Electronic Structures of Asymmetrically Substituted Phthalocyanines and Their Second Non-linear Optical Properties

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Quantum-chemical AM1 calculations were performed to study the geometries, the electronic structures and the second non-linear optical properties of phthalocyanine and some asymmetrically substituted phthalocyanines, which include *tert*-butyl, amino, dimethylamino, nitro, fluoro, chloro, bromo, iodo and nitrile substituents. The relationships of the second non-linear optical coefficients β with dipole moment μ, and β with the energy-gap differences of frontier orbitals ΔE_{DA} were discussed. Two relationships are regular and all $\Delta E_{DA} - \mu$ show very good linear relationship.

Keywords Asymmetrically substituted phthalocyanines, dipole moment, energy gap differences of frontier orbitals, second order non-linear optical coefficient

Introduction

Phthalocyanines are important organic compounds, on which much attention has been paid by experimental and theoretical study since their structures are concerned with those of some important natural products, *e. g.* chlorophyll, xanthematin. They are widely applied to dyes and photoconductors. In recent years, phthalocyanines are further used in wider fields, *e. g.* optical data storage, photoelectric appliances, liquid crystals, LB film, and non-linear optics *etc*. Especially in the field of non-linear optics, more and more scientists have noticed that phthalocyanines might have outstanding properties and brilliant applying prospects.

In 1935, Robertson[1] firstly determined the structure of the phthalocyanine by X-ray and obtained the structure data. X-ray can not detect H atom, so there exists some controversy about the positions of inner H atoms. One point[2-5] is that the two inner H atoms only connect with two single N atoms respectively, forming two normal chemical bonds, N—H bonds. The other point[6] is that the two inner H atoms are associated with two pairs of N atoms respectively, forming four well defined half-hydrogen bonds. In this paper, we will discuss the results according to our theoretical computation.

Since laser was invented in 1960s, non-linear optics and non-linear optical materials have been quickly developed. In recent years, people begin to put their interests in organic materials and high polymer materials. Zyss has discussed concepts useful in designing organic second non-linear optical compounds,[7] which show that for second non-linear optical materials, there are three requirements: (1) a highly electron-polarizable conjugated system; (2) an electron-pushing substituent and an electron-pulling substituent on conjugated system; (3) a non-centrosymmetric structure. Phthalocynine is a 42 π electron conjugated molecule with very good physical and chemical stability. All of the above requirements would be satisfied if an asymmetrically substituted phthalocyanine could be obtained. However, for a long time, almost all of the works concerned phthalocyanines were done on the structures and properties of metal-coordinated phthalocyanines. There were few reports about the structures and properties of asymmetrically substituted phthalocyanines, because of the difficulties in synthesis and purification.[8,9] Recently, the asymmetrically substituted nitro-tri-*tert*-butylphthalocyanines have been synthesized.[10] By adding electron-pushing and electron-pulling substituents to the peripheral ring of phthalocya-

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nine, the charge transfer occurs in π conjugated system. According to our preliminary results,[11] asymmetrically substituted phthalocyanines will exhibit good second non-linear optical properties.

In this paper, some asymmetrically substituted phthalocyanines have been designed, and their geometry structures, electron structures, dipole moments, energy-gap differences of frontier orbital and second non-linear optical properties have been studied with the quantum-chemical AM1 method. We hoped to find the relationship between the electronic structures and the second non-linear optical properties, and to supply as plentiful as possible information to help look for good second non-linear optical materials.

Computational model and method

There have been a lot of experimental reports concerning the structure of phthalocyanine,[1-6] all of which showed that the carbon-nitrogen backbone of phthalocyanine is in a plane. The theoretical D_{2h} constraint condition provides a highly delocalized structure with almost equal carbon-nitrogen bond lengths in the C_8N_8 central ring,[12] but the experimental structure data do not completely comply with D_{2h} symmetry. We think this must be owing to the experimental determination always being taken in crystal state, the intermolecular action makes the geometry of a single phthalocyanine molecule deviate from D_{2h} symmetry. In this paper, the molecular geometry structure of phthalocyanine was optimized by quantum-chemical AM1 method in the MOPAC-7, using D_{2h} symmetry constraint except for the two inner hydrogen atoms. The geometric parameters, which were obtained by AM1 method, basically agreed with experimental data and with those obtained by PM3 method.[12]

