www.asianpubs.org

ARTICLE

Synthesis, Characterization, Crystal and Molecular Structure Analysis of 1-(2-Chlorophenyl)-3-methyl-4-(*p*-tolylthio)-1*H*-pyrazol-5-ol

Ronak D. Kamani[1], Rahul P. Thummar[1], Nirav H. Sapariya[2], Beena K. Vaghasiya[1], Jemin R. Avalani[3], Vishal B. Purohit[3], Kirit H. Patel[1] and Dipak K. Raval[1,✉]

Asian Journal of Organic & Medicinal Chemistry

Volume: 4 Year: 2019
Issue: 4 Month: October–December
pp: 267–272
DOI: https://doi.org/10.14233/ajomc.2019.AJOMC-P189

Received: 23 March 2019
Accepted: 18 December 2019
Published: 31 December 2019

ABSTRACT

The synthesis of a novel tolylthiopyrazol bearing methyl group has been achieved by transition metal free N-chlorosuccinimide mediated direct sulfenylation of 1-aryl pyrazolones at room temperature. The product obtained was characterized by spectroscopic techniques and finally confirmed by X-ray diffraction studies. The compound 1-(2-chlorophenyl)-3-methyl-4-(*p*-tolylthio)-1*H*-pyrazol-5-ol (m.f. $C_{17}H_{15}N_2OSCl$) crystallizes in monoclinic crystal class in space group $P2_1/c$ with cell parameters a = 9.6479(5) Å, b = 15.1233(8) Å, c = 11.4852(6) Å, β = 108.374(2)°, V=1590.4(2) $Å^3$ and Z = 4. The final residual factor R_1 = 0.0499.

KEYWORDS

Pyrazolone, Sulfenylation, Crystal structure, Hydrogen bonding.

Author affiliations:

[1]Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar-388120, India
[2]Department of Chemistry, Natubhai V. Patel College of Pure and Applied Sciences, Vallabh Vidyanagar-388120, India
[3]Department of Chemistry, Shree A.N. Patel P.G. Institute of Science and Research, Anand-388001, India

✉To whom correspondence to be addressed:

Fax: +91 2692 236475
Tel: +91 2692 226856 Ext. 208
E-mail: dipanalka@yahoo.com

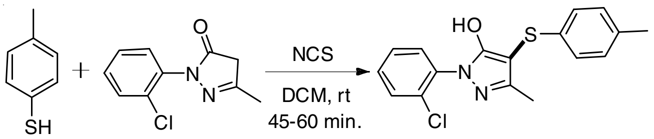
Available online at: http://ajomc.asianpubs.org

INTRODUCTION

Sulfur-containing compounds play essential role in natural products and bioactive compounds such as drugs, agrochemicals and functional materials [1-4]. In previous years, attempts have been dedicated to develop new methods for C–S bond construction. Accordingly, novel and efficient approaches for the formation of C–S bonds is an essential issue in modern organic chemistry. Highly efficient synthetic approach to sulfenylated pyrazoles *via* palladium [5], iodine [6], copper [7] and iron [8-11] catalyzed cross couplings of thiols or disulfides with aryl halides are reported. In recent years, transition metal-free syntheses for C–S bond formation *via* C–H bond sulfenylation reactions have also been intensively studied. In these transformations, various sulfenylating reagents such as aryl sulfonyl hydrazides [12-14], diaryl disulfides [15-17], aryl sulfonyl chlorides [18], sulfinic acids [19] and sodium sulfinates [20,21] have been extensively used. Hence, directly using thiols as sulfenylation reagent appears synthetically attractive.

Pyrazolones or pyrazoles have received huge attention in recent years due to their wide applications in dyes and agrochemicals [22]. The pyrazole derivatives occur in many biologically active natural and clinical products such as pyrazofurin, 4-methoxywithasomnine and formycin [23], crizotinib, fipronil and celebrex [24], respectively. The introduction of thiols into pyrazole in a regioselective fashion could enhance or alter its biological and pharmacological activity [25]. Pyrazole and its derivatives represent one of the most active classes of compounds, which exhibit broad spectrum of pharmacological activities like antimicrobial [26,27], anticonvulsant [28,29], anticancer [30,31], analgesic [32], anti-inflammatory [30,33], antitubercular [34,35], cardiovascular [36] *etc*.

Considering the importance of the pyrazole and thiol frameworks, together with our growing interest in sulfur-containing compounds synthesis, herein we wish to report a novel and single step reaction strategy for the construction of thiol-substituted pyrazoles C–H bond sulfenylation under transition metal free conditions (**Scheme-I**) [37].



