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The investigation of second harmonic generation from novel molecules [(*E*)-*N*-alkyl-4-{2-[4-(dialkylamino)phenyl]ethenyl}pyridazinium iodide]

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(*E*)-*N*-Methyl-4-{2-[4-(dihexadecylamino)phenyl]ethenyl}pyridazinium iodide (MHPd), (*E*)-*N*-octadecyl-4-{2-[4-(dimethylamino)phenyl]ethenyl}pyridazinium iodide (OMPd), (*E*)-*N*-octadecyl-4-{2-[4-(diethylamino)phenyl]ethenyl}pyridazinium iodide (OEPd), (*E*)-*N*-octadecyl-4-{2-[4-(dibutylamino)phenyl]ethenyl}pyridazinium iodide (OBPd) have been designed and synthesized. Their Langmuir–Blodgett film forming properties and second harmonic generation were studied. According to the results observed, MHPd is the best among the four congeners. By comparing the NLO properties of OMPd with those of a known compound, OMPy [(*E*)-*N*-octadecyl-4-{2-[4-(dimethylamino)phenyl]ethenyl}pyridinium iodide], the impairing effect of the second nitrogen in the six-membered pyridazine ring was examined experimentally and theoretically.

Since organic materials have higher nonlinear polarizability compared with inorganic ones, research on second harmonic generation today focuses on finding organic materials containing donor–π–acceptor conjugation systems.[1–5]

Both experimental observations[3,4] and model calculations[6–8] have been used in studying the relationship between the strength of second harmonic generation (SHG) (function) of organic molecules and their structures. It has been demonstrated that there is an optimal combination of donor and acceptor strength required to maximize $\mu\beta$ (where μ is the dipole moment of the molecule) for a given connective segment and beyond that point increasing the donor–acceptor strength leads to a diminution of the hyperpolarizability.[9] The nontrivial dependence of SHG upon bond length alternation (BLA, peaks at ~0.04 Å) is predictable and has also been observed.[10,11] Molecules with aromatic ground states tend to have greater bond length alternation than non-aromatic polyenes of comparable length, because of the energy which must be overcome for the loss of aromaticity while polarizing to a charge separated state. Heterocyclic rings such as thiazole[12] or thiophene[13] were thus introduced to replace benzene. Six-membered diazine rings might give better bond length alternation than five-membered thiazole or thiophene, but studies on such compounds have not been reported. Also, the function of heteroatoms such as sulfur or oxygen studied by other researchers are directly related to SHG.[14] Here, we attempt to study the function of the additional nitrogen in the title system.

In this work we have designed and synthesized a series of new compounds: (*E*)-*N*-methyl-4-{2-[4-(dihexadecylamino)phenyl]ethenyl}pyridazinium iodide (MHPd) and its congeners (*E*)-*N*-octadecyl-4-{2-[4-(dimethylamino)phenyl]ethenyl}pyridazinium iodide (OMPd), (*E*)-*N*-octadecyl-4-{2-[4-(diethylamino)phenyl]ethenyl}pyridazinium iodide (OEPd) and (*E*)-*N*-octadecyl-4-{2-[4-(dibutylamino)phenyl]ethenyl}pyridazinium iodide (OBPd). Their nonlinear optics (NLO) properties were measured and compared with each other. For the purposes of comparison, a known compound, OMPy [(*E*)-*N*-octadecyl-4-{2-[4-(dimethylamino)phenyl]ethenyl}pyridinium iodide], was also synthesized and measured.[15]

Experimental Section

Methods and materials

Melting points were determined with an X_4 micromelting-point apparatus. EI mass spectra were recorded with a VG ZAB-HS model spectrometer. ^{1}H NMR spectra were measured using a Bruker ARX400 NMR spectrometer with tetramethylsilane as an internal standard (in $CDCl_3$). Elemental analyses were carried out on a Carlo Erba 1102 and a Heraeus CHN-Rapid instrument. UV–VIS spectra were recorded using Shimadzu UV-3100 spectrometer.

