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Novel push–pull π-conjugated compounds suffering steric hindrance between donor and acceptor subunits

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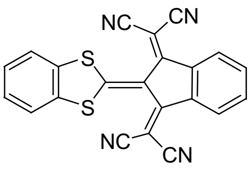
ABSTRACT

A novel push–pull compound with a 1,3-bis(dicyanomethylene)indan-2-ylidene moiety as an acceptor subunit has been prepared along with its two derivatives. These molecules are severely distorted from its planar structure and in solution undergo dynamic interconversion between bent structures. The structural features and UV–vis spectroscopic results indicate that the zwitter-ionic nature of the molecule is enhanced in the ground state, which is also supported theoretically by density functional calculations.

π-Conjugated compounds that possess an electron-donating group at one end and an electron-accepting group at another end, designated as push–pull compounds, have received much attention owing to the interesting optoelectronic properties they exhibit.[1] Many of the reported push–pull systems have 1,3-dithiol-2-ylidene and dicyanomethylene groups as a donor unit and an acceptor unit, respectively, which are connected by π-conjugated spacers such as polyenic,[2] quinoidal, [3] heterocyclic,[4] and heteroquinoidal[5] substructures. Thus, the size and nature of these spacers govern the ground-state polarization and electronic properties. With the presumption that a distorted spacer would enhance a single bond character of the push–pull π-conjugation and zwitter-ionic nature of the molecule as well, we designed a new molecule in which the donor and acceptor moieties are linked as closely as possible to suffer steric hindrance with each other. Among a variety of push–pull π-conjugated compounds investigated up to now, those incorporating anthraquinoidal spacers are unique sterically crowded systems.[6,3a] In this Letter, we describe the synthesis and characterization of new push–pull π-conjugated compounds, in which steric hindrance is introduced using a 1,3-bis(dicyanomethylene)indan framework (A) as an acceptor moiety.[7]



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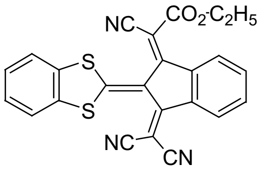

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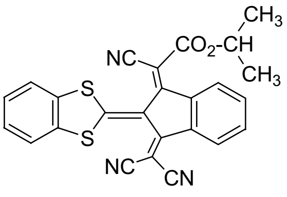

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2-(Benzo-1,3-dithiol-2-ylidene)-1,3-bis(dicyanomethylene)indan (**1**) was prepared by the condensation reaction of 1-dicyanomethylene-3-indanone with 1,3-benzodithiolylium tetrafluoroborate followed by the Knoevenagel reaction using malononitrile in chloroform (Scheme 1).[8] Ethyl cyanoacetate and isopropyl cyanoacetate, instead of malrononitrile, were also used in the condensation reaction in chlorobenzene to obtain **2** and **3**, respectively. The yields in these reactions were extremely low, but the products could be isolated as sufficiently pure compounds by GPC and recrystallization from dichloromethane.

The molecular and crystal structures of **1** were determined by X-ray crystal analysis (Figs. 1 and 2).[9,11] The molecule is not planar but bent to a butterfly structure contrary to our presumption that the molecule is twisted. The donor and acceptor entities, either of which is composed of a five membered-ring and a condensed benzene ring, exhibit planar geometries (D and A planes, respectively), whereas the sp^2 carbon atom at the 2 position of the indan moiety is subject to pyramidal deformation. Thus, the D and A planes intersect each other by 130°. The dicyanomethylene side chains

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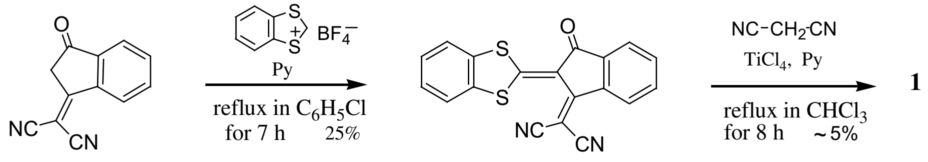

Scheme 1.

