# A comparative theoretical study of pseudo-linear dyes suitable for incorporation in electro-optically active poled polymers

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Eight structures, four quinonoid (Class A) and four non-quinonoid(Class B) have been assessed with regard to their suitability for inclusion as guest molecules, or as side-chains (bound, say, by *N*-alkyl) in polymers in order to produce electro-optically active poled polymers. The mode of assessment was by means of calculated transition moments, dipole moments and components (especially $\beta$-$x$, with the $x$-axis as the polar, long, molecular axis) of the $\beta$-tensor for second harmonic generation (SHG). The optical darkness of Class A render them suitable for SHG at incident wavelengths of about 1300 nm or longer. The best of Class A, which we are now attempting to synthesize, is VI(1-(4-aza-cyclohexa-2,5-diene-1-ylidenyl)-2-(4-(1,1-dicyanovinylidenyl)-cyclohexa-2,5-diene-1-ylidenyl)ethene). Class B, albeit with substantially smaller values of $\beta$-$x$, can be used over a much wider wavelength range (about 900 nm or longer); the best of class B is VIII (4-nitro-phenyl-4-amino-phenyl-diacetylene).

## 1. Introduction

The purpose of the work described in this paper is to identify molecular structures that are particularly suitable for producing electro-optically active poled polymers [1]. There are three major pre-requisites that such molecular structures must exhibit:

1. a high ground-state molecular electric dipole moment;
2. a large change in molecular electric dipole moment upon optical excitation;
3. the excitations with large changes in dipole moment must also have large transition moments.

The calculated molecular parameter used herein to assess suitability for applications in non-linear optics (NLO) is the third-rank tensor for second harmonic generation (SHG), $\beta(-2\omega, \omega, \omega)$ [2]. Although pre-requisite (1) above does not have a direct bearing upon the calculated value of $\beta$, it is essential in the context of poling due to the need for strong interactions between the permanent molecular electric dipole moment and an applied electric d.c. field. The latter interactions will tend to align the dipolar molecules co-facially, i.e. with like charge facing like charge, thereby counteracting the tendency for an array of dipoles to form centrosymmetric ensembles under the influence of attractive forces between neighbours, i.e. unlike charge facing unlike charge. The presence of a centre of symmetry gives a net zero value for $\beta$ (or for the related bulk susceptibility, $\chi^{(2)}$) because $\beta$ and $\chi^{(2)}$ are classified as ungerade (odd) in a centrosymmetric environment.

The types of molecular structures selected (see Fig. 1) consist of those already synthesized at Bristol Polytechnic (III, IV), those being studied at Cranfield Institute of Technology (II) [3] or elsewhere (VII) [4] and those that are under active investigation with regard to the design and testing of new synthetic routes as a direct result of the outcome of the theoretical investigation reported upon herein (I, V, VI).

In accord with established practice [5], emphasis has been placed upon pseudo-linear conjugated molecules with distinct electron-donating groups, e.g. $-NH_2$, $>NH$, and electron-accepting groups, e.g. $NO_2$, $=C(CN)_2$ at opposite ends of the long molecular axis (the $x$-axis in this work). The types of molecule can be divided into two classes (A and B). Class A can exhibit two types of structure: the quinonoid form* involving no formal separation of charge (as shown in Fig. 1, I, II, V, VI) and the zwitterionic form. The latter contain conventional benzenoid rings, a positively charged, quadruply-bound nitrogen and a triply-bound, negatively charged carbon atom in the guise of the $-\bar{C}(CN)_2$ group. Class B (Fig. 1, III, IV, VII, VIII) cannot exhibit a quinonoid structure without invoking dual separation of charge. We report the results for the planar structures depicted in Fig. 1.