N,*N*-Dihexadecylaminobenzene was synthesized by reacting aniline with 1-bromohexadecane quantitatively in a mixture of aqueous sodium hydroxide and toluene. *N*,*N*-Dihexadecylaminobenzaldehyde was synthesized by following reference 16. 4-Methylpyridazine-3,6-diol, 4-methyl-3,6-dichloropyridazine and 4-methylpyridazine were synthesized by following reference 17. All of them had satisfactory ^{1}H NMR and mass spectra.

The synthetic methods of the following materials are first reported in this work. The procedures are as shown in Scheme 1.

1,4-Dimethylpyridazinium iodide. 4-Methylpyridazine (0.94 g, 0.01 mmol) was dissolved in 5 ml of benzene (dried) with 1.25 ml (0.02 mol) of methyl iodide. The mixture was stirred at room temp. for 24 h. The dark brown liquid (1,4-dimethylpyridazinium iodide) which separated out from the reaction mixture was washed with diethyl ether twice. Yield: >90%; *m*/*z*: 108 ($M^+ - 1$).

MHPd. To 3 ml of a tetrahydrofuran solution of 0.190 g (0.34 mmol) of 4-*N*,*N*-dihexadecylaminobenzaldehyde, 2 ml of an ethanol (dried) solution of 0.08 g (0.34 mmol) of 1,4-dimethylpyridazinium iodide and 0.04 ml of piperidine were added to form a homogeneous solution. The mixture was stirred at room temp. for 5 d. The reaction mixture was then poured into water to which chloroform was added to extract the product. The organic phase was dried over magnesium sulfate and purified on a silica gel column; eluent: chloroform–methanol (50:1). After evaporation of the solvent, a waxy

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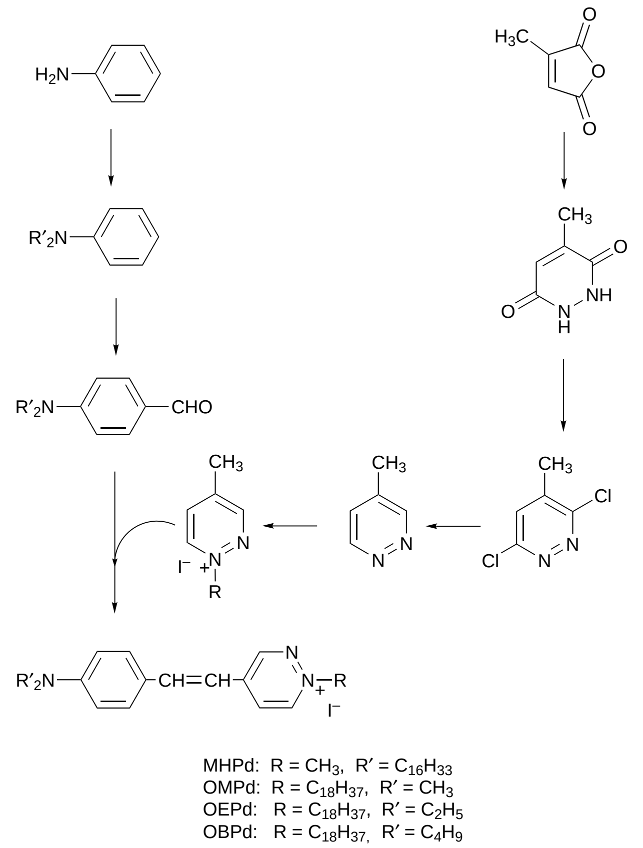

Scheme 1

purple product was obtained. Yield: 15–20%. MHPd: Calc. for $C_{45}H_{78}N_3I$(%): C, 68.59; H, 9.98; N, 5.33; Found: C, 68.59; H, 10.02; N, 5.65; δ_H (400 MHz, $CDCl_3$): 0.72 (t, *J* 6.6, 6H, 2 CH_3), 1.10–1.27 (m, 52H, 26 CH_2), 1.47 (t, *J* 6.2, 4H, 2 CH_2), 3.21 (t, *J* 7.6, 4H, 2 CH_2-N), 4.33 (s, 3H, $R_3-N^+-CH_3$), 6.50 (d, *J* 8.8, 2H, ArH), 6.6 (d, *J* 15.4, 1H, =CH−), 7.43 (d, *J* 8.8, 2H, ArH), 7.7 (d, *J* 15.6, 1H, =CH−), 8.19 (d, *J* 5.70, 1H, ArH), 8.78 (d, *J* 5.68, 1H, ArH), 9.86 (s, 1H, ArH); λ_{max}/nm ($CHCl_3$): 578 (ε 64000 dm^3 mol^{-1} cm^{-1}), 296; λ_{max} (EtOAc) 534, 292.

