

of these bands (cm.^{-1}): ν C-H (LiF prism) 3100 m; δ C-H, (NaCl prism) 1915-1940 w, broad, 1410 s, 1342 w, 1257 m, 1188 w, 1100 s, 1050 w, 1003 s, 996 s, 803 w, 775s. These closely parallel the bands reported for $(\text{C}_5\text{H}_5)_2\text{ReH}^7$ except for the noteworthy absence in our spectrum of a sharp band in the region where $\nu\text{Tc-H}$ would be expected ($\nu\text{Re-H cm.}^{-1}$, LiF prism, 2020 m).

Magnetic susceptibility for I was determined by nuclear magnetic resonance as already described in a previous work.⁴ For a solution of 66.1 mg. of I and 224 mg. (0.26 ml.) of toluene in an inner coaxial tube, the separation between the resonance of methyl protons of toluene and of protons of cyclohexane in the outer tube was found to be 18.4 cps., demonstrating diamagnetic character for I. Proton n.m.r. for I was obtained for solutions both in toluene and tetrahydrofuran, the latter permitting higher concentration of solute. A resonance at 5.61 τ ⁸ was observed (width, 0.8 δ cps.) whose ringing pattern displayed the exponential decay attributable to a single line. Scrutiny of the high field region up to 30 τ revealed no additional resonances. The n.m.r. of a sample of $(\text{C}_5\text{H}_5)_2\text{ReH}$ was investigated for comparison in our laboratory under similar conditions of measurement. A doublet centered at 5.69 τ ($A = 1.17$ cps., multiplet width, 1.8 δ cps.) and a peak at 23.4 τ (relative intensity 1/10, width 9 cps.) was found, in reasonable agreement with the previously reported data.⁷

The absence of a technetium bonded hydrogen atom, as ascertained by spectroscopic methods, demanded some explanation for the diamagnetic character of I. A molecular weight was obtained for the compound using the micro-tensimetric method.⁹ We observed a vapor pressure lowering of 3.75 mm. for a solution of 36.1 mg. of I in 852.7 mg. of diethyl ether ($P_0 = 535.6$ mm. at bath temperature during determination, 25.2 $^\circ$); found, 445 \pm 20. These results, taken together with the spectroscopic data above which attest to the presence solely of the (C_5H_5) group, strongly indicate the composition and molecular constitution for I to be $[(\text{C}_5\text{H}_5)_2\text{Tc}]_2$; mol. wt., 458. Analysis¹⁰ for carbon and hydrogen was carried out, using great care to exclude oxygen during the weighing: found: C, 52.87; H, 4.71; required for $(\text{C}_{10}\text{H}_{10}\text{Tc})_x$: C, 52.17; H, 4.82. The yield of I was of the order of 8%, based on ammonium pertechnetate.

The cyclopentadienyl derivative of technetium is not decomposed by water at room temperature; it dissolves in 10% aqueous tetrahydrofuran to give a pale yellow solution whose n.m.r. spectrum shows the resonance reported above, essentially un-

changed. Solution of I in tetrahydrofuran reacts with gaseous hydrogen chloride to yield an off-white precipitate. This redissolves upon addition of water, giving an air-sensitive, pale yellow solution for which a resonance appearing to be a singlet is observed at 4.60 τ .¹¹ Again, no resonances at high field in the region of absorptions of transition-metal bonded protons could be observed. Similar acid treatment of $(\text{C}_5\text{H}_5)_2\text{ReH}$ yielded a colorless aqueous tetrahydrofuran solution of $(\text{C}_5\text{H}_5)_2\text{ReH}_2^+\text{Cl}^-$ which in agreement with previous workers⁷ displays a barely resolvable triplet centered at 4.54 τ and broader resonance at 23.9 τ (1/5 relative intensity). The behavior under hydrolytic conditions thus indicates nature of ring-to-metal bonding in $[(\text{C}_5\text{H}_5)_2\text{Tc}]_2$ must be similar to that in $(\text{C}_5\text{H}_5)_2\text{ReH}$ rather than to that in $(\text{C}_5\text{H}_5)_2\text{Mn}$.

Acknowledgment.—This work was supported by National Science Foundation Research Grant G 16819.

