

## A simple method for the estimation of hyperpolarisabilities: Application to diamino substituted dicyanoquinodimethane molecules

M RAVI

School of Chemistry, University of Hyderabad, Hyderabad 500 046, India  
Present address: Department of Physics, University of Durham, South Road,  
Durham DH 1 3LE, UK

MS received 2 January 1998, revised 23 February 1998

**Abstract.** Two-level hyperpolarisabilities,  $\beta_2$  of a series of amine substituted dicyanoquinodimethane molecules were investigated utilising a simple solvatochromic method developed by us for the determination of excited state dipole moments. The hyperpolarisability,  $\beta$  as well as the two-level approximation to it,  $\beta_2$ , of these quinonoid systems were estimated computationally. Using a parallel study on a set of well known coumarin dyes and their reported electric field induced second harmonic generation (EFISHG)  $\beta$  for calibration, the experimental static  $\beta$ 's of quinonoid molecules are estimated and found to be very large, approximately in the range of  $-50$  to  $-60 \times 10^{-30}$  e.s.u.

**Keywords.** Two-level model; quinonoid compounds; hyperpolarisability.

### 1. Introduction

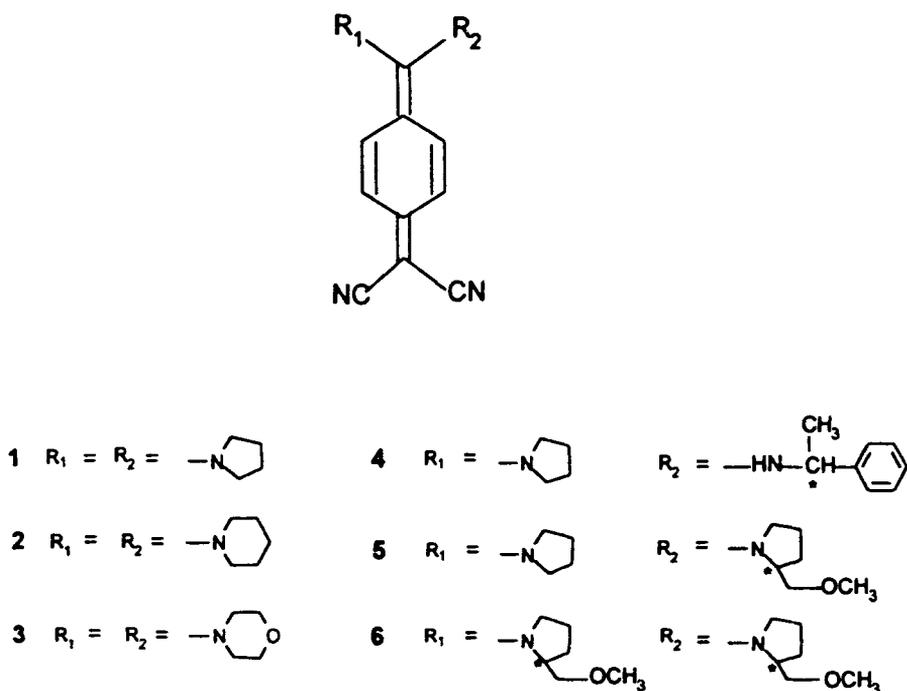
Molecules with the “donor-conjugated unit-acceptor” framework are of considerable interest in nonlinear optics (NLO) <sup>1-3</sup>. Several such molecules having large hyperpolarisabilities ( $\beta$ ) are useful in designing solid state devices for a variety of second order NLO applications like second harmonic generation (SHG) i.e. doubling the frequency of laser radiation, electro-optic effect and optical parametric oscillation.

Push-pull quinonoid systems are potential candidates for second order NLO materials. Amine substituted dicyanoquinodimethane molecules, first synthesised by a du Pont group <sup>4</sup> and investigated briefly by Nicoud <sup>5</sup> are an attractive class of molecules for the fabrication of NLO materials. The prototypical molecule 2-(4-dicyanomethylenecyclohexa-2,5-dienylidene)imidazolidine (in figure 1, ( $R_1$ ,  $R_2$ ) = -NH-CH<sub>2</sub>-CH<sub>2</sub>-NH-) was reported <sup>6</sup> to have a very large  $\beta$  value of  $(-240 \pm 60) \times 10^{-30}$  e.s.u. at an excitation energy of 1.17 eV. Our theoretical studies showed that they have appreciable  $\beta$  values and that the  $\beta$  could be fine-tuned by controlling the electron donating and accepting capability of the push-pull groups <sup>7</sup>. Our recent experimental studies on this class of materials revealed several positive features like (i) easy synthesis and flexibility to introduce a variety of donor groups (ii) good crystal growth of several derivatives, (iii) thermal stability up to 250–300°C and (iv) optical transparency through most of the visible region with absorption maxima typically around 350–400 nm <sup>8,9</sup>. We obtained noncentric structures by introducing chiral groups at the donor end of these systems. The chiral compounds showed moderate to strong phase matchable powder SHG capability (ranging from 3U to 55U) <sup>10,11</sup>.

