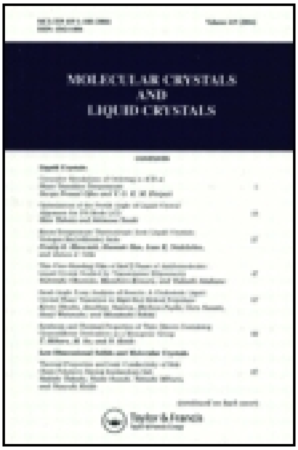

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Chemistry, Symmetry and Optics

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Version of record first published: 13 Dec 2006.

To cite this article: J. Zyss & G. Tsoucaris (1986): Chemistry, Symmetry and Optics, Molecular Crystals and Liquid Crystals, 137:1, 303-328

To link to this article: http://dx.doi.org/10.1080/00268948608070930

Mol. Cryst. Liq. Cryst., 1986, Vol. 137, pp. 303-328
0026-8941/86/1374-0303$25.00/0

Printed in the United States of America

CHEMISTRY, SYMMETRY AND OPTICS

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Abstract The remarkably high quadratic optically nonlinear efficiency of some organic molecular crystals can be ascribed to properly "tailored" structural features at both molecular and crystalline levels. Introduced within the framework of an oriented gas model, symmetry considerations play a foremost part, as detailed in the case of a monoclinic $P2_1$ crystal composed of planar molecular units, and lead to experimentally confirmed structural relations between macroscopic susceptibility coefficients. A hierarchy of point groups in connection with nonlinear efficiency can be established. This helps define the optimum molecular packing for each crystal point group. Different engineering strategies, such as those based on chirality, cancellation or dipole-dipole interaction forces and hydrogen bonding are defined and exemplified in specific cases. Except in the case of chiral molecular units, it is impossible to infer the crystalline symmetry type. Statistical correlations between molecular and crystalline symmetry types are nevertheless highly desirable to help guide chemical synthesis towards the right crystalline objective.

I-MICROSCOPIC AND MACROSCOPIC OPTICAL NONLINEARITIES :

The advent of nonlinear optics as a major field of optical physics followed with almost no delay[1] the invention of the laser. Although nonlinear effects in optics had been predicted much earlier[2], their actual observation was subordinated to the availability of higher optical power densities such as could only be obtained from the strong focusing of powerful coherent sources in appropriate materials. The early developments of nonlinear optics were based on the use of inorganic insulating or semiconductor materials[3] which had been generally conceived for other applications. It was only after a decade of learning, in the early seventies, that the concept of "tailor-made" materials emerged and the search for new materials with nonlinear efficiency surpassing that of state-of-the-art Lithium-Niobate ($LiNbO_3$), or dihydrogeno-potassium phosphate (KDP) actively started. This pointed out the relevance of organic and polymeric structures[3,4]. Among various driving forces which stimulate this research, the major one is the development of "all-optical" devices[5] suitable for optical communication or optical signal processing components which allow for larger bandwith or shorter switching times and are more readily compatible with efficient parallel architectures than their classical electronic counterparts. High nonlinearities are required as these components are expected to perform efficiently when driven by low-power semiconductor laser sources (a few 10's of mw over interaction length (a few mm's or less).

order	crystal	molecule	effects	possible utilization
1	$\chi^{(1)}$	α	refraction	optical fibers
2	$\chi^{(2)}$	β	generation of second harmonic $\omega + \omega \rightarrow 2\omega$	frequency doublers
			frequency mixing $\omega_1 \pm \omega_2 \rightarrow \omega_3$	optical mixers
			parametric amplification $\omega_3 \rightarrow \omega_1 + \omega_2$	optical parametric oscillators
			Pockels effects $\omega + 0 \rightarrow \omega$	electro optical modulators
3	$\chi^{(3)}$	γ	3-wave mixing	Raman coherent spectroscopy
			phase	real time holography
			Kerr effect	ultra high speed optical gates
			optical bistability	amplifiers, amplitude choppers, etc.

Table I. The various linear and nonlinear susceptibilities related to the relevant dielectric properties of matter.

Table I sums up a number of optical effects and their possible utilization which can be accounted for by second- or third-order nonlinear susceptibilities[6]. Such effects show up when a material is irradiated at an optical power density level which breaks up the usual linear dependency of the induced polarization in terms of the perturbating field. Higher order terms have to be introduced in the expansion of the polarization and this has to be done consistently at both macroscopic and microscopic scales yielding respectively:

$$P_i^{\omega} = P_i^{o,\omega} + \chi_{ij}^{(1)} \cdot E_j^{\omega} + \chi_{ijk}^{(2)} : E_j^{\omega_1} E_k^{\omega_2} + \chi_{ijkl}^{(3)} : E_j^{\omega_1'} E_k^{\omega_2'} E_l^{\omega_3'} \quad (1)$$

$$p_i^{\omega} = p_i^{o,\omega} + \alpha_{ij} \cdot E_{j\ell}^{\omega} + \beta_{ijk} : E_{j\ell}^{\omega_1} E_{k\ell}^{\omega_2} + \gamma_{ijk} E_{j\ell}^{\omega_1'} E_{k\ell}^{\omega_2'} E_{l\ell}^{\omega_3'} \quad (2)$$

where P is the polarization of the unit volume of material while p is the microscopic dipole refering to a bond in a covalent crystal or to a molecule in a Van-der-Waals lattice. E_j and $E_{j\ell}$ refer respectively to components of the applied and local fields which can be classically related within the Lorentz model[6] by a tensorial relation of the form:

$$\overline{E_l^{\omega}} = f(\omega)\, \overline{E^{\omega}} \quad (3)$$

where f is a second-order tensor, which in the case of isotropic or cubic media is given by the well known Lorentz correction

$$f = \frac{\varepsilon_{\omega} + 2}{3}\, I_d$$

I_d is here the identity operator.

