Introduction

Bisindolylmaleimide derivatives such as arcyriarubin and arcyriaflavin, which are isolated from the fruiting bodies of the slime mold (Arcyria denuudata), contain both two indole subunits and a maleimide subunit. These compounds correspond to a core structure of competitive inhibitors of protein kinase C (PKC) or DNA topoisomerase, as staurosporine, rebeccamycin, and ICP-1,4 which have a bisindolylmaleimide or indolocarbaazole skeleton with a C–N linkage to a sugar moiety. The ability of selective inhibition or regulation of the metabolism of cells makes them therapeutically important anticancer agents.5 The phosphorylation assays available for a specific detection.16,17 Most bisindolylmaleimides are vivid red crystals1 and some of them exhibit red luminescence in their solid phase; amorphous films of N-methylated derivatives have been applied for fabrication of red light-emitting diodes (LEDs).18

The origin of the large Stokes shift of the emission of bisindolylmaleimides in solution has not been fully understood. In general, it is caused by a significant difference between the absorption wavelength, which leads to suitable luminescence assays available for a specific detection.16,17 Most bisindolylmaleimides are vivid red crystals and some of them exhibit red luminescence in their solid phase; amorphous films of N-methylated derivatives have been applied for fabrication of red light-emitting diodes (LEDs).18

The photophysical properties of two bisindolylmaleimide derivatives, 3,4-bis(3-indolyl)-1-H-pyrrole-2,5-dione (acyriarubin A) and indol(2,3-a)pyrrolo(3,4-c) carbazole-5,7-(6 H)-dione (arcyriaflavin A), are investigated by using ab initio molecular orbital (MO) and multireference perturbation theory. These compounds are suggested to exist as monovalent anions deprotonated from an indole NH group in aprotic polar solvents. The analysis of MOs shows that the electronic structures of the S1 and S2 states are described by the single- or double-electron excitation between the naturally localized MOs on an indole moiety and on the maleimide part. This indicates that the intramolecular charge transfer (ICT) transfer may occur by photoexcitation. The minimum-energy structure of the arcyriarubin A anion is twisted; the dihedral angles between the indole and maleimide rings are 83.4° and 20.2° for the S1 and S0 states, respectively. The analysis of the minimum energy path along the coordinate of the twist angle is performed to explore the emission process from the S1 state. It has been shown that the magnitude of the Stokes shift increases with increasing the twist angle, but the oscillator strength decreases. It has been suggested that the experimentally observed fluorescence arises on the way toward the energy minimum of the S1 state. The Stokes-shifted emission of arcyriaflavin A is contributed by the S1→S0 electronic relaxation after the excitation in the S2 state.

Theoretical Study of Photophysical Properties of Bisindolylmaleimide Derivatives

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On another matter, fluorescent, chemiluminescent, and bioluminescent compounds have been developed for luminescence assays,8–10 especially for specific detection of certain biomolecules.11–13 Various indole derivatives were also synthesized, and their luminescent characteristics were investigated.14,15 A number of bisindolylmaleimide derivatives exhibit strong fluorescence accompanying a large Stokes shift with respect to the absorption wavelength, which leads to suitable luminescence

Figure 1. Molecular structures of BIM and C-BIM.
energies against Souza pointed out that the slopes of the plots of emission immediately after the report of Kaletas et al., Kosower and de for the relative energy to the S0 state of the most stable isomer. They finally concluded cannot expect ICT in which the electron density transferred from of the electron density over the whole molecule, therefore, we are involved in the electronic transitions exhibit a delocalization functional theory (DFT) indicate that all of the orbitals, which However their quantum chemical calculations with density their quantum chemical calculations with density functional theory (DFT) indicate that all of the orbitals, which are involved in the electronic transitions exhibit a delocalization of the electron density over the whole molecule, therefore, we cannot expect ICT in which the electron density transferred from one indole unit to the maleimide part. They finally concluded that no ICT occurs in BIM and C-BIM. On the other hand, immediately after the report of Kaletas et al., Kosower and de Souza pointed out that the slopes of the plots of emission energies against E(T30) for these bisindolylmaleimide derivatives, BIM (0.37) and C-BIM (0.54), would establish that the emissions arise from the charge transfer.25 Thus, it is still a subject of controversy whether ICT does occur in BIM and C-BIM or not. Furthermore, the DFT calculation is suitable to explore the features of the electronic ground state around the equilibrium geometry, whereas it could not be enough to describe the electronic structures related to the electronically excited states, especially in the donor—acceptor type of the electronic state. At least two configuration state functions (CSFs) are required for the ab initio calculation of the present molecular system. In order to look into the possibility of the donor—acceptor type transition, the multiconfiguration self-consistent field (MCSCF) calculations with the complete active space (CAS) is employed to determine the molecular orbitals (MOs), and then the multireference perturbation calculation is performed with CSFs obtained by the MOs.

