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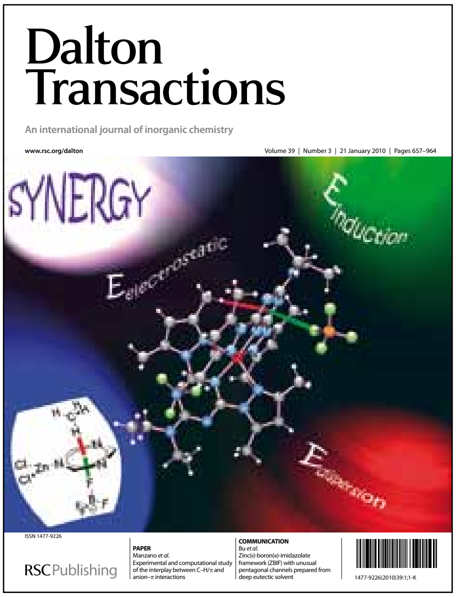

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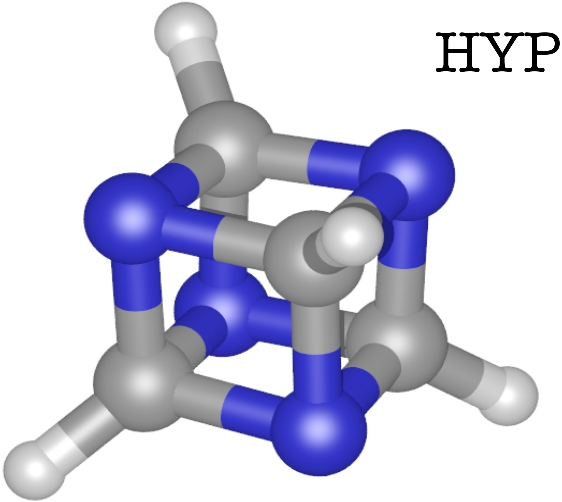

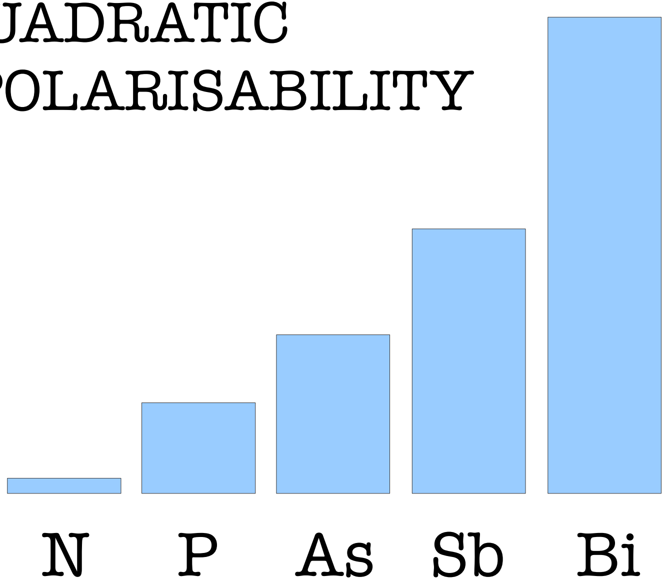

Enhancement of nonlinear optical properties in late group 15 tetra-substituted cubanes

Bruce F. Milne

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The optical absorption spectra and quadratic hyperpolarisabilities of 1,3,5,7-tetra-substituted cubane derivatives containing group 15 atoms have been investigated computationally using Coulomb-attenuated time-dependent density functional theory. The non-linear optical responses of these octupolar systems are shown to be highly dependent on the group 15 heteroatom with the bismuth-containing derivative displaying large enhancement of its quadratic hyperpolarisability, β, relative to 1,3,5,7-tetraazacubane *in vacuo* and with acetonitrile solvation. Spin-orbit coupling and scalar relativistic corrections play an important part in determining the value of β for compounds containing As, Sb and Bi.

1 Introduction

Materials displaying non-linear optical (NLO) properties are important for optoelectronics applications such as data transmission, manipulation and storage where electronic and magnetic devices can be replaced with ultrafast low energy loss photonic systems. NLO properties are also exploited in fields such as microfabrication, sensing and (bio)imaging[1–3] Photonics is seen as one of the Key Enabling Technologies that will play a central role in social and economic development in the 21st century.[4,5]

The optical properties of macroscopic materials originate in the induced polarisation, P, that comes about when the material is subject to an external time-dependent electromagnetic field, $E(t)$[6,7]

$$P(t) = \chi^{(1)}E(t) + \chi^{(2)}E(t)^2 + \chi^{(3)}E(t)^3 + \cdots \qquad (1)$$

where $\chi^{(i)}$ are the electromagnetic susceptibilities of the system and non-linear effects come about through the higher order terms of the expansion.