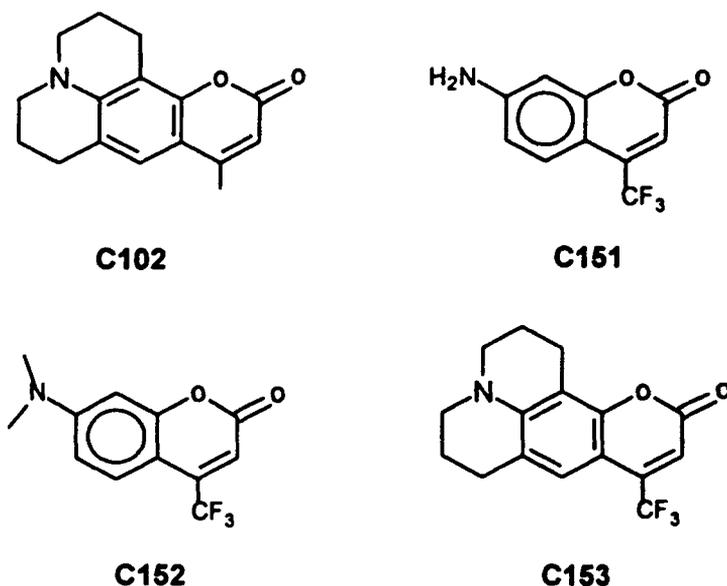
We have also observed an interesting phenomenon of solvate switchable powder SHG in one of these materials <sup>12</sup>.

Detailed investigation of the hyperpolarisabilities of organic molecules is very important in designing systems for the fabrication of optimised NLO materials. The popular experimental techniques to measure  $\beta$  are the electric field induced second harmonic generation (EFISHG) and the hyper Rayleigh scattering (HRS). Both techniques require coherent light sources and relatively expensive and sophisticated equipment for data collection. A simpler method to estimate the  $\beta$  values using a two-level approximation was first reported by Ouder <sup>13</sup>. The  $\beta$ 's of various organic molecules were determined using a solvatochromic method and compared with the results from other methods by Paley and his co-workers <sup>14</sup> and Qin <sup>15</sup> and his co-workers<sup>15</sup>. They showed that the agreement was very good and made a case for the utility of the simple method.

In this paper, we report for the first time, the two-level hyperpolarisabilities,  $\beta_2$  of several diamino substituted dicyanoquinodimethane molecules (figure 1); we note that  $\beta_2$  is also sometimes referred to as  $\beta_{ct}$ , to highlight the fact that the only excited state considered for the evaluation of  $\beta$  is the intramolecular charge transfer (ct) state. They were determined using a solvatochromic method we have developed recently to



**Figure 1.** Quinonoid molecules considered in this study; 7,7-dipyrrolidino-8,8-dicyanoquinodimethane (1), 7,7-dipiperidino-8,8-dicyanoquinodimethane (2), 7,7-dimorpholino-8,8-dicyanoquinodimethane (3), 7-S(-)- $\alpha$ -methylbenzylamino-7-pyrrolidino-8,8-dicyanoquinodimethane (4), 7-S(+)-2-methoxymethylpyrrolidino-7-pyrrolidino-8,8-dicyanoquinodimethane (5), 7,7-di(S(+)-2-methoxymethylpyrrolidino)-8,8-dicyanoquinodimethane (6)



**Figure 2.** Molecular structures of the coumarins considered in this study

estimate dipole moment changes on excitation. We have recently determined the solvatochromic  $\Delta\mu_{ge}$  of a family of coumarin molecules (C102, C151, C152 and C153; see figure 2) widely used as laser dyes (16). Their experimental (EFISHG)  $\beta$ 's have been published by Moylan <sup>17</sup>. Now we have determined their  $\beta_2$  using similar solvatochromic methods as employed for the quinonoid molecules.

