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MICROWAVE SPECTRA OF ISOTOPIC PYRROLES. MOLECULAR STRUCTURE, DIPOLE MOMENT, AND ^{14}N QUADRUPOLE COUPLING CONSTANTS OF PYRROLE

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SUMMARY

Microwave spectra of pyrrole and the six monosubstituted isotopic species have been investigated. Except for the [^{15}N] species, some of the lines were split by nuclear quadrupole coupling, and coupling constants for pyrrole have been determined:

$\chi_{aa} = 1.45 \pm 0.02$ $\chi_{bb} = 1.21 \pm 0.02$ $\chi_{cc} = -2.66 \pm 0.02$ MHz

From center frequencies the effective rotational constants and centrifugal distortion constants were computed by a method of least squares.

The substitution structure of pyrrole was derived: N–C = 1.370, C(2)–C(3) = 1.382, C(3)–C(4) = 1.417, N–H = 0.996, C(2)–H(2) = 1.076, C(3)–H(3) = 1.077 Å. CNC = 109.8°, NCC = 107.7°, CCC = 107.4°, NCH = 121.5°, H(3)C(3)C(4) = 127.1°.

The dipole moment of pyrrole was measured on the $0_{0,0} \rightarrow 1_{0,1}$ transition of the parent compound. $\mu = \mu_a = 1.74 \pm 0.02$ D.

INTRODUCTION

An earlier investigation[1] of microwave spectra of isotopic pyrroles has been extended and completed to include all non-equivalent atomic positions in the molecule.

Microwave spectra of the parent species were reinvestigated, dipole moment, quadrupole coupling constants and centrifugal distortion constants were determined.

The ring-substituted species were prepared as already published[2] and microwave spectra of the enriched samples were studied.

Earlier measurements of the monodeuterated species were redone on samples prepared and controlled as described below. In a few cases inconsistencies with earlier data were detected. Among other results it was found that the inertial defect of the [3-D] species is very much like that of the other isotopic species. Only for [1-D]pyrrole did we get a lower value for the inertial defect. This can be explained by a rather low frequency out-of-plane N–H(D) vibration.

EXPERIMENTAL

Pyrrole puriss. was dried over CaO in vacuo. The identity of the sample was checked by its IR spectrum.

[1-D]Pyrrole, with deuterium on nitrogen, was prepared by repeated exchange of pyrrole puriss. with deuterium oxide. The deuterated pyrrole was dried on molecular sieves. ^{1}H NMR (60 MHz) and IR spectra of the dried sample were identical with known spectra.

After several unsuccessful attempts to prepare specifically [2-D]pyrrole and [3-D]pyrrole, it was decided to make a statistical mixture of monodeuterated pyrroles and the parent species by 24 h exchange of 3.986 g (59.3 mmole) pyrrole puriss. with 0.744 g (37.2 mmole) 0.1 *N* D_2SO_4. This gave also some di- and trideuterated pyrroles. Deuterium on nitrogen was exchanged with hydrogen (by water) and the deuterated sample was distilled and dried over CaO. The final sample had a composition of approximately 40 % pyrrole, 20 % [2-D]pyrrole, 20 % [3-D]pyrrole, and 20 % higher deuterated pyrroles. The composition was in accordance with the ^{1}H NMR, IR and microwave spectra of the mixture.

[^{15}N]Pyrrole was 33 % enriched, the two monosubstituted [^{13}C]pyrroles each 22 % enriched[2].

The microwave spectrograph was of the conventional Stark-modulated type.

The reported transitions of the isotopic pyrroles were in each case Stark identified and measured at room temperature and at a pressure of 0.020 mm Hg. For the relatively weak *a*-type lines of [2-D]pyrrole and *b*-type lines of [3-D]-pyrrole, however, a pressure of 0.040 mm Hg was employed.

If the calculated hyperfine structure was more than 0.5 MHz, attempts were made to resolve the quadrupole pattern by lowering the pressure to 0.003–0.005 mm Hg and by using a slower sweep. For the weaker lines this was not attempted.

MICROWAVE SPECTRA

The planar pyrrole molecule is a near-oblate top with a twofold *a*-axis[3] (Fig.1). The majority of the available lines are *Q*-branch transitions, which can be found for rather high *J* values.

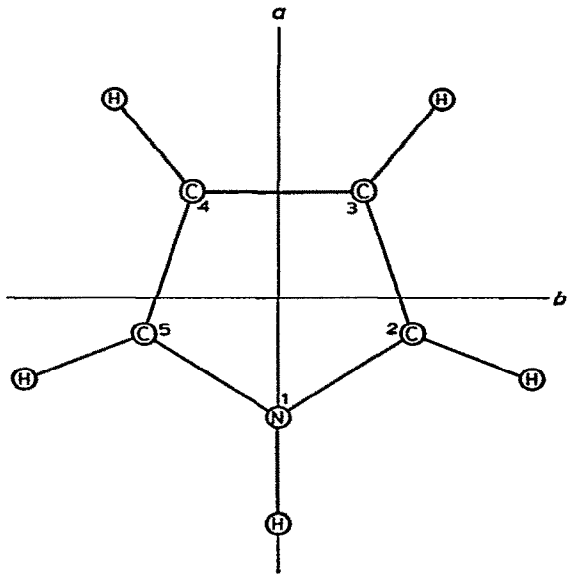

Fig. 1. Pyrrole principal axis system.

When off-axis substitutions are made, rather drastic rotations of the in-plane inertial axes occur, as shown in Table 1. The angle v given in this Table is found from the substitution coordinates a and b by the equation $\tan 2v = 2\mu ab/(I_b - I_a + \mu(a^2 - b^2))$. I_a and I_b are parent principal moments of inertia and μ the reduced mass $M\Delta m/(M+\Delta m)$, where M is the pyrrole mass and Δm the mass change on substitution.

