J. Phys. Chem. A **1997,** *101,* 9773−9777 **9773**

Push−Pull Phthalocyanines: A Hammett Correlation between the Cubic Hyperpolarizability and the Donor−Acceptor Character of the Substituents

A. Sastre,[†] M. A. Díaz-García,[†] B. del Rey,[†] C. Dhenaut,[‡] J. Zyss,[‡] I. Ledoux,*,[‡] F. Agulló-López,*,[†] and T. Torres*,[†]

Departments of Organic Chemistry C-I and Physics of Materials C-IV, Universidad Autónoma de Madrid, Cantoblanco, Madrid-28049, Spain, and France Telecom, CNET Paris-B; Dep. d'Electronique Quantique et Moléculaire, 196, Av. Henri Ravera, 92225 Bagneux, France

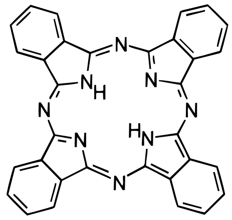
Received: July 18, 1997; In Final Form: September 29, 1997[⊗]

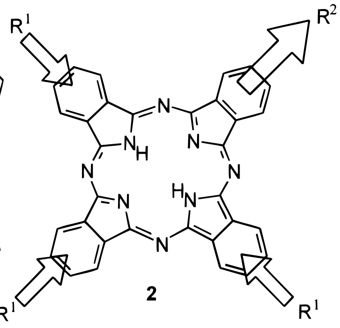
The nonlinear optical (NLO) properties at the molecular level of a family of unsymmetrically substituted metal-free phthalocyanines (**3**−**9**) have been studied for the first time. NLO characterization has been performed by electric field-induced second harmonic (EFISH) generation and third harmonic generation (THG) experiments in solution at 1.064 and 1.34 mm, respectively. The NLO response has been investigated for different types of substituents. Although no experimental evidence of a quadratic hyperpolarizability (β) contribution to γ_{EFISH} has been obtained, a significant influence of intramolecular charge transfer (ICT) on the cubic nonlinear response has been evidenced and correlated to the relative strengths of donor and acceptor substituents. Thus, γ_{THG} shows a clear absolute minimum for low Hammett parameters values of the substituents and becomes maximal for high values, i.e., for compounds having strong donor or acceptor groups such as alkoxy **(3)** or nitro **(8)** substituents. Such an enhancement effect of the γ_{THG} values due to the high dipolar moment associated with strong donor or acceptor substituents follows the trend previously observed in some porphyrin and phthalocyanine systems.

In recent years organic chromophores have been the object of a continuous interest in nonlinear optics (NLO), due to the potential advantages of their application in optoelectronics and integrated optical devices.[1,2] Besides reaching large and fast nonresonant NLO responses, they can be easily incorporated into useful macroscopic assemblies, mostly thin films. Furthermore, organic synthesis offers enormous possibilities of molecular engineering and tailoring of the NLO behavior to the required technological demands.

Whereas there are no particular symmetry requirements to have cubic molecular hyperpolarizabilities (γ), compounds need to be noncentrosymmetric in order to present quadratic hyperpolarizabilities (β). The most investigated systems, which have generally shown efficient second order NLO properties, are those presenting intramolecular charge transfer (ICT). These ICT processes, usually of one-dimensional character, are associated with large dipole moment changes $\Delta\mu$ between the ground state and the first excited state, currently identified as the "charge transfer state".[3] Typical compounds showing these types of properties are π-conjugated molecules with a D−π−A structure, where D and A are electron donor and acceptor, respectively, and π is a conjugated polyenic system.

Phthalocyanines (Pcs, **1**) present a large 18 π-electron conjugated macrocyclic ring. Their electronic distribution can be easily modified by organic synthesis, making them attractive systems for NLO applications.[4] Most of the NLO studies on Pcs have focused on third-order applications since they have been concerned with centrosymmetric compounds, i.e., nonsubstituted or identically substituted in the periphery. Extensive research has been devoted to the investigation of the third-order susceptibility $\chi^{(3)}$ of thin films.[5] However, much less information is available at a molecular level and only a few degenerate four wave mixing (DFWM) and THG studies in solution have been reported for several Pcs and naphthalocyanines[5a] and, more recently, for various octasubstituted Pcs.[6]


1



2

Theoretical calculations have proposed unsymmetrical "push−pull" phthalocyanines **2** with donor and/or acceptor substituents as novel materials for second-order NLO.[7] However, their properties remain practically unexplored, mainly due to the difficulty in their synthesis and purification. Recently, second harmonic generation (SHG) experiments from Langmuir−Blodgett (LB) films of nitrotri-*tert*-butyl-Pc have been reported.[8] However, as far as we know, no available information exists at a microscopic level.

