

Calculations of Hyperpolarizabilities for *Para*-disubstituted Benzenes with the QSPR

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Abstract: A quantitative structure-property relationship (QSPR) was made for the prediction of the hyperpolarizabilities(β) of *para*-disubstituted benzenes with the nonlinear optical properties, and the $\beta_{\text{cal}2}$ calculated by this model accorded better with the experimental values (β_{expt}) compared with the $\beta_{\text{cal}1}$ calculated at the CPHF/6-31G**//HF/STO-3G level of theory, especially when β was big.

Keywords: QSPR, hyperpolarizabilities, *para*-disubstituted benzenes, nonlinear optical properties.

When a laser beam propagates through the nonlinear optical (NLO) material, there will be great changes in the properties of the light beam, which are named NLO properties. The NLO properties include the Pockels effect, the second and the third harmonic generation *etc.*¹. More generally the NLO material can be used to control the frequency of light, and then it can be used to shorten the wavelength for high-density optical recording and optical switching for optical computing. So the NLO material is regarded as an important material in the information age².

A variety of the microcosmic measurements, such as the dipole moments (μ), polarizabilities (α), hyperpolarizabilities (β) and so on, are available for the properties of the nonlinear responses of bulk materials³. The predictions of the μ, α can be done very well by *ab initio* method, but the prediction of β is still not satisfactory. It is well known that the properties of a compound are determined by its microstructure, but little attention has been put on the statistical method — quantitative structure -property relationship (QSPR) which can be used to improve the precision of the same series compounds by theoretical calculation. The electronic structure and the α, β of 32 *para*-disubstituted benzenes with the NLO properties were calculated by coupled perturbed Hartree-Fock (CPHF) method at the 6-31G* level of theory.

Methodology

The electronic structures were optimized by HF/STO-3G method after primarily optimized by PM3 method.

The components of the molecular hyperpolarizability tensors(β_{ijk}) were obtained by means of the CPHF at the 6-31G* level⁴. β_{μ} is its projection on the direction of dipole

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moment. To keep the comparability with the experimental results and the results from semiempirical method in the reference⁵, β_μ was calculated using the following expression:

$$\beta_\mu = (3/5)(\beta_x\mu_x + \beta_y\mu_y + \beta_z\mu_z)/(\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}$$

$$\beta_i = \sum_j \beta_{ij} \quad i, j=(x, y, z)$$

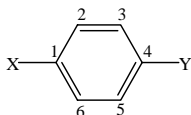
A great variety of the quantum chemical indices were taken from the calculation results, such as the lowest unoccupied molecular orbital energy E_{LUMO} , the highest occupied molecular orbital energy E_{HOMO} , $DELH=E_{LUMO} - E_{HOMO}$, total energy E , μ and solvent-excluded volume V *etc.*. Based on these quantum chemical indices, the stepwise regression analysis was used to build a quantitative structure-property relationship model, the regression function (1), for hyperpolarizability of *para*-disubstituted benzenes.

Results and Discussion

Table 1 Some of the quantum chemical indices of studied *para*-disubstituted benzenes*

NO.	X	Y	μ / Debye	DELH / Hartree	$V / \text{\AA}^3$	NO.	X	Y	μ / Debye	DELH / Hartree	$V / \text{\AA}^3$
1	SO ₂ Me	OH	3.9	0.44505	127.624	17	NO	NMe ₂	4.5	0.36836	126.917
2	SO ₂ C ₃ F ₇ OMe		4.9	0.41360	210.668	18	NO ₂	Me	4.6	0.40582	107.028
3	CN	Me	4.0	0.43525	100.544	19	NO ₂	Br	2.9	0.39377	110.429
4	CN	Cl	2.0	0.43095	98.625	20	NO ₂	OH	4.2	0.39939	94.769
5	CN	Br	2.3	0.42193	103.951	21	NO ₂	OPh	4.7	0.36448	159.08
6	CN	OPh	4.0	0.40517	152.558	22	NO ₂	OMe	4.7	0.39626	113.845
7	CN	OMe	4.1	0.43135	107.351	23	NO ₂	SMe	4.5	0.36744	125.234
8	CN	SMe	3.8	0.40223	118.723	24	NO ₂	N ₂ H ₃	5.6	0.38397	107.099
9	CN	NH ₂	5.2	0.41751	90.622	25	NO ₂	NH ₂	5.8	0.37721	97.123
10	CN	NMe ₂	5.4	0.40686	127.732	26	NO ₂	NMe ₂	6.1	0.36593	134.226
11	CHO	Me	2.9	0.42345	103.81	27	NO ₂	CN	0.6	0.4007	103.781
12	CHO	OPh	3.3	0.40487	158.952	28	NO ₂	CHO	2.7	0.39311	107.034
13	CHO	OMe	3.6	0.41862	110.624	29	CHC(CN) ₂	OMe	6.3	0.36294	145.138
14	CHO	SMe	3.4	0.39108	122.02	30	CHC(CN) ₂	NMe ₂	6.8	0.34622	166.173
15	CHO	NMe ₂	4.2	0.39174	131.033	31	C ₂ (CN) ₃	NH ₂	7.4	0.31999	142.395
16	COCF ₃	OMe	3.9	0.40327	209.456	32	C ₂ (CN) ₃	NMe ₂	7.9	0.31059	179.258

