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The Molecular Zeeman Effect and Magnetic Susceptibility Anisotropies of Oxazole and Isoxazole. A Magnetic Measure of Aromatic Character
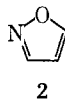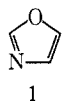
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Abstract: The microwave spectra of oxazole-^{15}N and isoxazole-^{15}N have been assigned and the molecular Zeeman effect observed and measured. The values of the rotational constants are $A = 10041.00 \pm 0.14$, $B = 9394.06 \pm 0.05$, $C = 4851.80 \pm 0.03$ for oxazole and $A = 9773.54 \pm 0.07$, $B = 9348.04 \pm 0.07$, and $C = 4775.25 \pm 0.04$ for isoxazole. The molecular g values are $g_{aa} = -0.0963 \pm 0.0024$, $g_{bb} = -0.1214 \pm 0.0021$, and $g_{cc} = 0.0394 \pm 0.0016$ for oxazole and $g_{aa} = -0.1044 \pm 0.0006$, $g_{bb} = -0.1220 \pm 0.0009$, and $g_{cc} = 0.0406 \pm 0.0007$ for isoxazole. The values of the magnetic susceptibility anisotropies in units of 10^{-6} erg/(G^2 mol) are $2\chi_{aa} - \chi_{bb} - \chi_{cc} = 39.2 \pm 3.0$ and $2\chi_{bb} - \chi_{aa} - \chi_{cc} = 35.2 \pm 3.4$ for oxazole and $2\chi_{aa} - \chi_{bb} - \chi_{cc} = 35.7 \pm 1.3$ and $2\chi_{bb} - \chi_{aa} - \chi_{cc} = 45.6 \pm 1.4$ for isoxazole. Subtraction of the local atom contributions to the magnetic susceptibilities indicates both molecules have nonlocal out-of-plane contributions which are within experimental error of one another and of the nonlocal out-of-plane contributions in furan. Neither the replacement of a carbon–carbon double bond by a carbon–nitrogen double bond nor the relative positions of the heteroatoms in the heteroaromatic ring have a major effect on the electron delocalization as measured by the magnetic susceptibility.

Experimental and theoretical analyses of aromatic character often begin with benzene and progress by consideration of the effects of perturbations on that aromatic system.[1] For example, furan is formally derived from benzene by replacement of two π electrons of a carbon–carbon double bond by two π electrons of an oxygen, an effect which appears to reduce delocalization in the heteroaromatic ring, provided that delocalization is considered to be measured by magnetic susceptibility anisotropy. On the other hand substitution of a carbon–nitrogen double bond for a carbon–carbon double bond appears to reduce delocalization in pyridine relative to that in benzene much less by this criterion.[2]

In a previous report from these laboratories we have noted that formal insertion of a carbonyl group into benzene, to give tropone, or into furan, to give 2-pyrone or 4-pyrone, results in a suppression of the magnetic characteristics of delocalization.[3] In further studies designed to test the effect of atom position on aromatic character as manifest in magnetic properties we have measured the molecular Zee-

man effects in the formally aromatic molecules oxazole (**1**) and isoxazole (**2**). Our data suggest that both molecules have slightly lower nonlocal contributions to the out-of-plane magnetic susceptibility than does furan.

Experimental Section

Purified samples of the nitrogen-15 isotopes of oxazole and isoxazole were obtained by synthesis of **1**[4] from formamide-^{15}N and of **2**[5] from hydroxylamine-^{15}N hydrochloride. The products were characterized by nmr as well as microwave spectroscopy. The ^{15}N isotopes were used to eliminate nitrogen quadrupole interactions, thus simplifying the spectra considerably.

The zero-field microwave spectra of the normal isotopes of both compounds have been previously assigned.[6] Reasonable structures were determined from the previous results and these structures were used to predict the microwave spectra of the ^{15}N isotopes. Both a-dipole and b-dipole transitions were observed in oxazole and isoxazole and assignments were readily achieved by standard techniques. The lines that were observed and assigned at Dry Ice temperature are listed in Table I. The resulting least-squares fit produced the rotational constants given in Table II.

