

An Electron Diffraction Investigation of the Molecular Structure of 1,3,4-Thiadiazole in the Vapour Phase

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The electron diffraction intensities obtained are consistent with a planar molecule having C_{2v} symmetry. Bond distances and angles are in good agreement with those determined by microwave spectroscopy. The following values were found for bond lengths and bond angles: $r(\text{C}-\text{H})=1.081 (\pm 0.028) \text{ \AA}$, $r(\text{N}-\text{C})=1.304 (\pm 0.010) \text{ \AA}$, $r(\text{N}-\text{N})=1.381 (\pm 0.016) \text{ \AA}$, $r(\text{S}-\text{C})=1.722 (\pm 0.006) \text{ \AA}$, $\angle \text{CSC}=86.4 (\pm 0.4)^\circ$, $\angle \text{SCN}=114.8 (\pm 0.5)^\circ$, $\angle \text{CNN}=112.0 (\pm 0.4)^\circ$, $\angle \text{SCH}=124.1 (\pm 3.0)^\circ$, and $\angle \text{HCN}=121.1 (\pm 3.0)^\circ$. Values in parentheses are estimated error limits. Bond distances and angles are those consistent with the average structure (r_α).

Both diagonal and non-diagonal weight matrices have been used in the least-squares refinements, and the results thus obtained have been compared.

Several investigations of the molecule 1,3,4-thiadiazole** exist, including microwave,¹ infra-red,² and ultraviolet³ spectra. Mean amplitudes of vibration (u -values) have been calculated from spectroscopic information.⁴ Theoretical treatment of the electron distribution have also been reported.^{3,5}

The present investigation was undertaken to compare the electron diffraction results with the structure determined by microwave spectroscopy.

EXPERIMENT AND DATA PROCESSING

The sample of 1,3,4-thiadiazole was supplied by Professor B. Bak.¹

Diffraction photographs were obtained in the usual way with the Oslo apparatus.⁶ The nozzle temperature was approximately 95°C. The electron wavelength was determined from a gold foil diffraction pattern and corrected by an experiment with CO₂. Plates from two different nozzle-to-plate distances of about 48 cm (48.292) and 19 cm (20.160) were obtained. The corresponding

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** Numbering of atoms is shown in Fig. 5.

electron wave lengths were 0.064842 Å and 0.064854 Å, determined with an uncertainty of *ca.* 0.14 %.

Five plates from each camera distance were photometered, and the intensity data treated in the usual way.⁷

A statistical analysis of each set of data was carried out on the modified molecular intensity curves.⁸ In Fig. 1 are presented the 48 cm average intensities and curves (I, II, III, IV, V) corresponding to the difference between each individual intensity curve and the average curve. An individual curve consists of data from one plate. The average deviation for an individual curve was calculated according to the following expression:

$$100 \times (\sum_s |A_s| / \sum_s |I_s|)$$

A_s is the difference between an individual intensity and the average intensity (I_s) at a point s . The average deviations thus obtained were 7.8, 9.0, 9.1, 7.8, and 9.9 for the 48 cm curves and 21, 22, 25, 24, and 22 for the 19 cm curves.

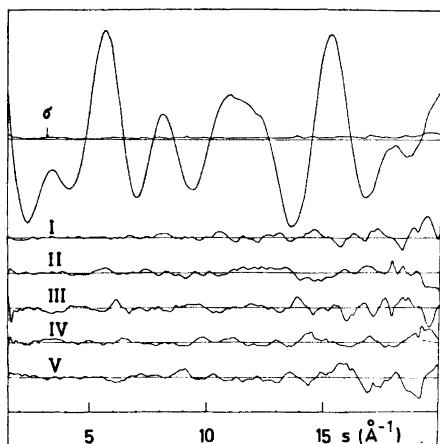


Fig. 1. Experimental 48 cm average intensity curve, and the curves (I, II, III, IV, V) corresponding to the difference between an individual intensity curve (from one plate) and the average curve. The curve labelled σ represents the standard deviation on the average intensities.

