Table 2. Summary of Observed Rate Constants (k_{obs}, min^{-1}) for the Reaction of *p*-Nitrophenyl Acetate with *m*-Chlorophenoxide and Benzohydroxamates in 0.1 M Borate Buffer (pH=9.27) Containing Various Concentrations of CTAB at 25.0℃ [a]

10^4[CTAB], M	k_{obs}, min^{-1}			
	(1)	(2)	(3)	(4)
0.0	.037	.038	.148	.028
4.0	.059	.085	1.47	.115
8.0	.097	.139	3.37	.192
14.0	.133	.193	6.33	.237
20.0	.164	.218	7.59	.264
28.0	.185	.233	9.25	.266
36.0	.198	.248	10.2	.267
48.0	.208	.247	11.4	.267
60.0	.207	.246	12.1	–
76.0	.213	.246	12.0	.265

[a] [PNPA]=1.0×10^{-5} M, [NuH]=2.00×10^{-4} M.

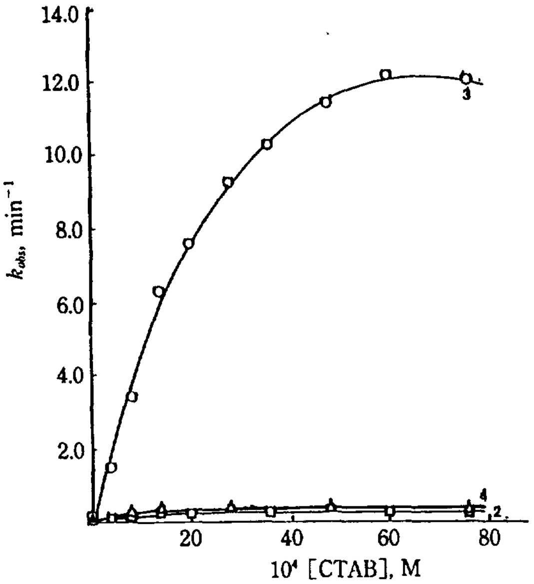

Figure 2. Plots showing micellar effect on rates for reactions of PNPA with *m*-chlorophenoxide (**4**) and benzohydroxamates (**2**, **3**) in 0.1 M borate buffer (pH=9.27) at 25.0℃.

is typical of nucleophilic substitution reactions with anionic nucleophiles in cationic micellar solutions.[4,6,11] However, the rate enhancement is most significant for the reaction of **3** and, therefore, the α-effect shown by **3** in pure H_2O retains in the presence of CTAB. This result is quite opposite from the one for the reaction of the hydroxamates having an N-H bond (**1** and **2**).

Therefore, the present study would lead to a conclusion that an equilibrum of I with II or III for the hydroxamates having an N-H bond appears to be responsible for the disappearance of the α-effect in the previous system. However, more systematic studies are required for a complete understanding of the present results.

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Theoretical Study of the Nonlinear Optical Properties of Nonsubstituted-, Methyl-fluoro-, and Amino-nitro-Polyenes

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Development of highly nonlinear optical materials is currently an area of intense interest in photonics or optoelectronics.[1] Polyenes with large delocalized π electrons exhibit extremely large nonlinear responses, thus, are becoming one of the possible material classes for nonlinear optical applications.[2,3] The first and second hyperpolarizabilities are directly related with the second and third harmonic generation in nonlinear optics, respectively. Thus, it is of importance to investigate the hyperpolarizabilities of polyene systems with respect to the chain length.

We have investigated three polyene systems, X-(-HC=CH-)$_n$ -Y, where X/Y=H/H, F/CH_3, and HN_2/NO_2. A number of theoretical studies of the polyene systems are available, but most of them centered on the nonsubstituted polyenes.[4] The hyperpolarizabilities were calculated with both the PM3 semiempirical[5] and Hartree-Fock self-consistent-field (SCF) *ab initio* methods, using MOPAC 6[6] and with Gaussian 90[6], respectively. The SCF calculations (which are much more reliable than any semiempirical calculation) were performed with the Huzinaga-Dunning double zeta (DZ) basis sets.[7] In our calculations, the three polyene systems have planar structures with all trans conformers. All the structures were fully optimized, and have all positive vibrational frequencies. Thus, these should be at least at the local minima of the energy hypersurface. With our limited configurational energy studies, the all-*trans* conformers seem to be in the global minima.

