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NEW SECOND-ORDER NONLINEAR OCTUPOLAR MATERIALS

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We investigated second-order nonlinear optical properties of non-centrosymmetric crystals built of oblate, trigonal molecules: triphenylamine and adducts (complexes) of arsenic triiodide with sulfur, $AsI_3{\cdot}3S_8$, and antimony triiodide with sulfur, $SbI_3{\cdot}3S_8$. The efficiency of powder second-harmonic generation (SHG) in triphenylamine and in the adducts was comparable to that for urea. However, the SHG merit factor derived from coefficients of the NLO susceptibility tensor obtained from measurements on single crystals, is about two orders of magnitude larger in the adduct crystals than in urea. The vector and septor (octupolar) parts of quadratic susceptibility tensors are discussed on the basis of semiempirical quantum computations for triphenylamine and the experimental results in the adducts.

Keywords: $AsI_3{:}3S_8$; hyperpolarizability; MOPAC; powder SHG; $SbI_3{:}3S_8$; triphenylamine

INTRODUCTION

The optical properties of second-order nonlinear optical (NLO) molecules and materials have been receiving a lot of attention. They exhibit potential for electro-optic applications and various schemes of molecular architecture are being investigated, both theoretically and experimentally [1–5]. A molecular structure based on elongated, rod-like, highly polarizable one-dimensional molecules built on a donor – conjugated π-electron

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bridge – acceptor system paradigm such as occurring in *para*-nitroaniline, disubstituted stilbenes, or push-pull linear conjugated polyenes is indicated from a conventional molecular engineering viewpoint. In these highly nonlinear dipolar materials, the component β_{333} of the tensor of the first hyperpolarizability β, parallel to the one-dimensional intramolecular charge transfer axis, becomes predominant over other components.

The theoretical work of Jerphagnon [6,7] and Zyss [8–10] showed the decomposition of third-rank tensors of the second-order susceptibility $\chi^{(2)}$ and of β into the sum of components irreducible under the three-dimensional rotation group: the vector (dipolar) part and the septor (octupolar) part. For a purely octupolar molecule all dipolar-like quantities, the dipole moment, and the vector part of β, vanish, while the symmetry allowed octupolar components remain. Various molecular engineering routes have been proposed towards the optimization of β and $\chi^{(2)}$ of octupolar nonlinear molecules in both planar and nonplanar geometries [8–10]. A class of planar 2-dimensional octupolar noncentrosymmetric molecules with a 3-fold symmetry axis is represented by π-electron conjugated non-dipolar analogues of nitroaniline, in which donor and acceptor groups are located at alternate positions on the benzene ring, for example 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) [8–12], 1,3,5-methoxy-2,4,6-tris(styryl)benzene derivatives [13], 2,4,6-triphenoxy-1,3,5-triazine (TPOT) [14], and trigonal polyenoctupoles [15] of the C_{3h} point group symmetry (the international class $\overline{6}$). In these molecules the symmetry requires that the ground and excited state dipole moments vanish [12].

Another approach is based on the so-called "central atom" strategy where a planar octupolar trigonal charge-transfer molecule or ion of D_3 (class 32) or D_{3h} (class $\overline{6}m2$) symmetry is built of a central donating (or accepting) group interacting with three peripheral groups by means of intramolecular electronic charge transfer [8–10]. Examples are crystal violet [10] and ethyl violet [16,17], which belong to the family of ionic triphenylmethane dyes. An interesting class of octupolar molecules are the chiral charge-transfer ruthenium (II) complexes in which the charge-transfer feature is associated with metal-to-ligand electron transfer, and the chirality is induced by torsion of the ligand moieties [10].

A 3-dimensional nonlinear octupolar scheme can be realized with the tetrahedral symmetry point group T (class 23) and T_d (class $\bar{4}3m$) of the cubic system [6,7,18,19]. The molecule of CCl_4, having symmetry of the regular tetrahedron, T_d, is an example [20,21].

We are interested in NLO properties of materials composed of the pyramidal molecules of trigonal C_3 (class 3) and C_{3v} (class $3m$) symmetry. We have shown [22–25] that the trigonal rhombohedral, R3m symmetry class, isomorphous crystals of adducts (complexes) of triiodomethane and antimony triiodide with octa-sulfur: $CHI_3{\cdot}3S_8$, and $SbI_3{\cdot}3S_8$ showed

efficient second-harmonic generation (SHG). For crystals of the complex of iodoform with sulfur, $CHI_3{\cdot}3S_8$, we determined the electrooptic (Pockels) coefficient r_{22} to be about 4 pm/V [22,23]. We also investigated the angle tuned phase-matched frequency doubling [24] and observed a remarkable anisotropy of the linear and NLO properties. The octupolar part of the second susceptibility tensor for $CHI_3{\cdot}3S_8$ is larger than the vector (dipolar) part [24]. A similar anisotropy in the Pockels effect coefficients was found in trigonal crystals of the (1:3) iodoform-quinoline complex of $R3$ symmetry [24,26]. This anisotropy is, however, reversed in the isomorphous $SbI_3{\cdot}3S_8$ crystal [25]. Studies were undertaken to analyze the third isomorphous member of this new class of trigonal second-order NLO materials, the complex of arsenic triiodide with sulfur, $AsI_3{\cdot}3S_8$ crystal [27,28].