## 2. Theory and calculations

The components of the third-rank Cartesian tensor, $\beta$ $(-2\omega, \omega, \omega)$, now abbreviated as $\beta$, describing the generation of the second harmonic of an incident beam of rotational frequency $\omega$, can be evaluated

*The term "quinonoid" refers to a six-membered ring, which is usually depicted with three double bonds, having four double-bonds in parallel—two in the ring and two exocyclic.
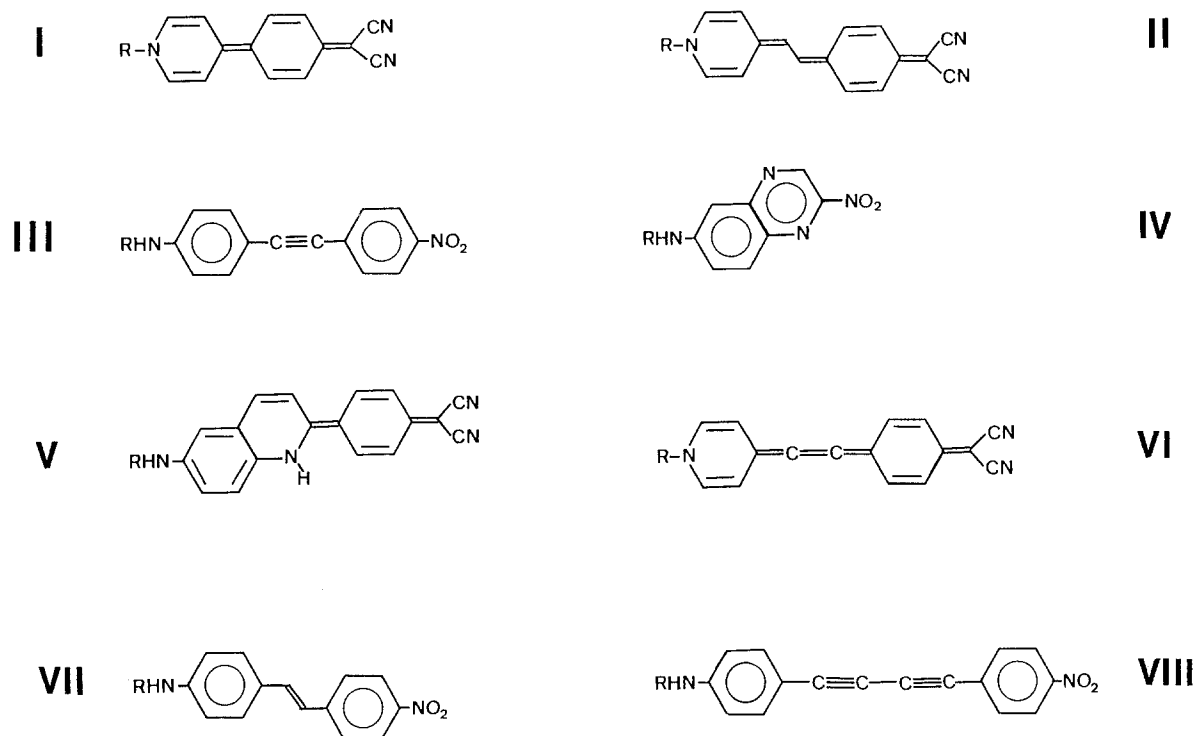
*Figure 1* Structures of planar ($x-y$ plane) conjugated systems for which calculations of $\beta$-$x$ are reported herein. The direction of the positive $x$-axis is from the electron accepting group ($NO_2$ or $=C(CN)_2$) along the bond connecting that group to the main molecular framework. The substituent, R, indicates a group suitable either for enhancement of solubility in a polymer melt, or for chemical binding to a polymer chain.

from the following equation [6]:

$$\beta_{ijk}(-2\omega, \omega, \omega) = -(e^3/8\hbar^2) \sum_{n'} \sum_{n} \{(\langle ikj\rangle$$

