Molecular Structure, Hirshfeld Surface Analysis, Optical and Electrochemical Studies of Stable Solid Diazonium Salt of p-Sulphophenyl-3-methyl-5-pyrazolone

Ghulam Shabir

Quaid-i-Azam University Islamabad: Quaid-i-Azam University

Ghulam Hussain

Punjab University: Panjab University

Aamer Saeed (✉ aamersaeed@yahoo.com)

Quaid-i-Azam University <https://orcid.org/0000-0002-7112-9296>

Hafiz Tasawwar Hussain

Government College University Faisalabad

Tuncer Hokelek

Hacettepe University: Hacettepe Universitesi

Mauricio Erben

National University of La Plata: Universidad Nacional de la Plata

Ulrich Flörke

Paderborn University: Universitat Paderborn

Research Article

Keywords: p-Sulphophenyl-3-methyl-5-pyrazolone, diazotization, Hirshfeld surface analysis, UV, Energy Gap, crystal structure

Posted Date: April 12th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-365936/v1>

License: This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Abstract

The title compound is a new pyrazolone derivative which was synthesized starting from *p*-sulphophenyl-3-methyl-5-pyrazolone (**1**) by nitrosation at low temperature to afford the corresponding *p*-sulphophenyl-3-methyl-4-nitroso-5-pyrazolone which can exist both in nitroso (**2a**) and oxime tautomeric forms (**2b**). Reduction of the latter using zinc with hydrochloric acid furnished the 4-amino-*p*-sulphophenyl-3-methyl-5-pyrazolone (**3**). The diazotization of (**3**) under careful control of temperature and pH afforded the *p*-Sulphophenyl – 3-methyl-5-pyrazolone diazonium salt (**4**) which was re-crystallized from acidified ethanol to afford crystal suitable for X-ray studies. UV-visible spectrum and cyclic voltammetric studies were also carried out indicating λ_{max} at 420 nm and HOMO-LUMMO energy gap was also calculated (E_g) of 2.95 eV. The molecular and crystal structures of the compound were clarified by single crystal X-ray diffraction indicated that it crystallizes as the sodium salt in the triclinic space group *P*-1, with the 4-azo-pyrazolone and the sulphophenyl groups being nearly coplanar. To get an insight to the intermolecular interactions in the crystal a Hirshfeld surface analysis was also carried out.

Research Highlights

- Solid stable diazonium salt, synthetic precursor towards acid Azo dyes
- Triclinic geometry with coplanar 4-azo-pyrazolone and the sulphophenyl groups
- Absorption maximum (λ_{max}) in visible range at 420 nm.

Introduction

Aryl diazonium salts are versatile intermediates having a variety of applications in organic syntheses [1]. In addition, aryl diazonium salts are surrogate to aryl halides, which are mostly used in transition metal mediated cross coupling reactions for carbon-carbon and carbon-hetero atom bond formation [2]. Good leaving nature of the stable N_2 molecule found in diazonium salts makes them versatile electrophiles which do not interfere with the reaction mixture and allows the use of ambient reaction conditions. The chemistry of diazonium salts has been studied for long starting around 1858. There are several named reactions associated with aryl diazonium salts including the Sandmeyer reaction (1884), the Pschorr cyclization (1896), the Gomberg-Bachmann reaction (1924), and the Meerwein arylation (1939) [3]. Meerwein first reported the arylation of coumarin, cinnamic acid, and acrylic acid with aryl diazonium salts catalyzed by copper (II) salts [4]. Later, the scope of this reaction was further extended to electron rich olefins [5]. New improved variants of Meerwein and Pschorr reactions have been developed by several researchers to achieve the syntheses of complex organic molecules [6]. The syntheses of benzothiophenes from the corresponding *o*-methylthio aryl diazonium salts have been investigated by Zanradi [7]. Heinrich and coworkers reported different types of Meerwein arylation reactions by employing TiCl_3 and FeSO_4 as chemical reductants [8–10]. Schiesser reported the syntheses of benzoselenophene and benzothiophene through a radical cyclization process involving the addition of aryl radicals to alkynes [11]. Alternatively, aryl radicals can also be generated from diazonium salts using organic

reducing agents such as tetrakis(dimethylamino)ethylene (TDAE) [12]. The aryl diazonium salt generates an aryl radical and dinitrogen by taking up an electron from the reducing agent; in the classical reactions the catalytic or stoichiometric amounts of transition-metal salts have been used. Visible light can also provide the required redox energy and it is an ideal reagent for organic syntheses [13]. Many research groups focus on the heterocyclic azole compounds, especially pyrazolone derivatives which have a wide range of pharmacological applications such as analgesic [14], anti-inflammatory, anti-cancer [15] and antimicrobial activities [16]. The pyrazolone scaffold was widely used in treating neurodegenerative disorder [17], cardiovascular diseases, rheumatoid arthritis (RA), osteoarthritis (OA) and Crohn's disease. Though the pyrazolone derivatives exhibit widespread pharmacological properties, the literature review shows that they are highly related to the treatment of inflammatory diseases [19–22].