4-Methyl-1-octadecylpyridazinium iodide. 4-Methylpyridazine (1.54 ml, 16.4 mmol) and 1-iodooctadecane (6.2 g, 16.4 mmol) were dissolved in 15 ml of ethanol (dried). After the mixture had been refluxed for 2 h, it was cooled. The precipitate was collected by suction. The product, 4-methyl-1-octadecylpyridazinium iodide, was recrystallized from ethanol. Yield: 71%.

OEPd, OMPd and OBPd (general method). The appropriate *N*,*N*-dialkylaminobenzaldehyde and 4-methyl-1-octadecylpyridazinium iodide (1 : 1) were dissolved in methanol. The mixture was stirred at room temp. (~20 °C) for 2 h after the addition of piperidine. The purple, waxy product was separated by column chromatography on silica gel using $CHCl_3$ as eluent. Yield: ~30%.

OEPd: Calc. for $C_{34}H_{56}N_3I$ (%): C, 64.44; H, 8.91; N, 6.63; Found: C, 64.22; H, 9.23; N, 6.44; δ_H (400 MHz, $CDCl_3$): 0.88 (t, *J* 6.0, 3H, 1 CH_3), 1.11–1.35 (m, 28H, 14 CH_2), 1.60 (m, 8H, 2CH_3, 1 CH_2), 2.03 (t, *J* 6.96, 2H, 1 CH_2), 3.48 (dd, *J* 7.05, 4H, 2 CH_2-NR_2), 4.65 (t, *J* 7.24, 2H, 1 $CH_2-N^+R_3$), 6.70 (d, *J* 8.9, 2H, 2ArH), 6.82 (d, *J* 15.64, 1H, 1 Ar−CH=), 7.60 (d, *J* 8.92, 2H, 2 ArH), 7.88 (d, *J* 15.64, 1H, 1 Ar−CH=), 8.45 (d, *J* 4.6, 1H, ArH), 8.93 (s, 1H, ArH), 10.04 (d, *J* 6.08, 1H, ArH); λ_{max}/nm ($CDCl_3$) 569 (ε 48900 dm^3 mol^{-1} cm^{-1}), 293.

OMPd: Calc. for $C_{32}H_{52}N_3I$ (%): C, 63.64; H, 8.65; N, 6.94; Found: C, 63.17; H, 9.04; N, 6.45; δ_H (400 MHz, $CDCl_3$): 0.88 (t, *J* 6.60, 3H, 1 CH_3), 1.16–1.43 (m, 30H, 15 CH_2), 2.06 (t, *J* 6.72, 2H, 1 CH_2), 3.10 (s, 6H, 2 CH_3-NR_2), 4.57 (t, *J* 7.48, 2H, 1 $CH_2-N^+R_3$), 6.72 (d, *J* 8.92, 2H, 2 ArH), 6.92 (d, *J* 15.64, 1H, ArCH=), 7.68 (d, *J* 8.92, 2H, 2 ArH), 7.97 (d, *J* 15.64, 1H, 1 Ar−CH=), 8.33 (d, *J* 4.64, 1H, ArH), 9.22 (s, 1H, ArH), 9.74 (s, 1H, ArH); λ_{max}/nm ($CHCl_3$): 558.5 (ε 31700 dm^3 mol^{-1} cm^{-1}), 294.5.

