3 b-1 and 3 b-2) and ignores the constructed quantities ΔI_a^* and ΔI_b^*. On the basis of this comparison of the three schemes of structure calculation, the remaining discrepancies between parameter values in Tables 3 a-2, 3 a-2, R, and 3 b-2 could perhaps be viewed as an indication of the degree of success with which a vibrating structure may be approximated by the unrealistic picture of a rigid molecule with an isotopically invariant structure.

For the present case of furazan such a structure was extracted by averaging over corresponding parameter values in columns I and II of the three tables mentioned, with uncertainties adjusted so as to encompass all individual results. This structure is shown in Fig. 2, which indicates that the O – N distance is noticeably shorter (0.007 Å) and that the N – C length is 0.003 Å longer than originally suggested by the work of Saegebarth and Cox [2].

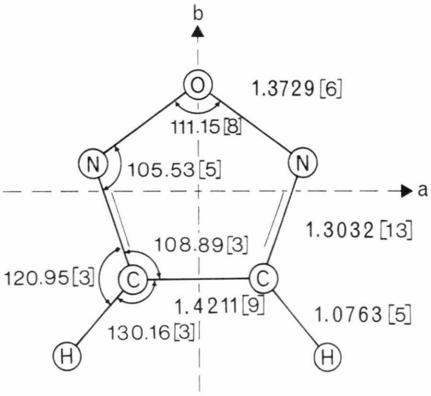


Fig. 2. The substitution structure of furazan. – The uncertainties given here encompass differences between the results in the two reference frames as well as variations arising from different schemes of structure calculation.

Appendix

The multitude of coordinate values presented in Table 3 a-1 seems to demand a more detailed description of the derivation of these coordinates than is usually necessary.

Hydrogen or deuterium positions: – These are calculated firstly by combination of the moments of the 3-d$_1$ form with either those of the normal form or with those of the 3,4-d$_2$ species (row 4, 4 R). They

		I Normal axis system		II 3,4-d_2 axis system		III Shift of C. o. G.	IV Combined data (Normal axis system)	
	a) Selected coordinates (in Å)							
		±a	b	±a	b	$\lvert b^{II} - b^{I}\rvert$	±a	b
1	O(1)	--	+1.08065[108]	--	+1.12947[100]	0.04882	--	+1.08060 [6] a)
2	N(2/5)	*1.13235 [25]*	*+0.30491 [88]*	*1.13228 [25]*	*+0.35311 [80]*	*0.04820*	*1.13232 [4]*	*+0.30455 [37]*
3	C(3/4)	0.71072 [29]	-0.92895 [30]	0.71069 [22]	-0.87909 [25]	0.04986	0.71070 [2]	-0.92849 [46]
4	H/D	1.40470 [5]	-1.75104 [5]	1.40460 [14]	-1.70222 [7]	0.04882	1.40465 [5]	-1.75110 [5]
					average shift:	0.04893		
					expected shift:	0.04893		
	c) Deduced bond lengths (in Å)					$\lvert$Difference$\rvert$		
11	O - N	1.3726 [13]		1.3729 [12]		0.0003	1.3727 [2] a)	
12	N - C	1.3039 [14]		1.3023 [12]		0.0016	1.3031 [8]	
13	C - C	1.4214 [6]		1.4214 [5]		--	1.4214 [-]	
14	C - H/D	1.0758 [5]		1.0766 [5]		0.0008	1.0762 [4]	
	d) Deduced bond angles (in degrees)							
15	∠ N O N	111.17 [15]		111.13 [13]		0.04	111.15 [2]	
16	∠ O N C	105.54 [12]		105.55 [11]		0.01	105.54 [1]	
17	∠ N C C	108.87 [4]		108.89 [4]		0.02	108.88 [1]	
18	∠ C C H/D	130.17 [3]		130.13 [3]		0.04	130.15 [2]	
	∠ N C H/D	120.96 [7]		120.98 [7]		0.02	120.97 [1]	

a) The square brackets in column IV express the compatibility of the combined data with their counterparts in column I and II.

Table 3b-2. Results of GEOM fits with rotational constants of ^{18}O forms adjusted to suppress negative ΔI-values.