The microwave spectrometer and high-field electromagnet used in the Zeeman study reported here have been described previously.[7] The measurements were made in a C-band waveguide at $-60°$. The theory of the rotational Zeeman effect in diamagnetic molecules has been given by Hüttner and Flygare.[8] They have shown that five independent parameters may be obtained from the Zeeman spectra: the three molecular g values, and two magnetic susceptibility anisotropies. In the usual microwave spectrograph employing plane polarized radiation, the absolute sign of the M transitions cannot be determined, thus only the relative signs of the three g values can be obtained. From the g values and magnetic susceptibility anisotropies obtained from the Zeeman spectra and the rotational constants obtained from the zero-field assignments for the molecules, the molecular quadrupole moments may be calculated. For a given choice of relative signs of the g values, a given set of molecular quadrupole moments are obtained. Usually only one choice of relative signs will give reasonable values for the molecular quadrupole moments.[9] The Zeeman parameters for oxazole and isoxazole are listed in Table III. The values listed are for the choice of signs for the g values which give reasonable values for the quadrupole moments compared to similar molecules in the literature.[10]

If other information is known about the molecule it often can be combined with the Zeeman results to obtain other molecular parameters.[10] If the bulk susceptibility is known, one can calculate the diagonal elements of the susceptibility tensor in the principle inertial axis system. The bulk value has been determined for isoxazole by an nmr technique.[11] The structure of isoxazole is also known[12] which allows the second moments of the electronic charge distributions and paramagnetic contribution to the magnetic susceptibility elements to be calculated. The total and paramagnetic

Table I. Observed Transitions (MHz) for Oxazole-^{15}N and Isoxazole-^{15}N

Transition	Obsd freq	Obsd − calcd
Oxazole-^{15}N		
a-Dipole		
$0_{00} \rightarrow 1_{01}{}^a$	14245.96	0.10
$1_{01} \rightarrow 2_{02}{}^a$	24532.08	−0.01
$1_{11} \rightarrow 2_{12}{}^a$	23949.44	−0.02
$1_{10} \rightarrow 2_{11}{}^a$	33033.95	−0.02
$2_{12} \rightarrow 2_{11}$	13626.76	−0.03
$2_{02} \rightarrow 2_{21}$	15631.76	−0.14
b-Dipole		
$0_{00} \rightarrow 1_{11}$	14892.90	0.10
$1_{01} \rightarrow 2_{12}{}^a$	24596.40	0.01
$1_{11} \rightarrow 2_{02}{}^a$	23885.15	−0.01
Isoxazole-^{15}N		
a-Dipole		
$0_{00} \rightarrow 1_{01}{}^a$	14123.31	0.02
$1_{01} \rightarrow 2_{02}{}^a$	24070.92	−0.02
$1_{11} \rightarrow 2_{12}{}^a$	23673.78	0.00
$2_{12} \rightarrow 2_{11}{}^a$	13718.39	0.00
$2_{02} \rightarrow 2_{21}{}^a$	15023.21	0.00
b-Dipole		
$0_{00} \rightarrow 1_{11}{}^a$	14548.80	0.02
$1_{01} \rightarrow 2_{12}{}^a$	24099.29	0.01
$1_{11} \rightarrow 2_{02}{}^a$	23645.44	−0.01
$2_{02} \rightarrow 2_{11}{}^a$	13746.71	−0.01
$2_{12} \rightarrow 2_{21}{}^a$	14994.87	−0.01

^{a} Used in a least-squares fit to obtain the rotational constants in Table II.

Table II. Rotational Constants^a (MHz) and Moments of Inertia^b (amu Å^2)

Parameter	Oxazole-^{15}N	Isoxazole-^{15}N
A	10041.00 ± 0.14	9773.54 ± 0.07
B	9394.06 ± 0.05	9348.04 ± 0.07
C	4851.80 ± 0.03	4775.25 ± 0.04
$(A + C)/2$	7446.40 ± 0.06	7274.39 ± 0.04
$(A − C)/2$	2594.60 ± 0.08	2499.15 ± 0.03
κ	0.750660 ± 0.00004	0.829743 ± 0.000004
I_{aa}	50.331	51.709
I_{bb}	53.798	54.062
I_{cc}	104.163	105.833
$I_{aa} + I_{bb} − I_{cc}$	−0.034	−0.062

^{a} Errors indicated are twice the least-squares standard deviations. ^{b} Conversion factor = 505377 MHz amu Å^2.