In this paper we investigate the photophysical properties of BIM and C-BIM on the grounds of our results of quantum chemistry calculations. The molecular structures at the potential minima and the potential energies for the electronic ground (S0) state, the lowest electronic excited (S1) state, and the second excited (S2) state of these conformers (isomers) were obtained using the multireference perturbation theory along with use of CASSCF calculations. Details of these calculations are described in the method section. In the results and discussion section, we discuss the properties with our findings from BIM and those of C-BIM separately. In order to assign the species that are responsible for the absorption in an aprotic polar solvent, N,N-dimethylformamide (DMF), the vertical excitation energies and the transition dipole moments of the isomers are compared with

### Table 1: Potential Energies of the S0, S1, and S2 States and the Oscillator Strengths and the Excitation Energies for the Electronic Transitions of the Three Isomers of Neutral BIM

<table>
<thead>
<tr>
<th>electronic state</th>
<th>E/cm⁻¹</th>
<th>oscillator strength</th>
<th>λ/nm</th>
<th>our theo.</th>
<th>exp</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1 S0</td>
<td>0</td>
<td>0.32</td>
<td>327</td>
<td>366</td>
<td></td>
</tr>
<tr>
<td>S1</td>
<td>30508</td>
<td>0.14</td>
<td>268</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S2</td>
<td>37317</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N2 S0</td>
<td>0 (325)</td>
<td>0.28</td>
<td>327</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S1</td>
<td>30574 (30899)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S2</td>
<td>36548 (36873)</td>
<td>0.16</td>
<td>274</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N3 S0</td>
<td>(1254)</td>
<td>0.12</td>
<td>267</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S1</td>
<td>28949 (30245)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S2</td>
<td>37456 (38712)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Figures in parentheses in the column of E(energy)/cm⁻¹ stand for the relative energy to the S0 state of the most stable isomer.

<table>
<thead>
<tr>
<th>electronic state</th>
<th>E/cm⁻¹</th>
<th>oscillator strength</th>
<th>λ/nm</th>
<th>our theo.</th>
<th>exp</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1(-) S0</td>
<td>0</td>
<td>0.32</td>
<td>327</td>
<td>366</td>
<td></td>
</tr>
<tr>
<td>S1</td>
<td>30835</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S2</td>
<td>35146</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M2(-) S0</td>
<td>0 (1030)</td>
<td>0.28</td>
<td>327</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S1</td>
<td>30375 (31405)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S2</td>
<td>34042 (35072)</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>I1(--) S0</td>
<td>0 (1156)</td>
<td>0.16</td>
<td>274</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S1</td>
<td>22231 (23387)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S2</td>
<td>30590 (31746)</td>
<td>0.05</td>
<td>327 (366)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>I2(--) S0</td>
<td>0 (3307)</td>
<td>0.12</td>
<td>267</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S1</td>
<td>24592 (27899)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S2</td>
<td>31348 (34655)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Figures in parentheses in the column of E(energy)/cm⁻¹ stand for the relative energy to the S0 state of the most stable isomer.

* Two of the four are the deprotonated form of the maleimide NH group (M1(--)) and M2(--)), and the other are the deprotonated form of the indole NH group (I1(--) and I2(--)). Figures in parentheses in the column of E(energy)/cm⁻¹ stand for the relative energy to the S0 state of the most stable isomer.

---

**Figure 2.** Optimized structures of neutral BIM obtained by CASPT2/cc-pVDZ calculations and their relative potential energies are indicated in units of kcal mol⁻¹.