We have recently described the preparation of a family of noncentrosymmetrically substituted Pcs (**3**−**9**)[9], and preliminary data about their molecular nonlinear optical properties have been presented in a communication.[10] We now report an extension of the previous work on the effects of the substituents on the second- and third-order NLO properties of Pcs **3**−**12** (Figure 1).

NLO characterization has been performed by electric field-induced second harmonic (EFISH) generation[3] and third harmonic generation (THG)[11] experiments in solution at 1.064 and 1.34 mm, respectively. The NLO response of unsymmetrical Pcs has been investigated for various donor and acceptor groups. A significant influence of intramolecular charge transfer on the

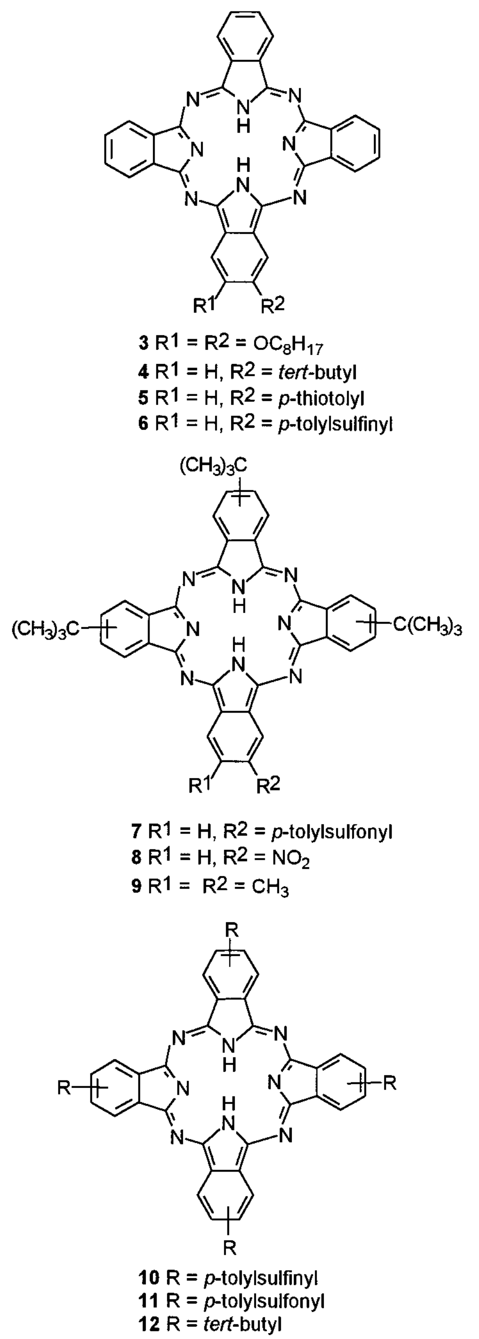
---

[†] Universidad Autónoma de Madrid.

[‡] CNET.

[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1997.

S1089-5639(97)02361-X CCC: $14.00



3 $R^1 = R^2 = OC_8H_{17}$
4 R^1 = H, R^2 = *tert*-butyl
5 R^1 = H, R^2 = *p*-thiotolyl
6 R^1 = H, R^2 = *p*-tolylsulfinyl

7 R^1 = H, R^2 = *p*-tolylsulfonyl
8 R^1 = H, R^2 = NO_2
9 $R^1 = R^2 = CH_3$

10 R = *p*-tolylsulfinyl
11 R = *p*-tolylsulfonyl
12 R = *tert*-butyl

Figure 1. Substituted Phthalocyanines **3**−**12**.

cubic nonlinear response has been evidenced and correlated to the relative strengths of donor and acceptor substituents.

Results and Discussion

Optical spectra of unsymmetrical Pcs **3**−**9** are similar to those of centrosymmetric metal-free Pcs, but weakly shifted to the blue. Most of the compounds (Pcs **3**−**6**) display the typical split Q-band (a typical example is included in Figure 2) in the lower energy region (at around 690 and 660 nm) and the B or Soret band centered at around 340 nm, associated to $\pi-\pi^*$ transitions. This splitting of the Q-band is smaller in Pc **8** and not visible in Pc **7**.