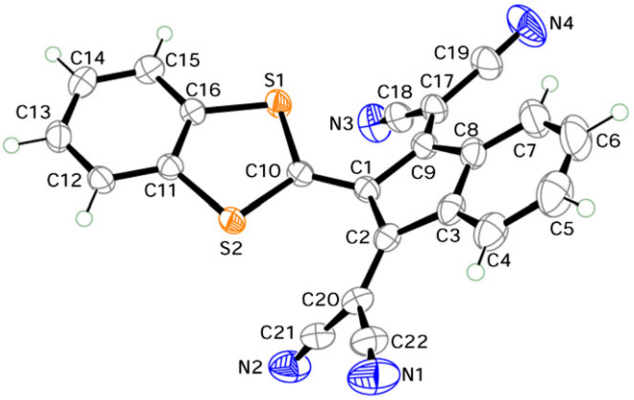

Figure 1. Perspective view of **1**. Ellipsoids are drawn at 50% probability.

are slightly twisted from the D and A planes. The central C=C bond length is 1.397 Å, being longer than that of a typical double bond and corresponding to that of benzene. These results indicate that the zwitter-ionic nature is extremely enhanced in the ground state of **1**. The structural features of **1** are well reproduced by theoretical calculations. Thus, the molecular geometries were optimized at the B3LYP/6-31G** level to show that the bent angle is 130.8° and the central C=C bond distance is 1.392 Å, both being well compared to the observed values.

Significantly short intramolecular contacts were observed between the N and S atoms: 3.216 and 3.187 Å. The charge distribution calculated based on B3LYP/6-31G** shows high negative and positive charges in these N and S atoms, respectively (Fig. 3). Thus, the short contacts could be attributed principally to electrostatic interactions. It could be anticipated that the molecule of **1** gains the stabilization of intramolecular electrostatic S–N attraction by

