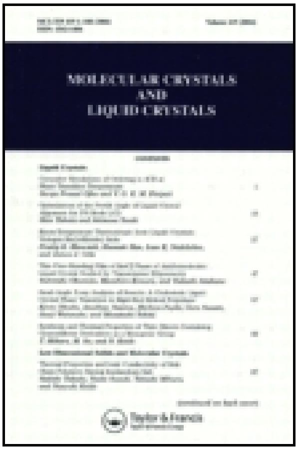

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EXPERIMENTAL CHARACTERIZATION OF NOVEL MATERIALS FOR NONLINEAR OPTICS REPRESENTED BY IODOFORM COMPLEXES

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Abstract: We report on nonlinear optical properties of a new class of efficient nonlinear optical compounds built of trihalides interacting weakly with donor type molecules. Adducts of iodoform with sulphur ($CHI_3 \cdot 3S_8$) and quinoline ($CHI_3 \cdot 3C_9H_7N$) exhibit sizeable electrooptic effects and second harmonic generation comparable to POM and better than urea. Angle-tuned phase matching of type I and II has been observed for both compounds. The comparison between the electrooptic effect and the second harmonic generation suggests that the electrooptic effect is mostly electronic in origin. The atomic force microscope was used to record the molecular structure on free-standing iodoform-sulphur crystal plates. The intermolecular spacings on the crystal surface correspond remarkably closely with those in the bulk.

INTRODUCTION

Trihalogenides AX_3,A=CH,Sb, X=I_3,Br_3,Cl_3 are far from the usual notion of a nonlinear molecule: They do not contain any aromatic rings and, in the special case of iodoform CHI_3 , only possess a small permanent dipole moment. In the bulk iodoform crystal, no second order nonlinearity can be measured, since the orientations of the individual iodoform molecules are statistically disordered, therefore a pure iodoform crystal is macroscopically centrosymmetric[1]. However, with a suitable partner molecule, the iodoform molecules can be perfectly aligned. In the iodoform-sulphur complex (figure 1), the iodoform molecules are perfectly aligned in the plane of the sulphur rings. The high polarizability of the sulphur rings may also help to increase the nonlinearity of the iodoform molecules. The structure of the iodoform-urotropine complex is shown in figure 2. This complex has the highest density of iodoform as well as the highest second harmonic efficiency (in powder samples) in all the investigated systems. One of the advantages of the iodoform complexes are their wider transparency ranges compared to π-electron systems.

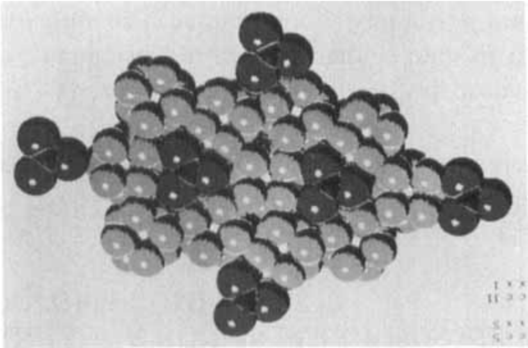

FIGURE 1 Molecular arrangement in the unit cell of iodoform-sulphur. All iodine atoms are positioned within a plane consisting of sulphur rings, all iodoform molecules are identically orientated.

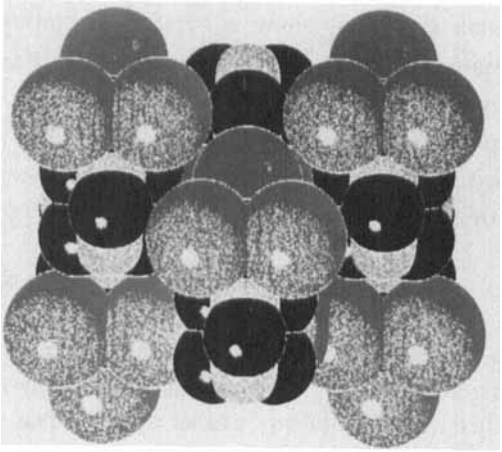

FIGURE 2 Molecular arrangement in the unit cell of iodoform-urotropine. There are two different orientations of the iodoform molecules, both of which contain an identically orientated I-C-I plane.