Despite many attempts, hitherto it has not been possible to separate and characterize all structural isomers of the tetra and pentasubstituted Pcs **7**−**11**. Isomers of compound **12** were separated previously by HPLC.[12] According to data previously reported,[13] a statistical mixture of four isomers (2,9,16,23-, 2,10,16,24-, 2,9,17,24-, and 2,9,16,24−) in a 1:1:2:4 ratio can be expected for compounds **10**−**12**. Compounds **7** and **8** are actually mixtures of eight isomers **(I**−**VIII)** (Figure 3), and were prepared by two routes: (a) statistical cyclotetramerization of the differently substituted diiminoisoindolines in the appropriate ratio or (b) by reaction of the tri-*tert*-butylsubphthalocyanine with the corresponding diiminoisoindoline.[9] In both cases the calculated ratio for each of the eight isomers in the condensation mixtures is the same, assuming in route (a) a free statistical distribution of the isoindol moieties and in route (b) a free statistical insertion of the diiminoisoindoline in all reactive positions of the subphthalocyanine. By the same reasoning described above, pentasubstituted phthalocyanine **9** would consist of a statistical mixture of four isomers in a ratio of 1:1: 1:1. Compounds **3**−**6** are not mixtures of isomers.

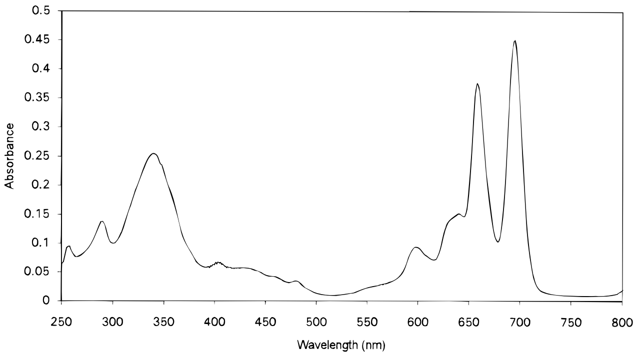


Figure 2. UV−Vis spectrum of phthalocyanine **3** in chloroform (10^{-6} M) solution.

Nonlinear Optical Measurements. Neglecting the imaginary parts, the cubic hyperpolarizabilities $\gamma_{THG} = \gamma(-3\omega;\omega,\omega,\omega)$ and $\gamma_{EFISH} = \gamma_e(-2\omega;\omega,\omega,0) + (\mu\beta\,(-2\omega;\omega,\omega)/5kT)$, measured for compounds **3**−**12** at 1.34 mm and 1.064 mm, respectively, are summarized in Table 1. To the best of our knowledge, no previous experimental molecular NLO data in other noncentrosymmetric Pcs have been reported. Also in Table 1 are listed the highest concentrations used in each experiment, at which Pc aggregates were not formed, as evidenced by their UV−visible spectra. The high dilution did not allow to determine the imaginary part of γ, nor the ground-state dipole moment (μ_0) to be measured. The μ_0 values previously reported by us[10] for compounds **3**−**12**, taken in chloroform solution, have a large error, as pointed out by repetitive measurements. For this reason those data have not been taken into account in the present paper. Unfortunately, the compounds are not soluble enough in other more adequate solvents (like dioxane or toluene) to allow reliable μ_0 determinations.

For the identically tetrasubstituted Pcs (**10**−**12**) γ_{EFISH} $(-2\omega;\omega,\omega,0)$ values are of the same sign (negative) and magnitude as those previously reported for an identically octasubstituted PcH_2 at the same excitation wavelength.[6] On the other hand, for the THG results, our present γ_{THG} $(-3\omega;\omega,\omega,\omega)$ values are 1 order of magnitude lower than that measured for the octasubstituted PcH_2.[6] These differences may be due to the different resonant processes operating in the two experiments (see below).

For the noncentrosymmetric Pcs **3**−**9**, γ_{EFISH} $(-2\omega;\omega,\omega,0)$ values are also negative and similar in magnitude to those obtained for the tetrasubstituted molecules. This suggests that the vector part of the β tensor is not important and should not yield any relevant harmonic intensity, the main contribution to the EFISH signal arising from the third-order electronic contribution γ_e. On the other hand, γ_{THG} $(-3\omega;\omega,\omega,\omega)$ values for Pcs **3**−**9** vary significantly with the nature of substituents.

Identification of Conjugated Sites and Intramolecular Charge Transfer (ICT) Paths. Phthalocyanines with a large number of conjugated π-electrons have an essentially two-