$$+ \langle ijk\rangle) [f(3, 1) + f(\bar{3}, \bar{1})]$$

$$+ (\langle jki\rangle + \langle kji\rangle) [f(\bar{1}, \bar{3})$$

$$+ f(1, 3)] + (\langle kij\rangle + \langle jik\rangle$$

$$\times [f(\bar{1}, 1) + f(1, \bar{1})]\} \qquad (1)$$

in which $e$ is the unit of electronic charge (a negative number), $\hbar$ is Planck's constant divided by $2\pi$, and the $\langle ijk\rangle$ etc. are shorthand for $T^i_{gn'}$, $T^j_{n'n}$, $T^k_{ng}$, $T^i_{ng}$ and $T^j_{n'n}$, say, respectively represent the matrix elements of the vector operator, $\hat{r}$, $\langle g/r^i/n\rangle$ and $\langle n/r^i/n'\rangle$ where $n$ and $n'$ refer to excited states and $g$ signifies the ground state. The frequency terms, $f(3, 1)$ etc. are defined elsewhere [6]. When $n = n'$, the so-called diagonal terms, the $T^i_{nn'}$ represent the change in molecular dipole moment between $g$ and $n$, and we have used the alternative notation $\Delta^i_{ng}$ for this circumstance. The matrix elements $T^i_{gn'}$ and $T^i_{ng}$ are transition moments along a particular Cartesian axis ($x$, $y$, or $z$).

Only 21 out of 27 tensor components contribute to the vectorial part ($\beta$-$x$, $\beta$-$y$, $\beta$-$z$) of a third rank tensor:

$$\beta\text{-}x = \beta_{xxx} + (\beta_{xyy} + \beta_{yxy} + \beta_{yyx} + \beta_{xzz}$$

$$+ \beta_{zxz} + \beta_{zzx})/3 \qquad (2)$$

$$\beta\text{-}y = \beta_{yyy} + (\beta_{yxx} + \beta_{xyx} + \beta_{xxy}$$

$$+ \beta_{yzz} + \beta_{zyz} + \beta_{zzy})/3 \qquad (3)$$

$$\beta\text{-}z = \beta_{zzz} + (\beta_{zyy} + \beta_{yzy} + \beta_{yyz} + \beta_{zxx}$$

$$+ \beta_{xzx} + \beta_{xxz})/3 \qquad (4)$$

The average value $\beta$-VEC is always positive, and is given by:

$$\beta\text{-VEC} = [(\beta\text{-}x)^2 + (\beta\text{-}y)^2 + (\beta\text{-}z)^2]^{1/2} \qquad (5)$$

For flat molecules in the $x-y$ plane, and with the added restriction that electron motion is confined to this plane, (i.e. in-plane to out-of-plane electron-dipole transitions are strictly forbidden, all matrix elements in Equation 1 that include the $z$-component of the vector operator, $\hat{r}$, are zero. Therefore, in this work, we are able to use the simplified formulae:

$$\beta\text{-}x = \beta_{xxx} + (\beta_{xyy} + \beta_{yxy} + \beta_{yyx})/3 \qquad (6)$$

$$\beta\text{-}y = \beta_{yyy} + (\beta_{yxx} + \beta_{xyx} + \beta_{xxy})/3 \qquad (7)$$

$$\beta\text{-VEC} = [(\beta\text{-}x)^2 + (\beta\text{-}y)^2]^{1/2} \qquad (8)$$

At zero applied frequency (the static approximation) we have the equalities $\beta_{xyy} = \beta_{yxy} = \beta_{yyx}$ and $\beta_{yxx} = \beta_{xyx} = \beta_{xxy}$. At non-zero applied frequency, in the case of SHG, the equalities involving $\beta_{xyy}$ and $\beta_{yxx}$ are removed, but we retain the equalities $\beta_{yxy} = \beta_{yyx}$ and $\beta_{xyx} = \beta_{xxy}$.

If, in addition to the mirror symmetry in the $x-y$ plane, the $x$-axis is a two-fold axis of rotational symmetry, the structure transforms as the $C_{2v}$ point group, e.g. structures I, III, VI and VIII. In this case, all the separate components in Equation 7 are formally zero. At non-zero applied frequency, there are now only three independent components, $\beta_{xxx}$, $\beta_{xyy}$ and $\beta_{yxy}$ (or $\beta_{yyx}$): at zero applied frequency, there are only two independent components, $\beta_{xxx}$ and, say, $\beta_{xyy}$. Note that in a linear molecule with different end groups, e.g. NC-C≡C-O⁻ transforming as $C_{\infty v}$, only $\beta_{xxx}$ is non-zero for both $\omega = 0$ and $\omega > 0$.

