The Structure of 1,2,5-Thiadiazole as Determined by Gas Electron Diffraction[1]

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A detailed analysis of the molecular structure of the five-membered ring 1,2,5-thiadiazole as determined by the sector-microphotometer method of gas electron diffraction is reported. The final refined molecular parameters are: r_g(S–N) = 1.632 Å., r_g(N–C) = 1.329 Å., and r_g(C–C) = 1.413 Å.; l(S–N) = 0.048 Å. and ∠N–S–N = 99.4°. The root mean square amplitude of vibration values for the N–C and C–C bonds were assumed to have the values l(N–C) = 0.040 Å. and l(C–C) = 0.043 Å. in order to obtain least squares estimates for r_g(N–C) and r_g(C–C). Without making these assumptions it was found that the weighted average of these two distances was 1.356 Å.

It is the purpose of this paper to report the final refined structural parameters and the details of the structural analysis for the new five-membered ring compound containing sulfur–nitrogen bonds, first synthesized by Carmack and co-workers.[2a,b] As 1,2,5-thiadiazole and thiophene are the sulfur analogs of pyrazine and benzene, respectively, it is of some interest to compare the structures of these molecules to see if the effects of sulfur and nitrogen atoms on the aromaticity of the systems can be observed in terms of changes in various molecular parameters. Precise data on pyrazine are not available at present. However, the structural data available for benzene[3] and thiophene,[4,5] coupled with the data presently available for thiadiazole,[2,6] should be sufficient to draw some tentative conclusions about this problem.

Experimental Procedure

Samples of 1,2,5-thiadiazole of better than 99% purity were obtained from the laboratory of Professor Marvin Carmack at Indiana University. Electron diffraction photographs were obtained with an r^3 sector using the sector electron diffraction camera in Professor L. S. Bartell's laboratory at Iowa State University. Specimen pressures of 20 to 80 mm. with exposure times of 1 to 4 sec. were used at a temperature of 298°K. The beam current was 0.3 μa. and the accelerating voltage was 40 kv. Four research grade plates at each of two camera distances were obtained for each molecule. The photographic plates were microphotometered in Professor L. O. Brockway's laboratory at the University of Michigan.

The microphotometer traces of the electron diffraction photographs were read at 0.25-mm. intervals to four significant figures in the optical density with the aid of a Bausch and Lomb 7 power measuring magnifier. The photographic emulsion was calibrated by a procedure due to Bartell and Brockway.[7]

The indices of resolution were found to be 0.97 for the 21.35-cm. camera distance and 1.00 for the 10.66-cm. camera distance. It was felt that the values of the index of resolution indicated the absence of any serious extraneous scattering effects.

Structure Analysis.—The experimental data were analyzed according to schemes outlined elsewhere.[4,8] Bond lengths and vibrational amplitudes[9] were all obtained by least squares analysis of the radial distribution curve, corrected for anharmonicity and series termination effects, with a mathematical model including corrections for the failure of the Born approximation.[10] The calculated experimental radial distribution curve made use of experimental data at integral values of q (q = 40 sin [θ]/λ) over

the range q = 12 to 90. An artificial convergence factor e^{-dq^2} was employed where d was chosen so that the experimental value of $M(q)$ at q = 90 was reduced to a tenth of its value. The missing data in the region $0 < q < 12$ were obtained both from the available experimental data, by a technique described in ref. 4, and by use of calculated data from an assumed theoretical model. Both techniques gave the same results.

The standard correlation technique using the experimental intensity curve was employed to obtain an estimate of the planarity of the molecule and as a further check on the analysis. It was found that the molecule was planar to better than 0.1 Å. The background needed for the correlation and radial distribution analysis was obtained by using the smoothness criterion and the Karle's nonnegative area criterion.[11]

As an additional check, a sharpened radial distribution function was used as a correlation technique.[12] The missing data in the region $0 < q < 12$ are not needed in this analysis and the method is very insensitive to the choice of the background function. When properly used, this method yields molecular parameters which correspond closely to the $r_m(1)$ parameters defined by Bartell.[13]

In order to carry out the structural analysis, the parameters for the hydrogen atoms were assumed to be those found in ethylene.[14] Furthermore, the reasonable values l(N–C) = 0.040 and l-(C–C) = 0.045 were assumed in order that a dissection of the composite peak, containing the information on the r_g(N–C) and r_g(C–C) parameters, could be made. Without this assumption, it is of course still possible to obtain the average of the two r_g-(N–C) and one r_g(C–C) distance quite accurately.

