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

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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 \( \lambda_{\text{max}} \) at 420 nm and HOMO-LUMO 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 (\( \lambda_{\text{max}} \)) 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 \( \text{N}_2 \) 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 \( \text{TiCl}_3 \) and \( \text{FeSO}_4 \) 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 \(K_a\) radiation (\(\lambda = 0.71073 \text{ Å}\)) [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 \(U_{iso}(H) = 1.2 U_{eq}(C)\) or \(1.5 U_{eq}(\text{CH}_3)\) and C-H 0.95–0.98 Å. 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 eÅ\(^{-3}\), 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 | C\(_{10}\)H\(_9\)N\(_4\)O\(_5\)S·Na·2(H\(_2\)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) |
| \(\alpha\), \(\beta\), \(\gamma\) (°) | 102.452 (5), 104.497 (6), 92.293 (6) |
| \(V\) (Å\(^3\)) | 704.1 (3) |
| \(Z\) | 2 |
| Radiation type | Mo \(K\alpha\) |
| \(\mu\) (mm\(^{-1}\)) | 0.30 |
| Crystal size (mm) | 0.47 \(\times\) 0.14 \(\times\) 0.09 |

| Data collection |  |
|----------------|---|
| Diffractometer | Bruker AXS SMART APEX |
| Absorption correction | Multi-scan (SADABS, Sheldrick, 2004) |
| \(T_{\text{min}}, T_{\text{max}}\) | 0.873, 0.974 |
| No. of measured, independent and observed \([I > 2\sigma(I)]\) reflections | 6673, 3344, 2059 |
| \(R_{\text{int}}\) | 0.063 |
| \((\sin \theta/\lambda)_{\text{max}}\) (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), SHELXL 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 NaNO\(_2\) and HCl as described by Knorr\(^1\) to afford the nitroso compound (2) which was filtered to remove some tarry 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 ºC. The excessive un-reacted zinc was removed by filtration. The amine hydrochloride (3) was diazotized very carefully by using an aqueous solution of NaNO\(_2\) 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 \textit{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-Diazo-2-methyl-5-nitro-3-oxo-2,3-dihydropyrazol-1-ide (WETGEJ)\(^x\) 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···O11\(^{iii}\) [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···O12\(^{l}\) [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 (°).

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|-------|-------|---------|
| C6—H6A···O1 | 0.95 | 2.21  | 2.878 (4) | 126 |
| O10—H12···O12i | 0.84 (1) | 2.01 (2) | 2.808 (3) | 161 (3) |
| O10—H11···O11iii | 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···O12iv | 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-((ρ-sulphophenyl))-3-methyl-4-azo-5-pyrazolone.

| Bond Configuration | Distance (Å)     | Bond Configuration | Distance (Å)     |
|--------------------|------------------|--------------------|------------------|
| Na—O1\(^{i}\)     | 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 \(d_{\text{norm}}\) (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 π ... π stacking by the presence of adjacent red and blue triangles; if there are no adjacent red and/or blue triangles, then there are no π ... π interactions. Figure 5 clearly suggests that there are no π ... π interactions in (I). The overall two-dimensional fingerprint plot, Fig. 6a, and those delineated into H ... H, H ... O/O ... H, H ... N/N ... H, O ... NA/NA ... O, N ... O/O ... N, C ... C, C ... N/N ... C, H ... C/C ... H, N ... N, H ... NA/NA ... H, C ... O/O ... C, O ... O, N ... NA/NA ... N and H ... S/S ... H [31] are illustrated in Figs. 4b–o, respectively, together with their relative contributions to the Hirshfeld surface. The most important interaction is H ... 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 Å. The pair of spikes in the fingerprint plot delineated into H ... O/O ... 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 Å. The pair of characteristic wings resulting in the fingerprint plots delineated into H ... N/N ... H, Fig. 6d, contacts with 8.9% contribution to the HS arises from the H ... N/N ... H contacts (Table 4) and is viewed as pair of spikes with the tips at d_e + d_i = 1.96 Å. The O ... NA/NA ... O contacts (8.1%, Fig. 6e) have a scissor-shaped distribution of points with the tips at d_e + d_i = 2.31 Å. The N ... O/O ... N contacts (7.5%, Fig. 6f) have a fringed-shaped distribution of points with the tips at d_e + d_i = 2.79 Å and d_e + d_i = 2.82 Å for inner and outer fringes, respectively. The C ... 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 Å. The C ... N/N ... 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 Å. In the absence of C–H ... π interactions, the pair of characteristic wings in the fingerprint plot delineated into H ... C/C ... H (Table 4) contacts (Fig. 6i, 3.2% contribution to the HS) has the tips at d_e + d_i = 2.96 Å. The N ... 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 Å. The H ... NA/NA ... H contacts have an unsymmetrical distribution of points (1.6% contribution, Fig. 6k) with the tips at d_e + d_i = 3.28 Å. Finally, the C ... O/O ... C (0.7%, Fig. 6l), O ... O (0.7%, Fig. 6m), N ... NA/NA ... N (0.5%, Fig. 6n) and H ... S/S ... 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 ... H, H ... O/O ... H, H ... N/N ... H and O ... NA/NA ... 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 ... H and H ... O/O ... 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).

