Cocrystallization of Diphenylamine and Picric acid (1:2)

Kamini KAPOOR,* Vivek K. GUPTA,* R. VELMURUGAN,** M. SEKAR,*** and Rajnikant*†

*X-ray Crystallography Laboratory, Post-Graduate Department of Physics & Electronics, University of Jammu, Jammu Tawi - 180 006, India

**Department of Chemistry (Post Graduate and Research), Kongunadu Arts and Science College, Coimbatore - 641 029, Tamil Nadu, India

***Post Graduate and Research Department of Chemistry, Sri Ramakrishna Mission Vidyalaya College of Arts and Science, Coimbatore - 641 020, Tamil Nadu, India

The title compound, diphenylamine-picric acid (1:2) ($C_{12}H_{11}N \cdot 2C_6H_3N_3O_7$), crystallizes in the monoclinic space group $P2_1/a$ with the following unit-cell parameters: $a = 25.4238(14)$, $b = 6.9922(5)$, $c = 15.1311(8)$ Å, $\beta = 92.335(5)^\circ$, $Z = 4$. The crystal structure was solved by direct methods, and refined by full-matrix least-squares procedures to a final R -value of 0.0770 for 2426 observed reflections. In the title molecular complex, both of the picric acid molecules are disordered, corresponding to a rotation about one H-C...C-N axis, resulting in two sites for the hydroxyl group. In the diphenylamine molecule, the two phenyl rings are rotated with respect to each other by a dihedral angle of $33.0(1)^\circ$. The crystal structure is stabilized by N-H...O and C-H...O hydrogen bonds and π - π stacking interactions.

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The applications and properties of diphenylamine are similar to those of aniline. Diphenylamine is used as a parent compound for vulcanization accelerators, and for antioxidants (and antiozonant) for the rubber industry. These derivatives are added to rubber products to retard degradation by oxidants and ozone. They are intermediates for the production of dyes, pH indicators, polymers and fibers, and curing agents. Diphenylamine is used as a test for oxidizing agents and in detecting DNA in labs. Diphenylamine is used to absorb decomposed catalysts in a solid-fuel rocket propellant.¹ 2,4,6-Trinitro phenol, popularly known as picric acid, was primarily used to manufacture explosives, and also as an intermediate in dye manufacturing. It is well known that picric acid forms charge-transfer molecular complexes with a number of aromatic compounds, such as aromatic hydrocarbons and amines through electrostatic or hydrogen bonding interactions.^{2,3} The crystal structures of a large number of picrate salts and picric acid complexes have been studied to understand the conformational features and charge -transfer processes.⁴⁻⁶ Here, we report on the crystal structure of the title adduct, where the hydrogen

atom was not transferred from the picric acid to the diphenylamine molecule, as expected, thus forming a neutral 1:2 molecular adduct.

Co-crystals of diphenylamine and picric acid were prepared by dissolving equimolar amounts of picric acid and diphenylamine in methanol. Slow evaporation of the solution resulted in the formation of black block-shaped single crystals

Fig. 1 Chemical structure of the title compound.

† To whom correspondence should be addressed.
E-mail: rkvk.paper11@gmail.com

Table 1 Crystal and experimental data

Chemical formula: $C_{12}H_{11}N \cdot 2C_6H_3N_3O_7$	
Formula weight = 625.43	
$T = 293(2)$ K	
Crystal system: monoclinic	Space group: $P2_1/a$
$a = 25.4238(14)$ Å	
$b = 6.9922(5)$ Å	$\beta = 92.335(5)^\circ$
$c = 15.1311(8)$ Å	
$V = 2687.6(3)$ Å ³	$Z = 4$
$D_x = 1.546$ g/cm ³	
Radiation: Mo K_α ($\lambda = 0.71073$ Å)	
$\mu(\text{Mo } K_\alpha) = 0.131$ mm ⁻¹	$F(0\ 0\ 0) = 1280$
Crystal size = $0.30 \times 0.20 \times 0.20$ mm ³	
No. of reflections collected = 10437	
No. of independent reflections = 4726	
θ range for data collection: 3.43 to 25.00°	
Data/Restraints/Parameters = 4726/1/430	
Goodness-of-fit on $F^2 = 1.026$	
R indices [$I > 2\sigma(I)$]: $R1 = 0.0770$, $wR2 = 0.2218$	
R indices (all data): $R1 = 0.1345$, $wR2 = 0.2833$	
$(\Delta/\sigma)_{\text{max}} = 0.001$ for U_{33} O2A	
$(\Delta\rho)_{\text{max}} = 0.541$ e Å ⁻³ $(\Delta\rho)_{\text{min}} = -0.255$ e Å ⁻³	
Measurement: X'calibur system — Oxford diffraction make, U.K.	
Programs system: SHELXL-97, CrysAlis RED	
Structure determination: SHELXS-97	
CCDC deposition number: 866195