(11) For aqueous solutions, central peak of $\beta\text{-CH}_2$ (high field) resonance of tetrahydrofuran was used as internal standard. Measurements were converted to τ -values using separation of tetramethylsilane given in ref. 8.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
LOS ANGELES 24, CALIFORNIA

D. K. HUGGINS
H. D. KAESZ

RECEIVED SEPTEMBER 15, 1961

THE STRUCTURE OF 1,2,5-THIADIAZOLE¹

Sir:

The detailed molecular structure of a new five-membered ring compound, containing sulfur-nitrogen bonds, first synthesized by Carmack and co-workers,² has been determined by electron diffraction. The preliminary results of this investigation are presented in this note.

The molecule 1,2,5-thiadiazole is isoelectronic with pyrazine, if of course the $1s^2$ electrons of the sulfur are not considered, so that the comparison of the chemistry and the structure of the two molecules provides a comparison of the effects of ethylene and sulfur as constituent groups. The available chemical evidence supports a planar ring structure with aromatic properties. Thiadiazole is isoelectronic with thiophene and electron diffraction data for thiophene also were obtained for comparison purposes. Structurally thiadiazole is also of interest since it provides a chance to obtain accurate bond length measurements of S-N and C-N bonds in what may be an aromatic system.

The electron diffraction data were obtained on the Iowa State University sector electron diffraction apparatus in Professor Bartell's laboratory and the photographic plates were microphotometered on the University of Michigan microphotometer in Professor Brockway's laboratory. The data analysis was carried out in a manner described elsewhere.³ The preliminary structural parameters

(1) Contribution number 994 from the Chemical Laboratories of Indiana University. The authors wish to thank the National Science Foundation and the Atomic Energy Commission for their financial support of this work.

(2) M. Carmack, L. M. Weinstock and D. Shew, Abstracts of Papers, 136th Meeting of the ACS, Atlantic City, N. J., September, 1959, page 37-P.

(3) R. A. Bonham and L. S. Bartell, *J. Chem. Phys.*, **31**, 702 (1959).

(7) M. L. H. Green, L. Pratt and G. Wilkinson, *J. Chem. Soc.*, 3916 (1958).

(8) Proton resonances observed at 40 Mc. (Varian V-43104 spectrometer) were measured for solutions in tetrahydrofuran with 1-2% internal toluene standard. Tetramethylsilane (1-2% internal standard) under these conditions appeared at 91.5 \pm 0.8 cps., on the high field side of the methyl protons of toluene, and also 69.3 cps. on the high field side of the center peak of the $\beta\text{-CH}_2$ (high field) resonance of tetrahydrofuran. Frequency measurements were made by the side-band method, using a calibrated Hewlett Packard Model 200 D audio-frequency oscillator.

(9) To be fully described in a forthcoming paper; for preliminary account, see ref. 4.

(10) We gratefully acknowledge the help of Miss Heather King, Microanalytical Laboratory, U.C.L.A.

are reported in Table I. The reported uncertainties were calculated from formulas 12a and 12b of reference (3) with the addition of a scale factor uncertainty of two parts per thousand. The resulting uncertainties obtained from this procedure were multiplied by a factor of two since the structural data have not been refined completely. It should be pointed out that the error estimates do not include uncertainties from lack of exactness of the kinematic theory for electron scattering. In the analysis of the data the hydrogen parameters were assumed and bond length and bond angle data for the hydrogen positions were taken from an earlier electron diffraction structure determination of ethylene.⁴

TABLE I

PRELIMINARY STRUCTURAL PARAMETERS FOR 1,2,5-THIA-DIAZOLE BY ELECTRON DIFFRACTION

	$r_e(0)$	l	r
C—H	1.085 ^a	0.077 ^a	
S—N	1.628 ± 0.008 Å	0.048 ± 0.008	1.60 ^b
N—C	1.329 ± 0.010 Å	0.040 ± 0.012	1.34 ^b
C—C	1.400 ± 0.022 Å	0.045 ± 0.026	1.41 ^b
<N-S-N	99.4 ± 2°		102 ^b
<C—C—H	122 ^a		

^a Assumed values taken from data on ethylene (see ref. 4).

^b See ref. 5.

The electron diffraction intensity data of thiadiazole and thiophene are almost identical feature for feature except for a scale factor shift of nearly 5%. The direction of the shift is such that thiadiazole must on the average possess distances shorter than those in thiophene by 5%. The fact that the shape of the two curves is similar is an indication that the molecule must possess nearly the same shape as the thiophene molecule.