Our result of the geometry structure of non-substituted phthalocyanine was shown in Fig. 1. A series of asymmetrically substituted phthalocyanines were computed in which electron-pushing substituents were *tert*-butyl (*t*-Bu), amino (NH_2), dimethylamino ($(CH_3)_2N$), and electron-pulling substituents were nitro (NO_2), fluoro (F), chloro (Cl), bromo (Br), iodo (I), nitrile (CN). In order to express and read conveniently, we defined the writing symbol as follows. The symbol of non-substituted phthalocyanine is Pc. The electron-pushing substituent is written on the left of Pc, and the electron-pulling substituent is written on the right of Pc,

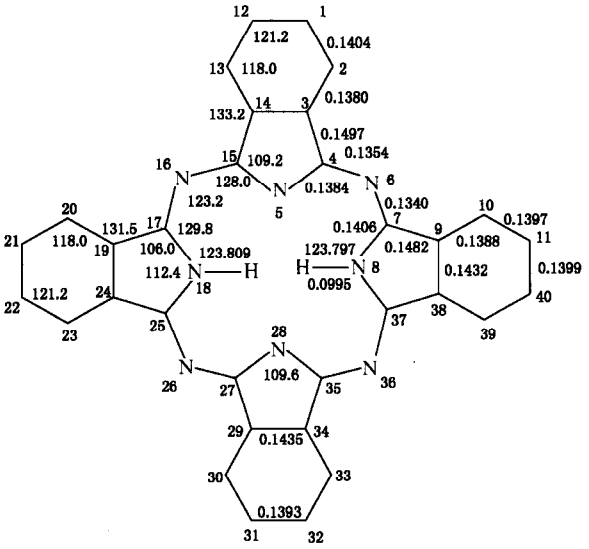

Fig. 1 Structure of phthalocyanine (unit: nm, °).

e. g. *t*-Bu-Pc-NO_2 means *tert*-butyl-nitro-phthalocyanine. If the substituent is connected on the peripheral ring along the lines of inner hydrogens, H atom is inserted in the symbol. For example, *t*-Bu-HPc, means *tert*-butyl is connected on the peripheral ring along the lines of inner hydrogens; PcH-NO_2 means nitro is connected on the peripheral ring along the lines of inner hydrogens; *t*-Bu-HPcH-NO_2 symbolizes *tert*-butyl and nitro are respectively connected on the peripheral rings along the lines of inner hydrogen atoms. When two substituents are connected on the opposite positions of phthalocyanine, there are two situations. The first situation is that the distance of two substituents is relatively near; the second situation is that the distance of two substituents is relatively far. For example, in Fig. 1 the distance of position 1 and position 32, and the distance of position 21 and position 11 are relatively near, however, the distance between position 1 and 31, and the distance between position 21 and position 40 are relatively far. We use symbol (F) to show the second situation, *e. g.* *t*-Bu-Pc-NO_2(F) means the phthalocyanine is substituted by two substituents *tert*-butyl and nitro whose distance was relatively far. The electronic structures of all kinds of substituted phthalocyanines were further optimized by AM1 method on the basis of optimized non-substituted phthalocyanine. On the basis of obtained AM1 wave function, the electron distribution, the dipole moment μ, the energy-gap difference of frontier orbitals ΔE_{DA} and the second non-linear optical coefficient β were

computed by MOPAC-6.

Molecular structure of non-substituted phthalocyanine

Bond lengths and angles in non-substituted phthalocyanine, which were optimized by AM1 method, are shown in Fig 1. There always exists controversy in literature concerning the locations of two inner hydrogen atoms in phthalocyanine,[1-6] so when optimized, the locations of the inner two hydrogen atoms were not constrained by symmetrical constraint. Computational results show that the bond lengths of two nitrogen-hydrogen bonds are a little shorter than that of normal N—H bond (0.0995 nm), and the two hydrogen atoms are not completely in line with nitrogen, but they deviate from co-line a little, showing C_i symmetry. All of these mentioned above may be led by the repulsion of the two hydrogen atoms. We think the two inner hydrogen atoms connect with two single N atoms respectively, forming two N—H bonds, but are not associated with two pairs of N atoms respectively, forming four well-defined half-hydrogen bonds.