| Distance | Value  | Distance | Value  |
|----------|--------|----------|--------|
| H12···S1 | 2.90 (4) | O20···H10A | 2.87 |
| S1···H4C | 3.1624 | N2···C7 | 3.446 (4) |
| S1···H11 | 3.13 (4) | N3···C9 | 3.323 (4) |
| H21···S1 | 3.02 (5) | N3···N4 | 3.091 (4) |
| O1···N3 | 2.948 (4) | N4···C9 | 3.437 (4) |
| O1···C6 | 2.878 (4) | N4···N4 | 2.950 (4) |
| O10···O11 | 2.774 (3) | H22···N2 | 2.14 (3) |
| O11···N4 | 2.814 (4) | N2···H10A | 2.46 |
| O20···O12 | 2.810 (4) | H9A···N4 | 2.66 |
| O13···N4 | 3.016 (4) | C1···C10 | 3.543 (4) |
| O13···C2 | 3.259 (4) | C1···C5 | 3.589 (4) |
| O13···N3 | 2.873 (4) | C1···C9 | 3.585 (4) |
| O13···N4 | 3.117 (4) | C2···C10 | 3.500 (4) |
| O20···N2 | 2.981 (4) | C2···C5 | 3.585 (4) |
| O1···H6A | 2.21 | C3···C6 | 3.555 (5) |
| O11···H11 | 1.93 (4) | C3···C7 | 3.568 (4) |
| O11···H9A | 2.79 | C3···C8 | 3.559 (4) |
| O12···H7A | 2.45 | C5···C5 | 3.498 (4) |
| H12···O12 | 2.01 (4) | C1···H6A | 2.66 |
| H21···O12 | 1.98 (4) | C3···H22 | 2.91 (3) |
| O12···H4C | 2.66 | H4A···H22 | 2.47 |
| O20···H4B | 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 (\(\lambda_{\text{max}}\)) of diazonium was taken in ethanol (1x10\(^{-5}\) M solution) to observe the molar extinction coefficient of the compound. The molar extinction was found to be \(\log \varepsilon = 6.5\) and \(\lambda_{\text{max}}\) 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 \(\lambda_{\text{max}}\) due to the presence of \(\alpha\)-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 TBAPF\(_6\) 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 \(\alpha\)-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.

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

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

Eq. 3 \(E_g = 1240\, \text{eV nm/}\, \lambda\)

Where,

\(E_{\text{HOMO}} = \) energy of HOMO level (eV)
\[ E_{\text{LUMO}} = \text{energy of LUMO level (eV)} \]

\[ E_g = \text{band gap energy (eV)} \]

\[ E_{\text{red}} = \text{half-wave potential (V)} \]

\[ \lambda = \text{cut-off wavelength of the absorption band (nm)} \]

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 ºC. The best diazotization temperature for this amine has been found to be -5 to -3 ºC. 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
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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.

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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 dnorm 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 ⋯ H, (c) H ⋯ O/O ⋯ H, (d) H ⋯ N/N ⋯ H, (e) O ⋯ NA/NA ⋯ O, (f) N ⋯ O/O ⋯ N, (g) C ⋯ C, (h) C ⋯ N/N ⋯ C, (i) H ⋯ C/C ⋯ H, (j) N ⋯ N, (k) H ⋯ NA/NA ⋯ H, (l) C ⋯ O/O ⋯ C, (m) O ⋯ O, (n) N ⋯ NA/NA ⋯ N and (o) H ⋯ S/S ⋯ H interactions. The di and de values are the closest internal and external distances (in Å) from given points on the Hirshfeld surface contacts.
Figure 7

The Hirshfeld surface representations with the function dnorm plotted onto the surface for (a) H ··· H, (b) H ··· O/ O ··· H, (c) H ··· N/ N ··· H and (d) O ··· NA/ NA ··· 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

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