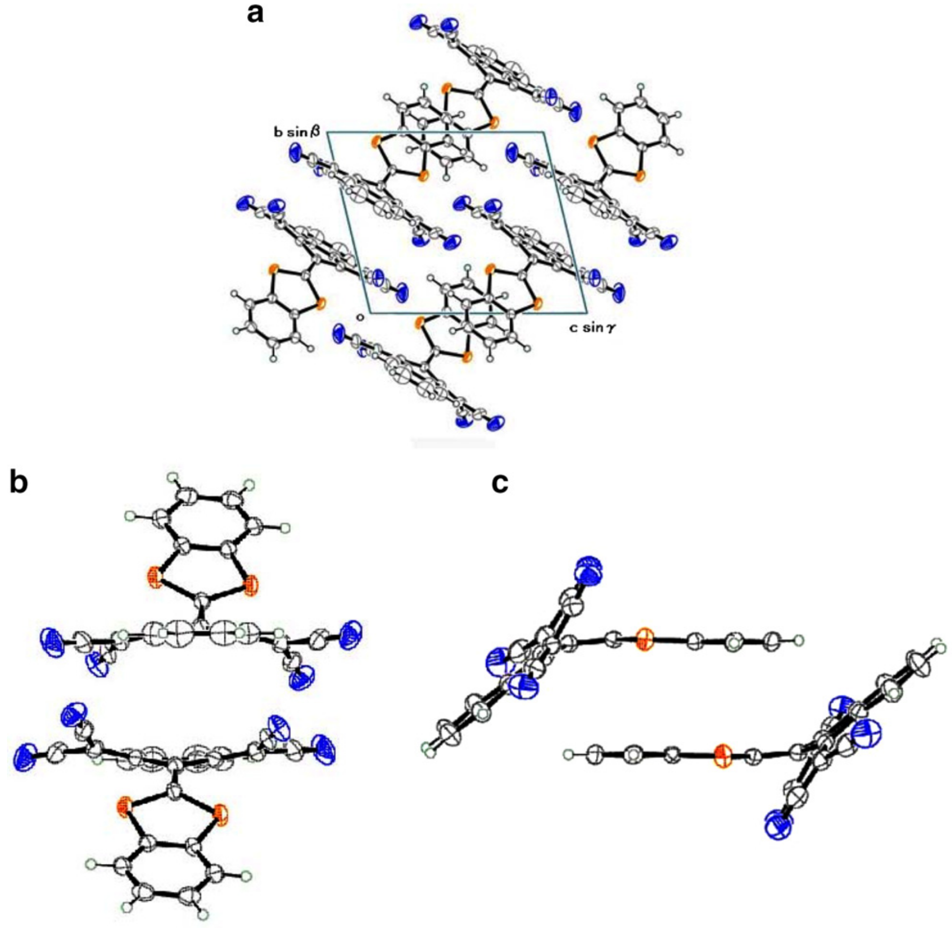

Figure 2. (a) Projection of the crystal structure of **1** along the *a-axis. (b) Side view of the indan subunit in* **1** showing overlap diagram. (c) Side view of the benzo-1, 3-dithiol subunit in **1** showing overlap diagram. Ellipsoids are drawn at 50% probability.

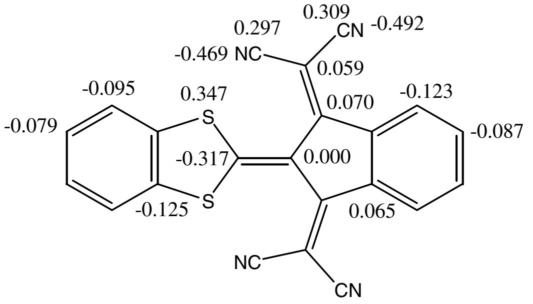

Figure 3. Charge distribution based on B3LYP/6-31G** calculation.

bending at the expense of the stabilization due to push–pull π-delocalization through the planar π-system.

In the crystal lattice, the molecules align perpendicularly to the [0 1 1] plane by facing the A planes with an interplanar distance of 3.84 Å (Fig. 2). The D planes are also in a face-to-face arrangement between neighboring molecules, as shown in Figure 2. Its interplanar distance is 3.88 Å. This outcome of the crystal structure is in contrast to our presumption that D–A stacking would be realized.

Taking into account the bent structure of **1**, its derivative **2**, which is substituted by different electron-withdrawing groups at the 1 and 3 positions of the framework, should furnish a chiral structure. The crystal structure of **2** was determined by X-ray crystal analysis and revealed to be nonplanar and therefore chiral molecule (Fig. 4).[9,10] The benzene rings of the donor and acceptor moieties intersect mutually by 130°. The central C=C bond is as long as 1.383 Å. An intramolecular short contact is observed for the ethoxycarbonyl group directed to the 1,3-dithiol ring, showing the S–O=C (2.956 Å) interaction.[12] Another intramolecular contact occurs on the other side of the molecule between the nitrogen and sulfur atoms (S–N 3.221 Å). In contrast to **1**, the cyano group on the same side as the ester functionality has an intermolecular short C–S contact with the neighboring sulfur atom (3.138 Å).

To determine whether **1** and **2** would take a bent structure in solution, **3** with an isopropyl group as a probe for the NMR spectral investigation was designed and prepared. The ^{1}H NMR spectra of **3** display two doublet and two triplet signals due to the indan moiety along with two symmetrical signals of the AA'BB' profile assigned to the protons of the benzo-1,3-dithiol fragment. The protons of the isopropyl group occurred in a doublet signal and the variable low-temperature ^{1}H NMR did not bring about splitting into two doublet resonances. However, in the variable low-temperature ^{13}C NMR, the line shape changed (Fig. 5); the isopropyl signals displayed broadening at around −40 °C and decoalescence at around −55 °C, retaining the other 23 signals unchanged in their sharpness and chemical shifts. These observations clearly indicate that the bent structure of **3** undergoes dynamic inversion to experience a time-averaged planar structure at room temperature and the inversion is slowed down at low temperature to exhibit diastereotopic isopropyl signals in the NMR time scale. The activation energy was estimated by a coalescence method to be approximately 43.2 kJ mol^{-1} at −55 °C.