Computational results

Affected by electron-pushing substituents and electron-pulling substituents, the electron distribution of conjugated system is asymmetric, which engenders obvious non-linear optical respondence.[13, 14] In order to find a suitable parameter to characterize the ability of electron transfer of substituents, the relationship of second non-linear optical coefficient with dipole moment, and second non-linear optical coefficient with energy-gap difference of frontier orbitals ΔE_D, ΔE_A, ΔE_{DA} are discussed.

The data of single substituted phthalocyanines are shown in Table 1 and those of double substituted phthalocyanines are shown in Table 2, in which ΔE_D and ΔE_A symbolize the electron-pushing ability of D (Donor) group and the electron-pulling ability of A (Acceptor) group respectively,

$$\Delta E_D = E(\mathrm{HOMO})_D - E(\mathrm{HOMO})_P$$
$$\Delta E_A = E(\mathrm{LUMO})_A - E(\mathrm{LUMO})_P$$

where $E(\mathrm{HOMO})_D$(or $E(\mathrm{LUMO})_A$) is HOMO (or LUMO) energy of single substituted Pc by D group (or A group), and $E(\mathrm{HOMO})_P$ is HOMO energy of non-substituted Pc and $E(\mathrm{LUMO})_P$ is LUMO energy of non-substituted Pc. The larger the ΔE_D (or ΔE_A) is, the stronger the electron-pushing (or electron-pulling) ability of Donor (or Acceptor) is. For double substituted Pc, ΔE_{DA} symbolizes the ability of electron-pushing and electron-pulling of substituents. $\Delta E_{DA} = \Delta E_D - \Delta E_A$. According to this definition, we computed all substituents we selected.

Table 1 μ, ΔE_D, ΔE_A, and β of single substituted phthalocyanines

D	Model compound	μ (Debye)	ΔE_D (eV)	β (10^{-30} esu)
t-Bu	*t*-Bu-Pc	0.837	0.0315	-130.069
t-Bu	*t*-Bu-HPc	1.001	0.0359	-248.454
NH_2	NH_2-Pc	3.270	0.1227	-328.172
NH_2	NH_2-HPC	3.481	0.1237	-512.484
$(CH_3)_2N$	$(CH_3)_2N$-Pc	3.633	0.1351	-351.525
$(CH_3)_2N$	$(CH_3)_2N$-HPc	3.946	0.1395	-569.982
A	**Model compound**	**μ (Debye)**	**ΔE_A (eV)**	**β (10^{-30} esu)**
NO_2	Pc-NO_2	9.370	-0.3495	-789.232
NO_2	PcH-NO_2	9.401	-0.2171	-957.782
CN	Pc-CN	5.633	-0.2058	-575.089
CN	PcH-CN	5.728	-0.1318	-891.537
F	Pc-F	2.799	-0.1061	-347.301
F	PcH-F	2.925	-0.0693	-549.039
Cl	Pc-Cl	2.410	-0.0988	-328.763
Cl	PcH-Cl	2.484	-0.0619	-530.473
Br	Pc-Br	2.783	-0.1161	-382.137
Br	PcH-Br	2.775	-0.0736	-582.353
I	Pc-I	2.746	-0.1150	-381.519
I	PcH-I	2.710	-0.0732	-573.337

Second non-linear optical properties and dipole moment

From Table 1 and Table 2, it can be seen that the dipole moments of substituted phthalocyanines are directly concerned with the electron-pushing and electron-pulling abilities of substituents. Both the electron-pushing abilities and the electron-pulling abilities of the substituted groups have been currently arranged in descending sequence such as $(CH_3)_2N$ > NH > *t*-Bu for electron-pushing substituted groups and NO_2 > CN > F > Br > I > Cl for electron-pulling substituted groups. In order to find stronger electron transfer system, we combined these electron-pushing substituents and electron-pulling

