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行政院國家科學委員會補助專題研究計畫

■成果報告 □期中進度報告

線型分子器件的量子化學與電子過程之理論研究

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摘要

我們在本研究中，運用 Molecule-in-molecule 方法探討有機共軛雙子激發態的特性，特別是通過空間與通過鍵的相對貢獻，利用半經驗方法與從頭法精確的激發態計算，再配合 MIM 分析，我們可以迅速有效地得到雙子激發態的重要特性，對於有機材料的發光特性之了解應有很大的用處，部份結果以發表在 J. Org. Chem. 上。我們也利用中介激子裡論，計算一維螺旋共軛高分子的激發態構造，探討了螺旋式共軛分子與其光物理性質間的關連。我們有系統地研究許多混價有機分子中的電子－聲子耦合強度以及弛豫能之計算。

Abstract

We apply Molecule-in-molecule method to the excited states of molecular dimers. The relative contributions of through-space and through-bond charge-transfer exciton in vinyl-group bridged cyclophanes were investigated using this method. In addition, the puzzling absorption spectra of a new class of cyclophane based on biphenylene moiety were successfully rationalized by this technique, the preliminary result was published in J. Org. Chem. Another topic we have worked on is the application of the intermediate exciton theory to the helically coiled conjugated polymers. We have extended our MIM method to systems with many unit cells, particularly electronic structures of helically coiled polyacetylenes. The interplay of electron-hole attraction and dipole-dipole interaction was investigated systematically in the relevant parameter space.

I. Quantum Chemical Studies of anti-[2,2](1,4)Biphenylenophane

The nature of electronic excited states of cyclophane consisted of two cyclic π-electron systems derived from 4N-electron perimeter is quite different from those systems based on (4N+2)-electron perimeter. To explore the effect of the transannular interaction on the most important low-lying electronic excited states, particularly, the relative weights of local exciton and charge-transfer exciton, we adopt the composite-molecule method of Longuet-Higgins and Murrel[1] to perform configuration interaction. The usual supermolecular calculation treats the two moieties in the phane as a single quantum system, therefore the important details concerning the charge transfer cannot be achieved in a straightforward way. The composite-molecule method is based on the local molecular oribials, the excited state wavefunction of cyclophane is expressed in terms of a superposition of an local exciton and charge resonance configurations:

$$\Psi_{\pm} = \sum_i c^{ex}_{\pm,i} 1/\sqrt{2} \left(L^*_i R_0 \pm L_0 R^*_i \right) + \sum_{a,r} c^{ct}_{\pm,ar} 1/\sqrt{2} \left(L^+_a R^-_r \pm L^-_r R^+_a \right)$$

where L^*_i (R^*_i) is the i-th singlet state of monomer L(R) and $L^+_a R^-_r$ ($L^-_r R^+_a$) corresponds to a charge-transfer(CT) configurations in which an electron moves from local molecular orbital φ_a of molecule L (R) to unoccupied orbital φ_r of molecule R (L). The percentage of exciton resonance component and charge resonance component can be calculated:

$$w_{LE} = \sum_i |c^{ex}_i|^2$$

$$w_{CT} = \sum_{ar} |c^{ct}_{ar}|^2$$

for which $w_{LE} + w_{CT} = 100\%$. Therefore, the relative weights w_{LE} and w_{CT} stand for a useful measure of transannular interaction for the two moieties in a cyclophane, which is hard to obtain from supermolecular approach commonly used by many researchers.

Our composite-molecule calculation is based on standard PPP model. This model has recently been shown to reproduce low-lying singly excited states pretty well[2]. Two types of biphenylene cyclophanes, face-to-face and head-to-tail arrangements, are investigated in the present paper. The perpendicular distance between two plarnar biphenylenes is chosen to be within $3.0 - 4.5$ A. For a qualitative discussion, only situation with d=4.0 is reported, a detailed investigation on the distance dependence will be presented later. To facilitate the discussion, we show a schematic diagram of six local perimeter molecular orbitals and corresponding energy diagram of a monomeric biphenylene in figure 1. There are two types of electronic excitations: those excitations involve the creation of local exciton and those configurations with charge transfer among two moieties in the cyclophane. The notation and classification of molecular orbitals and electronic states closely follow the perimeter labels proposed by Fleischhauer et al[2]. Only five (out of ten) essential local exciton states and five (out of ten) charge-transfer configurations are shown in the figure.

