Structure Calculations on 1,3,4-Thiadiazole with Computer Programs

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Dedicated to Professor Helmut Dreizler on the Occasion of His 60th Birthday

Insertion of the 14 available sets of isotopic moments of 1,3,4-thiadiazole into the computer programs GEOM or RU 111/115 confirms the previously hand-calculated structure parameters of this molecule, but does not further improve the accuracy of those results.

I. Introduction

In a recent publication [1] we have reported the results of a structure determination on 1,3,4-thiadiazole ($N_2C_2H_2S$, abbreviated as 1,3,4-TDA) on the basis of the rotation spectra of 14 molecular isotopes. That study contained a little novelty in that the "shift of the centre of gravity" and the "swing of inertial axes" between the different "parent" forms (normal, 2-d_1- and d_2-form of 1,3,4-TDA) were used to derive the otherwise undeterminably small coordinates of the near-axis hydrogen and carbon atoms in this compound. The results of that study were hand-calculated.

It is the purpose of this note to present the results of computer fits of the structure of 1,3,4-TDA to the above mentioned experimental data ([1], Table 1). These fits were carried out with the program GEOM [2], which was one of the earliest programs written for that purpose, and with the program RU 111/115 [3], which is perhaps the most recent addition to a family of computer programs designed for the extraction of the molecular geometry of a compound from the moments of inertia of the various molecular isotopes of that substance.

II. Structure Calculations on 1,3,4-TDA

a) Calculations with the Program GEOM

The most distinctive feature of the GEOM program [2] may be seen in the fact that this routine completely ignores the possibility of vibrational contributions to the observed moments of inertia to which the molecular structure is being fitted. The inertia defects which, even for planar molecules such as 1,3,4-TDA, do rarely vanish exactly, and which vary slightly from one molecular isotope to the next, are treated as statistical errors of the input data (experimental rotational constants or moments of inertia). The computer routine is laid out to adjust the parameters of the given "input structure" so as to minimize the discrepancies between the moments of inertia of the adjusted (optimised) structure and the moments of the observed molecular isotopes.

The program offers the options of a least-squares fit of the input structure to *either* the moments (I_g, $g = a, b, c$) of the parent form and their changes (ΔI_g) under isotopic substitution, *or* to those changes alone. For the present purpose we have chosen the latter option which has become known as the "pseudo-Kraitchman" method because it is closely akin to the original Kraitchman method [4], which has been used in [1] for the calculations on 1,3,4-TDA.

The structure results obtained by a GEOM fit to all 14 observed molecular isotopes are given in column I of the Table 1. The N–N bond distance and the CNN- and NCH bond angles were not required to specify the input structure and, accordingly, they were not fitted by the program. The values of those three parameters are, of course, readily extracted from the atomic coordinates, for which the GEOM routine does not derive error limits, however. To obtain error margins on those parameters, the program was re-run

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Table 1. Comparison of the hand-calculated structure results for 1,3,4-TDA with those obtained from the computer programs GEOM and Ru 111/115.

	I		II		III	
	Program GEOM (see [2])		Hand-calculated (see [1])		Program RU 111/115 (see [3])	
	Bond lengths (in Å)					
S−C	1.7192 (5) [a]		1.7200 [3] [b]		1.7204 (4), (44) [c]	
C−N	1.3042 (9)		1.3031 [5]		1.3044 (7), (46)	
N−N	1.3703 (14) [d]		1.3711 [5]		1.3711 (9), (47)	
C−H	1.0779 (5)		1.0771 [4]		1.0780 (4), (42)	
	Bond angles (in degrees)					
∢CSC	86.37 (3)		86.38 [2]		86.37 (3), (24)	
∢SCN	114.68 (3)		114.64 [3]		114.67 (2), (16)	
∢CNN	112.13 (2) [d]		112.17 [1]		112.15 (2), (5)	
∢SCH	122.50 (10)		122.49 [2]		122.23 (11), (100)	
∢NCH	122.82 (9) [d]		122.86 [1]		123.11 (11), (92)	
	Atomic coordinates (in Å)					
	a	±*b*	*a*	±*b*	*a*	±*b*
S (1)	+1.1763 [a]	–	+1.1761 [<1]	–	+1.1767 (2), (39)	–
C (2/5)	−0.0773	1.1766	−0.0778 [<1]	1.1773 [4]	−0.0778 (4), (17)	1.1774 (3), (34)
N (3/4)	−1.2854	0.6852	−1.2847 [<1]	0.6856 [3]	−1.2859 (3), (44)	0.6856 (4), (24)
H (2/5)	+0.1226	2.2358	+0.1220 [<1]	2.2357 [<1]	+0.1271 (18), (157)	2.2357 (2), (68)
Shift of C.o.G. (in Å)	0.0028 [f]		0.0028 [g]		0.0029 [f]	
Swing of axes (in degree)	0.53_8 [f]		0.53_5 [g]		0.55_7 [f]	