$\chi^{(1)}$, $\chi^{(2)}$, $\chi^{(3)}$ and α, β, γ are the macroscopic and microscopic susceptibility tensors respectively. The rank of tensor $\chi^{(n)}$ is n+1. The interacting field frequencies satisfy energy conservation relations of the type

$$\varepsilon_1\omega_1 + \varepsilon_2\omega_2 = \omega \quad \text{or} \quad \varepsilon_1\omega_1 + \varepsilon_2\omega_2 + \varepsilon_3\omega_3 = \omega$$

with $\varepsilon_i = \pm 1$ depending on whether the corresponding field or its complex conjugate are handled (absorption or emission cases). An "oriented-gas" description of the medium[7] allows for the straightforward connection of microscopic and macroscopic nonlinearities and will serve as the main stepping-stone in the optimization of the crystalline lattice nonlinear response from the understanding of the molecular properties. To symplify the formalism, we will hereafter refer to second-harmonic generation where $\omega_1 = \omega_2 = \omega$. In the "oriented gas" formalism, the macroscopic dipolar response is viewed as originating from the sum of presumably independent individual molecular contributions. This assumption is valid in view of the relatively loose structure of molecular crystals where intramolecular covalent bonds are more energetic than intermolecular ones by one to two orders of magnitude depending on the presence of hydrogen bonding in addition to Van-der-Waals interaction forces. These considerations support the notion of molecules tending to preserve their individuality in condensed phases and justify the oriented gas assumption. Terms of equivalent orders in field amplitude, either local or applied, can be accordingly and independently related, namely $\chi^{(1)}$ to α, $\chi^{(2)}$ to β and $\chi^{(3)}$ to γ. We shall call i,j,k, cartesian indices related to a molecular reference frame and I,J,K, cartesian indices for a laboratory-related frame. The crystal unit cell of volume N^{-1} contains n molecules, indexed by s. $\chi^{(2)}$ may then be related to β by [8,9]:

$$\chi^{(2)} = N f_I^{2\omega} f_J^{\omega} f_K^{\omega} \sum_{\substack{s=1\\ i,j,k}}^{n} [\cos I,i(s)] \cos[J,j(s)] \cos[K,k(s)] \beta_{ijk}(s) \quad (4)$$

where $f_I^{2\omega}$, f_J^{ω} and f_K^{ω} are Lorentz local-field correction factors, $f_I^{\omega} = \left[(n_I^{\omega})^2 + 2\right]/3$. The cosine factors apply to angles between unit vectors of the molecular and laboratory reference frames. If the crystal point-group g allows for n(g) equivalent positions in the unit cell (for example n(622) = 12 or n(222) = 4), Eq.(4) can be cast in a more condensed form, introducing a new tensor b, highly suitable for the general geometric discussion to follow:

$$\chi_{IJK}^{(2)} = N f_I^{2\omega} f_J^{\omega} f_K^{\omega} b_{IJK} \quad (5)$$

with b_{IJK} defined as :

$$b_{IJK} = \frac{1}{n(g)} \sum_{s=1}^{n(g)} \cos[I,i(s)] \cos[J,j(s)] \cos[K,k(s)] \beta_{ijk} \quad (6)$$

N is the total number of molecules in the crystal unit volume. The index s has been removed from β_{ijk} as the molecular reference frames correspond to each other by the same point-group operations as their attached molecules, resulting in identical expressions of the β tensor. It may happen that the actual number of molecules in the unit cell is a multiple or a submultiple of n(g), the former case when the crystal is composed of geometrically unrelated molecular sublattices, the latter case when intramolecular symmetry operations coincide with crystalline symmetry operations (as for example in urea where the unit cell accomodates only two molecules, while $n(\bar{4}2m)=8$, this reduction corresponding to the coincidence of molecular and crystalline mirror planes). The integer $n(g)/n$ can be viewed as a degeneracy factor accounting for possible coincidences between molecular and crystalline symmetry elements. Assuming P independent sublattices, individually labeled by t and N_t the number of molecules per unit volume in sublattice t, Eq.(5) and (6) can be straightforwardly generalized on to Eq.(7) and (8).

$$\chi^{(2)}_{IJK} = f^{2\omega}_{I} f^{\omega}_{J} f^{\omega}_{K} \sum_{t=1}^{P} N_t \, b^{t}_{IJK} \tag{7}$$

$$b^{t}_{IJK} = \frac{1}{n(g)} \sum_{s=1}^{n(g)} \cos|I,i_t(s)| \cos|J,j_t(s)| \cos|K,k_t(s)| \, \beta_{ijk} \tag{8}$$

