

A new class of nonlinear optical materials based on push-pull quinonoid molecules

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Diamino-substituted dicyanoquinodimethane molecules are shown to be promising new candidates for nonlinear optical materials. The molecular hyperpolarizabilities are large and the materials are nearly transparent in the visible region; they are also chemically and thermally stable. Suitable strategies can be used to induce noncentrosymmetry and, consequently, capability for second-harmonic generation.

ORGANIC molecules with large first-order hyperpolarizability, β , and polymers with large second-order hyperpolarizability, γ are of great interest in the fabrication of nonlinear optical (NLO) materials¹. The former, when assembled into a noncentrosymmetric crystal lattice are useful for applications like second-harmonic generation (SHG), electrooptic modulation, frequency mixing and optical parametric oscillation². Design of molecules with large β and transparency in the visible range along with acceptable thermal and chemical stability is an interesting and challenging problem. Obtaining bulk nonlinear optical effects from these molecules continues to be an even more difficult proposition.

We have examined a class of push-pull quinonoid compounds which appear to be promising candidates to develop second-order NLO materials. The prototypical systems **1**, **2** and **3** (Figure 1) and some derivatives were prepared by a Du Pont group³ and electric-field-induced second-harmonic generation studies (EFISHG) in solution indicated unexpectedly large β in one of these compounds⁴, namely, **1**. We have computed the β values of several of such molecules and found them to be quite large, considering the short extent of conjugation present in them. We have also synthesized several new members in this class of molecules and present in this paper three typical cases (**4**, **5**, **6**) Molecule **4** and **5** did not show any SHG in the solid state, since they formed centrosymmetric crystal lattices. Since a centre of symmetry (S_2 operation) would necessarily be absent in the crystal lattice of a pure enantiomer, we prepared **6** to provide a noncentric crystal. This strategy¹ led to a material with moderate SHG. These studies are expected to initiate investigations of push-pull

quinonoid molecules for the fabrication of novel nonlinear optical organic materials.

The molecular structure of all the compounds were optimized using the AM1 semiempirical method. The dipole moments of ground and excited states and hyperpolarizabilities were computed using the SCAMP routine⁵. This program provides theoretical estimates of β in good agreement with experiments; in the case of **1** the reported experimental value⁴ of $\beta(\hbar\omega = 1.17 \text{ eV})$ is $-(245 \pm 60) \times 10^{-30} \text{ esu}$ and the value calculated (as discussed below) using SCAMP is $-243 \times 10^{-30} \text{ esu}$. Typically, all single and pair excitations within the manifold of 12 molecular orbitals bracketing the HOMO-LUMO were included in the CI scheme. Hyperpolarizabilities presented in this paper are at zero excitation energies, calculated as the projection of the β tensor on the strongest dipole axis. The $\beta(\hbar\omega = 0 \text{ eV})$ is particularly relevant since it avoids any resonance enhancement from absorption.

The computational results for six typical molecules from our studies are provided in Table 1. The ground state dipole moments are quite large. These arise from the zwitterionic character due to the intramolecular charge transfer from the diaminomethylene end to the dicyanomethylene end. On excitation the back charge transfer leads to decreased dipole moments. The negative $\Delta\mu$ is supported by the negative solvatochromism observed in these molecules using a procedure we have proposed recently⁶.

The calculations indicated notable oscillator strengths only for two excited states in all the molecules, one in the visible range with low oscillator strength (≈ 0.2) and the other in the UV with high oscillator strength (≈ 0.6). The $\beta(\hbar\omega = 0 \text{ eV})$ are quite appreciable in these systems in view of the fact that these do not have very extended π electron conjugation paths (*p*-nitroaniline, for example⁵, has a $\beta(0)$ value of