Also given in Table 1 are the components of the dipole moment and the diagonal quadrupole coupling constants calculated for the isotopic molecules by proper transformation of parent properties (assumed to be constant).

The dipole components were used in computing the relative intensities of spectral lines. This was especially helpful for the [2-D]–[3-D]–parent mixture where both a- and b-type spectra were found for the two monodeuterated species. Quadrupole hyperfine structure was computed for all expected transitions and, in

TABLE 1

ANGLE v BETWEEN a-AXES OF PYRROLE AND SUBSTITUTED PYRROLE, DIPOLE MOMENT COMPONENTS AND NUCLEAR QUADRUPLE COUPLING CONSTANTS

For all species $\chi_{cc} = -(\chi_{aa}+\chi_{bb})$

Substituent	^{15}N	2-^{13}C	3-^{13}C	1-D	2-D	3-D
v (degrees)	0	57.3	23.8	0	66.9	32.4
μ_a (D)	1.74	0.94	1.59	1.74	0.68	1.47
μ_b (D)	0	1.46	0.70	0	1.60	0.93
χ_{aa} (MHz)	0	1.28	1.41	1.45	1.25	1.38
χ_{bb} (MHz)	0	1.38	1.25	1.21	1.41	1.28

several cases where the Stark pattern was inconclusive, used in the identification of lines.

NUCLEAR QUADRUPOLE COUPLING

One of the first things we found in the reinvestigation of pyrrole was that some of the low-J lines in the frequency region not earlier investigated were split by small amounts, with a maximum value about 2 MHz. This was ascribed to quadrupole coupling of the ^{14}N nucleus with the molecular rotation. Similar splittings were later observed in all the isotopic species, except [^{15}N]pyrrole. From ten splittings of more than 1.0 MHz in five patterns of the parent compound (Table 2) the diagonal coupling constants were derived by least-squares analysis to be

$$\chi_{aa} = 1.45 \pm 0.02 \qquad \chi_{bb} = 1.21 \pm 0.02 \qquad \chi_{cc} = -2.66 \pm 0.02 \text{ MHz}$$

TABLE 2

^{14}N NUCLEAR QUADRUPOLE PATTERNS OF PYRROLE MICROWAVE LINES USED IN DETERMINATION OF QUADRUPOLE COUPLING CONSTANTS

Transition		*Frequency (MHz)*			
$J_{K_{-1},K_{+1}} \rightarrow J'_{K'_{-1},K'_{+1}}$	$F \rightarrow F'$	*exp.*	*calc. hyperfine structure*	*(intensity)*	*center*
$0_{0,0} \rightarrow 1_{0,1}$	$1 \rightarrow 0$	13532.74	−0.73	(0.111)	13533.46
	$1 \rightarrow 2$	3.39	−0.07	(0.555)	
	$1 \rightarrow 1$	3.81	+0.36	(0.333)	
$2_{1,2} \rightarrow 2_{1,1}$	$2 \rightarrow 2$	13406.88	−0.97	(0.231)	13407.84
	$2 \rightarrow 3$		−0.58	(0.052)	
	$2 \rightarrow 1$		−0.36	(0.050)	
	$3 \rightarrow 2$		−0.11	(0.052)	
	$3 \rightarrow 3$	8.13	+0.28	(0.415)	
	$1 \rightarrow 2$		+0.36	(0.050)	
	$1 \rightarrow 1$	8.78	+0.97	(0.150)	
$2_{0,2} \rightarrow 2_{2,1}$	$2 \rightarrow 2$	13797.20	−1.03	(0.231)	13798.23
	$2 \rightarrow 3$	7.66	−0.56	(0.052)	
	$2 \rightarrow 1$	7.96	−0.30	(0.050)	
	$3 \rightarrow 2$		−0.17	(0.052)	
	$3 \rightarrow 3$	8.53	+0.28	(0.415)	
	$1 \rightarrow 2$		+0.30	(0.050)	
	$1 \rightarrow 1$	9.25	+1.03	(0.150)	
$3_{1,3} \rightarrow 3_{1,2}$	$3 \rightarrow 3$	22656.35	−0.83	(0.280)	22657.19
	$4 \rightarrow 4$	7.48	+0.28	(0.402)	
	$2 \rightarrow 2$	7.85	+0.66	(0.212)	
$3_{0,3} \rightarrow 3_{2,2}$	$3 \rightarrow 3$	22670.18	−0.83	(0.280)	22671.02
	$4 \rightarrow 4$	1.29	+0.28	(0.402)	
	$2 \rightarrow 2$	1.71	+0.67	(0.212)	

TABLE 3

MICROWAVE SPECTRUM OF PYRROLE (MHz)