These expressions have the practical advantage of leading to a general (group dependent only) expression of b_{IJK} which can be termed as the quadratic crystalline nonlinearity per molecule and is independent of the actual number of molecules in the unit cell. Eq.(8) offers a very operational guideline toward the optimization of a molecular crystal for quadratic nonlinear applications. The optimization procedure[10,11] may be formally decomposed into two steps: the first one consists in selecting a molecule which will exhibit β enhancing features while the second one is to ensure that the crystalline lattice orientation fully promotes the molecular response. A centrosymmetric lattice appears to be ruled out but we shall see further on that it is possible to define for each crystal point group the optimal molecular orientation maximizing the efficiency of phase-matched nonlinear quadratic processes. When these two steps are successfully addressed, there remains the difficult task of growing and shaping a crystal of sufficient size and optical quality for use in nonlinear optical devices. A still embryonic though promising technology is starting to yield organic crystalline samples of satisfactory quality and of various interesting shapes[12] such as bulk crystals, organic cored capilaries, planar thin films etc...

II- CONSIDERATIONS ON THE DIMENSIONALITY OF CHARGE-TRANSFER MOLECULAR CRYSTALS AND MATERIAL OPTIMIZATION

A - QUADRATIC NONLINEAR PROPERTIES OF INTRAMOLECULAR CHARGE TRANSFER CRYSTALS

A number of concurring experiments and related models have suggested as the prototype of highly nonlinear molecular systems a conjugated intramolecular charge transfer molecule of the paranitroaniline type[13]. The combined asymmetrizing influence of the electron acceptor and donor groups distorts the polarization response of the electron system thus radiating harmonics of the fundamental incoming field. Such molecular systems have been studied at length by theoretical chemists and it is common to account for their optical properties by means of a quantum two-level system. For such a system, the following expression of β can be derived by use of perturbation theory within the dipolar approximation[8] :

$$\beta_{ijk} = \frac{1}{2h^2}\left[\frac{\delta_i m_j m_k}{\omega_1{}^2 - \omega^2} + m_i\ (m_j\delta_k + \delta_j m_k\ )\ \frac{\omega_1{}^2 + 2\omega^2}{(\omega_1^2-4\omega^2)(\omega_1\ -\omega^2)}\right] \quad (9)$$

where $h\omega_1$ is the energy difference between the fundamental and excited states, δ is the difference between excited - and ground-state dipole moments and m is the transition dipole moment. It is seen from Eq.(9) that b involves only tensor products of the two vectors $\bar{\delta}$ and m making it a third-rank tensor confined to the $(\bar{\delta},\bar{m})$ plane. The quantum two-level nature of the molecular system results in a reduction of its geometric dimensionality to two. Assuming Kleinman symmetry relations, i.e. index permutation symmetry of the b tensor independent of frequency permutation, as valid far-away from resonances, one ends up with only 4 distinct β components, instead of 27 in the absence of symmetry namely : β_{aaa}, β_{bbb}, β_{abb}, β_{baa}, where a and b may be arbitrary directions within the molecular plane. This will be seen to have important consequences on the crystalline $\chi^{(2)}$ coefficients of monoclinic crystals when the oriented gas model as defined in Section I is called on to relate molecular and crystalline entities. We shall exemplify the general discussion to follow in the case of MAP[14] (methyl - (2,4-dinitrophenyl) - aminopropanoate) which belongs to the low-symmetry $P2_1$ class frequently encountered in organic crystals. The b tensor may be seen to have only four coefficients owing to the y two-fold axis symmetry reduction namely : b_{YXX}, b_{YYY}, b_{YZZ} and b_{YZX}. When the crystalline and molecular frameworks are chosen, according to Fig.1, the relation between b and β takes the simple form :

$$b_{YXX} = \cos\alpha\ \beta_{yxx} \tag{10}$$

$$b_{YYY} = \cos^3\alpha\ \beta_{yyy} \tag{11}$$

$$b_{YZZ} = \cos\alpha\ \sin^2\alpha\ \beta_{yyy} \tag{12}$$

$$b_{XYZ} = -\sin\alpha\ \cos\alpha\ \beta_{xyy} \tag{13}$$

It may be seen that β_{xxx}, the fourth component of the 2-D tensor β, is missing from the linear equations system[10,13] making it singular for essentially geometric reasons. It follows from this singularity that

$$b_{YZZ}\ /\ b_{YYY} = \tan^2\alpha \tag{14}$$

This new "structural" relation can be compared to independent $\chi^{(2)}$ coefficient measurements by Maker fringes techniques and crystallographic structure analysis. In the case of MAP, the agreement was found to be excellent as the experimental ratio (Eq.14) is 0.54 as compared to 0.56 for $\tan^2\alpha$ (for $\alpha = 36.9°$). A similar oriented-gas model analysis applied at the linear level helps relate the index of refraction (or the dielectric constant) to the molecular polarizability. A crystalline polarizability per molecule, labeled a, can be defined following similar considerations to those used to define b. Assuming in addition an isotropic in-plane polarizability tensor, i.e. $\alpha_{aa} = \alpha_{bb}$ as suggested by semi-empirical finite-field calculations[9], leads to the cancellation of $\chi^{(1)}_{XZ}$ and to the assignment of X and Z as principal dielectric axis. X, which is the direction common to the two unit-cell molecular planes cannot be predicted to be a principal axis by pure symmetry considerations as is the case for Y. The approach used here thus illustrates the combined power of joint chemical, structural and optical considerations.