Results

In Table I the final results for bond lengths and amplitudes of vibration, as determined by least squares analysis of the radial distribution curve, are presented. The listed uncertainties include a scale factor error of two parts per thousand and uncertainties due to random errors which have been estimated by using eq. 12a and 12b of ref. 8. Errors due to possible uncertainties in the theory have not been included. Figures 1 and 2 indicate the experimental intensity curves and background functions used in the analysis. Figure 3 shows the experimental and theoretical $M(q)$ curves and their difference and Fig. 4 presents the same curves in the radial distribution space.

TABLE I

STRUCTURAL PARAMETERS DERIVED FROM RADIAL DISTRIBUTION CURVES AND CALCULATED PRECISIONS

	$r_g(0)$	δr	l	δl
C–H	1.080	0.010	0.078	0.010
S–N	1.632	.005	.048	.007
N–C	1.329	.008	.040[a]	
C–C	1.413	.010	.043[a]	
∠N–S–N	99.4 ± 0.2°			
∠S–N–C	106.5 ± 0.4°			

[a] Assumed values.

In Table II the available structural results for the molecules benzene, thiophene, and 1,2,5-thiadiazole are presented. The 1,2,5-thiadiazole distances appear to

(1) The authors wish to thank the National Science Foundation and the Atomic Energy Commission for their financial support of this work.

(2) (a) M. Carmack, L. M. Weinstock, and D. Shew, Abstracts, 136th National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1959, p. 37-P; (b) R. A. Bonham and F. A. Momany, J. Am. Chem. Soc., 83, 4475 (1961).

(3) (a) A. Almenningen, O. Bastiansen, and L. Fernholdt, Kgl. Norske Videnskab. Selskabs Skrifter (1958); (b) I. L. Karle, J. Chem. Phys., 20, 65 (1952).

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(6) Sr. V. Dobyns and L. Pierce J. Am. Chem. Soc., 85, 3553 (1963).

(7) L. S. Bartell and L. O. Brockway, J. Appl. Phys., 24, 656 (1953).

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

(9) The term vibrational amplitude as used in this paper corresponds closely to the term l_m defined by several authors in previous publications. See for instance: L. S. Bartell and K. Kuchitsu, J. Chem. Phys., 35, 1945 (1961); R. A. Bonham and J. L. Peacher, ibid., 38, 2319 (1963).

(10) R. A. Bonham and T. Ukaji, ibid., 36, 72 (1962). See ref. 4, footnote 9, for errata to this paper.

(11) I. L. Karle and J. Karle, J. Chem. Phys., 17, 1052 (1949).

(12) M. Traetteberg and R. A. Bonham, ibid., to be published.

(13) L. S. Bartell, ibid., 23, 1219 (1955).

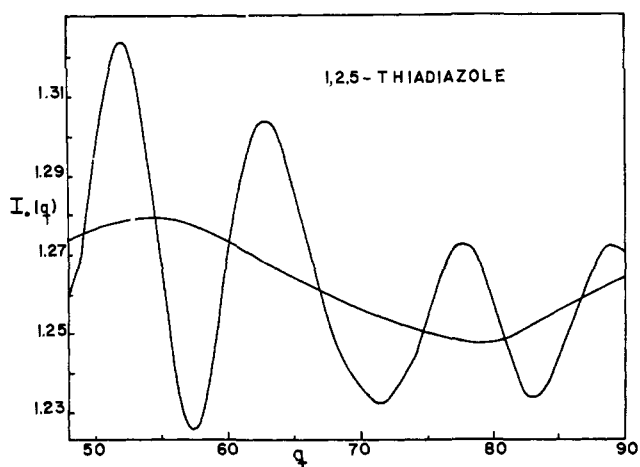(14) L. S. Bartell and R. A. Bonham, ibid., 31, 400 (1959).