The results of calculations for the biphenylene cyclophane in two different spatial arrangements

are shown in table 1, 2 and figure 2. The lowest two electronic states (**1** and **2**) originate from symmetric and antisymmetric linear combinations of monomeric s-→s+ local transitions. Both states have vanishing oscillator strength as expected from the null value of corresponding monomeric transitions. The experimental observations of weak fluorescence progression around 500nm are probably due to the vibronic borrowing effect. In addition, the larger overlap between two moieties in the H-type cyclophane with face-to-face arrangement leads to a small mixing of charge-transfer configuration. The exciton coupling two moieties estimated from the energy splitting between these two states ranges from 0.1 eV (J-cyclophane) to 0.5 eV (H-cyclophane). With such a small exciton coupling, we expect that these two low-lying electronic states exhibit the characters of trapped localized excitation in the presence of exciton-phonon coupling. The state correlation diagram of these two states between monomer and two types of cyclophanes is shown in figure 2.

The next two electronic states (**3** and **4**) have their origin as h+→s+ local excitations. These two states are mostly consisted of delocalized neutral exciton states with almost no any charge transfer in the J-type cyclophane with two moieties in head-to-tail alignment. The state with in-phase oscillation of transition dipole of two local excitons (N_{1+} in J-type and N_{1-} in H-type cyclophane) generates small absorption intensity. Hence we believe that the observed tiny peak around 370 nm in experiment is due to this exciation. States **5** and **6** are two degenerate dark electronic states involve symmetric and antisymmetric combinations of charge transfer configurations from $s1^-{\rightarrow}s2^+$ and $s2^-{\rightarrow}s1^+$.

The two electronic states originated from two local P_1 excitations (**7** and **10** in J-cyclophane; **7** and **12** in H-cyclophane) have largest exciton splittings: 2.56 eV and 4.91 eV, respectively(figure 2), This indicates that there exists a strong dipole-dipole coupling between these two moieties. For both arrangements, the delocalized exciton with higher energy carries most of the intensity in agreement with the experimental observation that an intensive absorption around 260 nm is seen. Interestingly, this brightest state also contains 5% (11% in H-cyclophane) of charge-transfer characteristics. This kind of excimeric character of the excited states becomes even more dramatic when the distance between two moieties is closer, for instance w_{CT}=50% when d=3.5 A in the case of H-type cyclophane. Hidden behind the strong absorption band due to P_{1+}, there are several forbidden and weakly allowed electronic states originated from N_2 and N_1^{CT} local states. Detailed discussion of the nature and classification of these electronic states will be presented in the other publication.