In this paper, we compare SHG in the adducts $AsI_3{\cdot}3S_8$, and $SbI_3{\cdot}3S_8$, to SHG in another interesting model system for investigations of dipolar vs. octupolar components of the second-order optical nonlinearity: triphenylamine, $(C_6H_5)_3N$. To our knowledge frequency doubling has not previously been observed in triphenylamine crystals.

THE MOLECULES AND CRYSTAL STRUCTURES

Triphenylamine

Triphenylamine is a tertiary aromatic amine which is often chosen as an electron donor in highly nonlinear π-conjugated chromophores, multibranched conjugated NLO dendritic structures [29] and polymer systems. The molecular structure of triphenylamine has been discussed in relation to the p-π conjugation [30,31]. An efficient interaction between the lone electron pair of the nitrogen atom and π electrons of adjoining aromatic system requires the nitrogen and the adjacent carbons to be coplanar and the C−N−C angles all to be 120°. The dipole moment of such a molecule ought to be zero. This is in conflict with the reported experimental values of dipole moment of triphenylamine in benzene solutions, which were measured to be 0.26 D at 15°C [32] and 0.47 D at 20°C [33]. A number of results have been obtained at 25°C: 0.52 D [34], 0.55 D [35] and 0.70 D [36].

Electron diffraction studies [30] of the triphenylamine molecule in the gaseous state suggested a pyramidal, propeller-like structure of C_3 symmetry with the angle C−N−C = 116° ± 2° and the twist angle (the torsion angle) of phenyl groups about their C−N bonds of 47° ± 5° [30]. The structure of triphenylamine crystals has been examined with the X-ray technique several times [31,37]. The more recent study [31] indicated the non-centrosymmetric monoclinic space group Bb (class m). The

asymmetric unit contains four independent molecules (Z = 16). The N−C bond lengths in the molecules are in the range 1.408–1.427 Å, the mean value is 1.419(6) Å. The phenyl rings are planar. The mean value of the dihedral angles between phenyl ring planes and the plane of the N-bonded C atoms in the four molecules is 44(5)°. The molecules have C_3 symmetry. They have the shape of a propeller, and they are weakly pyramidal. The N atom deviates from the plane of the N-bonded carbon atoms by 0.085, 0.104, 0.013 and 0.116 Å in the four molecules; the mean distance is 0.08(4) Å [31]. The mean value of the bond angle C−N−C is 119.6(7)° [31]. It corresponds to the sp^2 hybridization of N bonding orbitals. Therefore triphenylamine can be viewed as an octupolar trigonal molecule representing the molecular engineering approach based on the "central atom" strategy where the central atom, N, has a potential to utilize the lone electron pair in charge-transfer interaction with electron accepting groups.

A literature search shows that little is known about optical properties of triphenylamine. The molecule is highly polarizable. We found the refractive index ${n_{\mathrm{D}}}^{20}$ of triphenylamine extrapolated from measurements in chloroform solutions to be equal to 1.7084 [38]. This value is in a disagreement with the value quoted in a commonly used handbook [39], but it is comparable to the data derived from molar refraction measured in benzene solutions [34]. Large third-order optical nonlinearity was found in the copolymer of triphenylamine and a derivative of *p*-phenylenevinylene (TPA-PPV) [40]. Worthy of note are the relatively strong imaginary and real parts of the third-order nonlinearity measured in solutions of triphenylamine in chloroform (which are colorless) with femtosecond degenerate four-wave mixing at 800 nm [38].

We performed computations of the dipole moment μ, the first (α), second (β) and third-order polarizability (γ) of the triphenylamine molecule at zero frequency using the MOPAC-93 semiempirical quantum chemical program [41]. The AM1 approximation was used for the geometry optimization of the molecule and for calculation of the polarizabilities by the time-dependent coupled perturbed Hartree-Fock method. Figure 1 shows the computed molecular structure of triphenylamine rendered with the Chem3D program [42].

The minimum energy gradient test led to the symmetry class 3 (the molecular point group C_3) for the free triphenylamine molecule. The carbon atoms C(5), C(8), and C(9) connected to the central nitrogen atom lie on a common plane perpendicular to the three-fold symmetry axis. The C−N bond length is 1.414 Å, the valence angle C−N−C is 119.7°. The molecule is weakly pyramidal. The distance of the N atom out of the plane of the 3 adjacent C atoms is about 0.07 Å. The computed dipole moment of triphenylamine molecule is rather low, $\mu = 0.2\ D$. The molecule is chiral.