In this work, a new diazonium pyrazolone derivative, namely *p*-sulphophenyl-3-methyl-5-pyrazolone diazonium, is synthesized by diazotization of 4-amino-*p*-sulphophenyl-3-methyl-5-pyrazolone under careful control of temperature and pH. The molecular and crystal structures of the sodium salt were determined by X-ray diffraction technique. The electronic and electrochemical properties were determined in aqueous media by UV-visible and cyclic voltammetric studies.

Experimental

2.1 Materials and Method

p-Sulphophenyl-3-methyl-5-pyrazolone was obtained from Sigma-Aldrich, sodium nitrite and hydrochloric acid were purchased from Daejing Korea. Zinc dust, sulfamic acid and sodium hydroxide were common laboratory grade chemicals.

General Procedure for Synthesis of Diazonium Salt:

a) Nitrosation of *p*-Sulphophenyl-3-methyl-5-pyrazolone

Hydrochloric acid (45 ml) was added to a well stirred suspension of 1-(*p*-methylphenyl)-3-methyl-5-pyrazolone (**1**) (25.4 g, 0.1 mol) in H₂O (250 ml). The reaction mixture was cooled to 0–5 °C in an ice bath. A previously cooled solution of NaNO₂ (6.9 g, 0.1 mol) in H₂O (25 ml) at 0 °C, was then added to the reaction mixture over a period of 35 min with stirring which was continued for 1 h maintaining the same temperature, until a positive test for nitrous acid formation. The excess of nitrous acid was destroyed with required amount of sulphamic acid till the (nitroso/oxime) (**2**) was filtered after salting out. The nitroso was reduced by stirring in water (200 ml) containing HCl (85 ml) and Zinc metal (23 g) at reflux for 4 h. On completion of the reaction, the pH was raised to 9 using 6N NaOH, to precipitate the 1-(*p*-methylphenyl)-3-methyl-4-aminopyrazolone (**3**).

b) Diazotization and Crystallization

To the well stirred ice jacketed aqueous solution (2.69 g) of 1-(*p*-methylphenyl)-3-methyl-4-aminopyrazolone (**3**) at 0–5 °C was added sodium nitrite solution (0.7 g). It was added the 3.5 mL of

concentrated HCl. The reaction mixture was vigorously stirred for 1 h at low temperature to achieve the formation of 4-amino-*p*-sulphophenyl-3-methyl-5-pyrazolone diazonium (**4**).

2.2 X-ray crystallography

The crystallographic data of the diazonium salts were collected on a Bruker AXS SMART APEX diffractometer using Mo K_{α} radiation ($\lambda = 0.71073 \text{ \AA}$) [23]. The multi-scan absorption correction [SADABS] [24] applied data were processed by SHELX97 program package [*SHELXS97* and *SHELXL97*] [25] for solving and refining the structures, and ORTEP-3 [26] and PLATON [37] programs were used in drawings. All non H-atoms were refined anisotropically, water hydrogen atoms were clearly located from difference Fourier maps. Remaining hydrogen atoms were geometrically positioned and refined by riding on the carbon atoms with isotropic displacement parameters $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ or $1.5 U_{\text{eq}}(\text{CH}_3)$ and C-H 0.95–0.98 $\text{\AA}$. O-H distances were restrained with DFIX 0.84. Refinement converged at $R_1 = 0.057 [I > 2\sigma(I)]$, $wR_2 = 0.102 [all\ data]$ and $S = 0.96$; $\Delta\rho_{\text{max}}$ and $\Delta\rho_{\text{min}}$ were 0.38 and $-0.35 \text{ e\AA}^{-3}$, respectively. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1452211. Copies of available material can be obtained free of charge via www.ccdc.cam.ac.uk. The experimental details are given in Table 1.

Table 1
Experimental Details for the Diazonium Salt.

Crystal data	
Chemical formula	$\text{C}_{10}\text{H}_9\text{N}_4\text{O}_5\text{S}\cdot\text{Na}\cdot 2(\text{H}_2\text{O})$
M_r	338.28
Crystal system, space group	Triclinic, $P-1$
Temperature (K)	130
a, b, c (Å)	7.2912 (19), 9.793 (2), 10.482 (3)
α, β, γ (°)	102.452 (5), 104.497 (6), 92.293 (6)
V (Å ³)	704.1 (3)
Z	2
Radiation type	Mo K_α
μ (mm ⁻¹)	0.30
Crystal size (mm)	0.47 × 0.14 × 0.09
Data collection	
Diffractometer	Bruker AXS <i>SMART APEX</i>
Absorption correction	Multi-scan (<i>SADABS</i> , Sheldrick, 2004)
$T_{\min}, T_{\max}$	0.873, 0.974
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	6673, 3344, 2059
R_{int}	0.063
$(\sin \theta/\lambda)_{\max}$ (Å ⁻¹)	0.658
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.057, 0.102, 0.96
No. of reflections	3344
No. of parameters	216
No. of restraints	6

Computer programs: *SMART* (Bruker, 2002), *SAINT* (Bruker, 2002), *SAINT*, *SHELXTL* (Sheldrick, 2008), *SHELXL2013* (Sheldrick, 2013), *SHELXTL* and local programs.