Transition $J\ K_{-1}K_{+1} \rightarrow J'K'_{-1}K'_{+1}$	*Obs. frequency*[a]	*calc. −obs.*	*Centrifugal distortion corr.* *total*	*from* τ_{cccc}
0 0 0 — 1 0 1	13533.46	−0.040	−0.006	−0.003
1 0 1 — 2 0 2	22724.13	−0.064	−0.030	−0.023
1 1 1 — 2 1 2	22597.48	0.081	−0.031	−0.023
2 0 2 — 2 2 1	13798.23	0.054	−0.061	−0.007
2 1 2 — 2 1 1	13407.84	−0.117	−0.056	−0.007
3 0 3 — 3 2 2	22671.02	0.026	−0.167	−0.031
3 1 3 — 3 1 2	22657.19	0.015	−0.161	−0.031
3 1 2 — 3 3 1	14004.70	0.146	−0.156	−0.007
3 2 2 — 3 2 1	13215.61	−0.120	−0.134	−0.007
4 1 3 — 4 3 2	22678.64	−0.003	−0.366	−0.031
4 2 3 — 4 2 2	22636.95	0.077	−0.346	−0.031
4 2 2 — 4 4 1	14294.13	−0.057	−0.295	−0.007
4 3 2 — 4 3 1	12960.52	−0.169	−0.228	−0.007
5 2 3 — 5 4 2	22694.36	0.057	−0.620	−0.031
5 3 3 — 5 3 2	22597.12	0.049	−0.570	−0.031
5 3 2 — 5 5 1	14677.48	0.032	−0.486	−0.007
5 4 2 — 5 4 1	12643.58	−0.159	−0.332	−0.007
6 3 3 — 6 5 2	22722.75	0.034	−0.934	−0.031
6 4 3 — 6 4 2	22528.19	−0.010	−0.826	−0.031
6 4 2 — 6 6 1	15169.10	−0.033	−0.744	−0.008
6 5 2 — 6 5 1	12266.27	−0.029	−0.436	−0.007
7 4 3 — 7 6 2	22769.10	0.116	−1.316	−0.031
7 5 3 — 7 5 2	22419.38	−0.039	−1.106	−0.031
8 5 3 — 8 7 2	22840.50	−0.119	−1.776	−0.031
8 6 3 — 8 6 2	22259.26	0.059	−1.397	−0.031
8 6 2 — 8 8 1	16540.14	0.042	−1.541	−0.008
9 6 3 — 9 8 2	22944.20	0.053	−2.328	−0.031
9 7 3 — 9 7 2	22037.00	0.049	−1.684	−0.031
9 7 2 — 9 9 1	17452.91	−0.094	−2.132	−0.008
10 7 3 — 10 9 2	23090.26	−0.026	−2.989	−0.031
10 8 3 — 10 8 2	21742.72	−0.012	−1.947	−0.031
10 8 2 — 10 10 1	18537.45	−0.010	−2.892	−0.008
11 8 3 — 11 10 2	23289.29	−0.025	−3.786	−0.031
11 9 3 — 11 9 2	21368.68	−0.049	−2.167	−0.030
11 9 2 — 11 11 1	19806.80	−0.087	−3.857	−0.009
12 9 3 — 12 11 2	23553.90	0.006	−4.749	−0.031
12 10 3 — 12 10 2	20909.88	0.057	−2.322	−0.030
12 10 2 — 12 12 1	21269.90	0.108	−5.065	−0.009
13 11 3 — 13 11 2	20364.84	−0.059	−2.391	−0.030
25 22 4 — 25 22 3	24350.68	0.000	0.136	−0.080
26 23 4 — 26 23 3	23177.61	−0.009	2.651	−0.079
27 24 4 — 27 24 3	21934.67	0.022	5.488	−0.078
28 25 4 — 28 25 3	20633.62	0.023	8.607	−0.076
38 34 4 — 38 34 4	24118.16	−0.086	44.217	−0.165
39 35 5 — 39 35 4	22435.65	0.053	52.291	−..161

[a] ±0.10 MHz.

These and the calculated coupling constants in Table 1 were used to compute splittings for all the spectra. The calculated splittings were combined with measurements for the partly resolved patterns to give center frequencies in the complete material (Tables 3–9). Insufficient splittings were found to determine separately the coupling constants of each isotopic species.

For all the pyrroles the following is valid: for $J > 3$, a maximum of two quadrupole components could be expected, the difference between two of the three main components being less than 0.20 MHz. For $J > 6$, the maximum distance was calculated to be less than 0.30 MHz, and no splittings were observed.

TABLE 4

MICROWAVE SPECTRUM OF [^{15}N]PYRROLE (MHz)

Transition $J\ K_{-1}K_{+1} \rightarrow J'K'_{-1}K'_{+1}$	*Obs. frequency*[a]	*calc. −obs.*	*Centrifugal distortion correction*
0 0 0 — 1 0 1	13289.98	−0.256	−0.005
1 0 1 — 2 0 2	22560.88	0.068	−0.030
1 1 1 — 2 1 2	22254.57	0.059	−0.030
2 0 2 — 2 2 1	13963.49	−0.152	−0.062
2 1 2 — 2 1 1	12974.68	−0.341	−0.055
3 0 3 — 3 2 2	22444.60	0.058	−0.167
3 1 3 — 3 1 2	22356.80	0.046	−0.162
3 1 2 — 3 3 1	14529.49	−0.129	−0.161
3 2 2 — 3 2 1	12499.93	−0.157	−0.132
4 1 3 — 4 3 2	22494.77	0.184	−0.366
4 2 3 — 4 2 2	22231.59	−0.088	−0.348
4 2 2 — 4 4 1	15368.65	0.010	−0.308
5 2 3 — 5 4 2	22600.00	0.186	−0.621
5 3 3 — 5 3 2	21988.84	−0.074	−0.571
6 3 3 — 6 5 2	22791.73	0.064	−0.939
6 4 3 — 6 4 2	21584.72	0.106	−0.822
6 4 2 — 6 6 1	18125.10	0.035	−0.818
7 4 3 — 7 6 2	23110.35	0.091	−1.332
7 5 3 — 7 5 2	20984.96	0.053	−1.087
7 5 2 — 7 7 1	20163.30	0.156	−1.232
8 5 3 — 8 7 2	23607.04	−0.074	−1.819
8 6 3 — 8 6 2	20171.28	−0.021	−1.349
9 6 3 — 9 8 2	24342.51	−0.097	−2.425
9 7 3 — 9 7 2	19144.14	0.008	−1.591
9 7 2 — 9 9 1	25736.55	−0.078	−2.556
10 7 3 — 10 9 2	25386.15	−0.010	−3.187
10 8 3 — 10 8 2	17919.93	−0.070	−1.793
12 10 3 — 12 10 2	14994.18	0.002	−2.016
16 13 4 — 16 13 3	23320.24	0.047	−5.329
17 14 4 — 17 14 3	21366.49	−0.011	−5.243
18 15 4 — 18 15 3	19275.07	0.006	−4.993
24 20 5 — 24 20 4	23206.75	−0.014	−9.040

[a] ±0.10 MHz.