OBPd: Calc. for $C_{38}H_{64}N_3I$ (%): C, 66.16; H, 9.35; N, 6.09; Found: C, 66.08; H, 9.11; N, 6.05; δ_H (400 MHz, $CDCl_3$): 0.88 (t, *J* 6.86, 3H, CH_3), 0.99 (t, *J* 7.26, 6H, 2 CH_3), 1.26–1.42 (m, 34H, 17 CH_2), 1.62 (m, 4H, CH_2), 2.00 (t, *J* 6.83, 2H, 1 CH_2), 3.38 (t, *J* 7.4, 4H, 2 R_2NCH_2-), 4.61 (t, *J* 7.21, 2H, 1 $R_3N^+CH_2-$), 6.60 (d, *J* 9.09, 2H, ArH), 6.94 (d, *J* 15.67, 1H, ArCH=), 7.65 (d, *J* 8.99, 2H, ArH), 7.95 (d, *J* 15.67, 1H, ArCH=), 8.43 (d, *J* 6.75, 1H, ArH), 9.11 (d, *J* 6.73, 1H, ArH), 9.85 (s, 1H, ArH); λ_{max}/nm ($CHCl_3$): 573.5 (ε 51200 dm^3 mol^{-1} cm^{-1}), 321.5.

π–*A* isotherm and film deposition

The monolayer of MHPd, OMPd, OEPd or OBPd was obtained by spreading a chloroform solution of MHPd (OMPd, OEPd or OBPd, 10^{-3}–10^{-4}M) on to a pure water subphase (pH 5.6) in a one-compartment computer-controlled Nima Technology trough at 25 °C and the surface layer was then compressed at a speed of 80 cm^2 min^{-1} to a pressure of 35 mN m^{-1} for MHPd (35 mN m^{-1} for OMPd, 30 mN m^{-1} for OEPd, 25 mN m^{-1} for OBPd). The monolayer was transferred at a rate of 5 mm min^{-1} on to a hydrophilically pretreated quartz slide in the upstroke. The transfer ratios were 1.0 ± 0.1.

SHG and UV–VIS spectra measurement

The second harmonic generation measurements were made in transmission geometry with a Y-cut quartz plate as reference and with a Q-switched Nd:YAG laser (1.064 µm). A 1/2 λ plate and a Glan–Taylor polarizer were used to vary the polarization direction of the laser beam. The laser light, linearly polarized either parallel (p) or perpendicular (s) to the plane of incidence, was directed at an incident angle of 45° onto the vertically mounted sample. A set of 1.064 µm filters and a monochromator were used to ensure that the signal detected by the photomultiplier was generated by second-harmonic radiation. The average output signal was recorded on a digital storage recorder (HP54510A). All the SHG data in this work are average values of at least three individual measurements.

The second harmonic intensities ($I_{2\omega}$) obtained from the monolayer were analyzed by the general procedure described by Ashwell.[18]

The UV–VIS spectra of LB monolayers were recorded on a Shimadzu UV-3100 spectrometer with uncoated quartz substrates as reference.

Results and Discussion

Pressure–area isotherms

The surface pressure–area (π–*A*) isotherms for all the compounds are shown in Fig. 1. The sequence of film forming properties is MHPd > OMPd > OEPd > OBPd.

As shown in Table 1, although their collapse pressures are about the same, the isotherm of OMPd in the condensed region is steeper than that of OMPy (slope for OMPd is 2.83, for OMPy is 2.0 mN mÅ^{-2}) and the area per molecule for OMPd (41 Å^2) is smaller than that for OMPy (55 Å^2). These indicate that with one more nitrogen on the conjugation ring, the hydrophilic property is suitably enhanced, the film forming

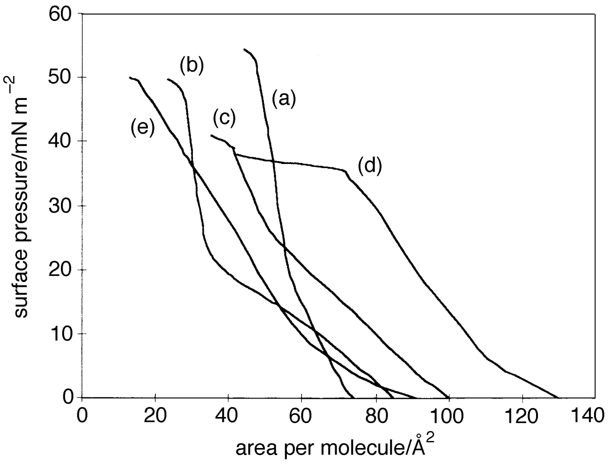

Fig. 1 π–A Isotherm of (E)-N-alkyl-4-{2-[4-(dialkylamino)phenyl]-ethenyl}pyridazinium iodide (a) MHPd; (b) OMPd; (c) OEPd; (d) OBPd; (e) OMPy

