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SYNTHESIS AND OPTIMIZED GEOMETRY OF 3, 5-DIAMINO-1,2,4-TRIAZOLINIUM PICRATE

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1.Introduction

Triazole compounds exhibit a variety of biological functions and have been extensively explored in the fields of medicine and insecticides. Triazole compounds exhibit substantial internal fungicidal action in addition to being antifungal, herbicidal, and insecticidal properties. The study on these compounds has so far been on the rise because of the numerous effects of the triazole structure. The modification of these compounds chemical structures as well as research into using them as human and veterinary pharmaceuticals have long been frontier topics both domestically and internationally in order to produce variants that are more effective [1].

3,5-diamino-1,2,4-triazole, one of the triazole derivatives, is a significant energetic intermediate that has been researched and used to create several active molecules [2]. Its nitrogen concentration is 70.67%.Picric acid's active electron clouds and ionic bonds cause it to combine with other organic molecules to generate stable picrate compounds.3,5-Diamino-1,2,4-Triazolinium Picrate single crystals have been effectively produced in the current study's organic material employing a slow evaporation procedure using ethanol and water as the solvents.

2.Computational details

All the computations for the 3,5-DTAZPA were carried out using the Gaussian 09 software with the B3LYP and the 6-311++G (d, p) basis sets[3,4,5,6]. Gaussian 09 software was used to calculate Optimized geometry.

3.Synthesis

3, 5-Diamino-1,2,4-Triazolinium and picric acid were dissolved in mixture of methanol and acetone using a mechanical stirrer for about two hours. The clear solution obtained was filtered off and kept aside in a dust-free environment without any mechanical vibrations. Bright yellow colour transparent 3,5-Diamino-1,2,4-Triazolinium picrate crystals (3, 5-DTAZPA) were collected after 9 days.

4.Optimized Geometry

Fig1 depicts the molecular architecture of the molecule in its optimized stable state along with the atom's number.

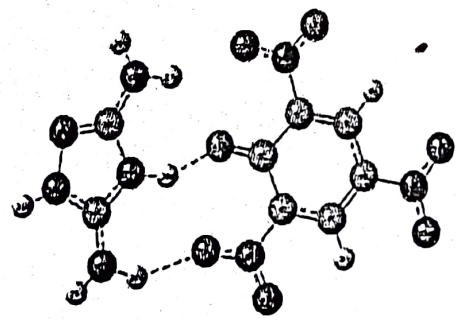

Fig1 Optimized molecular structure of 3, 5-DTAZPA

Six C-C bonds, nine C-N bonds, two C-H bonds, one C=O bond, six N-H bonds, and six N-O bonds are present in 3, 5-DTAZPA. The computed geometrical parameters and the XRD data differ slightly in 3, 5-DTAZPA. This is so that the estimated values can be obtained from the gas phase while the experimental values are obtained from the solid phase. **Table1** lists the 3, 5-DTAZPA molecules optimized bond lengths.

Table1 Optimized bond length of 3, 5-DTAZPA molecule

Bond lengths	Calc. (Å)	Expt (Å)	Bond lengths	Calc. (Å)	Expt. (Å)
C_1-C_2	1.3854	1.3734	N_{11}-O_{15}	1.2434	1.2183
C_1-C_7	1.3974	1.3844	O_{15}-H_{26}	1.9615	2.2810
C_1-N_9	1.4617	1.4433	O_{16}-H_{30}	1.6166	1.8630
C_2-H_3	1.081	0.9300	C_{19}-N_{22}	1.3421	1.3443
C_2-C_4	1.3863	1.3764	C_{19}-N_{24}	1.3350	1.3213
C_4-C_5	1.4576	1.4424	C_{19}-N_{25}	1.3445	1.3133
C_4-N_{11}	1.4489	1.4483	C_{20}-N_{21}	1.3467	1.3343
C_5-C_6	1.4543	1.4443	C_{20}-N_{22}	1.3857	1.3763
C_5-O_{16}	1.2492	1.2463	C_{20}-N_{23}	1.3132	1.3053
C_6-C_7	1.3739	1.3623	N_{21}-H_{27}	1.0165	0.8651
C_6-N_{10}	1.4677	1.4553	N_{21}-H_{28}	1.0067	0.8361
C_7-H_8	1.0814	0.9300	N_{22}-H_{30}	1.0509	0.9430
N_9-O_{12}	1.2271	1.2183	N_{23}-N_{24}	1.3953	1.3973
N_9-O_{13}	1.2272	1.2333	N_{24}-H_{31}	1.0065	0.8930
N_{10}-O_{17}	1.2249	1.2183	N_{25}-H_{26}	1.0177	0.8391
N_{10}-O_{18}	1.2293	1.2283	N_{25}-H_{29}	1.0070	0.8401
N_{11}-O_{14}	1.2237	1.2363			