[1]H. C. Longuet-Higgins and J. N. Murrell. *Proc. Phys. Soc. A*. **1955**, 68, 601.
[2]Fleischhauer, J; Ho1weler, U.; Spanget-Larsen, J.; Raabe, G; Michl, J. *J. Phys. Chem. A*. **2004**, 108, 3225.
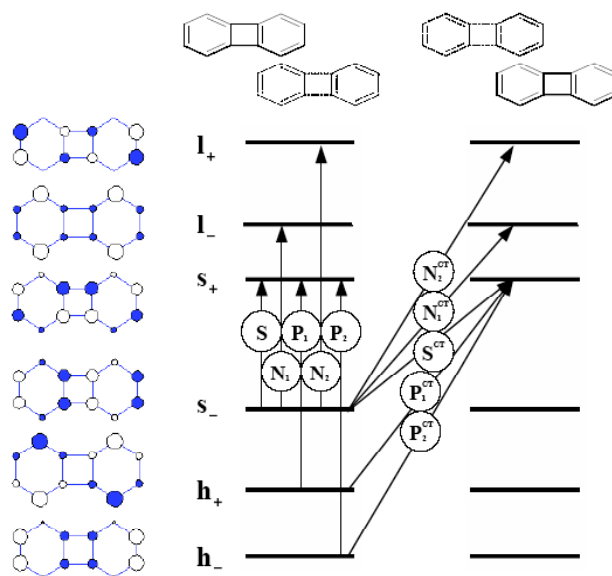
Figure 1. The PPP self-consistent MOs of biphenylene, their energies and perimeter labels. The five local excitons involved local excitations in one of the two moieties and five charge transfer configurations moving one electron from one to the other moity.
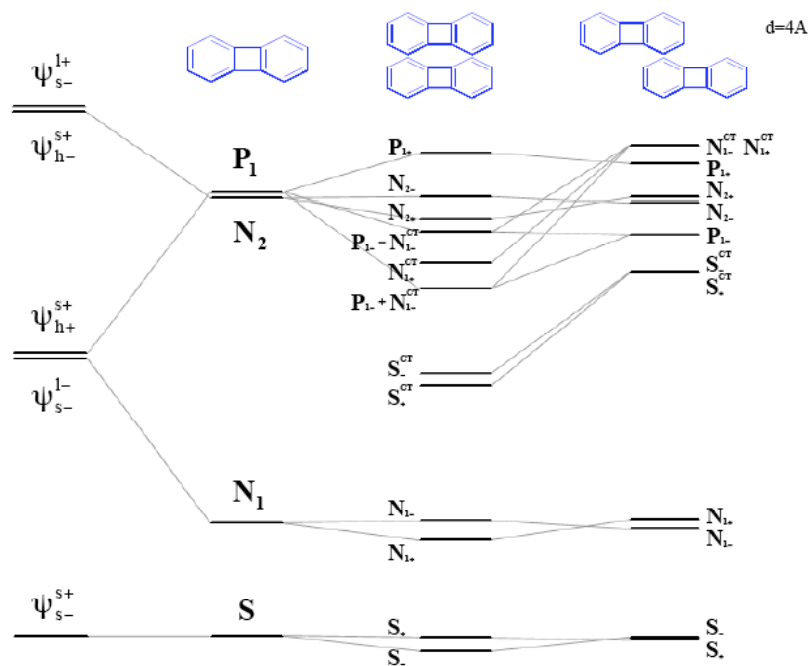

Figure 2.The state correlation diagram for the lowest 12 electronic states in two types of cyclophanes and monomeric excitations based on PPP calculation. Correlation with excitations using perimeter model is shown on the left.

State	E	f	state function
1	26.96	0	$0.69\,S_{1-} + 0.15\,S_{1-}^{CT}$
2	27.46	0	$0.70\,S_{1-}$
3	31.02	0	$0.69\,N_{1+} + 0.12\,N_{1-}^{CT}$
4	31.71	0.19	$0.70\,N_{1-}$
5	36.67	0	$0.70\,S_{1+}^{CT}$
6	37.09	0	$0.69\,S_{1-}^{CT} + 0.15\,S_{1-}$
7	40.24	0	$0.52\,P_{1-} + 0.44\,N_{1-}^{CT} + 0.18\,P_{1-}^{CT}$

8	41.19	0.03	$0.70\,N_{1+}^{CT}$
9	42.33	0	$0.54\,N_{1-}^{CT} - 0.42\,P_{1-} - 0.14\,P_{1-}^{CT}$
10	42.76	0	$0.68\,N_{2+} - 0.19\,N_{2-}^{CT}$
11	43.54	0.22	$0.70\,N_{2+} + 0.11\,N_{2+}^{CT}$
12	45.15	3.60	$0.66\,P_{1+} - 0.24\,P_{1+}^{CT}$

Table 1: Calculated electronic transitions for [2,2]biphenyle cyclophane in the face-to-face arrangement.   (Energy in 10^3 cm^{-1}).