Table 1 Slope of π–A curve in condensed region, collapse pressure, and area per molecule of (E)-N-alkyl-4-{2-[4-(dialkylamino)phenyl] ethenyl}pyridazinium iodide (25 °C)

compound	slope in cond. reg./mN mÅ^{-2}	collapse pressure/ mN m^{-1}	area per molecule/ Å^2
MHPd	4.12	54.5	60
OMPd	2.83	48.5	41
OEPd	1.23	39.6	70
OBPd	0.91	38.2	115
OMPy[16]	2.0	50	55

property is ameliorated and molecules could be aligned with each other more closely.

Significant differences in slope (in the condensed region), collapse pressure and area per molecule have been observed between MHPd and OMPd (OEPd, OBPd). The film forming properties of MHPd are remarkably better than the others because of its higher collapse pressure and larger isotherm slope (in the condensed region). Apparently, the attachment of long hydrophobic alkyl chains to the amino side of the chromophore is beneficial to the film forming property and *vice versa.* Moreover, the area per molecule of MHPd is larger than that of OMPd, suggesting that MHPd has a greater volume. The substitution of two long alkyl chains on the amino group is responsible for this.

Along with the increase in length of alkyl chains substituted on amino groups, a decline in both slope and collapse pressure and an increase in area per molecule have been observed in the series of OMPd, OEPd and OBPd. Obviously attachment of long hydrophobic alkyl chains onto both sides of the chromophore will cause the loss of amphiphilic character and result in worse film forming properties.

UV–VIS spectra

Table 2 shows the data from UV–VIS spectra. The maximum absorption wavelength ($\lambda_{\max}$) of OMPd (558.5 nm) is 62.5 nm longer than that of OMPy (496 nm) and the $\lambda_{\max}$ of MHPd is 19.5 nm longer than OMPd. Also $\lambda_{\max}$ of OBPd is longer than that of OEPd and $\lambda_{\max}$ of OEPd is longer than that of OMPd. Generally, there are four main factors which may lead to a red shift of the absorption band: longer conjugation length; stronger electron accepting and donating power of substituted groups; the formation of anions or cations; a greater degree of electron delocalization.[19] Between OMPd and OMPy, the only difference is in their conjugational chromophore. They do not have the same extent of electron delocalization. Therefore the lone pair of electrons on the additional nitrogen of OMPd provides a unique contribution. This function of nitrogen is so called auxochromation. The fact that 1,4-dimethylpyridinium iodide is white and 1,4-dimethylpyridazinium iodide is pale yellow provides further evidence for the existence of auxochromation. In the pyridazine system, the absorption differences resulted from the fact that they have substituted groups with different electron donating and accepting strength. Longer alkyl chains exert stronger electron repulsion power and weaker electron attracting ability than shorter chains.

Second harmonic generation

The SHG properties of all four compounds are shown in Table 3. Among these four molecules, $\chi_{zzz}^{(2)}$ of MHPd is the highest. Unfortunately the $\lambda_{\max}$ of MHPd in LB films (530 nm) is the closest to the second harmonic wavelength (532 nm), so its resonance enhancement is also the largest.

