The Microwave Spectrum of Oxazole
I. The Complete Structure by DRM Microwave Spectroscopy

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Double resonance modulation (DRM) microwave spectroscopy has been used to determine the complete substitution structure of oxazole. Isotopic species spectra associated with ^{13}C, ^{15}N and ^{18}O were studied in their natural abundances, while the mono-deuterated species were examined in a mixture of slightly enriched forms.

With uncertainties below 0.002 Å and 0.1° for distances and angles, respectively, the structure parameters of oxazole are as follows:

$O(1)-C(2) = 1.357_4$ Å
$C(2)-N(3) = 1.291_5$ Å
$N(3)-C(4) = 1.395_4$ Å
$C(4)-C(5) = 1.352_5$ Å
$C(5)-O(1) = 1.369_6$ Å
$C(2)-H(2) = 1.075_0$ Å
$C(4)-H(4) = 1.075_1$ Å
$C(5)-H(5) = 1.073_2$ Å

$C(5)O(1)C(2) = 103.9_1°$
$O(1)C(2)N(3) = 114.9_9°$
$C(2)N(3)C(4) = 103.9_2°$
$N(3)C(4)C(5) = 109.0_4°$
$C(4)C(5)O(1) = 108.1_4°$
$O(1)C(2)H(2) = 117.0_9°$
$N(3)C(4)H(4) = 121.8_9°$
$O(1)C(5)H(5) = 116.8_6°$

The geometry of oxazole is compared with that of isoxazole and with the structures of the closely related compounds furan and 1,3,4-oxadiazole.

I. Introduction

During the past two decades research into the electron distribution and the accurate geometry of heterocyclic molecules has attracted a great deal of interest from microwave spectroscopists, partly because these substances, besides playing a fundamental role in a flourishing branch of chemistry, are well suited as test cases or as applications of the rapidly progressing methods of quantum chemistry. Five-membered heterocyclics have been a particularly active area [1] of study and, up to 1974, the geometries, dipole moments, nuclear quadrupole coupling constants and magnetic susceptibilities of nearly two dozen substances of this type had been fully or partially investigated by microwave techniques.

While C_{2v}-symmetrical molecules such as furan [2], thiophene [3] and 1,2,5-thiadiazole [4] were studied at the beginning of this development primarily for reasons of spectral simplicity and preparative economy, progress was noticeably slowed for the rings without a C_{2v} axis; Due to restricted financial resources and preparative difficulties, together with the spectral complexity and the limited molecular selectivity of Stark effect modulation (SEM) spectrometers, it was often not possible to study all the isotopic species necessary for the complete determination of the geometries. However, following developments in microwave-microwave double radiation techniques [5] during the past ten years, such difficulties have now been considerably reduced, and the replacement of SEM by double resonance modulation (DRM) has been shown [6] to offer both sufficient sensitivity and molecular selectivity so as to allow the identification of rare isotopic species in their natural abundances irrespective of spectral complexity. As a result, the molecular structures of simple heterocyclic molecules can now be readily determined since the preparation of enriched species containing ^{13}C, ^{15}N or ^{18}O is no longer necessary. The power of this technique has been most clearly demonstrated in the case of isoxazole [6c] where even the deuterium species were studied in their natural abundance, and the optimistic outlook derived from that investigation has since been justified through succesful structure studies on ten more molecules [6d–g, 7].

Against this background, and in view of the isomerism of oxazole and isoxazole, — as reflected also in a Zeeman study of this pair of compounds [8] —, it seemed desirable to resume earlier work [9] from this laboratory and, along with the refinement of dipole and quadrupole data, to determine the molecular structure of oxazole. Accordingly, enriched

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samples of the deuterated forms of oxazole were prepared and the dipole moments and quadrupole coupling constants of these forms were investigated by conventional SEM spectroscopy [10]. The molecular structur was then determined by DRM techniques and, after the previously deduced rotational constants had been further refined during this stage of the work, the DRM data were used for the final evaluation of the orientation of the dipole moment and of the principal values and direction of the electric field gradient tensor.