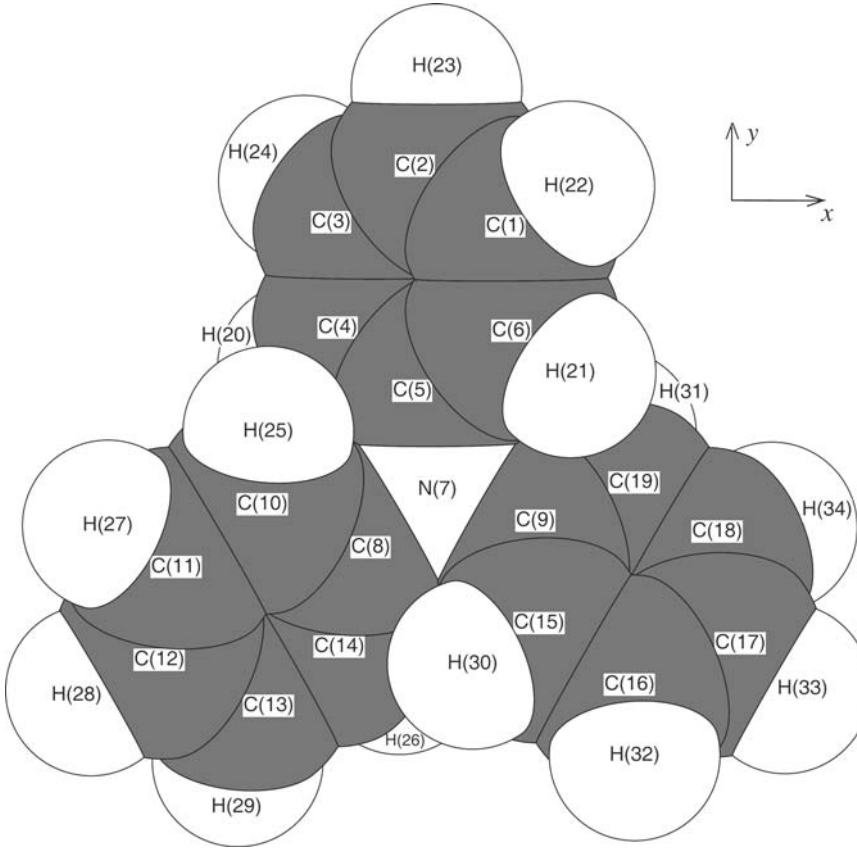

FIGURE 1 Space filling model of the triphenylamine molecule of C_3 symmetry obtained from MOPAC/AM1 computations. The view is down the 3-fold symmetry axis parallel to the z axis. The Cartesian xyz coordinates of the carbon atoms attached to nitrogen atom are: N(7) (0.00, 0.00, −0.11); C(5) (−0.01, 1.41, −0.04); C(8) (−1.22, −0.71, −0.04); C(9) (1.23, −0.70, −0.04).

A propeller conformation of the molecule is predicted: the phenyl rings are twisted around the C−N bonds. The dihedral angles between phenyl-ring planes and the plane of the N-bonded C atoms are 35°.

Prolonged geometry optimization led to the triphenylamine molecule of the symmetry D_3 (class 32) in which the heat of formation was 15 calories smaller than for the molecule of C_3 symmetry. The conformation of the D_3 symmetry molecule was a propeller with a planar central part (C−N bonds) and without a dipole moment (a propeller-like structure of triphenylamine of D_3 symmetry has been considered in ref. [43]). This is in contrast to the

dipole moment experimental observations therefore we concentrate on the results of computations of the molecule of class 3 symmetry.

The MOPAC calculations for triphenylamine molecule of C_3 symmetry gave the zero frequency polarizability tensor components: $\alpha_{11} = \alpha_{22} = 33.5 \times 10^{-24}\text{cm}^3$, $\alpha_{33} = 12.7 \times 10^{-24}\text{cm}^3$. The isotropic average polarizability $\alpha = (\alpha_{11} + \alpha_{22} + \alpha_{33})/3$ is $26.6 \times 10^{-24}\text{cm}^3$. This zero frequency value is similar to the experimental value of $\alpha = 32.2 \times 10^{-24}\text{cm}^3$ derived from our refractive index study of triphenylamine in chloroform solutions at $\lambda = 589.3\,\text{nm}$ [38].

The first hyperpolarizability tensor obtained for the C_3 geometry of triphenylamine molecule, specified in Figure 1, is given by Eq. (1):

$$\beta_{ijk}\left(10^{-31} esu\right) = \begin{bmatrix} & xx & yy & zz & yz & xz & xy \\ x & -0.7 & 1.5 & 0.0 & -0.1 & -4.1 & 75.2 \\ y & 75.2 & -74.4 & 0.0 & -4.2 & -0.1 & 1.5 \\ z & -4.1 & -4.2 & -0.2 & 0.0 & 0.0 & -0.1 \end{bmatrix} \quad (1)$$