Similarly, for a microscopic system such as an atom, molecule or cluster this can be expressed in the dipole approximation as

$$\mu(t) = \alpha E(t) + \beta E(t)^2 + \gamma E(t)^3 + \cdots \qquad (2)$$

where $\mu(t)$ is the field-induced dipole polarisation. Here the macroscopic susceptibilities are replaced by the microscopic polarisability α and the quadratic and cubic hyperpolarisabilities β and γ. The susceptibilities, $\chi^{(i)}$, and the (hyper)polarisabilities are tensors containing information about the system's optical response in different directions.

Various NLO effects are employed for different scientific and technological applications but possibly the most widely used (at this time) is second harmonic generation (SHG).[3] SHG, as a special case of the more general phenomenon of sum frequency generation, involves the mixing of two incident electromagnetic waves of frequency ω (within the semi-classical dipole formalism used in Eqn. (2)) to produce a scattered wave with frequency 2ω. Alternatively, a fully quantised model can be invoked where two photons of frequency ω are annihilated and one photon of frequency 2ω is created in the scattering process. The quadratic dependence on the field $E(t)$ means that the second term on the right hand side of eqn 2 is the origin of this effect. At the microscopic/molecular level this means that the magnitude of the quadratic hyperpolarisability tensor β must be enhanced in order to produce improved SHG characteristics.

For some time organometallic systems have been investigated for their potential uses in NLO and a great deal of attention has focussed on transition metal containing systems.[8] A great advantage that organometallics have over purely organic compounds is the greater freedom to tailor their electronic and optical properties due to the peculiarities of the metal(s) involved. Similarly, the p-block elements present a source of atomic building blocks with which to tune the NLO susceptibilities of organic host systems. In addition to the shell structure effects that dominate the characteristics of the metals from the earlier parts of the periodic table, heavier metals offer the possibility of introducing electronic structure alterations arising from the influence of special relativity that can contribute significantly to the overall properties of their compounds/complexes.

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1.1 Present work

Derivatives of the highly strained organic compound cubane[9] have been a source of great interest for many years due to their intrinsic structural novelty and for their potential as high energy density materials.[10] The introduction of heteroatoms into the cubane skeleton has been investigated as a way to modulate the explosive nature of the parent compound through reduction in the strain energy of the system. The group 15 atoms N and P in particular have been investigated experimentally and the strain energies and electrostatic properties of N, P and As analogues have been the subject of several theoretical studies.[11–16]

In the current work the (non)linear optical properties of octupolar 1,3,5,7-tetra-substituted cubane derivatives (Figure 1) containing group 15 elements N, P, As, Sb and Bi have been evaluated using TDDFT methods. Of particular interest was the effect of introducing heavy elements into a molecular structure with an insignificant quadratic hyperpolarisability, β, with the aim of enhancing the system's NLO response. In agreement with previous work it will be shown that a significant heavy-atom enhancement of β can be expected in these systems.[17,18]

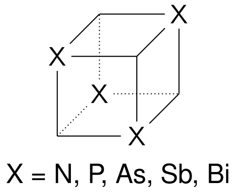

Fig. 1 Schematic structure of octupolar tetra-substituted cubanes ($C_4H_4X_4$)

2 Methods

The cubane derivative geometries were optimised using the GAMESS-US software (01 October 2010 (R1) release).[19] Geometries were optimised in D_2 symmetry at the B3LYP[20,21] level with the polarised split-valence Def2-TZVP basis set.[22] Solvent effects were modelled using the polarisable continuum model (PCM).[23,24] Acetonitrile was chosen as it is a commonly used solvent in experimental studies of hyperpolarisability that has been employed in several previous theoretical studies of NLO chromophores.[25] Also, the intermediate polarity of this solvent provides a reasonable model of the environment that can be expected for these organic/organometallic compounds in the condensed phase.

Dynamic quadratic hyperpolarisabilities were calculated with TDDFT quadratic response (QR) theory using Dalton 2011 at the common laser frequencies of 0.65, 1.165 and 1.55 eV (λ = 1907, 1064 and 800 nm).[26–29] Based on its good performance in previous calculations of (non)linear response properties the range-separated CAM-B3LYP hybrid functional was used.[17,30–33] TD-CAM-B3LYP excitation energies for the cubane derivatives were calculated using the TDDFT linear response module in Dalton2011.[34,35] PCM (acetonitrile) solvation was applied in all TDDFT calculations.

