

Optical nonlinearities in twin chromophores: An odd story

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It is part of the acquired lore of the neophyte chemist that while the temperatures at which linear alkanes C_nH_{2n+2} boil increase smoothly with increasing chain length n , the temperatures at which they melt show less usual behaviour – alkanes with odd n melt at lower-than-expected temperatures (Figure 1).

The explanation is that in the crystalline state, geometric concerns dictate that even n alkane molecules pack more efficiently¹, (at least for $n > 1$) making them just a trifle more refractory than odd n alkanes. In the liquid state, packing concerns do not play as important a role and the boiling temperatures display the expected monotonic increase with increase in formula weight. These trends have long served as an early, and rather pretty illustration of how structural details at the Ångstrom scale can manifest in something as coarse-grained and commonplace as the melting temperature of a wax.

In an interesting new twist to this familiar tale, chemists at the Indian Institute of Science have recently shown^{2,3} that pack-

ing constraints similar to those influencing the melting of wax can affect something as exotic as optical nonlinearities in chromophoric molecular solids. [Nonlinear optical (NLO) materials double the frequency (halve the wavelength) of the light transmitted by them.]

The systems studied were twin nonlinear optical chromophores such as 4-hydroxy-4'-nitroazobenzene or 4-nitrophenol linked in pairs by polymethylene chains $-(CH_2)_n-$ through the phenolic groups in the *para* position. The studies were aimed at determining the role, if any, of the lengths of the spacers (in other words, of n) on nonlinear optical properties. The azobenzene derivatives² display transitions into nematic liquid crystalline phases with the various transition temperatures (to the liquid crystal, and then to the isotropic liquid) showing the anticipated odd-even oscillations as a function of n . More interestingly, the NLO properties of the polycrystalline powders also display such odd-even oscillations; the odd n members possessing significantly

larger SHG efficiencies. While less impressive in their SHG efficiencies, it is the nitrophenol derivatives that we focus on³ since their crystal structures have recently been determined by X-ray diffraction.

From Figure 2 it is seen that while even n molecules made by linking the phenol groups of two 4-nitrophenol molecules through $-(CH_2)_n-$ spacers display polycrystalline powder SHG intensities that are smaller than the limits of detection, the molecules with odd n display measurable effects. What is very interesting is that even when the molecules were dispersed in a polymer film and aligned through poling by a DC electric field, even-odd oscillations in the SHG efficiencies were observed (not shown here). In the case of the chromophores being dispersed in a polymer matrix, the effects do not arise from the manner in which the molecules pack in the unit cell but from the *intramolecular* conformation, viz. the nature of torsions in the polymethylene chains.

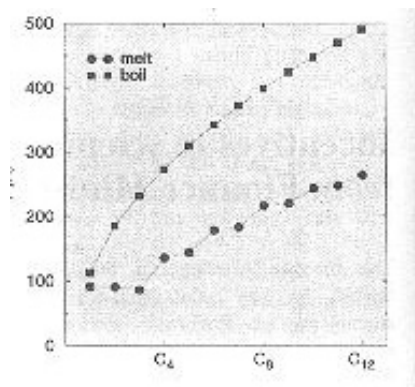


Figure 1. Melting and boiling points of the alkanes as a function of chain size n . Data from ref. 5.

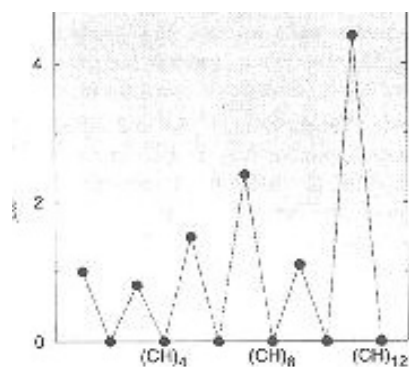


Figure 2. Powder SHG intensities relative to urea of twin 4-nitrophenol chromophores linked through the *para* positions by $-(\text{CH}_2)_n-$ units. Data are relative to urea powder. Excitation was at 1064 nm. Data from ref. 3.

The availability of single crystals of most of the members between $n = 1$ and $n = 12$ and the solution of their structures⁴ has confirmed earlier speculations³ that the even n molecules pack in the crystal in a centrosymmetric manner while odd n do not. Centrosymmetric crystals do not normally display optical nonlinearities. Figure 3 shows the structures of the $n = 1$ and $n = 2$ molecules determined by X-ray diffraction. Assuming that the molecular structures determined by X-ray diffraction are retained even when the chromophores are dispersed in polymer films, the larger



Figure 3. Molecular structures of the $n = 1$ and $n = 2$ molecules obtained from single-crystal X-ray diffraction. Dark grey, carbon; blue, nitrogen; yellow, oxygen. Unpublished data from T. N. Guru Row.

SHG efficiencies found for the odd n molecules can then be attributed to the greater ease with which the chromophores separated by odd n are aligned by the poling electric field. When n is even, the molecules appear to resist such alignment.

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