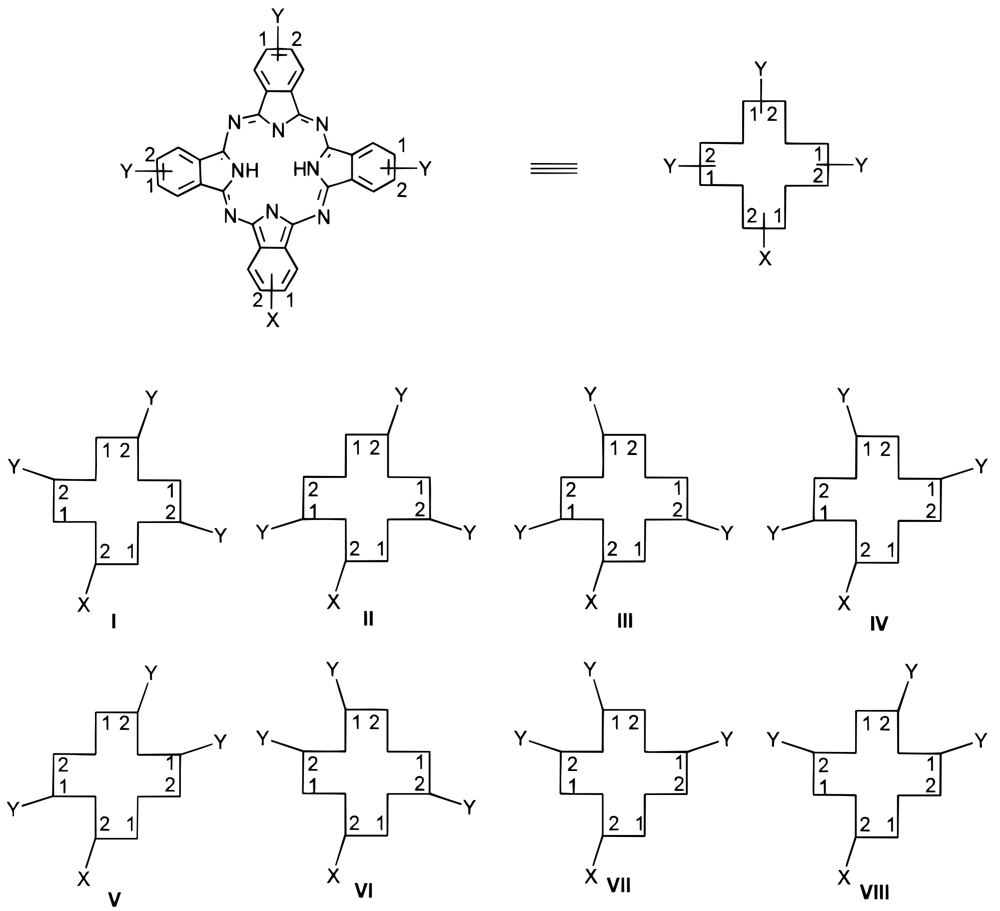


Figure 3. Compounds **7** and **8** consist of a mixture of eight regioisomers.

TABLE 1: Second-Order Microscopic Hyperpolarizability γ ($\times 10^{-34}$ esu) of Phthalocyanines 3−12 from THG and EFISH Experiments at 1.340 and 1.064 μm, Respectively, and Calculated Hammett's Parameters $\sum(\sigma_Y - \sigma_X)$ for Unsymmetrical Phthalocyanines 3−9

compd	concn (mol/L)	$\gamma_{EFISH}(-2\omega;\omega,\omega,0)$ ($\times 10^{-34}$ esu)	$\gamma_{THG}(-3\omega;\omega,\omega,\omega)$ ($\times 10^{-34}$ esu)	$\sum(\sigma_Y - \sigma_X)$
3	5.2×10^{-4}	−13	−42	1.29
4	5.2×10^{-4}	−34	−20	0.39
5	1.0×10^{-3}	−25	−36	0.57
6	1.0×10^{-3}	−23	−15	0
7	1.2×10^{-3}	−12	−19	−0.37
8	6.5×10^{-4}	−19	−41	−0.70
9	1.2×10^{-3}	−16	−21	0.10
10	3.8×10^{-5}	−22	−14	
11	3.8×10^{-5}	−15	−50	
12	1.3×10^{-3}	−13	−14	

dimensional structure. For this reason, taking into account the positions of the substituents in compounds **3**−**9** (see for example Figure 3), it is important to identify, for a given position X of an acceptor (or a donor, as the case may be) group, the corresponding "activated" sites Y where conjugation and therefore ICT can occur. Figure 4 gives the three possible conjugation patterns. A remarkable feature of such molecular systems is the noncoincidence of the molecular symmetry with that of the ICT. Three sites are actually active for π-electron donor−acceptor conjugation: one of them (Figure 4a) is located on the diametrically opposed site with respect to the acceptor group ("diametrical site", close to the vertical axis), and the two other ones (Figure 4b,c) are located on the same phenyl ring, along the horizontal axis ("lateral sites"). It must be pointed out that one benzene ring does not present any "conjugated" sites (right in the figures).

Taking into account the above statements and the considerations made before about the ratio of isomers in the regioisomeric mixtures of phthalocyanines **7**−**9**, the following conclusions can be inferred.