Previous studies[17,25,31,36] have highlighted the importance of diffuse functions relative to extensive sets of polarisation functions and so the multiple diffuse-augmentation approach was employed in order to test for convergence of the calculated properties. The correlation-consistent valence double-ζ basis set, cc-pVDZ, was used in the TDDFT calculations and was augmented with single, double and triple sets of diffuse functions producing the aug-cc-pVDZ, d-aug-cc-pVDZ and t-aug-cc-pVDZ sets, respectively.[37,38] The t-aug-cc-pVDZ basis set was used in the TDDFT excitation energy calculations. Scalar relativistic effective core potentials (ECP's) were employed for the elements As, Sb and Bi.[39]

An important point to note about the ECP's used in this work is the fact that the number of explicitly treated valence electrons is the same for As, Sb and Bi and consisted of the highest lying *s*-, *p*- and *d*-shells with all other electrons being subsumed into the ECP core. Thus, the same number of electrons contribute to the NLO properties of the compounds containing these elements and any difference must be ascribed to alteration of the potential experienced by the valence electrons.

The importance of the level of treatment of relativistic effects was investigated using the DIRAC11 software package. The geometries were re-optimised and the dynamic quadratic hyperpolarisability (ω = 0.65 eV) calculated *in vacuo*. As for the previous Dalton calculations the CAM-B3LYP TDDFT method was employed as was the aug-cc-pVDZ basis set on the elements C, N, P and H. For As, Sb and Bi the relativistically-optimised all-electron polarised double-*zeta* basis set of Dyall was used (including diffuse augmentation functions).[40,41] All basis sets were used in uncontracted form. Non-relativistic (NR) calculations were performed using the Levy-Leblond Hamiltonian whilst relativistic calculations were performed using the exactly-decoupled two component method (X2C) and included atomic mean-field interaction (AMFI) spin-orbit corrections.[42–44] For comparison the commonly used second order Douglas-Kroll-Hess (DKH-2) method was employed, with and without spin-orbit (SO) corrections.[45–47]

3 Results and discussion

3.1 Geometries

Selected geometrical parameters for the B3LYP/Def2-TZVP optimized cubane derivatives both in acetonitrile and *in vacuo*

Table 1 Selected B3LYP/Def2-TZVP geometrical parameters of heterocubanes in PCM acetonitrile (*in vacuo* data in parentheses)

Heteroatom (X)	C-X / Å	C-H / Å	C-X-C / °	X-C-X / °	X-C-H / °
N	1.5097 (1.5089)	1.0865 (1.0875)	85.27 (85.09)	94.55 (94.71)	121.98 (121.86)
P	1.8911 (1.8925)	1.0856 (1.0860)	85.22 (86.06)	94.59 (94.74)	121.95 (121.84)
As	2.0223 (2.0238)	1.0860 (1.0863)	83.57 (83.42)	96.08 (96.22)	120.83 (120.73)
Sb	2.2123 (2.2134)	1.0871 (1.0872)	83.22 (83.18)	96.39 (96.44)	120.59 (120.57)
Bi	2.3116 (2.3118)	1.0900 (1.0900)	82.34 (82.00)	97.46 (97.47)	119.78 (119.79)

are presented in Table 1. On going down the group bond lengths involving heteroatoms increased by ~0.8Å whilst bond angles increased by ~3 degrees at carbon atoms suggesting less strained structures for the lower group 15 analogues. That such a lowering of strain energy might reasonably be expected to accompany these changes is in line with the results of a previous study on the 1,3,5,7-tetraphosphacubane and 1,3,5,7-tetraarsacubane structures.[13]

The differences between the vacuum and acetonitrile structures were minimal (less than 0.001 Å in bond lengths and 0.2 degrees in bond angles).

3.2 Linear response

The calculated first excitation energies were predicted to fall in the UV region for the N, P and As heterocubanes (see Table 2). The Sb- and Bi-containing analogues had excitation energies shifted into the blue end of the optical spectrum at 2.94 and 2.73 eV, respectively. In all cases the first excitation displayed two-fold degeneracy due to the symmetry of the systems being studied.