The irreducible scalar invariants of the β spherical third-order tensor in the case of the class 3 (C_3) symmetry [6] are given by Eq. (2) for the vector part, $\beta_{\text{v}} = \beta_{\text{J}=1}$, and Eq. (3) for the septor (octupolar) part, $\beta_{\text{s}} = \beta_{\text{J}=3}$,

$$\beta_V = 2\beta_{311} + \beta_{333} \quad (2)$$

$$\beta_S = \left[\frac{2}{5}(2\beta_{311} - \beta_{333})^2 + 4(\beta_{211})^2 + 4(\beta_{111})^2\right]^{0.5} \quad (3)$$

The theoretical values $\beta_{\text{v}} = -0.85 \times 10^{-30}$ esu (-3.5×10^{-40} m^4/V), and $\beta_{\text{s}} = 15.1 \times 10^{-30}$ esu (63.1×10^{-40} m^4/V) were calculated from the tensor coefficients given in Eq. (1) for the coordinates $x = 1$, $y = 2$, $z = 3$. The octupolar part of β tensor is about 18 times bigger than the dipolar part. These theoretical values are in the range of values expected for small organic chromophores. The experimental values of β coefficients for triphenylamine are not known yet.

The average values of the second hyperpolarizability γ calculated with MOPAC for third harmonic generation, $\gamma(-3\omega;\omega,\omega,\omega)$, and the intensity dependent refractive index, $\gamma(-\omega;\omega,-\omega,\omega)$, are equal at zero frequency ω, $\gamma = 33.0 \times 10^{-36}$ esu. This value is close to the experimental third-order nonlinearity of triphenylamine, $|\gamma(-\omega;\omega,-\omega,\omega)| = 23 \times 10^{-36}$ esu, which we obtained from solution measurements of degenerate four-wave mixing at 800 nm, using a femtosecond laser [38]. The hyperpolarizability values have to be taken in the context of triphenylamine being a relatively small

molecule of moderate nonlinearity compared to usual organic nonlinear chromophores. We found that the computed β and γ values for the derivatives of triphenylamine, equipped with strong acceptor groups in the *para* position in the phenyls, were 1–2 orders of magnitude bigger than those of their parent triphenylamine molecule.

The $RI_3{\cdot}3S_8$ Adducts

These molecules are $RI_3{\cdot}nD$ (RI_3:nD) type complexes. Triiodides, RI_3, where R is CH, Sb, As, are pyramidal molecules of trigonal symmetry, and are weak electron acceptors. Complexes can be formed by addition (association) of the triiodides to various donor, D, molecules, for example sulfur, quinoline, urotropine [44]. The adducts $CHI_3{\cdot}3S_8$ [45], $SbI_3{\cdot}3S_8$ [46], $AsI_3{\cdot}3S_8$ [28,47] crystallize in a stoichiometric ratio 1:3 in a trigonal rhombohedral structure without inversion centre, space group is $R\bar{3}m$, crystal symmetry class $\bar{3}m$, and point group C_{3v}.

The crystals are of the van der Waals type with the absence of strong binding interactions. The triiodide molecules are apparently held in a sterically fixed position by the surrounding associating molecules due to weak intermolecular charge-transfer interaction between the iodine atoms, acting as electron acceptors, and free electron pairs of the donor molecules [44]. The bond lengths and bond angles of the triiodide molecules in the adducts remain nearly the same as those found in crystals of the pure compounds. A slight distortion of the bond angles occurs in the sulfur eight-member ring in the crown conformation [28]. No charge-transfer absorption bands are seen in the UV-Visible spectral range, and only small shifts in the infrared and Raman spectra of adducts crystals have been observed [48,49].

Figure 2 shows the X-ray crystal structure of $AsI_3{\cdot}3S_8$ [28]. The diagrams were prepared with ORTEP III [50] and POV-Ray [51]. Figure 2a shows the unit cell packing diagram viewed normal to the (001) plane, i.e., down the crystal 3-fold *c* axis. Figure 2b shows the (010) plane of the unit cell, where the molecules can be seen in the direction normal to the crystal *c* axis. The broken lines indicate the direction of the possible intermolecular charge transfer interactions between iodine and sulfur atoms in the adduct molecules. The interatomic distance I(1)... S(1) in the $AsI_3{\cdot}3S_8$ adduct crystal is shorter than the sum of van der Waals radii by about 0.43 Å. The arrangement of the involved atoms is nearly linear, the angle As-I... S being 169.67°. Similar features were observed in the isomorphous $CHI_3{\cdot}3S_8$ and $SbI_3{\cdot}3S_8$ adducts.