		I Normal axis system		II 3,4-d_2 axis system		III	IV Combined data (Normal axis system)	
i	Species fitted	6		6			9	
ii	$\Sigma\ (\delta I^2)$	2.3×10^{-5}		2.1×10^{-5}			3.8×10^{-5}	
	a) Fitted bond lengths (in Å)		D a)		D	II - I		D
11	O - N	1.3726 (7) b)	--	1.3724 (8)	- 5	-0.0002	1.3726 (3)	- 1
12	N - C	1.3039 (9)	--	1.3035 (8)	+12	-0.0004	1.3039 (5)	+ 8
13	C - C	1.4213 (11)	- 1	1.4202 (11)	-12	-0.0011	1.4209 (7)	- 5
14	C - H/D	1.0760 (7)	+ 2	1.0766 (7)	--	+0.0006	1.0760 (6)	- 2
	b) Fitted angles (in degrees)							
15	∠ N O N	111.21 (6)	+ 4	111.21 (6)	+ 8	--	111.22 (6)	+ 7
16	∠ O N C	105.51 (6)	- 3	105.48 (6)	- 7	-0.03	105.50 (6)	- 4
17	∠ N C C	108.88 (4)	+ 1	108.91 (4)	+ 2	+0.03	108.89 (4)	+ 1
18	∠ C C H/D	130.16 (3)	+ 1	130.17 (3)	+ 4	+0.01	130.18 (3)	+ 3
	∠ N C H/D	120.96 (7)	--	120.92 (7)	- 6	+0.01	120.92 (7)	- 5
	c) Deduced coordinates (in Å)							
		±a	b	±a	b	$\lvert b^{II} - b^{I}\rvert$	±a	b
1	O(1)	--	+1.08030	--	+1.12895	0.04865	--	+1.08027
2	N(2/5)	1.13261	+0.30494	1.13245	+0.35372	0.04897	1.13267	+0.30494
3	C(3/4)	0.71066	-0.92875	0.71010	-0.87948	0.04927	0.71045	-0.92875
4	H/D	1.40465 c)	-1.75105	1.40465 c)	-1.70212	0.04893	1.40465 c)	-1.75091
					Average shift of C.o.G.:	0.04896		

a) Difference between GEOM results and the Kraitchman parameters of Table 3a-2,R in units of the last quoted digit.

b) Uncertainties of all parameters are obtained from fits of different input structures. c) In the final GEOM fits this coordinate was held fixed, leaving four lengths and one angle to be fitted.

may equally be obtained from the combination of the moments of the two parent forms (row 5a). In addition, the value of the a-coordinate can be deduced from the moments of the ^{18}O-forms of normal and 3,4-d_2 furazan (row 5b), but the b-coordinate will be larger in this case than in the parent forms due to the shift of the origin towards the ^{18}O-atom.

Oxygen position: – While the a-coordinate must be zero by symmetry, the b-coordinate may be calculated either from ΔI_a and ΔI_a^* (row 1) or by inclusion of the value derived from the observed ΔI_c alone (row 1R). Coordinate values derived from the similar quantities ΔI_a and ΔI_a^* differ significantly (~ 0.02 Å) from that derived from ΔI_c alone, so that the averaged values obtained in the two schemes also differ noticeably. The shift of the centre of gravity (C.o.G.), however, turns out virtually indentical in both schemes and is equal to the C.o.G. shift deduced from the b_H- and b_D-values in row 4 and row 5.

Carbon position: – The a-coordinates turn out very consistent (row 3, 3R) between the normal and the 3,4-d_2 frame, irrespective of whether they are calculated under inclusion of the value from the combination of ΔI_a^* with ΔI_b^* or without it. The same holds true for each pair of b-coordinates, but it should be noted that the shift of the C.o.G. (column III) turns out 0.001 Å larger than in rows 1, 4 and 5.

Nitrogen position: – Comparison of row 2a with row 2aR shows again that the inclusion of coordinate values derived from the combination of ΔI_a^* with ΔI_b^* does not have a significant influence, nor does it remove the obvious inconsistency between the a-values in the two reference frames. These a-coordinates, which ought to be the same in column I and column II, differ by as much as 0.0006 Å, and the b-coordinates are too small in either axis system to satisfy the first-moment condition. Moreover, their difference, $b_N^{II} - b_N^{I}$, is seen to be 0.002 Å smaller than deduced from H/D or O positions. For this reason, the smallish b_N-values were redetermined from the first-moment condition $\sum m_i b_i = 0$. This may be done either by taking the b_O- and b_C-coordinates from rows 1 and 3, or from rows 1R and 3R. For b_H and b_D the averaged values from tows 4 and 5 were used (-1.75104 and -1.70222). The results (in row 2b and 2bR) suggest that the b_N-coordinate is undercalculated by 0.0035 Å in the normal axis frame and by 0.005 Å in the 3,4-d_2 frame. The shift of the C.o.G. deduced from the revised b_N-values does still not reach the expected value of 0.0489 Å, but it does come closer to that limit than the shift derived from the 'raw' substitution coordinates.

If it is acceptable to ascribe the discrepancy between a_N^I and a_N^{II} to the use of incorrect values of ΔI_a, one may contemplate to revise these a-coordinates by use of ΔI_c and the improved b-coordinates. From $|a| = \{(\Delta I_c/\mu) - b^2\}^{1/2}$ one then obtains the more compatible a_N-values of row 2b and row 2bR.

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