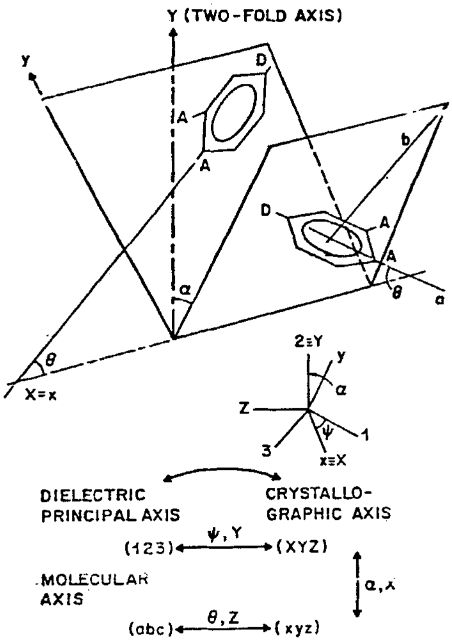
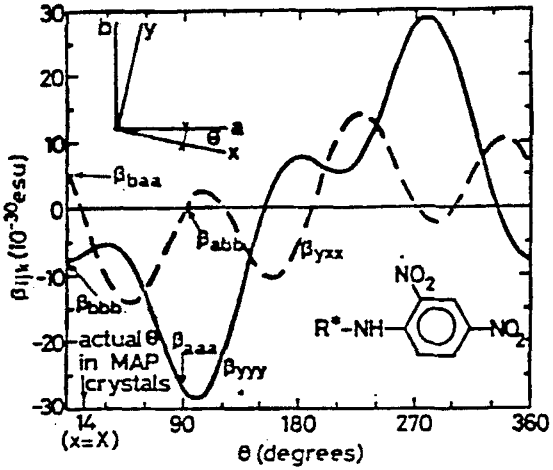


FIGURE 1. An "artist view" of the monoclinic crystal unit cell of MAP. The two molecular planes are symmetric with respect to the two-fold axis y. α and θ define the angular positions of the molecular planes with respect to the binary axis and of each molecule within its plane. The proper crystalline (X,Y,Z) and molecular (x,y,z) reference frames which help simplify the relation between macroscopic and microscopic nonlinear susceptibilities are defined from classical dielectric (1,2,3) and molecular (a,b,c) reference frames.

B - OPTIMIZATION AND HIERARCHY OF POINT CRYSTAL GROUPS FOR N.L.O.

The oriented-gas model offers a convenient framework for discussing the optimization of structures in view of increasing the yield of phase-matched quadratic parametric processes. Fig.2 shows the dramatic influence of the variation of



SHG optimum

$(d_{YXX})_{max} = 6.7 d_{YXX} = 2.7\ 10^{-7}$ e.s.u.

$(\alpha = 0,\ \theta = 47.6°)$

E.O. optimum

$(d_{YYY})_{max} = 14 d_{YYY} = 6.1\ 10^{-7}$ e.s.u.

$(\alpha = 0,\ \theta = 100.6°)$

FIGURE 2. Variation of the molecular β_{ijk} components upon rotation of MAP molecules in the ab plane.

angular parameters θ associated with the rotation of MAP molecules within fixed molecular planes. Optimized d_{YXX} and d_{YYY} coefficients are respectively 6.7 and 14 times larger than the corresponding actual MAP coefficients, reaching respectively values of 2.7 10^{-7}e.s.u and 6.1 10^{-7}e.s.u, compared to 14 10^{-9}e.s.u, for $LiNbO_3$. It is possible to generalize this approach to all Kleinman compatible non-centrosymmetric point groups and define, for each of them, the optimal relative orientation of the polarization of the collinearly propagating waves and of molecular charge transfer axis with respect to crystalline symmetry axis. When such optimal

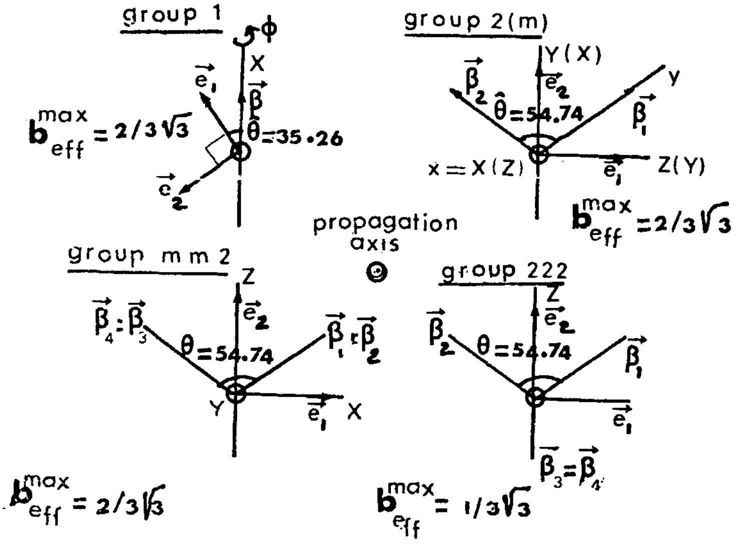


FIGURE 3. Optimal molecular orientations (one-dimensional case) and phase-matching configurations for biaxial crystal groups.