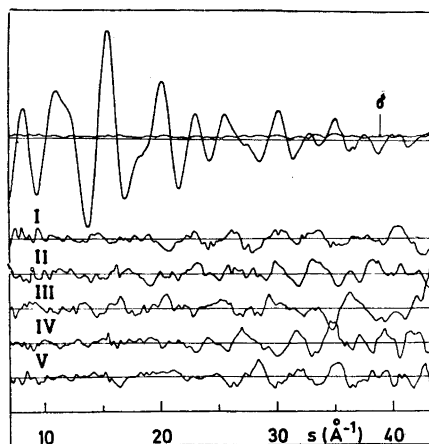


Fig. 2. Experimental 19 cm average intensity curve, and the curves (I, II, III, IV, V) corresponding to the difference between an individual intensity curve (from one plate) and the average curve. The curve labelled σ represents the standard deviation on the average intensities.

The curve labelled σ in Fig. 1 represents the standard deviation on the average intensity.

19 cm curves corresponding to those previously discussed for 48 cm have been presented in Fig. 2.

The general trend in the curves for standard deviations is very much the same as found for several sets of data investigated in this laboratory.⁸ From the error curves in Figs. 1 and 2 it is seen that the errors are not quite randomly distributed, and a certain correlation should be expected.⁸

Individual curves for both sets of data show satisfactory mutual agreement. The two average curves were used in the refinements. The 48 cm data cover the s range $1.50-20.0 \text{ \AA}^{-1}$ with $\Delta s = 0.125 \text{ \AA}^{-1}$, while the 19 cm data cover the s range $7.0-43.25 \text{ \AA}^{-1}$ with $\Delta s = 0.25 \text{ \AA}^{-1}$.

Average intensity curves, modified ⁷ by

$$s/|f_s'| |f_c'|$$

are presented in Fig. 3. The curves show satisfactory mutual agreement in the overlap region.

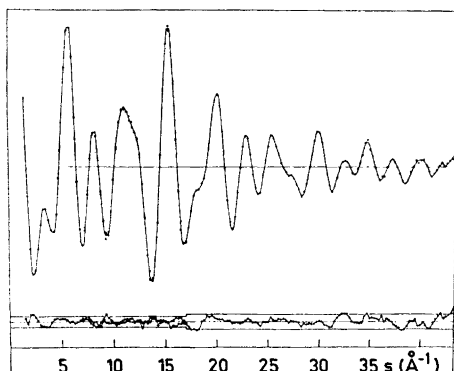


Fig. 3. 48 cm (—) and 19 cm (---) experimental average intensity curves. Residuals corresponding to parameters in Table 1 column b_1 , are plotted below together with the experimental error limits. On the 48 cm curve only every second point is plotted.

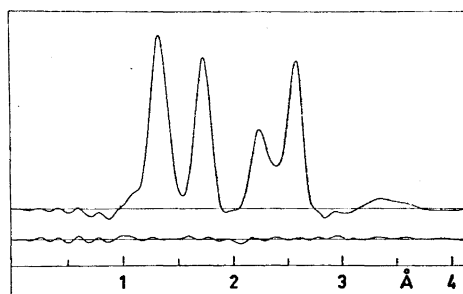


Fig. 4. Experimental radial distribution function, and residuals corresponding to parameters in Table 1 column b_1 . An artificial damping constant equal to 0.0005 \AA^2 has been applied.

In Fig. 4 is presented the experimental radial distribution (RD) function.⁷ Approximate values for the bond lengths may be obtained from the RD curve. The bond distances C—H (1.08 \AA), N—C (1.30 \AA), and N—N (1.38 \AA) contribute to the complex peak between 1.0 \AA and 1.5 \AA , while the peak between 1.6 \AA and 1.9 \AA corresponds to the bond distance S—C (1.72 \AA). Short non-bonded distances contribute to the complex peak between 2.0 \AA and 2.7 \AA , and the contributions from the longer non-bonded distances are found in the range $3.1-4.6 \text{ \AA}$.

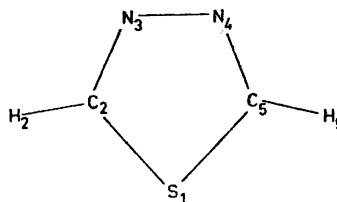


Fig. 5. Numbering of atoms in 1,3,4-thiadiazole.

The numbering of atoms is shown in Fig. 5.