ROTATIONAL AND CENTRIFUGAL DISTORTION CONSTANTS

The unperturbed rotational frequencies given in Tables 3–9 for all the isotopic species were analyzed by a least-squares method to give the rotational and centrifugal distortion constants shown in Table 10. According to an earlier paper by

TABLE 5

MICROWAVE SPECTRUM OF [2-^{13}C]PYRROLE (MHz)

Transition $J\ K_{-1}K_{+1} \rightarrow J'K'_{-1}K'_{+1}$	*Obs. frequency*[a]	*calc. —obs.*	*Centrifugal distortion correction*
0 0 0 — 1 0 1	13370.41	0.057	−0.006
0 0 0 — 1 1 1	13499.69	−0.080	−0.006
1 0 1 — 2 1 2	22455.06	−0.001	−0.030
1 1 1 — 2 0 2	22323.11	0.013	−0.031
2 0 2 — 2 1 1	13247.83	−0.096	−0.057
2 1 2 — 2 2 1	13632.51	−0.139	−0.057
3 1 2 — 3 2 1	13066.95	−0.092	−0.142
3 2 2 — 3 2 1	13053.00	−0.097	−0.146
3 2 2 — 3 3 1	13827.83	−0.106	−0.145
4 2 2 — 4 3 1	12839.71	0.118	−0.253
4 2 2 — 4 4 1	14131.04	−0.043	−0.250
4 3 2 — 4 3 1	12798.01	0.013	−0.266
4 3 2 — 4 4 1	14089.19	0.002	−0.264
5 2 3 — 5 3 2	22325.74	0.107	−0.611
5 3 2 — 5 4 1	12578.65	0.041	−0.387
5 3 2 — 5 5 1	14514.68	0.107	−0.382
5 4 2 — 5 4 1	12481.43	−0.006	−0.420
5 4 2 — 5 5 1	14417.42	0.099	−0.415
6 3 3 — 6 5 2	22451.88	−0.050	−0.848
6 4 2 — 6 5 1	12298.21	0.035	−0.539
6 4 3 — 6 5 2	22448.69	−0.029	−0.852
6 4 2 — 6 6 1	15007.11	−0.016	−0.531
6 5 2 — 6 5 1	12104.70	−0.047	−0.609
6 5 2 — 6 6 1	14813.55	−0.049	−0.601
9 6 3 — 9 7 2	21793.60	0.090	−2.203
10 7 3 — 10 8 2	21526.09	0.047	−2.762
10 8 3 — 10 8 2	21461.99	0.094	−2.857
12 10 3 — 12 10 2	20622.88	0.036	−4.346
12 11 2 — 12 12 1	18639.47	−0.044	−2.643
13 10 3 — 13 11 2	20366.59	0.012	−4.761
13 11 3 — 13 11 2	20074.35	−0.052	−5.242
13 12 2 — 13 13 1	19517.21	0.124	−3.194
14 11 3 — 14 12 2	19886.68	−0.021	−5.479
14 12 3 — 14 12 2	19440.37	−0.038	−6.240
14 13 2 — 14 14 1	20460.77	0.029	−3.829
15 12 3 — 15 13 2	19384.20	−0.024	−6.176
15 14 2 — 15 15 1	21467.55	−0.072	−4.560
23 21 2 — 23 22 1	20060.47	0.002	4.553
27 24 3 — 27 25 2	19170.30	−0.004	3.819

[a] ±0.10 MHz.

TABLE 6

MICROWAVE SPECTRUM OF [3-^{13}C]PYRROLE (MHz)

Transition $J\ K_{-1}K_{+1} \rightarrow$	$J'K'_{-1}K'_{+1}$	*Obs. frequency*[a]	*calc. −obs.*	*Centrifugal distortion correction*
0 0 0	1 0 1	13276.72	0.090	−0.005
1 0 1	2 0 2	22505.44	0.030	−0.031
1 0 1	2 1 2	22520.20	−0.067	−0.030
1 1 1	2 0 2	22209.57	−0.091	−0.030
1 1 1	2 1 2	22224.06	0.082	−0.030
2 0 2	2 2 1	13890.95	0.006	−0.058
3 1 2	3 3 1	14402.22	−0.005	−0.149
4 1 3	4 2 2	22220.80	0.098	−0.344
4 2 3	4 2 2	22217.69	0.029	−0.345
5 2 3	5 3 2	22025.62	0.040	−0.574
5 2 3	5 4 2	22526.03	0.089	−0.572
5 3 3	5 3 2	22012.89	0.089	−0.575
5 3 3	5 4 2	22513.53	−0.092	−0.573
5 3 2	5 5 1	16204.93	−0.117	−0.461
6 3 3	6 4 2	21707.65	−0.038	−0.842
6 4 3	6 4 2	21669.85	−0.102	−0.845
6 4 2	6 6 1	17609.12	0.018	−0.710
7 4 3	7 6 2	22949.66	−0.024	−1.175
7 5 3	7 5 2	21154.87	−0.041	−1.148
8 5 3	8 7 2	23360.75	−0.038	−1.556
8 6 2	8 8 1	21674.42	−0.010	−1.511
9 6 3	9 8 2	23969.09	−0.045	−2.001
9 7 3	9 7 2	19543.20	−0.007	−1.809
10 7 3	10 9 2	24832.80	0.086	−2.522
10 9 2	10 10 1	21914.49	0.015	−2.552
16 13 4	16 13 3	24532.15	0.013	−7.418
17 14 4	17 14 3	22788.08	−0.010	−7.964
27 23 5	27 23 4	18252.53	0.002	−19.056

[a] ±0.10 MHz.

