

Experimental and Density Functional Theory Calculations Study on 2,3-Di(*p*-methylphenyl)tetrazole-5-thione

P.S. ZHAO[†], F.F. JIAN^{*}, R.R. ZHUANG and J. ZHENG

*New Materials & Function Coordination Chemistry Laboratory,
Qingdao University of Science and Technology, Qingdao Shandong-266042, P.R. China
E-mail: zhaopusu@163.com*

2,3-Di(*p*-methylphenyl)tetrazole-5-thione has been synthesized and characterized by elemental analysis, FTIR, electronic absorption spectra and X-ray single crystal diffraction. Density functional theory method calculations at B3LYP/6-31G* level of the structure, atomic charges distribution, vibration frequencies and the thermodynamic properties at different temperatures have been performed and the results show that the exocyclic sulfur atom has the biggest negative charge values and this site is the most likely site of protonation and methylation as well as the potential coordination site with metallic ions. The calculation of the second order optical nonlinearity has been carried out, and the molecular hyperpolarizability is 13.994×10^{-30} esu, indicating that 2,3-di(*p*-methylphenyl)tetrazole-5-thione is a good candidate as second-order nonlinear optical material.

Key Words: 2,3-Di(*p*-methylphenyl)tetrazole-5-thione, Density function theory, Vibrational frequency, Thermodynamic property, Second-order nonlinear optical hyperpolarisability.

INTRODUCTION

Many substituted tetrazoles show a variety of interesting properties. For instance, they exhibit certain types of physiological activity by affecting the nervous system in a number of ways¹. They are commonly used as good weed killers in agriculture, as well as applied in various industrial branches (pharmaceutics, photography)². The physical and chemical properties of some 2,3-diaryl-tetrazole-5-thione, including synthesis, structure, protonation, electronic absorption spectra, *etc.* have been studied by several groups of researchers³⁻⁵. In their investigations, 2,3-diaryl-tetrazole-5-thione were regarded as mesoionic compounds. In literature, neither complete theoretical investigations nor the comparison between the calculations and experimental results for derivations of tetrazole-5-thione are available. As a matter of fact, in order to characterize the correlation

[†]Jiangsu Key Laboratory for Chemistry of Low-Dimensional Materials, Huaiyin Teachers College, Huaian 223300, P.R. China.

between molecular structure and macroscopic properties in the studied compounds, it is essential to undertake a detailed comparative study of the isolated molecule and the solid state unit. So we synthesized 2,3-di(*p*-methylphenyl)tetrazole-5-thione by a new method and determined its crystal structure for the first time. Density functional theory (DFT) method is also applied B3LYP/6-31G* to optimize the geometry of this compound, since DFT provided a sound basis for the development of computational strategies for obtaining information about the energetics, structure and properties of molecules at much lower costs than traditional *ab initio* wave function techniques⁶. Herein we report the DFT calculations at B3LYP/6-31G* level and experimental results of the 2,3-di(*p*-methylphenyl)tetrazole-5-thione.

EXPERIMENTAL

The C, H and N elemental analysis was performed on a Yanaco CHN FOER MT-3 elemental analyzer. IR spectra (FTIR) were recorded on a Perkin-Elmer 2000 FTIR spectrometer using KBr pellet. Ultraviolet spectra were recorded in a GBC UV/Vis spectrophotometer.

Synthesis: All chemicals were obtained from a commercial source and used without further purification.

p,p'-Dimethyl dithizone (5.0 g, 17.5 mmol) was dissolved in 200 mL methyl cyanide. Then, carbon disulfide (35.0 mmol) and sodium hydroxide (17.5 mmol) 50 % aqueous solution were added dropwise with stirring at 40°C. The mixture was kept at 40°C for 4 h and the orange precipitate was formed, the mixture was cooled to room temperature. The products were collected and the orange crystals were obtained by recrystallization from EtOH. Yield: 88 %. m.p. 169-171°C; anal. calcd. for C₁₅H₁₄N₄S: C 63.83, H 5.00, N 19.85 %; found: C 63.62, H 5.32, N 19.58%. Electronic absorption spectra in EtOH (nm, log ε): λ_{max} = 211 (1.293), λ = 342 (0.889), λ = 324 (0.518), λ = 420 (0.656).