We have evaluated the components of the $\beta$-tensor cited in Equations 6 and 7 for a range of $\hbar\omega$ from zero

to 1.398 eV, in increments of 0.1165 eV, thereby including 1.165 eV which corresponds to the Nd:YAG line at 1064 nm, for which wavelength calculated values of the components of $\beta$ are often cited [7].

The influence of a d.c. electric field, applied and maintained whilst a polymer, containing a polar dye as either a guest or as a bound side-chain, cools through a phase transition from a fluid (or glassy) state to a solid state, is to impose some degree of orientational ordering of the long molecular dipolar ($x$-) axis along the direction of the applied field. For this reason, we report the values of $\beta$-$x$ (as defined in Equation 6) (see Table II and accompanying caption).

Using standard choices of parameters for the $H$ [8, 9] and $G$ [10] matrices, and standard formulae for the elements of the Hartree–Fock Operator matrix [11], we have obtained the eigenvalues and eigenvectors representing the electron-pair-filled molecular orbitals and the empty, virtual levels (or unoccupied molecular orbitals) by standard numerical methods. (The programmes were written by the author in FORTRAN IV and were run using the virtual FORTRAN compiler of the PRIMOS operating system. A NAG subroutine for matrix diagonalization was used.)

Following Garito et al. [12], we have only used those molecular orbitals (filled and unoccupied) that are constituted of $2p_z$ atomic orbitals (a.o.) in ensuing calculations of state energies and components of the $\beta$-tensor. The $2p_z$ a.o. change sign upon reflection through the $x$-$y$ molecular plane, and molecular orbitals constituted from such atomic orbitals are referred to as $\pi$ if they are occupied and $\pi^*$ if they are not. The eigenvectors were used to calculate the transition moments and accompanying dipole changes induced by one-electron excitations.

In order to improve the ground-state binding energy, and to improve the excitation energies, extensive configuration interaction was utilized to obtain the

positions, above the ground state, of 48 spin-singlet electronic excited states [13]. The 48 state energies, and the composition of the states in terms of the relative contributions from the original $\pi$-$\pi^*$ excitations, were used to obtain the values of the state–state transition moments and changes in molecular dipole moments required for the calculation of the components of $\beta$ (see Equation 1; Tables I and II).

## 3. Results and discussion
### 3.1. Class A: Molecules with an excited state at circa 550 nm
The quinonoid systems I, II, V and VI (see Fig. 1), with their lowest energy singlet electronic states at 2.34, 2.12, 2,17 and 2.10 eV respectively, comprise Class A.

In the expressions for the components of $\beta$, there is a term $(\omega_{ng}^2 - 4\omega^2)$ in the denominator. When this term goes to zero we have a resonance condition: Orr and Ward [14] have given the expressions that are applicable at or near resonance, the use of which will be the subject of a further communication. For I, II, V and VI and resonance condition will hold when $\hbar\omega = 1.17$, 1.06, 1.09 and 1.05 eV respectively, i.e. in the range 1050–1180 nm, which lies close to the Nd:YAG line at 1064 nm. Due to the difference in the sign of the denominator on opposite sides of the resonance condition, there is an accompanying change in the sign of $\beta$-$x$ as shown in Table II.

The lowest-lying excited state in all the Class A materials has a profound effect on the calculated values of $\beta$-$x$ at all values of $h$ lower than the resonance condition. The reasons for this may be seen in Table I. In each case, a large transition moment $(T_{ng}^x)$ in the $x$-direction, i.e. long molecular axis, is accompanied by a large (and negative) value of the change in molecular dipole moment $(\Delta_{ng}^x)$ in the $x$-direction. The large magnitudes of $T_{ng}^x$ and $\Delta_{ng}^x$, and the negative sign of the

TABLE I Energies (nm), transition moments, $T^x$, $T^y$, (Debye) and dipole moment changes, $\Delta^x$, $\Delta^y$ (Debye) of the four lowest energy states of molecules I through VIII (see Fig. 1).