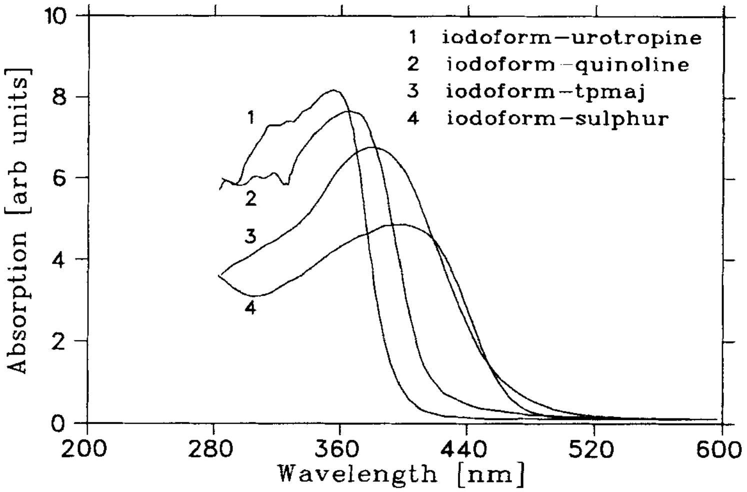

FIGURE 3 Wavelength dependence of the absorption coefficients of several iodoform adducts (tpmaj: Trimethylphenylammoniumodide).

Figure 3 shows the low wavelength absorption edges of some prominent compounds. It can be seen that the iodoform-urotropine complex, which has the highest nonlinearity, also has the largest transparency range down to approximately 400nm, which is a basic requirement for frequency doubling of standard laser diodes.

EXPERIMENTAL AND DISCUSSION

Reference 2 gives a detailed description of the measurements of the refractive indices and the electrooptic and second harmonic coefficients. The results for iodoform-sulphur (point group 3m) and quinoline (3) are summarized in table 1.

		χ_{ijk}^{SHG}, $\lambda = 937$nm, $d_{11}^{q} = 0.48$	$\beta_{ijk}^{a)}$	χ_{ijk}^{EO}, $\lambda = 632.8$nm
Iodoform	(111)	7.1	8.4	4.8
Quinoline	(222)	16.2	19	10.8
tensor	(333)	4.0	6.7	2.6
elements	(113)	-	5.4	4.9
Iodoform	(111)	0	0	0
Sulphur	(222)	38.2	23	38.7
tensor	(333)	5.2	7.5	3.8
elements	(113)	-	8.8	10.0

a) calculated with $\chi_{ijk}^{SHG}(-\omega_3;\omega_1,\omega_2) = N f_i^{\omega_3} f_j^{\omega_1} f_k^{\omega_2} \beta_{ijk}(-\omega_3;\omega_1,\omega_2)$

TABLE 1 The susceptibilities χ_{ijk}^{SHG} and χ_{ijk}^{EO} [pm/V] and the calculated microscopic susceptibilities β_{ijk} $[10^{-40} m^4/V]$ of the iodoform molecule.

A striking result of the measurement is the anisotropy of the nonlinear coefficients in both compounds, the nonlinearity is weakest along the dipole (333) axis of the iodoform molecule. More advanced quantum chemical calculations of the hyperpolarizabilities of iodoform confirm this anisotropy[3]. As can be seen, the second harmonic coefficients are close to the data reported for many efficient organic materials[4]. It is evident that iodoform compounds can be placed among the well recognized efficient nonlinear π-electron materials.

The high birefringence allows phasematching in both compounds. In figure 4, the measurements of both type I and type II phasemaching are compared to the calculated values determined from refractive index measurements. As can be seen, the correspondence is perfect.

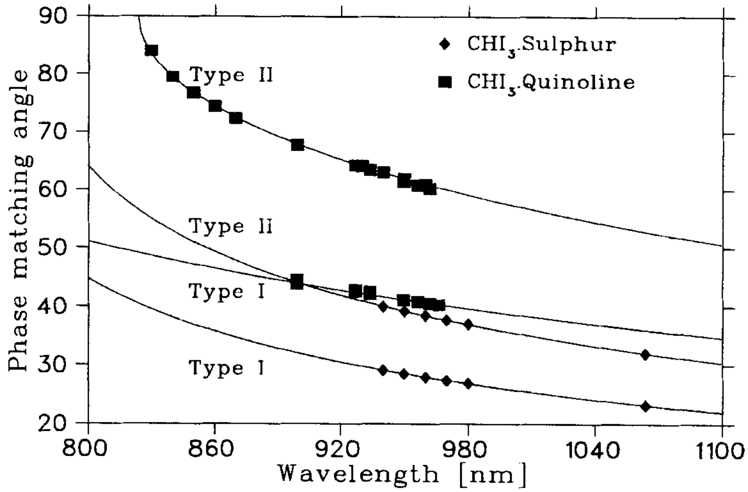

FIGURE 4 Type I and II phasematching in the iodoform-sulphur and iodoform-quinoline compound.

Noncritical (θ=90°) phase matching of type II in the iodoform-quinoline crystal is achieved at a wavelength of 823nm. Unfortunately, no second harmonic light is observed in this geometry, since the effective nonlinear coefficient χ_{22} is multiplied by $\cos\theta$.

