X-ray Structure Analysis Online

Crystal Structure of 2-[1-(2,4-Dinitrophenyl)ethyl]-1,10-Phenanthroline

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The crystal structure of 2-[1-(2,4-dinitrophenyl)ethyl]-1,10-phenanthroline was determined by X-ray crystallography. The compound crystallizes in a monoclinic system and was characterized thus: $P2_1/n$, a = 15.477(2), b = 5.1818(6), c = 21.754(2)Å, β = 96.295(3)°, Z = 4, V = 1734.12 Å^3. The crystal structure was solved by direct methods and refined by full-matrix least-squares on F^2 to final values of R = 0.0600.

(Received April 20, 2010; Accepted June 10, 2010; Published on web July 10, 2010)

2-(2,4-Dinitrobenzyl)pyridine and some of its derivatives (DNBPs) are well known as photochromic substance.[1-3] The photochromism of DNBPs takes place through photoinduced and thermally activated tautomerization. The title compound was synthesized in the following manner. A suspension of zinc (1.2 g, 18.5 mmol, fine dust) in dry THF, under argon, was activated using 0.1 mL of a dry solution of HCl in 1,4-dioxane (4 M). 1-Phenylethyl bromide (1.9 ml, 14 mmol) was added (drop by drop during 15 min). The solution was stirred at room temperature for 1 h, and then filtered. The (1-phenylethyl)zinc bromide was added to a solution of 2-chloro-1,10-phenanthroline[4] (1 g, 4.7 mmol) and $(Ph_3P)_4Pd$ (2.6 g, 0.2 mmol) in 15 mL of THF, and the solution was heated to 50°C for 2 h. The reaction mixture was filtered and then the precipitate was basified and extracted with CH_2Cl_2. It was purified by column chromatography (on an alumina column; 30% ethyl acetate in hexane), and a pale-yellow oil (1.03 g) was obtained. This oil was dissolved in concentrated sulfuric acid, and the mixture was cooled to –10°C. Ten milliliters of fuming HNO_3 was added to the mixture, and the solution was allowed to reach room temperature. After stirring the solution for three hours at room temperature, the solution was poured into iced water and made basic using an ammonia solution and extracted with three portions of dichloromethane. The combined organic layers were concentrated and chromatographed (on an alumina column, 50% ethyl acetate in hexane) and recrystallized from ethyl acetate/hexane mixture. Yield 35%; ^{1}H-NMR (400 MHz, $CDCl_3$) δ9.23 (1H, dd), 8.67 (1H, d), 8.36 (1H, dd), 8.26 (1H, dd), 8.19 (1H, d), 8.14 (1H, d), 7.78 (2H, d), 7.65 (1H, dd), 7.51 (1H, d), 5.26 (1H, q), 2.05 (3H, d); ^{13}C-NMR (100 MHz, $CDCl_3$) δ161.2 s, 150.5 d, 149.3 s, 146.1 s, 145.9 s, 137.0 d, 136.1 d, 132.6 d, 129.1 s, 127.5 s, 126.7 d, 126.3 d, 123.0 d, 122.8 d, 119.6 d, 42.7 d, 21.7 q; HRMS (FAB) m/z [M+H]$^+$ found: 375.1098, calc: 375.1093.

Colorless crystals of the title compound suitable for X-ray

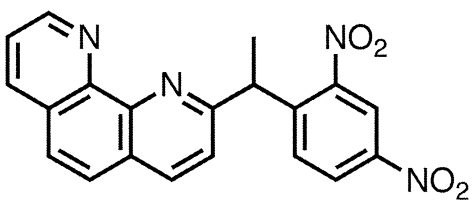

Fig. 1 Chemical diagram of the title compound.

Table 1 Crystal and experimental data

Chemical formula: $C_{20}H_{14}N_4O_4$
Formula weight = 374.35
T = 173 K
Crystal system: monoclinic
Space group: $P2_1/n$ Z = 4
a = 15.477(2)Å
b = 5.1818(6)Å
c = 21.754(2)Å
β = 96.295(3)°
V = 1734.12 Å^3
D_x = 1.434 g/cm^3
Radiation: Mo K_α (λ = 0.7107 Å)
F(0 0 0) = 776.00
No. of reflections collected = 16988
No. of independent reflections = 3944
Data/Restraints/Parameters = 3944/0/268
Goodness-of-fit on F^2 = 1.000
R indices [$I > 2\sigma(I)$]: $R1$ = 0.0600, $wR2$ = 0.1560
$(\Delta/\sigma)_{max}$ = 0.000
$(\Delta\rho)_{max}$ = 0.65 eÅ^{-3}
$(\Delta\rho)_{min}$ = –0.51 eÅ^{-3}
Measurement: Rigaku RAXIS-RAPID.
Program system: CrystalStructure 3.6.0, CRYSTALS
Structure determination: SIR97
Refinement: full-matrix least-squares on F^2