X-ray structure determination: The selected crystal of the 2,3-di(*p*-methylphenyl)tetrazole-5-thione was mounted on a Rigaku Raxis-IV diffractometer. Reflection data were measured at 20°C using graphite monochromated Mo-K_α (λ = 0.71073 Å) radiation. The collected data⁷ were reduced by using the program SAINT. The structure was solved by direct methods and refined by full-matrix least-squares method on F_{obs}^2 using the SHELXTL software package⁸. All non-H atoms were anisotropically refined. The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent carbon atoms. The final least-square cycle gave $R = 0.1082$, $R_w = 0.2929$ for 1036 reflections with $I > 2\sigma(I)$; the weighting scheme, $w = 1/[\sigma^2(F_o^2) + (0.2000P)^2]$, where $P = (F_o^2) + 2F_c^2/3$. Atomic scattering factors and anomalous dispersion corrections

were taken from International Table for X-Ray crystallography⁹. A summary of the key crystallographic information of the 2,3-di(*p*-methylphenyl)tetrazole-5-thione is given in Table-1.

TABLE-1
CRYSTAL DATA AND STRUCTURE REFINEMENT FOR THE
2,3-DI(*p*-METHYLPHENYL)TETRAZOLE-5-THIONE

Empirical formula	C ₁₅ H ₁₄ N ₄ S
Formula weight	282.37
Temperature (K)	293 ± 2
Wavelength (Å)	0.71073
Crystal system, space group	Orthorhombic, <i>P</i> _{mm} 2 ₁
Unit cell dimensions (Å)	<i>a</i> = 18.381(4) <i>b</i> = 6.1799(12) <i>c</i> = 6.1865(12)
Volume (Å ³)	702.7(2)
Z, Calculated density (Mg/m ³)	2, 1.334
Absorption coefficient (mm ⁻¹)	0.225
<i>F</i> (000)	296
Crystal size (mm ³)	0.3 × 0.3 × 0.6
θ Range	3.30-27.44°
Limiting indices	-23 ≤ <i>h</i> ≤ 23, 0 ≤ <i>k</i> ≤ 7, -7 ≤ <i>l</i> ≤ 7
Reflections collected/unique	2213/1310 (<i>R</i> _{int} = 0.0731)
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	1310/1/95
Goodness-of-fit on <i>F</i> ²	1.163
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.1082, <i>wR</i> ₂ = 0.2929
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1199, <i>wR</i> = 0.2997
Extinction coefficient	0.40(8)
Largest diff. peak and hole (e/Å ³)	0.924 and -0.435

Computational methods: Initial molecular geometry was optimized using MM+ molecular modeling and semi-empirical AM1 methods¹⁰ (HYPERCHEM 6.0, Hypercube, Ont., Canada). In the next step, the DFT calculations with a hybrid Functional B3LYP (Becke's Three parameter Hybrid Functional Using the LYP Correlation Functional) at 6-31G* basis set by the Berny method¹¹ were performed with the Gaussian 98 software package¹². Vibrational frequencies calculated ascertain the structure was stable (no imaginary frequencies). The thermodynamic properties of the present compound at different temperatures have been calculated on the basis of vibrational analyses. On the basis of the MNDO Hamiltonian¹³ and PM3 parametrization¹⁴ with the MOPAC¹⁵ program package, the molecular hyperpolarisability value was also calculated.

All calculations were performed on a Pentium IV computer using the default convergence criteria.