Scheme-I: Synthetic protocol for 1-(2-chlorophenyl)-3-methyl-4-(*p*-tolylthio)-1*H*-pyrazol-5-ol

EXPERIMENTAL

Synthesis of 1-(2-chlorophenyl)-3-methyl-4-(*p*-tolylthio)-1*H*-pyrazol-5-ol: In a round bottom flask, a mixture of aryl thiols (1.0 mmol) and N-chlorosuccinimide (NCS) (1.2 mmol) was magnetically stirred in 2 mL of dichloromethane (DCM) for 0.5 h. 1-Aryl pyrazolones (1.0 mmol) was added to it. Stirring was continued for further 15-30 min at room temperature and the reaction was monitored by TLC. After completion, the reaction mixture was poured into 20 mL of saturated sodium bicarbonate solution and extracted with dichloromethane. The remaining organic phase was dried with anhydrous Na_2SO_4 and the solvent was distilled off under reduced pressure. The resulting residues were purified by a simple wash with *n*-hexane to afford the target products. The method employed for synthesis is shown in **Scheme-I**.

FT-IR (KBr, ν_{max}, cm^{-1}): 3341 (-OH *str.*), 3025 (C–H *str.*, asymmetric), 2935 (C–H *str.*, symmetric), 1587, 1480, 1329, 1319, 1229, 1156, 1127, 1012, 831, 710 (C–S *str.*). ^1H NMR (400 MHz, DMSO-d_6) δ (ppm): 2.09 (s, 3H), 2.23 (s, 3H), 6.98 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.46-7.56 (m, 3H), 7.66 (dd, *J* = 7.6 Hz; 1.6 Hz, 1H), 11.09 (s, 1H). ^{13}C NMR DEPT-135 (100 MHz, DMSO-d_6) δ (ppm): 136.0, 130.6, 130.3, 130.2, 130.1, 129.6, 127.9, 124.9, 20.3, 12.34. MS (*m/z*): 330.83

Method of crystallization: The pure 1-(2-chlorophenyl)-3-methyl-4-(*p*-tolylthio)-1*H*-pyrazol-5-ol (0.12 g) was dissolved in 20 mL of ethyl acetate. The resulting solution was warmed with charcoal on a water bath and 1-3 drops of DMF were added to the solution. The solution was filtered while hot through Whatmann 2 filter paper. The solution was kept in a stopper conical flask slightly opened. Crystals grew after 8-10 days due to thin layer evaporation. They were filtered and washed with chilled *n*-hexane.

All the chemicals were purchased from commercial suppliers and used without further purification. All the reactions were monitored by thin layer chromatography (TLC). ^1H NMR and ^{13}C NMR spectra were determined in DMSO-d_6 on Bruker Avance 400 MHz and 100 MHz spectrometer respectively and reported in δ ppm. IR spectra were obtained with a FTIR Perkin Elmer spectrum 100 spectrometer in KBr pellets with absorption in cm^{-1}. Melting points were measured using the capillary method on µThermoCal10 (Analab Scientific Pvt. Ltd.) melting point apparatus and are uncorrected. IKA RV 10 control rotary evaporator was used to remove the solvents under vacuum. X-ray diffraction crystal structure analysis was obtained on the RIGAKU SCX mini X-ray Diffractometer. All measurements were made on a Rigaku SCX mini Diffractometer using graphite monochromated Mo-Kα radiation. Structure solution and refinement was solved by direct methods [38-40] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement [41] on F^2 was based on 3647 observed reflections and 199 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of: $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.0499$ and $wR2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma w(F_o^2)^2]^{1/2} = 0.1496$. The standard deviation of an observation of unit weight was 1.07. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.54 and -0.45 e/Å^3, respectively. Neutral atom scattering factors were taken from Cromer and Waber [42]. Anomalous dispersion effects were included in F_{calc} [43]; the values for Δf′ and Δf″ were those of Creagh and McAuley [44]. The values for the mass attenuation coefficients are those of Creagh and Hubbell [45]. All calculations were performed using the crystal structure [46] crystallographic software package except for refinement, which was performed using SHELXL-97 [47].

RESULTS AND DISCUSSION

A colourless block crystal of $C_{17}H_{15}N_2OSCl$ having approximate dimensions of 0.540 mm × 0.490 mm × 0.320 mm was mounted on a glass fiber. The data were collected at a temperature of 20 ± 1 °C to a maximum 2θ value of 55.0°. The crystal-to-detector distance was 52.00 mm and readout was performed in the 0.146 mm pixel mode given the total of 540 oscillation images and its collection. A sweep of data was done using ω oscillations from -120.0 to 60.0° in 1.0° steps, in which the exposure rate and detector swing angle was 8.0 [s/°], -30.80° respectively. Data were collected and processed using Crystal-clear (Rigaku), In which the total 15922 reflections were collected, out of them 3647 were unique (Rint = 0.0238) and equivalent reflections. The linear absorption coefficient, μ, for Mo-Kα radiation is 3.735 cm^{-1}. Empirical absorption correction was applied which resulted in transmission factors ranging from 0.700 to 0.887. The details of crystal data and refinement are given in Table-1.

