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Engineering of non-linear optical crystals displaying a quasi perfect polar alignment of chromophores

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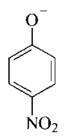
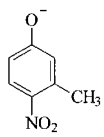
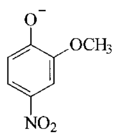
Four non-linear optically active crystals based on organic salts obtained by bis-protonation of four diamines (*trans*-(±)-1,2-, *trans*-(1*R*,2*R*)-(−)-, *cis*-1,2-diaminocyclohexane or *R*-(−)-2-methylpiperazine) by 2-methoxy-4-nitrophenol have been prepared. Their crystal structures and non-linear optical efficiencies have been studied. The two adjacent proton acceptor sites in 1,2-diaminocyclohexanes play an important role in aligning the 2-methoxy-4-nitrophenolate chromophores in a quasi-perfect polar arrangement by anchoring through short hydrogen bonds. In the case of the methylpiperazinium derivative the symmetrical 1,4 location of proton acceptor sites directs the chromophores to near antiparallel alignment by forming short hydrogen bonds. The second harmonic generation efficiencies at 1.064 μm of Nd^{3+} : YAG laser light are equivalent to that of POM (3-methyl-4-nitropyridine-1-oxide) for the three diammoniocyclohexane derivatives and equivalent to twice that of urea for the methylpiperazinium derivative.

Introduction

Organic materials based on hyperpolarisable chromophores have been proposed for quadratic non-linear ($\chi^{(2)}$-NLO) applications such as frequency conversion or electro-optical modulation.[1] Single crystals, poled polymers, Langmuir–Blodgett films and liquid crystals are the most commonly encountered material engineering routes for this kind of materials.[2] There is still an interest in the engineering of crystalline materials with satisfactory properties, not only for second harmonic generation (SHG), but also for parametric interactions (as the one used in an optical parametric oscillator, OPO) or electrooptical modulation.[3] Several efficient inorganic, organic and organomineral NLO crystals have been proposed in recent years, some of these have even reached a high level of development. However several problems concerning the overall quality of these materials remain to be solved, and more research is needed to improve their optical as well as mechanical properties. First of all, to get efficient $\chi^{(2)}$-NLO effects in a single crystal, one needs to achieve an optimised non-centrosymmetric assembly of the NLO chromophores. Ideally the NLO chromophores should self assemble in a non-centrosymmetric structure in such a way that a complete additive contribution of the individual β_{ijk} values results in high macroscopic tensor components of $\chi^{(2)}$. This route is still not predictive since we cannot calculate with sufficient accuracy the actual crystal structure of a new crystalline material; one meets success only after several trials and errors. However some crystal engineering rules have now emerged from studies in our own laboratories[4] and many others.[5,6] Secondly one needs to improve many other properties such as mechanical behaviour (robustness), optical damage threshold (thermal conductivity) or linear optical properties (refractive indices, birefringence). Generally, purely organic compounds in which van der Waals interactions dominate lack sufficient mechanical strength for practical uses. That is why we have developed recently a crystal engineering strategy based essentially on ionic interactions, with the aim of getting more cohesive crystalline structures. In this context we have investigated the use of the 4-nitrophenolate anion for building new NLO crystals. The use of 4-nitrophenolate itself or substituted entities has been justified in previous studies from the point of view of their remarkable hyperpolarisabilities and their easy anchorage onto host organic[7] or inorganic networks.[8] The 4-nitrophenol derivatives are weak acids. The proton loss induces a conjugate base with an electron-donating group O^- ($\sigma = -0.81$)[9] stronger than that of the hydroxy group OH ($\sigma = -0.38$),[10] as we can see from the respective Hammett σ coefficients. In these anions there is a strong charge transfer (CT) from the donor oxygen O^- towards the acceptor nitro group in the *para* position. Then the molecular hyperpolarisability β_{CT} along the O^-–NO_2 charge transfer axis is increased with respect to the original 4-nitrophenol. Only the molecular tensor component β_{CT} is taken into account here since even when the phenyl ring is substituted by other groups, the charge transfer $O^- \Rightarrow NO_2$ remains the strongest electronic effect so that these chromophores can be considered as unidimensional in a first approximation. The already reported calculated β_{CT} values (approximately β_{xxx} if x is along the charge transfer axis) are respectively 18.2×10^{-30} esu for 4-nitrophenolate,[7a] 17.4×10^{-30} esu for 3-methyl-4-nitrophenolate.[8d] For the new NLO chromophore 2-methoxy-4-nitrophenol (also called 4-nitroguaiacol) used here, the β_{xxx}, calculated on the optimised structures using semi-empirical AM1 parameters and the finite field method available in MOPAC 6, increases from 6.0×10^{-30} to 20.2×10^{-30} esu upon the removal of proton (Table 1). The 4-nitrophenolate anions have the capability to form Me–O bonds or hydrogen bonds with their three H-acceptor sites. Then several classes of crystalline NLO materials could be considered with this chromophore: organic salts having a metal cation (1) or an organic cation (2) (functionalized or chiral) and organometallic crystals containing a metal cation,

