



Synthesis and Crystal Structure of 2,2'-[Ethylenedioxybis(nitrilomethylidyne)]dinaphthalene

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A novel Schiff-base bisoxime compound, with the molecular formula $C_{24}H_{20}N_2O_2$, has been synthesized and characterized by elemental analysis, IR, 1H NMR and X-ray single-crystal diffraction. Structural analysis revealed that 2,2'-[ethylenedioxybis(nitrilomethylidyne)]dinaphthalene lies across a crystallographic inversion centre (symmetry code: $-x, -y, -z$) and adopts an E configuration with respect to the azomethine C=N bond. Within the molecule, the naphthalene units are parallel, but extend in opposite directions from the dimethylene bridge. In the crystal structure, weak intermolecular C-H...N hydrogen bonds and C-H... π stacking interactions link molecules into infinite three-dimensional supramolecular network structure.

Key Words: Bisoxime Compound, Synthesis, Crystal Structure.

INTRODUCTION

The design of new Schiff-base compounds has received long-lasting research interest not only because of their appealing structural and topological novelty but also due to their potential wide application in the fields of biochemistry, synthesis, catalysis and optical materials and conducting polymers¹. Some of Schiff-base compounds or their complexes play crucial roles in some biological processes, such as the biological functions of bacteriorhodopsin², radiopharmaceuticals for cancer targeting, model systems for biological macromolecules, catalysts, dioxygen carriers³ and models in understanding the structure of biomolecules. Schiff-base compounds can also be used to obtain optical materials and conducting polymers⁴. Many Schiff base complexes have been structurally characterized, but only a relatively small number of free Schiff base bisoxime compounds have been characterized. As an extension of our work⁵⁻⁷, a new Schiff base bisoxime compound, 2,2'-[ethylenedioxybis(nitrilomethylidyne)]dinaphthalene, was synthesized and the single crystal structure was also determined.

EXPERIMENTAL

2,2'-[Ethylenedioxybis(nitrilomethylidyne)]dinaphthalene was synthesized according to an analogous method reported earlier⁸. To an ethanol solution (5 mL) of 1-naphthaldehyde (624.8 mg, 2 mmol) was added an ethanol solution (5 mL) of 1,2-bis(aminoxy)ethane (184.3 mg, 1.00 mmol). The mixture solution was stirred at 328 K for 4 h. When cooled to room temperature, the precipitate was filtered and washed succes-

sively with ethanol and hexane, respectively. The product was dried under vacuum and purified with recrystallization from ethanol to yield 736.9 mg of the title compound. Yield, 60.1 %, m.p. 363-364 K. Anal. calcd. (%) for $C_{24}H_{20}N_2O_2$: C, 78.24; H, 7.60; N, 7.07; found (%): C, 78.38; H, 7.65; N, 6.93. IR (KBr, ν_{max} , cm^{-1}): C=N, 1624 and C-O, 1175. 1H NMR ($CDCl_3$, δ ppm): 4.65 (s, 4H), 7.48 (t, $J = 7.6$ Hz, 2H), 7.53 (t, $J = 7.6$ Hz, 4H), 7.78 (d, $J = 7.2$ Hz, 2H), 7.87 (d, $J = 2.4$ Hz, 4H), 8.57 (d, $J = 8.4$ Hz, 2H), 8.83 (s, 2H).

X-Ray structure determination: Colourless block-shaped single crystals suitable for X-ray diffraction studies were obtained after several weeks by slow evaporation from an ethanol-tetrahydrofuran mixed solution of the title compound. A crystal of dimensions 0.12 mm \times 0.03 mm \times 0.03 mm was used to determine the crystal structures by X-ray diffraction technique on Bruker SMART CCD area-detector diffractometer using MoK_{α} radiation ($\lambda = 0.71073$ Å, $T = 298(2)$ K) graphite monochromation radiation. All calculations were performed using the SHELXL-97 crystal graphic software package⁹. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located by difference synthesis and refined isotropically. The selected bond lengths and bond angles are listed in Table-1.

RESULTS AND DISCUSSION

The crystal structure of the title compound is only built up by the $C_{24}H_{20}N_2O_2$ molecules, within all bond lengths are in normal ranges (Table-2). The molecule lies across a crystallographic inversion centre (symmetry code: $-x, -y, -z$) and

TABLE-1
CRYSTAL DATA AND REFINEMENT
PARAMETERS FOR THE TITLE COMPOUND

| | |
|-----------------------------|--|
| Empirical formula | C ₂₄ H ₂₀ N ₂ O ₂ |
| Crystal colour | Colourless, block-shaped |
| Formula weight | 368.42 |
| Temperature | 298(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | C2/c |
| Cell dimensions | a = 36.583 (3) Å, b = 6.4156 (11) Å, c = 7.9654 (17) Å β = 100.667(2) |
| Volume | 1837.2 (5) Å ³ |
| Z | 4 |
| Density (calculated) | 1.332 mg/m ³ |
| Absorption coefficient | 0.085 mm ⁻¹ |
| F ₍₀₀₀₎ | 776 |
| Index ranges | -43 ≤ h ≤ 42, -7 ≤ k ≤ 6, -9 ≤ l ≤ 9 |
| Reflections collected | 4525 |
| Independent reflections | 1579 [R _{int} = 0.0502] |
| Data/restraints/parameters | 1579/0/127 |
| Goodness of fit indicator | 1.004 |
| Final R indices [I > 3σ(I)] | R ₁ = 0.0773, wR ₂ = 0.1273 |
| Largest diff. peak and hole | 0.251 and -0.166 e. Å |

adopts an E configuration with respect to the azomethine C=N bond. Within the molecule, the naphthalene units are parallel, with the distance 2.373(2) Å (intra-molecule plane-to-plane distance) and extend in opposite directions from the dimethylene bridge (Fig. 1).