TABLE 7

MICROWAVE SPECTRUM OF [1-D]PYRROLE (MHz)

Transition $J\ K_{-1}K_{+1} \rightarrow$	$J'K'_{-1}K'_{+1}$	*Obs. frequency*[a]	*calc. −obs.*	*Centrifugal distortion correction*
0 0 0	1 0 1	12699.46	0.017	−0.006
1 0 1	2 0 2	22100.32	0.114	−0.032
1 1 1	2 1 2	21416.89	−0.123	−0.031
2 0 2	2 2 1	14422.55	0.002	−0.059
3 0 3	3 2 2	21956.98	0.071	−0.170
3 1 3	3 1 2	21428.84	−0.040	−0.178
3 1 2	3 3 1	16082.93	−0.129	−0.144
4 1 3	4 3 2	22281.43	0.128	−0.365
4 2 3	4 2 2	20736.29	−0.041	−0.401
4 2 2	4 4 1	18731.29	−0.127	−0.241
5 2 3	5 4 2	22979.95	0.088	−0.587
5 3 3	5 3 2	19540.94	−0.058	−0.696
5 3 2	5 5 1	22562.19	−0.087	−0.335
6 3 3	6 5 2	24282.09	0.192	−0.800
6 4 3	6 4 2	17834.27	−0.111	−1.059

[a] ±0.20 MHz.

TABLE 8

MICROWAVE SPECTRUM OF [2-D]PYRROLE (MHz)

Transition $J\ K_{-1}K_{+1} \rightarrow J'K'_{-1}K'_{+1}$	*Obs. frequency*[a]	*calc. —obs.*	*Centrifugal distortion correction*
0 0 0 — 1 0 1	12700.10	0.030	—0.004
0 0 0 — 1 1 1	13356.90	—0.216	—0.004
1 1 1 — 2 0 2	21302.63	0.093	—0.025
2 0 2 — 2 1 1	12144.68	—0.091	—0.017
2 1 2 — 2 2 1	14040.31	—0.035	—0.017
3 0 3 — 3 1 2	21444.25	0.091	—0.057
3 1 3 — 3 1 2	21439.23	—0.138	—0.057
3 1 3 — 3 2 2	21803.07	—0.132	—0.056
3 2 2 — 3 3 1	15068.98	0.002	—0.033
4 1 3 — 4 2 2	20977.49	0.194	—0.096
4 2 3 — 4 3 2	21993.92	0.189	—0.092
5 2 3 — 5 3 2	20194.62	0.053	—0.145
5 2 3 — 5 4 2	22505.97	—0.006	—0.133
5 3 3 — 5 4 2	22362.14	—0.014	—0.135
5 4 2 — 5 5 1	18208.64	—0.058	—0.083
6 3 3 — 6 4 2	19147.04	—0.178	—0.204
6 4 3 — 6 5 2	22968.72	—0.010	—0.185
6 5 1 — 6 6 0	14167.44	—0.094	—0.028
6 5 2 — 6 6 1	20310.75	0.153	—0.116

[a] ±0.20 MHz.

TABLE 9

MICROWAVE SPECTRUM OF [3-D]PYRROLE (MHz)

Transition $J\ K_{-1}K_{+1} \rightarrow J'K'_{-1}K'_{+1}$	*Obs. frequency*[a]	*calc. —obs.*	*Centrifugal distortion correction*
0 0 0 — 1 0 1	12602.79	—0.149	—0.007
1 0 1 — 2 0 2	21965.47	—0.059	—0.034
1 0 1 — 2 1 2	22079.52	0.103	—0.033
1 1 1 — 2 1 2	21262.98	0.030	—0.033
2 0 2 — 2 2 1	14390.61	0.119	—0.074
3 0 3 — 3 2 2	21829.60	0.088	—0.208
3 1 3 — 3 1 2	21262.28	0.319	—0.219
3 1 2 — 3 3 1	16125.41	—0.099	—0.181
4 1 3 — 4 2 2	20594.69	—0.108	—0.501
4 1 3 — 4 3 2	22179.96	—0.210	—0.456
4 2 3 — 4 2 2	20524.73	—0.073	—0.506
4 2 3 — 4 3 2	22110.05	—0.225	—0.460
5 3 3 — 5 3 2	19261.99	0.006	—0.883
5 3 3 — 5 4 2	22660.88	0.088	—0.760
5 3 2 — 5 5 1	22906.30	0.073	—0.418
5 4 2 — 5 5 1	19507.50	—0.099	—0.541
6 3 3 — 6 5 2	24341.80	0.067	—0.997
6 4 3 — 6 4 2	17476.25	0.071	—1.347
6 5 1 — 6 6 0	16898.44	0.005	—0.189

[a] ±0.20 MHz.

TABLE 10

MEAN DEVIATION AND ROTATIONAL CONSTANTS, CENTRIFUGAL DISTORTION CONSTANTS, PRINCIPAL MOMENTS OF INERTIA AND INERTIAL DEFECT OF ISOTOPIC PYRROLES

(Conversion factor 505531 MHz × amu Å²)

Species	Parent	^{15}N	2-^{13}C	3-^{13}C
s (MHz)	0.077	0.128	0.072	0.069
A (MHz)	9130.610±0.013	9131.09±0.02	9021.879±0.012	9099.129±0.009
B (MHz)	9001.343±0.013	8807.26±0.02	8892.736±0.012	8803.137±0.009
C (MHz)	4532.083±0.013	4482.47±0.02	4477.737±0.012	4473.678±0.009
D_1 (kHz)	−9.90±0.07	−10.3±0.3	−9.72±0.08	−9.95±0.13
D_2 (kHz)	−8.93±0.08	−8.8±0.2	−9.78±0.08	−8.80±0.12
D_3 (kHz)	−9.80±0.09	−9.8±0.3	−9.47±0.08	−9.22±0.14
I_a(amuÅ²)	55.36662±0.00008	55.36368±0.00014	56.03389±0.00008	55.55818±0.00006
I_b(amuÅ²)	56.16173±0.00008	57.39933±0.00015	56.84763±0.00008	57.42623±0.00006
I_0(amuÅ²)	111.5450±0.0003	112.7797±0.0005	112.8988±0.0003	113.0012±0.0002
I.D.(amuÅ²)	0.0166±0.0003	0.0167±0.0005	0.0173±0.0003	0.0168±0.0002