Although OMPd, OEPd and OBPd also have resonance enhancement, their $\chi_{zzz}^{(2)}$ values are comparable. Their $\lambda_{\max}$ values in LB films are about the same. By comparing the $\chi_{zzz}^{(2)}$ of these three molecules, we know that there is a $\chi_{zzz}^{(2)}$ increasing trend from OMPd through OEPd to OBPd. This result is in accord with the theory that stronger electron donating substituents on the amino group give larger SHG signals.[16]

The $\chi_{zzz}^{(2)}$ value, tilt angle in LB films and the area per molecule (35 mN m^{-1}) of OMPd and OMPy are about the

Table 3 SHG of (E)-N-alkyl-4-{2-[4-(dialkylamino)phenyl]ethenyl}-pyridazinium iodide

compound	$\chi_{zzz}^{(2)}$/pm V^{-1}	ϕ/°	*ca.* l/Å
MHPd	257(150–400)	44	30
OMPd	75(52–99)	32	33.3
OEPd	110(100–120)	39	33.0
OBPd	132(86–200)	34	36.0
OMPy[a]	87(20–153)	32	34
OMPy[16]	90–150	41	

[a] Data obtained under the same experimental conditions in this work. ϕ° is the tilt angle of chromophore in LB films. l is the calculated length of molecules.

Table 2 UV–VIS data of (E)-N-alkyl-4-{2-[4-(dialkylamino)phenyl]ethenyl}pyridazinium iodide

	$\lambda_{\max}$/nm			
compound	in chloroform	in LB films	in ethyl acetate	ε/dm^3 mol^{-1} cm^{-1}
MHPd	578	530	534.2	64000
OMPd	558.5	545		31700
OEPd	569.5	545		48900
OBPd	573.5	540		51200
OMPy[a]	495.6	460	465.6	
OMPy[16]	496	460		

[a] Data obtained under the same experimental conditions in this work.

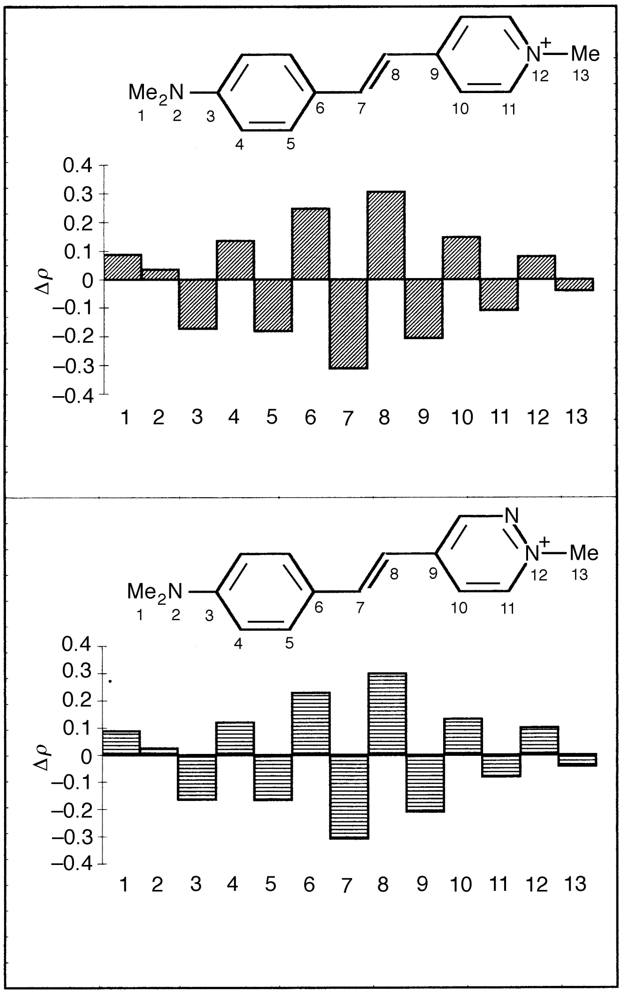

Fig. 2 The charge difference $\Delta\rho$ between the first excited singlet state and the ground state of MMPy (top) and MMPd (bottom) ($\Delta\rho = \rho_e - \rho_g$). Each numbered column refers to the $\Delta\rho$ of the correspondingly numbered part of its structure. $\Delta\rho$ refers to the sum of charges of all heavy atoms and hydrogen atoms in each numbered part of the structure. A positive charge difference indicates loss of negative charge upon excitation.

same. But obviously the resonance enhancement part of OMPd is greater than that of OMPy, because the λ_{max} (in LB films) of OMPd is much closer to 532 nm than that of OMPy. So if this enhancement part is subtracted, the net $\chi_{zzz}^{(2)}$ of OMPd should be smaller than for OMPy. This result suggests that other than the lower aromaticity, which is beneficial to SHG enhancement,[9] there must be an unknown factor unfavorable for SHG. Considering that the second nitrogen is the only difference between OMPd and OMPy, this second nitrogen in the pyridazine ring may be that unfavorable factor.