Fig2 depicts the 3, 5-DTAZPA intermolecular hydrogen bond and packing. Via the N-H···O=C interaction, the picrate ion is connected to the 1,2,4 triazolium ring by protonating hydrogen. As a result, the protonating C-N bonds are bigger (1.3857 Å) than the non-protonated nitrogen atom's (1.3132 Å), which distributes resonance among the C=O bonds in the picrate ion [7]. In the 3, 5-DTAZPA crystal, the proton donor (N_{22}-H_{30}) is stretched from 1.0108 Å to 1.0509 Å due to intermolecular hydrogen bonding, whereas the proton acceptor (C=O) C_5-O_{16} is elongated from 1.2234 Å to 1.2492 Å [8].

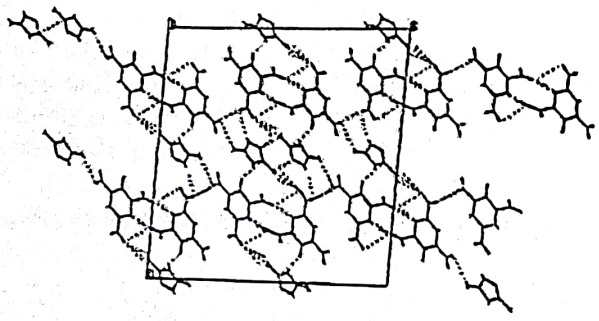

Fig2 Packing and intermolecular hydrogen bonds of 3, 5-DTAZPA

The N-C bonds N_9-C_1 (1.4617 Å), N_{11}-C_4 (1.4489 Å), and N_{10} -C_6 (1.4677 Å) exhibit a single bond character, while N_{22}-C_{19} (1.3421 Å), N_{24}-C_{19} (1.3350 Å), N_{25}-C_{19} (1.3445 Å), N_{21}-C_{20} (1.3467 Å) and N_{23}-C_{20} (1.3132 Å) showed double bond characters [9]. N_{22}-H_{30} bond length elongation (1.0509 Å) is due to the influence of N_{22}-H_{30}···O_{13} intermolecular hydrogen bonding [10]. In 3, 5-DTAZPA the bond length of both C_4-C_5 and C_5-C_6 is longer than all the other C-C bonds due to hydrogen bonding. C-NO_2 bonds such as C_7-NO_2, C_4-NO_2, and C_6-NO_2 bonds are lengthier than all other covalent bonds, indicating that their bond is prone to rupture in the decomposition process [11]. In 1,2,4 Triazole ring N_{24}-C_{19} (1.3350 Å) double bond distance is shorter than the N_{22}-C_{19} (1.3421 Å) double bond, and this is due to the effect of the electronic factors associated with substituent's the large electron densities. In 3, 5-DTAZPA the 1,2,4 Triazole ring has some multiple bond characters that exist due to the bond lengths N_{24}-C_{19} and N_{22}-C_{19} which are slightly longer than C=N (1.22 Å) also smaller than C-N (1.47 Å) [12]. The intermolecular O-H bond is of the order of 1.61-1.96 Å. C_5=O_{16} bond length (1.2492 Å) is consistent with the literature.

5.Conclusion

Compounds for 3,5-DTAZPA were produced using a slow evaporation technique. Through protonating hydrogen and the N-H···O=C interaction, the picrate ion is connected to the 1,2,4 triazolinium ring. By increasing the size of the CN bonds in the protonating position (1.3857 Å) relative to the nonprotonated nitrogen atom (1.3132 Å), resonance is distributed throughout the C=O bonds in the picrate ion. The benzene ring's symmetry is disturbed by the electron-withdrawing substituents, resulting in ring angles that differ from 120°. The presence of hyperconjugation contact between the phenyl ring and the lateral chain is indicated by a deviation from exoangle (120°). The effect of N_{22}-H_{30}···O_{13} intermolecular hydrogen bonding is responsible for the lengthening of the N_{22}···H_{30} bond (1.0509 Å).

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