Table 2 μ, ΔE_{DA} and β of double substituted phthalocyanines

Model compound	μ (Debye)	ΔE_{DA} (eV)	$\beta \times 10^{-30}$ (esu)	Model compound	μ (Debye)	ΔE_{DA} (eV)	$\beta \times 10^{-30}$ (esu)
t-Bu-Pc-NO_2	10.228	0.3810	-889.208	NH_2-Pc-CN	8.784	0.3286	-833.568
t-Bu-Pc-NO_2(F)	10.480	0.3810	-859.041	NH_2-Pc-CN(F)	8.937	0.3286	-689.681
t-Bu-HPcH-NO_2	10.327	0.2529	-969.501	NH_2-HPcH-CN	8.928	0.2555	-909.259
t-Bu-HPcH-NO_2(F)	10.576	0.2529	-903.641	NH_2-HPcH-CN(F)	9.028	0.2555	-790.036
t-Bu-Pc-F	3.530	0.1376	-474.375	NH_2-Pc-Br	6.029	0.2388	-717.589
t-Bu-Pc-F(F)	3.642	0.1376	-471.978	NH_2-Pc-Br(F)	6.102	0.2388	-606.678
t-Bu-HPcH-F	3.766	0.1051	-738.754	NH_2-HPcH-Br	6.171	0.1973	-863.448
t-Bu-HPcH-F(F)	3.886	0.1051	-728.373	NH_2-HPcH-Br(F)	6.176	0.1973	-767.494
t-Bu-Pc-Cl	3.203	0.1303	-483.986	NH_2-Pc-I	6.009	0.2377	-727.171
t-Bu-Pc-Cl(F)	3.314	0.1303	-477.060	NH_2-Pc-I(F)	6.072	0.2377	-607.137
t-Bu-HPcH-Cl	3.402	0.0977	-744.579	NH_2-HPcH-I	6.188	0.1969	-889.039
t-Bu-HPcH-Cl(F)	3.500	0.0977	-747.232	NH_2-HPcH-I(F)	6.136	0.1969	-766.693
t-Bu-Pc-CN	6.460	0.2373	-735.217	$(CH_3)_2$N-Pc-NO_2	12.860	0.4846	-873.734
t-Bu-Pc-CN(F)	6.563	0.2373	-704.022	$(CH_3)_2$N-Pc-NO_2(F)	13.240	0.4846	-748.359
t-Bu-HPcH-CN	6.629	0.1677	-1024.843	$(CH_3)_2$N-HPcH-NO_2	12.964	0.3566	-754.252
t-Bu-HPcH-CN(F)	6.770	0.1677	-1005.700	$(CH_3)_2$N-HPcH-NO_2(F)	13.273	0.3566	-644.633
t-Bu-Pc-Br	3.622	0.1476	-558.329	$(CH_3)_2$N-Pc-F	6.255	0.2412	-650.378