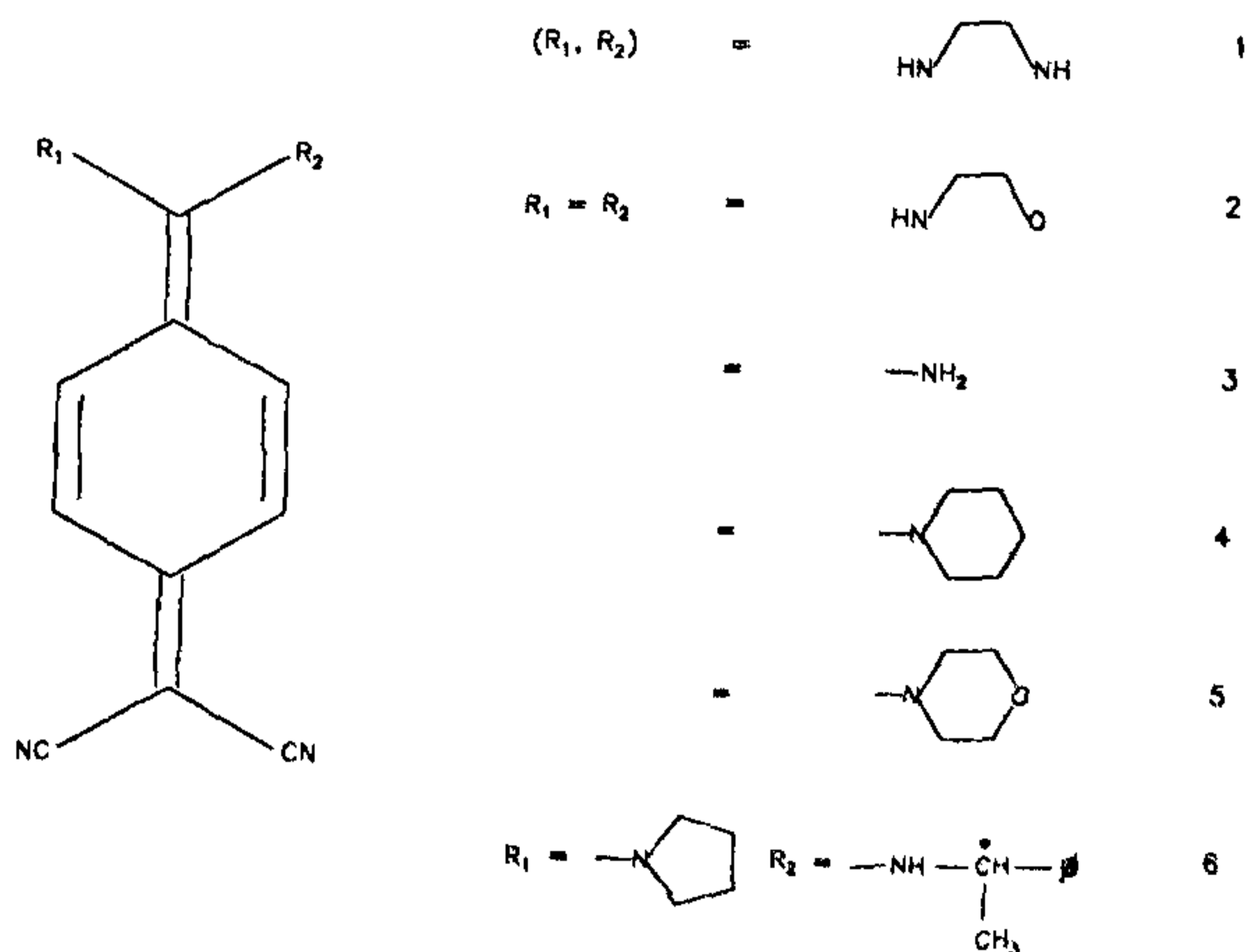


Figure 1. Molecules considered in the study

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Table 1. The calculated ground state dipole moment (μ_g), dipole moment change on excitation ($\Delta\mu$) and the static hyperpolarizability ($\beta(0)$) as well as the experimental absorption maxima and melting points of compounds 1-6

| Molecule | $\mu_g(D)$ | $\Delta\mu(D)$ | $\beta(0)^*$ | λ_{max}^* | m.p. ($^{\circ}C$) |
|----------|------------|----------------|--------------|-------------------|----------------------|
| 1 | 14.8 | -9.2 | -57.2 | 405 | >350 |
| 2 | 12.5 | -4.5 | -29.0 | 370 | >350 |
| 3 | 14.5 | -10.2 | -58.6 | 403 | >350 |
| 4 | 15.0 | -8.0 | -73.3 | 410 | 302 |
| 5 | 12.5 | -9.3 | -67.7 | 420 | >350 |
| 6 | 12.5 | -3.0 | -31.5 | 368 | 245 |