Crystal data	
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}, \Delta\rho_{\min}$ (e Å ⁻³)	0.38, - 0.35
<i>Computer programs: SMART</i> (Bruker, 2002), <i>SAINT</i> (Bruker, 2002), <i>SAINT</i> , <i>SHELXTL</i> (Sheldrick, 2008), <i>SHELXL2013</i> (Sheldrick, 2013), <i>SHELXTL</i> and local programs.	

Results And Discussion

3.1 Synthesis and X-Ray Crystal Study

Synthesis of diazonium salt of (**4**) was achieved according to the route sketched in Scheme 1.

1-(4-sulphophenyl) 3-methyl-2-pyrazolin-5-one (**1**) was nitrosated at -2-0 °C using NaNO₂ and HCl as described by Knorr¹ to afford the nitroso compound (**2**) which was filtered to remove some terry material. The nitroso derivative (**2a**), usually exists in its tautomeric oxime (**2b**) form as indicated by its FTIR spectrum, was salted out by common salt, and dried after filtration. Reduction of (**2**) was achieved and zinc metal in the presence of HCl added in small portions at reflux to afford a colorless solution. A small amount of additional zinc was added, and the resultant amine hydrochloride was quenched to -7 °C. The excessive un-reacted zinc was removed by filtration. The amine hydrochloride (**3**) was diazotized very carefully by using an aqueous solution of NaNO₂ and HCl at -5 to -3 °C to provide the title compound (**4**). The careful control of temperature is essential to avoid the formation of rubazoic acid, which is routinely formed during this reaction on increasing temperature due to oxidizing action of nitrous acid formed *in situ*.

In the molecular structure of diazonium salt the phenyl- as well as the pyrazolone-rings lie almost in plane, the relevant torsion angle C1-N1-C5-C6 measures 3.3(5)°. Essential bonding parameters of the pyrazolone moiety are N1-N2 [1.407(3) Å], C1-O1 [1.230(3) Å], C2-N3 [1.325(4) Å], N3-N4 [1.110(3) Å] and C2-N3-N4 [177.3(3)°]. These are in close agreement with those of 4-Diazonio-2-methyl-5-nitro-3-oxo-2,3-dihydropyrazol-1-ide (WETGEJ)^{x1} with N-N [1.362 Å], C-N2 [1.323 Å], (C)N-N [1.116 Å] and C-N-N [177.7°].

The crystal structure (Fig. 2) shows various hydrogen bonding patterns with the solvent water molecules. Strongest interactions are O10-H11...O11ⁱⁱⁱ [symmetry code: (iii) -x + 1, -y + 1, -z + 2] with H...O of 1.94(1) Å, O20-H21...O12^{iv} [symmetry code: (iv) x, y + 1, z] with 1.98(1) Å, O10-H12...O12ⁱ [symmetry code: (i) x - 1, y + 1, z] with 2.01(2) Å and O20-H22...N2 with 2.14(1) Å. An intramolecular C6-H6A...O1 bond is connected with the planar arrangement of both the aromatic ring planes.

The asymmetric unit of diazonium salt is depicted in Fig. 1; the unit cell with intermolecular H-bonding pattern is shown in Fig. 2 (Table 2). Table 3 gives the selected bond lengths (Å) and angles (°).

Table 2
Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
C6—H6A···O1	0.95	2.21	2.878 (4)	126
O10—H12···O12 ⁱ	0.84 (1)	2.01 (2)	2.808 (3)	161 (3)
O10—H11···O11 ⁱⁱⁱ	0.84 (1)	1.94 (1)	2.774 (3)	173 (4)
O20—H22···N2	0.85 (1)	2.14 (1)	2.981 (4)	173 (4)
O20—H21···O12 ^{iv}	0.84 (1)	1.98 (1)	2.810 (4)	172 (5)
Symmetry codes (i) $x - 1, y + 1, z$; (iii) $-x + 1, -y + 1, -z + 2$; (iv) $x, y + 1, z$.				

Table 3
Selected geometric parameters (Å) of 1-(*p*-sulphophenyl)-3-methyl-4-azo-5- pyrazolone.

