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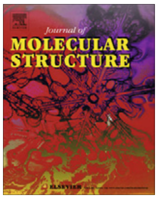

Structure, spectroscopy, and theory calculations on 1,3-bis((5,6-dimethyl-1H-benzo[d]imidazol-1-yl)methyl)benzene

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HIGHLIGHTS

- The title compound was characterized by UV–Vis, IR spectra and X-ray diffraction.
- The optimized geometries could well reproduce the crystal structural parameters.
- The theoretical absorption spectra showed good agreement with UV–Vis values.
- The FMO analysis of title compound was investigated by theoretical calculations.

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ABSTRACT

The molecule, 1,3-bis((5,6-dimethyl-1H-benzo[d]imidazol-1-yl)methyl)benzene (short for **T**, $C_{26}H_{26}N_4$), was synthesized and characterized by UV–Vis spectroscopy, infrared spectroscopy and single crystal X-ray diffraction. The molecular geometry, vibrational frequencies, absorption spectrum of the compound **T** have been calculated by using the density functional theory (DFT/B3LYP) method with TZVP basis sets, and have been compared with the experimental data. The calculated results showed that the optimized geometries can well reproduce the crystal structural parameters, and the theoretical absorption spectra show good agreement with experimental UV–Vis values. Besides, frontier molecular orbitals analysis of the title compound was investigated by theoretical calculations.

1. Introduction

Research on benzimidazoles has been paid more and more attention in recent years, as benzimidazoles are regarded as important bioactive heterocyclic compounds. This compound have been used in a wide range of applications, including organic synthesis and catalysis [1,2], inorganic synthesis [3], chromatography [4–7] and biological systems [8]. The most prominent benzimidazole compound in nature is N-ribosyl-dimethylbenzimidazole, which serves as an axial ligand for cobalt in vitamin B_{12} [9,10]. Especially, this heterocyclic system is present in numerous antioxidant [11], antiparasitic [12], antihelmintics [13], antiproliferative [14], anti-HIV [15], anti-inflammatory [16,17], and anticancer [18] activities. Owing to the immense importance and versatile bioactivities exhibited by benzimidazoles, efforts have been made to screened them for potential biological activities. These different applications have attracted many experimentalists and theorist to investigate the spectroscopic and structural properties of benzimidazole [19,20] and some of its derivatives coordination compounds containing benzimidazole group [21].

In general, free imidazole molecule does not have visible light absorption [22–24]. To improve the photoabsorption properties of imidazole, it is possible to introduce some groups with conjugated structures, into the imidazole skeleton, such as benzene. In this work, we present results of a detailed investigation of the experimental and theoretical characterization of 1,3-bis((5,6-dimethyl-1H-benzo[d]imidazol-1-yl)methyl)benzene (short for **T**, shown as Fig. 1), using infrared spectroscopy, UV–Vis spectroscopy, and single crystal X-ray diffraction. We select this benzimidazole compound because of its remarkable advantages in the coordination-polymer construction: (i) the bisbenzimidazole nitrogens have strong coordination ability and the $-(Ph-CH_2)-$ group is semirigid; (ii) it contains both the imidazole ring and a larger conjugated π-system, capable of acting as hydrogen bond donors and for π–π stacking interactions.

To further understand the photophysical properties, density functional theory (DFT) and time-dependent density functional

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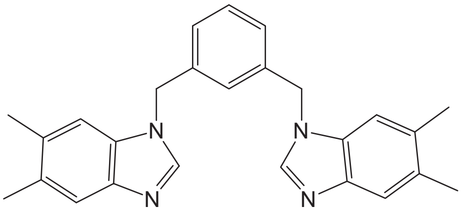

Fig. 1. Structures of 1,3-bis((5,6-dimethyl-1H-benzo[d]imidazol-1-yl)methyl) benzene.

theory (TDDFT) could be used to clarify fundamental aspects concerning the photophysical properties. Using these methods, the photophysical properties of some organic molecules have been successfully described [25–28], including some imidazole-containing molecules. Herein, the quantum-chemical calculations are credible and valuable for providing insight into molecular parameters and the spectra. The calculation aims to provide a complementary view on the molecular spectra and the structural parameters of the molecule. In particular, we have focused our attention on the comparison of predictions from DFT and TDDFT calculations with experimental observations.

2. Experimental and computational methods

2.1. Synthesis

All the reagents and solvents for synthesis were purchased from commercial sources and used without further purification. The compound **T** was prepared according to the literature [29].