[a] Uncertainties are given in units of the last quoted decimal.
[b] Quantities in square brackets are limits of compatibility between the three separate determinations.
[c] The second error margin represents the estimated deviation from equilibrium parameters.
[d] Uncertainty derived from fit of differently specified input structure.
[e] Uncertainties of coordinates are not computed by GEOM.
[f] Hand-calculated from hydrogen coordinates. – [g] Derived from experimental data in [1].

with the same input structure, but specified differently to include those three parameters.

The last two rows of the Table 1 give the values of the "shift of the centre of gravity (C.o.G.)" between the normal and the d_2-form, and the "swing of inertial axes" in the 2-d_1-species against the C_{2v}-symmetrical forms, as calculated from the small *a*-coordinate of the hydrogens in the optimised structure of 1,3,4-TDA.

b) Hand-Calculated Structure Results

These results are given in column II of Table 1 for comparison with those obtained with the two computer programs. Their derivation has been adequately described in [1], but it should be recalled that the uncertainties in square brackets are compatibility limits of the lengths and angles separately deduced in three reference frames. The set of atomic coordinates, which was not included in [1], was obtained by transformation of the coordinates derived in the 2-d_1-frame (Table B-3 of [1]), and of those derived in the d_2-frame (Table A-2 of [1]) into the axis system of the normal form. Corresponding coordinates from three sets were than averaged to yield the here quoted values. The agreement between the three sets must be considered very good for six of the eight coordinates (where deviations from the quoted averages are 0.00006 Å or less). The *b*-coordinates of carbon and nitrogen deviate by ±0.0004 Å from the averages quoted in the Table 1.

The values for the "shift" and the "swing" of axes were derived from multiple substitution data, as explained in [1].

c) Calculations with the Program RU 111/115

In contrast to the GEOM program, the rountine devised by Rudolph [3] attempts to take the rovibrational contributions to the moments of inertia into account. From the outset, the observed moments $I_{g,o}^{(i)}$

(where i denotes the molecular isotope) are treated as quantities which differ from the equilibrium moments $I^{(i)}_{\mathrm{g,e}}$ by a small, but not precisely known amount ε. The experimental error of the $I^{(i)}_{\mathrm{g,o}}$ is assumed to be negligible in comparison with ε. Thus,

$$I^{(i)}_{\mathrm{g,e}} = I^{(i)}_{\mathrm{g,o}} + \varepsilon^{(i)}_{\mathrm{g}}.$$

The rovibrational contributions $\varepsilon^{(i)}_{\mathrm{g}}$ to the observed moments $I^{(i)}_{\mathrm{g,o}}$ are then assumed to be generally representable in the form

$$\varepsilon^{(i)}_{\mathrm{g}} = p(I^{(i)}_{\mathrm{g,o}})^q$$

with the coefficient $p = 0.00223(7)$ and the exponent $q = 1.247(5)$ for polyatomic molecules taken from a study by Demaison and Nemes [5].