Na—O1ⁱ	2.2763 (15)	N1—C6	1.417 (2)
Na—O5	2.2907 (17)	N2—C9	1.303 (2)
Na—O6	2.3630 (16)	N3—N4	1.109 (2)
Na—O4	2.3733 (15)	N3—C8	1.328 (2)
Na—O6 ⁱⁱ	2.4951 (16)	C1—C2	1.382 (3)
Na—S1	3.3338 (9)	C1—C6	1.387 (3)
Na—Na ⁱⁱ	3.6887 (14)	C1—H1	0.9300
S1—O2	1.4387 (16)	C2—C3	1.380 (3)
S1—O4	1.4439 (14)	C2—H2	0.9300
S1—O3	1.4543 (16)	C3—C4	1.385 (3)
S1—C3	1.7720 (18)	C4—C5	1.383 (3)
O1—C7	1.225 (2)	C4—H4	0.9300
O1—Na ⁱⁱⁱ	2.2763 (15)	C5—C6	1.386 (2)
O5—H1	0.79 (3)	C5—H5	0.9300
O5—H2	0.75 (3)	C7—C8	1.433 (2)
O6—Na ⁱⁱ	2.4951 (16)	C8—C9	1.413 (3)
O6—H3	0.80 (3)	C9—C10	1.488 (3)
O6—H4	0.84 (3)	C10—H10A	0.9600
N1—C7	1.385 (2)	C10—H10B	0.9600
N1—N2	1.405 (2)	C10—H10C	0.9600
Symmetry codes: (i) $x-1, y, z-1$; (ii) $-x-1, -y+1, -z$; (iii) $x+1, y, z+1$.			

3.2 Hirshfeld surface analysis

To visualize the intermolecular interactions in the crystal of the title compound, a Hirshfeld surface (HS) analysis [27] was carried out by using *Crystal Explorer 17.5* [28]. In the HS plotted over d_{norm} (Fig. 3), the

white surface indicates contacts with distances equal to the sum of van der Waals radii, and the red and blue colours indicate distances shorter (in close contact) or longer (distinct contact) than the van der Waals radii, respectively [29]. The bright-red spots appearing near Na, N2, O11, O12 and hydrogen atoms H11, H12, H21, H22 indicate their roles as the respective donors and/or acceptors; they also appear as blue and red regions corresponding to positive and negative potentials on the HS mapped over electrostatic potential [30] as shown in Fig. 4. The blue regions indicate positive electrostatic potential (hydrogen-bond donors), while the red regions indicate negative electrostatic potential (hydrogen-bond acceptors). The shape-index of the HS is a tool to visualize the $\pi \dots \pi$ stacking by the presence of adjacent red and blue triangles; if there are no adjacent red and/or blue triangles, then there are no $\pi \dots \pi$ interactions. Figure 5 clearly suggests that there are no $\pi \dots \pi$ interactions in (I). The overall two-dimensional fingerprint plot, Fig. 6a, and those delineated into $H \dots H$, $H \dots O/O \dots H$, $H \dots N/N \dots H$, $O \dots NA/NA \dots O$, $N \dots O/O \dots N$, $C \dots C$, $C \dots N/N \dots C$, $H \dots C/C \dots H$, $N \dots N$, $H \dots NA/NA \dots H$, $C \dots O/O \dots C$, $O \dots O$, $N \dots NA/NA \dots N$ and $H \dots S/S \dots H$ [31] are illustrated in Figs. 4b–o, respectively, together with their relative contributions to the Hirshfeld surface. The most important interaction is $H \dots H$ (Table 4) contributing 27.5% to the overall crystal packing, which is reflected in Fig. 6b as widely scattered points of high density due to the large hydrogen content of the molecule with the tip at $d_e = d_i = 1.08 \text{ \AA}$. The pair of spikes in the fingerprint plot delineated into $H \dots O/O \dots H$ contacts (Table 4) have a symmetrical distribution of points (26.6% contribution, Fig. 6c) with the tips at $d_e + d_i = 1.78 \text{ \AA}$. The pair of characteristic wings resulting in the fingerprint plots delineated into $H \dots N/N \dots H$, Fig. 6d, contacts with 8.9% contribution to the HS arises from the $H \dots N/N \dots H$ contacts (Table 4) and is viewed as pair of spikes with the tips at $d_e + d_i = 1.96 \text{ \AA}$. The $O \dots NA/NA \dots O$ contacts (8.1%, Fig. 6e) have a scissor-shaped distribution of points with the tips at $d_e + d_i = 2.31 \text{ \AA}$. The $N \dots O/O \dots N$ contacts (7.5%, Fig. 6f) have a fringed-shaped distribution of points with the tips at $d_e + d_i = 2.79 \text{ \AA}$ and $d_e + d_i = 2.82 \text{ \AA}$ for inner and outer fringes, respectively. The $C \dots C$ contacts (6.6%, Fig. 6g) (Table 4) have a bullet-shaped distribution of points with the tip at $d_e = d_i = 1.72 \text{ \AA}$. The $C \dots N/N \dots C$ contacts (Table 4) contribute 5.9% to the overall crystal packing, which are reflected in Fig. 6h with the small tips at $d_e + d_i = 3.28 \text{ \AA}$. In the absence of $C-H \dots \pi$ interactions, the pair of characteristic wings in the fingerprint plot delineated into $H \dots C/C \dots H$ (Table 4) contacts (Fig. 6i, 3.2% contribution to the HS) has the tips at $d_e + d_i = 2.96 \text{ \AA}$. The $N \dots N$ contacts (Table 4) contribute 2.2% to the overall crystal packing, which are reflected in Fig. 6j with the tip at $d_e = d_i = 1.46 \text{ \AA}$. The $H \dots NA/NA \dots H$ contacts have an unsymmetrical distribution of points (1.6% contribution, Fig. 6k) with the tips at $d_e + d_i = 3.28 \text{ \AA}$. Finally, the $C \dots O/O \dots C$ (0.7%, Fig. 6l), $O \dots O$ (0.7%, Fig. 6m), $N \dots NA/NA \dots N$ (0.5%, Fig. 6n) and $H \dots S/S \dots H$ (0.1%, Fig. 6o) contacts with contribution smaller than 1.0% to the HS have scattered points of very low density.