^{*}In units of 10^{-30} esu

^{*}In acetonitrile solution (in nm).

-9.1×10^{-30} esu). This seems to arise from the large $\Delta\mu$ associated with the electronic excitations. A detailed theoretical analysis we have recently carried out⁷ on 7,7'-diamino-8,8'-dicyanoquinodimethane (**3**) indicates that the usual two-level approximation⁸ to β reproduces only 50% of the full β and that appreciable contributions from several excited states lead to large values of β in these systems. The negative effects of the rather large excitation energies with strong oscillator strengths in these molecules are offset by these large $\Delta\mu$ contributions.

Encouraged by the theoretical results, we have synthesized several compounds in this class with a view to investigating, in particular, the NLO properties of the bulk materials, which are practically more relevant than the molecular properties like β . The synthesis is quite simple and follows the general procedure outlined in ref. 3. In the case of molecule with two different donor amines, the monopyrrolidine-substituted 7,7',8,8'-tetracyanoquinodimethane was prepared initially, followed by the replacement of the second cyano group by the appropriate second amine. Table 1 provides the experimental absorption wavelengths of the six molecules recorded in acetonitrile solution. In every molecule only a single absorption is seen, which appears close to the UV-visible interface or outside the visible window. The solid materials are all either colourless or pale yellow. The melting points provided in Table 1 point to the general thermal stability of these compounds, showing that poling techniques can be applied on them and that laser irradiation damage will be minimal. We present below the preliminary studies on **4**, **5** and **6**.

The bis-piperidine and bis-morpholine derivatives (**4**, **5**) gave crystals suitable for X-ray analysis from acetonitrile; the crystal structure analysis⁹ of these two compounds indicated centric space groups $P1$ and $P2_1/n$, respectively. This was not unexpected as the dipole moment of these compounds is very large. As indicated by the space group symmetry, no SHG was detected in these compounds.

Since chirality in the molecule forces the crystal packing to be noncentric, we have prepared the S(-)- α -methylbenzylamine derivative (**6**). Crystals grown from acetonitrile were protected from solvent loss and structure analysis was carried out⁹. The noncentric space group