An important fact is that the symmetry class $3m$ (C_{3v} point group) of RI_3 triiodide molecules is fully preserved in the adduct crystals. These molecules occupy C_{3v} symmetry sites with the molecular 3-fold symmetry

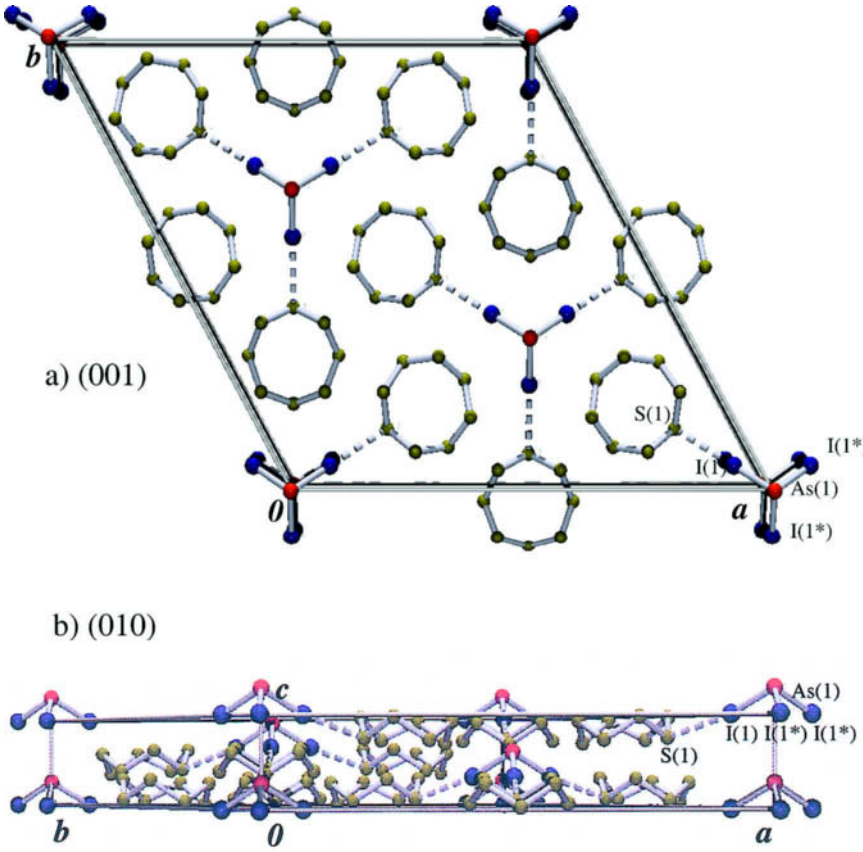

FIGURE 2 Unit cell packing diagrams for $AsI_3 \cdot 3S_8$ adduct crystal: a view normal to (001) plane – Figure 2a, a view normal to (010) plane – Figure 2b. The broken lines indicate the closest contacts between iodine I(1) and sulfur S(1) atoms in the adduct molecules. Asterisks indicate atoms generated by crystallographic symmetry. The cell constants are a 24.739(2) Å, c 4.412(3) Å, V 2338(1) Å^3, Z 3.

axis parallel to the crystal c 3-fold axis. The molecules of adducts are weakly polar due to a small dipole moment of the triiodides, being about 1 Debye. The vector of the dipole moment is aligned parallel to the molecular and crystal trigonal axis.

The adduct crystals are optically anisotropic, uniaxial negative. The ordinary refractive index, $n_o = n_{11} = n_{22}$, is bigger in the ab plane (the plane of iodine atoms) than the extraordinary index, $n_e = n_{33}$ along the crystal trigonal c axis.

EXPERIMENTAL

Materials

Triphenylamine (98%) was purchased from Aldrich. Both the raw material and the material purified by crystallization and sublimation were used in the powder SHG experiments. No essential difference in the second-harmonic responses was observed from the raw and purified materials. The size of the grains (10–200 μm) was measured under a microscope. The powders were kept in glass plane parallel cells equipped with spacers, 0.3–0.5 mm thick. The experiments were carried both on dry powders (in air) and in the index matching medium. Diiodomethane ($n_D^{20} = 1.75$) and divinylbenzene ($n_D^{20} = 1.5740$) mixed in proportion about 3:1 served as index matching fluid for polycrystalline triphenylamine. Refractive index of solid triphenylamine was assumed to be 1.71 similar to this measured in solutions. The cell thickness was about 0.5 mm.

Crystals of adducts (needles of a diameter 0.7–1.0 mm, 2–4 mm long) were used in Maker fringes experiments. Adducts crystals were prepared according to the procedures described for $SbI_3{\cdot}3S_8$ in Ref. [25] and for $AsI_3{\cdot}3S_8$ in Ref. [28]. A powdered material (of crushed needles) of grain size 10–150 μm, placed in 0.3 mm thick glass cells was used in powder SHG experiments. The index matching liquid for adducts was made of a solution of CH_2I_2 and sulfur which contained about 3 wt% of S_8. Average refractive indices of the crystals are 2.06 in $AsI_3{\cdot}3S_8$, 2.08 in $SbI_3{\cdot}3S_8$ at the fundamental wavelength 1053 nm.