Cell constants and an orientation matrix for data collection corresponded to a primitive monoclinic cell with dimensions: a = 9.6479(5) Å, b = 15.1233(8) Å, c = 11.4852(6) Å, β = 108.374(2)°, volume = 1590.4(2) Å^3, Z = 4, f.w. = 330.83 and the calculated density is 1.382 g/cm^3. The reflection conditions h0l: l = 2n and 0k0: k = 2n uniquely determine the space group to be: $P2_1/c$ (#14). The value of bond angles and bond lengths

TABLE-1 CRYSTAL DATA AND STRUCTURE REFINEMENT	
Empirical formula	$C_{17}H_{15}N_2OSCl$
Formula weight	330.83
Temperature	20 ± 1 °C
Space group	$P2_1/c$
Crystal colour, Habit	Colourless, block
Crystal dimensions	0.540 mm × 0.490 mm × 0.320 mm
Crystal system	Monoclinic
Lattice type	Primitive
Lattice parameters	a = 9.6479(5) Å; b = 15.1233(8) Å c = 11.4852(6) Å; β = 108.374(2)°
Volume	1590.4(2) $Å^3$
Space group	$P2_1/c$ (#14)
Z	4
Density (calculated)	1.382 g/cm^3
F_{000}	688.00
Reflections collected	15922
Independent reflections	3647 were unique (R_{int} = 0.0238)
Refinement method	Full-matrix least-squares on F2
Theta range for data collection	2.0°-55.0°
μ (MoKα)	3.735 cm^{-1}
Reflections/variables	3647/199
Reflection ratio	18.33
Final R indices [I>2.00σ(I)] 0.0499 (R_1)	Final R indices [I>2.00σ(I)] 0.0499 (R_1)
R indices (all data) R = 0.0570 and wR_2 = 0.01496	R indices (all data) R = 0.0570 and wR_2 = 0.01496
Largest diff. peak and hole	0.540 and -0.450 e $Å^{-3}$

were described in Table-2. In which, the C–S and C–O bond distances 1.740 Å and 1.251 Å are in good agreement with literature values of 1.744 Å [48] and 1.255 Å [49], respectively. The C–S bond length and bond angle of C2-S1-C4 (101.97°) also confirmed the bond formation of C2-S1-C4 (Table-2).

In the title compound the pyrazole ring shows the pentagonal-planer conformation with perpendicular to the phenyl rings was also confirmed by the value of torsion angle between the atoms of C3-N1-N2-C1 = -1.4(2)°, N1-N2-C1-C2 = 1.3(3)°, N2-N1-C3-C2 = 0.9(2)°, N2-C1-C2-C3 = -0.8(3)° and C1-C2-C3-N1 = -0.1(3)° (Table-3). The torsion angle about C2–S1–C4–C5 being -165.36(17)° and that about N1–C11–C12–C13 is 176.77(3)° shows antiperiplanar conformation. The atoms C3–N1–C11–C12 and C1-C2-S1-C4 gives *syn*-clinal conformation with a value of -64.7(4)° and -98.32(18)°, respectively.

Subsequent refinements were carried out with equivalent thermal parameters for non-hydrogen atoms and isotropic temperature factors for the hydrogen atoms, which were placed at chemically acceptable positions. The hydrogen atoms were allowed to ride on their parent atoms (Table-4).

The ORTEP of the molecule with thermal ellipsoids drawn at 50 % probability is shown in Fig. 1. The structure exhibits

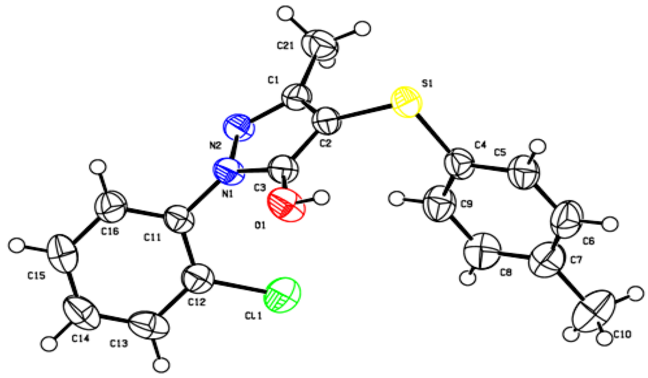


Fig. 1. ORTEP diagram with thermal ellipsoids drawn at 50 % probability (CCDC: 1561633)