All eight isomers of compounds **7** and **8 (I**−**VIII**, Figure 3) display an ICT between the acceptor group and the donor group located on the closest benzene ring ("lateral sites"). The corresponding ICT has a strong 1-D character.

Only four (**I, II, V, and VIII**, Figure 3**)** out of the eight regioisomers of each compound display an ICT between the acceptor group and the opposite donor group (along the vertical axis). The total charge-transfer axis of such compounds results from composition of the "lateral" and "diametrical" ICT's, and displays a stronger two-dimensional character than the previous one.

Therefore, in our case the contribution to the cubic nonlinearity due to the ICT is the sum of contributions from two different kinds of molecules with two different ICT's.

It is interesting to plot the measured γ_{THG} as a function of an adequate parameter reflecting the different donor−acceptor strength of the substituents responsible for the ICT. The Hammett free-energy relationship is the most used description of how substituents alter the electronic structure in simple aromatic systems. The Hammett's equation is usually expressed in the form: $\log K = \log K_0 + \rho\sigma$, where the symbols K and K_0 denote the equilibrium constants for the ionization of substituted and unsubstituted benzoic acids respectively; of the two empirical constants, σ is characteristic of the substituents, indicating its behavior as electron donors or electron acceptors, whereas ρ is determined by the sensitivity of the process to changes in substitutents. To evaluate the "sum" of the effects of the subtituents according to the operating paths indicated above, we take here the resonance Hammett's constants of the substituents (σ_R) as defined in ref 14. We choose as an adequate parameter the difference between the Hammett's constants of

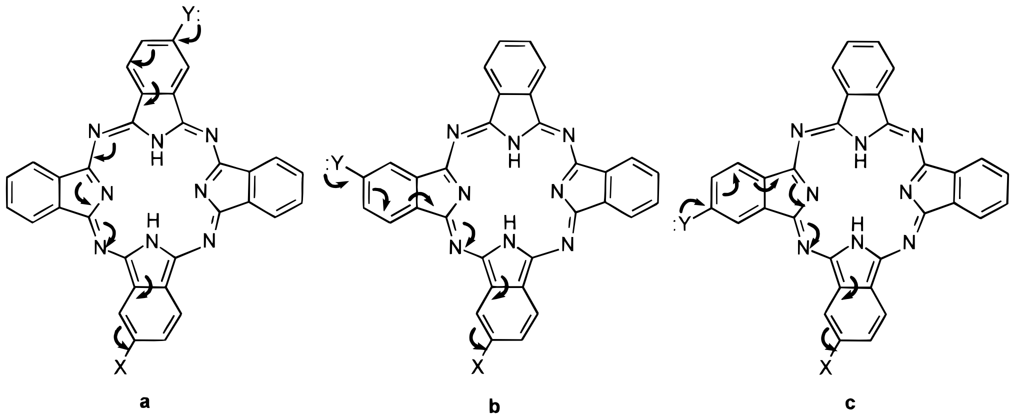


Figure 4. "Activated" sites (Y), in a Pc substituted by an acceptor group (X), where ITC can occur by substitution for a donor.

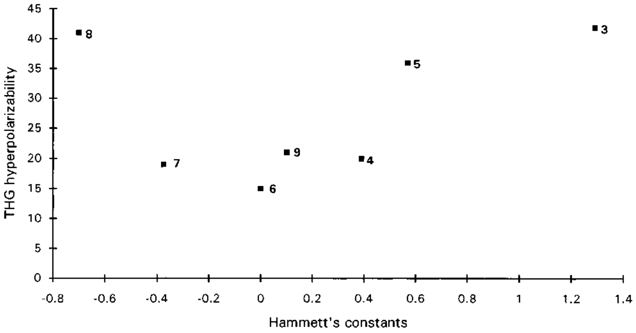


Figure 5. Plot of second-order nonlinear optical hyperpolarizability $|\gamma_{\mathrm{THG}}|$ ($\times 10^{-34}$ esu) as a function of Hammett's parameters $\sum(\sigma_Y - \sigma_X)$ for unsymmetrical phthalocyanines **3**−**9**.

the substituents $\sum(\sigma_Y - \sigma_X)$. This procedure for each path is similar to that chosen in ref 14 for aniline derivatives. Thus for a given compound **(3**−**9)** the $\sum(\sigma_Y - \sigma_X)$ values for *each* operating path in *each* regioisomer were calculated and weighed taking into account the corresponding ratio of *each* regioisomer as indicated above. The results are collected in Table 1 and are plotted against THG values in Figure 5. γ_{THG} displays a clear absolute minimum for low $\sum(\sigma_Y - \sigma_X)$ values and becomes maximal for high Hammett constant parameters, i.e., for compounds having strong donor or acceptor groups such as alkoxy **(3)** or nitro **(8)** substituents. This indicates that a significant contribution to the molecular third-order nonlinearity arises from the ICT. Such an enhancement effect of the γ_{THG} values due to the high dipolar moment associated with strong donor or acceptor substituents is in accordance with the behavior previously observed in some phthalocyanine and porphyrin systems.[15]