RESULTS AND DISCUSSION

Crystal Structure: The crystal structure of the 2,3-di(*p*-methylphenyl)-tetrazole-5-thione with the atomic numbering is given in Fig. 1. A perspective view of the crystal packing in the unit cell is shown in Fig. 2. Atomic parameters and equivalent isotropic thermal parameters of non-H atoms are given in Table-2. Some selected X-ray diffraction data together with the optimized geometrical parameters at B3LYP/6-31G* level, including the total energy, zero-point vibrational energy and energy of HOMO and LUMO are listed in Table-3.

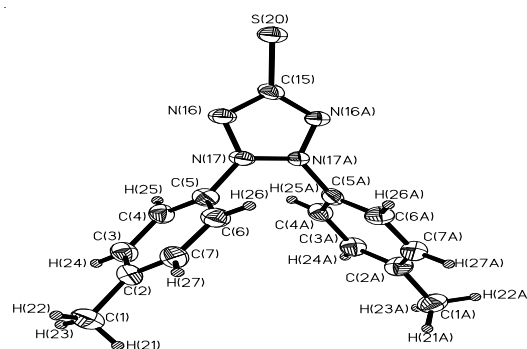


Fig. 1. Molecular structure with the atomic numbering scheme for 2,3-di(*p*-methylphenyl)tetrazole-5-thione

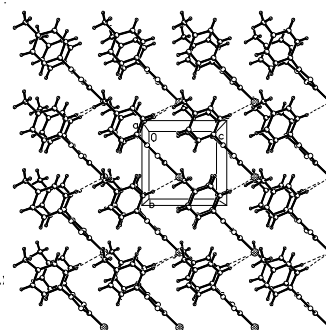


Fig. 2. View of the crystal packing down the *a* axis for 2,3-di(*p*-methylphenyl)tetrazole-5-thione

TABLE-2
ATOMIC COORDINATES ($\times 10^4$) AND EQUIVALENT ISOTROPIC
DISPLACEMENT PARAMETERS ($\text{\AA}^2 \times 10^3$)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}	Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
S(20)	0	3288(4)	9473(4)	61(1)	C(6)	1030(4)	10898(10)	4695(14)	57(2)
N(17)	363(3)	7513(7)	5202(9)	43(1)	C(5)	816(4)	8873(11)	3903(10)	49(2)
N(16)	612(3)	6092(9)	6599(9)	51(2)	C(4)	1045(4)	8096(11)	1915(12)	53(2)
C(1)	2211(5)	12856(14)	65(15)	75(3)	C(3)	1506(4)	9417(11)	643(12)	57(2)
C(2)	1728(4)	11449(11)	1428(15)	60(2)	C(15)	0	5205(18)	7498(16)	53(2)
C(7)	1504(4)	12136(12)	3445(13)	56(2)	-	-	-	-	-

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

The crystal structure contains two discrete 2,3-di(*p*-methylphenyl)-tetrazole-5-thione molecules. In each molecule, the sulfur atom and the carbon atom in the tetrazole ring lie on a twofold axis, and the remaining atoms are related by this twofold axis. There are no true single or double-bond distances of N-N and N-C in the tetrazole ring. The C-S distance is 1.702(8) Å, which is intermediate between a double-bond and a single-bond distance. The tetrazole ring and the exocyclic sulfur atom are almost

exactly planar, with the largest deviation 0.023 Å from the least-squares plane. These phenomena indicate that there is considerable electron delocalization in the tetrazole ring and the exocyclic sulfur atom. The only single-bond distance in the molecule is from the nitrogen atom N (17) in the tetrazole ring to the carbon atom C(5) of the phenyl group. The phenyl ring with the conjunction C(1) atom in methyl group are also coplanar, the maximum deviation being 0.016 Å. The tetrazole ring and the phenyl ring are almost perpendicular and the dihedral between them is 89.82°.