TABLE-2 BOND LENGTHS (Å) AND BOND ANGLES (°)					
Bond lengths (Å)		Bond angles (°)			
Atom	Distance	Atom	Angle	Atom	Angle
C11-C12	1.725(3)	C2-S1-C4	101.97(10)	C2-S1-C4	101.97(10)
S1-C4	1.786(3)	N2-N1-C11	121.23(17)	N2-N1-C11	121.23(17)
N1-N2	1.380(3)	N1-N2-C1	108.37(17)	N1-N2-C1	108.37(17)
N1-C11	1.422(3)	N2-C1-C21	120.7(2)	N2-C1-C2	109.48(19)
C1-C2	1.381(4)	S1-C2-C1	127.60(17)	C2-C1-C21	129.80(19)
C2-C3	1.423(3)	C1-C2-C3	107.57(17)	S1-C2-C3	124.59(17)
C4-C9	1.388(4)	O1-C3-C2	133.12(19)	O1-C3-N1	121.96(19)
C6-C7	1.387(5)	S1-C4-C5	118.15(19)	N1-C3-C2	104.91(19)
C7-C10	1.510(5)	C5-C4-C9	118.8(2)	S1-C4-C9	123.08(16)
C11-C12	1.389(3)	C5-C6-C7	121.5(3)	C4-C5-C6	120.2(3)
C12-C13	1.387(4)	C6-C7-C10	121.8(3)	C6-C7-C8	117.6(3)
C14-C15	1.371(4)	C7-C8-C9	121.5(3)	C8-C7-C10	120.6(3)
S1-C2	1.7406(19)	N1-C11-C12	120.84(17)	C4-C9-C8	120.4(3)
O1-C3	1.251(3)	C12-C11-C16	119.72(19)	N1-C11-C16	119.42(19)
N1-C3	1.380(3)	Cl1-C12-C13	119.53(18)	Cl1-C12-C11	120.64(17)
N2-C1	1.327(3)	C12-C13-C14	119.9(3)	C11-C12-C13	119.8(2)
C1-C21	1.487(4)	C14-C15-C16	120.4(3)	C13-C14-C15	120.5(3)
C4-C5	1.388(3)	N2-N1-C3	109.66(17)	C11-C16-C15	119.7(3)
C5-C6	1.387(4)	C3-N1-C11	127.43(19)	N2-C1-C2	109.48(19)
C7-C8	1.387(4)	N2-C1-C21	120.7(2)	C2-C1-C21	129.80(19)
C8-C9	1.383(4)	O1-C3-N1	121.96(19)	S1-C2-C3	124.59(17)
C11-C16	1.379(3)	N1-C3-C2	104.91(19)	–	–
C13-C14	1.365(4)	–	–	–	–
C15-C16	1.383(4)	–	–	–	–

TABLE-3
TORSION ANGLES (°)

Atom 1	Atom 2	Atom 3	Atom 4	Torsion angle	Atom 1	Atom 2	Atom 3	Atom 4	Torsion angle
C2	S1	C4	C5	-165.36(17)	C2	S1	C4	C9	14.1(3)
C4	S1	C2	C1	-98.32(18)	C4	S1	C2	C3	75.27(19)
N2	N1	C3	O1	-179.68(18)	N2	N1	C3	C2	0.9(2)
C3	N1	N2	C1	-1.4(2)	N2	N1	C11	C12	99.0(2)
N2	N1	C11	C16	-82.4(3)	C11	N1	N2	C1	-167.65(16)
C3	N1	C11	C12	-64.7(4)	C3	N1	C11	C16	114.0(3)
C11	N1	C3	O1	-14.5(4)	C11	N1	C3	C2	166.07(19)
N1	N2	C1	C2	1.3(3)	N1	N2	C1	C21	-178.11(15)
N2	C1	C2	S1	173.71(16)	N2	C1	C2	C3	-0.8(3)
C21	C1	C2	S1	-6.9(4)	C21	C1	C2	C3	178.6(2)
S1	C2	C3	O1	5.9(4)	S1	C2	C3	N1	-174.76(14)
C1	C2	C3	O1	-179.4(3)	C1	C2	C3	N1	-0.1(3)
S1	C4	C5	C6	-179.58(17)	S1	C4	C9	C8	-179.11(17)
C5	C4	C9	C8	0.3(4)	C9	C4	C5	C6	1.0(4)
C4	C5	C6	C7	-1.3(5)	C5	C6	C7	C8	0.2(5)
C5	C6	C7	C10	-179.9(3)	C6	C7	C8	C9	1.1(5)
C10	C7	C8	C9	-178.8(3)	C7	C8	C9	C4	-1.4(5)
N1	C11	C12	Cl1	-2.6(4)	N1	C11	C12	C13	176.77(19)
N1	C11	C16	C15	-177.3(2)	C12	C11	C16	C15	1.3(4)
C16	C11	C12	Cl1	178.8(2)	C16	C11	C12	C13	-1.9(4)
Cl1	C12	C13	C14	-179.71(19)	C11	C12	C13	C14	0.9(4)
C12	C13	C14	C15	0.6(5)	C13	C14	C15	C16	-1.1(5)
C14	C15	C16	C11	0.1(5)	–	–	–	–	–

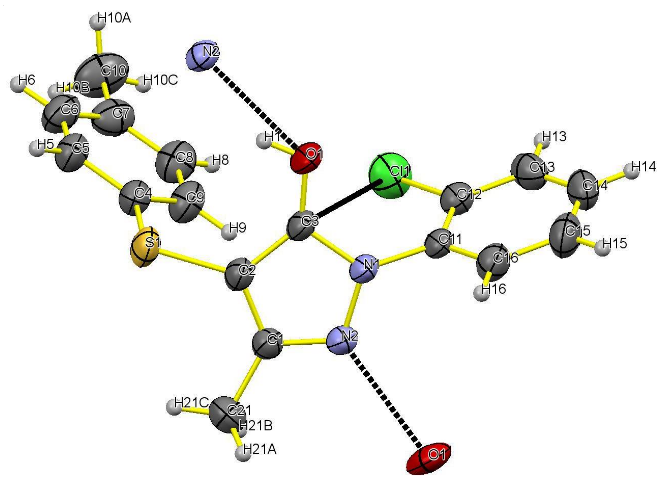
inter-molecular hydrogen bonds of the type O–H---N. O1–H1---N2 has a length of 2.619(3) Å with an angle of 148.64° along with the symmetry codes X, -Y+1/2, Z+1/2-1 respectively (Fig. 2). The stability of the crystal structure can be accounted by the hydrogen bonds.