Table 1 Calculated values of molecular hyperpolarisabilities β_{xxx} for three 4-nitrophenolate NLO chromophores (in 10^{-30} esu)

4-Nitrophenolate NLO chromophore			
$\beta_{xxx}(10^{-30}$ esu)	18.2	17.4	20.2

the 4-nitrophenolate and a ligand (3). Materials illustrating the class (1) are sodium 4-nitrophenolate dihydrate (Ima2),[8a] sodium 3-methyl-4-nitrophenolate dihydrate (Cc)[8d] and magnesium 4-nitrophenolate dihydrate (C2)[11] with a herringbone arrangement of chromophores. The class (2) is represented by the efficient crystal, 4-dimethylaminopyridinium/4-nitrophenolate/4-nitrophenol ($P2_12_12_1$).[7a] To our knowledge materials obtained from the class (3) route have not yet been reported. In the present paper we report on the synthesis and study of a series of crystals belonging to the class (2), utilising optically pure chiral cations to favour the non-centrosymmetric packing of chromophores. The optically pure chiral cations are the bisammonium ones obtained by protonation of *trans*-(1*R*,2*R*)-(−)-diaminocyclohexane and *R*-(−)-2-methylpiperazine. For comparison the analogous crystalline salts from optically inactive *cis*-1,2-diaminocyclohexane and racemic *trans*-1,2-diaminocyclohexane have also been prepared. Such amines favour the anchorage of 2-methoxy-4-nitrophenolate chromophores through short hydrogen bonds. Four non-centrosymmetric crystals showing a non-linear quadratic efficiency were studied. Three crystal structures among the four reveal a quasi-perfect polar alignment of chromophores.

Experimental

The four diammonio-2-methoxy-4-nitrophenolate salts have been prepared by dissolving 10^{-3} mole of respective *trans*-(±)-1,2-, *trans*-(1*R*,2*R*)-(−)-, *cis*-1,2-diaminocyclohexane or *R*-(−)-2-methylpiperazine and 2×10^{-3} mole of 2-methoxy-4-nitrophenol in 20 cm^3 of water. The solutions were stirred at 50 °C for 1 h. The so formed yellow solutions were filtered then slowly evaporated in air during a week yielding yellow crystals of good quality. Such crystals can be grown up to $10\times5\times5$ mm^3 in size. The crystals were characterised by elemental analysis, thermal analysis (SETARAM, TG92), X-ray diffraction (Nonius CAD4) and second harmonic generation measurements by the Kurtz and Perry powder test.[12]