Note that the dynamic behavior does not accompany the rotation of the central carbon–carbon double bond. If such were the case, the ^{13}C signals of the benzo-1,3-dithiole framework should also be observed as a time-averaged ones with respect to the longest molecular axes. We envisaged that the free rotation of the central double bond would be observed at high temperatures. However, in variable-temperature ^{13}C NMR measurement, the spectrum showed no change to a time-averaged structure of C_s symmetry even up to 100 °C in $CD_2Cl_2CD_2Cl_2$.

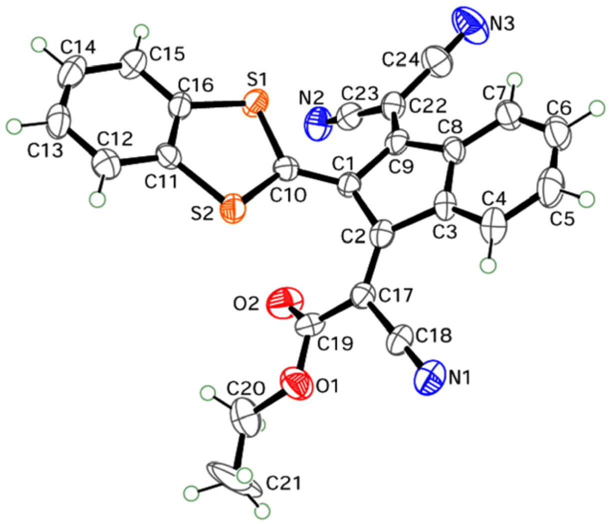

Figure 4. Perspective view of **2**. Ellipsoids are drawn at 50% probability.

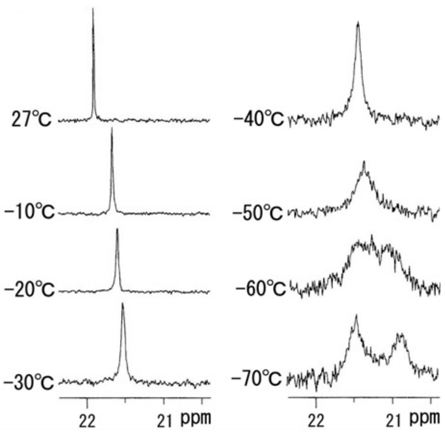

Figure 5. Variable-temperature ^{13}C NMR of **3** in acetonitrile (150 MHz), showing signals of methyl carbons in isopropyl group.

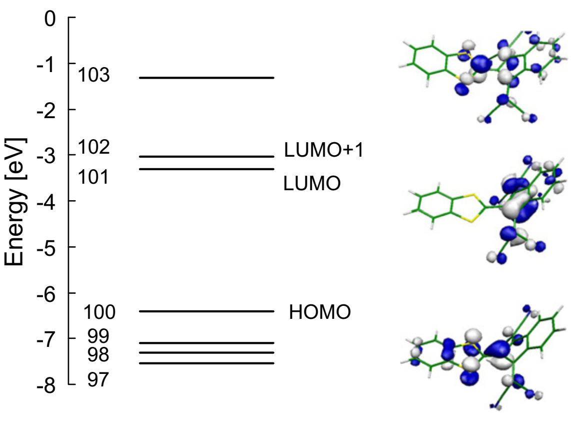

Figure 6. MO scheme for **1** based on DFT calculations with the B3LYP functional.

The UV–vis spectrum of **1** shows two strong absorption bands at 322 nm (ε 27,310) and 450 nm (ε 31,960) in chloroform. To characterize the energy transition of **1**, excitation energy and absorption intensity were computed using time-dependent DFT calculations with the B3LYP functional (Fig. 5).