While the  $\Delta\mu_{ge}$  of the quinonoid molecules is negative, it is positive for the coumarins. This would lead to opposite signs for the hyperpolarisabilities of the two classes of compounds. However, the sign of  $\beta$  is of no consequence to NLO properties; only the magnitude is important. Therefore we have utilised the  $\beta_2$  determination of the coumarins as a parallel study to the investigation on quinonoid molecules. The hyperpolarisability,  $\beta$  and the 2-level approximation to it,  $\beta_2$  for the quinonoid systems and the coumarins were estimated by computational methods. This allowed us to obtain a scaling between the  $\beta_2$  and  $\beta$  in these systems. With the additional information or the EFISHG determined  $\beta$  values of coumarins, we are able to make semiquantitative predictions for the actual hyperpolarisabilities of the quinonoid systems without carrying out expensive EFISHG or HRS measurements.

## 2. Theoretical

When a molecule is placed in an external electric field ( $E$ ), a dipole moment is induced in the molecule and the induced dipole moment per unit volume is called the polarisation ( $P$ ). It is related to the electric field as follows

$$P_i = \alpha_{ij}E_j + \beta_{ijk}E_jE_k + \gamma_{ijkl}E_jE_kE_l + \dots \quad (1)$$

where  $P_i$  is the electronic polarisation induced along the  $i$ th molecular axis,  $E_j$ ,  $E_k$ ,  $E_l$  etc. are the  $j$ ,  $k$ ,  $l$ th components of the applied electric field,  $\alpha_{ij}$  is the  $ij$ th component of

the polarisability tensor,  $\beta_{ijk}$  is the  $ijk$ th component of the second hyperpolarisability tensor and  $\gamma_{ijkl}$  is the  $ijkl$ th component of the second hyperpolarisability tensor respectively. The terms beyond the first describe the nonlinear response of the molecule to the radiation field and importantly the even order tensor like the  $\beta$  which is responsible for SHG, vanishes in a centrosymmetric system.

### 2.1 Calculation of two-level hyperpolarisability, $\beta_2$

To estimate the hyperpolarisability that is free of any resonance contribution, we have calculated the static hyperpolarisability (*i.e.* excitation energy = 0 eV) throughout this study.

The simple two-level model (13) which describes the second order molecular response (excluding the dispersion factors) in terms of electronic charge transfer excitation between the ground state  $g$  and first excited state  $e$ , is given in the form of (2)

$$\beta_2 = \frac{3e^2 h^2 f \Delta\mu_{ge}}{2m \Delta E_{ge}^3} \quad (2)$$

where  $\Delta E_{ge}$ , is the energy,  $\Delta\mu_{ge}$ , the dipole moment change and  $f$ , the oscillator strength for the first excitation. We have used AMI optimised geometries for the coumarin dyes and crystal structure geometries for quinonoid molecules to compute the  $\Delta E_{ge}$ ,  $f$  and  $\Delta\mu_{ge}$  for the lowest excitation, using the Austin Model 1 method (MOPAC93) (Fujitsu Inc.)<sup>18</sup> invoking a configuration interaction (CI) scheme. This CI involved single and pair excitations within a manifold of 10 molecular orbitals (5 HOMO's and 5 LUMO's). Then we have calculated the  $\beta_2$  using the above equation.

### 2.2 Calculation of hyperpolarisability, $\beta$

The hyperpolarisability,  $\beta$  of organic molecules are usually determined experimentally using EFISHG or HRS techniques. The EFISHG technique provides the major vector part of the hyperpolarisability,  $\beta_x$  defined as

$$\beta_x = \beta_{xxx} + \frac{1}{3}(\beta_{xyy} + 2\beta_{yxy} + \beta_{xzz} + 2\beta_{zxx}) \quad (3)$$

where  $x$  is the direction of the permanent dipole moment of the molecule. In most organic molecules having donor and acceptor groups, this is the direction of charge transfer. We have computed the  $\beta$  (actually the  $\beta_x$ ) directly from the MOPAC93 program which utilises the time dependent Hartree-Fock method<sup>19</sup>. The MOPAC calculations were carried out on a Sun Sparc 10 Workstation.