Results and discussion

Chemical analysis

The same chemical composition is found for all three phases of 1,2-diammoniocyclohexane derivatives as confirmed both by the elemental analyses and the X-ray crystal structure determinations. The elemental analysis of freshly prepared crystals confirms the chemical composition as $C_6H_{16}N_2^{+2}\cdot(C_7H_6O_4N^-)_2\cdot3H_2O$ (Calculated: C=47.43%, H=6.72%, N=11.07%, O=34.78%; Observed for racemic *trans*-1,2-diammoniocyclohexane derivative (crystal (I)) : C=47.53%, H=6.71%, N=11.12%, O=34.35%; for *trans*-(1*R*,2*R*)-(−)-diammoniocyclohexane derivative (crystal (II)): C=47.51%, H=6.75%, N=11.08%, O=34.28%; for *cis*-1,2-diammoniocyclohexane derivative (crystal (III)): C=47.59%, H=6.75%, N=11.14%, O=33.02%). The chemical composition of (*R*)-(−)-2-methylpiperazine derivative (crystal (IV)) was found to be $C_5H_{14}N_2^{+2}\cdot(C_7H_6O_4N^-)_2\cdot2H_2O$, as confirmed both by elemental analysis and X-ray structure determination (Calculated: C=48.10%, H=6.33%, N=11.81% and O=33.76%; Observed: C=47.98%, H=6.25%, N=11.76%, O=33.64%).

Thermal stability

The *trans*-1,2-diammoniocyclohexane derivatives (crystals (I) and (II)) are stable at ambient temperature and pressure indefinitely whereas the *cis*-1,2-diammoniocyclohexane derivative (crystal (III)) slowly loses water molecules after a few days and becomes yellow opaque powder. The TG-DTA experiments show that crystals (I) and (II) lose water molecules around 100 °C and melt at 168 °C and 146 °C respectively. After the loss of water molecules at room temperature the dehydrated crystal (III) melts at 149 °C and decomposes above 160 °C. Crystal (IV) loses one molecule of water around 100 °C, melts at 131 °C and decomposes above 160 °C.

X-Ray diffraction

The space groups and cell parameters were determined using an Enraf-Nonius CAD-4 four-circle diffractometer with MoKα radiation. Diffracted intensities were corrected for Lorentz and polarisation factors. No absorption correction was applied due to favourable crystal geometry and a low absorption coefficient in each case. The crystal data, details of the diffracted intensity measurements and refinement conditions for crystals (I), (II) and (IV) are summarised in Table 2. The respective space groups were confirmed by the diffraction limiting conditions associated to the second harmonic signal

Table 2 Crystal data, intensity measurements and structural refinement parameters

Formula	$C_{20}H_{34}O_{11}N_4$ (I)	$C_{20}H_{34}O_{11}N_4$ (II)	$C_{19}H_{30}O_{10}N_4$ (IV)
Molecular weight	506.51	506.51	474.47
Space group	*Cc*	*P*1	*P*2$_1$
a/Å	24.350(6)	6.935(1)	9.156(1)
b	6.938(1)	8.223(1)	11.250(1)
c	16.271(3)	11.596(1)	12.487(2)
α, β, γ (°)	90, 114.69(2), 90	101.81(1), 101.65(1), 99.01(1)	90, 111.26(2), 90
V/Å^3	2497.4(9)	620.3(1)	1198.8(3)
Z, D_x/g cm^{-3}	4, 1.347	1, 1.356	2, 1.314
μ/cm^{-1} λ(MoKα)	1.100	1.110	1.070
Temperature/°K	296	296	296
Radiation/Å	0.7107 (MoKα)	0.7107 (MoKα)	0.7107 (MoKα)
Monochromator	graphite (220)		
Bragg angle limits (°)	3–30	3–33	3–35
Reflections collected	7834	4636	5434
Unique data	1389 ($R_{int}=0.028$)	3650 ($R_{int}=0.009$)	2783 ($R_{int}=0.02$)
Data in refinement	1389, $I>3\sigma(I)$	3650, $I>3\sigma(I)$	2783, $I>3\sigma(I)$
Refined parameters	351	361	321
R, R_w	0.033, 0.039	0.038, 0.038	0.043, 0.054
Weighting scheme	$w=1/[\sigma^2(F_o)+0.0002F_o^2]$	$w=1/[\sigma^2(F_o)+0.0001F_o^2]$	$w=1/[\sigma^2(F_o)+0.0002F_o^2]$