t-Bu-Pc-Br(F)	3.684	0.1476	-529.187	$(CH_3)_2$N-Pc-F(F)	6.427	0.2412	-605.948
t-Bu-HPcH-Br	3.770	0.1095	-818.932	$(CH_3)_2$N-HPcH-F	6.583	0.2087	-796.924
t-Bu-HPcH-Br(F)	3.808	0.1095	-797.950	$(CH_3)_2$N-HPcH-F(F)	6.694	0.2087	-803.139
t-Bu-Pc-I	3.591	0.1465	-560.441	$(CH_3)_2$N-Pc-Cl	5.982	0.2339	-685.238
t-Bu-Pc-I(F)	3.645	0.1465	-528.390	$(CH_3)_2$N-Pc-Cl(F)	6.132	0.2339	-620.204
t-Bu-HPcH-I	3.785	0.1091	-850.778	$(CH_3)_2$N-HPcH-Cl	6.274	0.2013	-852.424
t-Bu-HPcH-I(F)	3.754	0.1091	-798.025	$(CH_3)_2$N-HPcH-Cl(F)	6.365	0.2013	-815.908
NH_2-Pc-NO_2	12.441	0.4722	-845.741	$(CH_3)_2$N-Pc-CN	9.172	0.3409	-868.125
NH_2-Pc-NO_2(F)	12.482	0.4722	-728.873	$(CH_3)_2$N-Pc-CN(F)	9.374	0.3409	-733.374
NH_2-HPcH-NO_2	12.763	0.3408	-748.231	$(CH_3)_2$N-HPcH-CN	9.394	0.2713	-934.863
NH_2-HPcH-NO_2(F)	12.745	0.3408	-638.991	$(CH_3)_2$N-HPcH-CN(F)	9.561	0.2713	-824.278
NH_2-Pc-F	5.891	0.2288	-626.805	$(CH_3)_2$N-Pc-Br	6.410	0.2511	-755.570
NH_2-Pc-F(F)	6.025	0.2288	-564.450	$(CH_3)_2$N-Pc-Br(F)	6.509	0.2511	-650.612
NH_2-HPcH-F	6.139	0.1930	-756.269	$(CH_3)_2$N-HPcH-Br	6.642	0.2131	-911.775
NH_2-HPcH-F(F)	6.183	0.1930	-744.923	$(CH_3)_2$N-HPcH-Br(F)	6.683	0.2131	-823.054
NH_2-Pc-Cl	5.609	0.2215	-655.059	$(CH_3)_2$N-Pc-I	6.392	0.2501	-767.789
NH_2-Pc-Cl(F)	5.731	0.2215	-577.469	$(CH_3)_2$N-Pc-I(F)	6.480	0.2501	-651.609
NH_2-HPcH-Cl	5.812	0.1856	-806.374	$(CH_3)_2$N-HPcH-I	6.664	0.2127	-938.913
NH_2-HPcH-Cl(F)	5.860	0.1856	-757.354	$(CH_3)_2$N-HPcH-I(F)	6.642	0.2127	-822.823