LEAST-SQUARES REFINEMENT

The refinements⁷ were carried out using the two average intensity curves simultaneously. Preliminary results from the 19 cm data alone have been reported elsewhere.⁸ An individual scale factor was refined for each curve. The relative weight between the curves was chosen to obtain approximately equal values for $V'PV$ for the two curves.⁸ A reasonable change in the relative weight resulted in quite negligible changes in the parameters refined. The standard deviations for parameters were influenced more by such changes as might be expected.⁸

For each set of data an individual weight matrix was applied. A diagonal weight function was chosen taking into consideration the variation in the standard deviations for the intensities.^{7,8} In the final refinements the outer part of the 48 cm data and the inner part of the 19 cm data were given a lower weight than the one predicted from experimental uncertainty alone. However, such changes in the diagonal weights resulted in negligible changes in the parameters and their standard deviations.

Three types of refinements were carried out:

I. A planar model with C_{2v} symmetry was used to introduce relations between the internuclear distances due to geometry. Bond distances and the angles C-S-C and S-C-H were chosen as independent parameters.⁷ Non-bonded distances and the angles S-C-N, C-N-N, and N-C-H were treated as dependent parameters. Results using two different weight matrices are presented in columns a_1 and b_1 in Table 1.

II. All distances were treated as independent parameters. The multiplicity of distances was the same as in I. Distances that could not be refined were given values reported in columns a_1 and b_1 . Results using two different weight matrices are presented in columns a_2 and b_2 in Table 1.

III. The last type of refinements corresponds to the refinements in I. However, correction terms were included in the refinements to obtain the average structure.⁹ Results using two different weight matrices are presented in columns a_3 and b_3 in Table 1.

Perpendicular amplitude correction coefficients (K) and u -values have been calculated by Cyvin *et al.*^{4,10}

	u (Å)	K (Å)		u (Å)	K (Å)
C-H	.0772	.0194	C...N	.0522	.0011
S-C	.0435	.0011	N ₃ ...H ₅	.0933	.0062
C-N	.0462	.0022	N ₃ ...H ₂	.1000	.0105
N-N	.0462	.0018	C ₂ ...H ₅	.0886	.0056
S...N	.0442	.0003	S...H	.0969	.0082
C...C	.0505	.0007	H...H	.1161	.0079

When r_a is the interatomic distance which most directly emerges from the refinements,⁷ then the mean distance (r_g) and the distance of the average structure (r_α) are obtained according to^{4,9}

$$r_g = r_a + u^2/r_a \text{ and } r_\alpha = r_g - K$$

Correction for centrifugal distortion is thus neglected.

Some u -values could not be refined and for these parameters the values reported above have been used.

Small differences in the parameters obtained from the two weight matrices might be expected.^{8,11} The difference between values in columns b and a has been divided by the standard deviation (σ_b) in b , and the absolute value of this ratio is found in columns marked d . The d -values are in most cases acceptable. For the angles and bond distances the d -values are approximately $\sigma_b/3$ except for C-H, where the d -value is as large as twice the standard deviation. Rather large d -values are found for non-bonded distances involving hydrogen. For the u -values the situation is very much the same as for the geometrical parameters.

In columns marked c are given the ratios σ_b/σ_a where σ_b is the standard deviation obtained with a non-diagonal weight matrix, while σ_a was obtained with a diagonal matrix. The values in c_2 illustrate that the ratio σ_b/σ_a depends on the interatomic distance both for the r and u -values.⁸ The general decrease in this ratio with increasing distance is not so clearly seen in column c_1 . This is due to the fact that the refinements corresponding to a_1 and b_1 were carried out with constraints on the parameters, while the distances were treated as independent parameters in a_2 and b_2 .

The discussion of structural parameters is based on the results in columns b_1 , b_2 , and b_3 .

DISCUSSION

In Fig. 3 are presented the average experimental modified molecular intensity curves.

Theoretical intensities were calculated according to the parameters in column b_1 .⁷ The residuals between the theoretical intensities and the experimental ones are also plotted together with the experimental error limits for the intensities. Twice the average standard deviation for the intensities was chosen as an experimental error limit. Practically all the residuals fall within the experimental error limits. R -factors⁸ are given in Table 1. The deviation between theory and experiment is not significant.

In Fig. 4 is presented the experimental RD-curve together with the curve of residuals corresponding to parameters in column b_1 .