Table 2 Two-fold degenerate TD-CAM-B3LYP/t-aug-cc-pVDZ first excitations in acetonitrile

Heteroatom	eV	nm
N	6.00	207
P	3.66	339
As	3.38	366
Sb	2.94	421
Bi	2.73	454

Overall, the excitation energies form three groups containing N in the first, P and As in the second and Sb and Bi in the third. Involvement of empty d-orbitals in forming the unoccupied electronic states of the P and As derivatives can be seen to be a distinct difference between these and the tetraazacubane. A similar shell-structure model can be invoked for the grouping of the Sb and Bi heterocubanes (including empty 5f states for Bi) but these can be expected to be distinct from the lighter group 15 compounds because for these elements relativistic effects become significant and alter the potential experienced by the valence electrons.[48–50]

These excitations (and all others up to the tenth excitation level) were found to display extremely small oscillator strengths of the order of 10^{-8} or smaller. The reason for this was found to be that the calculated molecular excitations were dominated by one-electron excitations that conserved symmetry meaning that these would be Laporte (symmetry) forbidden.[51] For example, the first excitations shown in Table 2 were dominated by two one-electron excitations of $B_2 \rightarrow B_2$ and $B_3 \rightarrow B_3$ symmetry. Higher energy excitations were found to possess dominant contributions from two one-electron excitations that in fact broke symmetry e.g. $B_2 \rightarrow B_3$ and $B_3 \rightarrow B_2$ that had excitation amplitudes of equal strength leading to an overall conservation of symmetry in the optical response of the total charge density.

3.3 Quadratic hyperpolarisability

In addition to the observed degeneracy of transitions in the absorption spectrum of the cubanes, the high symmetry and octupolar nature of these systems means that the quadratic hyperpolarisability tensor (β) components are almost all zero. The exceptions to this are the components $\beta_{i,j,k}$ ($i \neq j \neq k$) which are identical for all *i, j, k*.

Figure 2 shows the values in atomic units of the symmetry-unique $\beta_{i,j,k}$ tensor components for the substituted cubanes calculated at the CAM-B3LYP level. The three plots correspond to the nonlinear response to three common fundamental laser wavelengths of 1907 nm (0.65 eV), 1064 nm (1.165 eV) and 800 nm (1.55 eV).

A trend can clearly be seen at all three plots whereby substitution with increasingly heavy group 15 atoms leads to a steady increase in β. For the triply-augmented t-aug-cc-pVDZ basis set the β enhancement on going from N to Bi substitution in the cubanes is 36-fold and $\omega = 0.65$ eV whilst for 1.165 and 1.55 eV this rises to 39- and 56-fold, respectively. These trends agree with those found previously for hyperpolarisibilities in group 15 substituted organic compounds.[17,18]

Caution should be exercised in the interpretation of the 1.55 eV results since for this energy of incident radiation the second harmonic at 3.1 eV is in the region of the first absorption band of the cubanes containing P, As, Sb and Bi meaning that artificial enhancement of β by the QR method is a possibility. This problem can be avoided by using the complex polarisation propagator (CPP) approach as shown recently for a group of marine natural products, the dermacozines.[52] However, in the present case only minor alterations to the overall results obtained were expected and so the CPP method was not employed. This also ensured compatibility between the results obtained with and without explicit relativistic treatments since these methods are currently only available within the QR formalism.

As noted in section **2** (Methods) above, the nature of the ECP basis sets used in this work means that the number of electrons explicitly included in the calculations of β for the As-, Sb- and Bi-cubanes was identical. This has the consequence that the increase in hyperpolarisability observed on going from As to Bi cannot be explained by an increased number of electrons contributing to the value of β.[53,54] The change must therefore be due to alteration of the potential experienced by the valence electrons, coming both from alterations in the shielding of the nucleus and lower electronic shells and from the small changes in geometry (Table 1) occurring in these three derivatives.

This is supported by several detailed discussions by Kuzyk and co-workers who have shown that the potential experienced by electrons plays a key part in controlling nonlinear optical response.[55–58] Making use of this argument it is possible to include in the present analysis the N and P cubane derivatives which, although they do not possess any filled *d*-electron shells, share the same *s, p* valence configuration as the heavier group 15 analogues and alterations in their NLO response can therefore reasonably be attributed to changes in the potential acting on their valence electrons.