Table 3 Intramolecular distances for crystal (I), $C_{20}H_{34}O_{11}N_4$

Distances/Å (esd's in parentheses)

O1	C14	1.289(6)	C1	C2	1.509(9)
O2	N3	1.238(6)	C1	C6	1.528(7)
O3	N3	1.211(6)	C2	C3	1.48(1)
O4	C19	1.379(5)	C3	C4	1.517(8)
O4	C20	1.426(7)	C4	C5	1.545(7)
O5	C7	1.309(5)	C5	C6	1.505(7)
O6	N4	1.229(6)	C7	C8	1.393(6)
O7	N4	1.234(6)	C7	C12	1.432(6)
O8	C12	1.368(5)	C8	C9	1.367(7)
O8	C13	1.426(6)	C9	C10	1.378(7)
N1	C5	1.499(6)	C10	C11	1.395(7)
N1	H7	0.88(5)	C11	C12	1.365(7)
N1	H8	0.91(5)	C14	C15	1.403(6)
N1	H9	1.02(5)	C14	C19	1.419(6)
N2	C6	1.498(6)	C15	C16	1.376(7)
N2	H10	0.91(5)	C16	C17	1.365(7)
N2	H11	0.82(5)	C17	C18	1.400(7)
N2	H12	0.96(5)	C18	C19	1.349(7)
N3	C17	1.447(7)	N4	C10	1.431(6)

Intramolecular bond angles (°)

C19	O4	C20	116.8(4)	C9	C8	C7	122.4(4)
C12	O8	C13	117.8(4)	C8	C9	C10	118.9(4)
O3	N3	O2	123.3(5)	C9	C10	C11	121.9(4)
O3	N3	C17	118.9(5)	C9	C10	N4	119.0(4)
O2	N3	C17	117.8(6)	C11	C10	N4	119.1(4)
O6	N4	O7	121.2(5)	C12	C11	C10	118.4(4)
O6	N4	C10	119.4(5)	C11	C12	O8	125.1(4)
O7	N4	C10	119.4(5)	C11	C12	C7	121.7(4)
C2	C1	C6	110.7(5)	O8	C12	C7	113.2(4)
C3	C2	C1	111.6(6)	O1	C14	C15	122.0(4)
C2	C3	C4	111.1(5)	O1	C14	C19	121.7(4)
C3	C4	C5	111.6(5)	C15	C14	C19	116.3(4)
N1	C5	C6	111.2(4)	C16	C15	C14	122.5(5)
N1	C5	C4	106.1(4)	C17	C16	C15	118.3(4)
C6	C5	C4	111.4(4)	C16	C17	C18	121.9(4)
N2	C6	C5	111.5(4)	C16	C17	N3	119.0(5)
N2	C6	C1	108.2(4)	C18	C17	N3	119.1(5)
C5	C6	C1	111.4(4)	C19	C18	C17	118.9(4)
O5	C7	C8	123.2(4)	C18	C19	O4	125.4(4)
O5	C7	C12	120.2(4)	C18	C19	C14	122.1(4)
C8	C7	C12	116.7(4)	O4	C19	C14	112.6(4)

based on the Kurtz and Perry powder test:[12] crystal (I), *hkl* with $h+k=2n$, $h01$ with $l=2n$, symmetry *Cc*; crystal (II), *hkl* without conditions, symmetry *P*1; crystal (III), *hkl* without conditions, symmetry *P*1; crystal (IV), only $0k0$ with $k=2n$, symmetry $P2_1$. The structures were solved by direct methods using the SIR 92 program.[13] Full matrix least-squares refinements were performed on F with teXsan software.[14] Scattering factors for neutral atoms and f', $\Delta f'$, f'', $\Delta f''$ were taken from *International Tables for X-ray Crystallography*.[15] The crystal structures were drawn using the ORTEP program[16] included in teXsan software and the MOLVIEW program.[17] The main interatomic distances and bond angles are described in Tables 3–8. Final atomic parameters, anisotropic thermal factors and isotropic for H atoms and a list of observed and calculated structure factors are available as deposited materials.†