Conclusion

In conclusion, we have developed an efficient and simple protocol for the synthesis of N-chlorosuccinimide mediated sulfenylated pyrazoles at room temperature. N-Chlorosuccinimide was demonstrated to facilitate this transformation possibly by generating more reactive phenyl hypochlorothioite *in situ* from thiophenols. The synthesized product was characterized by spectroscopic techniques and X-ray diffraction studies. The X-ray studies shows that the inter-molecular hydrogen bonding of the type O–H---N and the pyrazole ring gives pentagonal-planer conformation perpendicular to the phenyl rings.

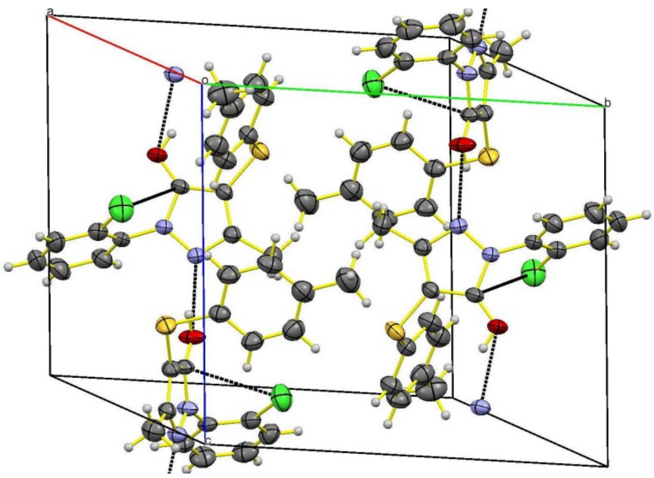
ACKNOWLEDGEMENTS

The authors are thankful to Head, Department of Chemistry, Sardar Patel University for providing necessary research facilities. We are also thankful to Center of Excellence NFDD Complex, Department of Chemistry, Saurashtra University, Rajkot for Single crystal XRD analysis.



Possible hydrogen bonds (Å):

Donor	H	Acceptor	
O1	H1	N2[1]	
D---A	D–H	H---A	D–H---A
2.619(3)	0.82	1.88	148.64



Symmetry operators:
X, -Y+1/2, Z+1/2-1

Fig. 2. Possible hydrogen bonds, symmetry operators and crystal packing arrangement view along the b-axis showing N-H---O hydrogen bonds

TABLE-4
ATOMIC COORDINATES AND EQUIVALENT THERMAL PARAMETERS OF THE NON-HYDROGEN ATOMS

Atom	x	y	z	Beq
Cl1	0.66727(7)	0.05292(5)	0.47096(7)	5.05(2)
S1	0.59025(7)	0.36797(4)	0.27472(5)	3.72(2)
O1	0.8377(2)	0.2085(1)	0.3446(2)	4.18(4)
N1	0.8345(2)	0.2229(1)	0.5432(2)	2.96(3)
N2	0.7647(2)	0.2753(1)	0.6058(2)	2.89(3)
C1	0.6806(3)	0.3326(2)	0.5273(2)	2.84(4)
C2	0.6908(3)	0.3178(2)	0.4117(2)	2.97(4)
C3	0.7903(3)	0.2467(2)	0.4210(2)	2.92(4)
C4	0.4520(3)	0.2873(2)	0.2103(2)	3.32(4)
C5	0.3707(3)	0.2952(2)	0.0873(2)	3.92(5)
C6	0.2616(3)	0.2345(2)	0.0335(3)	4.51(6)
C7	0.2325(3)	0.1639(2)	0.0994(3)	4.32(5)
C8	0.3162(3)	0.1561(2)	0.2217(3)	4.31(5)
C9	0.4234(3)	0.2171(2)	0.2771(3)	3.98(5)
C10	0.1140(4)	0.0974(3)	0.0413(4)	6.03(7)
C11	0.9096(3)	0.1447(2)	0.5966(2)	2.75(4)
C12	0.8443(3)	0.0623(2)	0.5678(2)	3.19(4)
C13	0.9223(3)	-0.0135(2)	0.6163(3)	4.00(5)
C14	1.0622(4)	-0.0066(2)	0.6934(3)	4.44(5)
C15	1.1260(3)	0.0747(2)	0.7243(3)	4.57(6)
C16	1.0502(3)	0.1508(2)	0.6761(2)	3.70(4)
C21	0.5948(3)	0.4000(2)	0.5694(3)	4.12(5)