Species	1-D	2-D	3-D
s	0.118	0.130	0.145
A	9130.77±0.02	9018.39±0.03	9089.06±0.02
B	8340.83±0.02	8361.84±0.03	8272.45±0.02
C	4358.66±0.02	4338.30±0.03	4330.20±0.02
D(kHz)	−10.3±1.4	−1.8±1.3	−13.1±1.7
I_a	55.36565±0.00014	56.05556±0.00018	55.61971±0.00015
I_b	60.60923±0.00017	60.45692±0.0002	61.11020±0.00018
I_0	115.9832±0.0005	116.5276±0.0007	116.7455±0.0006
I.D.	0.0083±0.0006	0.0151±0.0008	0.0156±0.0006

one of us[4], it is usually possible to select linear combinations of the four "planar" centrifugal distortion constants in such a way that the observed frequencies are almost independent of one of the new constants. Instead of the D–R constants previously used[4] for the analysis of the near-oblate symmetric rotor spectra, we have here preferred to use the simpler combinations

$$D_1 = \tau_{aaaa} - 2\tau_{cccc} \quad D_2 = \tau_{bbbb} - 2\tau_{cccc} \quad D_3 = \tau_{abab} + 2\tau_{cccc} \quad D_4 = \tau_{cccc}$$

In all calculations the fourth constant τ_{cccc} was fixed at the value -1.9 kHz, which is of the correct order of magnitude according to calculations from a reasonable harmonic force field. It can be seen from Table 3 that the contributions to the total centrifugal distortion from the fixed constant are almost negligible. The reason for this is that the coefficient of D_4 in the rearranged expression for the perturbation energy is approximately equal to $\frac{1}{2}J^2(J+1)^2 - \frac{1}{4}\langle P_c^4 \rangle$, from which we can estimate the contributions by replacing $\langle P_c^4 \rangle$ by K_{+1}^4. For a Q-branch transition with a change in K_{+1}, e.g. from 5 to 4, a contribution of -0.175 MHz is obtained in fair agreement with the actual calculations (compare Table 3).

For an oblate symmetric rotor $D_1 = D_2 = D_3$. Because only a small number of rather low-J transitions have been measured in the spectra of the deuterated species, we have used this equality to reduce the number of parameters to be adapted. The constant D in Table 10 is the common value obtained for D_1, D_2 and D_3. The usefulness of this approximate method of centrifugal distortion correction was shown by its application to the transitions with $J \leqq 6$ in the parent and ring-substituted species. The rotational constants obtained by the two methods agree well.

DIPOLE MOMENT

The dipole moment of pyrrole was determined by measuring the Stark coefficient of the $0_{0,0} \rightarrow 1_{0,1}$ transition[5]. The $0 \rightarrow 1$ transition of OCS was used to calibrate the electric field[6]. $\Delta\nu$(pyrrole)/$\Delta\nu$(OCS) $= 5.27 \pm 0.05$. In calculating the dipole moment, the quadrupole coupling could be ignored, since the Stark perturbation was at least an order of magnitude greater than the quadrupole perturbation. The dipole moment of pyrrole is then $\mu = \mu_a = 1.74 \pm 0.02$ D.

MOLECULAR STRUCTURE

Substitution coordinates of each atom in pyrrole were determined from differences in I_a^0 and I_b^0; the results are in Table 11. The experimental uncertainties are considerably less than 0.001 Å and also lower than the errors expected in substitution coordinates, errors which may well be a few thousandths of an Å[7]. The [^{15}N] and [1-D] species of pyrrole show ΔI_a^0-values of -0.0029 and -0.0010

TABLE 11

PYRROLE SUBSTITUTION COORDINATES (Å)

Atom	*a*	*b*	
N	−1.12220±0.00008[a]	0	$M^{-1}\sum_i m_i a_i = -0.0005$ Å
C(2)	−0.33395±0.00012	±1.12111±0.00010	
C(3)	0.98522±0.00007	±0.70837±0.00017	$I_a^\circ - I_a$(calc.) = 0.461 amu Å² (ca. 0.8 %)
H(1)	−2.11771±0.00004	0	$I_b^\circ - I_b$(calc.) = −0.005 amu Å²
H(2)	−0.7605 ±0.0007	±2.1089±0.0003	
H(3)	1.8443 ±0.0003	±1.3578±0.0004	

[a] Experimental uncertainty.

amu Å², respectively, which is the usual order of magnitude for zero-point effects for substitution on a principal axis. Using Costain's average $\Delta I^0 = 0.0024$ amu Å² we get the following expected errors in the coordinates, $\delta r = 0.0012/r$ Å:

	δa_1	δb_1		δa_1	δb_1
N	0.0011	—	H(1)	0.0006	—
C(2)	0.0036	0.0011	H(2)	0.0016	0.0006
C(3)	0.0012	0.0017	H(3)	0.0007	0.0009

Another way of estimating the order of magnitude of systematic errors in the coordinates makes use of bond-shortening effects[8]. Assuming that average C–D bonds are shorter than C–H bonds by 0.003 Å and that ^{13}C or ^{15}N substitution makes the involved bonds (except to hydrogen) shorter by 0.00005 Å, errors in coordinates can be estimated as given below:

	δa_2	δb_2		δa_2	δb_2
N	0.0015	—	H(1)	0.0060	—
C(2)	0.0004	0.0014	H(2)	0.0020	0.0057
C(3)	0.0009	0.0009	H(3)	0.0045	0.0041

The two sets of numbers are seen to be considerably greater than the pure experimental uncertainty, and for the ring atoms of roughly the same size, except for $a_{C(2)}$. For the hydrogen atoms the bond-shortening effect is up to ten times higher than the Costain expectation.