Urea (99.5%, Analytical UNIVAR Reagent, Ajax Chemicals) was used as a reference for powder SHG measurements. The urea samples were in a form of polycrystalline needles (40–200 μm) and a powder (40–150 μm) immersed in optical index matching media, like optical cement, epoxy adhesives and liquid divinylbenzene, which were effective in improving light transmission. The urea cells were 0.3–0.4 mm thick. These index matching media were chosen to match an average refractive index, 1.54, of urea crystals at the fundamental wavelength [52].

Linear Absorption Spectra

Since some of the compounds studied here have absorption edges close to the second harmonic (526.5 nm) of the fundamental wavelength of the Nd:YLF laser (1053 nm) a resonance enhancement of second-order NLO response is possible. The transmission spectra of solutions of triphenylamine in benzene and chloroform and the reflectance spectra of polycrystalline $SbI_3{\cdot}3S_8$ and $AsI_3{\cdot}3S_8$ adducts mixed with KBr powder are shown in Figure 3. The transmission spectra were measured with a Shimadzu

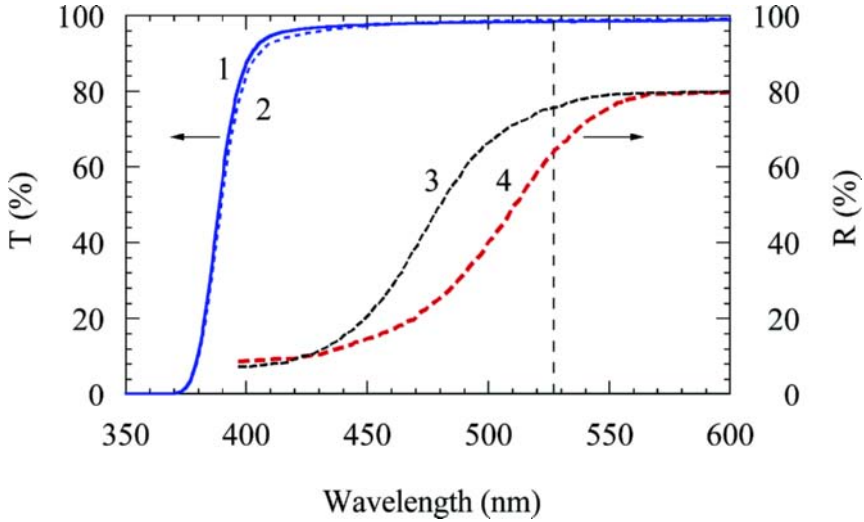

FIGURE 3 UV/VIS transmission spectra of triphenylamine, 31.8 wt% in benzene solution – curve 1 (solid line), 19.1 wt% in chloroform – curve 2 (dotted line); and the diffuse reflectance spectra, normalized to 80% maximum reflectance, of solid adducts: $SbI_3{\cdot}3S_8$ – curve 3, $AsI_3{\cdot}3S_8$ – curve 4.

UV-3101PC spectrophotometer, the reflectance spectra were recorded with a Varian Cary-45 spectrophotometer using a diffuse reflectance attachment. The absorption onset is at about 540 nm in $SbI_3{\cdot}3S_8$ and 560 nm in $AsI_3{\cdot}3S_8$.

The arsenic iodide adduct (yellow-orange solid) has a significant absorption at 526.5 nm. $SbI_3{\cdot}3S_8$ adduct (yellow solid) absorbs a little at this wavelength. Triphenylamine and urea are colorless and do not absorb light in the visible range. The absorption threshold in triphenylamine was estimated from the absorption spectra of concentrated solutions of triphenylamine in benzene, and chloroform. It is near 395–400 nm. Table 1 shows absorption thresholds of studied materials. Absorption maximum, $\lambda_{max} = 303$ nm, the molar absorption coefficients $\varepsilon_{max} = 2.4 \times 10^4\,M^{-1}cm^{-1}$, and $\varepsilon_{400\,nm} = (0.6–0.7)\,M^{-1}cm^{-1}$ were observed in solutions of triphenylamine in chloroform. Urea is transparent in the UV-VIS range. The absorption threshold in urea crystal is known to be at about 200 nm [52].

NLO Measurements and results

The laser system used in the SHG tests consisted of a diode-end-pumped 1053 nm mode-locked Nd:YLF laser [53] and a Nd:YLF amplifier operating at 20 Hz (approximately 6 ps pulse duration, 0.3 mJ/pulse). The SHG tests

TABLE 1 Absorption Thresholds and Efficiencies of the Second Harmonic Relative to Urea in Powder Samples Immersed in Index Matching Media

Material	λ_{edge} (nm)	$I^{2\omega}/I^{2\omega}_{urea}$ (526.5 nm)
Triphenylamine	400	0.6
$AsI_3{:}3S_8$	560	1.2
$SbI_3{:}3S_8$	540	0.9
Urea	200	1.0

were performed using a powder technique in transmission [54,55]. The second-harmonic intensity was measured with a photomultiplier connected to a two-channel oscilloscope, which also monitored intensity of the fundamental beam. A weakly focussed laser beam, about 2 mm diameter, was incident on one side of the powder sample. The second harmonic generated in the powders was detected after the sample with a photomultiplier tube in the direction of the fundamental radiation. The second-harmonic output intensity was collected only within a narrow solid angle of the total angular distribution. The laser fundamental beam was separated from the second harmonic by means of suitable glass and interference filters. The results are shown in Table 1.