## 3. Experimental

To determine experimentally, the  $\beta_2$  of any molecule using the above two-level formulation we need to measure (i)  $\Delta\mu_{ge}$ , the dipole moment change (ii)  $\Delta E_{ge}$  the energy and (iii)  $f$ , the oscillator strength for the first excitation(charge transfer excitation).

### 3.1 Determination of $\Delta E_{ge}$ and $f$

The absorption band shape is very close to Gaussian for the molecules reported in this paper. The energy of transition,  $\Delta E_{ge}$  can be found simply from band maximum of the

UV-vis absorption spectrum of the molecule. The oscillator strength,  $f$  of the transition can be determined<sup>20</sup> from the area under the band by means of (4).

$$A = \int \varepsilon(\nu) d\nu$$

$$f = 1.44 \times 10^{-19} \times A (\text{M}^{-1} \text{cm}^{-1} \text{sec}^{-1}) \quad (4)$$

where  $A$  is the integral absorption coefficient,  $\varepsilon(\nu)$  = molar extinction coefficient at frequency,  $\nu$  ( $\nu(\text{Hz}) = \Delta E/hc$ ) and the integral is over the entire absorption band.

### 3.2 Determination of $\Delta\mu$ using a simple solvatochromic method

There are various techniques available for the determination of excited state dipole moments and the most popular method is based on the Lippert-Mataga equation<sup>21,22</sup>. In this method, the shifts of the absorption and fluorescence band maxima are followed using the solvent polarity, normally described by functions of the dielectric constant,  $D$  and refractive index,  $n$ . Due to the simplicity of the experimental procedure and the ease of data analysis, the solvatochromic method has become popular for the determination of the excited state dipole moments.

The solvatochromic shifts of dipolar molecules should correlate much better with microscopic solvent polarity parameters such as  $E_T^N$  or  $E_T(30)$ <sup>23</sup> rather than traditionally used bulk solvent polarity functions involving  $D$  and  $n$ . The theoretical basis for such a correlation has been formulated by us recently<sup>24</sup>. The following expression is used for the determination of the excited state dipole moments,

$$\Delta\bar{\nu}_{af}/\text{cm}^{-1} = 11307.6 \left( \frac{\Delta\mu}{\Delta\mu_D} \right)^2 \left( \frac{a_D}{a} \right)^3 E_T^N + \text{const.} \quad (5)$$

where  $E_T^N$  is the solvent polarity function proposed by Reichardt<sup>23</sup>, based on the absorption wavenumber,  $\bar{\nu}_a$  of a standard betaine dye in the solvent. In (5)  $\Delta\bar{\nu}_{af}$  is the Stokes shift ( $\bar{\nu}_a - \bar{\nu}_f$ ;  $\bar{\nu}_a$  is the wavenumber of absorption,  $\bar{\nu}_f$  the wavenumber of fluorescence).  $\Delta\mu_D$  and  $a_D$  are the dipole moment changes on excitation and the Onsager radius of the betaine dye respectively;  $\Delta\mu$  and  $a$  are the corresponding quantities of the molecule of interest. The Onsager radius of the molecules were estimated using the length of the dipole. The ratio  $a/a_D$  was found to be approximately equal to 1 for all the quinonoid molecules ( $a_D = 6.2 \text{ \AA}$ )<sup>24</sup>. It may be noted that since a ratio of  $a_D/a$  is involved, errors involved in the estimation of the Onsager radius may be ameliorated to some extent. The possible applications and advantages of this method, namely the utilisation of mixed solvents and the facility to collect larger data sets for analysis has been discussed. The  $\Delta\mu$ 's of several coumarin dyes were successfully determined by us<sup>16</sup> and some of this data are used in this study for the determination of their  $\beta_2$ .

Synthesis and purification procedures for all the quinonoid compounds are reported elsewhere<sup>10,11</sup>. Laser-grade coumarin dyes (Kodak) were used without any further purification. Spectroscopic grade solvents (E-Merck, India) were dried over 4 Å molecular sieves. The purity of the solvents was checked by measuring the  $E_T^N$  using the betaine dye. The betaine dye, a gift from Prof Reichardt was used without any further purification for  $E_T^N$  measurements. The absorption and fluorescence spectra of all the compounds were measured on a Jasco Spectrophotometer (Model 7800) and a Jasco spectrofluorimeter (Model FP-777) respectively.