In order to get a better understanding on the analysis above, some theoretical calculations have been carried out by using MINDO/3 of MOPAC 6.00 on two model molecules, MMPd [(*E*)-*N*-methyl-4-{2-[4-(dimethylamino)phenyl]ethenyl}-pyridazinium iodide] and MMPy [(*E*)-*N*-methyl-4-{2-[4-(dimethylamino)phenyl]ethenyl}pyridinium iodide]. It is well known that the β value for SHG is often described by the two-level model and $\Delta\mu_{eg}$ is in direct proportion to β and consequently to $\chi_{zzz}^{(2)}$, where $\Delta\mu_{eg}$ is the change of dipole moments between ground states and excited states.[20] Results show that $\Delta\mu_{eg}$ is $|-12.52|$D for MMPd and $|-13.26|$D for MMPy. Fig. 2 shows the charge differences $\Delta\rho$ between the first excited singlet state and the ground state of MMPd and MMPy. The charge differences refer to the sum of charges of all heavy atoms and hydrogen atoms in each correspondingly numbered column. A positive charge difference indicates loss of negative charge upon excitation. It is also known that when a molecule with larger $\Delta\mu_{eg}$ is excited to the first excited state, it loses more negative charge in the electron donating part and gains more negative charge in the electron accepting part. Fig. 3 describes the difference between $\Delta\rho$ of MMPd and MMPy ($\Delta\rho_{MMPd} - \Delta\rho_{MMPy}$). It can be seen from Fig. 3 that the dimethylamino group (column 1 and 2) of MMPy loses negative charge more easily than that of MMPd and the electron accepting part (columns 11–13) of MMPy gets negative charge more easily or loses less negative charge than that of MMPd. It is obvious that the main contribution of MMPd getting less negative charge in the electron accepting part comes from column 11 where the additional nitrogen is located. Therefore because of this contribution of the additional nitrogen, $\Delta\mu_{eg}$ of MMPd is smaller than that of MMPy. A similar situation should arise when OMPy is compared with OMPd. So the negative effect of the second nitrogen in this system may not be negligible.

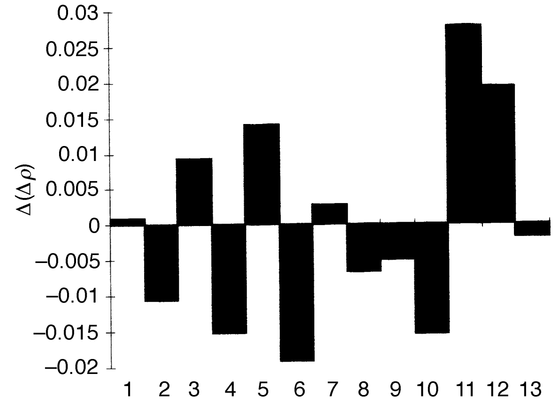

Fig. 3 The difference between $\Delta\rho$ of MMPd and MMPy [$\Delta(\Delta\rho) = \Delta\rho_{MMPd} - \Delta\rho_{MMPy}$]. Each numbered column refers to the $\Delta(\Delta\rho)$ of the correspondingly numbered part of structures in Fig. 2.

Conclusions

The novel pyridazinium compounds MHPd, OMPd, OEPd and OBPd were synthesized and characterized for the first time. Strong SHG was obtained. Among the factors which affect the second harmonic generation in the pyridazinium system, besides bond length alternation, aromaticity, resonance enhancement *etc*., high electron density around the second nitrogen in the six-membered diazine ring is the one which could not be ignored. This last factor should be taken into account when an aromatic ring with more than one heteroatom is considered in finding new and high SHG materials.

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