| State | | Molecules | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | I | II | III | IV | V | VI | VII | VIII |
| 1 | Energy | 529 | 584 | 347 | 355 | 571 | 590 | 357 | 361 |
| | $T^x$ | 11.48 | 13.41 | 7.68 | −3.34 | −10.45 | −14.06 | −7.27 | 8.95 |
| | $T^y$ | 0.0 | 1.54 | 0.0 | 2.81 | −1.13 | 0.0 | −1.55 | 0.0 |
| | $\Delta^x$ | −13.20 | −12.64 | 23.56 | 12.94 | −15.53 | −14.76 | 21.34 | 26.12 |
| | $\Delta^y$ | 0.0 | −1.07 | 0.0 | −0.76 | 0.18 | 0.0 | 2.53 | 0.0 |
| 2 | Energy | 462 | 438 | 251 | 307 | 408 | 444 | 256 | 264 |
| | $T^x$ | 0.0 | −0.25 | 0.80 | 1.06 | −4.57 | 0.0 | 0.65 | 0.30 |
| | $T^y$ | −0.30 | 0.30 | 0.0 | −0.24 | −0.63 | −0.29 | 0.56 | 0.0 |
| | $\Delta^x$ | −23.51 | −29.00 | 15.24 | 9.92 | −21.99 | −31.35 | 15.11 | 19.55 |
| | $\Delta^y$ | 0.0 | −4.28 | 0.0 | −2.34 | 0.37 | 0.0 | 1.76 | 0.0 |
| 3 | Energy | 295 | 345 | 240 | 259 | 343 | 341 | 244 | 251 |
| | $T^x$ | −1.35 | −0.64 | −2.12 | −4.81 | −0.84 | 1.35 | 1.63 | −2.04 |
| | $T^y$ | 0.0 | −0.90 | 0.0 | −1.79 | −2.61 | 0.0 | 1.08 | 0.0 |
| | $\Delta^x$ | −9.46 | −4.77 | 14.99 | 11.19 | 14.98 | −6.73 | 14.75 | 19.36 |
| | $\Delta^y$ | 0.0 | 0.03 | 0.0 | −2.83 | −3.31 | 0.0 | 1.74 | 0.0 |
| 4 | Energy | 224 | 244 | 199 | 221 | 255 | 242 | 201 | 208 |
| | $T^x$ | 0.0 | 0.07 | 0.99 | −3.64 | −2.61 | 0.0 | 1.28 | 1.17 |
| | $T^y$ | −0.96 | −0.76 | 0.0 | 2.55 | −0.84 | 0.75 | −0.60 | 0.0 |
| | $\Delta^x$ | −20.00 | −22.42 | 7.01 | 8.20 | 8.54 | −24.55 | 9.11 | 13.56 |
| | $\Delta^y$ | 0.0 | −3.36 | 0.0 | −4.57 | −3.09 | 0.0 | 1.04 | 0.0 |

latter, give a large and negative value for $\beta_{xxx}$, and for $\beta$-$x$ which has $\beta_{xxx}$ as by far its largest component in this work. The influence of interactions between different pairs of excited states, the so-called off-diagonal interactions, upon all components of $\beta$ is very small in all the Class A systems. Although we have evaluated the off-diagonal contributions, in order to assess their importance relative to the diagonal contributions, we have shown that Class A systems offer examples to which the "diagonal-terms-only" expression of Pugh and Morley [6] is applicable:

$$\beta_{ijk}^{\text{DIAG}} = -(e^3/\hbar^2) \sum_n \left[ T_{gn}^i(T_{gn}^j\Delta_{gn}^k + T_{gn}^k\Delta_{gn}^j) \right.$$
$$\left. \times \frac{(\omega_n^2 + 2\omega^2)}{(\omega_n^2 - 4\omega^2)(\omega_n^2 - \omega^2)} + T_{gn}^k T_{gn}^j\Delta_{gn}^i \cdot (\omega_n^2 - \omega^2)^{-1} \right]$$