**Table 1.** Extinction coefficient at maximum absorption ( $\epsilon_{max}$ ) and integral absorption coefficient ( $A$ ) (see text for details) measured for molecules 1–6 and coumarin dyes C102, C151, C152, C153 (see figure 2)

Molecule	$\epsilon_{max}$ ( $M^{-1} cm^{-1}$ )	$A/10^{15}$ $M^{-1} cm^{-1} s^{-1}$
1	18436	2674
2	26987	2922
3	24612	3212
4	15012	2690
5	23856	2905
6	23142	2619
C102	25117	3074
C151	23014	3325
C152	22401	3074
C153	33470	4304

**Table 2.** The experimental energy ( $\Delta E_{ge}$ ), the dipole moment change ( $\Delta\mu_{ge}$ ) and the oscillator strength ( $f$ ) for the lowest excitation, the experimental and theoretical two-level hyperpolarizability ( $\beta_2$ ) and  $\beta$  from EFISHG (reported earlier) and from semiempirical computation, for the coumarin dyes C102, C151, C152 and C153 (figure 2); all  $\beta^{\dagger}$  are at  $h\omega = 0 eV$

Molecule	$\Delta E_{ge}$ (eV)	$\Delta\mu_{ge}$ (D)	$f$	$\beta_2$ (exp)	$\beta$ (exp)*	$\beta_2$ (calc)	$\beta$ (calc)
C102	3.24	2.11	0.443	4.5	12.4	1.3	6.0
C151	3.38	1.58	0.479	3.2	9.0	1.3	5.0
C152	3.15	2.16	0.443	5.0	10.6	2.2	8.3
C153	2.95	2.22	0.620	8.8	15.8	2.4	9.4

$\dagger$ In units of  $10^{-30}$  e.s.u.

\*Ref. 17

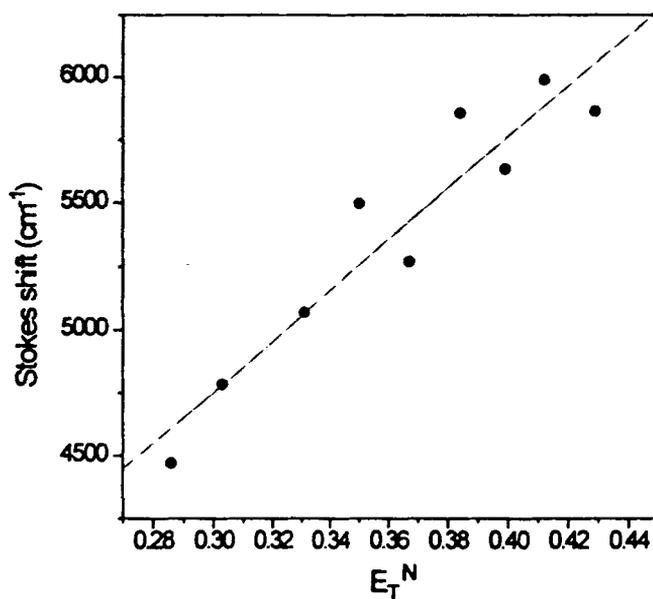
#### 4. Results and discussion

The molecular extinction coefficient  $\epsilon_{max}$  (at  $\lambda_{max}$ ) and the integral absorption coefficient,  $A$  (from which the oscillator strength was calculated) for the molecules 1–6 and the coumarin dyes are presented in table 1.  $\Delta E_{ge}$ ,  $f$ ,  $\Delta\mu_{ge}$  determined as described above for the coumarin dyes and for the molecules, 1–6 are tabulated in tables 2 and 3 respectively. As mentioned in section 3 the  $\Delta\mu_{ge}$ 's of coumarin dyes were taken from published results<sup>16</sup>.  $\Delta\mu_{ge}$  of the quinonoid compounds (1–6) were determined using the acetonitrile-benzene binary mixtures of nine different compositions by measuring the Stokes shifts of the molecules. Figure 3 shows the plot of the Stokes shifts vs the  $E_T^N$  polarity parameter at compositions ranging from 20% to 100% of acetonitrile for the molecule 6. The correlation is found to be excellent ( $r = 0.946$ ). Similar correlations were obtained for the other molecules as well. The  $\Delta\mu_{ge}$ 's of these quinonoid molecules are large and negative and indicate a benzenoid ground state going over to a quinonoid excited state.