As a proper reflection of this interrelation between the DRM study of the molecular structure and the final evaluation of the earlier SEM data, we report in the present part I the complete structure of oxazole, while the dipole and quadrupole results from the preceeding SEM work will be given in part II.

II. Experimental

a) Samples — Work on the parent species and on the isotopic forms involving ^{13}C, ^{15}N and ^{18}O in natural abundance was conducted on a purified sample which had been prepared according to the method of Bangert [11]. Deuterated species were studied on an enriched sample which had been prepared for the preceeding work by SEM spectroscopy (part II), and which initially contained an estimated concentration of 25% and 15% of the 4-d_1- and 5-d_1-species, respectively, along with the normal and the 2-d_1-species. At the time of the structure study by DRM spectroscopy a large portion of this sample had decomposed but, luckily, the remaining oxazole still contained comparable amounts of all three mono-deuterated forms, giving absorption signals of about the same intensity as the naturally occurring ^{13}C-species of the pure substance.

b) Instrumental — Rotational spectra of the parent and isotopic forms of oxazole were studied with the DRM spectrometer, and in the mode of operation, described previously [12]. The instrument uses frequency modulation of the pump radiation, and its absorption cell consists of a 20 m section of K-band waveguide (cut-off frequency: 14.1 GHz). The range of pump frequencies was taken from 18—26 GHz, with signal frequencies varying from 28—40 GHz. Medium-powered klystrons (~ 200 mW) were used as sources of both the signal and pump radiation. DRM signals were observed on the oscilloscope. All measurements were made at room temperature and with sample pressures near 40 mtorr.

III. Spectroscopic Results

a) Characterisation of Spectra

From the early work [9] and the renewed efforts [10] which preceeded the present structure study by DRM, the rotation spectrum of oxazole has been identified as that of a planar, near-oblate, asymmetric rotor ($\varkappa \sim 0.9$) with a- and b-type transitions of comparable intensity. Q-branch transitions are predominant while R-branch lines are scarce; The conventional microwave range from 10—40 GHz contains only 12 R-branch transitions, the highest J-value being the $J = 2 \rightarrow 3$ transition. While easily resolved in low-J transitions, the hyperfine splitting due to the quadrupolar ^{14}N nucleus receeds with increasing J-values so that many of the high-J Q-branch transitions appear as singlets with others still showing a close doublet or triplet structure resulting from the most intense transitions between the hyperfine levels.

As is typical for planar, near-oblate rotors, the orientation of the principal inertial axes a and b with respect to the molecular geometry is not easily deduced from the observed moments of the parent species alone, and it undergoes large changes upon isotopic substitution (see Fig. 1 and row 3 of Table 1). As a result, the components of the dipole moment along the axes vary considerably between isotopic species, leading to nearly pure a-type spectra for the

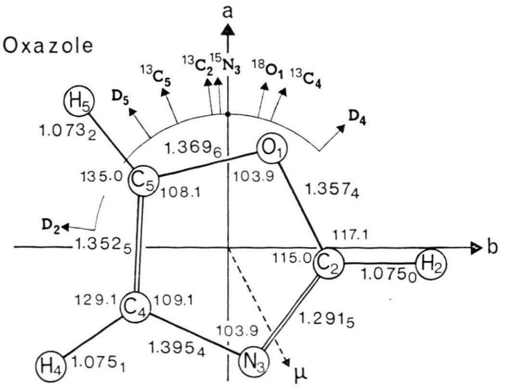

Fig. 1. The "best" structure of oxazole, and the orientation of the inertial axis a in the parent and the eight isotopic species.