**Figure 3.** Optimized structures of deprotonated anions (M1(--), M2(--), I1(--), and I2(--)) of BIM obtained by CASPT2/cc-pVDZ calculations and their relative potential energies are indicated in units of kcal mol⁻¹.
the spectroscopic data.16,17 Detailed discussions of the characters of the low-lying electronic states and the occurrence of the ICT are made on the basis of the results of the multireference perturbation calculation. We also discuss in this section the origin of the Stokes-shifted fluorescence of these bisindolylmaleimides. Finally we summarize and compare the results of BIM and C-BIM in the conclusion section.

**Computational Methods**

Our previous paper suggested that BIM and C-BIM exist as the monovalent or divalent anions in aprotic polar solvents such as DMF (N,N-dimethylformamide) on the grounds of the comparison between absorption maxima and vertical excitation energies calculated with the MRCI (multireference configuration interaction) method by using the optimized geometries at the B3LYP/cc-pVDZ level of theory.16 However, we still have a doubt whether the most stable structure can be optimized by the single electronic configuration method based on DFT; the optimized structures we have reported might be misleading because the natural orbitals were not employed for the geometry optimization, especially for the charge-transfer system. In addition, only one anionic species which was deprotonated from the indole NH group has been theoretically explored in the previous paper, although the hydrogen atom of the maleimide NH group could be detachable.17,26 We should take into account two monovalent anions, a deprotonated form of the NH group of the maleimide moiety and a deprotonated form of the NH group of one of the indole moieties, for each derivative since the two indole subunits were equivalent. Therefore, we again carried out geometry optimization of electronic neutral species of BIM, C-BIM, and their monovalent anions with the more reliable CASPT2 method,27 because the MRCI method used in the previous paper was time-consuming for the system consisting of 25 heavy atoms and 13 (BIM) or 12 (C-BIM) hydrogen atoms to accomplish fully geometry optimizations. We employed Dunning’s cc-pVDZ (correlation consistent, polarized valence, double-ζ) basis set.28 In each step of the molecular geometry optimization, we first performed three-state-averaged complete active space self-consistent field (CASSCF) calculations to determine the molecular orbital set for subsequent multireference perturbation calculations. Then the potential energy and the analytical gradient for the molecular geometry were obtained from the multireference perturbation calculations using second-order Rayleigh–Schrödinger perturbation theory (RS2).27 The active spaces were employed as CAS(8,6) and CAS(6,5) for BIM and C-BIM, respectively. The main electronic configurations of the ground state of BIM (C₁ symmetry) and C-BIM (C₅ symmetry) are written as

BIM (1^1A (S₀)): (inner occupied orbitals)⁸(82a)²(83a)²(84a)²(85a)²(86a)⁰(87a)⁰,

C-BIM (1^1A (S₀)): (inner occupied orbitals)⁶(82a”)²(83a”)²(84a”)²(85a”)²(86a”)⁰.

The characters of each MO are mentioned in the later section. The canonical orbitals were obtained by the CASSCF calcula-
tion, and the configuration state functions (CSFs) were generated by single and double electron excitations based on the reference configurations obtained from the CASSCF calculations. In this work, the CSFs were generated with:

BIM: \([\{82a(83a)84a(85a)86a(87a)\}]^8\),

C-BIM: \([\{82a''(83a'')84a''(85a'')86a''\}]^9\)\).

The total number of configurations for multireference perturbation calculations with RS2 (CASPT2) of BIM was about 24,000,000, and that of C-BIM was about 19,000,000.

All of these quantum chemistry calculations were performed using the electronic structure program MOLPRO (revision 2006.1). The computers on which calculations were performed were PRIMEQUEST 580 and PRIMERGY RX200S3 (Fujitsu) and SR11000 (Hitachi) owned by the computer center of Kyushu University.

### Results and Discussion

#### 1. Bisindolylmaleimide (BIM)/Arcyriaarubin A

i. Identification of Conformer in N,N-Dimethylformamide (DMF) Solution

Three stable conformers (N1–N3) of neutral BIM have been obtained by the geometry optimization for the S0 state. These optimized structures are displayed in Figure 2 together with the relative potential energies. The relative energies are 0.0, 0.93, and 4.01 kcal mol\(^{-1}\) for N1, N2, and N3, respectively. The geometry optimization calculations have been performed in vacuo. The molecule in solution would walk up and down around these energy minima of these conformers.