Table III. Molecular g Values, Magnetic Susceptibility Anisotropies, and Molecular Quadrupole Moments^a

Parameter	Oxazole-^{15}N	Isoxazole-^{15}N
g_{aa}	−0.0963 ± 0.0024	−0.1044 ± 0.0006
g_{bb}	−0.1214 ± 0.0021	−0.1220 ± 0.0009
g_{cc}	0.0394 ± 0.0016	0.0406 ± 0.0007
$2\chi_{aa} − \chi_{bb} − \chi_{cc}$	39.2 ± 3.0	35.7 ± 1.3
$−\chi_{aa} + 2\chi_{bb} − \chi_{cc}$	35.2 ± 3.4	45.6 ± 1.4
Q_{aa}	−4.9 ± 2.9	+0.1 ± 1.1
Q_{bb}	+9.5 ± 3.1	+3.0 ± 1.3
Q_{cc}	−4.6 ± 4.9	−3.1 ± 1.6

^{a} The magnetic susceptibilities are in units of 10^{-6} erg/(G^2 mol) and the quadrupole moments are in units of 10^{-26} esu cm^2. The indicated errors are double standard deviations.

susceptibilities may then be combined to find the diamagnetic contribution. The structural coordinates[12] are given in Table IV and the resultant additional molecular parameters are listed in Table V.

Discussion

Oxazole and isoxazole, like furan, are clearly formally aromatic. All have six π electrons and undergo electrophilic

Table IV. Atomic Center-of-Mass Coordinates (Å) for Isoxazole-^{15}N from Reference 12^a

Atom	a	b
O	−0.095	1.102
N	−1.144	0.178
C_1	−0.570	−1.003
C_2	0.854	−0.907
C_3	1.073	0.433
H_1	−1.186	−1.887
H_2	1.579	−1.703
H_3	1.964	1.036

^{a} These coordinates give rotational constants of A = 9773.7, B = 9349.0, and C = 4778.3 MHz.

Table V. Second Moments of Charge Distribution and Magnetic Susceptibilities of Isoxazole-$^{15}N^a$

χ_{bulk}	−38.0 ± 0.5^b	$\chi_{aa}{}^p$	148.3 ± 0.2
χ_{aa}	−26.1 ± 0.9	$\chi_{bb}{}^p$	156.0 ± 0.3
χ_{bb}	−22.8 ± 1.0	$\chi_{cc}{}^p$	235.7 ± 0.1
χ_{cc}	−65.1 ± 1.4	$\chi_{aa}{}^d$	−174.4 ± 1.1
$\langle a^2 \rangle$	36.0 ± 0.4	$\chi_{bb}{}^d$	−178.8 ± 1.2
$\langle b^2 \rangle$	34.9 ± 0.5	$\chi_{cc}{}^d$	−300.8 ± 1.5
$\langle c^2 \rangle$	6.2 ± 0.4		

^{a} The total (χ), paramagnetic (χ^p), and diamagnetic (χ^d) susceptibilities are in units of 10^{-6} erg/(G^2 mol) and the charge distributions ($\langle x \rangle^2$) are in units of 10^{-16} cm^2. ^{b} Reference 11.

Table VI. Comparison of Magnetic Parameters for Various Aromatic Molecules (in units of 10^{-6} erg/(G^2 mol))

Molecules	$[\chi_{cc}]_{\text{nonlocal}}{}^a$	
	A	B
Benzene	−33.6 ± 5.5^b	−36.4
Pyridine	−28.5 ± 6.5^c	−28.4
Pyrrole	−35.4 ± 5.0^c	−33.2
Thiophene	−33.0 ± 4.5^c	−35.2
Furan	−22.9 ± 2.5^c	−24.4
Oxazole	−18.4 ± 8.5	
Isoxazole	−21.9 ± 6.5	−18.6

^{a} $A = [\chi_{cc} − \frac{1}{2}(\chi_{aa} + \chi_{bb})]_{\text{exp}} − [\chi_{cc} − \frac{1}{2}(\chi_{aa} + \chi_{bb})]_{\text{local atom}}$. $B = [\chi_{cc}]_{\text{exp}} − [\chi_{cc}]_{\text{local atom}}$. The local contribution was calculated from the local atom values in ref 12, with the exception of those for doubly bonded nitrogen, obtained from T. G. Schmalz, private communication, which are $x = −0.2$, $y = −5.0$, and $z = −9.9$. ^{b} Experimental susceptibilities taken from A. Bothner-By and J. A. Pople, *Ann. Rev. Phys. Chem.*, **16**, 43 (1965). ^{c} Experimental susceptibilities contained in ref 10.