Structure description

The structures of crystals (I) and (II) display a quasi-polar alignment of two independent 2-methoxy-4-nitrophenolate anions (Fig. 1–4). In crystal (I) the angle between the charge transfer axes of the two anions is (N3–O1, N4–O5) = 13.6°. The anion planes are almost perpendicular to the *b* axis, a situation which induces a great crystal anisotropy. The three-dimensional alternated distribution of the two enantiomeric cations *trans*-(1*R*,2*R*)- and *trans*-(1*S*,2*S*)-diammoniocyclohexane due to the effect of both the glide mirror *c* and $a/2+b/2$ network translation frames a racemic crystal. The chromophore alignment is mainly induced by the adjacent chiral carbon atoms C5, C6 onto which the ammonium groups are fixed: two pairs of short hydrogen bonds originating from N1 and N2 atoms anchor the anions onto the enantiomeric cations (Table 4). An aggregate of three water molecules connected between them forms a H-bond network with the CO and nitro groups. The atoms O4, O8 of methoxy groups are not involved in H-contacts. Except for the three-centre H-bond O9–H5···O6,O7 between a water molecule and a nitro group

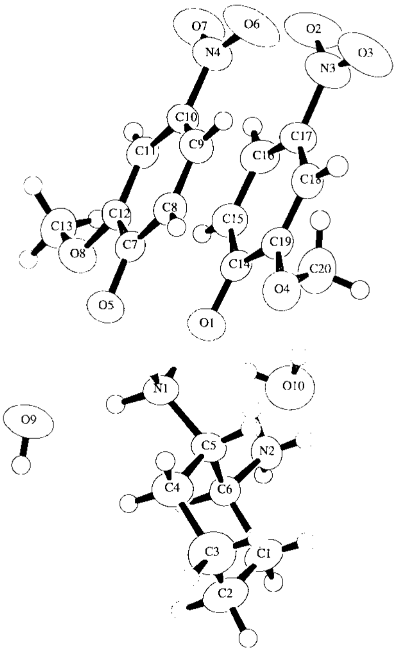


Fig. 1 Motif in racemic crystal (I). Atomic numbering scheme and thermal ellipsoids drawn at 50% probability.

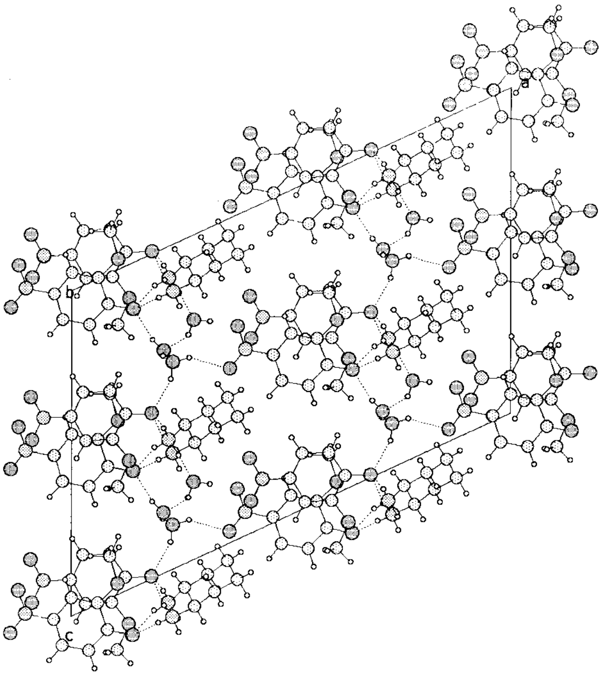


Fig. 2 Projection in (*a*,*c*) plane of crystal (I) structure. H-bond network is detailed.