The Hirshfeld surface representations with the function d_{norm} plotted onto the surface are shown for the $H \dots H$, $H \dots O/O \dots H$, $H \dots N/N \dots H$ and $O \dots NA/NA \dots O$, interactions in Figs. 7a–d, respectively.

The Hirshfeld surface analysis confirms the importance of H-atom contacts in establishing the packing. The large number of $H \dots H$ and $H \dots O/O \dots H$ interactions suggest that van der Waals interactions and hydrogen bonding play the major roles in the crystal packing [32].

Table 4
Selected interatomic distances (Å).

H12...S1ⁱ	2.90 (4)	O20...H10A	2.87
S1...H4C ⁱⁱ	3.1624	N2...C7 ⁱⁱ	3.446 (4)
S1...H11 ⁱⁱⁱ	3.13 (4)	N3...C9 ^v	3.323 (4)
H21...S1 ^{iv}	3.02 (5)	N3...N4 ^{ix}	3.091 (4)
O1...N3	2.948 (4)	N4...C9 ^v	3.437 (4)
O1...C6	2.878 (4)	N4...N4 ^{ix}	2.950 (4)
O10...O11 ⁱⁱⁱ	2.774 (3)	H22...N2	2.14 (3)
O11...N4 ^v	2.814 (4)	N2...H10A	2.46
O20...O12 ^{iv}	2.810 (4)	H9A...N4 ^{vi}	2.66
O13...N4 ⁱⁱ	3.016 (4)	C1...C10 ^v	3.543 (4)
O13...C2 ⁱⁱ	3.259 (4)	C1...C5 ^v	3.589 (4)
O13...N3 ⁱⁱ	2.873 (4)	C1...C9 ⁱⁱ	3.585 (4)
O13...N4 ^{vi}	3.117 (4)	C2...C10 ^v	3.500 (4)
O20...N2	2.981 (4)	C2...C5 ^v	3.585 (4)
O1...H6A	2.21	C3...C6 ^v	3.555 (5)
O11...H11 ⁱⁱⁱ	1.93 (4)	C3...C7 ⁱⁱ	3.568 (4)
O11...H9A ^{vii}	2.79	C3...C8 ⁱⁱ	3.559 (4)
O12...H7A	2.45	C5...C5 ⁱⁱ	3.498 (4)
H12...O12 ⁱ	2.01 (4)	C1...H6A	2.66
H21...O12 ^{iv}	1.98 (4)	C3...H22	2.91 (3)
O12...H4C ⁱⁱ	2.66	H4A...H22	2.47
O20...H4B ^{viii}	2.85	H10A...H22	2.35
O20...H4A	2.84		

Symmetry codes: (i) $x-1, y+1, z$; (ii) $-x+2, -y+1, -z+1$; (iii) $-x+1, -y+1, -z+2$; (iv) $x, y+1, z$; (v) $-x+1, -y+1, z+1$; (vi) $x+1, y, z+1$; (vii) $-x+2, -y+1, -z+2$; (viii) $-x+1, -y+2, -z+1$; (ix) $-x+1, -y+1, -z$.

3.3 Optical and Electrochemical Studies

The optical and electrochemical studies of newly synthesized diazonium salt were conducted to get information regarding the absorption intensity and redox behavior.

The UV-visible absorption spectrum of diazonium salt of 4-amino-*p*-sulphophenyl-3-methyl - 5-pyrazolone in ethanol is shown in Fig. 8. The absorption maximum (λ_{max}) of diazonium was taken in ethanol (1×10^{-5} M solution) to observe the molar extinction coefficient of the compound. The molar extinction was found to be $\log \epsilon = 6.5$ and λ_{max} of diazonium was found at 420 nm. This transition can be assigned as due to $n-\pi^*$ and $\pi-\pi^*$ transitions of the azo linkage. This value of the molar extinction coefficient is the evidence of the high absorption intensity. These transitions are bathochromic shifted to higher λ_{max} due to the presence of *o*-hydroxy group to diazo linkage. The hydroxy group has the ability to donate the lone pair of electrons to ring which increases the electron density at the chromophoric motif and hence decreases the energy required for electronic transitions. Moreover, this compound undergoes tautomerism and keto form is formed which increases the stability of azo linkage through strengthening the carbon to nitrogen atom of azo linkage.