The potential energies of the S0, S1, and S2 states and the vertical excitation energies (S1 → S0) are listed in Table 2. It is particularly worth noting that the potential energies of the electronic excited states of 11(1) and 12(2) are lowered remarkably, whereas those of 11(1) and 12(2) are similar to the neutral species. The S1 → S0 vertical excitation energy of isomer 11(1) is in good agreement with the excited state (\(\lambda_{\text{max}} = 452\) nm); furthermore, in terms of the calculated oscillator strength (f0), the electronic transitions of 11(1) and 12(2) are almost forbidden (f0 < 0.01), although the S1 → S0 transitions of 11(1) and 12(2) are allowed. Hence, it is suggested that the BIM molecule exists as the 11(1) form in DMF solution. The relative energies of the S0 state of M1(1), M2(2), I1(1), and I2(2) are 0.0, 2.95, 3.30, and 9.46 kcal mol\(^{-1}\), respectively. It is interesting to note that the isomers, which are deprotonated from the maleimide NH group, are energetically more stable than the isomers deprotonated from an indole group. In vacuo, it is suggested that the deprotonation from the maleimide unit could occur more easily than that from an indole unit, because in the neutral isomers (N1–N3), the Coulombic attracting force between the N and H atoms of the indole units is stronger than that of the maleimide unit from viewpoints of the N–H bond lengths and of Mulliken population analysis. Generally speaking, however, the subtraction of hydrogen atoms from solute by the solvent may cause the deprotonation of nonacidic compounds in solution. Such an interaction between neutral BIM molecules and solvents is necessary to generate the BIM anions. In the previous paper, we have attempted the geometry optimization of the BIM and DMF (N,N-dimethylformamide) complexes, and finally obtained only one configuration having a hydrogen bond between the H atom of indole NH and the O=C group of the DMF molecule (see also the Supporting Information of ref 16). The subtraction of an H atom from an NH group of the indole moiety would occur more easily than from the maleimide NH in DMF solution. Thus, the major species in DMF solution is assigned as 11(1).\)

### ii. MOs and Electronic Configurations of Isomers in Franck–Condon Region

The main electronic configuration of the ground state of BIM in CASPT2 is described as (1A (S0)): (inner occupied orbitals) 16(82a)2(83a)2(84a)2(85a)2(86a)2(87a)0. However, there are additional contributions from electronic excitations such as

- (inner occupied orbitals) 16(82a)2(83a)2(84a)2(85a)2(86a)2(87a)0,
- (inner occupied orbitals) 16(82a)2(83a)2(84a)2(85a)2(86a)2(87a)0, and
- (inner occupied orbitals) 16(82a)2(83a)2(84a)2(85a)2(86a)2(87a)0.

The molecular orbitals (MOs) are characterized by 83a (highest occupied molecular orbital, HOMO-2), 84a (HOMO-1), 85a (HOMO), and 86a (lowest occupied molecular orbital, LUMO) under C1 symmetry. At least four MOs should be included in the active space. Finally, the six active orbitals are important to describe the low-lying electronic states, and these orbitals are occupied by eight electrons in CASSCF (8 electrons/6 MOs).

The primary configuration for the S1 state of neutral BIM (N1–N3) is the single electron excitations to LUMO from HOMO which is indicated as (HOMO)1 (LUMO)1 and that of the S2 state is (HOMO-1)1 → (LUMO)1. Figure 4 illustrates these MOs, (HOMO-1), HOMO, and LUMO of N1–N3. The vertical excitation energies of all the conformers of neutral BIM are inconsistent with a low energy absorption band (\(\lambda_{\text{max}} = 452\) nm), and all of the electronic transitions could not be ascribed to the ICT process since the corresponding MOs are delocalized over the center of the molecule.