TABLE-3
SELECTED BOND LENGTHS, ANGLES AND TORSION ANGLES BY X-RAY AND
THEORETICAL CALCULATIONS

Bond lengths (Å)	Exp.	Calc.	Bond angles (°)	Exp.	Calcd.
S(20)-C(15)	1.702(8)	1.6751	N(16)-N(17)-N(17A)	110.3(3)	110.11
N(17)-N(16)	1.314(7)	1.3142	N(16)-N(17)-C(5)	124.1(5)	122.86
N(17)-N(17A)	1.336(9)	1.3509	N(17A)-N(17)-C(5)	125.6(3)	124.00
N(17)-C(5)	1.430(8)	1.4319	N(17)-N(16)-C(15)	104.5(5)	105.77
N(16)-C(15)	1.369(8)	1.3914	C(7)-C(2)-C(3)	120.0(7)	118.22
C(1)-C(2)	1.502(8)	1.5097	C(7)-C(2)-C(1)	120.4(7)	120.75
C(2)-C(7)	1.380(7)	1.4027	C(3)-C(2)-C(1)	119.6(8)	121.03
C(2)-C(3)	1.407(8)	1.4019	C(2)-C(7)-C(6)	121.3(7)	121.44
C(7)-C(6)	1.394(9)	1.3919	C(7)-C(6)-C(5)	118.1(7)	118.83
C(6)-C(5)	1.400(9)	1.3963	C(4)-C(5)-C(6)	122.4(7)	121.19
C(5)-C(4)	1.385(8)	1.3954	C(4)-C(5)-N(17)	118.2(6)	117.87
C(4)-C(3)	1.416(7)	1.3923	C(6)-C(5)-N(17)	119.5(6)	120.83
C(15)-N(16A)	1.369(8)	1.3914	C(5)-C(4)-C(3)	118.4(6)	118.92
			C(2)-C(3)-C(4)	119.7(7)	121.38
			N(16)-C(15)-N(16A)	110.4(8)	108.24
			N(16)-C(15)-S(20)	124.8(4)	125.88
			N(16A)-C(15)-S(20)	124.8(4)	125.88
Torsion angles (°)					
N(17A)-N(17)-N(16)-C(15)	-0.5(7)	-0.71	C(1)-C(2)-C(7)-C(6)	177.1(7)	179.10
C(5)-N(17)-N(16)-C(15)	178.7(6)	177.09	C(7)-C(6)-C(5)-C(4)	-1.7(9)	-1.52
N(16)-N(17)-C(5)-C(4)	-88.6(8)	-47.34	C(7)-C(6)-C(5)-N(17)	176.4(6)	177.71
N(17A)-N(17)-C(5)-C(4)	92.3(6)	135.16	C(6)-C(5)-C(4)-C(3)	-0.5(9)	-1.17
N(16)-N(17)-C(5)-C(6)	89.6(8)	128.96	C(1)-C(2)-C(3)-C(4)	-179.4(7)	-178.74
N(17A)-N(17)-C(5)-C(6)	-89.5(6)	-48.54	N(17)-C(5)-C(4)-C(3)	178.7(6)	177.47
N(17)-N(16)-C(15)-N(16A)	0.8(9)	0.31	N(17)-N(16)-C(15)-S(20)	178.6(7)	179.69
Total energy	-1197.1300667 au		Energy of HOMO	-0.16450 au	
Zero-point vibrational energy	696.2851 kJ/mol		Energy of LUMO	-0.08724 au	

Optimized geometries: Comparing the optimized geometry with the experimental data in Table-3, it is found that most of the optimized bond lengths are slightly larger than the experimental values, which is due to the theoretical calculations belong to isolated molecules in gaseous phase at 0

K and the experimental results belong to molecules in solid phase. The largest deviation of bond lengths and angles between the theoretical and experimental geometry are 0.0277 Å and 2.16°, respectively, indicating those calculational precision is satisfactory¹⁶. Nevertheless, the differences in the torsion angles are evident, which mainly occur in phenyl ring group and the largest deviation is about 42.86°. In the crystal structure, the close packing style of molecules and the existence of crystal field bring with stronger twisting of the phenyl ring, which makes the torsion angle of N(17A)-N(17)-C(5)-C(6) from predicted -48.54° to experimental -89.5(6)°. In spite of this, the resonance situation between tetrazole ring and exocyclic sulfur atom is still existent and the phenyl ring with the conjunction C(1) atom of methyl group are also coplanar, suggesting that the theoretical calculations about the present compound still have important significance.