geometry is reached for a given wavelength the effective crystalline nonlinear coefficient per molecule b, that is a properly weighed combination of individual b_{IJK} coefficients taking into account angular parameters, reaches a maximal value, namely b_{eff}^{max}. Fig.3 depicts a number of such optimal configurations for the most frequently encountered low-symmetry monoclinic or orthorhombic groups 1,2,m,mm2, and 222. In table II, the corresponding values of b_{eff}^{max} coefficients are given in units of β_{uuu}, the hyperpolarizability coefficient along the charge transfer axis u. It should be noted that the most favourable groups, i.e. those for which b reaches the highest maximal value ($2/3\sqrt{3}$=38%) are also those of lower symmetry where organic molecular crystals tend to concentrate as demonstrated by recent systematic investigations of crystallographic data banks.

TABLE II. Hierarchy of non-Centrosymmetric Point Groups with respect to collinear phase-matched efficiency of quadratic nonlinear processes as measured by b_{eff}^{max}

group	b_{eff}^{max}
1, 2, m, m m 2	$2/3\sqrt{3}$
$\bar{6}2m$, $\bar{6}$, 3, 3m, 32	1/4
222, 6mm, 6, 4mm, 4, $\bar{4}2m$, 23, $\bar{4}3m$	$1/3\sqrt{3}$
$\bar{4}$	0

III - MOLECULAR CRYSTAL ENGINEERING

Derived from the above general principles, a molecular crystal engineering approach can now be initiated, at two levels, that of the molecular structure and of the crystalline structure. This approach requires, first, the definition of criteria for the choice of chemical families to be explored, and the subsequent optimization within each family. In order to substantiate such a choice, several kinds of criteria are to be formulated.

A. MOLECULAR CRITERIA

1. Lack of Inversion Center

This requirement, common to all physical effects driven by a third-order cartesian tensor applies primarily to the molecular point group.

2. Presence of a Conjugated System

The presence of mobile electron, provided by a conjugated system significantly enhances optical nonlinearities of all orders. The contribution of σ electrons is one order of magnitude below that of π electrons.

3. Presence of Charge Transfer (CT)

Further enhancement may be obtained from the simultaneous presence and interaction within a molecular system, of an electron attracting and an electron withdrawing group. Such a system can satisfactorily be accounted for by the two-level model described above.

4. Transparency

Clearly, increasing the dimensions of the system results in the increase of the short wavelength limit of the transparency domain. This criterion has, of course, to be defined with respect to the various wavelengths involved. These wavelengths, in turn, correspond to available laser sources. Thus, the widely used YAG:Nd^{3+} beam (1.06 μm) requires transparency at least 100 nm beyond the 0.53 μm second harmonic. Fig.4 displays the transmittance dependence of three currently investigated molecules. But the need for highpower U.V. coherent sources is felt in many areas, especially in connection with laser fusion research. Up to now, the crystals used have been KDP or other isomorphous derivatives. However, they may be rivalled by urea which is transparent up to 200 nm and displays

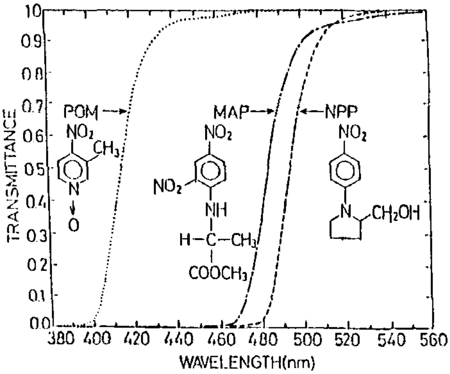


FIGURE 4. UV absorption edge in solution of highly nonlinear organic compounds

higher nonlinearities[15]. Practical applications require the growth of larger high quality crystals, so as to allow for the defocusing of high power laser beams below the damage threshold power density, which presently limits the actual implementation of urea in high power laser systems.

5. Steric reduction of the optically non active part of the molecule

The origin of the NLO phenomena is localized within the π system and CT region. Any other portion of the molecular system will "dilute" the active part, although it may, as such, favourably influence from another point of view the overall performance of the material. Examples of such situations are chiral radicals leading to non-centrosymmetry, intermolecular H-bonding groups to increase the cohesion, hydrophobic or mesogenic features for Langmuir-Blodgett or nematic ordering.