The electronic configuration of the S0 state of anionic BIM (M1(1), M2(2), I1(1), and I2(2)) is also described as (1A (S0)): (inner occupied orbitals) 16(82a)2(83a)2(84a)2(85a)2(86a)2(87a)0, since the isomers are deprotonated anions. The other electronic configurations which contribute to the electronic ground and excited states are listed in Table 2. Figure 5 illustrates their MOs, (HOMO-2), (HOMO-1), HOMO, and LUMO of these isomers, which are determined by our MCSCF calculations. For all these isomers, a main character of the S1 state corresponds to a single electron excitation of (HOMO)1 → (LUMO)1, and that of the S2 state corresponds to (HOMO-1)1 → (LUMO)1. The difference between M1(1), M2(2), I1(1), and I2(2) is seen in the secondary or the tertiary electronic configurations (the configurations are listed in Table S2 of the Supporting Information). It is clearly seen that these excitation, HOMO–LUMO, or (HOMO-1)–LUMO, of isomer I1(1) corresponds to the electron transfer from \(\pi\)-MO localized on the deprotonated indole moiety to \(\pi^*\)-MO localized on the maleimide moiety, i.e., this electronic transition corresponds to the ICT process. Although the single electron excitation to an antibonding \(\pi^*\)-MO causes destabilization of the molecule, it is suggested that the charge–charge interaction stabilizes the excited states. On the other hand, HOMO–LUMO or (HOMO-1)–LUMO of isomer I1(1)
1) (LUMO) excitation of \(M_1(-)\) and \(M_2(-)\) corresponds to the \(\pi-\pi^*\) transition localized on the maleimide moiety. In the other words, the ICT process is not involved in the electronic transition of \(M_1(-)\) and \(M_2(-)\).

### iii. Optimized Structure of \(S_1\) and Origin of Stokes Shift.

In order to investigate the origin of the large Stokes shift of the BIM molecule in solution\(^{16,17}\), we have carried out the molecular geometry optimization to search the energy minimum in the \(S_1\) potential surface of the monovalent anion, which is deprotonated from an indole NH group assigned above to the species existing in solution. The optimized structure in the \(S_1\) state of monovalent anions of BIM denoted by \(I(-)^*\) is displayed in Figure 6, while the potential energies and the vertical transition energies to the \(S_0\) corresponding to theoretical emission energies are listed in Table 3. The optimized geometry of \(I(-)^*\) changes dramatically. The deprotonated indole subunit in \(I(-)^*\) is twisted, and it makes a dihedral angle of 83.4° with the maleimide unit, which is close to a right angle. The potential energy at the optimized geometry in the \(S_1\) state of \(I(-)^*\) prominently decreased by 5920 cm\(^{-1}\) from the energy of the Franck−Condon (FC) region in the potential surface of \(I_1(-)\). The HOMO−LUMO single excitation is the primary configuration even for the optimized geometry in the \(S_1\) state of \(I(-)^*\); HOMO that is localized in the deprotonated indole ring is almost orthogonal to LUMO (see Figure 7). The extensive localization of the MOs depending on the two functional moieties (i.e., the indole ring and the maleimide ring) could enhance the ICT character of \(I(-)^*\) and simultaneously this enhancement stabilizes the potential energy of the \(S_1\) state. On the other hand, the potential energy of the \(S_0\) state at the twisted structure increases by 6956 cm\(^{-1}\) (19.9 kcal mol\(^{-1}\)) in comparison with that at the equilibrium geometry. Such a significant destabilization in the \(S_0\) state suggests that a high potential barrier exists against the twisting motion, and finally a drastic twisting results in the large Stokes shift. As seen in Table 3, however, the vertical transition energy between the \(S_1\) and \(S_0\) states at the minimum of \(S_1\) is 9296 cm\(^{-1}\), which corresponds to 1076 nm emission. This wavelength is vastly different from an experimental value (600 nm).\(^{16}\) The calculated emission frequency is red-shifted by 12 935 cm\(^{-1}\) from an absorption (22 231 cm\(^{-1}\)) for \(I_1(-)^*\), which means that the theoretically predicted value of Stokes shift is about 2.4 times larger than the experimental value (5457 cm\(^{-1}\)).\(^{16}\) Furthermore, since the calculated oscillator strength (\(f_0\)) is 0.002, the \(S_1-S_0\) transition has a forbidden character due to the orthogonality of MOs discussed above. Thus, in anionic BIM, the potential minimum would not correspond to the minimum that provides emission. We however found the two minimum energy structures of the \(S_0\) and the \(S_1\) states are quite similar to each other.