The materials studied here are highly refractive both at the fundamental and the second-harmonic wavelengths, which causes high scattering losses at the grain surfaces and reduction of light transmission. The index matching liquids improved transparency of the powders. The second-harmonic intensities measured in the suspensions were 2–3 times greater than in dry powders.

The data in Table 1 indicate that all compounds display non-linear responses comparable to urea. The data were reproducible within 10% for the adducts, and about 20% for triphenylamine. The efficiency data obtained from the powder SHG measurements are only of semi-quantitative value. This is apparent if one compares results in Table 1 with the values of components of the second-order susceptibility tensor d_{ijk} of the adducts which were obtained from measurements of Maker fringes in adduct crystals (Table 2). The adducts have relatively high second-order susceptibilities, $\chi^{(2)}$ ca. 10^{-11} m V^{-1} [25,27,28], about an order of magnitude higher than urea.

DISCUSSION

When comparing the SHG of different materials one needs to take into account the fact that its efficiency depends not only on the value of

TABLE 2 Refractive Indices, the Coefficients d_{ijk} of the SHG Susceptibility Tensor and the Figures of Merit M_{ijk} in Uniaxial Crystals of Adducts and Urea

Material, crystal class	n^A	n^{ω} (1064 nm)	$n^{2\omega}$ (532 nm)	SHG tensor element	$d_{ijk}{}^B$(pm/V)	M_{ijk}(pm^2/V^2)
$AsI_3{:}3S_8$,[C]	n_o	2.209	2.345	(222)	26	59
$3m$	n_e	1.819	1.882	(333)	11.4	21
$SbI_3{:}3S_8$,[D]	n_o	2.209	2.332	(222)	8.1	6
$3m$	n_e	1.858	1.931	(333)	11.3	19
Urea,[E]	n_o	1.477	1.490	(123) = (213)	1.4	0.6
$\bar{4}2m$	n_e	1.583	1.596	= (312)		

[A] Refractive index $n_o = n_{11} = n_{22}$, $n_e = n_{33}$.
[B] The second-order nonlinear susceptibility $\chi_{ijk}{}^{(2)} = 2d_{ijk}$.
[C] Refs [27,28];. [D] Ref. [25]; [E] Ref. [52].

nonlinear coefficients but also on the refractive indices of the material, determining the coherence length, l_c, ($I^{2\omega} \sim l_c{}^2$) for various types of interactions and the possibility of phase matching [19]. The discrepancy between the relatively low powder SHG of the triiodide adducts and their high d_{ijk} values compared to urea is not readily explained on the basis of coherence lengths alone, which are similar and rather short. The l_c at normal incidence of the fundamental 1064 nm derived for the second-order susceptibility tensor elements (222) and (333) are 2.0 μm and 4.2 μm in $AsI_3{\cdot}3S_8$ crystal, 2.2 μm, 3.6 μm in $SbI_3{\cdot}3S_8$ crystal. Urea crystal which belongs to the tetragonal class $\bar{4}2$m has $d_{14} = d_{25} = d_{36}$. The coherence length $l_{36} = l_{312}$ calculated from urea crystals refractive indices, is equal to 2.2 μm, however the l_c is in the range 3 to 20 μm the when d_{14}, and d_{25} coefficients are effective.

Miller's rule [19] predicts that large d values are usually accompanied by large refractive index values. Refractive indices of adducts crystals are bigger than of urea crystal. The merit factor $M = d^2/n^3$ is thus useful for comparing various NLO materials. We calculated the figure of merit $M_{ijk} = d_{ijk}{}^2/(n_i{}^{2\omega}\ n_j{}^{\omega}\ n_k{}^{\omega})$ for elements of SHG tensor in the adducts and urea crystals using refractive indices at the appropriate wavelengths. The results are given in Table 2. The SHG figure of merit for arsenic triiodide – sulfur is about two orders of magnitude bigger than that for urea. This indicates that the powder SHG efficiency data in Table 1 must have been influenced by additional factors reducing the SHG in the adduct powders.

The data in Table 2 indicate that both the linear and the nonlinear optical properties of $AsI_3{\cdot}3S_8$ and $SbI_3{\cdot}3S_8$ adduct crystals are highly anisotropic. The anisotropy of refractive indices is such that n_{22} in the crystal ab

plane is bigger than n_{33} perpendicular to it (the crystals are uniaxial negative). As mentioned above, the microscopic trigonal symmetry of triiodide molecules (C_{3v}) coincides with the macroscopic trigonal $3m$ symmetry of the adduct crystals. Consequently, the polarizability tensor of the adduct molecule is anisotropic: $\alpha_{11} = \alpha_{22} > \alpha_{33}$. The molecule is an oblate spheroid for which the equatorial radius is greater than the polar radius, the largest polarizability component, $\alpha_{22} = \alpha_{11}$, is parallel to the plane of iodine atoms, and the orthogonal, short axis, α_{33}, is in the direction of the molecule dipole moment.