6. Chemical Stability

This obvious requirement acquires a special importance in view of the possibly long time exposure to laser light experienced by devices. Chemical stability during the crystal growth process is also required, especially in melt growth methods where degradations are likely. Even when low concentrations of impurities are present and a very small part of the material altered, this may lead to a catastrophic degradation of the overall crystalline quality.

B. CRYSTAL STRUCTURE CRITERIA

The term structure recovers several concepts at different levels basically :

- Symmetry Features, such as crystal system, point group, space group.

- Molecular Arrangement within the Unit Cell (packing) : for a given space group, the molecules are located and oriented within the unit cell so as to minimize the free-energy of the whole system. Clearly, the NLO coefficients essentially depend on the mutual orientation of the molecules.
- Molecular Structure : if the molecule is totally rigid "by construction", as, for instance, in m-dinitrobenzene, the molecular structure in the crystal does not significantly differ from that in solution or gas. However, if free rotation is possible, significant modifications of the molecular characteristics may result therefrom.

We will here emphasize different crystal structure related considerations which are of relevance towards NLO.

1. The Chirality Concept

Among the symmetry elements intervening in the point (and space) group, the center of inversion or center of symmetry plays a pivotal role. Indeed, its absence is an absolute prerequisite for nonlinear effects. Thus, we have been led to examine systematically the relationships between molecular and crystalline symmetry. In order to clarify these relations, the following new notation will be used. Small letters will represent molecular point group types, capital letters crystal point group types.

Type a (or A) denotes the presence of direct rotation axes only. In other words a represents the ensemble of homochiral molecules and A the ensemble of proper point groups (examples : 2, 222)

Type m (or M) denotes the presence of mirrors (plane of symmetry) or inverse 4 rotation and, eventually, the presence of direct rotation axis (examples : m, mm2, $\bar{4}2m$). This ensemble is that of non-chiral groups which do not comprise an inversion center among their elements.

Type i (or I) characterises the presence of an inversion center among the group elements, and eventually, any other element (example : $\bar{1}$, mmm). Special reference should be made to the case of a racemic crystal (obtained from a 50% - 50% mixture in solution). The molecular level symmetry type should be symbolized by $a_R + a_S$, the crystal symmetry is generally of type M or I, but A cannot be excluded per se. We note that this classification encompasses the 32 crystallotraphic point groups. First, the eleven proper (chiral) groups are numbered, then eleven new groups are obtained by simply introducing an inversion center to the element of each proper group. Finally, the ten other groups are obtained from the proper groups by a more involved process, starting from the ten subgroups of index 2 (subgroup of order equal to half the order of the group). Note that the odd-order groups 1 and 3 have no subgroup, while, on the other hand, groups 422 and 622 each have two distinct subgroups of index 2. Table III[16] results from the inspection of 8789 structures, both organic and inorganic. In parenthesis is the number of structures which are found in a given group. Such statistics have recently been updated[17]. They quantify the well known tendancy of organics to gather in low symmetry monoclinic or orthorhombic space groups such as $P2_1/c$, $P\bar{1}$, $P2_12_12_1$ and $P2_1$, while inorganic compounds have a pronounced tendancy to crystallize in highly symmetric groups of the cubic, orthorhombic and hexagonal classes. This gives a "statistical" advantage to organic structures for nonlinear applications as can be seen from inspection of Table II as already mentionned at the end of section II.

This is a purely mathematical classification ; the physical implication, at the crystalline level, is simply that both

TABLE III. Construction of the 32 crystal Point Groups and their classification in A,M,I classes. The first number in parenthesis is the total number observed of structures, the second, that of organic structures according to 1966 statistics[16].

Proper Groups		Sub-Groups of Index 2	Improper Groups			
G_p	A		$\overline{G_i}$ or M		G_i or I	
C_1 (41,35)	1				C_i (249, 152)	$\bar{1}$
C_2 (367, 325)	2	C_1	C_s (70,38)	m	$C_{2h}=C_i\times C_2$ (1908, 1203)	$\frac{2}{m}$
$D_2=C_2\times C'_2$ (596, 510)	222	C_2	$C_{2v}=C_2\times C'_s$ (226,127)	2mm	$D_{2h}=C_i\times(C_2\times C'_2)$ (1158, 323)	mmm
C_3 (25, 13)	3				$C_{3i}=C_i\times C_3$ (152, 38)	$\bar{3}$
$D_3=C_3\times C'_2$ (72, 10)	32	C_3	$C_{3v}=C_3\times C'_s$ (106,37)	3m	$D_{3d}=C_{3i}\times C'_2$ (444, 29)	$\bar{3}m$
C_4 (17, 12)	4	C_2	S_4 (47,17)	$\bar{4}$	$C_{4h}=C_i\times C_4$ (135, 38)	$\frac{4}{m}$
$D_4=C_4\times C'_2$ (68, 43)	427	C_4	$C_{4v}=C_4C'_s$ (14,6)	4mm	$D_{4h}=C_i\times C_4\times C'_2$ (579, 59)	$\frac{4}{m}mm$
		$C_2\times C'_2$	$V_d=S_4\times C'_2$ (107,29)	$\bar{4}2m$		
C_6 (18, 9)	6	C_3	C_{3h} (1)	$\bar{6}$	$C_{6h}=C_i\times C_6$ (97, 15)	$\frac{6}{m}$
$D_6=C_6\times C'_2$ (52, 14)	622	C_6	$C_{6v}=C_6\times C'_s$ (80,6)	6mm	$D_{6h}=C_i\times(C_6\times C'_2)$ (355, 8)	$\frac{6}{m}mm$
		$C_3\times C'_2$	$D_{3h}=C_{3h}\times C'_2$ (42,4)	$\bar{6}2m$		
$T=C_3\times(C_2\times C'_2)$ (87, 15)	23				$T_h=C'_{3i}\times(C_2\times C'_2)$ (212, 15)	m3
$O=C'_3\times(C_4\times C''_2)$ (21, 9)	432	$C'_3\times(C_2\times C''_2)$	$T_d=C'_3\times(S_4\times C''_2)$ (219,16)	$\bar{4}3m$	$O_h=C'_{3i}\times(C_4\times C''_2)$ (1223, 62)	m3m