![Figure 6](image)

**Figure 6.** Optimized structure in the \(S_1\) state of the monovalent anions of BIM (\(I(-)^*\)) and that of the neutral BIM (\(N^*\)).

### Table 3: Potential Energies of the \(S_0\) and \(S_1\) States and the Oscillator Strengths and the Value of Stokes Shift for the Optimized Structure in the \(S_1\) State of Monovalent Anions of BIM (\(I(-)^*\))

<table>
<thead>
<tr>
<th>electronic state</th>
<th>(E/cm^{-1})</th>
<th>oscillator strength</th>
<th>Stokes shift/cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(I(-)^*)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(S_0)</td>
<td>0</td>
<td>0.002</td>
<td>12935</td>
</tr>
<tr>
<td>(S_1)</td>
<td>9296</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(exp^a)</td>
<td>16667</td>
<td></td>
<td>5457</td>
</tr>
</tbody>
</table>

\(^a\) Reference 16.
The obtained potential energy curves are shown in Figure 8, as a function of the corresponding dihedral angle. The potential curve of the S1 state suggests that the photoexcited molecule at the FC region of the S1 state. In other words, the twisting. This electronic transition is allowed since the structure of anionic N* is only slightly shifted from the equilibrium geometry of N1 (FC region). The dihedral angle of the two indole units with respect to maleimide unit for N* is 17.2°; this value decreased by 15.6° from that of N1 in the S0 state (32.8°). The S1−S0 vertical excitation energy (24 497 cm⁻¹) at the minimum of the S1 state is also inconsistent with the experimental data, and a theoretical value of Stokes shift from that of the FC region (30 508 cm⁻¹) is 6012 cm⁻¹.

Table 4: Potential Energies of the S0, S1, and S2 States and the Oscillator Strengths and the Excitation Energies for the Electronic Transitions of the Neutral Isomer (cN), the Deprotonated Anions (cI⁻, cM⁻) of C-BIM.

<table>
<thead>
<tr>
<th>electronic state</th>
<th>S0</th>
<th>S1</th>
<th>S2</th>
<th>S1</th>
<th>S2</th>
<th>λ (nm)</th>
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<tbody>
<tr>
<td>E/cm⁻¹</td>
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<td>37581</td>
<td>32086</td>
<td>34938</td>
<td>43627</td>
<td>296</td>
</tr>
<tr>
<td>oscillator strength</td>
<td>0.18</td>
<td>0.12</td>
<td>0.15</td>
<td>0.04</td>
<td>0.62</td>
<td>286</td>
</tr>
</tbody>
</table>

*S cM(1) is the deprotonated form of the indole NH group, and cM(2) is the deprotonated form of the maleimide NH group. Figures in parentheses in the column of E(energy)/cm⁻¹ stand for the relative energy to the S0 state of the most stable isomer. Reference 16.

II. Connected Bisindolylmaleimide (C-BIM)/Arcyrialflavin A. i. Identification of Conformer in N,N-Dimethylformamide (DMF) Solution. Figure 10 shows the minimum-energy structures of a neutral isomer (cN) and monovalent anionic isomers (cI⁻ and cM⁻) of arcyrialflavin A (connected bisindolylmaleimide, C-BIM) in the S0 state. Isomer cI⁻ is the deprotonated form of an indole NH subunit, and isomer cM⁻ is the deprotonated form of the maleimide NH group. Only one stable conformer has been obtained for each species of C-BIM since the indole subunits are not flexible due to the existence of central C−C (2−2') bond connecting the two indole moieties. The potential energies of the S0, S1, and S2 states and the vertical excitation energies (S1−S0, S2−S0) for isomer cN, cI⁻, and cM⁻ are given in Table 4. In contrast to BIM, the deprotonated form of an indole NH group (cI⁻) is more stable by 13.50 kcal mol⁻¹ than the deprotonated form of the maleimide NH group (cM⁻). The potential energies of the S1 and S2 states of the monovalent anion cI⁻ are remarkably lowered, whereas those of the other isomers are quite high. The vertical excitation energies of the S1−S0 and the S2−S0 transitions of isomer cI⁻ are in good agreement with the experimental data. In addition, the relationship between the calculated oscillator strengths (f0) for these electronic transitions is consistent with the intensities of the two absorption bands. These results suggest that the C-BIM molecule exists as the cI⁻ form in DMF solution.