$B_{eq} = 8/3\ \pi^2\ (U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$

REFERENCES

1. D.J. Ager, Silicon-Containing Carbonyl Equivalents, *Chem. Soc. Rev.*, **11**, 493 (1982); https://doi.org/10.1039/cs9821100493.
2. T. Kondo and T.-A. Mitsudo, Metal-Catalyzed Carbon-Sulfur Bond Formation, *Chem. Rev.*, **100**, 3205 (2000); https://doi.org/10.1021/cr9902749.
3. T. Konosu, S. Oida, Y. Nakamura, S. Seki, T. Uchida, A. Somada, M. Mori, Y. Harada, Y. Kamai, T. Harasaki, T. Fukuoka, S. Ohya, H. Yasuda, T. Shibayama, S. Inoue, A. Nakagawa and Y. Seta, Synthesis and *in vitro* Antifungal Activities of Novel Triazole Antifungal Agent CS-758, *Chem. Pharm. Bull.*, **49**, 1647 (2001); https://doi.org/10.1248/cpb.49.1647.
4. A.Y. Sizov, A.N. Kovregin and A.F. Ermolov, Fluorine-Containing Alkyl(aryl) Vinyl Sulfides, *Russian Chem. Rev.*, **72**, 357 (2003); https://doi.org/10.1070/RC2003v072n04ABEH000784.
5. S. Guo, W. He, J. Xiang and Y. Yuan, Palladium-Catalyzed Direct Thiolation of Ethers with Sodium Sulfinates, *Tetrahedron Lett.*, **55**, 6407 (2014); https://doi.org/10.1016/j.tetlet.2014.09.098.
6. X. Zhao, L. Zhang, T. Li, G. Liu, H. Wang and K. Lu, *p*-Toluene-sulphonic Acid-Promoted, I_2-Catalysed Sulphenylation of Pyrazolones with Aryl Sulphonyl Hydrazides, *Chem. Commun.*, **50**, 13121 (2014); https://doi.org/10.1039/C4CC05237D.
7. P. Saravanan and P. Anbarasan, Palladium Catalyzed Aryl(alkyl)thiolation of Unactivated Arenes, *Org. Lett.*, **16**, 848 (2014); https://doi.org/10.1021/ol4036209.
8. A. Correa, M. Carril and C. Bolm, Iron-Catalyzed S-Arylation of Thiols with Aryl Iodides, *Angewandte Chemie*, **120**, 2922 (2008); https://doi.org/10.1002/ange.200705668.
9. H. Tian, C. Zhu, H. Yang and H. Fu, Iron or Boron-Catalyzed C–H Arylthiation of Substituted Phenols at Room Temperature, *Chem. Commun.*, **50**, 8875 (2014); https://doi.org/10.1039/C4CC03600J.
10. T.-T. Wang, F.-X. Wang, F.-L. Yang and S.-K. Tian, Palladium-Catalyzed Aerobic Oxidative Coupling of Enantioenriched Primary Allylic Amines with Sulfonyl Hydrazides Leading to Optically Active Allylic Sulfones, *Chem. Commun.*, **50**, 3802 (2014); https://doi.org/10.1039/C4CC00275J.
11. W.-Y. Wu, J.-C. Wang and F.-Y. Tsai, A Reusable $FeCl_3 \cdot 6H_2O$/Cationic 2,2'-Bipyridyl Catalytic System for the Coupling of Aryl Iodides with Thiols in Water under Aerobic Conditions, *Green Chem.*, **11**, 326 (2009); https://doi.org/10.1039/b820790a.
12. I.P. Beletskaya and V.P. Ananikov, Transition-Metal-Catalyzed C–S, C–Se, and C–Te Bond Formation *via* Cross-Coupling and Atom-Economic Addition Reactions, *Chem. Rev.*, **111**, 1596 (2011); https://doi.org/10.1021/cr100347k.
13. S.S. Mansy and J. Cowan, Iron-Sulfur Cluster Biosynthesis: Toward an Understanding of Cellular Machinery and Molecular Mechanism, *Acc. Chem. Res.*, **37**, 719 (2004); https://doi.org/10.1021/ar0301781.
14. T. Punniyamurthy, S. Velusamy and J. Iqbal, Recent Advances in Transition Metal Catalyzed Oxidation of Organic Substrates with Molecular Oxygen, *Chem. Rev.*, **105**, 2329 (2005); https://doi.org/10.1021/cr050523v.