**Table 3.** The experimental energy ( $\Delta E_{ge}$ ), the dipole moment change ( $\Delta\mu_{ge}$ ) and the oscillator strength ( $f$ ) for the lowest excitation, the experimental and theoretical two-level hyperpolarizability and  $\beta$  from semiempirical computation, for the molecules 1–6 (figure 1); all  $\beta^{\dagger}$  are at  $\hbar\omega = 0$  eV

Molecule	$\Delta E_{ge}$ (eV)	$\Delta\mu_{ge}$ (D)	$f$	$\beta_2$ (exp)	$\beta_2$ (calc)	$\beta$ (calc)
1	2.99	−9.4	0.385	−22.1	−11.5	−52.6
2	2.74	−8.2	0.421	−27.4	−13.5	−54.9
3	2.69	−8.1	0.462	−31.4	−11.7	−54.3
4	3.12	−10.0	0.387	−20.8	−14.7	−51.0
5	2.89	−8.7	0.418	−24.6	−14.5	−51.4
6	2.86	−9.5	0.377	−25.1	−16.9	−50.2

<sup>†</sup>In units of  $10^{-30}$  e.s.u.



**Figure 3.** Stokes shifts vs the  $E_T^N$  values for the molecule 6 in acetonitrile-benzene mixtures at nine different compositions

The  $\beta_2$  values determined using these spectroscopic parameters (using equation 2) are also presented in the respective tables. The  $\beta_2$  values estimated theoretically using the  $\Delta E_{ge}$ ,  $f$  and  $\Delta\mu_{ge}$  from semiempirical AM1/CI calculations for the coumarins and quinonoid systems are collected in tables 2 and 3 respectively. These tables also provide the  $\beta$  values for these systems computed using the time dependent Hartree-Fock (TDHF) method. Table 2 contains additionally, the  $\beta$  values of coumarins reported<sup>17</sup> earlier, using EFISHG studies.

In table 2 it is seen that the experimental  $\beta_2$  are approximately 3–4 times that of the theoretical  $\beta_2$ . In the case of  $\beta$ , this ratio is roughly about 1.5 to 2. In table 3, we find that the  $\beta_2$  (experimental) is again 1.5 to 2 times larger than  $\beta_2$  (theoretical).

This trend of higher values of experimental  $\beta$  with respect to theoretical values is in accordance with the earlier reports<sup>25</sup>. This overestimation in the experimental values could be due to the effect of solvent dielectric environment and local field factors on  $\beta$ <sup>26</sup>.

What is more pertinent here is the comparison of  $\beta_2$  values to the  $\beta$  values, either from experiment or from theory. In table 2, it is seen that the theoretical  $\beta$  to  $\beta_2$  ratio is about 4, and the experimental  $\beta$  to  $\beta_2$  ratio is roughly 2–3. For the quinonoid molecules, the theoretical  $\beta$  to  $\beta_2$  ratio is again about 4 which is consistent with the case of coumarins. Our earlier detailed theoretical analysis carried out on a model compound 7,7-diamino-8,8-dicyanoquinodimethane using a sum-over-states method indicated that the contribution of the first excited state to  $\beta$  is approximately 50% and the rest is made up of contributions from a large number of excited states<sup>7</sup>. The present theoretical analysis shows that the  $\beta_2$  is only 25% that of  $\beta$ . This may be ascribed to the different computational method we have used in this study. However, the experimental results on coumarins show that the  $\beta_2$  is nearly 50% of  $\beta$  as seen in several molecules. Significantly, these observations allow us to make an estimate of the experimental (EFISHG) hyperpolarisabilities expected for the quinonoid systems. Based on the transferability of the  $\beta_2/\beta$  ratios between coumarins and the quinonoids, the EFISHG  $\beta$  values of the quinonoids are expected to be 2–3 times their experimental  $\beta_2$  values *ie.* about  $-50$  to  $-60 \times 10^{-30}$  e.s.u (at  $\hbar\omega = 0$  eV).

Some comments about the hyperpolarisabilities of the quinonoids are in order. These systems have potentially large  $\beta$  values as seen from the 2-level approximation, theoretical estimates or the projected EFISHG values. These values are large compared to well known NLO organic molecules<sup>27</sup>. In particular these  $\beta$ 's are interesting in view of the short conjugation lengths of these molecules which leads to relatively high absorption energies and near transparency in the visible range. They are inherently negative values, which are consistent with the negative solvatochromism arising from the decrease in the dipole moment on excitation. The static  $\beta$  (or  $\beta_2$ ) values in these molecules are very similar irrespective of the donor groups. The moderate to strong powder SHG (**4**, **5** and **6** showed 3U, 28U and 55U respectively)<sup>11</sup> found in these systems have been engineered by fine tuning the crystal structures.