The results in b_2 are also consistent with a planar molecule. The sum of angles in the ring is 540.5° and the sum of angles on the C-atom is 361.9° as calculated from b_2 . Deviations from the theoretical values 540° and 360° are negligible, as well as the deviations between parameters in b_2 and b_1 . R -factors⁸ in b_1 and b_2 are nearly identical.

In column b_3 are found distances and angles corresponding to the average structure. The results in b_3 show that the structure obtained in b_1 is practically identical with the average structure. Actually the parameters in b_1 give R -factors which are slightly better than those in b_3 .

The correlation matrix^{7,12} for the parameters is practically the same for columns b_1 and b_3 in Table 1. In Table 2 is presented the matrix corresponding to parameters in b_3 . Correlation coefficients between refined parameters have been included in the calculation of standard deviations for dependent distances and angles.⁷

Table 1. Least-squares results for 1,3,4-thiadiazole.

	a_1	a_2	a_3	b_1	b_2	b_3	c_1	c_2	d_1	d_2
$r(\text{C}-\text{H})$	1.1274 (66)	1.1202 (76)	1.1174 (68)	1.0932 (143)	1.0916 (191)	1.0834 (144)	2.2	2.5	2.4	1.5
$r(\text{N}-\text{C})$	1.3068 (19)	1.3058 (19)	1.3069 (20)	1.3076 (43)	1.3080 (65)	1.3075 (45)	2.3	3.4	0.1	0.5
$r(\text{N}-\text{N})$	1.3880 (33)	1.3886 (34)	1.3877 (34)	1.3840 (71)	1.3802 (117)	1.3841 (73)	2.2	3.4	0.6	0.7
$r(\text{S}-\text{C})$	1.7269 (5)	1.7267 (6)	1.7270 (5)	1.7266 (12)	1.7265 (13)	1.7266 (12)	2.4	2.2	0.3	0.2
$r(\text{N}_3 \cdots \text{H}_2)$	2.1248 (101)		2.1152 (103)	2.0953 (207)		2.0850 (208)	2.1		1.5	
$r(\text{N} \cdots \text{C})$	2.2342 (11)	2.2344 (13)	2.2339 (11)	2.2318 (24)	2.2317 (28)	2.2316 (24)	2.2	2.2	1.0	1.0
$r(\text{C} \cdots \text{C})$	2.3659 (21)		2.3652 (21)	2.3637 (45)		2.3630 (45)	2.1		0.5	
$r(\text{S} \cdots \text{H})$	2.5336 (93)	2.5406 (155)	2.5262 (93)	2.5062 (193)	2.4919 (242)	2.5000 (192)	2.1	1.6	1.4	2.0
$r(\text{S} \cdots \text{N})$	2.5657 (8)	2.5653 (12)	2.5662 (8)	2.5661 (13)	2.5669 (12)	2.5666 (13)	1.6	1.2	0.3	1.1
$r(\text{N}_3 \cdots \text{H}_3)$	3.2994 (79)		3.2889 (80)	3.2632 (171)		3.2525 (173)	2.2		2.1	
$r(\text{C}_3 \cdots \text{H}_3)$	3.4829 (78)		3.4725 (79)	3.4471 (163)		3.4370 (163)	2.1		2.2	
$r(\text{H} \cdots \text{H})$	4.5902 (145)		4.5702 (146)	4.5214 (307)		4.5024 (308)	2.1		2.2	
$\angle \text{C}-\text{S}-\text{C}$	86.47 (9)	86.49 (9)	86.44 (9)	86.40 (18)	86.50 (18)	86.36 (19)	2.0	2.0	0.4	0
$\angle \text{S}-\text{C}-\text{H}$	123.79 (71)	124.99 (155)	123.86 (71)	123.89 (147)	122.71 (252)	124.05 (148)	2.1	1.6	0.1	0.9
$\angle \text{S}-\text{C}-\text{N}$	114.79 (11)	114.84 (15)	114.82 (12)	114.80 (25)	114.84 (40)	114.84 (25)	2.3	2.8	0	0
$\angle \text{C}-\text{N}-\text{N}$	111.97 (8)	112.01 (17)	111.96 (8)	112.00 (17)	112.21 (49)	111.98 (17)	2.1	2.9	0.2	0.4
$\angle \text{H}-\text{C}-\text{N}$	121.41 (70)	122.11 (69)	121.31 (70)	121.31 (147)	124.37 (183)	121.11 (148)	2.1	2.7	0.1	0.1

Table 1. Continued.