^{13}C(2)-, ^{15}N(3)-, ^{13}C(5)- and 5-d$_1$-species, while in the 4-d$_1$-spectrum only *b*-type transitions are observed (see Fig. 1 for numbering of atoms). This rotation of the inertial axes also leads to large variations between different isotopic forms of the field gradient at the ^{14}N nucleus in the direction of the inertial axes, with χ_{aa} varying from -4.03 MHz in the ^{13}C(2)-species to $+1.22$ MHz in the 2-d$_1$-species, while χ_{bb} changes from $+1.65$ MHz in the ^{13}C(2)-species to -3.60 MHz in the 2-d$_1$-species (compare row 5 of Table 1).

b) Isotopic Species Spectra

Knowledge of the hydrogen positions in oxazole, as deduced from the preceeding SEM work on deuterated species, made the DRM identification of the isotopic species spectra due to ^{13}C, ^{15}N and ^{18}O a rather simple exercise; In conjunction with assumed C-H bond lengths of 1.075 ± 0.005 Å, and with reasonable values for the ring bonds as estimated from the known lengths in related compounds [2, 6c, 13], it allowed the coordinates of the carbon atoms to be estimated to within a few hundredths of an angstrom unit. The *b*-coordinate of the carbon atom C(2), in particular, could be anticipated to within ± 0.005 Å from the known position of H(2) and the observation that the C-H bond would be approximately parallel to the *b*-axis (see Figure 1). Due to the proximity to the *b*-axis of H(2), and hence also of C(2), the uncertainties in the small *a*-coordinate of C(2) were of no significant influence on the expected *B*-constant of the ^{13}C(2)-species, and its spectrum could therefore be predicted closely enough for instant identification by the standard DRM methods [12].

Utilisation of the accurately deduced position of this first ring atom C(2), together with the other, less precise isotopic data in the remodelling of the ring structure, subsequently allowed improved predictions for the ^{13}C(4)- and ^{13}C(5)-spectra, which were then readily assigned. The ^{15}N-species was studied next and, with seven out of the eight atoms located, the ^{18}O(1)-spectrum was predicted and observed without difficulty.

As a considerable number of DRM signal transitions of the parent species of oxazole had been observed and measured during the described investigation of the ring isotopes, it seemed desirable at this point to refine the previously derived information on the deuterated species, especially since the least squares fits of transitions measured in the preceeding SEM investigation had led to considerably larger standard deviations than the DRM work, with uncertainties in the rotational constants up to ten times larger for the deuterated forms than for the isotopic species of the ring atoms. The reinvestigation of the deuterium spectra by DRM spectroscopy revealed these discrepancies to be due to a number of misassigned transitions with *J*-values above 10 in the case of the 2-d$_1$- and the 4-d$_1$-species, while in the case of the particularly difficult 5-d$_1$-species with only *a*-type transitions, none of the previous SEM measurements agreed to within less than ± 0.3 MHz with the values deduced in the DRM analysis.

With the exception of 12 R-branch transitions (5, 4, 1 and 2 for the parent, ^{15}N, 2-d$_1$ and 4-d$_1$-species, respectively) all experimental data underlying the present structure determination were thus obtained, refined or verified by DRM spectroscopy.

c) Derivation of Rotational Parameters

The derivation of rotational constants and, particularly, of the distortion constants for oxazole and its isotopic species was made difficult by the small number of R-branch transitions. In the most favourable cases of the parent, the ^{18}O(1)-, ^{13}C(4)- and the 2-d$_1$-species with comparable dipole components along the *a*- and *b*-axis, there occurred six R-branch transitions between 28—40 GHz (DRM signal range) of which only the four $J = 2 \rightarrow 3$ transitions could be modulated via the $J = 1 \rightarrow 2$ R-branches or the $J = 3$ Q-branch transitions in K-band (DRM pump range). For the other isotopic species only two R-branch signals remained as either the two *a*-type or the two *b*-type transitions faded into undetectability due to the small value of the corresponding dipole component (see Table 1, row 4).

As was to be expected in such circumstances, least squares fits of the observed spectra to the previously used Hamiltonian with four quartic distortion terms [14] did not allow the distortion constant τ_{aabb} to be determined and, even in the case of the parent species with nine observed R-branch transitions (five from the preceeding SEM work), the uncertainty in this constant remained $\pm 200\%$, entailing correspondingly large uncertainties (60% to 70%) in the other three distortion constants. Guided by the small value ($\sim$ 1 kHz) of τ_{aabb} in similar, planar ring compounds [6c—g] we thought it

Table 1. Rotational parameters of the parent and isotopic species of oxazole.