The electroptic data indicate that the iodoform compounds can be classified as moderate electrooptic materials. The lowest half wave voltages, 9kV in iodoform-sulphur and 28kV in iodoform-quinoline, are obtained when the light beam is parallel to the optic axis and the electric field is applied perpendicular to it. It is worthwhile to notice that bulk crystals, as well as waveguide samples grown between plates, grow in the optimal configuration for electrooptic applications. A comparison between a reference Kerr cell filled with nitrobenzene and a bulk iodoform-sulphur crystal and showed that in both cases the light modulation followed the 1ns drive signal without showing any lattice resonances.

This indicates that the main contribution to the electrooptic effect is of electronic origin. Much faster low voltage devices can be built with waveguide structures and using the transverse electrooptic effect.

The bulk structures of the iodoform adducts are well known using standard analytical methods such as electron and x-ray-diffraction[5,6]. With the inception of the field of scanning force microscopies[7], the low concentration of surface molecules no longer eludes analysis. A commercially available Atomic Force Microscope[8] was used to scan the surface of a crystal plate of iodoform-sulphur. The scans were recorded under ambient atmosphere, at room temperature.

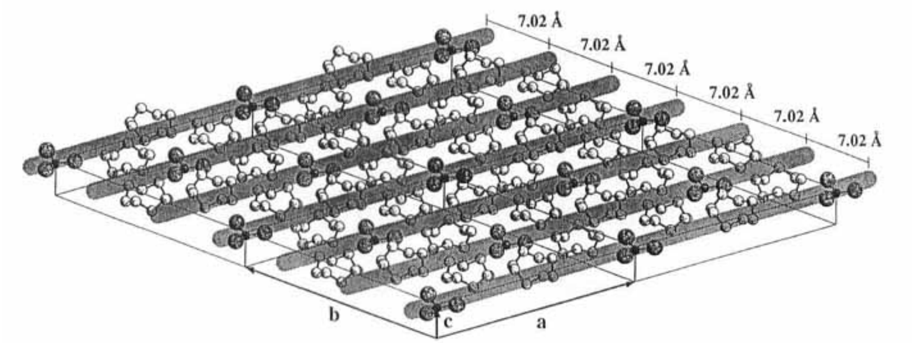

FIGURE 5 Unit cell of iodoform-sulphur (a=b=24.32Å,c=4.44Å). The distance between successive rows of iodoform molecules is 7.02Å.

Figure 5 shows four unit cells of the uniaxial iodoform-sulphur compound, the optic axis is along the three-fold c-axis.

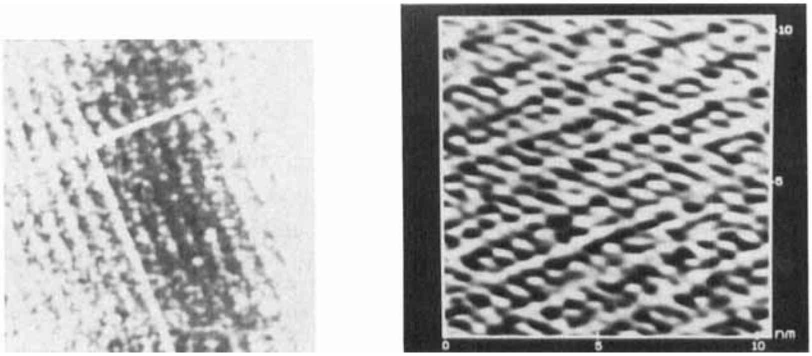

FIGURE 6 left: bc or ac plane, the optic axis is along the drawing plane. The clearly visible structure corresponds to the stacking of the iodoform- sulphur planes within the bulk crystal.
right: ab plane, the optic axis is perpendicular to the drawing plane. The structure can be associated to the position of the iodoform molecules within the bulk crystal.

The AFM scans revealed flat surfaces on the molecular level. On the left of figure 6 is an scan perpendicular to the optic axis. The stacking of the unit cell layers can be clearly seen (every second sulphur layer). On the right of figure 6 is a high resolution image taken along the optic axis with a clearly visible superstructure, which can be associated to the positions of the iodoform molecules within the compound.

TABLE 2 Comparison of bulk and surface values. It can be seen that the arrangement of the iodoform and sulphur molecules on the surface corresponds closely to that of the bulk.

	AFM surface	Literature bulk
a=b	24.4Å	24.36Å
c	4.5Å	4.44Å
γ	120°	120°

CONCLUSIONS

For a detailed discussion of the origins of the nonlinearity in iodoform compounds, we refer to the paper of Samoc et al[2]. The excellent quality of the iodoform-sulphur complex allowed us to build electrooptic switches with 1ns switching time, and much faster devices are possible using waveguide structures. The atomic force microscope has provided information on the arrangement of molecules on the surface of the iodoform-sulphur complex.

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