$u(\text{C}-\text{H})$.0898	(74)	.0888	(71)	.0889	(76)	.0861	(151)	.0857	(152)	.0867	(153)	2.0	2.1	0.3	0.2
$u(\text{N}-\text{C})$.0489	(21)	.0484	(22)	.0491	(21)	.0509	(38)	.0520	(51)	.0508	(37)	1.8	2.3	0.5	0.7
$u(\text{N}-\text{N})$.0552	(43)	.0534	(43)	.0564	(44)	.0585	(88)	.0592	(119)	.0592	(90)	2.1	2.8	0.4	0.5
$u(\text{S}-\text{C})$.0615	(8)	.0618	(8)	.0614	(8)	.0619	(16)	.0620	(16)	.0618	(16)	2.0	2.0	0.3	0.1
$u(\text{N}\cdots\text{C})$.0504	(15)	.0505	(14)	.0504	(15)	.0536	(24)	.0544	(24)	.0535	(24)	1.6	1.7	1.3	1.6
$u(\text{S}\cdots\text{N})$.0545	(9)	.0548	(9)	.0545	(9)	.0565	(15)	.0557	(15)	.0565	(15)	1.7	1.7	1.3	0.6
k (48 cm)	1393	(10)	1397	(10)	1394	(10)	1449	(24)	1443	(24)	1451	(24)	2.4	2.4	2.1	1.9
k (19 cm)	1378	(17)	1382	(17)	1377	(17)	1398	(30)	1396	(29)	1399	(30)	1.7	1.7	0.7	0.5
R_1	7.56		7.45		7.62		8.37		8.36		8.41					
R_2	6.30		6.27		6.35		7.22		7.20		7.24					
R_3	6.30		6.27		6.35		15.59		15.57		15.62					
$V'PV \times 10^{-3}$	1113		1104		1129		284.7		284.0		285.6					

Results for diagonal weight matrices are in columns marked by a , off-diagonal elements have been included in columns marked b , and the ratios in columns c are σ_b/σ_a , where σ is the standard deviation given in parentheses. The difference between values in columns b and a has been divided by the standard deviation in column b , and the *absolute* value of this ratio is found in columns d .

In a_1 , b_1 , c_1 , and d_1 some distances were regarded as *dependent* parameters, and the geometrical restrictions correspond to a planar model, with C_2v symmetry for the molecule.

In a_2 , b_2 , c_2 , and d_2 all distances were *independent* parameters. (The distances $N_3\cdots H_3$, $C\cdots C$, $N_3\cdots H_5$, $C_2\cdots H_5$, and $H_2\cdots H_5$ could not be refined together with the other distances). The multiplicity of distances was the same as in a_1 .

The restrictions in columns a_3 , and b_3 are the same as in a_1 , and b_1 , however correction terms to obtain the r_x -structure have been included. Distances and angles are consistent with the r_x -structure.

Distances and u -values are in Å and angles in degrees. The k -values are scale factors for the two camera distances and the quantities R_1 , R_2 , R_3 , and $V'PV$ are defined in a previous paper.⁸

For all refinements the diagonal weight w for the 48 cm data was given by $w = \exp[-0.10(s-3.0)^2]$ for $s < 3.0$, $w = 1$ for $3.0 \leq s \leq 18.0$, $w = \exp[-0.50(s-18.0)^2]$ for $s > 18.0$. The corresponding weight w for the 19 cm data was given by $w = w_0 \exp[-0.10(s-8.0)^2]$ for $s < 8.0$, $w = w_0$ for $8.0 \leq s \leq 20.0$, $w = w_0 \exp[-0.0025(s-20.0)^2]$ for $s > 20.0$. In the refinements a_1 , a_2 , and a_3 , $w_0 = 0.7$ while in b_1 , b_2 , and b_3 , $w_0 = 0.9$.

