# Conformational and Vibrational Properties of Indigo Dye: DFT Approach

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**Abstract:** In our present study, we report conformational and vibrational properties of Indigo dye. Indigo dye was found to have two isomerization structures, namely Cis and Trans isomers. We report optimized molecular structural parameters, vibrational spectra, thermodynamical parameters, total dipole moment and HOMO-LUMO energies for Indigo using Density Functional Theory DFT/B3LYP utilizing 6-311G(d,p) basis set. The Cis-Indigo was found to be a promising material for application in optoelectronic devices due to its high calculated dipole moment (7 Debye) and HOMO-LUMO energy gap of 3 eV which indicates its strong reactivity within the surrounding molecules. The Trans-Indigo has no dipole moment and HOMO-LUMO energy gap of ~ 2.5 eV. Our comparative study of Cis- Trans Indigo derivatives service as mean to pick the right Indigo isomer for intended applications.

## 1 Introduction

As is well-known, hetero-cycles compounds are widespread in natural products and have attracted considerable attention from a wide area of science, including physical chemistry, medicinal chemistry, natural product chemistry, synthetic organic chemistry and polymer science [1-2]. Among various hetero-cycles compounds, Indigo dyes attracted more attention because of their high applicability as vat dyestuffs that used for coloring textiles since ancient times [3-4]. Their reduced (leuco, colorless) chemical form is highly soluble and allows for the use of large dyeing baths, the color appearing after simple oxidation by air. Furthermore, once chlorinated or brominated, they show an enhanced affinity to fibers such as wool or cotton [5-6].
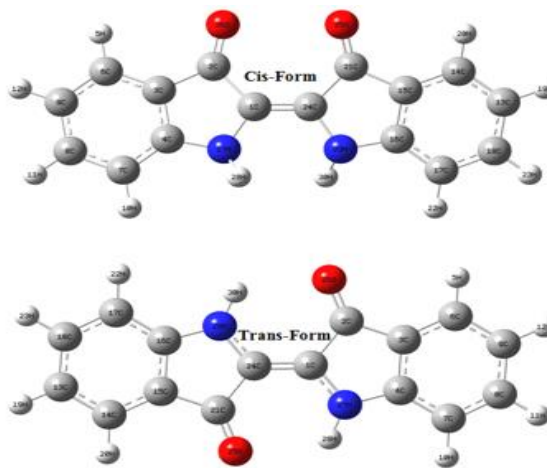


**Figure 1:** Optimized molecular structure of Indigo isomers at B3LYP/6-311G(d,p).

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Indigo is a dark blue crystalline powder that sublimes at 390–392 °C. It is insoluble in water, alcohol, or ether but soluble in DMSO, chloroform, nitrobenzene, and concentrated sulfuric acid. Indigo has a chemical formula of $C_{16}H_{10}O_2N_2$ as shown in Fig. 1. Indigo had been prepared by many methods such as Baeyer-Drewson and Pfleger synthesis. [7-8]. In spite of this, it is worth to mention that experimental and/or molecular modeling studies for the molecular structure of Indigo are still limited. Accordingly, The present investigation was carried out for studying the optimized molecular structural parameters, vibrational frequencies, thermo-dynamical parameters, total dipole moment and HOMO-LUMO energy gap for Indigo isomers using DFT/B3LYP utilizing 6-311G(d,p) basis set.

## 2 Experimental Details

A commercially available sample of Indigo in solid form was purchased from Aldrich (99%) and used without further purification. FT-IR analysis was performed using Thermo Scientific Nicollet 460$_{plus}$ Spectrophotometer at room temperature in the spectral range 500–4000 cm$^{-1}$.

## 3 Computational Details

All the computations were performed using Gaussian (09W) program package [9]. Gauss View 5 [10] was used for visualization of the structure and simulation of the vibrational spectra. Cis and Trans Indigo and corresponding vibrational harmonic frequencies were calculated using Becke3–Lee–Yang–Parr (B3LYP) with 6-31G(d,p) basis set on a PC Core I5/2.8 GHz without any constraint on the geometry. The harmonic vibrational frequencies have been analytically calculated by taking the second order derivative of energy using the same level of theory. The ground state optimized geometry of Indigo isomers is shown in Fig. 1. We add polarization functions for better treatment of polar bonds such as C=O, C=C, C-N, C-C, N-H and C–H groups.