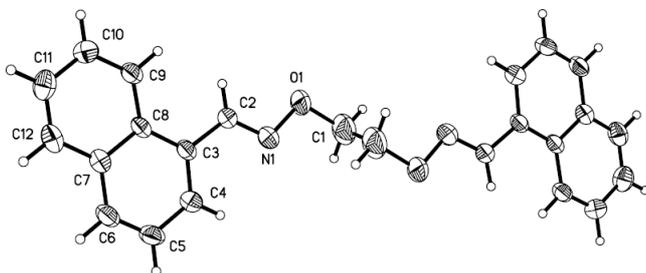


Fig. 1. Molecular structure of the title compound

In the crystal structure, C-H...π(Ph) stacking interactions and weak intermolecular C1-H1B...N1 hydrogen bonds link molecules into infinite three-dimensional supramolecular structure (Fig. 2). The crystals are held together by a pair of

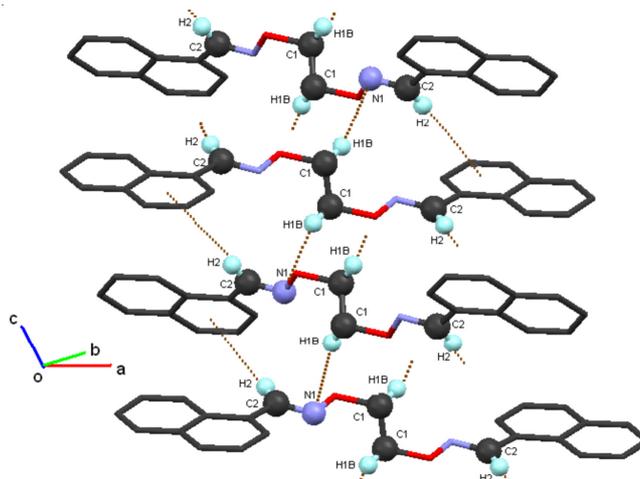


Fig. 2. Part of intermolecular hydrogen bonds and C-H...π interactions

weak intermolecular hydrogen bonds C1-H1B...N1 between dimethylene groups and the oxime nitrogen atoms ($d(\text{H1B}\cdots\text{N1}) = 2.175(3)$ Å, $d(\text{C1}\cdots\text{N1}) = 3.643(2)$ Å, $\angle\text{C1-H1B}\cdots\text{N1} = 160.40^\circ$), which link each molecule to 4 others to form infinite helix chains along b axis (Fig. 3). In addition, the molecules are further linked by a pair of intermolecular C2-H2...π(C3-C8) interactions to form the other infinite helix chains along c axis. The intermolecular C-H...π_{centroid} separations are equal ca. 3.304 Å and lie in the accepted distance range for this type of contacts¹⁰. Thus, these crosslinked hydrogen-bonded and C-H...π(Ph) chains constitute a three-dimensional supramolecular network structure.

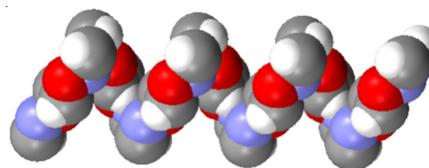


Fig. 3. Infinite helices chains along b axis. For clarity, the non-contact atoms not involved in the interactions have been omitted

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TABLE-2
SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR THE TITLE COMPOUND

| Atom | Distance | Atom | Distance | Atom | Distance |
|------------|----------|-----------|----------|-------------|----------|
| N1-C2 | 1.232(4) | C3-C8 | 1.390(4) | C7-C8 | 1.416(5) |
| N1-O1 | 1.391(4) | C4-C5 | 1.404(5) | C8-C9 | 1.397(4) |
| O1-C1 | 1.475(5) | C5-C6 | 1.322(4) | C9-C10 | 1.340(4) |
| C2-C3 | 1.453(5) | C6-C7 | 1.375(5) | C10-C11 | 1.405(6) |
| C3-C4 | 1.347(4) | C7-C12 | 1.379(5) | C11-C12 | 1.338(5) |
| Atom | Angle | Atom | Angle | Atom | Angle |
| C2-N1-O1 | 110.2(3) | C3-C4-C5 | 120.3(3) | C3-C8-C9 | 124.8(3) |
| N1-O1-C1 | 106.2(3) | C6-C5-C4 | 119.9(4) | C3-C8-C7 | 118.8(3) |
| N1-C2-C3 | 118.5(4) | C5-C6-C7 | 122.1(4) | C9-C8-C7 | 116.4(3) |
| C4-C3-C8 | 120.3(3) | C6-C7-C12 | 122.0(4) | C10-C9-C8 | 123.3(4) |
| C4-C3-C2 | 119.1(3) | C6-C7-C8 | 118.5(3) | C9-C10-C11 | 119.0(4) |
| C8-C3-C2 | 120.6(3) | C12-C7-C8 | 119.4(4) | C12-C11-C10 | 119.6(4) |
| C11-C12-C7 | 122.2(4) | - | - | - | - |

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