CHEMISTRY LETTERS, pp. 969-972, 1986.

INTRAMOLECULAR CHARGE TRANSFER TRANSITION FOR SYMMETRY ALLOWED CHARGE TRANSFER INTERACTION IN THE MOLECULES OF C_s SYMMETRY AND A POTENTIAL MODEL TO INTRODUCE NEW INTERSTACK INTERACTION

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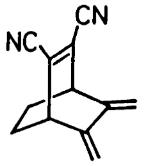
Three intramolecular charge transfer (CT) compounds, which exhibit clear CT transition for symmetry allowed CT interaction, have been synthesized and examined. In addition, a possible way to introduce new type of interstack interactions in the solid state was proposed from the crystal structure of 7,10-ethenocyclohepta[de]naphthalene-8,9-dicarbonitrile.

Generally, the intramolecular charge transfer (CT) transitions between the donor and the acceptor components fixed in a rigid framework of C_{2v} or C_s molecular symmetry are classified into the following two types:[1)] CT transition (i) for symmetry allowed CT interaction, and (ii) for symmetry forbidden CT interaction. Utilizing the structural features of such rigid frameworks, we have reported the existence of the type-ii transitions along with the unequivocal experimental evidence.[2)]



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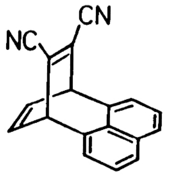

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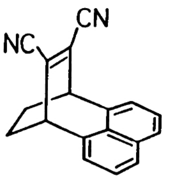

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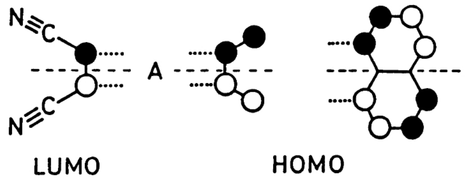

Fig. 1.

In order to observe type-i transitions, we design three molecules of C_s molecular symmetry, 5,6-dimethylenebicyclo[2.2.2]oct-2-ene-2,3-dicarbonitrile (**1**), 7,10-ethenocyclohepta[de]naphthalene-8,9-dicarbonitrile (**2**), and 7,10-ethanocyclohepta[de]naphthalene-8,9-dicarbonitrile (**3**), selecting cis-dicyanoethylene group as an acceptor component and S-cis-butadiene or naphthalene group as a donor component. Figure 1 shows the symmetry allowed interaction mode between the donor HOMO and the acceptor LUMO. We now report the syntheses and electronic spectra for the three examples of the type-i category together with a new aspect on the crystal structure of **2**.

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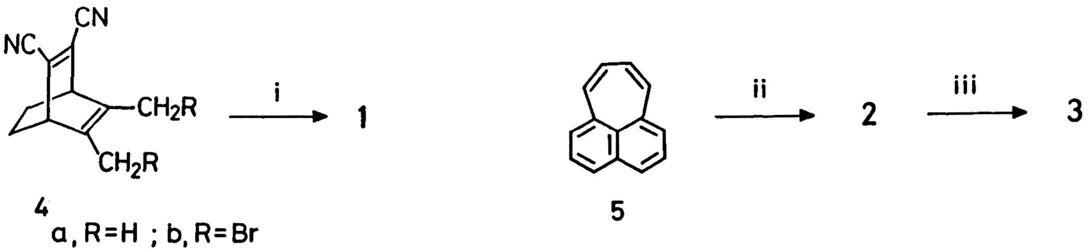
The Diels-Alder adduct **4a** of 2,3-dimethylcyclohexadiene[3] with dicyanoacetylene was treated with NBS to give **4b**, and then debromination with zinc to afford the butadiene **1**[4] (70% overall yield from 2,3-dimethylcyclohexadiene). Diimide reduction of **2**,[4] prepared in 72% yield from pleiadiene (**5**)[5] and dicyanoacetylene, with p-toluenesulfonylhydrazine and pyridine afforded **3**[4] (70%).



i, Zn/AcOH, rt 1 h; ii, NCC≡CCN, rt 21 h; iii, $TosNHNH_2$/Py, EtOH, refl. 12 h

The electronic spectra of **1**, **2**, and **3** are illustrated in Fig. 2. The diene **1** shows the locally excited transitions around 240-250 nm for the donor and the acceptor chromophores, and around 265 (shoulder) nm for the donor chromophore.[6] The bands around 260-290 nm of **2** and **3** are reasonable as ^1L_a band of the naphthalene chromophore,[7] whereas the local excitation of the dicyanoethylene chromophore overlaps with the ^1L_a band or is hidden under the intense ^1B_a band of the naphthalene chromophore. Additional absorption maxima shifted outside of these local excitations are observed for **1**, **2**, and **3** at 303, 348, and 346 nm, respectively, which can be assigned to the intramolecular CT transitions.[8] Therefore, these transitions are simple examples of the intramolecular CT transitions for symmetry allowed CT interaction in the intramolecular CT compounds of the C_s molecular symmetry.