## 4 Results and Discussions

### 4.1. Geometry Optimization

Our calculated optimized geometrical parameters for Indigo at B3LYP/6-311G(d,p) basis set are listed in Table 1. Since the exact crystal structure of Indigo is not available this time, our optimized structure can be only compared with other similar systems for which the crystal structures have been solved.

**Table 1:** Optimized structural parameters for indigo isomers at B3LYP/6-311G(d,p).

| Bond Length (Å) | | Bond Angle (°) | | | |
|---|---|---|---|---|---|
| C1-C2 | 1.5 | C2-C1-C24 | 130.9 | C15-C16-C17 | 121.3 |
| C1-C24 | 1.4 | C2-C1-N27 | 107.5 | C15-C16-N29 | 109.9 |
| C1-N27 | 1.4 | C24-C1-N27 | 121.5 | C17-C16-N29 | 128.8 |
| C2-C3 | 1.5 | C1-C2-C3 | 103.8 | C16-C17-C18 | 117.4 |
| C2-O26 | 1.2 | C1-C2-O26 | 128.3 | C16-C17-H22 | 121.6 |
| C3-C4 | 1.4 | C3-C2-O26 | 127.8 | C18-C17-H22 | 121.0 |
| C3-C6 | 1.4 | C2-C3-C4 | 108.7 | C13-C18-C17 | 121.8 |
| C4-C7 | 1.4 | C2-C3-C6 | 130.4 | C13-C18-H23 | 119.3 |
| C4-N27 | 1.4 | C4-C3-C6 | 120.9 | C17-C18-H23 | 118.9 |
| C5-C6 | 1.1 | C3-C4-C7 | 121.3 | C15-C21-C24 | 103.8 |
| C6-C9 | 1.4 | C3-C4-N27 | 109.9 | C15-C21-O25 | 127.8 |
| C7-C8 | 1.4 | C7-C4-N27 | 128.8 | C24-C21-O25 | 128.3 |
| C7-H10 | 1.1 | C3-C6-H5 | 119.7 | C1-C24-C21 | 130.9 |
| C8-C9 | 1.4 | C3-C6-C9 | 118.5 | C1-C24-N29 | 121.5 |
| C8-H11 | 1.1 | H5-C6-C9 | 121.8 | C21-C24-N29 | 107.5 |
| C9-H12 | 1.1 | C4-C7-C8 | 117.4 | C1-N27-C4 | 109.7 |
| C13-C14 | 1.4 | C4-C7-H10 | 121.6 | C1-N27-H28 | 119.0 |
| C13-C18 | 1.4 | C8-C7-H10 | 121.0 | C4-N27-H28 | 119.6 |
| C13-H19 | 1.1 | C7-C8-C9 | 121.8 | C16-N29-C24 | 109.7 |
| C14-C14 | 1.4 | C7-C8-H11 | 118.9 | C16-N29-H30 | 119.6 |
| C14-H20 | 1.1 | C9-C8-H11 | 119.3 | C24-N29-H30 | 119.0 |
| C15-C16 | 1.4 | C6-C9-C8 | 120.2 | | |
| C15-C21 | 1.5 | C6-C9-H12 | 120.2 | | |
| C16-C17 | 1.4 | C8-C9-H12 | 119.6 | | |
| C16-N29 | 1.4 | C14-C13-C18 | 120.2 | | |
| C17-C18 | 1.4 | C14-C13-H19 | 120.2 | | |
| C17-H22 | 1.1 | C18-C13-H19 | 119.6 | | |
| C18-H23 | 1.1 | C13-C14-C15 | 118.5 | | |
| C21-C24 | 1.5 | C13-C14-H20 | 121.8 | | |
| C21-O25 | 1.2 | C15-C14-H20 | 119.7 | | |
| C24-N29 | 1.4 | C14-C15-C16 | 120.9 | | |
| N27-H28 | 1.0 | C14-C15-C21 | 130.4 | | |
| N29-H30 | 1.0 | C16-C15-C21 | 108.7 | | |
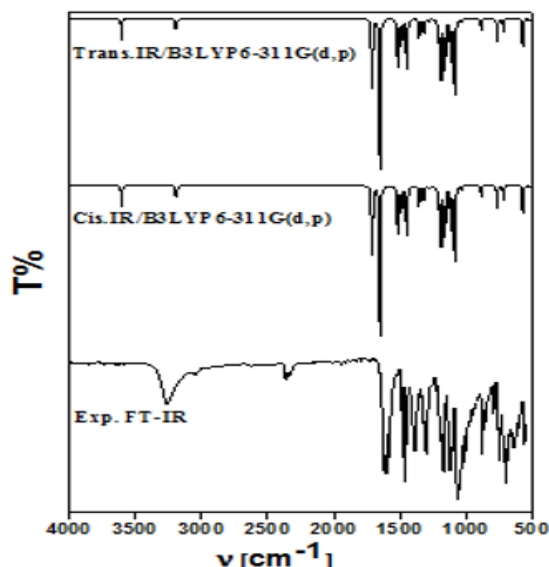