1	Species		Parent	^{18}O(1)	^{13}C(2)	^{15}N(3)
2	Concentration		Natural abundance			
3	Rotation of inertial axes[a]		—	+12.75°	−9.28°	−5.32°
4	Dipole components μ_a^2/μ_b^2[b]		1.86/0.40	1.42/0.84	2.10/0.16	2.01/0.25
5	Quadr. constants χ_{aa}/χ_{bb}[c]		−3.92/1.54	3.30/0.92	−4.03/1.65	—
6	Signal transitions in fit Range of J-values		9 R & 64 Q 2−3 & 4−39	4 R & 29 Q 2−3 & 7−22	2 R & 50 Q 2−3 & 5−29	6 R & 36 Q 1−3 & 5−24
7	Standard deviation (in MHz)		0.05	0.08	0.09	0.07
8	A	in MHz	10050.99 (2)[d]	10014.29 (3)	9835.02 (3)	10042.26 (2)
9	B		9645.73 (2)	9232.01 (3)	9636.68 (3)	9395.35 (2)
10	C		4919.41 (2)	4801.01 (2)	4864.75 (3)	4851.38 (2)
11	τ_{aaaa}	in kHz[e]	−14.92 (5)	−14.89 (40)	−14.52 (5)	−15.02 (21)
12	τ_{bbbb}		−15.73 (5)	−14.33 (27)	−16.28 (5)	−15.30 (15)
13	τ_{abab}		− 7.85 (2)	− 7.68 (10)	− 7.34 (3)	− 7.40 (6)
14	I_a	in μÅ^2	50.28122 (6)[f]	50.46546 (13)	51.38538 (17)	50.32495 (10)
15	I_b		52.39377 (6)	54.74171 (14)	52.44298 (17)	53.79004 (11)
16	I_c		102.73097 (24)	105.26458 (43)	103.88529 (63)	104.17168 (39)
17	Inertia defect		0.05598 (32)	0.05741 (48)	0.05693 (69)	0.05670 (42)

[a] The angles of rotation are calculated from the r_S-coordinates given in Table 2. See also Figure 1.

[b] The dipole components are calculated from those of the parent species in conjunction with the angles of rotation given in row 3.

[c] The principal values of the coupling constants were deduced from the χ-values observed in the normal and the 2-d$_1$-species.

justified, therefore, to fit the oxazole spectra to the abbreviated Hamiltonian

$$H = A P_a^2 + B P_b^2 + C P_c^2$$
$$+ (1/4)\,(\tau_{aaaa} P_a^4 + \tau_{bbbb} P_b^4 + \tau_{abab} P_a P_b P_a P_b)$$

with $\tau_{aabb} = 0$. Through this constraint the remaining three distortion constants turned out determinable to ~ 1%, while the uncertainties in the rotational constants were reduced to about one third of their previous values.

For all spectra the rotational parameters were initially derived from transitions without hyperfine splitting. The resulting rotational constants, together with the expected or previously measured quadrupole coupling constants, were then used to calculate the fine structure and to deduce the hypothetical centre frequencies of the split transitions, which were then incorporated in the final LSQ fits. In all cases the computed splittings were found to agree within experimental uncertainty (~ 0.1 MHz) with the patterns that had been observed. This not only allowed the hypothetical centres to be determined to better than ± 0.05 MHz, but also provided strong evidence that the orientation and magnitude of the electric field gradient tensor had been determined with good accuracy (Part II).

The rotational parameters of oxazole and its isotopic species are listed in the lower half of Table 1 (rows 8—17). The upper half of this table summarises relevant information concerning the rotation of the inertial axes with respect to the parent form under isotopic substitution (row 3), the squared dipole moment components (row 4) and the quadrupole coupling constants (row 5), as well as the number of transitions (N) contained in the final LSQ fit for every isotopic form (row 6). The standard deviation (row 7) of observed transition frequencies ($\nu_{\text{obs.}}$) was calculated as $\{\sum(\nu_{\text{calc.}} - \nu_{\text{calc}})^2/(N-6)\}$. Listings of the observed transition frequencies for each isotopic species have been deposited with the "Zentrum für Struktur-Dokumentation" of the University of Ulm. They may also be obtained from the authors (O.L.S.).