Quasi-tetrahedral symmetry in octupolar NLO chromophores has been studied previously by Zyss and co-workers for purely organic paracyclophane derivatives.[59,60] This feature of the hyperpolarisability tensor at the molecular level could have important consequences for any applications of these compounds in NLO materials because, unlike the case with more common dipolar donor-π-acceptor (D-π-A) chromophore types, the quadratic susceptibility $\chi^{(2)}$ (Eqn. (1)) should be more isotropic and therefore not require that strict phase matching criteria be adhered to.[1]

The occurrence of significant quadratic hyperpolarisabilities in octupolar cubic tetraorganotin compounds has been observed experimentally by Persoons and co-workers using hyper Rayleigh scattering and lends support to the heavy-atom β enhancement found in the present work.[61] The combination of this heavy-atom effect with the symmetry properties of the substituted cubanes suggests a potentially useful role for these compounds (or related derivatives) in NLO materials.

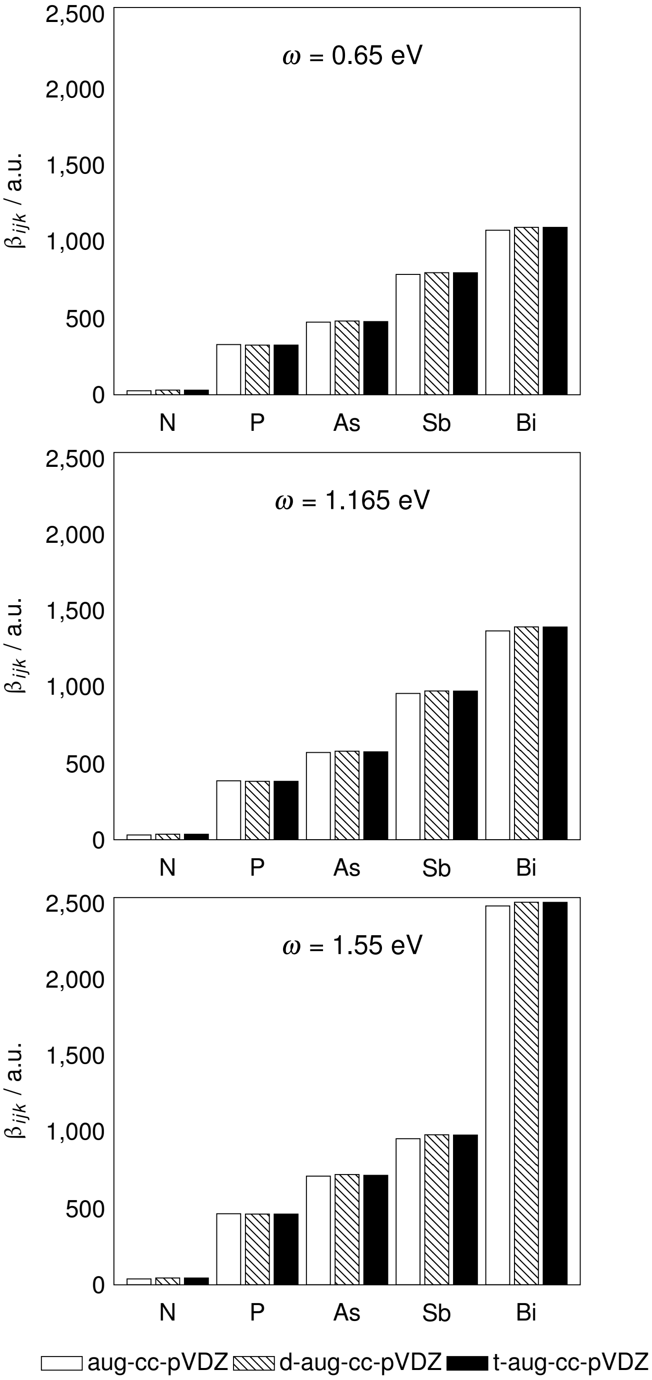

Fig. 2 Cubane derivatives in PCM acetonitrile: symmetry unique quadratic hyperpolarisability tensor components, β_{ijk} $(i \neq j \neq k)$

3.4 Relativistic effects on β

Table 3 shows β values for the cubanes calculated in the gas phase both at the non-relativistic (NR) level and also including relativistic treatments at varying levels of sophistication (see Methods section). The benchmark in these calculations comes from the values obtained at the X2C level which provides an excellent two-component approximation to the full four-component Dirac-Coulomb Hamiltonian and provides both scalar relativistic and spin-orbit contributions to the hyperpolarisability.