A and M groups are compatible with 2nd order NLO effects. This naturally leads to a thorough examination of the molecular symmetry (as defined above, i.e. a,m,i) and its implications for crystal symmetry (A,M,I) characteristics. Clearly, if some sort of correlation shows up this will serve as useful molecular guidelines for the synthetic chemist. But the only certain correlation, i.e. the only implication is :

$$a \Rightarrow A$$

This has been the basis of the "chirality concept" in NLO[14,18]

Indeed, the introduction of a chiral group into a molecule is readily achieved in chemistry. The above implication then ensures that the corresponding crystal is non centrosymmetrical. We recall that two chirality patterns are distinguished in chemistry : presence of a central asymmetric atom (usually an asymmetric carbon) and of an inherently disymmetric group (helicenes are classical examples , but other groups such as substituted biphenyl or binaphthyl are well known). Up to now, only the influence of asymmetric carbon groups has been explored in NLO, as shown in section IV. But inherently dissymmetric groups may have the additional interest of not "diluting" the NLO active part by the additional inactive chiral radical. It would be preferable to induce the formation of noncentrosymmetrical crystals without necessarily resorting to the introduction of a chiral group of either kind into the molecule. But any implication other than $a \twoheadrightarrow A$ is not geometrically valid, and one can only invoke statistical inference.

2. Statistical Inference for Lack of Inversion Center

If the $a \twoheadrightarrow A$ implication is the only strict relation between molecular and crystal symmetry, it remains possible to infer relationships which retain some statistical validity. Such relationships pertain (a) to pure symmetry considerations (examples : statistics on crystallization from racemic mixtures[19], (b) to preferential behaviour upon crystallization of certain chemical families (for instance, meta-disubstituted benzenes exhibit a tendency towards M type symmetry).

3. Crystal Group Effect

The "hierarchy" of point groups shown in section I may also play an incitive role in materials research.

4. Optimization of the Molecular Orientation

It is a general fact that a priori considerations are of little use in inferring the crystal structure. However, the NLO coefficients geometrical dependence as exemplified in Fig.2 may well incite new research work on intermolecular interactions and preferential packing for specific chemical families.

C. CRYSTAL GROWTH AND CRYSTAL QUALITY CRITERIA

Several types of characteristics are included in this section.

1. Crystal Dimensions. The importance of the crystal dimensions may be illustrated as follows. In nuclear fusion experiments, where laser beams are focused on the target, it has been demonstrated that the yield is increased by using up converted UV radiation rather than the primary IR laser beam. A large surface high power UV beam is obtained by successive harmonic generations in a KDP crystal approaching 1 m^2 in surface. The device consists in fact in the accurately parallel juxtaposition of several KDP crystals with transverse dimensions of the order of 30-40cm. On the other hand, urea displays equal or perhaps better NLO intrinsic characteristics and is still transparent in the UV, but good quality single crystals obtained up to now do not exceed a few cubic centimeters. The crystal growth description of NLO materials would rightfully deserve a paper of its own. If this is really the bottle-neck for large scale NLO materials, it is certainly desirable to take into account possible crystal growth related parameters at the design level of new molecular materials for NLO. However, for telecommunication devices, and especially in "integrated optics", the necessary dimensions are relatively small, which makes the growth problem less

critical but requires higher nonlinearity.

2. Optical Quality. Growing large crystals is naturally connected with their quality which can be impaired by two kinds of defects : bulk or surface defects. We meet again here the general field of crystal growth which is not the purpose of this paper.

3. Optical Damage Threshold. This feature surprisingly stands out as a potential asset in the domain. Indeed, the optical damage threshold for organic crystals is higher than that of mineral crystals. This could be ascribed to the weaker cohesion forces involved in molecular crystals, allowing thus for easier heat relaxation, through vibrational modes, after the laser energy impact.

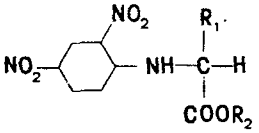
In summary, for bulk crystal applications, dimension is the principal prerequisite while for thin layer devices, it is the high value of $\chi^{(2)}$. In both cases, ultimate crystalline quality is required.