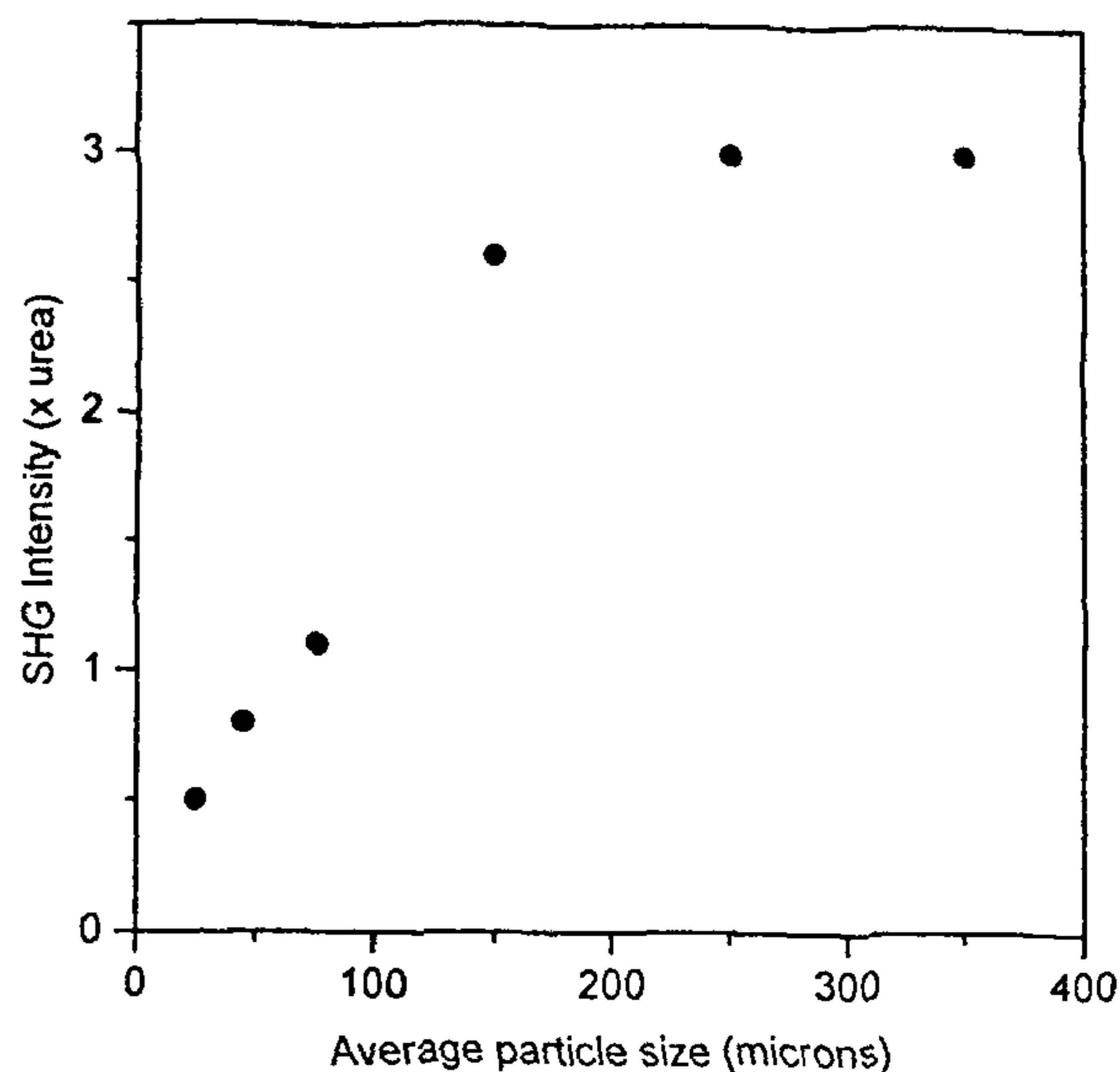


Figure 2. Variation of the powder SHG intensity with particle size of **6**

$P2_1$ was observed. SHG studies were carried out using a Nd:YAG laser with 1064 nm radiation. The samples were loaded between glass plates with uniform teflon sheets to control the sample thickness. Powder material of different particle sizes were selected by grading with standard sieves. Particle size dependence of the SHG (Figure 2) was analysed following the Kurtz and Perry method¹⁰, and **6** showed a phase-matchable SHG three times stronger than urea at particle sizes above 150 μm . Crystals also produced the same moderate SHG. It is noteworthy that this compound shows an absorption at about 368 nm in acetonitrile solution and is light yellow in colour in the solid state. The material is stable to extended laser irradiation (6 ns and 10 Hz) at 1 GW/cm^2 and has a melting point (m.p.) of $245^{\circ}C$. It holds promise for applications involving visible light, especially in view of the phase-matchability of the SHG observed.

We have presented theoretical results on hyperpolarizabilities of a new class of push-pull quinonoid systems. The β values are very promising for these molecules, which also show only weak absorption in the visible region. Experimental studies indicate that compounds of this group are easily synthesized and are chemically and thermally very stable. They are also amenable to a variety of chemical modifications. For example, introduction of chirality is shown to produce noncentric crystal structures and, consequently SHG activity. Crystal structures and NLO studies on these and other systems will be published later. Experimental determination of molecular hyperpolarizabilities are also being planned.

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