**Figure 2:** Experimental and calculated IR spectra for Indigo isomers at B3LYP/6-311G(d,p).

*4.2 Vibrational Assignments*

Indigo has 30 atoms and 84 normal vibrations are distributed as 57 Á + 27 A″ considering $C_s$ symmetry. For comparison with our experimental FT-IR data, we select only 18 active modes for both Cis and Trans Indigo, distributed as 12 A' + 6 A". The modes A' are in plane and stretching vibrations while modes A" correspond to the out-of-plane vibrations. According to the DFT/B3LYP calculations, All calculated wavenumbers had been scaled with factor 0.96 [11-13].

**Table 2:** Experimental and Computational Calculated Vibrational Wavenumbers (Harmonic Frequency (cm$^{-1}$)), IR Intensities, Species and Assignments for Indigo isomers at B3LYP/6-311G(d,p).

| No | Cis-Form | | | | Trans-Form | | | | Exp. | Species | Vibrational Assignments |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Wavenumber (cm$^{-1}$) | | IR Intensity | | Wavenumber (cm$^{-1}$) | | IR Intensity | | | | |
| | Unscaled | Scaled | Rel. | Abs. | Unscaled | Scaled | Rel. | Abs. | | | |
| 1 | 525 | 515 | 16 | 3 | 557 | 546 | 0 | 0 | 550 | A" | γ C-C + γ C-N |
| 2 | 561 | 550 | 37 | 8 | 571 | 560 | 0 | 0 | 660 | A" | |
| 3 | 664 | 651 | 23 | 5 | 689 | 675 | 0 | 0 | 680 | A' | β C-C + β C-N |
| 4 | 688 | 674 | 25 | 5 | 718 | 704 | 49 | 7 | 700 | A' | |
| 5 | 715 | 701 | 10 | 2 | 733 | 718 | 0 | 0 | 720 | A" | |
| 6 | 780 | 764 | 0 | 0 | 780 | 764 | 10 | 1 | 780 | A" | γ C-H |
| 7 | 808 | 792 | 0 | 0 | 818 | 802 | 0 | 0 | 820 | A" | |
| 8 | 869 | 852 | 2 | 0 | 874 | 857 | 0 | 0 | 880 | A" | γ N-H |
| 9 | 901 | 883 | 0 | 0 | 952 | 933 | 0 | 0 | 960 | A' | υ C-N+ υ C-C |
| 10 | 1092 | 1070 | 157 | 34 | 1116 | 1094 | 189 | 27 | 1025 | A' | |
| 11 | 1096 | 1074 | 0 | 0 | 1118 | 1096 | 0 | 0 | 1080 | A' | β C-H |
| 12 | 1175 | 1169 | 467 | 100 | 1208 | 1184 | 0 | 0 | 1180 | A' | |
| 13 | 1288 | 1262 | 280 | 60 | 1343 | 1316 | 0 | 0 | 1250 | A' | |
| 14 | 1480 | 1450 | 98 | 21 | 1517 | 1487 | 0 | 0 | 1500 | A' | β N-H |
| 15 | 1602 | 1570 | 182 | 39 | 1653 | 1620 | 691 | 100 | 1560 | A' | υ C=C |
| 16 | 1761 | 1726 | 238 | 51 | 1765 | 1730 | 0 | 0 | 1700 | A' | υ C=O |
| 17 | 3104 | 3042 | 4 | 1 | 3168 | 3105 | 0 | 0 | 3100 | A' | υ C-H (aromatic) |
| 18 | 3507 | 3437 | 13 | 3 | 3605 | 3533 | 102 | 15 | 3400 | A' | υ N-H |