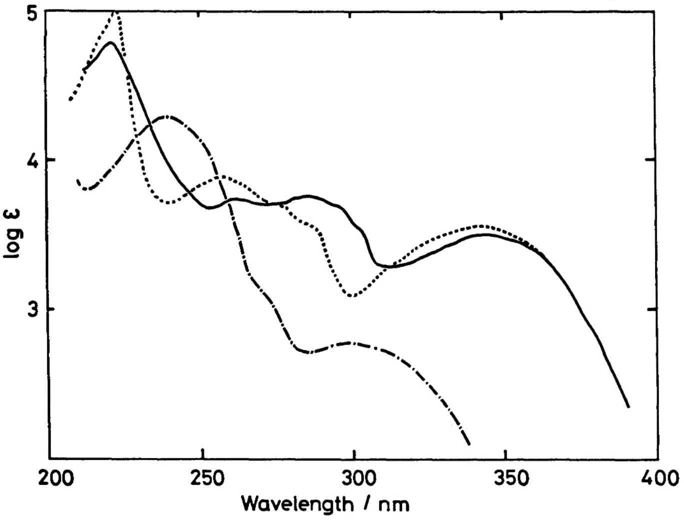


Fig. 2. Electronic absorption spectra of **1**, **2**, and **3** in EtOH.

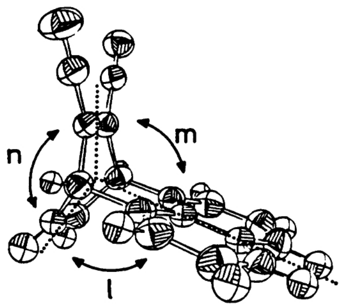


Fig. 3. Molecular structure of **2**.

Here, we would like to comment some aspects of the crystal structure of **2** which provides a model for a new type of interstack interactions in the solid state. Generally, interstack interactions are shown to be an important feature to realize metallic behavior of organic conductors. Usually such interactions have been materialized by close intermolecular contacts between S···S, S···N, and so forth.[9] Recently, we have mentioned an idea for enhancement of the dimensionality in organic conductors as a potential application of three-dimensionally modified molecules.[10] The crystal structure of **2** which belongs to such molecules suggests a way for chemical modifications to design new component molecules for organic conductors.

In the molecular structure of **2**[11] (Fig. 3), the naphthalene and the dicyanoethylene moieties are nearly planar with the maximum deviations of 0.021 and 0.017 Å, respectively. The dihedral angles of l, m, and n are 113.9, 112.5, and 133.4°, respectively. Figure 4 shows the stereoview of the molecular packing in the crystal structure. The naphthalene moieties are aligned in columnar stacks along the c axis. The interplanar distances between the naphthalenes are 3.63 and 3.99 Å, which indicate dimeric structures within the stacks. The residual bulky groups arrange in opposite directions alternately, reducing their steric repulsion. Interestingly, the dicyanoethylene moieties form isolated dimeric structures, interacting with those in adjacent stacks with interplanar distance of 3.29 Å.

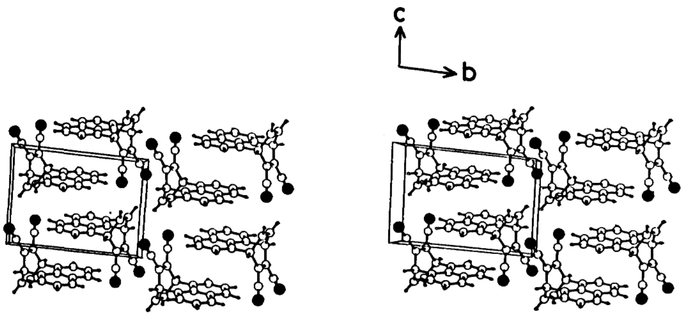


Fig. 4. Stereoview of the crystal packing of **2**.