The electrochemical characterization of diazonium salt was made by cyclic voltammetry using DMSO containing 0.1 M TBAPF₆ as a supporting electrolyte with glassy carbon electrode. All redox potentials, HOMO (highest occupied molecular orbital), LUMO (lowest unoccupied molecular orbital) and band gap energies (E_g) were calculated from this technique.

The reduction potential of diazonium compound was observed from cyclic voltammogram (Fig. 9) and was found to be of valued 0.9 V. By utilizing the reduction potential of the compound, the HOMO and LUMO levels were determined which were found at levels of -6.45 and - 3.5 eV, respectively, with the help of Bredas Equations (Eqs. 1, 2 and 3). This diazonium has a high electron affinity (LUMO level - 3.5 eV) and may act as an acceptor material for organic heterojunction solar cells. The band gap energy (E_g) of the compound was 2.95 eV (Table 5). This band gap energy is moderate which is affected by the *o*-hydroxyl group. This OH group donates electron to pyrazole ring and pyrazole is formed which leads to extension of conjugation and decreasing the energy of LUMO levels too much which reduces the gap between the two.

$$\text{Eq. 1 } E_{\text{LUMO}} = - (4.4 + E_{\text{red}})$$

$$\text{Eq. 2 } E_{\text{HOMO}} = E_{\text{LUMO}} - E_g$$

$$\text{Eq. 3 } E_g = 1240 \text{ eV nm} / \lambda$$

Where,

E_{HOMO} = energy of HOMO level (eV)

E_{LUMO} = energy of LUMO level (eV)

E_g = band gap energy (eV)

E_{red} = half-wave potential (V)

λ = cut-off wavelength of the absorption band (nm)

Table 5
Band gap energy (E_g), HOMO and LUMO levels of 1-(*p*-sulphophenyl)-3-methyl-4-azo-5-pyrazolone.

Compound	E_g (eV)	LUMO (eV)	HOMO (eV)
Diazonium Salt	2.95	-3.5	-6.45

3.4 Application of Diazonium Salt in Acid Azo Dyes

The *p*-sulphophenyl – 3-methyl-5-pyrazolone diazonium salt was employed in the syntheses of a vast range of acid dyes and their Cr (III), Fe (II) and Cu (II) metal complexes with varied hues from yellow to dark brown, depending upon the nature of coupler component used (Scheme 2, Fig. 10–12). The absorption maxima of the synthesized complexes were found to be in the range of 475–530 nm. In order to observe the application properties, dyes were applied on leather and they exhibited high values of fastness properties (Tables 6 and 7).

Table 6
Fastness properties data of Cu (II) complexes (8a-g)

Dye	Wash Fastness	Light Fastness	Perspiration Fastness
8a	3–4	3–4	4–5
8b	3–4	3–4	4–5
8c	3–4	3–4	4–5
8d	3–4	3–4	4–5
8e	3–4	3–4	4–5
8f	3–4	3–4	4–5
8g	3–4	3–4	4–5

Table 7
Fastness properties data of the dyes 10a-f and their Iron complexes (12a-f)

Dye	Light Fastness	Wash Fastness	Rubbing Fastness	
			Dry	Wet
3a	4–5	4–5	4	3
3b	4–5	4–5	4	3
3c	4–5	4	5	4
3d	3–4	4–5	4–5	3–4
3e	3–4	4–5	4–5	3–4
3f	3–4	3–4	4–5	3–4
5a	4–5	4	4	3–4
5b	4–5	4	4–5	3–4
5c	4–5	5	4–5	3–4
5d	4–5	4–5	4–5	3–4
5e	4–5	4–5	4–5	3–4
5f	4–5	4–5	4–5	3–4

Conclusion

In this work it has been found that the amine hydrochloride of (**4**) was stable at -7 °C. The best diazotization temperature for this amine has been found to be -5 to -3 °C. At a temperature, above this range, amine hydrochloride is oxidized by nitrous acid to form rubazoic acid. Similarly, the formation of rubazoic acid is formed at higher pH as well. The higher rate of nitrite addition forms greater amount of nitrous acid that favored the formation of rubazoic acid, while a slow addition of nitrite lead to more of diazotization. The title diazonium compound has been isolated and found to be stable in dry form. It crystallizes in the triclinic space group *P*-1. Application of diazonium salt (**4**) provided a huge range of dyes with varied colors possessing high values of fastness properties of leather.

Declarations

Funding

There is no funding

Data availability statement

The manuscript has no associated data

Authors Contributions

Ghulam Shabir and Ghulam Hussain conducted the synthesis of compound. Aamer Saeed designed the work and wrote the manuscript. Hafiz Tasawwar Hussain conducted UV, Vis, FTIR, Electrochemical study, Application of Dyes and Fastness study on Leather. Tuncer Hökelek Mauricio F. Erben performed Hirshfield Analysis Study. Ulrich Flörke Conducted Single Crystal XRD study of compound.

Ethics Declarations

The authors declare that they have read the ethical guidelines of journal and completely follow them.