In summary, the solvatochromic method which we proposed (5) for the  $\Delta\mu_{ge}$  determination has many advantages over the other solvatochromic methods. The comparison of  $\beta_2$  to  $\beta$  from theory and experiment on a set of coumarin dyes and a consistent comparison of the theoretical  $\beta_2$  and  $\beta$  of the quinonoid systems has enabled us to make estimates of the experimental molecular  $\beta$ 's of the new class of quinonoid systems. Hence, we conclude from the study that the solvatochromic and theoretical methods with calibration studies on appropriately chosen systems together make a convenient tool to understand the range of experimental  $\beta$  values of novel and potentially interesting organic molecules.

### Acknowledgement

I am grateful to Dr T P Radhakrishnan for invaluable suggestions and fruitful discussions. I thank Dr A Samanta for providing the coumarin dyes and the Council of Scientific and Industrial Research, New Delhi for a fellowship and the Department of Science and Technology, New Delhi for funding some of the facilities used in this work.

## References

1. Chemla D S and Zyss J (eds) 1987 *Nonlinear optical properties of organic molecules and crystals* (New York: Academic Press)
2. Williams D J 1984 *Angew. Chem. Int. Ed. Engl.* **23** 690
3. Kanis D R, Ratner M A and Marks T J 1994 *Chem. Rev.* **94** 195
4. Hertler L R, Hartzler H D, Acker D S and Benson R E 1962 *J. Am. Chem. Soc.* **84** 3387
5. Nicoud J F 1988 *Mol. Cryst. Liq. Cryst.* **156** 257
6. Lalama S J, Singer K D, Garito A F and Desai K N 1981 *Appl. Phys. Lett.* **39** 940
7. Ravi M and Radhakrishnan T P 1995a *J. Phys. Chem.* **99** 17624
8. Ravi M, Rao D N, Cohen S, Agranat I and Radhakrishnan T P 1995b *Curr. Sci.* **68** 1119
9. Ravi M, Rao D N, Cohen S, Agranat I and Radhakrishnan T P 1996a *Struct. Chem.* **7** 225
10. Ravi M, Rao D N, Cohen S, Agranat I and Radhakrishnan T P 1996b *J. Mater. Chem.* **6** 1119
11. Ravi M, Rao D N, Cohen S, Agranat I and Radhakrishnan T P 1997 *Chem. Mater.* **9** 830
12. Ravi M, Rao D N, Cohen S, Agranat I and Radhakrishnan T P 1996c *J. Mater. Chem.* **6** 1853
13. Oudar J L 1977 *J. Chem. Phys.* **67** 446
14. Paley M S, Harris J M, Looser H, Baumert J C, Bjorklund G C, Jundt D and Twieg R J 1989 *J. Org. Chem.* **54** 3774
15. Qin J, Wu X, Zhang X, Zhan C and Liu D 1995 *Synth. Metals* **71** 1711
16. Ravi M, Soujanya T, Samanta A and Radhakrishnan T P 1995c *J. Chem. Soc., Faraday Trans.* **91** 2739
17. Moylan C R 1994 *J. Phys. Chem.* **98** 13513
18. MOPAC93©Fujitsu Inc.
19. Dupuis M and Karna S 1991 *J. Comp. Chem.* **12** 487
20. Atkins P W 1990 *Physical Chemistry* 5th edn., (Oxford: ELBS) p503
21. Lippert E Z 1955 *Z. Naturforsch., Teil A* **10** 541
22. Mataga N, Kaifu Y and Koizumi M 1956 *Bull. Chem. Soc. Jpn.* **29** 465
23. Reichardt C (ed.) 1988 *Solvents and solvent effects in organic chemistry* (Weinheim: VCH) p. 337
24. Ravi M, Samanta A and Radhakrishnan T P 1994 *J. Phys. Chem.* **98** 9133
25. Dehu C, Meyers F and Bredas J L 1993 *J. Am. Chem. Soc.* **115** 6198
26. Willettes A, Rice J E, Burland D M and Shelton D P 1992 *J. Chem. Phys.* **97** 7590
27. Eaton D F 1991 *Science* **253** 281