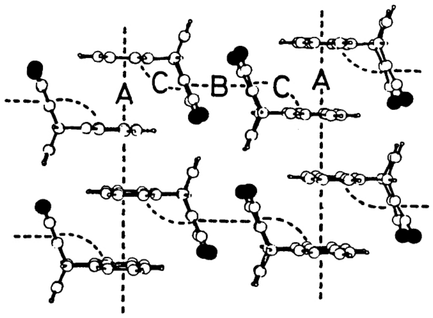


Fig. 5. Illustration of a model for interstack interaction.

As shown schematically in Fig. 5, there are principal intra- and interstack interactions through (i) the naphthalene π-systems (denote by A in Fig. 5) and (ii) dimeric dicyanoethylene moieties (B). Futhermore, these two interactions might be coupled by the symmetry allowed intramolecular CT interaction between naphthalene and dicyanoethylene moieties within a molecule **2** (C). Consequently, the electronic delocalization might occur to some extent throughout a sheetlike network. The application of such features in three-dimensionally modified molecules such as **2** seems to be an important clue to explore new organic conductors.

Support of this work by the Grant-in-Aid for Special Project Research on the Properties of Molecular Assemblies (No. 60104002) from the Ministry of Education, Science and Culture, Japan is gratefully acknowledged.

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4) **1**: a pale yellow oil; MS, m/e 182 (M^+, 13%) 154 ($M^+-C_2H_4$, 100%), exact MS calcd for $C_{12}H_{10}N_2$ 182.0843, found 182.0862; ^1H NMR ($CDCl_3$) δ 1.79 (4H, AB-like), 3.61 (2H, m), 5.04 (2H, s), 5.36 (2H, s); IR ($CDCl_3$) 2230 cm^{-1}; UV λ_{max} (CH_2Cl_2) 241 (log ε 4.29), 246 (sh, 4.26), 254 (sh, 4.11), 275 (sh, 3.05), 303 (2.78), (EtOH) 239 (4.28), 244 (sh, 4.24), 253 (sh, 4.06), 272 (sh, 3.08), 299 nm (2.77).

2: yellow plates, mp 210-212.5 °C (sealed capillary); ^1H NMR (CD_2Cl_2) δ 4.47 (2H, t-like), 6.58 (2H, t-like) 7.28-7.50 (4H, m), 7.71-7.92 (2H, m); IR (KBr) 2233, 2224 (sh) cm^{-1}; UV λ_{max} (CH_2Cl_2) 262.5 (log ε 3.74), 276 (sh, 3.72), 286.5 (sh, 3.77), 296 (sh, 3.71 , 322 (sh, 3.30), 326 (sh, 3.34), 348 (3.50), (EtOH) 205.5 (4.62), 209 (4.62), 221.5 (4.80), 262 (3.73), 275 (sh, 3.71), 285.5 (sh, 3.76), 295 (sh, 3.70), 322 (sh, 3.34), 326 (sh, 3.37), 344 nm (3.50).

3: yellow plates, mp 192-193 °C (sealed capillary); ^1H NMR (CD_2Cl_2) δ 2.32 (4H, AA'BB'-like), 4.00 (2H, m), 7.30-7.51 (4H, m), 7.72-7.90 (2H, m); IR (KBr) 2227, 2236 cm^{-1}; UV λ_{max} (CH_2Cl_2) 259 (log ε 3.90), 277 (sh, 3.71), 288 (sh, 3.58), 310 (sh, 3.19), 325 (sh, 3.40), 346 (3.56), (EtOH) 223 (5.00), 257.5 (3.88), 276 (sh, 3.70), 286 (sh, 3.57), 309 (sh, 3.24), 324 (sh, 3.44), 342 nm (3.56).

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11) Crystal data: $C_{18}H_{10}N_2$, M=254.3, triclinic, space group P1, a=8.17(2), b=10.92(1), c=7.683(4) Å, α=96.3(1), β=79.8(1), γ=108.1(2)°, U=639.9 $Å^3$, Z=2, Dm=1.31 g cm^{-3}, Dc=1.32 g cm^{-3}. Data were collected on a Rigaku automated 4-circle diffractometer with Ni-filtered Cu K_α radiation and averaged to give 2041 unique observed reflections. The structure was solved by direct method (MULTAN 80)[12] and refined by the block-diagonal anisotropic least-squares methods to an R value of 0.046.

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(Received March 28, 1986)