Fig. 2 ORTEP view of the molecules, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of arbitrary radii.

Fig. 3 Packing arrangement of molecules viewed down the *b*-axis.

suitable for X-ray analysis. A single crystal of the title compound, measuring $0.30 \times 0.20 \times 0.20$ mm, was picked up for X-ray intensity data collection on a CCD area-detector diffractometer (*X'calibur* system — *Oxford diffraction make*) having graphite-monochromated Mo K_α radiation ($\lambda = 0.71073$ Å). A total number of 10437 reflections were collected, of which 2426 reflections were treated as observed ($I > 2\sigma(I)$). Data were corrected for Lorentz, polarization and absorption factor. The structure was solved by direct methods using SHELXS97, and refined by SHELXL97.⁷ The hydrogen H4 atom was first determined in a difference electron density map, and placed at its idealized position with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{N})$.

Owing to the disorder, hydrogen atoms attached to phenolic O atoms were placed at idealized positions with $\text{O-H} = 0.82$ Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{N})$. The carbonic hydrogen atoms were positioned into their respective idealized positions, with $\text{C-H} = 0.93$ Å and $U_{\text{iso}}(\text{Haryl}) = 1.2U_{\text{eq}}(\text{Caryl})$. The final refinement cycles yielded an R-factor of 0.0770 [$wR(F^2) = 0.2218$] for 2426 observed reflections. The residual electron density ranged from -0.255 to 0.541 eÅ⁻³. The CIF for this structure has been deposited at Cambridge Crystal Data Centre (CCDC 866195). The crystallographic data are summarized in Table 1. Selected bond lengths and bond angles are given in Table 2S. An ORTEP⁸ view of the molecules indicating the atom numbering scheme is shown in Fig. 2.

The bond lengths and angles in the individual molecules are in agreement with literature values.⁹ In the diphenylamine molecule, C₁₂H₁₁N, two phenyl rings are bound to a central N atom. These rings are rotated with respect to one another by a dihedral angle of $33.0(1)^\circ$. The six C-C bond lengths in the phenyl rings lie in the range $1.355(6)$ Å – $1.393(6)$ Å (C7–C12); $1.351(5)$ Å – $1.415(5)$ Å (C13–C18). The N-C bond lengths in the diphenylamine molecule are: N4–C7 = $1.411(5)$ Å; N4–C13 = $1.393(5)$ Å. The phenolic oxygen in the picric acid molecules was found to be disordered over two positions. The final occupancies were refined to 0.58:0.42 (molecule A) and 0.62:0.38 (molecule B). The three nitro groups are almost coplanar with the aromatic picrate ring [dihedral angles: $10.3(4)$, $2.6(5)$ and $10.2(2)^\circ$ (molecule A); $12.9(4)$, $2.2(4)$ and $6.2(2)^\circ$ (molecule B)]. The six C-C bond lengths in the picrate ring lie in the range $1.366(5)$ Å – $1.392(5)$ Å (molecule A); $1.360(5)$ Å – $1.396(5)$ Å (molecule B).

A packing view of the molecules in the unit cell viewed down the *b*-axis is shown in Fig. 3. In the crystal structure, N-H...O and C-H...O hydrogen bonds are observed (Table 3S). In addition, π - π interactions involving the C1A–C6A (Centroid Cg1), C1B–C6B (Centroid Cg2), C7–C12 (Centroid Cg3) and C13–C18 (Centroid Cg4) benzene rings are also observed. Details of π - π interactions are given in Table 4S.

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