IV. Structure Calculation

a) r_S-Structure

The quasi-constancy of the inertial defect (Table 1, row 17) under all isotopic substitutions clearly confirms the complete planarity of the oxazole molecule. Accordingly, Kraitchman's equations [15] for the planar case were employed in the calculation of atomic coordinates. As in previous studies [6b—g],

Table 1 (Continued)

^{13}C(4)	^{13}C(5)	^{2}D(2)	^{2}D(4)	2D(5)
		Mixture of enriched species (~ 1−3% each)		
+19.46°	−17.18°	−82.16°	+44.72°	−33.50°
1.16/1.10	2.22/0.04	0.65/1.61	0.28/1.98	2.21/0.05
2.80/0.42	− 3.90/1.52	1.22/−3.60	− 0.40/−1.98	− 3.00/0.62
4 R & 52 Q	2 R & 28 Q	5 R & 54 Q	4 R & 35 Q	2 R & 22 Q
2−3 & 5−26	2−3 & 5−30	1−3 & 6−29	1−3 & 4−25	2−3 & 5−24
0.08	0.07	0.05	0.07	0.09
9899.08 (2)	9938.09 (3)	9649.62 (2)	9801.49 (2)	9884.48 (3)
9539.28 (2)	9512.53 (3)	9207.25 (2)	9005.67 (2)	8959.59 (3)
4855.27 (2)	4857.67 (3)	4709.21 (2)	4690.92 (2)	4697.26 (3)
−14.77 (8)	−14.99 (16)	−14.26 (7)	−15.79 (28)	−14.68 (73)
−14.80 (8)	−16.10 (15)	−12.98 (6)	−12.96 (19)	−13.58 (46)
− 7.91 (3)	− 7.07 (5)	− 7.09 (3)	− 6.47 (9)	− 6.22 (12)
51.05285 (11)	50.85243 (14)	52.37262 (9)	51.56115 (12)	51.12824 (18)
52.97841 (12)	53.12740 (15)	54.88893 (8)	56.11753 (14)	56.40614 (28)
104.08815 (43)	104.03676 (54)	107.31652 (27)	107.73486 (48)	107.58942 (72)
0.05690 (46)	0.05693 (57)	0.05497 (37)	0.05619 (51)	0.05504 (78)

[d] Uncertainties quoted are three times the least-squares standard deviations.
[e] The distortion constant τ_{aabb} was set to zero (see text).
[f] Conversion factor: 505376 MHz μÅ^2.

each a- and b-coordinate was calculated from the inertial changes ΔI_a and ΔI_b, then from ΔI_a and ΔI_c, and finally from ΔI_b and ΔI_c, separately. The resulting three coordinate values were then averaged, and the largest deviation from the average was taken as a measure for the reliability of the substitution coordinates. The set of r_S-coordinates derived in this way is given in the top left of Table 2.

As is generally to be expected in the case of near-axis atoms, the a-coordinate of C(2) and the b-coordinates of O(1) and N(3) are the most poorly determined r_S-coordinates within the oxazole ring, and these coordinates were therefore re-derived from the centre-of-mass and the product-of-inertia conditions; From the condition $\sum m_i a_i = 0$, the small a-coordinate of C(2) was calculated first and with all a-coordinates thus known, $b_{O(1)}$ and $b_{N(3)}$ were recalculated from the simultaneous conditions $\sum m_i b_i = \sum m_i a_i b_i = 0$.