$$(9)$$

We may also invoke a further simplification in the light of our evidence for the dominance of the "diagonal" contributions from State 1 (I, 99.6%, II, 99.9%, V, 90.0% and VI, 95.8%) to the value of $\beta$-$x$, and use the single-state version of Morley and Pugh's diagonal-term equation [6]:

$$\beta_{ijk}^{\text{DIAG}} = -(e^3/\hbar^2)\left[ T_{g1}^i(T_{g1}^j\Delta_{g1}^k + T_{g1}^k\Delta_{g1}^j) \right.$$
$$\left. \times \frac{(\omega_1^2 + 2\omega^2)}{(\omega_1^2 - 4\omega^2)(\omega_1^2 - \omega^2)} + T_{g1}^k T_{g1}^j\Delta_{g1}^i \cdot (\omega_1^2 - \omega^2)^{-1} \right]$$

$$(10)$$

Although only state 1 is involved in Equation 10, the composition of State 1, in terms of one-electron excitations amongst the original eigenvectors, must be determined by extensive configuration interaction [12]. In the Class A systems, despite our use of extensive configuration, State 1 is always composed of $> 96\%$ of the one-electron excitation from the highest occupied pair-filled molecular orbital (the accepted acronym is HOMO) to the lowest unoccupied molecular orbital (the accepted acronym is LUMO). We now adopt the abbreviation H $\rightarrow$ L for this key excitation.

The H $\rightarrow$ L excitations exhibit large transition moments and large and negative changes in molecular dipole moment: the latter correspond to pronounced movement of electron charge density to the donor group ($>$ NH) and its environs from the acceptor group, $=$ C(CN)$_2$. By convention [7], this leads to a negative $\Delta_{ng}^x$ (if the $x$-axis is the long, polar molecular axis) and to a negative $\beta_{xxx}$ and $\beta$-$x$. These negative values are somewhat unusual.

In all cases herein, the calculated values of the tensor components other than $\beta_{xxx}$ are always rather small in relative terms, although they do become large in absolute terms as the resonance condition is approached. The sensitivity of $\beta$-$x$ to the applied frequency, $\omega$, is caused by the low energy of the first excited state. The value of this energy is sensitive to the extent of configuration interaction (we have investigated variations when using 4, 9, 25, 36 and 48 states). Extensive configuration interaction is essential in Class A molecules.

### 3.2. Class B: Molecules with all excited states below 365 nm

The non-quinonoid systems III, IV, VII and VIII, with their first excited singlet electronic states at 3.57, 3.49, 3.47 and 3.43 eV respectively, comprise Class B.

For the foregoing molecules, the resonance condition $\omega_{ng}^2 = 4\omega^2$ is not reached until $\lambda(= 2\pi c/\omega)$ is of the order of 750 nm or less. For this reason, the calculated values of $\beta$-$x$ show a small and gradual wavelength dependence with no changes in sign when $\lambda > 887$ nm. This is in marked contrast to the Class A systems.

Another distinctive feature of the Class B systems is the small absolute magnitude of $\beta$-$x$. This is in part due to the relatively large value of the energy expression in the denominator: it is also due to the relatively low values of $T_{ng}^x$(and $T_{ng}^y$) of the first excited states (see Table I) when compared to those exhibited by the first excited states of the Class A systems.

The influence of the extent of configuration interaction on the state energies of Class B systems, and upon their values of $\beta$-$x$ is very slight (unlike Class A). However, more than one state makes a noteworthy

TABLE II $\beta$-$x$ values [$\beta$-$x$ = $\beta_{xxx}$ + ($\beta_{xyy}$ + $\beta_{yxy}$ + $\beta_{yyx}$)/3] calculated from 48 states evaluated by configuration between 48 one-electron transitions. The presence of a heavy horizontal line indicates the onset of the resonance condition $w_n^2 = 4w^2$ in which $w_n$, $w$ are (respectively) the state energy and the laser energy: attention is drawn to the sign-change in $\beta$-$x$ that ensues. The abbreviation, "Reson.", is used to indicate an on-resonance condition.