State	E	f	state function
1	27.40	0	$0.70\,S_{1+}$
2	27.51	0	$0.70\,S_{1-}$
3	31.45	0	$0.70\,N_{1-}$
4	31.77	0.23	$0.70\,N_{1+}$
5	40.79	0	$0.70\,S_{1+}^{CT}$
6	40.80	0	$0.70\,S_{1-}^{CT}$
7	42.22	0	$0.70\,P_{1-}$
8	43.38	0.04	$0.70\,N_{2-}$
9	43.59	0	$0.70\,N_{2+}$
10	44.78	3.84	$0.68\,P_{1+} - 0.16\,N_{1+}^{CT}$
11	45.42	0	$0.70\,N_{1-}^{CT}$
12	45.46	0.24	$0.68\,N_{1+}^{CT} + 0.16\,P_{1+}$

Table 2: Calculated electronic transitions for [2,2]biphenyle cyclophane in the head-to-tail arrangement.   (Energy in 10^3 cm^{-1}).

II. The reorganization energy analysis of sterically hindered aromatic compound
(In Collaboration with Wei-Guang Liu and Chung-Chih Wu)

Over the past two decades, the study of organic materials has been growing for the potential of the application on light emitting diodes, solar cells and organic thin film transistors. But the performances of these devices are often limited by the low mobility of organic materials. According to the Marcus theory, the electron transport rate constant in organic solid is governed by the famous equation:

$$k_{ET} = \frac{4\pi^2}{h}\frac{1}{\sqrt{4\pi\lambda k_B T}}t^2 e^{-\lambda/4k_B T}$$, where λ is the reorganization energy, which is caused by the

geometric difference of neutral and ionized states, and t is the transfer integral. The organic conjugated materials, for the loose bonded and highly delocalized π electrons, have lower

reorganization energy than saturated compounds, so they are usually the basic construction units for electroptical materials. In practical application, it is usually to connect several monomers to form oligomer or polymer in order to increase thermal stability or adjust the emission light wavelength and quantum yield. Although the connection of π conjugated monomers may let the charge distribute on more monomers, and then decrease the local charge alternation and the reorganization energy, the extra rotation degree of freedom on the connection site may be another source of reorganization energy. The magnitude of the reorganization energy contributed from this degree of freedom is related to the conjugation effect and the ortho-position repulsion, which are opposite forces. To make the π electrons more delocalized, the conjugation effect tends to increase the overlap between different π-electron rings and draws these rings to flat. But the flatter of these rings, the closer of ortho-position atoms attaching on them, and the repulsion energy will increase. The stable conformation is reached when these two forces are equal. This phenomenon has been studied for a long time in theory and experiment, and the simplest case is biphenyl. The earlier researches were focused on the relation of biphenyl UV-VIS spectroscopy and its neutral conformation, specifically the inter-ring torsion, in gas and solid state. After Marcus proposed the electron transfer theory, the reorganization energy of biphenyl and fluorene in solution are estimated in experiment and the results supported that the inter-ring torsional distortion do lead to a considerable magnitude of reorganization energy. This is also important in organic semiconductor, because many materials contain this type of freedom and it affects the electro-optic properties of materials.
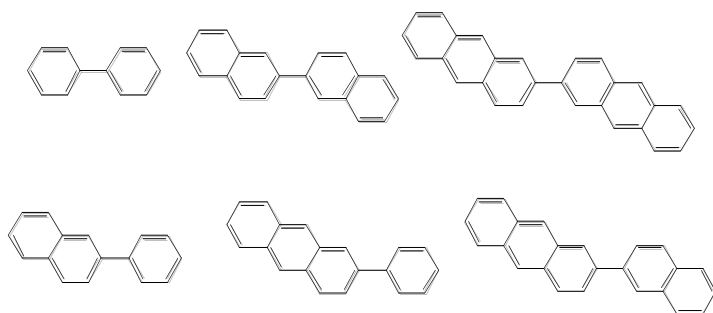
There has been lots of reorganization energy calculation for monomers containing inter-ring torsion freedom in ab initio level and point out the existence of rotation motion during neutral to charge state, but few paper reports what may affect the magnitude of reorganization energy from this part. In our work we find a simple method to estimate the reorganization energy from the rotation site, and predict how to decrease the contribution from it.