substitution.[13,14] Many years ago the resonance energy of isoxazole was estimated to be 50 kcal/mol,[15] as compared to 36 kcal/mol for benzene and 17 kcal/mol for furan,[16] but later authors have indicated that this value is much too high.[17,18] Del Re, using a π-electron "Hückel" method, recently calculated the delocalization energy of furan, oxazole, and isoxazole, relative to benzene, as 18, 33, and 6%, respectively.[19]

The magnetic criterion for aromaticity from the molecular Zeeman effect was recently discussed in detail by Schmalz, *et al.*[20] Their method involves the determination of the "nonlocal" contribution to the out-of-plane magnetic susceptibility by subtraction of the contribution calculated from "local" atom or bond values. The value of this nonlocal contribution for various aromatic compounds, including oxazole and isoxazole, is shown in Table VI. The large error limits on pyridine, oxazole, and isoxazole are due to the large uncertainty in the local atom value of doubly bonded nitrogen.

Comparison of the nonlocal out-of-plane magnetic susceptibility contributions of oxazole and isoxazole in Table VI shows these molecules to have nearly the same delocali-

zation in so far as that effect is measured by magnetic properties. Although such an insensitivity to atomic position would be expected for nonaromatic molecules, and has been demonstrated for cyclopent-2-en-1-one and cyclopent-3-en-1-one,[21] this appears to be the first demonstration in aromatic systems. Comparison of the oxazole and isoxazole results is noted to depend on the assumption that the local atom values are independent of the neighboring atoms more than for the cyclopentenone case. While this appears to be a valid assumption,[20] it is still open to question.

The relationship between magnetic and other criteria of aromaticity is of current interest.[22] A thermodynamic comparison of imidizole and pyrazole, molecules related to **1** and **2** by the replacement of oxygen by nitrogen, has been reported in which imidizole is assigned approximately one-half the resonance energy of pyrazole.[23] By the magnetic criterion no large difference exists in the electron delocalizations in oxazole and isoxazole.

An examination of the nonlocal values of the magnetic susceptibilities indicates that oxygen has a more significant effect than double-bonded nitrogen on suppressing the magnetic effects of delocalization. Comparison of benzene to pyridine and of furan to oxazole and isoxazole reveals a decrease in the nonlocal contribution of about 20% for the nitrogen-containing molecules, but this decrease is less than the experimental uncertainty. However, furan, oxazole, and isoxazole all seem to have significantly smaller contributions than the other six π-electron systems although substantial delocalization is still indicated.

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Optical Rotatory Power in the Ground State and Electronically Excited State of Diketopiperazines Containing Aromatic Side Chains

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Abstract: The circular dichroism and the circular polarization of the fluorescence of various cyclic dipeptides containing aromatic side chains has been studied. The optical rotatory power deduced from these measurements vanished upon electronic excitation in fluid media but is essentially the same in the ground and electronically excited states in highly viscous media. A change in conformation thus occurs upon excitation in fluid solution essentially before light emission takes place. The change responsible for the disappearance of the optical activity is faster than the rate of rotational relaxation as monitored by the linear polarization of the fluorescence.

The conformation of diketopiperazines has been the subject of a variety of studies. On the theoretical side, molecular orbital calculations performed for *cyclo*(Gly-Phe) predict a folded conformation for this compound.[1] Empirical energy calculations on *cyclo*(Gly-Phe), *cyclo*(Gly-Tyr), and *cyclo*(Gly-Val) also indicate that the minimum energy conformations have the side chains stacked over the piperazine ring.[2] Such conformations for cyclic dipeptides were deduced experimentally from X-ray structure analysis[3] and nmr[4,5] studies and gained support from CD measurements.[6,7]

The above studies are concerned with the molecular conformation of the cyclic dipeptides in the electronic ground state. Since the electronic charge distribution in an excited chromophore is different from that in the chromophore in the ground state, the interaction of the chromophore with its environment in the two states may be very different. The equilibrium conformation of the cyclic dipeptides with aromatic side chains may thus change upon electronic excitation of the aromatic chromophores. The lifetime of the excited chromophores (which falls in the nanosecond time range) is long enough to permit partial or complete relaxa-