substituents, and designed a series of double substituted phthalocynines. The variation of dipole moments of double substituted phthalocyanines displays a regular pattern. The dipole moments of substituted phthalocyanines whose substituents connect on the peripheral ring along the lines of inner hydrogens are respectively larger than those of their counterparts whose substituents connect on the peripheral ring not along the lines of inner hydrogens. This regularity is also fit for single substituted Pcs. The dipole moments of the double substituted phthalocyanines, in which the distance between two substituents is relatively far, are respectively larger than those of the double substituted phthalocyanines, in which the distance between two substituents is relatively near. The dipole moment of $(CH_3)_2$N-HPcH-NO_2(F) is the largest, 13.273 Debye.

The second non-linear optical coefficients of substituted phthalocyanines are also concerned with the electron-pushing and electron-pulling abilities of substituents. We hope to find a substituted Pc with large non-linear optical coefficient by enhancing electron transfer. For single substituted Pcs, the variation of second non-linear optical coefficient β shows similar regularity with the variation of dipole moment . By

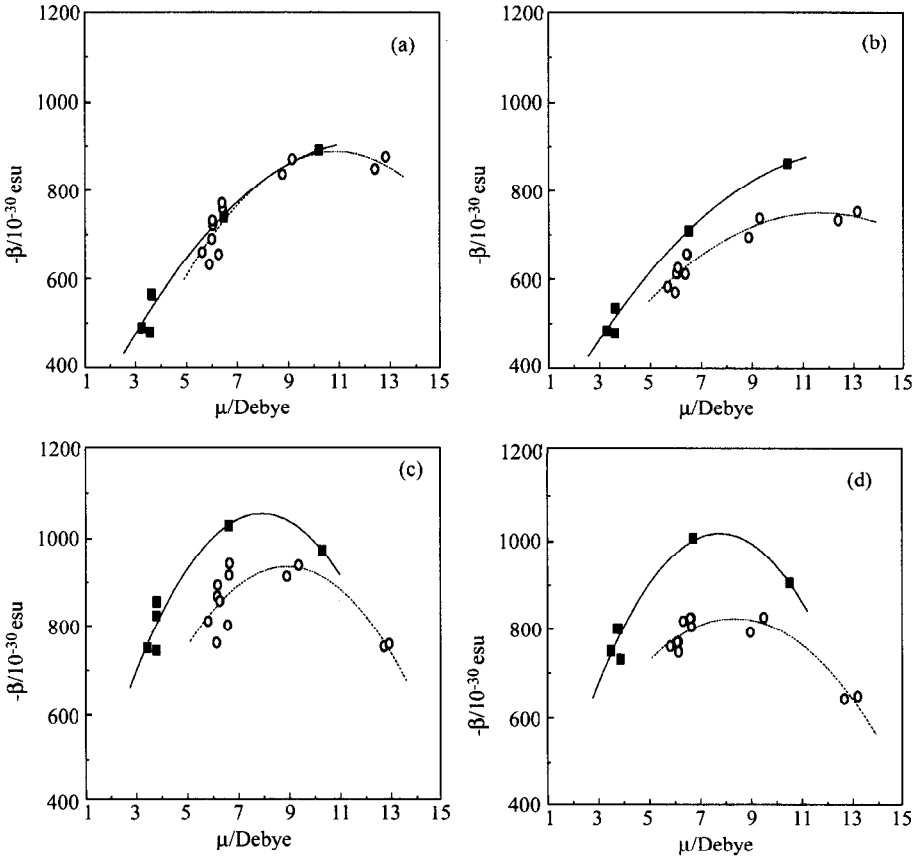

Fig. 2 The relationship of β and μ. (a) D-Pc-A system; (b) D-Pc-A(F) system; (c) D-HPcH-A system; (d) D-HPcH-A(F) system. —■D = *t*-Bu; ····○ D = NH_2, $(CH_3)_2N$.

adding electron-pushing substituents and electron-pulling substituents, we have obtained the substituted Pcs, which have large β values. The results show that this substitution model is useful for enhancing the second non-linear optical coefficient β of Pc. *t*-Bu-HPcH-CN has the largest β, $-1024.843 \times 10^{-30}$ esu, maybe it can be used to make good non-linear optical material. The variation of β of substituted Pcs shows regularity. For double substituted Pcs, the β values of substituted Pcs whose substituents connect on the peripheral ring along the lines of inner hydrogens are respectively always larger than those of their counterparts whose substituents connect on the peripheral ring not along the lines of inner hydrogens. This regularity is the same as that of dipole moment. The β values of the double substituted Pcs, in which the distance between two substituents is relatively near, are respectively always larger than those of the double substituted Pcs, in which the distance between two substituents is relatively far. This regularity is opposite to that of dipole moment.

Fig. 2 shows the relationship between second non-linear optical coefficient β and dipole moment μ for some systems. In order to observe relationship of β vs. μ in detail, we discussed the effects of NH_2, $(CH_3)_2N$ and *t*-Bu respectively, for *t*-Bu transfers electron towards backbone of Pc mainly by inducing effect, however, NH_2 and $(CH_3)_2N$ transfer electron towards backbones of Pcs mainly by conjugating effect. In Fig. 2, there is a maximum β value on each curve. It shows that there is always a largest β, when suitably combining the electron-pushing and electron-pulling substituents.

Second non-linear optical properties and energy-gap difference of frontier orbital

Yoshimura[15-17] thought that the largest β does not appear when charge separates completely. He found that in order to obtain large β, HOMO and LUMO of

