

Calculation of ¹⁴N and ³³S Quadrupole Coupling Constants on Optimized Molecular Structures of Thiazole

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¹⁴N and ³³S nuclear quadrupole coupling constants have been calculated for optimized molecular structures of thiazole. For nitrogen, the B3PW91/6-311+G (df, pd) model was used to calculate of the electric field gradients, and for sulfur, the B3LYP/6-311G (3df, 3p) model. The best results are obtained for the B3PW91/6-31G (2d, 2pd) optimized molecular structure. For this structure, the root mean square difference between the calculated and experimental nitrogen coupling constants is 3 kHz (0.14%), and that between the calculated and experimental sulfur coupling constants is 43 kHz (0.25%). Calculated coupling constants are given in the principal axes of both the inertia and coupling constant tensors. © 2001 Academic Press

INTRODUCTION

Accurate nuclear quadrupole coupling constants (nqcc) in heterocyclic thiazole for both ¹⁴N and ³³S have been determined by Fourier transform microwave spectroscopy by Kretschmer and Dreizler (1). The nitrogen nqcc's are an improvement in precision over previously determined values (2, 3). The off-diagonal components of the nqcc tensors could not be determined (1).

A substitution structure (r_s) of thiazole was reported some time ago by Nygaard *et al.* (3). It was noted by these authors that, due to a number of small and therefore uncertain coordinates, this structure is not without ambiguity.

It is the purpose of this work to calculate on optimized molecular structures the full nqcc tensors in the principal axes of both the inertia and nqcc tensors. Reliable methods for calculation of the nqcc's in conjunction with accurate experimental values provide for assessment of the several optimized structures. Where good agreement between the calculated and experimental nqcc's is found for the diagonal components in the principal axes of the inertia tensor, it can reasonably be assumed that the calculated off-diagonal components are equally accurate.

This line of investigation has recently been applied to pyridine and the monochloropyridines (4) and to pyrimidine (5).

METHOD

The nqcc is the spectroscopic measurement of the energy of interaction of the electric quadrupole moment of the nucleus of the atom with the gradient of the molecular electric field (efg) at the site of the nucleus. The components of the nqcc tensor χ_{ij} are related to those of the efg tensor q_{ij} by

$$\chi_{ij} = (eQ/h)q_{ij}, \quad [1]$$

where e is the proton electric charge, Q is the electric quadrupole moment of the nucleus, and h is Planck's constant; $i, j = a, b, c$ (principal axes of the inertia tensor) or x, y, z (principal axes of the efg tensor).

With eQ/h taken as a best-fit parameter determined by linear regression analysis of the calculated efg's versus the experimental nqcc's, the B3PW91/6-311+G (df, pd) model was shown to yield accurate nitrogen nqcc's for 39 molecules containing 45 nitrogen sites. These calculations were made on experimental molecular structures. The residual standard deviation (RSD) was found to be 30 kHz (1.3% of the average absolute experimental nqcc), with $eQ/h = 4.5617(43)$ MHz/a.u. (6). This model is applied here to calculation of the nitrogen nqcc's.

To calculate the sulfur nqcc's, the efg's were calculated using the B3LYP/6-311G (3df, 3p) model. This model was shown, for the experimental structures of 12 molecules, to yield a RSD of 0.42 MHz (1.8%), with $eQ/h = -15.578(40)$ MHz/a.u. (7).

The structure of thiazole was optimized using the B3LYP, B3P86, and B3PW91 methods in conjunction with Pople-type bases ranging from 6-31G (d, p) to 6-31G (3d, 3p). B3LYP is Becke's (8) hybrid Hartree–Fock theory/density functional theory method (HF/DFT) in conjunction with the correlation functional of Lee *et al.* (9, 10); B3P86 is Becke's method with the correlation functional of Perdew (11); and B3PW91 is Becke's method with the correlation functional of Perdew and Wang (12).

All calculations were performed using the GAUSSIAN 94 package of programs (13).

RESULTS

The experimental ¹⁴N and ³³S nqcc's for thiazole are shown in Table 1. Nitrogen nqcc's were measured for each of the ³²S, ³³S, and ³⁴S isotopomers (1).