The anisotropy of the second-order nonlinear tensor coefficients in this family of crystals is quite interesting. A ratio $d_{222,eff}/d_{333} = 2.5$ is found in $AsI_3{\cdot}3S_8$ crystal. An even bigger anisotropy was observed in $CHI_3{\cdot}3S_8$ crystals, where the $d_{222,eff}/d_{333}$ ratio was about 10 [24]. However, this anisotropy is reversed in $SbI_3{\cdot}3S_8$ crystal, where the ratio was found to be only about 0.7 [25]. The explanation of the origin of the difference in the behavior of these isomorphous crystals is still a challenge. It does appear to correlate with the increasing polarity of $SbI_3{\cdot}3S_8$ in comparison to $CHI_3{\cdot}3S_8$ and $AsI_3{\cdot}3S_8$ adducts.

The $3m$ symmetry class of the triiodide-octasulfur complexes requires knowledge of three independent d_{ijk} and β_{ijk} coefficients [6] to evaluate the scalar invariants of the SHG and electrooptic tensors. For the molecule of $CHI_3{\cdot}3S_8$ adduct the septor (octupolar) part of the first hyperpolarizability, $\beta_s = \beta_{J=3} = 11.3 \times 10^{-30}$ esu (47.5×10^{-40} m^4/V), is nearly twice bigger than the vector part, $\beta_v = \beta_{J=1} = 6.0 \times 10^{-30}$ esu (25.1×10^{-40} m^4/V) [24,25]. This trend is reversed in $SbI_3{\cdot}3S_8$ adduct [25]. The evaluation of the vector and octupolar contribution to the β tensor in $AsI_3{\cdot}3S_8$ adduct molecule is in progress.

We establish in this work that crystals of triphenylamine are also SHG active. This confirms that the crystal structure of triphenylamine is noncentrosymmetric [31,37]. Triphenylamine crystals belong to the monoclinic crystal class m. Thus they are optically biaxial [37] and possess a large number of non-zero elements of the second-order susceptibility tensor: six coefficients are expected under the Kleinman symmetry conditions, nine when Kleinman's symmetry is not valid [19]. The quantum-chemical calculations indicate that optical properties of triphenylamine molecule are highly anisotropic. The octupolar part of first hyperpolarizability tensor is about 18 times bigger than the vector part. Triphenylamine is thus another interesting model compound for experimental and theoretical investigations of second-order optical nonlinearity in octupolar systems.

It is worth noting that these trigonal molecules of high octupolar nonlinearity could be of interest for use in optical poling experiments [16,17,56,57] to make second-order nonlinear noncentrosymmetric materials by optical means.

CONCLUSIONS

The oblate nearly planar trigonal molecules of triphenylamine and the complex molecules of the triiodide – octasulfur adducts represent a new class of weakly polar molecules which may be packed in noncentrosymmetric crystal structures and exhibit a remarkable anisotropy of linear and nonlinear optical properties. The second-order susceptibility coefficients d_{ijk} determined in the adduct crystals with the Maker fringe technique are an order of magnitude bigger than in urea crystal.

The AsI_3:$3S_8$ adduct crystals show the quadratic susceptibility coefficient d_{222} (in the direction perpendicular to the crystal and the molecule 3-fold symmetry c axis) bigger than d_{333} (parallel to the c axis). It means that the hyperpolarizability β_{222} (in the plane of iodine atoms) is bigger than β_{333} (along the molecule dipole moment). The (222) coefficients significantly contribute to the octupolar part of quadratic susceptibility tensor of AsI_3:$3S_8$ crystal and the molecule.

We report here the first observation of second-harmonic generation in triphenylamine crystals. The results of the powder SHG experiments measured with the ps pulsed laser at the fundamental beam 1053 nm showed the second-harmonic efficiency being only slightly stronger in powders of $AsI_3{\cdot}3S_8$ and $SbI_3{\cdot}3S_8$ adducts than in triphenylamine and urea polycrystalline powders used as a reference. The differences could be caused by differences in absorption edges which were closer to second-harmonic wavelength in adducts than in triphenylamine and urea. However, the figure of merit M_{ijk} indicates that the capability to generate second harmonic in the $AsI_3{\cdot}3S_8$ complex is about two orders of magnitude bigger than in urea crystal. This discrepancy indicates that the powder SHG results are of semiquantitative value only.

We showed here that molecular structure of triphenylamine computed with quantum chemical program MOPAC/AM1 is of C_3 symmetry. It is chiral and has the shape of a propeller. The theoretical values of linear and nonlinear optical molecular polarizabilities indicate that triphenylamine molecule is highly anisotropic. The theoretical octupolar part of β in triphenylamine is remarkable bigger than the vector part.

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