No similar correlation with the substituents has been found for γ_{EFISH}. A possible explanation for the different behavior of γ_{THG} and γ_{EFISH} can be advanced through a qualitative analysis of their frequency dependences, as described next. An adequate description of the frequency dispersion of γ_{THG} and γ_{EFISH} should take into account the electronic properties of the ground state and of several relevant excited states. However, we will assume here that the Pc molecules can be described in terms of a two-level model, consisting of the ground state and a first excited state corresponding to the Q−band (Table 2). This is of course a rough approximation for a complete description of these complex systems, but it may illustrate in a simple way some key features determining the role of ICT paths on the cubic hyperpolarizabilities.

According to this two-level approximation, γ_{THG} and γ_{EFISH} can be expressed as follows:[16]

TABLE 2: $\lambda_{\max}$ and ϵ Values of the Most Relevant UV−Visible Absorptions for Compounds 3−12 in Chloroform Solution

product	λ	ϵ	product	λ	ϵ
3	695	162181	**6**	687	128824
	659	134896		661	134896
	640	54954		637	69183
	599	32359		608	43651
	431	19952		341	56234
	339	81283	**7**	711	sh
4	695	147910		687	100000
	658	134896		618	21379
	639	51286		341	38904
	597	29512	**8**	692	100000
	358	sh		679	102329
	339	74131		644	50118
5	700	100000		624	43651
	663	100000	**9**	701	125892
	641	50118		664	109647
	610	30902		644	37153
	424	sh		603	19054
	340	74131		342	63095

$$\gamma_{\mathrm{THG}}(-3\omega;\omega,\omega,\omega) = \frac{-\omega_1 {\mu_{10}}^4}{h^3({\omega_1}^2 - 9\omega^2)({\omega_1}^2 - \omega^2)} + \frac{\omega_1({\omega_1}^2 + \omega^2){\mu_{01}}^2(\Delta\mu)^2}{h^3({\omega_1}^2 - 9\omega^2)({\omega_1}^2 - 4\omega^2)({\omega_1}^2 - \omega^2)} \tag{1a}$$

$$\gamma_{\mathrm{EFISH}}(-2\omega;\omega,\omega,0) = \frac{-\omega_1 {\mu_{10}}^4}{h^3({\omega_1}^2 - 4\omega^2)({\omega_1}^2 - \omega^2)} + \frac{\omega_1(2{\omega_1}^2 - 5\omega^2){\mu_{01}}^2(\Delta\mu)^2}{2h^3({\omega_1}^2 - 4\omega^2)^2({\omega_1}^2 - \omega^2)} + \frac{\mu}{5kT}\frac{3{\omega_1}^2{\mu_{10}}^2\Delta\mu}{2h^2({\omega_1}^2 - 4\omega^2)({\omega_1}^2 - \omega^2)} \tag{1b}$$

ω_1 is the frequency of the first excited state, μ_{10} the transition dipole moment between the ground state (0) and the excited state (1), μ is the ground-state dipole moment of the molecule, and ω the fundamental frequency (corresponding to 1.34 μm for THG and 1.064 μm for EFISH). γ_{THG} is the sum of two contributions: the first one is present in all cases, whereas the second appears only if the molecule presents a dipolar ICT. The second term displays three possible resonances, at ω, 2ω, and 3ω; for ω, 2ω, and $3\omega \ll \omega_1$, its sign is opposite to that of the first term. On the other hand, γ_{EFISH} contains an additional term corresponding to the orientational contribution of the quadratic hyperpolarizability β.

First, one may comment that the negative sign of both γ_{THG} and γ_{EFISH} found for all investigated molecules is in accordance with previous results on centrosymmetric Pc's. The explanation for this behavior has been already advanced and requires a more detailed (four level) model including a two-photon transition.[6,17] However, our interest here is to understand the influence of the ICT terms, i.e., of the donor/acceptor subtituents, on the overall γ_{THG} and γ_{EFISH} values. This specific point can be reasonably discussed with reference to the dispersion terms in eq 1 taking into account that the Q-band transition (Table 2) is not appreciably modified by the substituents. For γ_{THG} our data show a significant variation with the nature of the substituents. They display a clear absolute minimum for weak Hammett constants and become maximal when using strong donor or acceptor species such as alkoxy or nitro groups. This behavior can be rationalized within our simple two-level model framework. First, the ICT term in eq 1a represents a negative contribution to γ_{THG} since $\omega_1{}^2-9\omega^2 < 0$ at $\lambda = 1.34$ μm. Moreover, it reaches a high value due to the strong resonance at 2ω ($\lambda_{2\omega} = 0.670$ μm), so it may markedly enhance the centrosymmetric contribution associated to the first term in eq 1a. In fact, the magnitude of this enhancement effect is related to the mesomeric factor $\Delta\mu^2$ appearing in the ICT term.