The molecular structure of thiazole was optimized, and on each optimized structure nitrogen and sulfur efg's were

TABLE 1
 ^{14}N and ^{33}S Nuclear Quadrupole Coupling
 Constants (MHz)

	Expt. ^a	Calc.
Thiazole ^{32}S		
χ_{aa} (^{14}N)	-2.7481 (15)	-2.747
χ_{bb} (^{14}N)	0.08505 ^b	0.081
χ_{cc} (^{14}N)	2.66305 ^b	2.666
χ_{ab} (^{14}N)		2.560
Thiazole ^{33}S		
χ_{aa} (^{14}N)	-2.7411 (49)	-2.740
χ_{bb} (^{14}N)	0.0767 (69)	0.074
χ_{cc} (^{14}N)	2.6644 ^c	2.666
χ_{ab} (^{14}N)		2.564
χ_{aa} (^{33}S)	7.1708 (61)	7.230
χ_{bb} (^{33}S)	-26.1749 (69)	-26.190
χ_{cc} (^{33}S)	19.0041 ^c	18.961
χ_{ab} (^{33}S)		0.739
Thiazole ^{34}S		
χ_{aa} (^{14}N)	-2.7359 (23)	-2.733
χ_{bb} (^{14}N)	0.0716 ^d	0.067
χ_{cc} (^{14}N)	2.6643 ^d	2.666
χ_{ab} (^{14}N)		2.567

^a Ref. (1).

^b Derived from χ_{aa} and $\chi_{bb} - \chi_{cc} = -2.5780(32)$ MHz.

^c Derived from zero trace condition.

^d Derived from χ_{aa} and $\chi_{bb} - \chi_{cc} = -2.5927(47)$ MHz.

TABLE 2
 Root Mean Square (rms) Difference (kHz)
 and eQ/h (MHz/a.u.)

Optimization Model	^{14}N		^{33}S	
	rms	eQ/h	rms	$-eQ/h$
B3LYP/6-31G(d,p)	29.2	4.5787	827	15.171
B3P86/6-31G(d,p)	1.8	4.5734	188	15.538
B3PW91/6-31G(d,p)	5.8	4.5776	320	15.495
B3LYP/6-31G(2d,2p)	21.0	4.5557	503	15.318
B3P86/6-31G(2d,2p)	4.7	4.5496	109	15.673
B3PW91/6-31G(2d,2p)	3.5	4.5660	46	15.640
B3LYP/6-31G(3d,3p)	6.4	4.5823	95	15.514
B3P86/6-31G(3d,3p)	19.7	4.5780	483	15.834
B3PW91/6-31G(3d,3p)	14.3	4.5874	386	15.795
B3PW91/6-31G(2d,p)	4.6	4.5666	44	15.634
B3PW91/6-31G(2d,2p)	3.5	4.5660	46	15.640
B3PW91/6-31G(2d,3p)	3.3	4.5713	58	15.658
B3PW91/6-31G(2d,pd)	4.4	4.5651	41	15.633
B3PW91/6-31G(2d,2pd)	2.7	4.5617	43	15.642
B3PW91/6-31G(2d,3pd)	2.6	4.5694	57	15.658
Expt. structure ^a	17.7	4.6094	371	15.779

^a Ref. (3).

TABLE 3
 Structure Parameters (\AA and $^\circ$)

Parameter	r_s^a	r_{opt}
S(1)C(2)	1.7239(9)	1.7313
C(2)N(3)	1.3042(11)	1.2988
N(3)C(4)	1.3721(2)	1.3690
C(4)C(5)	1.3670(4)	1.3635
C(5)S(1)	1.7130(3)	1.7188
C(2)H(2)	1.0767(18)	1.0817
C(4)H(4)	1.0798(1)	1.0818
C(5)H(5)	1.0765(2)	1.0781
C(5)S(1)C(2)	89.33(3)	89.03
S(1)C(2)N(3)	115.18(1)	115.14
C(2)N(3)C(4)	110.12(2)	110.28
N(3)C(4)C(5)	115.81(2)	116.09
C(4)C(5)S(1)	109.57(1)	109.46
S(1)C(2)H(2)	121.26(5)	120.56
N(3)C(4)H(4)	119.35(1)	119.18
C(4)C(5)H(5)	129.03(3)	129.10

^a Ref. (3).

calculated. The best-fit value of eQ/h for conversion of the efg's to nqcc's, and the root mean square (rms) difference between calculated and experimental nqcc's are given in Table 2 as functions of the optimization model. The results for the experimental structure are also given. The goal is to determine that structure on which the rms differences for both nuclei are small, and with best-fit values of eQ/h close to the calibration values. This latter requirement should be considered less stringent for sulfur than for nitrogen simply because of statistical differences due to sample size.