The notations for electrical properties used here are as follows. In presence of applied electric field (E_i), the energy of a molecule perturbed by a static uniform electric field can be expanded[8] as $H=H^o-\Sigma_i \mu_i E_i-\Sigma_{ij} \alpha_{ij} E_i E_j-\Sigma_{ijk} \beta_{ijk} E_i E_j E_k-\Sigma_{ijkl} \gamma_{ijkl} E_i E_j E_k E_l\cdots$. Here, H^o is the Hamiltonian for the free molecular system, and μ_i, α_{ij}, β_{ijk}, γ_{ijkl}, are the components of the dipole moment, polarizability, first hyperpolarizability, and second hyperpolarizability, respectively. Each dummy index (i, j, k, l) denotes one of x, y, and z. We assumed the Kleinmann symmetry[9]. Then, the mean polarizability is $\alpha=\frac{1}{3}\Sigma_i \alpha_{ii}$. The vector component of the (first) hyperpolarizability tensor is $\beta_i=\frac{1}{3}\Sigma_j \beta_{ijj}$. Then, the component of the hyperpolarizability along the dipole moment is $\beta_\mu=\Sigma_i \beta_i \mu_i/|\mu|$. The mean second hyperpolarizability is given by $\gamma=\frac{1}{5}\Sigma_{ij} \gamma_{iijj}$.

Table 1 lists the PM3 semiempirical results of the three polyene systems for $1 \leq n \leq 25$. Table 2 lists the SCF/DZ *ab initio* results for $1 \leq n \leq 8$. The predicted results are somewhat smaller than the experimental values[10] (see the footnote of Table 2), but are consistently underestimated; thus, the scaled values may be used so as to have near experimental values.

Kirtman *et al.*[11] fitted the electronic properties as a function of the second order of n^{-1}. We estimated the asymptotic values (for $n=\infty$) of the electronic properties with $\log A=a_0+a_1/(n+1)+a_2/(n+1)^2+a_3/(n+1)^3$, so that the case $n=0$ can be included in that equation. Here, A can be μ, β, $\alpha/(n+$

Table 1. The PM3-Predicted Electrical Preoperties (μ and α in a.u.; β in 10^{-30} esu; γ in 10^{-36} esu)

	X/Y	$n=1$	$n=2$	$n=3$	$n=5$	$n=8$	$n=10$	$n=15$	$n=20$	$n=25$	($n=\infty$)
μ	F/CH_3	0.63	0.68	0.73	0.79	0.83	0.84	0.86	0.86	0.86	0.90
	NO_2/NH_2	3.02	3.60	3.93	4.23	4.40	4.45	4.50	4.52	4.53	4.64
α	H/H	15.0	35.3	62.0	130.2	256.7	342.8	574.4	810.8	1048.8	50(n+1)
	F/CH_3	24.7	48.1	77.6	149.6	275.7	365.6	597.9	834.5	1072.6	49(n+1)
	NO_2/NH_2	41.7	75.2	114.2	197.2	327.3	417.5	649.6	886.2	1124.2	47(n+1)
$\beta\mu$	F/CH_3	0.05	0.50	1.61	5.91	13.83	18.11	24.25	26.67	28.0	54.4
	NO_2/NH_2	2.18	12.97	35.98	97.56	166.15	193.86	229.72	243.81	250.11	381.6
γ	H/H	0.02	2.34	13.55	110.41	585.5	1090.6	2903.9	5057.9	7362.9	422(n+1)
	F/CH_3	0.26	4.77	25.26	153.78	681.0	1244.6	3102.7	5288.6	7592.0	432(n+1)
	NO_2/NH_2	2.11	14.79	78.04	459.53	1359.4	2044.2	4005.5	6205.6	8350.5	442(n+1)