It is seen from Table 2 that the magnitude of all three small coordinates is increased by the application of the above conditions and this implies that, in accord with previous findings [6f, g], vibrational effects have made the effective changes in the relevant moments of inertia [I_b in the case of C(2), I_a in the case of O(1) and N(3)] smaller than they would have been for a completely rigid molecule (negative vibrational contribution). From Table 2 it is also noticed that the uncertainties in the three small coordinates are not improved by the described way of calculation, though it must be added here that the uncertainties quoted in Table 2 were deduced with the obviously too pessimistic assumption that the uncertainties in the values of the other 13 coordinates entering the calculation would combine in the most unfavourable way. On both these accounts, the coordinates calculated from the centre-of-mass and product-of-inertia conditions were preferred over the 'raw' r_S-values, and the former were therefore chosen as the basis for the calculation of the bond lengths and angles given in the lower half of Table 2. The unusually large uncertainties of these parameters resulted, of course, from the over-pessimistic assessment of the uncertainties in the coordinates, as outlined above.

b) Least Squares Fit of Internal Parameters

For comparison with the r_S-results, the isotopic information contained in Table 1 was also treated by the method devised by Nösberger, Bauder and Günthard [16], in which the structure parameters are adjusted by an iterative least squares procedure to match either the observed moments of inertia of the isotopic species (fit of I and ΔI), or to reproduce

Table 2. Structure calculations on oxazole.

	r_S-structure		LSQ-fit of internal parameters	
Coordinates				
O(1)	+ 1.0490 [4]	(+ 0.4475 [11])[c] + 0.4505 [19][d]	+ 1.0479 [5]	+ 0.4508 [8]
C(2)	(− 0.1546 [10])[c] − 0.1600 [19][d]	+ 1.0691 [2]	− 0.1595 [13]	+ 1.0697 [7]
N(3)	− 1.1795 [3]	(+ 0.2726 [15])[c] + 0.2758 [21][d]	− 1.1785 [3]	+ 0.2767 [3]
C(4)	− 0.6127 [4]	− 0.9983 [3]	− 0.6120 [9]	− 0.9995 [8]
C(5)	+ 0.7358 [4]	− 0.8824 [4]	+ 0.7346 [10]	− 0.8831 [9]
H(2)	− 0.1599 [25]	+ 2.1443 [3]	− 0.1584 [17]	+ 2.1444 [2]
H(4)	− 1.2164 [1]	− 1.8882 [1]	− 1.2154 [12]	− 1.8890 [9]
H(5)	+ 1.5569 [5]	− 1.5732 [5]	+ 1.5558 [6]	− 1.5745 [7]
Bond lengths				
O(1)−C(2)	1.3580 [26][e]		1.3568 [14][f]	
C(2)−N(3)	1.2918 [21]		1.2912 [15]	
N(3)−C(4)	1.3945 [25]		1.3963 [9]	
C(4)−C(5)	1.3534 [9]		1.3515 [17]	
C(5)−O(1)	1.3692 [17]		1.3701 [10]	
C(2)−H(2)	1.0752 [5]		1.0747 [5]	
C(4)−H(4)	1.0754 [6]		1.0748 [5]	
C(5)−H(5)	1.0730 [13]		1.0735 [13]	
Bond angles				
C(5)O(1)C(2)	103.88 [45]		103.94 [6]	
O(1)C(2)N(3)	115.01 [40]		114.97 [7]	
C(2)N(3)C(4)	103.90 [40]		103.95 [5]	
N(3)C(4)C(5)	109.08 [65]		108.99 [4]	
C(4)C(5)O(1)	108.13 [63]		108.15 [12]	
O(1)C(2)H(2)	117.10 [45]		117.08 [1]	
N(3)C(2)H(2)	127.89 [15]		127.95 [6]	
N(3)C(4)H(4)	121.87 [30]		121.91 [8]	
C(5)C(4)H(4)	129.04 [10]		129.10 [8]	
C(4)C(5)H(5)	135.02 [10]		134.97 [3]	
O(1)C(5)H(5)	116.85 [28]		116.87 [9]	
Effective and calculated moments				
$I_a^{\text{subst.}}$	50.0525		50.1276	
$I_a^{\text{eff.}} - I_a^{\text{subst.}}$	0.2287 ≙ 0.45%		0.1536 ≙ 0.31%	
$I_b^{\text{subst.}}$	52.3947		52.2398	
$I_b^{\text{eff.}} - I_b^{\text{subst.}}$	0.0541 ≙ 0.10%		0.1540 ≙ 0.29%	