On the experimental structure, the rms difference and eQ/h are respectively, for nitrogen, 17.7 kHz and 4.6094 MHz/a.u.,

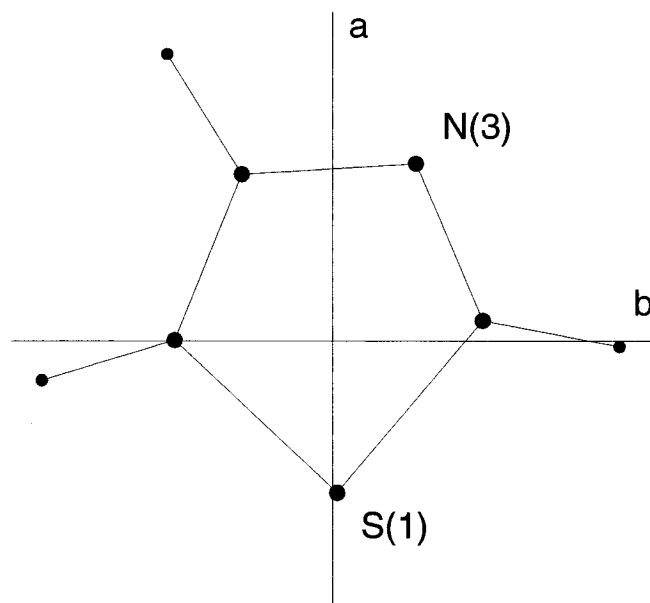


FIG. 1. Thiazole.

TABLE 4
³²S Isotopomer of Thiazole: Atomic Coordinates (Å)

Atom	a	b
S (1)	-1.1603	0.0418
C (2)	0.1447	1.1795
N (3)	1.3332	0.6558
C (4)	1.2497	-0.7107
C (5)	-0.0091	-1.2345
H (2)	-0.0529	2.2430
H (4)	2.1603	-1.2948
H (5)	-0.3155	-2.2681

and for sulfur, 371 kHz and -15.779 MHz/a.u. On the B3PW91/6-31G(2d, 2p) structure, these are respectively, for nitrogen, 3.5 kHz and 4.5660 MHz/a.u., and for sulfur, 46 kHz and -15.640 MHz/a.u. The latter is a notable improvement over the former with regard both to the rms differences and to the values of eQ/h .

Fine tuning the model by varying the polarization functions on the hydrogen atoms further improves the results. The best results for nitrogen are obtained with the B3PW91/6-31G(2d, 2pd) optimization model, and for sulfur with the B3PW91/6-31G(2d, pd) model. We choose to go forward with the former, for which the rms difference and eQ/h are respectively, for nitrogen, 2.7 kHz and 4.5617 MHz/a.u., and for sulfur, 43 kHz and -15.642 MHz/a.u. The difference of 2.7 kHz is 0.14% of the average absolute experimental nitrogen nqcc, and that of 43 kHz is 0.25% of the average absolute experimental sulfur nqcc; 4.5617 MHz/a.u. is the same as the nitrogen calibration value (6), while -15.642 MHz/a.u. differs from the sulfur calibration value (7) by 0.4%.

The nqcc's calculated on the B3PW91/6-31G(2d, 2pd) structure are given in Table 1 along with the experimental nqcc's. Structure parameters are given in Table 3 along with the experimental r_s parameters. As shown in Fig. 1, the S and N atoms are numbered 1 and 3, respectively; the C and H atoms are numbered accordingly. Atomic coordinates for the ³²S isotopomer are given in Table 4.

In the principal axes of the nitrogen nqcc tensor, $\chi_{xx} = 1.591$, $\chi_{yy}(\chi_{cc}) = 2.666$, and $\chi_{zz} = -4.257$ MHz. The z-principal

axis makes an angle of 0.8° with the external CNC bisector and tilts toward C(4)H(4). For sulfur, $\chi_{xx} = 7.246$, $\chi_{yy}(\chi_{cc}) = 18.961$, and $\chi_{zz} = -26.206$ MHz. The z-principal axis makes an angle of 2.1° with the external CSC bisector and tilts toward C(5)H(5). These coupling constants for sulfur differ little from those obtained by Kretschmer and Dreizler (1) by assuming, on the experimental structure of Nygaard *et al.* (3), that the z-principal axis coincides with the bisector of the CSC angle. They find $\chi_{xx} = 7.21$, $\chi_{yy} = 19.0041$, and $\chi_{zz} = -26.22$ MHz.

SUMMARY

¹⁴N and ³³S nuclear quadrupole coupling constants in good agreement with accurate experimental coupling constants have been calculated for the B3PW91/6-31G(2d, 2pd) optimized molecular structure of thiazole. The nqcc's are given in principal axes of both the inertia and nqcc tensors.

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