Conflicts of Interest/Competing Interests

The authors declare that they have no competing interests with respect to the research, authorship, and/or publication of this article.

References

1. Roglans A, Pla-Quintana A, Moreno-Manas M (2006) Diazonium salts as substrates in palladium-catalyzed cross-coupling reactions. *Chemical reviews* 106:4622–4643
2. Mahouche-Chergui S, Gam-Derouich S, Mangeney C, Chehimi MM (2011) Aryl diazonium salts: a new class of coupling agents for bonding polymers, biomacromolecules and nanoparticles to surfaces. *Chem Soc Rev* 40:4143–4166
3. Mo F, Dong G, Zhang Y, Wang J (2013) Recent applications of arene diazonium salts in organic synthesis. *Organic biomolecular chemistry* 11:1582–1593
4. Meerwein H, Büchner E, van Emster K (1939) Über die Einwirkung aromatischer Diazoverbindungen auf α , β -ungesättigte Carbonylverbindungen. *Journal für Praktische Chemie* 152:237–266
5. Heinrich MR (2009) Intermolecular olefin functionalisation involving aryl radicals generated from arenediazonium salts. *Chemistry-A European Journal* 15:820–833
6. Galli C (1988) Radical reactions of arenediazonium ions: an easy entry into the chemistry of the aryl radical. *Chem Rev* 88:765–792
7. Hari DP, König B (2013) The photocatalyzed Meerwein arylation: Classic reaction of aryl diazonium salts in a new light. *Angew Chem Int Ed* 52:4734–4743
8. Pratsch G, Anger CA, Ritter K, Heinrich MR (2011) Hydroxy-and Aminophenyl Radicals from Arenediazonium Salts. *Chemistry-A European Journal* 17:4104–4108

9. Heinrich MR, Blank O, Wölfel S (2006) Reductive carbodiazenylation of nonactivated olefins via aryl diazonium salts. *Org Lett* 8:3323–3325
10. Wetzel A, Pratsch G, Kolb R, Heinrich MR (2010) Radical arylation of phenols, phenyl ethers, and furans. *Chemistry-A European Journal* 16:2547–2556
11. Staples MK, Grange RL, Angus JA, Ziogas J, Tan NP, Taylor MK, Schiesser CH (2011) Tandem free-radical addition/substitution chemistry and its application to the preparation of novel AT 1 receptor antagonists. *Organic biomolecular chemistry* 9:473–479
12. Hari DP, König B (2013) The photocatalyzed Meerwein arylation: Classic reaction of aryl diazonium salts in a new light. *Angew Chem Int Ed* 52:4734–4743
13. Xiao T, Dong X, Tang Y, Zhou L (2012) Phenanthrene Synthesis by Eosin Y-Catalyzed, Visible Light-Induced [4 + 2] Benzannulation of Biaryldiazonium Salts with Alkynes. *Advanced Synthesis Catalysis* 354:3195–3199
14. Brogden RN (1986) Pyrazolone derivatives. *Drugs* 32:60–70
15. Wang X, Wang X, Liang Y, Shi Z, Zhang J, Chen L, Fu L (2010) A cell-based screen for anticancer activity of 13 pyrazolone derivatives. *Chin J Cancer* 29:980–987
16. Vijesh AM, Isloor AM, Isloor S, Shivananda KN, Shyma PC, Arulmoli T (2011) Synthesis of some new pyrazolone derivatives as potent antimicrobial agents. *Der Pharma Chemica* 3:454–463
17. Chen T, Benmohamed R, Kim J, Smith K, Amante D, Morimoto RI, Kirsch DR, Ferrante RJ, Silverman RB (2012) ADME-guided design and synthesis of aryloxanyl pyrazolone derivatives to block mutant superoxide dismutase 1 (SOD1) cytotoxicity and protein aggregation: potential application for the treatment of amyotrophic lateral sclerosis. *Journal of medicinal chemistry* 55:515–527
18. Lalit K, Chandresh T, Vivek S (2012) Biological Significance of Pyrazolone: A Review. *International Journal of Research in Pharmacy Science* 2:13–22
19. Soni JP, Sen DJ, Modh KM (2011) Structure activity relationship studies of synthesised pyrazolone derivatives of imidazole, benzimidazole and benztriazole moiety for anti-inflammatory activity. *Journal of Applied Pharmaceutical Science* 1:115–120
20. Antre RV, Oswal RJ, Kshirsagar SS, Kore PP, Mutha MM (2012) 2D-QSAR Studies of Substituted Pyrazolone Derivatives as Anti-Inflamma-tory Agents. *Med chem* 2:126–130
21. Dohutia, CH.A.N.D.R.A.J.I.T., Kaishap, PP, Chetia (2013) D.I.P.A.K. Synthesis and study of analgesic, anti-inflammatory activities of 3-methyl-5-pyrazolone derivatives. *Int J Pharm Pharm Sci* 5:86–90
22. Antre RV, Cendilkumar A, Goli D, Andhale GS, Oswal RJ (2011) Microwave assisted synthesis of novel pyrazolone derivatives attached to a pyrimidine moiety and evaluation of their anti-inflammatory, analgesic and antipyretic activities. *Saudi pharmaceutical journal* 19:233–243
23. Bruker SMART, Bruker SAINT AXS Inc. 2002, Madison, Wisconsin, USA
24. Sheldrick GMSADABS, 2004, University of Göttingen, Germany
25. Sheldrick GM (2008) A short history of SHELX. *Acta Cryst A* 64:112–122
26. Farrugia LJ (2012) WinGX and ORTEP for Windows: an update. *J Appl Crystallogr* 45:849–854