The off-diagonal elements⁸ of Q^{-1} are $p_2 = -0.64$ and $p_3 = 0.148$ for the 48 cm data, while $p_2 = -0.60$ and $p_3 = 0.120$ for the 19 cm data. These values are quite close to the average values found for several sets of data from this laboratory.⁸

FINAL RESULTS AND ERROR LIMITS

In Table 3 are listed the final results from this work together with parameters obtained by spectroscopic means.¹

Table 3. Final parameters. Bond distances and u -values are given in Å and angles in degrees. The values in parentheses are estimated error limits (twice the standard deviation).

	r_x -structure from electron diffraction	r_s -structure from spectroscopy
$r(\text{C-H})$	1.081 (± 0.028)	1.077 ^a
$r(\text{N-C})$	1.304 (± 0.010)	1.302
$r(\text{N-N})$	1.381 (± 0.016)	1.371
$r(\text{S-C})$	1.722 (± 0.006)	1.721
$\angle \text{C-S-C}$	86.4 (± 0.4)	86.4
$\angle \text{S-C-N}$	114.8 (± 0.5)	114.6
$\angle \text{C-N-N}$	112.0 (± 0.4)	112.2
$\angle \text{S-C-H}$	124.1 (± 3.0)	122.5
$\angle \text{H-C-N}$	121.1 (± 3.0)	122.9
$u(\text{C-H})$	0.087 (± 0.030)	0.077 ^b
$u(\text{N-C})$	0.051 (± 0.008)	0.046
$u(\text{N-N})$	0.059 (± 0.018)	0.046
$u(\text{S-C})$	0.062 (± 0.004)	0.044
$u(\text{N}\cdots\text{C})$	0.054 (± 0.004)	0.052
$u(\text{S}\cdots\text{N})$	0.057 (± 0.004)	0.044

^a r_s -structure determined by microwave spectroscopy.¹

^b u -values calculated by Cyvin *et al.*⁴

An experiment with CO_2 gave a correction of -0.25% in the s scale. The distances in Table 3 are thus -0.25% shorter than those in Table 1 column b_3 .

A final error limit is reported as twice the standard deviation where the uncertainty in the wavelength (0.14%) is included for the distances.

The structure parameters from electron diffraction are those consistent with the average structure (r_x), while the spectroscopic results correspond to the r_s -structure.¹ The two sets of parameters are therefore not directly comparable in principle.⁹ However, no significant deviations are found between the two sets of geometrical parameters. Two of the u -values, $u(\text{S-C})$ and $u(\text{S}\cdots\text{N})$, are significantly different from those calculated by Cyvin *et al.*⁴

CONCLUSIONS

The electron diffraction intensities obtained are consistent with a planar molecule having C_{2v} symmetry. Bond distances and angles show good agreement with those determined by microwave spectroscopy.¹

Table 2. Correlation matrix ($\times 100$) for parameters.

Parameter	1	2	3	4	5	6	7	8	9	10	11	12	13	14
$r(\text{S}-\text{C})$	100													
$r(\text{N}-\text{C})$	0	100												
$r(\text{N}-\text{N})$	-5	-89	100											
$\angle \text{CSC}$	4	79	-52	100										
$r(\text{C}-\text{H})$	-1	0	18	32	100									
$\angle \text{SCH}$	-22	1	7	22	-5	100								
$u(\text{S}-\text{C})$	-5	-5	-4	-16	-17	-6	100							
$u(\text{N}-\text{C})$	2	78	-86	42	-23	-2	13	100						
$u(\text{N}-\text{N})$	3	91	-86	65	-13	1	3	80	100					
$u(\text{C}-\text{H})$	7	19	-19	15	1	2	-13	25	18	100				
$u(\text{S}\cdots\text{N})$	-17	-12	8	-11	-5	32	34	6	-3	-12	100			
$u(\text{N}\cdots\text{C})$	-1	1	-1	-6	11	-14	14	5	3	-5	7	100		
k (48 cm)	-7	0	-6	-13	-36	8	38	21	13	-14	32	8	100	
k (19 cm)	-9	-5	-5	-19	-27	3	60	25	10	-19	58	19	43	100

The r_α and r_s structures determined are nearly identical.

Diagonal and non-diagonal weight matrices gave nearly identical parameters, while the standard deviations obtained using a diagonal weight matrix are too small.

Note added in proof. After this work had been completed, we have received a reprint from Dr. Lise Nygaard¹³ describing a reinvestigation of the microwave spectrum of 1,3,4-thiadiazole.

The estimated average (r_z) structure from this reinvestigation is very close to the r_z structure reported in Table 3, and the r_α structure from electron diffraction shows excellent agreement with the r_z structure.

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