The analysis of the γ_{EFISH} data is more problematic due to the additional presence of the orientational term. However, assuming that such term is negligible, one sees that the relative ICT contribution with regard to the centrosymmetric one in eq 1b is much smaller than in the case of γ_{THG} , since at $\lambda = 1.06$ μm one is far from the 2ω resonance. This might explain that the effects of the donor/acceptor substituents on γ_{EFISH} values have not been experimentally observed. This hypothesis is confirmed by the fact that γ data reported for centrosymmetric molecules are close to those for the similar noncentrosymmetric species.

In summary, we have studied for the first time the NLO properties at molecular level of a new family of unsymmetrically substituted metal-free phthalocyanines. Although no experimental evidence of a quadratic hyperpolarizability (β) contribution to γ has been obtained, a correlation between the THG hyperpolarizability $\gamma(3\omega;\omega,\omega,\omega)$ and the donor−acceptor character of the Pc substituents have been found. It appears to be related to a strong two-photon resonance enhancement of the ICT contribution to γ. This fact opens a way for the design of new Pcs with tailored third-order NLO properties. Additional NLO experiments are currently in progress with these and related molecules in order to discriminate the orientational contribution from the purely electronic one in the EFISH experiment. This would lead to an adequate estimation of the dipolar β value, whereas the octupolar contribution to the β tensor could be estimated using harmonic light scattering experiments.[18] These data will be reported in due course.

Experimental Section

Compounds **3**−**9** were obtained either by statistical condensation of the corresponding diiminoisoindoline or by ring expansion of the appropriate subphthalocyanine, as described previously.[9]

THG and EFISH experiments have been performed in chloroform solutions, as a function of concentration, at respectively, 1.340 and 1.064 nm fundamental wavelengths. Both are emitted by Q-switched Nd^{3+}:YAG lasers with 60 and 20 ns pulse duration, respectively. A liquid cell with thick windows in the wedge configuration was used to obtain the Maker fringe pattern (harmonic intensity variation as a function of liquid cell translation). In the EFISH experiments the incident beam was also synchronized with a DC field applied to the solution containing the nonlinear molecules. From the concentration dependence of the harmonic signal with respect to that of pure solvent the molecular hyperpolarizability γ (assumed to be real) was determined.

THG experiments provide the purely electronic cubic hyperpolarizability $\gamma_{THG}(-3\omega;\omega,\omega,\omega)$, whereas EFISH experiments give γ_{EFISH}, the sum of a purely cubic contribution $\gamma_e(-2\omega;\omega,\omega,0)$ and of a quadratic, orientational contribution $\mu\beta(-2\omega;\omega,\omega)/5kT$), where μ is the static dipole moment and β the vector part of the first−order hyperpolarizability.

Acknowledgment. This work was supported by CICYT (Spain) and the Comunidad Autónoma de Madrid through grants MAT96/0654, and TIC 96-0668 and 06T/017/96, respectively, and by the EC through Grant ERBCHRX-CT94-0558.

Supporting Information Available: Hammett's constant calculations of the substituents for compounds **3**−**9** (6 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a). Shen, Y. R. The Principles of Nonlinear Optics; Wiley: New York, 1984. (b) Sastre, A.; Torres, T.; Díaz-García, M. A.; Agulló-López, F.; Dhenaut, C.; Brasselet, S.; Ledoux, I; Zyss, J. *J. Am. Chem. Soc.* **1996**, *118*, 2746. (c) Samuel, Y. D. W.; Ledoux, I.; Dhenaut, C.; Zyss, J.; Fox, H. H.; Schrock, R. R.; Silbey, R. J. *Science* **1994**, *265*, 1070. (d) LeCours, S. M.; Guan, H.-W.; DiMagno, S. G.; Wang, C. H.; Therien, M. J. *J. Am. Chem. Soc.* **1996**, *118*, 1497. (e) Priyadarshy, S.; Therien, M. J.; Beratan, D. N. *J. Am. Chem. Soc.* **1996**, *118*, 1504.