*



structure of studied *para*-disubstituted benzenes

X : *meta*-orienting group ;

Y : *ortho-para*-directing group except (27,28) ;

Table 1 gave some of the quantum chemical indices introduced in the regression function that was given as below:

$$\beta = 36.9800 + 0.01165\exp(\mu) - 87.4506DELH + 0.005094V \quad (1)$$

$$N=32, R = 0.974, SD = 2.755, F=169.593$$

$$t_{\exp(\mu)} = 11.216, t_{DELH} = -3.441, t_V = 0.295, r_{\exp(\mu)} = 0.961, r_{DELH} = -0.841, r_V = 0.387$$

Where the correlation coefficient R was 0.974, the standard deviation SD was 2.755, and F -test value was 169.593. The QSAR model had good predictability. Eq. (1) showed that β was a positive correlation to $exp(\mu)$. The value of $r_{exp(\mu)}$, the single correlation coefficient $exp(\mu)$ to β reached 0.961, and $t_{exp(\mu)}$ was 11.216. It meant that higher μ led to higher β , and the subtle change of μ would affect β greatly, that is, μ was the primary factor. It also showed that the influence of $DELH$ cannot be ignored, and the r_{DELH} was 0.841. The molecule with small energy difference between the *HOMO* and the *LUMO*, $DELH$, was easily energized, and the modulus of $DELH$ in Eq. (1) showed that smaller $DELH$ led to bigger β , too. The molar volume V was introduced into Eq. (1) as a positive correlation factor. For *para*-disubstituted benzenes, the volume of molecules and the degree of delocalization increased with the increasing volume of substituents which contain the p_z orbital, which accorded with the relationship between the β and the π -conjugated condition as known³. β increased with the increasing degree of delocalization. **Table 2** gave concrete data for the following comparison, and the regression equations can be derived from it as below:

$$\beta_{\text{expt}} = 2.85 (\pm 1.21) + 0.64 (\pm 0.08) \beta_{\text{cal1}} \quad (2)$$

$$R = 0.792, SD = 5.7, F = 50.57, N = 32$$

$$\beta_{\text{expt}} = 0.38 (\pm 0.55) + 0.95 (\pm 0.04) \beta_{\text{cal2}} \quad (3)$$

$$R = 0.948, SD = 2.6, F = 545.12, N = 32$$

Both μ and α can be accurately calculated by the *ab initio*, and they fitted the experimental values better than those calculated using MNDO/PM3 method by Matsuzawa *et al.*⁵. **Table 2** showed that our theoretical prediction of β (β_{cal1}) was still not satisfactory, especially when β was large. Comparing Eq. (2) with Eq. (3), R increased from 0.792 to 0.948, F value raised sharply from 50.57 to 545.12, and the SD in Eq. (2) was bigger than that in Eq. (3). In Eq. (3), the coefficient of β_{cal2} was 0.95, and the constant was small. The differences were also indicated in **Figure 1** clearly.