Taking now the maximum value for each expected error as a vib–rot uncertainty we get the numbers in parentheses in Table 12, where the pyrrole substitution structure is also given. The distances are thought to be known to ± 0.005 Å and the angles to ±0.5°. Calculated moments of inertia are compared to the experimental values in Table 11. As expected, the differences are not completely vanishing. The value of the center of mass *a*-coordinate, also in Table 11, is small as expected.

The ΔI-values calculated for the earlier investigated [2,3,4,5-D_4] and [D_5] species are within 0.1 % of the experimental differences[1].

TABLE 12

PYRROLE SUBSTITUTION STRUCTURE

(Expected vib–rot errors in parentheses, see text)

N–C	1.370 Å(0)	CNC	109.8°
C(2)–C(3)	1.382 Å(+0.005)	NCC	107.7°
C(3)–C(4)	1.417 Å(+0.003)	CCC	107.4°
N–H	0.996 Å(+0.004)	NCH	121.5°
C(2)–H(2)	1.076 Å(+0.003)	H(3)C(3)C(4)	127.1°
C(3)–H(3)	1.077 Å(+0.004)		

DISCUSSION

In Table 13 are collected experimental and calculated dipole moments and nuclear quadrupole coupling data for pyrrole and some related molecules. The microwave (MW) results are for molecules in the gas phase, whereas the nuclear

TABLE 13

COMPARISON OF DIPOLE MOMENTS AND NUCLEAR QUADRUPOLE COUPLING DATA FOR PYRROLE AND SOME RELATED MOLECULES

molecule	pyrrole	N-methyl-pyrrole	pyridine	4-methyl pyridine
MW	*this work*	*ref. 9**	*ref. 4*	*ref. 10*
μ (D)	1.74±0.02	2.12±0.02	2.15±0.05	2.70±0.02
χ_{aa} (MHz)	1.45±0.02	2.05±0.05	−4.88±0.04	−4.82±0.04
χ_{bb} (MHz)	1.21±0.02	−1.69±0.3	1.43±0.03	1.0 } $\chi_{bb}-\chi_{cc}$ =
χ_{cc} (MHz)	−2.66±0.02	−0.37±0.3	3.45±0.02	3.8 } −2.8±0.4
η (%)	9±1		41.4±0.8	58±8
NQR	*refs. 11, 12*		*ref. 13*	*ref. 13*
χ (MHz)	2.06		4.58	4.41
η (%)	26.9		39.6	34.2
χ_1 (MHz)	±0.75		±1.38	±1.45
χ_2 (MHz)	±1.31		±3.20	±2.96
χ_3 (MHz)	∓2.06 (c)		∓4.58 (a)	∓4.41 (a)
MO	*ref. 14*		*ref. 14*	
μ (D)	2.11		2.16	
χ_{aa} (MHz)	4.91		−5.99	
χ_{bb} (MHz)	1.96		2.59	
χ_{cc} (MHz)	−6.87		3.40	

* See note added in proof on pag. 506

quadrupole resonance (NQR) data were measured at 77°K in the solid state. There is a considerable difference between the numbers for pyrrole, which might be caused by hydrogen bonding in the condensed phase. Even more surprising is the effect of substituting a methyl group for hydrogen at the nitrogen atom. This completely destroys the almost symmetrical electronic environment. On the contrary, the pyridine values are not very sensitive to the phase (no hydrogen bonding) and substituting a methyl group at the carbon atom opposite the nitrogen does not make a great change in the immediate environment of the nitrogen nucleus.

The dipole moments show the expected behaviour by methyl substitution, considering the dipole moment of toluene measured by the microwave (Stark) method, $\mu = 0.375 \pm 0.01$ D[15]. It can be seen that the dipole moments of pyrrole and pyridine must be oppositely oriented, both methyl derivatives having numerically higher moments than their parents.

The MO calculation referred to in Table 13 is in considerable disagreement with the experiments, especially for the pyrrole quadrupole coupling constants.

The present pyrrole structure is a considerable improvement of the earlier work[1] based on deuterated species only. It shows clearly that the slight variation in assumed C–H distances used previously to derive a ring structure can give results that are rather misleading:

distance	*present result* (Å)	*range of earlier models* (Å)	
N–C	1.370	1.366–1.401	(0.035)
C(2)–C(3)	1.382	1.353–1.389	(0.036)
C(3)–C(4)	1.417	1.412–1.446	(0.034)
N–H	0.996	0.978–1.008	(0.030)
C(2)–H(2)	1.076	1.070–1.080	assumed
C(3)–H(3)	1.077		

A second conclusion is that C–H = 1.08 Å and N–H = 1.00 Å are reasonable values in heterocyclic molecules. The C–H distances in pyrrole may be slightly shorter than the C–H distance in benzene.

Finally, it is of interest once more to compare the structures of cyclopentadiene (I)[16], furan (II)[17], and thiophene (III)[18] with that of pyrrole (IV), as given in Fig. 2. These four molecules have been treated in a uniform way, i.e. by the substitution method, except for the hydrogen atoms in (I). If we consider the difference between the C(3)–C(4) and C(2)–C(3) distances as a measure of electron delocalization, (IV) should be the most aromatic of the four molecules. However, the chemical properties of (III) are most benzene-like, which might be caused by the participation of the *d*-orbitals of sulphur, a possibility not present in (II) and (IV).