15. W. Ge and Y. Wei, Iodine-Catalyzed Oxidative System for 3-Sulfenylation of Indoles with Disulfides using DMSO as Oxidant under Ambient Conditions in Dimethyl Carbonate, *Green Chem.*, **14**, 2066 (2012); https://doi.org/10.1039/c2gc35337g.
16. C.D. Prasad, S.J. Balkrishna, A. Kumar, B.S. Bhakuni, K. Shrimali, S. Biswas and S. Kumar, Transition-Metal-Free Synthesis of Unsymmetrical Diaryl Chalcogenides from Arenes and Diaryl Dichalcogenides, *J. Org. Chem.*, **78**, 1434 (2013); https://doi.org/10.1021/jo302480j.
17. P. Sang, Z. Chen, J. Zou and Y. Zhang, K_2CO_3 Promoted Direct Sulfenylation of Indoles: A Facile Approach towards 3-Sulfenylindoles, *Green Chem.*, **15**, 2096 (2013); https://doi.org/10.1039/c3gc40724a.
18. Y. Liao, P. Jiang, S. Chen, H. Qi and G.-J. Deng, Iodine-Catalyzed Efficient 2-Arylsulfanylphenol Formation from Thiols and Cyclohexanones, *Green Chem.*, **15**, 3302 (2013); https://doi.org/10.1039/c3gc41671b.
19. C.-R. Liu and L.-H. Ding, Byproduct Promoted Regioselective Sulfenylation of Indoles with Sulfinic Acids, *Org. Biomol. Chem.*, **13**, 2251 (2015); https://doi.org/10.1039/C4OB02575J.
20. F. Xiao, S. Chen, J. Tian, H. Huang, Y. Liu and G.-J. Deng, Chemoselective Cross-Coupling Reaction of Sodium Sulfinates with Phenols under Aqueous Conditions, *Green Chem.*, **18**, 1538 (2016); https://doi.org/10.1039/C5GC02292D.
21. F. Xiao, H. Xie, S. Liu and G.J. Deng, Iodine-Catalyzed Regioselective Sulfenylation of Indoles with Sodium Sulfinates, *Adv. Synth. Catal.*, **356**, 364 (2014); https://doi.org/10.1002/adsc.201300773.
22. P. Khloya, S. Kumar, P. Kaushik, P. Surain, D. Kaushik and P.K. Sharma, Synthesis and Biological Evaluation of Pyrazolylthiazole Carboxylic Acids as Potent Anti-inflammatory–Antimicrobial Agents, *Bioorg. Med. Chem. Lett.*, **25**, 1177 (2015); https://doi.org/10.1016/j.bmcl.2015.02.004.
23. V. Kumar, K. Kaur, G.K. Gupta and A.K. Sharma, Pyrazole containing natural products: Synthetic preview and biological significance, *Eur. J. Med. Chem.*, **69**, 735 (2013); https://doi.org/10.1016/j.ejmech.2013.08.053.
24. A. Bell, Sildenafil (VIAGRA^{TM}), A Potent and Selective Inhibitor of Type 5 cGMP Phosphodiesterase with Utility for the Treatment of Male Erectile Dysfunction, *Bioorg. Med. Chem. Lett.*, **6**, 1819 (1996); https://doi.org/10.1016/0960-894X(96)00323-X.
25. V.B. Purohit, S.C. Karad, K.H. Patel and D.K. Raval, Palladium *N*-Heterocyclic Carbene Catalyzed Regioselective Thiolation of 1-Aryl-3-methyl-1*H*-pyrazol-5(4*H*)-ones using Aryl Thiols, *Tetrahedron*, **72**, 1114 (2016); https://doi.org/10.1016/j.tet.2016.01.012.
26. H. B'Bhatt and S. Sharma, Synthesis and Antimicrobial Activity of Pyrazole Nucleus Containing 2-Thioxothiazolidin-4-one Derivatives, *Arabian J. Chem.*, **10**, S1590 (2017); https://doi.org/10.1016/j.arabjc.2013.05.029.
27. S. Malladi, A.M. Isloor, S.K. Peethambar, B.M. Ganesh and P.S. Goud, Synthesis and Antimicrobial Activity of Some New Pyrazole Containing Cyanopyridone Derivatives, *Der Pharm. Chem.*, **4**, 43 (2012).
28. M. Abdel-Aziz, G.E.-D.A. Abuo-Rahma and A.A. Hassan, Synthesis of Novel Pyrazole Derivatives and Evaluation of their Antidepressant and Anticonvulsant Activities, *Eur. J. Med. Chem.*, **44**, 3480 (2009); https://doi.org/10.1016/j.ejmech.2009.01.032.