CCDC 752992 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

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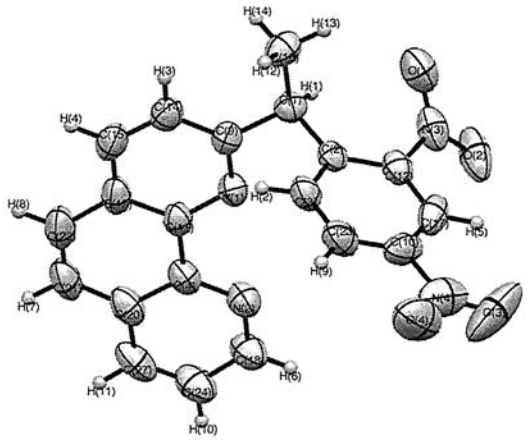

Fig. 2 ORTEP structure of 2-[1-(2,4-dinitrophenyl)ethyl]-1,10-phenanthroline. Thermal ellipsoids of non-H atoms are drawn at the 50% probability level.

Table 2 Significant intramolecular dimentions

Phenanthrolyl-Phenyl (˚)	82.4
o-Ntro group-Phenyl (˚)	36.4
p-Ntro group-Phenyl (˚)	11.3
O(1)···H(1) (Å)	2.290(2)
N(1)···H(1) (Å)	2.616(2)
C(12)-C(2)-C(1)-H(1) (˚)	–14.6(6)
N(1)-C(9)-C(1)-H(1) (˚)	–61.3(3)
C(16)-C(1)-C(9)-N(1) (˚)	179.5(2)

diffraction analysis were obtained by slow evaporation of an ethyl acetate/hexane mixture solution at room temperature. Data collections were performed at 173 K. All measurements were made on a Rigaku RAXIS-RAPID diffractometer using Mo K_α radiation (λ = 0.7107 Å).

Table 1 lists the crystal data and the experimental conditions. Figure 2 illustrates an ORTEP diagram of the molecule along with the atomic-labeling scheme.

The unit cell contains two homo dimers (AA and BB), where A or B refers to one of the two enantiomers (Fig. 3). The molecular packing observed for 2-[1-(2,4-dinitrophenyl)ethyl]-pyridine[5] is more or less closely related to that obtained in the present study. The planes of the *o*- and *p*-nitro groups are twisted about the mean plane of the phenyl ring by 36.4 and 12.1˚, respectively. The dihedral angle of 82.8˚ was determined for the mean planes of the phenanthrolyl moiety and the dinitrophenyl ring. The O(1) atom of the *o*-nitro group is within

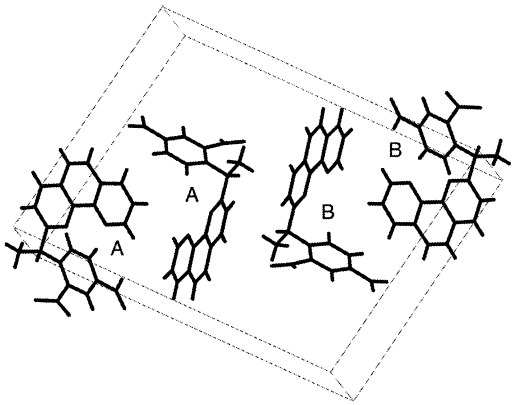

Fig. 3 Arrangement of 2-[1-(2,4-dinitrophenyl)ethyl]-1,10-phenanthroline in the unit cell.

the interaction distance and orientation to the benzylic H(6) atom, d(O···H) = 2.290(2)Å. The methyl conformation of the phenylethyl moiety is characterized as an *anti*-like with respect to N(9) atom adjacent to the C(9)–C(1) bond. The distance from the N(1) atom of the phenanthroline ring to the benzylic H(1) is 2.616(2)Å. According to these results, this crystal was expected to be photoactive because both the *o*-nitro group and the N atom of the phenanthroline ring can interact with the photolabile benzylic proton. We attempted to obtain a photochromic crystal from several solvents (acetone, H_2O, benzene, hexane, ether, ethyl acetate, DMF) and their mixtures. However, the available crystals were found to be photochemically unreactive. It can be presumed that the photo-induced tautomerization of this compound requires a large structural transformation, and therefore cannot take place in the solid state.

References

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