| Laser energy (nm$^{-1}$) | Calculated values of $\beta$-$x$ ($/10^{**}-30$ cgs esu$^3$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | I | II | III | IV | V | VI | VII | VIII |
| Static | $-248$ | $-304$ | 61 | 24 | $-367$ | $-501$ | 56 | 87 |
| 10640 | $-251$ | $-309$ | 61 | 24 | $-373$ | $-505$ | 56 | 88 |
| 5320 | $-263$ | $-326$ | 62 | 24 | $-392$ | $-532$ | 57 | 89 |
| 3547 | $-283$ | $-357$ | 64 | 25 | $-427$ | $-584$ | 59 | 92 |
| 2660 | $-316$ | $-410$ | 67 | 26 | $-487$ | $-673$ | 62 | 96 |
| 2128 | $-370$ | $-501$ | 71 | 27 | $-589$ | $-825$ | 65 | 102 |
| 1773 | $-461$ | $-674$ | 76 | 29 | $-774$ | $-1110$ | 71 | 110 |
| 1520 | $-633$ | 1080 | 82 | 31 | $-1180$ | $-1790$ | 78 | 120 |
| 1330 | $-1040$ | $-2910$ | 92 | 34 | $-2600$ | $-4760$ | 87 | 135 |
| 1182 | $-3030$ | 4280 | 105 | 38 | Reson. | Reson. | 101 | 155 |
| 1064 | 3630 | 1290 | 124 | 45 | 2080 | 2320 | 121 | 185 |
| 967 | 1220 | 796 | 153 | 54 | 1290 | 1490 | 154 | 233 |
| 887 | 792 | 632 | 202 | 71 | 1570 | 1230 | 213 | 319 |

contribution to the magnitude of $\beta$-x, which means that the simple expression in Equation 10 cannot be used. For example, State 3 of VII contributes more than 10% of the value of $\beta$-x. However, in common with Class A, the off-diagonal terms are small so that Equation 9 is applicable.

The composition of the excited states in terms of the contributions from one-electron excitations is more complex than in Class A. For example, State 1 is composed of only 85–90% of the H $\rightarrow$ L excitation with two or three excitations making circa 5% contributions. Also, States 3 and 4 are (respectively) difference and sum states involving almost equal contributions from two excitations. However, the H $\rightarrow$ L excitation (in common with Class A) still dominates $\beta_{xxx}$ and $\beta$-x.

In this Class, $\Delta^x_{gl}$ and the dipole moment change of the H $\rightarrow$ L excitation are both positive, which produces (the more usual) positive values for $\beta_{xxx}$ and $\beta$-x. Electron charge density is now transferred, during the H $\rightarrow$ L excitation, from the donor group ($>$ NH) and its environs to the acceptor group ($NO_2$) and its environs.

## 4. Conclusion

Maloney and Blau [15] have expressed the view that near-IR absorbing organic dyes, because of their large non-linear optical susceptibilities and fast response and decay times, should be strong candidates for all-optical signal processing devices at wavelengths in the region of 1300–1600 nm. The quinonoid structures (Class A: I, II, V and VI) fall into the above category.

Due to their large molecular ground-state dipole moments (about 20 D), and the colinearity of the major component of the permanent moment with the major component of the $\beta$-tensor, Class A structures are suitable for incorporation into poled polymers either as guest molecules or as side chains bound by, say, derivatization at –NH–. Means must be found (1) of stabilizing the rigid quinonoid structures and (2) of enforcing molecular planarity. We are currently making a major effort to obtain structure VI, or its zwitterionic analogue.

The Class B structures, albeit with smaller absolute values of $\beta$-x, are less optically dark than Class A and can be used over a wider range of wavelengths of

incident laser radiation of SHG. Of this Class, the diacetylene, VIII, is the most satisfactory: this has already been shown to have a high-temperature nematic phase [17]. For the foregoing reasons, we have selected VIII (and related derivatives) as the basis for further work on Class B systems. The suitability for poling is less than that for Class A, because the molecular dipole moments of Class B systems are all circa 25% of the moments of the Class A systems.

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