(2) (a) *Nonlinear Optical Properties of Organic Molecules and Crystals*; Chemla, D. S.; Zyss, J., Eds.; Academic Press: New York, 1987; Vols 1 and 2. (b) *Molecular Nonlinear Optics;* Zyss, J. Ed.; Academic Press: Boston, **1994**. (c) *Nonlinear Optics of Organic Molecules and Polymers*; Nalwa, H. S., Miyata, S., Eds.; CRC Press: Boca Raton, FL, 1997. (d) Dagani, R. *Chem. Eng. News* **1996**, *March 4*, 22.

(3) Oudar, J−L. *J. Chem. Phys.* **1977**, *67*, 446.

(4) (a) Nalwa, H. S.; Shirk J. S. *Phthalocyanines: Properties and Applications*; Leznoff, C. C., Lever, A. B. P., Eds.; VCH Publishers: Inc Weinheim, **1996**, Vol. 4; p 79. (b) de la Torre, G.; Torres, T.; Agulló-López, F.; *Adv. Mater.* **1997**, *9*, 265.

(5) (a) Nalwa, H. S. *Adv. Mater.* **1993**, *5*, 341. (b) Díaz-García, M. A.; Agulló-López, F.; Torruellas, W. E.; Stegeman. G. I. *Chem. Phys. Lett.* **1995**, *235*, 535. (c) Tajalli, H.; Jiang, J. P.; Schimidt, A.; Murray, J. T.; Armstrong, N. R.; Chandross, M.; Mazumdar S.; Peygambarian. N. *Appl. Phys. Lett.* **1995**. (d) Díaz-García, M. A.; Fernández-Lázaro, F.; Duro, J. A.; de la Torre, G.; Delhaes, P.; Mingotaud, C.; Torres, T.; Cabrera, J. M.; Agulló-López, F. *Appl. Phys. Lett.* **1996**, *69*, 295.

(6) Díaz-García, M. A.; Ledoux, I.; Duro, J. A.; Torres, T.; Agulló-López, F.; Zyss, J. *J. Phys. Chem.* **1994**, *98*, 8761.

(7) Li, D.; Ratner, A.; Marks, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 1707.

(8) (a) Liu, Y.; Xu, Y.; Zhu, D.; Wada, T.; Sasabe, H.; Liu, L.; Wang, W.; *Thin Solid Films* **1994**, *244*, 943. (b) Liu, Y.; Xu, Y.; Zhu, D.; Wada, T.; Sasabe, H.; Zhao X..; Xie, X.; *J. Phys. Chem.* **1995**, *99*, 6957. (c) Liu, Y.; Xu, Y.; Zhu, D.; Zhao, X.; *Thin Solid Films* **1996**, *289*, 282.

(9) Sastre, A.; del Rey, B.; Torres, T.; *J. Org. Chem.* **1996**, *61*, 8591.

(10) Díaz-García, M. A.; Agulló-López, F.; Sastre, A.; del Rey, B.; Torres, T.; Dhenaut, C.; Ledoux, I.; Zyss, J. 2nd International Conference on Organic Nonlinear Optics, Kusatsu, Gumma, Japan, 1995. Published as proceeding in *Nonlinear Optics* **1996**, *15*, 251.

(11) Kajzar F.; Messier, J. *Rev. Sci. Instrum.* **1987**, *58*, 2061.

(12) Hanack, M.; Schmid, G.; Sommerauer, M. *Angew. Chem., Int. Ed.. Engl.* **1993**, *32*, 1422.

(13) Leznoff, C. C.; Lever, A. B. P. In *Phthalocyanines: Properties and Applications*; Leznoff, C. C., Lever, A. B. P., Eds.; VCH Publishers: Inc, Weinheim, 1989; Vol. 1; p 29.

(14) Katritzky, A. R.; Topsom, R. D. *Chem. Rev.* **1977**, *77*, 639.

(15) (a) Suslick, K. S.; Chen, C. T.: Meredith, R.; Cheng, L. T. *J. Am. Chem. Soc.* **1992**, *114*, 6928. (b) Nalwa, H. S.; Kakuta, A. *Thin Solid Films* **1995**, *254*, 218.

(16) (a) Barzoukas, M; Fremaux, P.; Josse, D.; Kajzar, F.; Zyss J. *Mater. Res. Soc. Symp. Proc.* **1988**, *109*, 171. (b) Orr, B.; Ward, J. F. *Mol. Phys.* **1971**, *20*, 513. (c) Ward, J. F. *Rev. Mod. Phys.* **1985**, *37*, 1.

(17) Díaz-García, M. A.; Hutchings, M. G.; Gordon, P. F.; Agulló-López, F.; Kazjar, F.; *Nonlinear Optics* **1995**, *14*, 169

(18) Terhune, R. W.; Maker, P. D.; Savage, C. M. *Phys. Rev. Lett.* **1965**, *14*, 681. (b) Zyss, J.; Ledoux, I. *Chem. Rev.* **1994**, *94*, 77.