Fig. 1.—Long camera distance intensity data, $I_0(q)$, and the background function, $B(q)$ (smooth curve). The ordinate values refer to an arbitrary relative intensity scale.
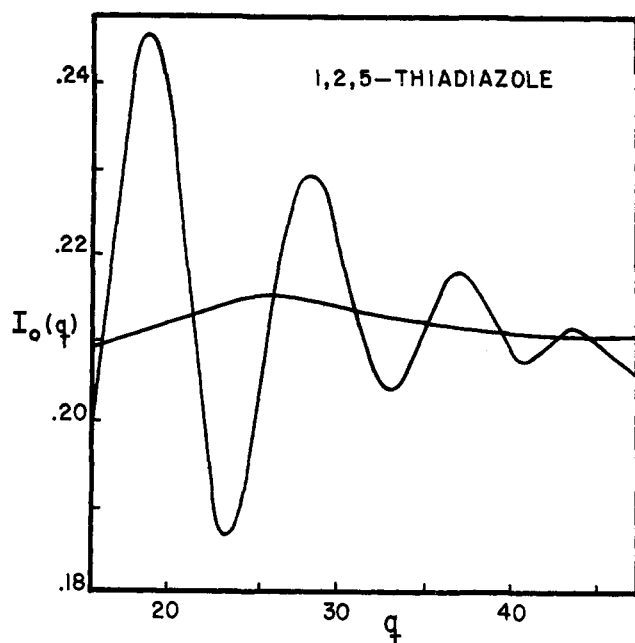
Fig. 2.—Short camera distance intensity data, $I_0(q)$, and the background function, $B(q)$ (smooth curve). The ordinate values refer to an arbitrary relative intensity scale.
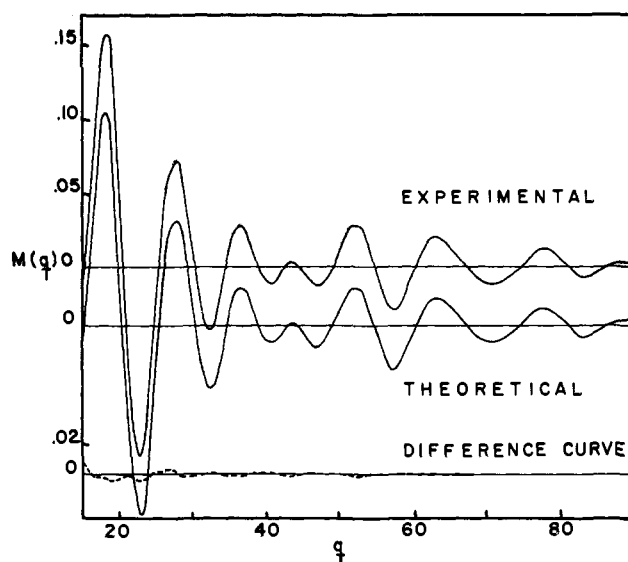
Fig. 3.—Experimental and theoretical reduced molecular intensity curves and their difference. The ordinate scale refers to the absolute value of $M(q)$.
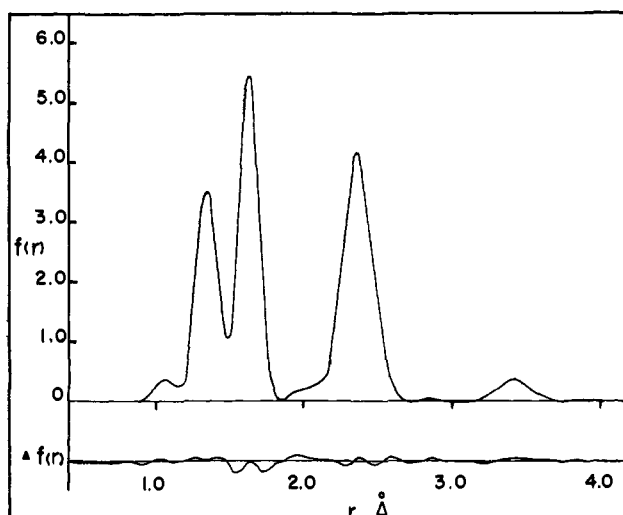
Fig. 4.—Radial distribution curve for 1,2,5-thiadiazole and the difference between the theoretical and experimental curves. The ordinate refers to the absolute scale of the radial distribution function.