υ (stretching); β (in plane bending); γ (out of plane bending)

Our theoretical and experimental wavenumbers, species and the corresponding assignments for Cis and Trans Indigo are collected in Table 2. Both experimental and calculated IR spectra for Cis and Trans Indigo at B3LYP/6-311G(d,p) basis set are shown in Fig. 2. Our computational results have shown a comparable agreement with the experimental ones. Any discrepancy observed between theoretical and experimental data may be attributed to the fact that our calculations actually performed on a single molecule in the gaseous state in contradictory to the experimental results that recorded in the solid state.

*4.2.1. N-H Vibrations*

The N-H group stretching vibrations are observed in range 3400 - 3500 cm$^{-1}$ [14]. The computed vibration (mode 18) is assigned to N-H aromatic stretching vibration at 3437 cm$^{-1}$ for Cis-Indigo and 3533 cm$^{-1}$ for Trans-Indigo which is comparable with the experimental result at 3400 cm$^{-1}$. The computed vibration (mode 14) is assigned to N-H in plane bending vibration at 1450 cm$^{-1}$ for Cis-Indigo and 1487 cm$^{-1}$ for Trans-Indigo which is comparable with the experimental result at 1500 cm$^{-1}$. The computed vibration (mode 8) is assigned to N-H out of plane bending vibration at 852 cm$^{-1}$ for Cis-Indigo and 857 cm$^{-1}$ for Trans-Indigo which is comparable with the experimental result at 880 cm$^{-1}$.

*4.2.2. C-H Vibrations*

The aromatic C-H stretching vibrations are observed in the region 3000–3100 cm$^{-1}$ [15]. The computed vibration (mode 17) is assigned to C-H aromatic stretching vibration at 3042 cm$^{-1}$ for Cis-Indigo and 3105 cm$^{-1}$ for Trans-Indigo which is comparable with the experimental result at 3100 cm$^{-1}$.

The C-H in plane bending vibration is observed in the region 1025-1280 cm$^{-1}$ and C-H out of plane bending vibration in the region 690–850 cm$^{-1}$ [16]. The computed vibrations (modes 13, 12, 11, 10) are assigned to C-H in plane bending vibrations at 1262, 1169, 1074, 1070 cm$^{-1}$ for Cis-Indigo and at 1316, 1184, 1096, 1094 cm$^{-1}$ for Trans-Indigo which are comparable with the experimental results at 1250, 1180, 1080, 1025 cm$^{-1}$. The computed vibrations (modes 7, 6, 5) are assigned to C-H out of plane bending vibrations at 792, 764, 701 cm$^{-1}$ for Cis-Indigo and at 802, 764, 718cm$^{-1}$ for Trans-Indigo which are comparable with the experimental result at 820 780, 720 cm$^{-1}$.

### 4.2.3. C=O Vibrations

The C=O stretching vibration is observed in the region 1750-1680 cm$^{-1}$ [17]. The computed vibration (mode 16) is assigned to C=O stretching vibration at 1726 cm$^{-1}$ for Cis-Indigo and 1730 cm$^{-1}$ for Trans-Indigo which is comparable with the experimental result at 1700 cm$^{-1}$.

### 4.2.4. C=C Vibrations

The C=C vibration is in general observed in the region 1480 – 1630 cm$^{-1}$ [18-19]. The computed vibration (mode 15) is assigned to C=C stretching vibrations at 1570 cm$^{-1}$ for Cis-Indigo and 1620 cm$^{-1}$ for Trans-Indigo which is comparable with the experimental result at 1560 cm$^{-1}$.

### 4.2.5. C-N, C-C Vibrations:

The computed vibration (mode 9) is assigned to both C-N and C-C stretching vibration at 883 cm$^{-1}$ for Cis-Indigo and 933 cm$^{-1}$ for Trans-Indigo which is comparable with the experimental result at 960 cm$^{-1}$.