Table 2. The *ab initio* SCF/DZ-Predicted Electrical Properties (μ and α in a.u.; β in 10^{-30} esu)

	X/Y	n=0	$n=1$	$n=2$	$n=3$	$n=4$	$n=5$	$n=6$	$n=7$	$n=8$	($n=\infty$)
μ	F/CH_3	1.11	1.12	1.23	1.33	1.42	1.49				2.00
	NO_2/NH_2	2.05	3.23	4.01	4.57	4.95	5.22	5.41	5.56	5.65	6.93
α	H/H	2.0	19.9[a]	44.7[b]	76.4	114.8	158.7	207.0	258.9	313.6	61(n+1)
	F/CH_3	11.0	30.4	55.9	88.5	127.5	171.9				56(n+1)
	NO_2/NH_2	21.1	44.6	78.4	120.3	168.2	220.1	274.5	331.2	388.6	63(n+1)
$\beta\mu$	F/CH_3	0.25	0.31	0.33	0.24	1.76	4.39				13
	NO_2/NH_2	0.10	2.07	8.96	23.62	46.64	76.04	108.31	141.12	170.93	1189

[a] The experimental mean polarizability of C_2H_4 is 28.7 a.u. (Ref. 10). [b] The experimental mean polarizability of C_4H_6 is 58.3 a.u. (Ref. 10).

1) or $\gamma/(n+1)$. Except for the calculation of $\gamma/(n+1)$, the parameter a_3 was negligible; thus, the asymptotic values were obtained within the second order of $(n+1)^{-1}$.

The PM3 underestimates the dipole moments, since the SCF results are much more reliable. But, from the PM3 trend of the electrical properties with increasing chain length, we expect the similar trend for the SCF calculation. The asymptotic polarizabilities and second hyperpolarizabilities of the three polyene systems should have the same values. Thus, using different polyene systems, the asymptotic values can be better estimated than the case with one polyene system. We expect that the SCF and PM3 values of $\alpha/(n+1)$ are 61~63 and 47~50 a.u., respectively, while the PM3 values for $\gamma/(n+1)$ are 422~442 10^{-36} esu. If the parameter a_3 is neglected, the PM3 values of $\gamma/(n+1)$ for X/Y=H/H, F/CH_3, and NH_2/NO_2 are 304, 319, and 379 10^{-36} esu, respectively. Thus, in this case the second order approximation is not suitable. The PM3-predicted asymptotic values of β_μ for X/Y=F/CH_3 and NO_2/NH_2 are ~54 and ~382 10^{-30} esu, respectively. The corresponding SCF-predicted asymptotic values are 13 and 1189 10^{-30} esu., respectively. For these asymptotic values, the SCF results are more reliable due to the higher level of theory, while the PM3 results can give better trend with more data for polyene systems with longer chain length.

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Unusual Solvatochromic Behavior of the Open-Chain Merocyanine Forms of 5-chlorinated 1,3,3-spiro(2H-1-benzo-2,2′-indoline) Derivatives

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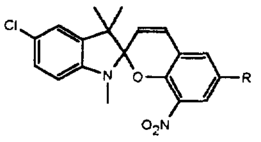
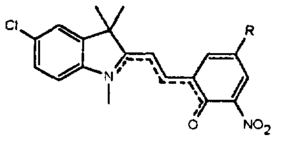
Thermo- and photochromic indolinobenzospiropyran dyes have attracted considerable attention in the last few decades, with regard to various practical applications such as recording, copying and displaying materials.[1,2] In addition, the open-chain merocyanine forms of spirobenzopyrans are of particular interest since merocyanine dyes are known to be used as empirical solvent polarity indicators.[3] Indolinobenzospiropyrans (I) are known to be in equilibrium with their metastable colored merocyanine forms (II) by UV-visible light, heat or spontaneously as we mentioned in previous papers.[4-6]



I



II

1; R=CH_3
2; =H
3; =Br

A number of studies[2,4-7] have reported important advances particularly towards understanding the backward spiro-ring formation processes in various solvents. The influence of solvents on the ring closure reaction rate could yield structural information of the ground state of open-chain merocyanine