vary somewhat between the methods of analysis, but the differences are within the assigned limits of error.

TABLE II

STRUCTURAL RESULTS FOR MOLECULES SIMILAR TO 1,2,5-THIADIAZOLE

	$r_{C_1-C_2}$[f]	$r_{C_2-C_3}$	r_{S-C}	r_{S-N}	r_{C-N}	$\angle$N–S–N
Benzene[a]	1.397					
Thiophene[b]	1.370	1.419	1.714			
1,2,5-Thiadiazole[c]		1.413		1.632	1.329	99.4°
1,2,5-Thiadiazole[d]		1.420		1.631	1.328	99.55
1,2,5-Thiadiazole-3,4-dicarboxamide[e]		1.437		1.621	1.322	98.75

[a] See ref. 3a and 3b. [b] R. A. Bonham and F. A. Momany, *J. Phys. Chem.*, **67**, 2474 (1963). [c] Present study. [d] See ref. 6. [e] Private communication with R. R. McDonald. [f] C_1-C_2 is the bond nearest the sulfur in thiophene.

If we assume the Pauling[15] equation for computing the double-bond character in these molecules, it can be shown that the C=C distances adjacent to the sulfur

(15) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1950.

atom in thiophene and the C=N distances in thiadiazole both have a rather high degree of double-bond character ($\sim$70%). The S=C and S=N values are somewhat ambiguous because of the lack of a precise single bond S—N distance; however, to a first approximation these values are again very close ($\sim$30%). From these results, it can be reasonably concluded that the subsequent introduction of two nitrogens into the thiophene ring at the 2,5-positions has little effect on the over-all aromaticity. This conclusion is compatible with the bond C–C lengths opposite the sulfur atom for thiophene and 1,2,5-thiadiazole. The very slight difference in bond lengths is within the probable errors given in the two experimental determinations.

gratefully acknowledge the use of the facilities of the Indiana University Research Computing Center. Thanks are also due Mr. Ralph Christofferson for read-

ing some of the microphotometer traces and Mrs. Joanne Knight for her help in preparing the manuscript.

Molecular Complexes and Their Spectra. XVII. The Iodine and the Chloranil Complexes with Thianthrene Analogs

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RECEIVED FEBRUARY 25, 1963

The thermodynamic properties of the iodine complexes with the thianthrene analogs I, II, and III in solution were spectroscopically studied. Their charge transfer bands were also studied in comparison with the ones of the chloranil complexes with the thianthrene analogs. From the obtained results, it is concluded that the thianthrene analogs are essentially n-donors for iodine. Furthermore, referring to the energies of the charge transfer bands of the chloranil complexes, the appropriate integral values for the thianthrene analogs in the Hückel MO method were studied.

Introduction

Many studies have hitherto been carried out with various charge-transfer type molecular complexes. But there have been only few works in which unsaturated heterocyclic compounds except for azines were used as donors. Recently, Lang[2] studied spectroscopically the iodine complexes with five-membered unsaturated heterocyclic compounds. Since thianthrene analogs have two heteroatoms, it is particularly interesting to study the charge transfer interaction between iodine and these molecules, the principal reason for undertaking the present study. In the present study, thianthrene (I), phenoxathiin (II), and diphenylene dioxide (III) were used as donors.
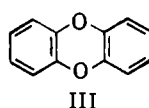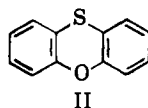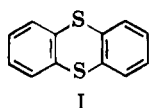
Experimental