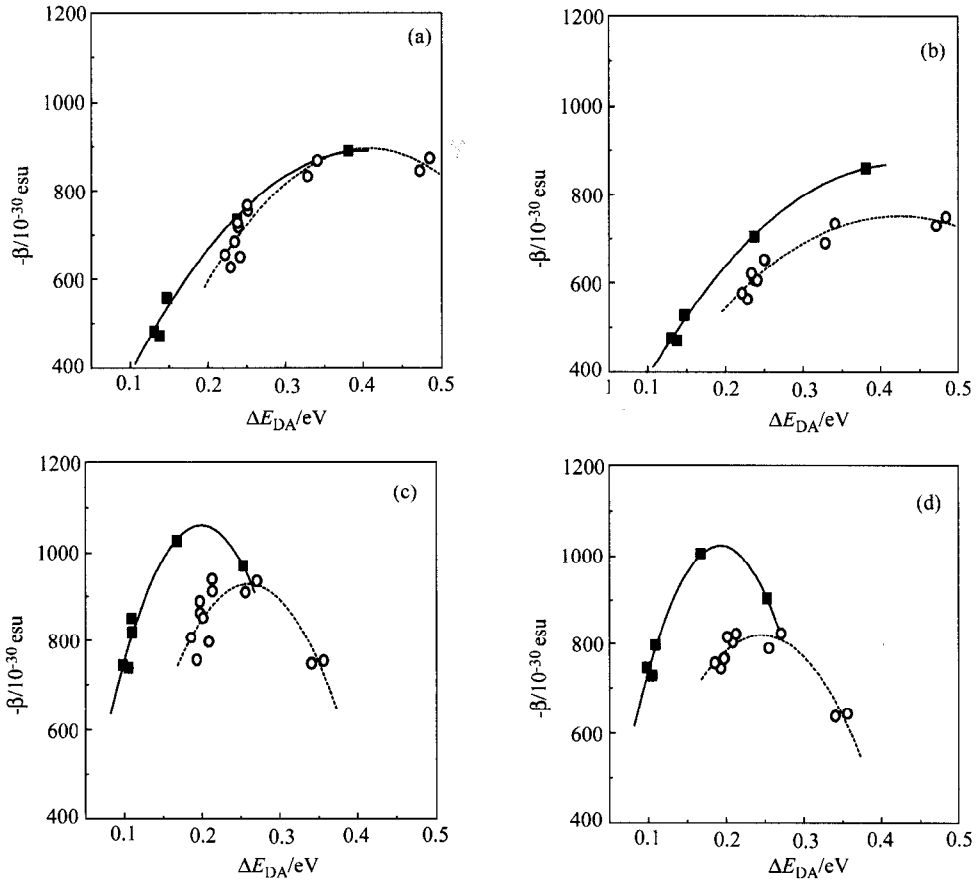

Fig. 3 The relationship of β with ΔE_{DA}. (a) D-Pc-A system; (b) D-Pc-A(F) system; (c) D-HPcH-A system; (d) D-HPcH-A(F) system. —■ D = *t*-Bu; ···○ D = NH_2, $(CH_3)_2N$.

molecule must be overlapped in bridge chain area. We used energy-gap of frontier orbitals to characterize substituents, which was proposed by Sheng and Jiang.[18-20] The basic idea of this model is that electron flows from HOMO of electron-pushing substituent (Donor) to LUMO of electron-pulling substituents (Acceptor) through bridge chain. The higher the HOMO of Donor or the lower the LUMO of Acceptor is, the more easily the electron flows. So after solving HOMO of Donor and LUMO of Acceptor, we can judge strength of a combination of D and A. According to this model, the subtraction of HOMO of non-substituted Pc from HOMO of substituted Pc by D group characterizes the electron-pushing ability of Donor; the subtraction of LUMO of non-substituted Pc from LUMO of substituted Pc by A group characterizes the electron-pulling ability of Acceptor. For electron-pushing substituents, the larger the absolute value of ΔE_D is, the stronger the electron-pushing ability is, the descending sequence of absolute value of ΔE_D being $(CH_3)_2N > NH_2 > t$-Bu. For electron-pulling substituents, the larger the absolute value of ΔE_A is, the stronger the electron-pulling ability is, the descending sequence of absolute value of ΔE_A being $NO_2 > CN > Br > I > F > Cl$.

The advantage of the frontier orbital model is that it concerns not only the electron-pushing and electron-pulling ability of substituents, but also the interaction between substituents and backbone. But the systems we study here are more complicated than those the literature reported.[18-20] Our systems are closed ring, but the systems the literature studied are opened chain. We have to consider not only the effect of substituents, but also the effect of substituted position. This model can not tell apart two kinds of double substituted Pcs, one being the substituted Pcs in which the distance between two substituents is relatively far, the other being the substituted Pcs in which the distance between two substituents is relatively near. In Fig. 3, the curves show that β is not a monotonic function of ΔE_{DA}, there being a maximum point.