Since the sign of $\varepsilon^{(i)}_{\mathrm{g}}$ (or p) cannot be ascertained with confidence for polyatomic molecules, the rovibrational contributions to the observed moments are modelled in the RU program as statistical errors of the form

$$\varepsilon^{(i)}_{\mathrm{g}} = 0 \pm p(I^{(i)}_{\mathrm{g,o}})^q,$$

and the moments to be reproduced by the molecular structure according to the least-squares method are therefore

$$I^{(i)}_{\mathrm{g}}\,(\text{fitted}) = I^{(i)}_{\mathrm{g,o}} \pm p(I^{(i)}_{\mathrm{g,o}})^q.$$

The observed moments are weighted according to their expected errors $|p(I^{(i)}_{\mathrm{g,o}})^q|$, which are assumed to be highly correlated within each $\mathrm{g} = a, b, c$ since the rovibrational contributions $\varepsilon^{(i)}_{\mathrm{g}}$ of all isotopic species i of a particular molecule can be expected to be very similar in magnitude and sign.

Despite these differences, the RU program should, on account of the last equation, yield roughly the same structural results as the GEOM program, but with *two* error margins. The first of these arises from the residual incompatibilities of the observed $I^{(i)}_{\mathrm{g,o}}$-values with a rigid (and in the present case: planar) structure. The second error margin which the RU program reveals, arises from the term $\pm p(I^{(i)}_{\mathrm{g,o}})^q$, and must be taken as an indication of the estimated deviations of the derived structure parameters from their equilibrium values.

Amongst other options, the RU program contains the possibility of fitting either all observed moments $I^{(i)}_{\mathrm{g,o}}$, which results in the r_0-structure, or of fitting only the differences $\Delta I^{(j)}_{\mathrm{g,o}}$ between the parent form and the molecular isotopes j, which results in the pseudo-Kraitchman structure $r_{\Delta I}$. To allow a comparison of the GEOM-results and of the hand-calculated results of [1] with the results of the RU program, the computations with the last were performed on the basis of $\Delta I_{\mathrm{g,o}}$-values. – The results may be inspected in column III of Table 1.

III. Discussion

A glance at the Table shows that the bond lengths in 1,3,4-TDA derived by computer programs and by hand-calculation agree with each other within about 0.001 Å. The ring angles coincide within 0.05°. The three coordinate sets show the largest discrepancy in the position of the hydrogen atoms: While the hand-calculation and the GEOM program lead to the fairly consistent values of $a_{\mathrm{H}} = 0.1220$ Å and 0.1226 Å, the RU program places the hydrogens about 0.004 Å further away from the b-axis (see the figure in [1]) of the molecule. As a result, the SCH and NCH angles are changed by ±0.3° from the consistent values indicated by the other two calculations, and the "shift of the C.o.G." as well as the "swing of axes" turn out larger than is expected on the basis of the GEOM results and than has been deduced from the multiple substitution data in [1].

The estimated deviations (second error in column III) of the $r_{\Delta I}$-parameters ($\cong r_{\mathrm{S}}$-values) from their unknown equilibrium values are seen to be of the order of 0.005 Å in the distances, and of up to 1° in the angles. They are thus roughly 10 times larger than the residual inconsistencies between the three approaches presented here, all of which are based either on the Kraitchman or the pseudo-Kraitchman ΔI_{g} method. However, the second errors of column III are meant to estimate the expected deviations from r_{e}-values. To the extent to which the results of structure calculations with schemes different from the above are indicative of the scatter of calculated values about true r_{e}-values, these larger errors must be considered more closely. For example, if differences of rotational constants are used in the RU program instead of differences in moments of inertia, the resulting bond lengths differ from those reported here by amounts which are an order of magnitude larger than the uncertainties which emerge from the least-squares fitting procedure of experimental data alone, and this fact is indeed reflected by the second errors of column III of Table 1.

IV. Summary

The overall result of this study, as displayed by the data of the Table 1, may be summarized in the conclusion that the parameters obtained with the help of two programs do neither contradict the values nor do they improve the apparent accuracy of the hand-calculated structure results for 1,3,4-thiadiazole.

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