Table 3 Relativistic effects on $\beta_{i,j,k}$ values *in vacuo* / a.u. (ω = 0.65 eV)

Heteroatom	NR	DKH-2	DKH-2-SO	X2C	ECP
N	1.2	1.2	1.2	1.2	1.4
P	214.3	216.5	216.5	216.5	213.7
As	297.4	308.2	307.8	307.9	311.6
Sb	476.9	509.6	505.7	506.4	518.0
Bi	601.0	733.8	679.3	683.2	735.4

A similar trend to that observed in acetonitrile solution was found for all cubanes at each level of theory. A reduction in $beta$ for each compound relative to the acetonitrile-solvated results was also seen which lead to a much greater relative increase in β on going from N to Bi substitution (~700-fold increase when relativistic effects were included).

As expected, the cubanes containing N and P displayed negligible relativistic changes in their β values. Relativistic effects on β start to appear for As but only become important for the heaviest species containing Sb and Bi. Overall, a good agreement is seen between the results of calculations using scalar relativistic ECPs and those performed at the all-electron level with the scalar relativistic DKH-2 treatment.

Whilst scalar corrections were seen to cause an increase in β for all of the cubane derivatives except the lightest N-cubane, spin-orbit effects were found to have the opposite effect and their inclusion at both the DKH-2 and X2C levels of theory noticably reduced the magnitude of the relativistic enhancement of β. However, the net relativistic effect on β remained positive even when spin-orbit effects were included.

These results suggest that whilst scalar relativistic ECPs can provide a reasonable approximation to the full X2C results in calculations of the quadratic hyperpolarisabilities of these systems (and at a greatly reduced computational expense) caution must be excercised if high accuracy is desired for compounds containing very heavy elements such as Bi. The all-electron DKH-2 method including spin-orbit effects (DKH-2-SO) provides results very similar to those obtained with the X2C method with only moderate computational expense.

3.5 Frontier molecular orbital energies

The *in vacuo* HOMO-LUMO gap energies for the cubane derivatives calculated at the same (non)relativistic levels of theory as above are shown in Table 4. The changes in both the absorption spectra and quadratic hyperpolarisabilities of the group 15 cubane derivatives seen above can be traced to the steady decrease in energy of the HOMO-LUMO gap on going from the top to the bottom of the group. The same grouping that was found for the first excitation energies (and to some extent the quadratic hyperpolarisabilities) is seen in the HOMO-LUMO energies. This is similar to the trend seen for the group 15 derivatives of N,N,N-trimethylglycine (betaine) but is much more pronounced in the cubane derivatives.[17]

Table 4 *In vacuo* HOMO-LUMO gap / eV

Heteroatom	NR	DKH-2	DKH-2-SO	X2C	ECP
N	9.17	9.16	9.16	9.16	9.16
P	6.93	6.92	6.90	6.90	6.92
As	6.57	6.56	6.47	6.48	6.53
Sb	5.91	5.92	5.72	5.73	5.90
Bi	5.63	5.66	5.15	5.16	5.65

Relativistic effects are seen to play an important role in determining the magnitude of the HOMO-LUMO gap energy for the cubanes containing As, Sb and Bi. Whereas in the quadratic hyperpolarisability results in Table 3 scalar relativistic effects produced the largest alteration in β the calculated HOMO-LUMO gaps display a much greater sensitivity to the inclusion of spin-orbit effects. In the case of the Bi-cubane scalar relativistic effects lead to an increase of ~ 0.02 eV whilst spin-orbit effects lead to a decrease in HOMO-LUMO gap energy of ~ 0.5 eV.

4 Conclusion

The substitution of 1,3,5,7-tetraazacubane with heavier group 15 elements has been shown to yield compounds with greatly enhanced quadratic hyperpolarisabilities. This is in line with previous studies of group 15 derivatives of betaine and pyrrole that also indicated a significant heavy-atom effect leading to increased quadratic hyperpolarisabilities with the heaviest members of the group, Sb and Bi.[17,18]

The incorporation of four heavy group 15 atoms into the 1,3,5,7-tetrasubstituted cubane structure effectively converts a compound with negligible nonlinear optical properties into a potentially useful building block for NLO materials, particularly if moieties such as *t*-butyl groups were substituted in place of the hydrogen atoms on the tertiary carbons in the structure to improve the stability of these systems.[11]

The cubanes are further distinguished from the compounds previously studied as heavy group 15 containing NLO chromophores by the fact that electronic excitations in the visible and near-UV regions of their absorption spectrum are symmetry forbidden. This suggests that, unlike more conventional NLO chromophores containing extensive organic π-electron systems, minimal absorption in these regions should occur making the compounds colourless and reducing absorption of scattered light produced in nonlinear processes such as harmonic generation.

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