Table 2 Comparison of calculated results with experimental values^a

X	Y	$\frac{10^{-30} \text{C} \cdot \text{m}^5/\text{esu}}{\text{expt cal}^1 \text{ cal}^2 \text{ cal}^c}$				X	Y	$\frac{10^{-30} \text{C} \cdot \text{m}^5/\text{esu}}{\text{expt cal}^1 \text{ cal}^2 \text{ cal}^c}$				X	Y	$\frac{10^{-30} \text{C} \cdot \text{m}^5/\text{esu}}{\text{expt cal}^1 \text{ cal}^2 \text{ cal}^c}$			
SO ₂ Me	OH	1.3	1.2	-0.6	0	CHO	OPh	1.9	0.9	2.8	4.6	NO ₂	SMe	6.1	1.1	6.7	8.1
SO ₂ C ₃ F ₇	OMe	3.3	4.4	3.8	2.5	CHO	OMe	2.2	2.8	1.4	3.7	NO ₂	N ₂ H ₃	7.6	9.2	7.9	8
CN	Me	0.7	1.6	0.2	1.4	CHO	SMe	2.6	4.3	3.8	8	NO ₂	NH ₂	9.2	11.7	9.7	6.3
CN	Cl	0.8	2.4	-0.1	4.6	CHO	NMe ₂	6.3	8.6	4.3	6.8	NO ₂	NMe ₂	12	15.7	12.9	8.4
CN	Br	1.1	2.8	0.7	1.5	COCF ₃	OMe	3.6	6.6	3.5	4.9	NO ₂	CN	0.6	3.4	2.5	0.5
CN	OPh	1.2	3.4	3.1	3.7	NO	NMe ₂	12	12.3	6.7	9	NO ₂	CHO	0.2	1.5	3.3	-0.4
CN	OMe	1.9	0.6	0.7	3	NO ₂	Me	2.1	4.7	3.5	1.4	CHC(CN) ₂	OMe	9.8	13.5	14.7	9
CN	SMe	2.8	5.8	3.0	6.8	NO ₂	Br	3.3	6.4	3.4	1.5	CHC(CN) ₂	NMe ₂	32	26.2	22.4	16
CN	NH ₂	3.1	5.8	3.6	5.7	NO ₂	OH	3	5.7	3.4	2.3	C ₂ (CN) ₃	NH ₂	39	3.2	36.5	6.4
CN	NMe ₂	5	7.7	5.4	7.2	NO ₂	OPh	4	11.3	7.6	4.5	C ₂ (CN) ₃	NMe ₂	50	48.8	53.6	16
CHO	Me	1.7	2.2	0.7	1.6	NO ₂	OMe	5.1	5.8	4.5	3.1						

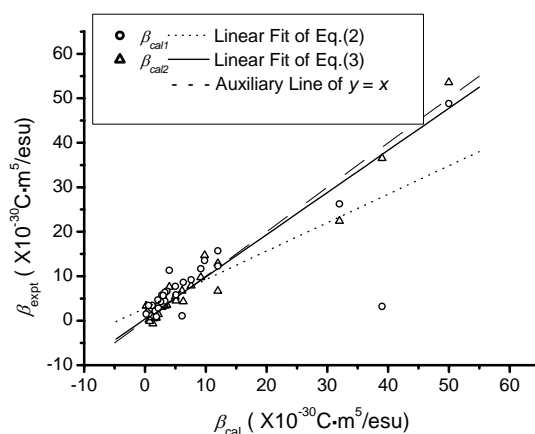
a. Experimental data and the value marked cal^c were both taken from Ref.5;

b. Calculated by CPHF/6-31G* method;

c. Calculated by QSPR model.

The regression line l_2 of Eq. (3) in **Figure 1** almost overlapped the dash line $y = x$, and the sample points uniformly distributed both sides of it, which meant systematic error was quite low. On the contrary, the regression line l_1 of Eq. (2) in **Figure 1** deviated from the dash line $y = x$, which meant that the theoretical predictions of β were prevalent smaller than experimental values, a systematic error existed in the theoretical method at present, and the prediction ability was limited for the compounds with great β . The comparison showed the statistical method—QSPR predict the hyperpolarizabilities β accurately for the series of *para*-disubstituted benzenes.

Figure 1 The plots of the Hyperpolarizabilities calculated by theoretical method and QSPR vs. the observed values



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