Atomic charges: The Mulliken atomic charges of the present compound at the B3LYP/6-31G* level are listed in Table-4. (Only half of the atoms are listed in view of the symmetry of the molecules).

TABLE-4
MULLIKEN ATOMIC CHARGES (IN e) OF THE TITLE COMPOUND AT
THE B3LYP/6-31G* LEVEL

Atom	Charges	Atom	Charges
S(20)	-0.336779	C(6)	-0.119837
C(15)	0.273509	C(7)	-0.193841
N(16)	-0.283780	C(1)	-0.533791
N(16A)	-0.283802	H(24)	0.148098
N(17)	-0.133784	H(25)	0.184004
N(17A)	-0.133848	H(26)	0.164096
C(2)	0.191219	H(27)	0.144017
C(3)	-0.194723	H(21)	0.175139
C(4)	-0.124930	H(22)	0.169767
C(5)	0.270958	H(23)	0.169037

According to the data in Table-4, due to the nitrogen atom has bigger electronegativity than carbon atom, the charges of nitrogen atoms are all negative and the atoms of C(15), C(5) have positive charges. On the contrary, the other carbon atoms in phenyl rings have negative charges and all the hydrogen atoms have positive charges. The exocyclic sulfur atom has the highest negative charge values, indicating that this site is the most likely site of protonation and methylation as well as the potential coordination site for metal ions. This phenomenon not only consists with many experimental facts reported early, but also provides helpful information for further study on its metal complexes. The dipole moment of the present compound is 14.4943 Debye.

Vibrational frequencies: The experimental and infrared spectra are shown in Fig. 3. Vibrational frequencies calculated at B3LYP/6-31G* level were scaled by 0.96, which is a typical scaling factor for the B3LYP level frequencies. Some selected calculated harmonic frequencies are listed in Table-5 and compared with the experimental data. The descriptions concerning the assignment have also been indicated in the Table-5. Gaussview program¹⁷ was used to assign the calculated harmonic frequencies.

The predicted harmonic vibration frequencies are similar to the experimental data. They show a strong peak for (C-S) stretch vibration, except for the peak at 3432 cm⁻¹ in experimental IR spectra, which is attributed to the $\nu(\text{O-H})$ of water molecules. The probable reason for the errors between the calculation and the experiment is considered presentation of the difference of intermolecular actions. The results of vibration frequencies containing known systematic errors due to the neglect of the electron corrected are in gaseous state, while the experimental data are in the solid state.