To deal with the problem of reorganization energy mainly coming from both C-C bonds and dihedral angle alternation in a more conceptual way, we adapt the Huckel model with bond-length-dependent resonance integral proposed by Longuet-Higgins and Salem, which has been demonstrated this model predicts reasonable reorganization energy for polyacenes and linear polyenes, and we modify it to take the rotation degree of freedom into account.

In order to deal with the variable dihedral angle, we consider a model molecular system, which

is constructed from one polyacene A connecting with the other polyacene B by a C-C bond (for example, a biphenyl) as shown in fig1. The Hamiltonian of this model molecular system is

$$H = \begin{pmatrix} H_A & V \\ V & H_B \end{pmatrix}$$

where H_A and H_B are corresponding Hamiltonian of polyacene A and B, and we set the dimension of H_A and H_B as m and n. V is the interaction between these two polyacene, containing only one nonzero element corresponding to the connecting C-C bond.

We compare the direct molecular geometry results from DFT and Huckel method to see if Huckel method is applicable to these π conjugation system with steric hindrance, and then consider how the magnitude and distribution of reorganization energy are affected. We take the DFT results as standard and the Huckel method are compared with it in the following table.

DFT

	1-1	1-2	1-3	2-2	2-3	3-3
Dihedral	38.2	37.8	37.3	36.4	35.5	34.3
angle	19.4	23.4	29.0	25.7	28.5	29.9
	7.1	17.7	25.8	20.1	25.2	27.3
Bridge bond	1.486	1.485	1.484	1.484	1.483	1.483
length	1.444	1.456	1.468	1.457	1.464	1.467
	1.439	1.453	1.468	1.453	1.463	1.465
R.E from __	127.0	71.4	23.9	40.4	17.6	9.8
	262.4	127.0	68.1	84.1	34.6	18.7
Total R.E	359.4	244.0	156.7	192.2	159.8	103.5
	557.7	363.0	223.8	294.9	206.0	154.9

	1-1	1-2	1-3	2-2	2-3	3-3
Neutral dihedral angle	* 36.8	36.8	36.8	37.8	37.8	38.3
	** 38.2	37.8	37.3	36.4	35.5	34.3
Charged dihedral angle	* 17.4	24.2	33.1	20.3	33.3	26.9
	** 13.3	20.6	27.4	22.9	26.9	28.6
Neutral bond length	* 1.486	1.486	1.486	1.486	1.486	1.486
	** 1.486	1.485	1.484	1.484	1.483	1.483
Charged bond length	* 1.437	1.460	1.478	1.450	1.477	1.465
	** 1.442	1.455	1.468	1.455	1.464	1.465
Neutral bond order	0.23	0.24	0.24	0.24	0.24	0.24
Charged	0.48	0.36	0.27	0.41	0.28	0.34

bond order						
R.E from $\Delta\theta$	*157.8(33%)	48.5(17%)	4.1(2%)	101.8(31%)	6.9(4%)	39.4(23%)
	***188.5	63.2	10.3	80.3	11.7	19.3
	**194.7(42%)	99.2(33%)	46.0(24%)	62.3(26%)	26.1(14%)	14.3(11%)
R.E from C-C bonds	*319.2	242.9	190.3	226.1	184.4	133.0
	**263.9	204.3	144.3	181.3	156.8	114.9
Total R.E	* 477.0	286.0	194.5	327.9	191.3	172.5
	** 458.6	303.5	190.3	243.6	182.9	129.2
Charge on larger parts	0.5	0.84	0.97	0.5	0.94	0.5
	0.5	0.65	0.78	0.5	0.68	0.5

Neutral state: For neutral state, the Huckel method provides good agreement with DFT in bond length and dihedral angle. DFT method gave a slight trend, which is increasing π electron accompanied larger dihedral angle and shorter bridge bond length, but Huckel method didn't show this trend. So this trend may be induced by exchange energy that is dependent on the number of electron and Huckel method doesn't include it.