[a] See Fig. 1 for choice of positive direction of axes,
[b] For derivation of coordinates from the LSQ-fits: See text.
[c] Substitution values.
[d] Values derived from first and second moment conditions.
[e] Uncertainties correspond to the largest possible errors in the coordinates.
[f] For computation of uncertainties: See text.

the observed differences between the moments of isotopic species and their counterparts in the parent form (fit of ΔI only). As recommended by the authors of this method for the refinement of structure parameters, the r_S bond distances and angles were used as the starting parameters in the LSQ fits and, on account of the general observation that the r_S-geometry slightly underpredicts the effective moments (see Table 2, last four rows) the internal parameters were matched only to the changes in the moments. Due to its cyclic configuration, only four out of the five ring bonds and only three out of the five ring angles of oxazole were needed, of course, to determine the molecular geometry, so that the values of one bond and its adjacent two angles had to be omitted from the starting parameters and the LSQ refinement. As there was little reason, however, to exclude any particular bond with its adjacent angles, and also as another check on the sensitivity of the LSQ method towards the input data, the fitting program was run five times with the origin of the coordinate system placed in each of the five ring atoms, and with the length of the opposite ring bond and its adjacent angles omitted from the refinement, in turn. While the fit with the coordinate origin in the poorly placed N(3) atom (bond length C(4)—C(5) and angles C(4)C(5)O(1) and C(2)O(1)C(5) not in fit) diverged after the first step, the remaining four runs all converged to give standard deviations for the 24 ΔI-values of ~ 0.0015 μÅ². The structure parameters indicated by these four fits were therefore averaged and the deviations of individual results from these averages were taken as a measure of the reliability of the LSQ results, reflecting the sensitivity of this method towards the starting values. They are given in square brackets in Table 2, where they are seen to be about a factor 2 smaller than the maximum uncertainties of the r_S-calculation. Atomic coordinates were derived from the internal parameters fits in the same fashion as described for distances and angles. Their values and uncertainties are given in the top half of Table 2, where they may be compared with the corresponding r_S coordinates.

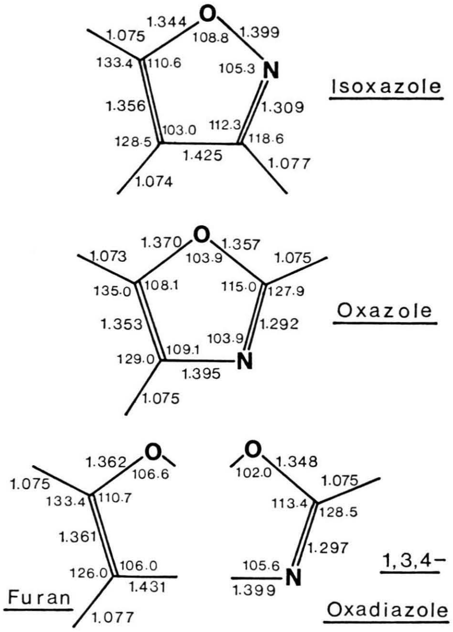

Fig. 2. Comparison of the structure of oxazole with the geometries of isoxazole, furan and 1,3,4-oxadiazole.

c) *Choice of the 'Best' Structure*

From Table 2 the r_S- and LSQ-values for bond distances and angles are seen to differ by no more than 0.002 Å and 0.1°, respectively, and we though it appropriate therefore to take the straight averages between the two sets of results as representing the 'best' structure parameters of oxazole. Their values are given in Figure 1. From the consistency of the two sets of results, the uncertainties in the averages seem to be no more than 0.001 Å and 0.05° in bond lengths and angles, respectively. However, as it would not seem reasonable to suppose that the structure calculation by two different methods, but from the same set of experimental data, can reduce the absolute uncertainties, we feel that at least 0.002 Å and 0.1° should be allowed on the 'best' parameter values of Figure 1.