Materials.—Fisher certified iodine was resublimed under reduced pressure. Fisher spectrograde dichloromethane and carbon tetrachloride were dried with Drierite and distilled with a Podbielniak column. Phillips 66 "pure" grade n-heptane was washed twice with concentrated sulfuric acid, then several times with water, dried with Drierite, and distilled with a Podbielniak column. Eastman Pure Chemicals of thianthrene, phenoxathiin, and chloranil were purified by recrystallization from n-heptane–ethanol (1:1) mixture, n-heptane, and toluene, respectively (m.p. 158.5–159.5° for thianthrene, 57–57.5° for phenoxathiin). Commercially available diphenylene dioxide was washed twice by dilute aqueous sodium hydroxide solution and, after drying, recrystallized repeatedly from n-heptane (m.p. 119–120°).

Method.—Absorption spectra were measured with a Beckman spectrophotometer Model DK-2 attached with a thermostated cell jacket. Square silica cells of 1-cm. path length were used. The molar extinction coefficients near the peaks of the charge transfer absorption bands[3] and the equilibrium constants were obtained by the formula of Ketelaar, et al.[4] In the cases of thianthrene and phenoxathiin, the concentrations of iodine were $4.6 \sim 5.3 \times 10^{-4}$ M and those of the donors $0.05 \sim 0.20$ M. In the case of diphenylene dioxide the concentration of iodine was 3.7×10^{-3} M and those of the donors were $0.21 \sim 0.36$ M. Since the tail of the long wave length absorption band of thianthrene and the CT band of its iodine complex considerably overlap with each other, especially in carbon tetrachloride, E_I in the formulas of Ketelaar, et al.,[4] was obtained by dividing the difference between the absorption of thianthrene and that of the complex solution by the iodine concentration. The absorption

intensities of thianthrene were always less than 7.5% those of the complex solutions. The CT bands of the complexes between chloranil and the thianthrene analogs were measured with equal volume mixtures of the chloranil and the thianthrene analogs solutions, both nearly saturated. The CT band shapes of the iodine and the chloranil complexes were obtained by subtracting the absorptions corresponding to the added quantities of both components of the complexes from the absorptions of the complex solutions. The oscillator strengths of the CT bands were calculated by the approximate formula given by Tsubomura and Lang.[5,6]

Results

Since the formula of Ketelaar, et al.,[4] was satisfied in all cases, it is clear that the one-to-one charge transfer complexes were formed in the concentration ranges used in this work. Table I shows the equilibrium constants and the molar extinction coefficients obtained. In the calculation of the equilibrium constants, the molarity was used as the units of the concentrations of iodine and the donors. As shown in Table I, the obtained molar extinction coefficients of the complexes somewhat fluctuated over the temperature range adopted in the present study, but it is likely that in all cases the molar extinction coefficients are independent of temperature. Therefore, the equilibrium constants shown in Table I were evaluated using the average values of the molar extinction coefficients obtained at various temperatures. As shown in Fig. 1, good linearities between the logarithms of the equilibrium constants and the reciprocals of temperatures were obtained in all cases. The binding energies (ΔH) and the entropies of formation (ΔS) of the complexes are obtained from the slope and the intercept of the straight lines shown in Fig. 1. The thermodynamic constants and the features of the CT bands obtained are shown in Tables II and III, respectively. The features of the CT bands of the chloranil complexes with the thianthrene analogs at 20° are also shown in Table III for the purpose of comparison; $\Delta\nu^-$ and $\Delta\nu^+$ in the sixth and the seventh columns of Table III are the differences in wave number between the peak positions of the CT bands and their half-height positions of the CT bands at the longer and the shorter wave length sides, respectively, and the sums of these two values are the half-widths $(\Delta\nu_{1/2})$ of the CT bands which are shown in the eighth column. The peak positions of the CT bands and the CT band shapes of the iodine complexes with the thianthrene analogs are almost independent of temperature. In the last column the oscillator strengths of the CT bands, f-values, are

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