2.2. Apparatus

The Infrared (IR) spectrum was recorded from KBr pellets in the range 4000–400 cm^{-1} on a Nicolet FT-IR 170SX spectrometer. The UV–Vis spectrum was recorded on Shimadzu UV-3600 spectrophotometer equipped with a PTC-348WI temperature controller in the range of 190–1100 nm.

2.3. X-ray crystallographic

Suitable single crystal of the title compound was mounted on glass fibers with epoxy cement for X-ray measurement. The crystallographic data were collected on a Bruker Smart 1000 CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and an $\omega - 2\theta$ scan mode at 293 K. All the measured independent reflections were used in the structure analyses, and semi-empirical absorption corrections were applied using the SADABS program [30]. Crystal structure was solved by the direct method and subsequently completed by the difference Fourier recycling. All the non-hydrogen atoms were refined anisotropically using full-matrix, least-squares technique. All the hydrogen atoms were positioned geometrically and refined using a riding model for the title complex. All the calculations were performed using the program SHELXTL and SHELXL-97 program [31]. The crystallographic data and experimental details of the data collection and the structure refinement are given in Table 1.

2.4. Computational details

All calculations on electronic structures were carried out using the ORCA 2.8 program [32]. Geometry optimizations and vibration analysis were performed using DFT and absorption spectrum were calculated using TDDFT method. Becke's three-parameter hybrid exchange functional with Lee–Yang–Parr gradient-corrected correlation (B3LYP functional) [33–37] was chosen as the functional. The triple-ξ valence quality with one set of polarization functions (TZVP) [38] was chosen as basis sets throughout, which was an appropriate basis set for such organic compound. No constrains for symmetry, bonds, angles, or dihedral angles were applied in the geometry optimization calculations. All of the local minima were confirmed by the absence of an imaginary mode in vibrational analysis calculations. In frequency analysis, we used tighter convergence criteria in SCF calculation.

Table 1
Crystal data and structure refinement for compound **T**.

Compound	**T**
Empirical formula	$C_{26}H_{26}N_4$
Formula weight	394.51
Wavelength/Å	0.71073
Crystal system	Monoclinic,
Space group	*Pc*
a/Å	9.6765(12)
b/Å	17.698(2)
c/Å	12.4705(16)
α/°	90
β/°	92.551(2)
γ/°	90
V/Å^3	2133.5(5)
Z	4
Dc/g cm^{-3}	1.228
Crystal size/mm	0.18 × 0.17 × 0.17
$F(000)$	840
θ Range/°	2.30–27.48
Limiting indices	$-12 \leqslant h \leqslant 12$; $-22 \leqslant k \leqslant 22$, $-16 \leqslant l \leqslant 16$
Reflections collected	19183
Independent reflections	9512
R_{int}	0.0254
Completeness to theta = 25.02	99.6%
Absorption coefficient/mm^{-1}	0.074
T/K	295(2) K
GOF on F^2	1.013
Final R indices $[I > 2\sigma(I)]^{[a,b]}$	$R_1 = 0.0458$ $wR_2 = 0.1093$
R (all data)$^{[a,b]}$	$R_1 = 0.0666$ $wR_2 = 0.1203$
$\Delta\rho_{max}$(e Å^{-3})	0.171
$\Delta\rho_{min}$(e Å^{-3})	−0.158

3. Results and discussion

3.1. Crystal structure and geometry optimization

Single-crystal X-ray structural analysis of **T** reveals that it crystallizes in the monoclinic space group *Pc*. The asymmetric unit consists of two independent units: 1 and 2, (Fig. 2a). Both independent molecules show trans-configuration with different dihedral angles. In 1, the dihedral angles between the mean-planes of the benzimidazole rings and the benzene ring (C11—C16) are 87.685(66)° (N1/N2/C2—C7) and 85.066(61)° (N3/N4/C19—C24), respectively. While in 2, the dihedral angles between the mean-planes of the benzimidazole rings and the benzene ring (C37—C42) are 84.321(69)° (N5/N6/C27—C32) and 80.735(66)° (N7/N8/C44—C49), respectively. The bond lengths and angles in **T** are all within a normal range and different torsion angles were observed in the two independent units (Table 2), which may be caused by the flexibility of **T** itself. The bond lengths of N1—C1 and N2—C1 in the 5,6-dimethylbenzimidazole moiety are not equal. The N1—C1 (1.308 Å) length is shorter than the N2—C1 length (1.353 Å), which indicates that the N1—C1 bond is close to the double bond and N2—C1 bond is close to the single bond. These