The computational results indicate that the HOMO–LUMO transition energy is 2.53 eV (490 nm), which seems to be in fairly good agreement with the observed longest-wavelength absorption, whereas its oscillator strength is remarkably small; as shown in the electron density contours in Figure 6, the HOMO–LUMO overlap is insufficient. On the other hand, for the transition from HOMO to LUMO + 1 with a transition energy of 3.04 eV (408 nm), the oscillator strength is 0.4163. Thus, we assigned the lowest transition to the HOMO–LUMO + 1 one, although the maximum λ value is strongly underestimated, being generally recognized for this method.

The LUMO is markedly concentrated in the indan subunit. On the other hand, the HOMO is less centered on the 1,3-dithiol-2-ylidene subunit. The LUMO + 1 is distributed in both donor and acceptor units. Thus, in the HOMO–LUMO + 1 transition, which is assigned to the lowest excitation, charge-transfer nature is hardly involved. In agreement with these results, the absorption band at 450 nm displayed neither bathochromic nor hypsochromic shift depending on the polarity of solvents (benzene, CH_2Cl_2, $CHCl_3$, and DMF). Generally, the intramolecular charge-transfer band exhibits bathochromic shift with increasing solvent polarity. The results obtained for **1** could be interpreted by assuming that the zwitter-ionic structure is developed already in the ground state to minimize the charge-transfer nature in electronic transition, which is also supported by charge distribution (Fig. 3) and large dipole moment (7.54 D) based on B3LYP/6-31G** calculation.

In cyclic voltammetry in dichloromethane, **1** exhibits one reversible oxidation wave at 1.39 V and one reversible reduction wave at −0.67 V versus SCE, respectively. The difference in the oxidation and reduction potentials, which reflects the HOMO–LUMO gap, is rather large for **1** compared with those of other related push–pull conjugated systems, indicating the rather large HOMO–LUMO gap.[7] This is also supported by the B3LYP/6-31G** calculations, showing that the HOMO–LUMO gap is as large as 3.11eV. These results could be also characteristic feature of sterically hindered push–pull conjugated compounds.

In summary, we prepared new push–pull π-conjugated compounds in which the donor and acceptor units are not connected through planar π-conjugation. A full structural characterization of this compound as a bent molecule has been carried out by X-ray diffraction analysis, ^{1}H and ^{13}C NMR spectra, and theoretical studies. In solution, the bent structure was found to be in dynamic inversion. Theoretical studies as well as UV–vis spectra showed that the contribution of the intramolecular charge-transfer nature is small and that the zwitter-ionic nature of the molecule is enhanced in the ground state.

Acknowledgment

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8. One-step synthesis of **1** from 1,3-bis(dicyanomethylene)-2-indanone and benzodithiolylium tetrafluoroborate was also carried out, but the yields were not improved.
9. Crystal data of **1**; $C_{22}H_8N_4S_2$ triclinic, $P\bar{1}$ (#2), $a = 9.195(4)$ Å, $b = 9.336(5)$ Å, $c = 11.\ 289(5)$ Å, $\alpha = 102.021(18)°$, $\beta = 106.888(16)°$, $\gamma = 92.833(19)°$, $V = 900.7(7)$ Å^3, $Z = 2$, $R = 0.0382$, $Rw = 0.0557$, GOF = 1.097.
10. Crystal data of **2**; $C_{24}H_{13}N_3O_2S_2$, monoclinic, $P2_1/c$ (#14), $a = 10.638(4)$ Å, $b = 15.088(5)$ Å, $c = 13.869(5)$ Å, $\beta = 113.289°$, $V = 2044.7(12)$ Å^3, $Z = 4$, $R = 0.0392$, $Rw = 0.0718$, GOF = 1.067.
11. Crystallographic data for the structural analysis of **1** and **2** have been deposited with the Cambridge Crystallographic Data Centre (CCDC 679925 for **1** and 679926 for **2**). These data can be obtained free of charge via www.ccds.cam.au.uk/conts/retrieving.html.
12. In the preparation of **2** and **3**, their isomer, in which the ester group is directed to the benzo-1,3-dithiol-2-ylidene moiety, could not be isolated.