### 4.3. Thermo-Dynamical Properties

In the framework of molecular orbital theory the ionization energy and electron affinity can be expressed by HOMO and LUMO orbital energies as I = -E$_{HOMO}$ and A = -E$_{LUMO}$. The global hardness is η = 1/2(E$_{LUMO}$–E$_{HOMO}$).

**Table 3:** The Optimized Calculations of Total Energies (a.u), Zero Point Vibrational Energies (kcal mol$^{-1}$), Rotational Constants (GHz), Entropies (cal k$^{-1}$), Specific Heat C$_V$ (cal k$^{-1}$), Total Dipole Moment (Debye), Nuclear Repulsion Energy (eV), E$_{LUMO}$ and E$_{HOMO}$ (eV), HOMO-LUMO Energy Gap (eV), Ionization Energy (I) (eV), Electron Affinity (A) (eV), Global Hardness (η) (eV), Electronic Chemical Potential (µ) (eV), Global Electrophilicity Index (ψ) (eV) and finally softness (ζ) (eV $^{-1}$) for Indigo isomers at B3LYP/6-311G(d,p).

| | | |
|---|---|---|
| **Total Energy** | -875.9119423 | -875.8864052 |
| **Zero Point Energy** | 140.89772 | 140.65091 |
| **Rotational Constants** | 1.15987 | 1.11461 |
| | 0.17367 | 0.17144 |
| | 0.15106 | 0.1491 |
| **Entropy** | | |
| Total | 121.49 | 122.51 |
| Transational | 42.59 | 42.59 |
| Vibrational | 33.62 | 33.69 |
| Rotational | 45.28 | 46.23 |
| **Nuclear Repulsion Energy** | 3.8 *10$^4$ | 3.8*10$^4$ |
| **Specific Heat Cv** | 59.74 | 59.89 |
| **Dipole Moment** | 0 | 7 |
| **E$_{LUMO}$** | -3.01 | -2.79 |
| **E$_{HOMO}$** | -5.52 | -5.76 |
| **HOMO-LUMO energy gap** | 2.5 | 3 |
| **Ionization energy (I)** | 5.52 | 5.76 |
| **Electron Affinity (A)** | 3.01 | 2.79 |
| **Global Hardness (η)** | 1.26 | 1.49 |
| **Chemical Potential (µ)** | 4.27 | 4.28 |
| **Global Electrophilicity Index (ψ)** | 7.24 | 6.15 |
| **Softness (ζ)** | 0.79 | 0.67 |
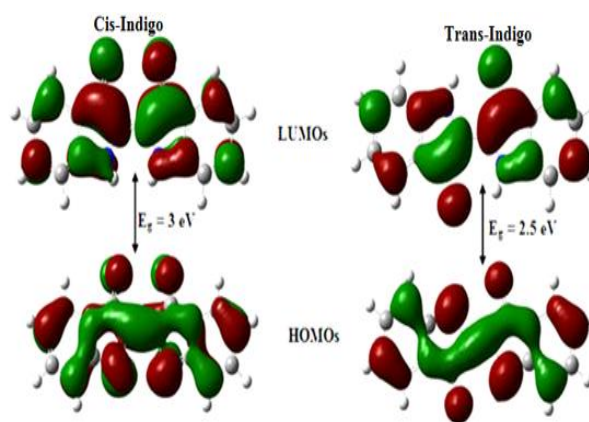


**Figure 3:** LUMO-HOMO energy gaps for Indigo isomers at B3LYP/6-311G(d,p).

The electron affinity can be used in combination with ionization energy to give electronic chemical potential, µ=

$1/2(E_{LUMO} + E_{HOMO})$. The global electrophilicity index, $\psi = \mu^2 /2\eta$ and softness, $\zeta = 1/\eta$ [20]. These parameters have been evaluated and tabulated in Table 3. Also, many calculated thermo-chemical parameters are evaluated and tabulated in Table 3 such as total energy, zero-point vibrational energy, rotational constants, entropy at room temperature, specific heat $C_V$, total dipole moment, nuclear repulsion energy and HOMO-LUMO energy gap for Indigo isomers at B3LYP/6-311G(d,p).