Assuming that the covalent radius of nitrogen is 0.05 Å shorter than the radius of carbon and ignoring differences in hybridization, the degree of delocalization in the CNC part of pyrrole is similar to that in the carbon chain. If a com-

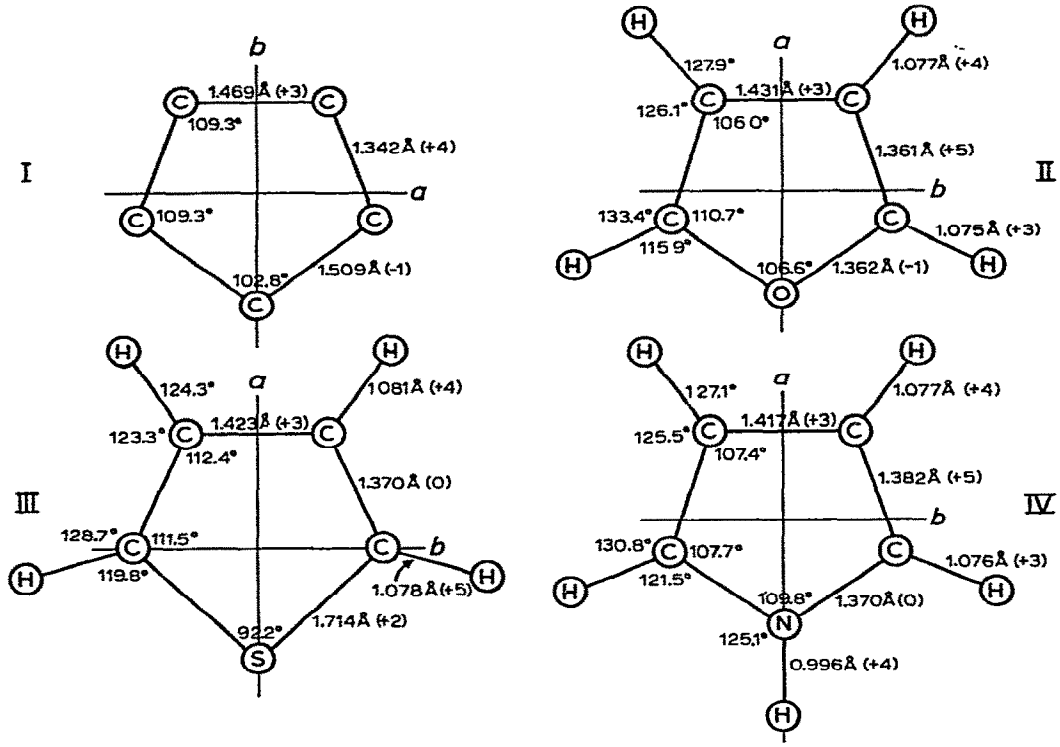

Fig. 2. Substitution structure of cyclopentadiene (I), furan (II), thiophene (III), and pyrrole (IV). Numbers in parentheses are estimated vib–rot errors (in thousandths of Å), see text.

parison with six-membered rings can be drawn, neglecting differences in hybridization (although this neglect is not justified to the same degree), it is observed that C(2)–C(3) is 0.015 Å shorter and C(3)–C(4) 0.02 Å longer than in benzene, and that N–C is 0.03 Å longer than the (quite different) N–C bond in pyridine[19]. This supports the view of a high degree of delocalization in pyrrole.

The C(2)–H(2) bonds in Fig. 2 show a considerable tilt in the direction of the electronegative hetero-atoms. In (II) the tilt is 17–18°, in (III) and (IV) about 9°. The C(3)–H(3) bonds show no significant tilt.

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REFERENCES

1 B. Bak, D. Christensen, L. Hansen and J. Rastrup-Andersen, *J. Chem. Phys.*, 24 (1956) 720.
2 B. Bak, T. Pedersen and G. O. Sørensen, *Acta Chem. Scand.*, 18 (1964) 275.

3 W. S. WILCOX AND J. H. GOLDSTEIN, *J. Chem. Phys.*, 20 (1952) 1656.
4 G. O. SØRENSEN, *J. Mol. Spectry.*, 22 (1967) 325.
5 S. GOLDEN AND E. B. WILSON, JR., *J. Chem. Phys.*, 16 (1948) 669.
6 S. A. MARSHALL AND J. WEBER, *Phys. Rev.*, 105 (1957) 1502.
7 C. C. COSTAIN, *Trans. Am. Cryst. Assoc.*, 2 (1966) 157.
8 V. W. LAURIE AND D. R. HERSCHBACH, *J. Chem. Phys.*, 37 (1962) 1687.
9 W. ARNOLD, H. DREIZLER AND H. D. RUDOLPH, *Z. Naturforsch.*, 23a (1968) 301.
10 H. D. RUDOLPH, H. DREIZLER AND H. SEILER, *Z. Naturforsch.*, 22a (1967) 1738.
11 L. GUIBÉ AND E. A. C. LUCKEN, *Mol. Phys.*, 14 (1968) 73.
12 E. SCHEMPP AND P. J. BRAY, *J. Chem. Phys.*, 48 (1968) 2380.
13 L. GUIBÉ, *Ann. Phys.*, 7 (1962) 177.
14 D. W. DAVIES AND W. C. MACKRODT, *Chem. Commun. (London)*, (1967) 1226.
15 H. D. RUDOLPH, H. DREIZLER, A. JAESCHKE AND P. WENDLING, *Z. Naturforsch.*, 22a (1967) 940.
16 L. H. SCHARPEN AND V. W. LAURIE, *J. Chem. Phys.*, 43 (1965) 2765.
17 B. BAK, D. CHRISTENSEN, W. B. DIXON, L. HANSEN-NYGAARD, J. RASTRUP-ANDERSEN AND M. SCHOTTLÄNDER, *J. Mol. Spectry.*, 9 (1962) 124.
18 B. BAK, D. CHRISTENSEN, L. HANSEN-NYGAARD AND J. RASTRUP-ANDERSEN, *J. Mol. Spectry.*, 7 (1961) 58.
19 B. BAK, L. HANSEN-NYGAARD AND J. RASTRUP-ANDERSEN, *J. Mol. Spectry.*, 2 (1958) 361; and unpublished results.

NOTE ADDED IN PROOF

Dr. H. Dreizler in a private communication (December 1968) gave the quadrupole coupling constants with uncertainties for N-methylpyrrole quoted in Table 13. These values differ from those published earlier[9].