27. Hirshfeld FL (1977) Bonded-atom fragments for describing molecular charge densities. *Theoretica chimica acta* 44:129–138
28. Spackman MA, Jayatilaka D (2009) Hirshfeld surface analysis. *CrystEngComm*, **2009**, 11, 19–32
29. Turner MJ, McKinnon JJ, Wolff SK, Grimwood DJ, Spackman PR, Jayatilaka D, Spackman M A. CrystalExplorer17. 2017, The University of Western Australia
30. Venkatesan P, Thamotharan S, Ilangoan A, Liang H, Sundius T (2016) Crystal structure, Hirshfeld surfaces and DFT computation of NLO active (2E)-2-(ethoxycarbonyl)-3-[(1-methoxy-1-oxo-3-phenylpropan-2-yl) amino] prop-2-enoic acid. *Spectrochim Acta Part A Mol Biomol Spectrosc* 153:625–636
31. McKinnon JJ, Jayatilaka D, Spackman MA (2007) Towards quantitative analysis of intermolecular interactions with Hirshfeld surfaces. *Chem Commun* 37:3814–3816
32. Hartwar VR, Sist M, Jorgensen MRV, Mamakhel AH, Wang X, Hoffmann CM, Sugimoto K, Overgaard J, Iversen BB (2015) Quantitative analysis of intermolecular interactions in orthorhombic rubrene. *IUCrJ* 2:563–574

Figures

Figure 1

The asymmetric unit of the title compound. Anisotropic displacement ellipsoids are drawn at the 50% probability level.

Figure 2

A partial crystal packing of p-Sulphophenyl -3-methyl-5-pyrazolone diazonium with hydrogen bonding patterns shown as dotted lines. H-atoms not involved are omitted for clarity.

Figure 3

View of the three-dimensional Hirshfeld surface of the title compound plotted over d_{norm} in the range of -0.6911 to 1.2708 a.u.

Figure 4

View of the three-dimensional Hirshfeld surface of the title compound plotted over electrostatic potential energy in the range -0.0500 to 0.0500 a.u. using the STO-3 G basis set at the Hartree–Fock level of theory. Hydrogen-bond donors and acceptors are shown as blue and red regions around the atoms corresponding to positive and negative potentials, respectively.

Figure 5

Hirshfeld surface of the title compound plotted over shape-index.

Figure 6

The full two-dimensional fingerprint plots for the title compound, showing (a) all interactions, and delineated into (b) H $\cdots$ H, (c) H $\cdots$ O/O $\cdots$ H, (d) H $\cdots$ N/N $\cdots$ H, (e) O $\cdots$ NA/NA $\cdots$ O, (f) N $\cdots$ O/O $\cdots$ N, (g) C $\cdots$ C, (h) C $\cdots$ N/N $\cdots$ C, (i) H $\cdots$ C/C $\cdots$ H, (j) N $\cdots$ N, (k) H $\cdots$ NA/NA $\cdots$ H, (l) C $\cdots$ O/O $\cdots$ C, (m) O $\cdots$ O, (n) N $\cdots$ NA/NA $\cdots$ N and (o) H $\cdots$ S/S $\cdots$ H interactions. The d_i and d_e values are the closest internal and external distances (in Å) from given points on the Hirshfeld surface contacts.

(a)

(b)

(c)

(d)

Figure 7

The Hirshfeld surface representations with the function d_{norm} plotted onto the surface for (a) $\text{H} \cdots \text{H}$, (b) $\text{H} \cdots \text{O}/\text{O} \cdots \text{H}$, (c) $\text{H} \cdots \text{N}/\text{N} \cdots \text{H}$ and (d) $\text{O} \cdots \text{NA}/\text{NA} \cdots \text{O}$ interactions.

Figure 8

UV-visible absorption spectrum of 1-(p-sulphophenyl)-3-methyl-4-azo-5-pyrazolone in ethanol.

Figure 9

Cyclic voltammogram of diazonium salt (4) in DMSO.

Figure 10

Application of Cu (II) complex acid dyes 8a-g on leather at 2 and 5 % depth.

Figure 11

Application of unmetallized acid dyes 10a-f on leather at 2 and 5 % depth.

Figure 12

Application of Fe (II) complexes (12a-f) of acid dyes (10a-f) on leather at 2 and 5 % depth.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [abstractfig.png](#)
- [scheme1.png](#)
- [scheme2.png](#)