### 4.4. Frontier molecular properties

Highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) determine the way the molecule interacts with other species. The HOMO-LUMO energy gap characterizes the chemical reactivity and kinetic stability of the molecule [21-22]. The HOMO-LUMO energy gaps are 3 and 2.5 eV for both Cis and Trans Indigo, respectively. We notice that the HOMOs of both Cis and Trans indigo are $\pi$ orbitals while the LUMOs are $\pi^*$ orbitals. Also, Fig. 4 shows the total calculated density of state (DOS) spectrum for Cis and Trans Indigo at B3LYP/6-311G(d,p). The total DOS spectrum was scaled by 0.5. Not only the frontier molecular orbitals affecting the way the molecule interacts with other species But also the dipole moment value which determine the reactivity of molecule to interact with the surrounding media [23].
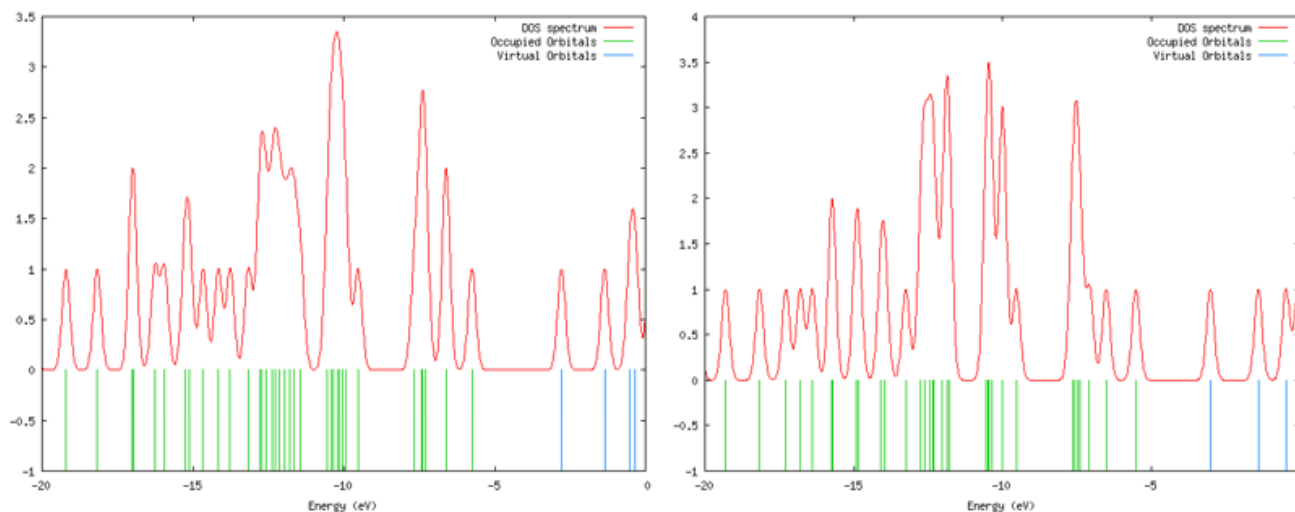


**Figure 4:** Density of state (DOS) spectra for Indigo isomers at B3LYP/6-311G(d,p).

The dipole moment of Cis-Indigo is calculated to be 7 Debye, which indicates its relatively high reactivity. By comparison, the Trans-Indigo has no dipole moment which indicates its high stability and low reactivity. Such results showed that only Cis-Indigo is IR active and Trans-Indigo is IR inactive. Consequently, FT-IR became the only spectroscopic tool to differentiate between Indigo isomers.

## 5 Conclusion

The Cis-Indigo is highly recommended to be a promising structure for many applications in optoelectronic devices due to its high calculated dipole moment value (7 Debye) which indicates its high reactivity to interact with the surrounding molecules and HOMO-LUMO energy gap of 3 eV rather than Trans-Indigo which has no dipole moment and HOMO-LUMO energy gap of 2.5 eV. Also, our calculations have shown that Trans-Indigo is IR inactive, and only Cis-Indigo is IR active due to its high dipole moment value (7 Debye).

### Highlights

1. B3LYP as well as FTIR were utilized to analyze Indigo forms.

2. Vibrational assignments for Indigo forms were aided at B3LYP/6-311G(d,p).

3. Cis-Indigo is a promising structure for solar cells due to its high dipole moment (7 Debye) and HOMO/LUMO band gap (3 eV).

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