Structural Aspects of Nonlinear Optics: the Configuration of IO_3 in $TlIO_3$

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Summary Optical second harmonic generation measurements on a single crystal of $TlIO_3$ ($d_{311}/d_{333} = 0{\cdot}54$) allow the first prediction of a molecular structure (intramolecular O–I–O of 90°) by such a technique.

As part of a continuing study of the relationships between molecular structures and hyperpolarizability[1–3] we have prepared and characterized $TlIO_3$. The observed ratio of two of the nonlinear coefficients (d_{311}/d_{333}) predicts that the intramolecular O–I–O bond angle will be 90° ± 5°. The water insoluble crystal also appears to be *ca.* 2·5 times more efficient as a $1{\cdot}06\,\mu$ doubler than the standard material $LiIO_3$.

Single crystals, *ca.* 2 mm each side were grown from a 50% aqueous solution of HF [reaction (1)]. The almost insoluble[4]

$$Tl^+ + IO_2F_2^- + H_2O \rightarrow TlIO_3 + 2HF\uparrow \qquad (1)$$

(*ca.* 0·6 g/l) salt, $TlIO_3$, crystallizes in space group $R3m$, with cell constants[5] $A_H = 6{\cdot}344$, and $C_H = 7{\cdot}925$ Å. There are 3 molecules per hexagonal cell; $D_c = 6{\cdot}86$ g/cm³.

Details of the experimental set up are given elsewhere.[1] The results of the second harmonic generation (SHG) measurements show that $d_{311}/d_{333} = 0{\cdot}54 \pm 0{\cdot}08$.

Using the three-dimensional microscopic model proposed by Buckingham and Orr,[6] where the hyperpolarizability terms ($\beta^{\parallel}$, $\beta^{\perp}$) for the I–O bonds and iodine lone pair are equivalent, as found in other iodates,[1] we find that d_{333} and

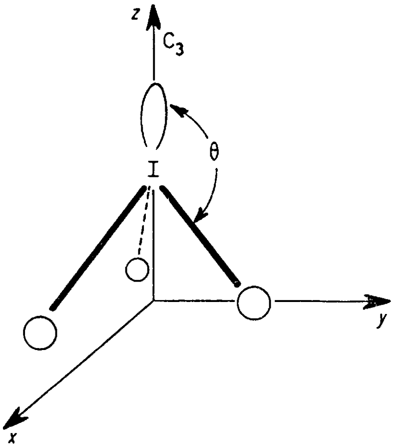

FIGURE. Iodate configuration in $TlIO_3$, showing the dipolar (3-fold) *c* axis which is coincident with the iodine lone pair. The *x* axis is orthogonal to the (*yz*) mirror plane.

d_{311} are given by equations (1) and (2), respectively, where

$$d_{333} = (3/V)\,[\beta^{\parallel}(1 + 3\cos^3\theta) + 9\beta^{\perp}\cos\theta\,\sin^2\theta] \qquad (2$$

$$d_{311} = (3/V)\,\{(3/2)\,\beta^{\parallel}\cos\theta\,\sin^2\theta + [1 + (3/2)\cos\theta\,(3\cos^2\theta - 1)]\beta^{\perp}\} \qquad (3)$$

θ is the trihedral angle shown in the Figure and V is the volume of the unit cell. Using the literature value[1] of $\beta^{\parallel}/\beta^{\perp} = 3{\cdot}6$ and our measured value of $d_{311}/d_{333} = 0{\cdot}54 \pm 0{\cdot}08$ we find $\theta = 125°$, which corresponds to an intramolecular O–I–O angle of 90 ± 5°. In general the average O–I–O angle is 98·5 ± 2·6°. Confirmation of the predicted IO_3 configuration by conventional (*X*-ray) methods is in progress.

The underlying assumptions of this bond additivity model are essentially the same as those used in linear bond polarizability models,[7] *i.e.* we neglect local field corrections, van der Waals interactions, *etc.*, and all interactions where one would not expect high concentrations of electron density which could respond to an optical field and re-radiate at the second harmonic. This dipolar requirement (second harmonic) simply means we can neglect any collection of electrons which possesses a centre of inversion such as core electrons and the 2(6*S*) electrons on the Tl^+. As an illustration, in considering a crystal of mixed ionic and covalent bonds such as lithium formate ($LiCO_2H$) one might expect $\beta_{C-O} \geqslant \beta_{C-H} >> \beta_{Li-O} \sim \beta_{O-O} \sim \beta_{H-O} >> \beta_{Li-H} \cdots$ because this is the order in which one might expect to find valence electron density distributed between these various dipolar interactions.[8]

In summary we have shown for the first time that the quantitative relations between bulk nonlinear optical coefficients (*d*'s) and microscopic bond hyperpolarizabilities (β's) can be readily used to determine molecular parameters.

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