V. Discussion

As it seems preferrable to postpone a correlation between the observed structure parameters and the likely electron distribution in the oxazole ring until the dipole and quadrupole data have been reported in part II, the following discussion is restricted to purely geometrical comparisons between oxazole, isoxazole [6c], furan [2] and 1,3,4-oxadiazole [13].

From a comparison of oxazole with the isomeric isoxazole it is noted (see Fig. 2) that within the section comprising H(4), C(4), C(5), H(5) and O(1), which is common to both isomers, only the length C(5)—O(1) is significantly affected by the interchange of the carbon and nitrogen atoms in the 2- and 3-position of the ring; while the bond lengths C(4)—H(4), C(5)—H(5) and C(4)=C(5) coincide within 0.003 Å in the two isomers, the C(5)—O(1) distance in oxazole (1.370 Å) is 0.025 Å longer than in isoxazole, and it exceeds the corresponding length in furan (1.362 Å) by about 0.01 Å. Not unexpectedly, the bonds emanating from O(1) and C(4) are altered by even larger amounts than the C(5)—O(1) bond and, together with the C=N-linkage itself, they are all shortened in comparison with isoxazole. Hence, the sum of the three bond lengths in the section O(1)—C(2)=N(3)—C(4) of the oxazole ring (4.044 Å) is 0.089 Å shorter than that of the O(1)—N(2)=C(3)—C(4) part in isoxazole, indicating that the interchange of the carbon and nitrogen atom is accompanied by a noticeable modification of the electron distribution within the ring. This must also be inferred from a consideration of the total circumference of the two isomeric ring structures, which shows that this quantity is about 0.06 Å smaller in oxazole (6.767 Å) than in isoxazole (6.833 Å).

According to an idea first formulated by Nygaard et al. [17] the structure parameters of oxazole would be expected to resemble closely those of furan in the molecular fragment O(1)C(5)C(4) and those of 1,3,4-oxadiazole in the section O(1)C(2)N(3), with the length N(3)—C(4) about equal to the average between the C—C bond of furan (1.431 Å) and the N—N bond of 1,3,4-oxadiazole (1.395 Å), and with the angle C(5)O(1)C(2) half-way between its values in these two molecules. From Figure 2 it is readily seen however that, although a qualitative correlation between the oxazole parameters and corresponding quantities in furan or 1,3,4-oxadiazole is fairly obvious, there is no ring bond in oxazole whose length would support the outlined hypothesis in a quantitative way. If the C—H bond lengths are ignored, the closest coincidence between observed and expected values occurs for the carbon-nitrogen double bond which in oxazole is 0.005 Å shorter than in 1,3,4-oxadiazole. While most angles deviate by 1—3° from the expected values, the angle C(5)O(1)C(2) (103.9°) approaches the expected average between the furan and the 1,3,4-oxadiazole values (106.6° and 102.0°, respectively) to within 0.4°, but the C—N bond, for which a value of 1.415 Å would be expected, falls outside the limits set by the C—C and N—N bonds in furan and 1,3,4-oxadiazole. These discrepancies between the observed values and the parameters expected from the 'composition hypothesis' are to some extent counterbalanced by the fact that the sum of the bond lengths O(1)—C(5) and C(5)—C(4) (2.723 Å) and the sum of the angles O(1)C(5)C(4) and C(5)C(4)N(3) (217.2°) coincide very closely with their counterparts in furan (2.723 Å and 216.7°, respectively), and that the sum of the lengths O(1)—C(2) and C(2)=N(3) (2.649 Å) and of the angles O(1)C(2)N(3) and C(2)N(3)C(4) (218.9°) in oxazole match the corresponding sums (2.645 Å and 219.0°) in 1,3,4-oxadiazole. This suggests that, although not valid in exact detail, the hypothesis of Nygaard and collaborators [17] remains a useful, qualitative guide for estimating the structures of heterocyclic molecules.

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