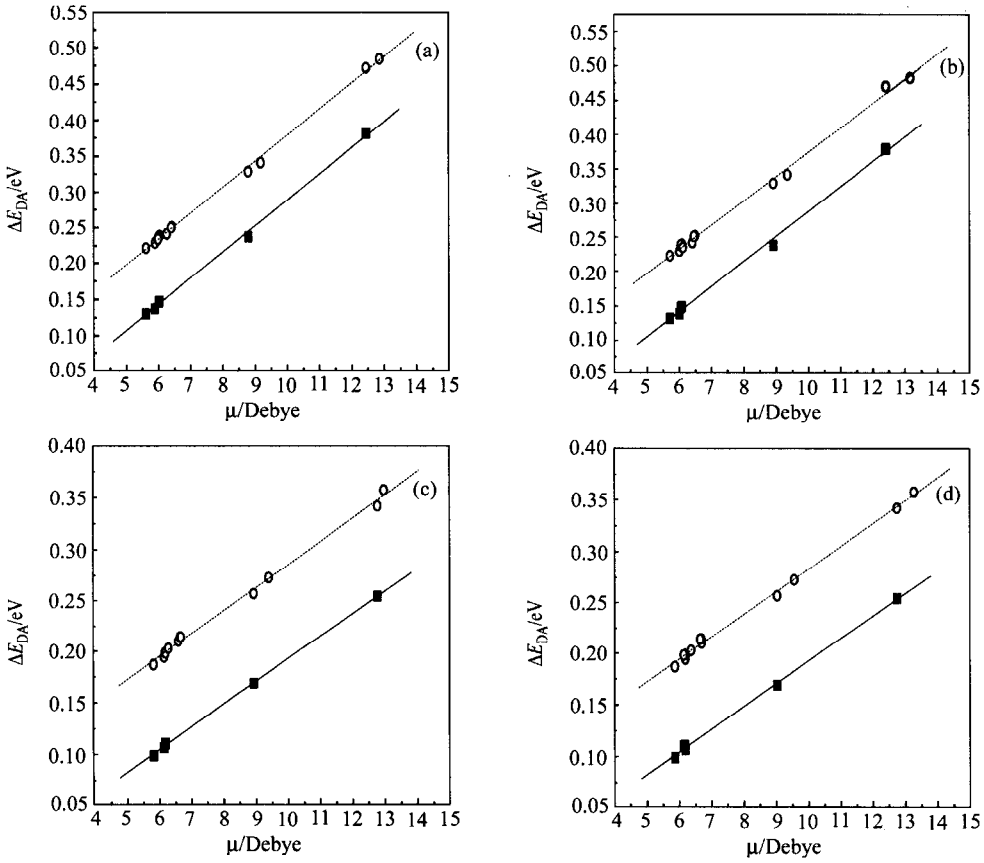

Fig. 4 The relationship of ΔE_{DA} with μ. (a) D-Pc-A system; (b) D-Pc-A(F) system; (c) D-HPcH-A system; (d) D-HPcH-A(F) system. —■ D = *t*-Bu; ····○ D = NH_2, $(CH_3)_2N$.

Energy-gap difference of frontier orbitals and dipole moment

From Fig. 2 and Fig. 3, it is observed that the curves $\beta - \mu$ and $\beta - \Delta E_{DA}$ have the same convex regularity, so that there might be a very interesting relationship to connect the ΔE_{DA} with μ, which is shown in Fig. 4. From Fig. 4, it shows that ΔE_{DA} is a very good linear function of dipole moment μ, so that ΔE_{DA} is equivalent to μ when they are used to describe the non-linear optical coefficient concerned with the ability of electron transfer of substituents.

Conclusion

The geometries, electronic structures and non-linear optical coefficient β of phthalocyanine and a series of asymmetrically substituted phthalocyanines were investigated by the quantum-chemical AM1 method. Geometry optimization showed that two inner hydrogen atoms connect with two single N atoms respectively and form two N—H bonds. The backbone geometries of asymmetrically substituted phthalocyanines do not deviate too much from that of non-substituted phthalocyanine.

The combination of electron-pushing and electron-pulling substituents results in large β for the asymmetrically substituted phthalocyanines (the largest β is $-1024.843 \times 10^{-30}$ esu). The relationships of β and μ, β and ΔE_{DA} were studied, which show a similar convex variation pattern with a maximum. They may be used to provide the useful structural information on combination of electron-pushing substituents and electron-pulling substituents for synthesizing asymmetrically substituted phthalocyanines with satisfactory non-linear optical properties.

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