A correlation study was made to determine the degree of planarity of the ring. This study indicated that the ring was planar to within 0.1 Å. The preliminary parameters also suggest that the ring system is highly aromatic since the C—C bond is nearly the benzene value and the C—N bonds are in nearly the same relation to the C—N double and single bond distances as the benzene C—C distance is to the normal C—C double and single bond distances. The S—N distances appear to be quite short but are in good agreement with existing X-ray data for a similar ring system in the molecule benzo-2,1,3-thiadiazole.⁵ A comparison of the relevant parameters between the two molecules is given in Table I.

Professor Louis Pierce of the University of Notre Dame has kindly furnished us with some preliminary results of a microwave determination of the molecular structure of 1,2,5-thiadiazole. The results to date indicate that the molecule is planar and the preliminary moments of inertia are $I_A = 59.2$, $I_B = 79.8$ and $I_C = 139.1$. The moments of inertia calculated from our preliminary electron parameters are $I_A = 58.4$, $I_B = 79.6$ and $I_C = 138.0$.

The authors wish to thank Professor Carmack for furnishing us with the chemical evidence for the structure and for providing a sample of thiadiazole.

(4) I. S. Bartell and R. A. Bonham, *J. Chem., Phys.*, **31**, 400 (1959).

(5) V. Luzzati, *Acta Cryst.*, **4**, 193 (1951).

We also wish to thank Professors Bartell and Brockway for the use of their equipment, Mr. Melvin Druelinger for his aid in reading some of the microphotometer traces and help with the computations, and Mr. Ralph Christofferson for his help in reading some of the traces. We also wish to thank Professor Pierce for his preliminary results and for kindly calculating the moments of inertia from our electron diffraction parameters.

CHEMISTRY DEPARTMENT
INDIANA UNIVERSITY
BLOOMINGTON, INDIANA

R. A. BONHAM
F. A. MOMANY

RECEIVED AUGUST 18, 1961

IMIDAZOLE- AND BASE-CATALYZED HYDROLYSIS OF PENICILLIN IN FROZEN SYSTEMS

Sir:

In studies on the penicillin amide bonds, we have observed an unusual lability of the β -lactam bond in frozen systems. Penicillin solutions containing imidazole or histidine lost antimicrobial activity when stored at -18° , but not when incubated for 17 hours at 38° . Further study showed that facile imidazole-catalyzed cleavage of the β -lactam in penicillin occurred only at temperatures between -5 and -30° in frozen, but not supercooled, systems (Table I). Splitting, which was routinely assayed by decreased hydroxamate formation at neutral pH,¹ was confirmed by changes in optical rotation, by formation of the hydroxamate under alkaline conditions, and by infrared and ultraviolet analyses of the products.

TABLE I

β -LACTAM HYDROLYSIS AT VARIOUS TEMPERATURES^a

Catalyst	Substrate	% Hydrolysis					
		22°	0° ^b	-8°	-18°	-28°	-78°
Imidazole	pen-G	23	4	71	64	20	4
Histidine	pen-G	12	4	3 ^b	14	0	6
Carnosine	pen-G	21	9	7 ^b	26	14	9
Histamine	pen-G	30	10	6 ^b	20	8	7
OH ⁻ , pH 9.9	pen-G	75	14		28	12	4
Imidazole	pen-V	24	8	72	70	48	4
Imidazole	6-APA	2	0	0 ^b	98	89	18
Histidine	6-APA	4	0	43	24	6	
Histamine	6-APA	9	0	0 ^b	46	24	
OH ⁻ , pH 9.9	6-APA	38	0		23	7	0

^a Conditions are 65 hours, pH 7.7, 0.01 M catalyst and substrate. Buffer at pH 9.9 is 0.05 M borate. ^b Unfrozen.

The reaction occurred in imidazole-penicillin mixtures with pH levels as low as 6.2. With 0.01 M penicillin G, 0.02 M imidazole, -18° , and pH 7.7, the reaction was 52% complete in 5 hours and 92% complete in 17 hours. The rate in frozen H₂O was about twice that in frozen D₂O. Catalysis of ring opening by hydroxide ion, which proceeds readily at room temperature, could not be detected in borate-buffered (imidazole-free) solutions of pH lower than 9.6 which were kept at 0 or -28° . However, at -18° , penicillin and 6-aminopenicillanic acid (6-APA) were hydrolyzed significantly. Freezing penicillin in the absence of catalyst does not induce susceptibility to later hydrolysis by imidazole or increase the rate of penicillinase

(1) A. O. Niedermeyer, F. M. Russo-Alesi, C. A. Lenzian and J. M. Kelly, *Anal. Chem.*, **32**, 664 (1960).