Charged state: For charged ones with ortho hydrogen close to each other, the Huckel method predicts a little shorter bridge bond length than DFT, because the recursion relation doesn't include the repulsion force from hydrogen. In general, the bond order at bridge is increased due to lose antibonding orbital electron or get bonding orbital electron at bridge site, and both calculation results reflect this trend: the shorter bridge bond length and the smaller dihedral angel comparing with neutral state.

For those molecules whose bridge connects the same polyacene (1-1, 2-2 and 3-3), the geometries predicted by Huckel method agree well with DFT results. Both results show that as the number of π electron increase, the magnitude of the change of bridge bond length and dihedral angle decrease. In fact, from Koopman's theory, we know the most important factor affecting the conjugation strength and the bridge site geometry is the frontier MO distribution at the bridge site in charge state. As the number of p_z orbital joining into hybridization increase, in average the p_z orbital weight of frontier MO at bridge site decrease, so the increase of bond order there become less severe. According to the Huckel calculation, the increase of bond order of 1-1, 2-2 and 3-3 are 0.25, 0.17 and 0.1 separately.

For those asymmetric molecules (1-2, 1-3 and 2-3), Huckel method predicts larger dihedral angle and longer bridge bond length comparing with DFT results, which means that Huckel method predict weaker conjugation effect than DFT in those cases. Further inspection revealed that in charged state predicted by Huckel method, the charge is not delocalized on whole molecular but almost completely localized on the larger ring in those asymmetric molecules, while DFT gave more charge-delocalized results. It hints that the Huckel model may overestimate the electron-phonon coupling, and the charge is easier localized by the phonon modes on the larger polyacene. The exaggerated electron-phonon coupling also reflects on the potential surface scan of charged symmetric cases. As the dihedral angle increasing, the value of resonance integral is reduced until lower than the value of electron-phonon coupling, the symmetry-breaking occurs

and the potential surface becomes discontinuous. It is also shown that as the polyacene become larger, the electron-phonon coupling also increase and the symmetry-breaking appears earlier; for 4-4 model system, the symmetry-breaking occurs even before the total energy minimum is reached, and the energy-minimum geometry is hard to be meaningful.

We demonstrated the Huckel model with bond-length-dependent resonance integral can predict qualitatively correct geometry and reorganization energy for the π-conjugation system with rotation degree of freedom and steric hindrance, but the deviation grows as the increasing of difference of electron-phonon coupling of subsystem.

附件一

參加 2004 夏天 Gordon Research Conference 之 Electornic Processes in Organic Materials 報告

本會議是有關有機材料光電性質最重要之會議，今年會議移到麻州中部的一小大學 Mount Holyoke University。會議一如往常，從星期天至星期五共六天。所有與會人員均住在開會的地方，與會人員有相當好的互動。會議主席是 Klafter，會議共有下列幾大主題：

1. 分子電子學
2. 奈米晶體與量子點
3. 單分子光譜與非線性光譜
4. 超分子
5. 生物系統：觸媒，折疊與傳送
6. 生物系統：光合作用
7. 有機材料與奈米導線中電荷轉移

我所提出的報告是 Vibrational Contributions in Nonlinear Optical Coefficients。

Attached Files:
1. Chia-Chun Chou and Bih-Yaw Jin, Vibrational Contributions to Linear and Nonlinear Optical Coefficients
2. Chia-Chun Chou and Bih-Yaw Jin, Vibrational contribution to the second hyperpolarizabilities of polyenes:the lattices relaxation approach

附件二
The Phane Properties of *anti*-[2.2](1,4)Biphenylenophane

Attached File:
3. Leung, Man-kit; Viswanath, M. Balaji; Chou, Pi-Tai; Pu, Shih-Chieh; Lin, Hsin-Chieh; Jin, Bih-Yaw, The Phane Properties of *anti*-[2.2](1,4)Biphenylenophane, *J. Org. Chem.* **2005**, 70, 3560-3568.