29. D. Kaushik, S.A. Khan, G. Chawla and S. Kumar, *N'*-[(5-Chloro-3-methyl-1-phenyl-1*H*-pyrazol-4-yl)methylene] 2/4-Substituted Hydrazides: Synthesis and Anticonvulsant Activityt, *Eur. J. Med. Chem.*, **45**, 3943 (2010); https://doi.org/10.1016/j.ejmech.2010.05.049.
30. K.M. Dawood, T.M. Eldebss, H.S. El-Zahabi, M.H. Yousef and P. Metz, Synthesis of Some New Pyrazole-Based 1,3-Thiazoles and 1,3,4-Thiadiazoles as Anticancer Agents, *Eur. J. Med. Chem.*, **70**, 740 (2013); https://doi.org/10.1016/j.ejmech.2013.10.042.
31. I. Koca, A. Özgür, K.A. Coskun and Y. Tutar, Synthesis and Anticancer Activity of Acyl Thioureas Bearing Pyrazole Moiety, *Bioorg. Med. Chem.*, **21**, 3859 (2013); https://doi.org/10.1016/j.bmc.2013.04.021.
32. A. Vijesh, A.M. Isloor, P. Shetty, S. Sundershan and H.K. Fun, New Pyrazole Derivatives Containing 1,2,4-Triazoles and Benzoxazoles as Potent Antimicrobial and Analgesic Agents, *Eur. J. Med. Chem.*, **62**, 410 (2013); https://doi.org/10.1016/j.ejmech.2012.12.057.
33. N. Gökhan-Kelekci, S. Yabanoglu, E. Küpeli, U. Salgin, Ö. Özgen, G. Ucar, E. Yesilada, E. Kendi, A. Yesilada and A.A. Bilgin, A New Therapeutic Approach in Alzheimer Disease: Some Novel Pyrazole Derivatives as Dual MAO-B Inhibitors and Antiinflammatory Analgesics, *Bioorg. Med. Chem.*, **15**, 5775 (2007); https://doi.org/10.1016/j.bmc.2007.06.004.
34. R.C. Khunt, V.M. Khedkar, R.S. Chawda, N.A. Chauhan, A.R. Parikh and E.C. Coutinho, Synthesis, Antitubercular Evaluation and 3D-QSAR Study of *N*-Phenyl-3-(4-fluorophenyl)-4-substituted Pyrazole Derivatives, *Bioorg. Med. Chem. Lett.*, **22**, 666 (2012); https://doi.org/10.1016/j.bmcl.2011.10.059.
35. R.B. Pathak, P.T. Chovatia and H.H. Parekh, Synthesis, Antitubercular and Antimicrobial Evaluation of 3-(4-Chlorophenyl)-4-substituted Pyrazole Derivatives, *Bioorg. Med. Chem. Lett.*, **22**, 5129 (2012); https://doi.org/10.1016/j.bmcl.2012.05.063.
36. D. Raffa, B. Maggio, M.V. Raimondi, S. Cascioferro, F. Plescia, G. Cancemi and G. Daidone, Recent Advanced in Bioactive Systems Containing Pyrazole Fused with a Five Membered Heterocycle, *Eur. J. Med. Chem.* **97**, 732 (2015); https://doi.org/10.1016/j.ejmech.2014.12.023.
37. R.D. Kamani, V.B. Purohit, R.P. Thummar, N.H. Sapariya, B.K. Vaghasiya, K.H. Patel, C.T. Pashavan, M.K. Shah and D.K. Raval, One-Pot Catalyst-Free Direct Sulfenylation of 1-Aryl Pyrazolones with Aryl Thiols at Room Temperature, *Chem. Select*, **2**, 9670 (2017); https://doi.org/10.1002/slct.201701924.
38. A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. Burla, G.T. Polidori and M. Camalli, SIR92 - A Program for Automatic Solution of Crystal Structures by Direct Methods, *J. Appl. Crystallogr.*, **27**, 435 (1994); https://doi.org/10.1107/S002188989400021X.
39. J.W. Pflugrath, The Finer Things in X-Ray Diffraction Data Collection, *Acta Cryst. D*, **55**, 1718 (1999); https://doi.org/10.1107/S090744499900935X.
40. L. Song and T. Iyoda, Supramolecular Framework Based on Pyridinio-diketone Ligand *via* Non-classic Hydrogen Bonding, *J. Inorg. Organomet. Polym. Mater.*, **19**, 124 (2009); https://doi.org/10.1007/s10904-008-9251-7.
41. T. Kimura, C. Chang, F. Kimura and M. Maeyama, The Pseudo-Single-Crystal Method: A Third Approach to Crystal Structure Determination, *J. Appl. Crystallogr.*, **42**, 535 (2009); https://doi.org/10.1107/S0021889809013430.
42. D.T. Cromer and J.-T. Waber, International Tables for X-Ray Crystallography, Kynoch Press: Birmingham, England (1974).
43. J.A. Ibers and W.C. Hamilton, Dispersion Corrections and Crystal Structure Refinements, *Acta Crystallogr.*, **17**, 781 (1964); https://doi.org/10.1107/S0365110X64002067.
44. A.J.C. Wilson, International Tables for Crystallography: Mathematical, Physical and Chemical Tables, International Union of Crystallography (1992).
45. D. Creagh and W.J. McAuley, ed.: A.J.C. Wilson, International Tables for Crystallography, Kluwer Academic Publishers, Bostan, pp. 200-206 (1992).
46. CRYSTAL STRUCTURE 4.0, Crystal Structure Analysis Package, Rigaku Corporation, Tokyo, Japan (2000-2010).
47. G.M. Sheldrick, Crystal Structure Refinement with SHELXL, *Acta Crystallogr. C: Struct. Chem.*, **C71**, 3 (2015); https://doi.org/10.1107/S2053229614024218.
48. A.-X. Tian, X.-B. Ji, N. Sun, R. Xiao, Y.-Y. Zhao, H.-P. Ni, Y. Tian and J. Ying, Four New Coordination Polymers Constructed by 2-(4-Thiazolyl)benzimidazole and 1,3,5-Benzenetricarboxylic Acid, *J. Chem. Crystallogr.*, **47**, 1 (2017); https://doi.org/10.1007/s10870-016-0674-7.
49. J. Bruno-Colmenarez, R. Atencio, M. Quintero, L. Seijas, R. Almeida and L. Rincón, Crystal Structure Analysis and Topological Study of Non-covalent Interactions in 2,2-Biimidazole:Salicylic Acid 2:1 Co-crystal, *J. Chem. Crystallogr.*, **47**, 47 (2017); https://doi.org/10.1007/s10870-017-0679-x.