ii. MOs and Electronic Configurations of Isomers. The number of the electrons in C-BIM is less than that in BIM by two, and the S0 state of C-BIM is composed of several electronic configurations:

(inner occupied orbitals)¹⁶²(82a)²(83a)²(84a)²(85a)²(86a)²
(inner occupied orbitals)¹⁶²(82a)²(83a)²(84a)²(85a)²(86a)²
(inner occupied orbitals)¹⁶²(82a)²(83a)²(84a)²(85a)²(86a)²

*References 16a-16c.
and the molecule de-excites, we carried out geometry optimization

The theoretical study of bisindolylmaleimides suggests that most part of the electronic transitions suggest the occurrence of ICT. The ICT character is localized on the maleimide moiety, and these electronic excitations correspond to an electron transfer from π-MO localized on the deprotonated indole moiety to π* MO localized on the maleimide moiety, and these electronic transitions suggest the occurrence of ICT. The ICT character lowers the energies of the excited states. This may be the reason why the S1−S0 or S2−S1 vertical excitation energies are lower than the other two species.

### Conclusions

In this paper we discuss the photophysical properties of two fluorescent indole derivatives, BIM (or arcyriarubin A) and C-BIM (or arcyriallav A) on the basis of quantum chemistry calculations. The occurrence of ICT in BIM and C-BIM is a subject of controversy. Our results have brought an explanation of the issue. The neutral species and the monovalent anion that is deprotonated from the maleimide NH group of BIM show no transitions containing the ICT character. The ICT character significantly depends on the shape of molecular orbitals. In these species, the MOs involved in low-energy electronic transitions are symmetric. The monovalent anion which is deprotonated from an indole NH group of BIM exhibits that some electron excitations correspond to the ICT. C-BIM shows a similar tendency to BIM. Single deprotonation from one of the indole NH groups makes the MOs asymmetric, which may be a reason why their photophysical aspects of the anions of BIM and C-BIM are similar to the asymmetric indolylmaleimides. The transition of electron to an antibonding π* MO causes destabilization of the molecule, but the ICT interaction stabilizes the excited states. These properties are consistent with solvatochromic trends. Consequently, we conclude that the ICT occurs in BIM and C-BIM in the aprotic polar solvents as N,N-dimethylformamide (DMF).

![Figure 11.](image)

**Figure 11.** (HOMO-1), HOMO, LUMO, and (LUMO+1) of cN, cl−, and cm−.

**TABLE 5: Potential Energies of the S0 and S1 States and the Oscillator Strengths and the Value of Stokes Shift of the S0−S1 Electronic Transition for the Optimized Structure in the S1 State of the Monovalent Anion of C-BIM (cl−).**

<table>
<thead>
<tr>
<th>Electronic state</th>
<th>E/cm⁻¹</th>
<th>Oscillator strength</th>
<th>Stokes shift/cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>cl−</td>
<td>S0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>S1</td>
<td>17809</td>
<td>0.07</td>
</tr>
<tr>
<td>exp</td>
<td></td>
<td>19802</td>
<td></td>
</tr>
</tbody>
</table>

* Reference 16.
In contradiction to the similarity of properties of the electronic ground state of BIM and C-BIM, the behavior of BIM in the electronic excited states after photoexcitation is quite different from that of C-BIM. In C-BIM, the S₂ → S₁ excitation is the initial process of the photoabsorption. In solution, the molecule in the S₂ state immediately relaxes after photoexcitation to the S₁ state, hence the Stokes-shifted emission arises from the minimum of the S₁ potential energy surface. The potential minimum geometry of C-BIM in the S₁ state is planar. However, such an intermediate structure has not been obtained as the local minimum of the potential energy surface in our geometry optimization procedure. To solve this question, ab initio molecular dynamics (ab initio MD) simulations would be useful.

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Supporting Information Available: Additional tables of data. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes


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