IV - EXAMPLE OF NLO MATERIALS

1. MAP (methyl-(2,4-dinitrophenyl)-aminopropanoate) AND THE CHIRALITY CONCEPT

The principle of this category of NLO materials consists in associating, within the same molecule, a NLO active part and a chiral radical. Then the resulting crystal is non centrosymmetrical in general, the only exceptions are the crystals displaying rotational or statistical disorder. However, a statistical survey of molecular crystal symmetry relations has shown that this case is very rare.

A convenient source of chiral radicals is encountered in natural substances : usually aminoacids and sugars. Their



R_1 \ R_2	H	CH_3	C_2H_5	$CH[CH_3]_2$
CH_3	225	1500	3000	100
$CH[CH_3]_2$	5	450		2500
$CH-CH_2-[CH_3]_2$	210			

$I_{2\omega}(X) \ / \ I_{2\omega}(SiO_2)$

FIGURE 5. SHG-Powder test results (versus SiO_2) for a series of chiral 2-4 dinitroaniline analogs (MAP corresponds to $R_1=R_2=CH_3$)

optical purity may reach 100%, as a result of rigorous natural selection (the living organisms possess specific enzymes which systematically destroy the D-aminoacids!). Marriage between the well known NLO active dinitrophenyl radical, and the natural L(+)-- alanine radical, results in the MAP molecule. Optimization with respect to the choice of the chiral radical is displayed in Fig.5, with $R_1=R_2=CH_3$. An indication of the NLO efficiency is given in this Figure. However, crystal growth problems possibly partially accounted for by racemization during the process, have not yet qualified this material for practical applications, despite a considerable improvement over the past years.

2. PYRIDINOXYDE DERIVATIVES (POM,3-methyl-4-nitropyridine-1-oxyde) AND THE VANISHING DIPOLE MOMENT CONCEPT

The remarkable mesomeric and charge transfer properties of this heteroatomic aromatic family have been the object of an early research work[20]. A recent prospective work has pointed out a new relevant fact of general importance : the vanishing dipole moment of the molecule is a favourable factor in the manifestation of the overall crystal NLO effect. Indeed, the dipole moment electrostatic interaction generally governs the crystal packing and tends to orient the molecular dipoles in opposite directions, thus favouring centrosymmetrical lattices. This and other considerations[21,22] pointed out the relevance of POM crystals (NLO efficiency about 14 times "KDP"). An interesting feature is the presence of the methyl group leading to an A class point group (222), whereas the p-nitropyridinoxyde crystal belongs to centrosymmetrical I class group. (short notation m/I for p-nitropyridinoxyde ; m/A for POM). Crystals of several cm^3 of good quality have been obtained and this material has recently successfully performed as a single-pass picosecond parametric emitter[23].

3. CHIRALITY AND HYDROGEN BONDING : NPP (N-(4-nitrophenyl)-L-prolinol)

NPP exemplifies an optimal structure as can be derived from Table II. Its structure[24] actually coincides with the theoretical optimal molecular orientations in a $P2_1$ unit cell. The angle between molecular dipoles and the two-fold axis is 58°6 which comes close to θ_o maximizing the $\cos\theta.\sin^2\theta$ factor relating the molecular hyperpolarizability to the crystalline d_{21} susceptibility, i.e. θ_o=54°7. The conjugated part of the molecule is quasi-planar and ideally contains the crystalline two-fold axis. The resulting structure is lamellar with strong intermolecular intraplanar hydrogen bonding coupling the acceptor nitro group's oxygens to the prolinol substituent alcohol function. The ideal crystal/laser beam phase-matched nonlinear interaction geometry is reached when the wave vectors are orthogonal to the molecular planes, the fundamental and harmonic waves being respectively perpendicular and parallel to the two-fold axis. Such a configuration promotes, without any costly projection factor, the optimized d_{21} coefficient (in addition, it is non critical as the wave-vectors direction coincide with a principal dielectric axis). Highly efficient second harmonic generation has just been observed in this geometry at a fundamental wavelength of 1.15 µm.

Owing to space constraints,we have arbitrarily restricted this brief account to CNET developed crystals. Other worthwhile structures deserve reference such as : MNA (3-methyl-4-nitroaniline)[25]; PNP(2-(N-prolinol)-5-nitropyridine)[26]; various urea derivatives, for example N-N' dimethylurea[27], MBA-NP[28].

In conclusion, it now appears that an important part of the molecular crystal engineering approach pertains to questions of symmetry, both in Chemistry and in Optics. Let us recall that Pasteur's fundamental breakthrough, in 1848, was to conjecture the "implication" :

$$A_R \longrightarrow a_R \tag{15}$$

$$A_S \longrightarrow a_S \tag{16}$$

where the left hand side symbols stand for the simultaneous observation for the same chemical species of mirror related macroscopic crystals. He could then infer a microscopic reality, i.e. asymmetric carbon, from a macroscopic symmetry observation. Here we particularly discussed the much simpler if not trivial, reverse implication : a ⟶ A . The application of this geometrically certain implication together with that of statistical correlations between molecular and crystalline symmetry types can be fruitfully used to provide synthesis guidelines towards nonlinear optics.

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