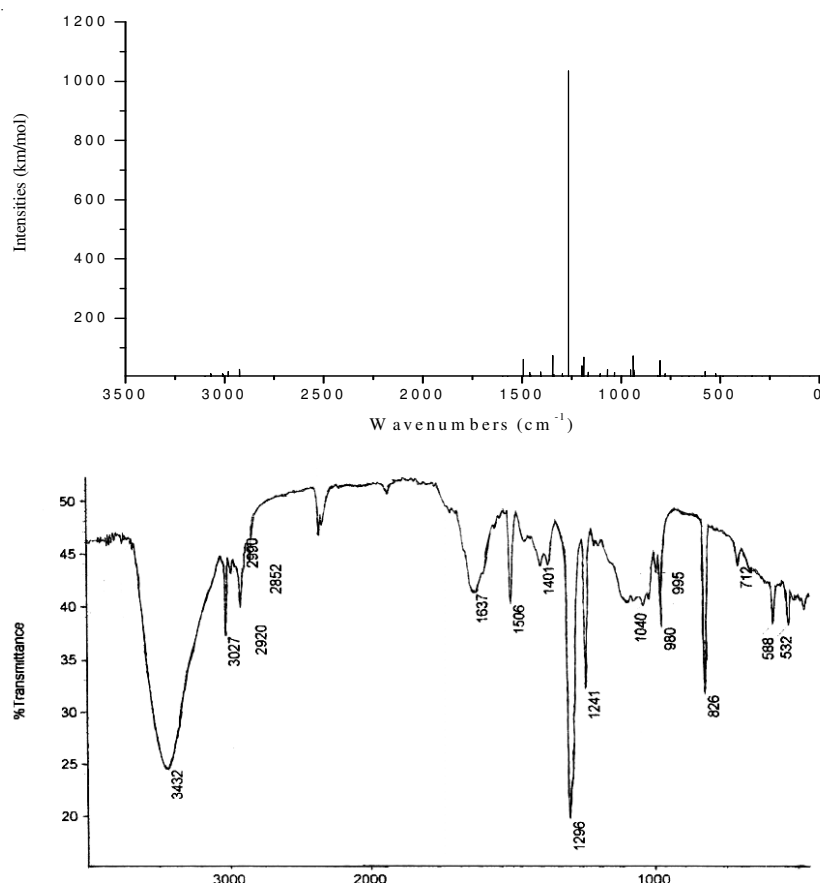


Fig. 3. Infrared spectra of 2,3-di(*p*-methylphenyl)tetrazole-5-thione

TABLE-5
COMPARISON OF THE EXPERIMENTAL AND CALCULATED
VIBRATIONAL FREQUENCIES (cm⁻¹)

B3LYP/6-31G*	Experimental	Assignment
3105.7 ~ 3066.6	3027	phenyl ring C-H str.
3010.1 ~ 2982.1	2990	CH ₃ group ν_{asy} (C-H)
2925.3 ~ 2925.1	2920	CH ₃ group C-H sym. str.
1597.1 ~ 1571.3	1637	phenyl ring C-C str.
1493.7 ~ 1493.4	1506	ip phenyl ring C-H def.
1460.9 ~ 1456.1	-	CH ₃ group C-H def.
1404.7 ~ 1402.0	1401	CH ₃ group C-H def. + in-plane phenyl ring C-H def.
1345.2 ~ 1339.3	-	N (tetrazole ring)-C (phenyl ring) str.
1264.4	1296	ν (C-S)
1197.3 ~ 1187.5	-	ν (N-N)
1068.4	1040	tetrazole ring ν_{asy} (C-N)
1033.5 ~ 1033.2	995	CH ₃ group C-H def.
1000.0 ~ 981.2	980	CH ₃ group C-H def.+ in-plane phenyl ring C-H def.
952.4	-	tetrazole ring C-N sym. str.
938.3 ~ 801.2	826	Out-of-plane phenyl ring C-H def.

Thermodynamic properties: On the basis of vibrational analysis and statistical thermodynamics, the standard thermodynamic functions-heat capacity ($C_{p,m}^0$), entropy (S_m^0) and enthalpy (H_m^0)- were obtained. The scaling factor for frequencies is also 0.96.

As observed, the standard heat capacities, entropies and enthalpies increase at any temperature from 200.00 K to 800.00 K, due to that the intensities of molecular vibration increase while the temperature increases. The correlation equations between these thermodynamic properties and temperature T are as follows:

$$C_{p,m}^0 = -9.17787 + 1.20721T - 5.6756 \times 10^{-4} T^2$$

$$S_m^0 = 297.36617 + 0.75473T$$

$$H_m^0 = -67.94869 + 0.36793T$$

These equations will be helpful for the further studies of the present compound.

Non-linear optical property calculations: On the basis of the MNDO Hamiltonian and PM3 calculation with the MOPAC program package, the molecular hyperpolarizability value, β_μ , the vector components along the dipole moment direction, of the present compound are calculated to be 13.994×10^{-30} esu, which is much greater than that of urea (0.14×10^{-30} esu). Therefore, the present compound is a good candidate as second-order nonlinear optical material.

Supplementary materials: CCDC-234730 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: (44)(1222)336033; email: deposit@ccdc.cam.ac.uk].

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