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† CCDC reference number 1145/163. See http://www.rsc.org/suppdata/jm/1999/2233 for crystallographic files in .cif format

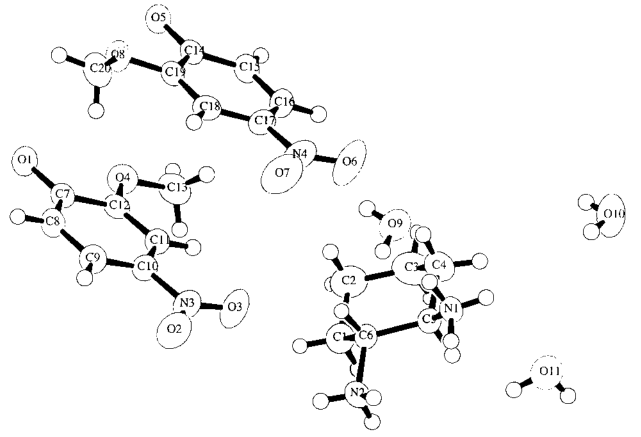

Fig. 3 Motif in enantiomeric crystal (II). Atomic numbering scheme and thermal ellipsoids drawn at 50% probability.

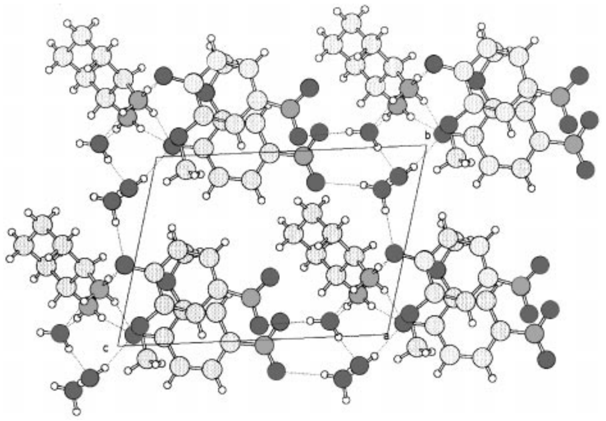

Fig. 4 Projection following the *a* direction of crystal (II) structure of *P*1 symmetry. H-bond network is evidenced.

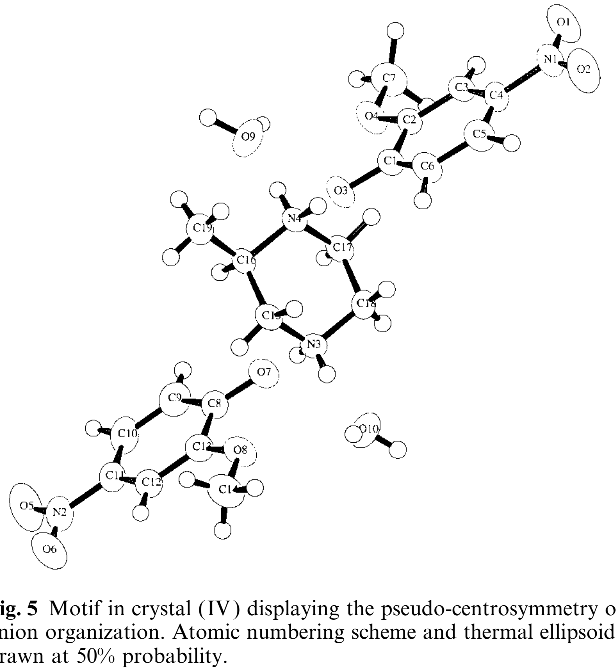

Fig. 5 Motif in crystal (IV) displaying the pseudo-centrosymmetry of anion organization. Atomic numbering scheme and thermal ellipsoids drawn at 50% probability.

Table 4 Hydrogen bonds for crystal (I), $C_{20}H_{34}O_{11}N_4$

D······	H······	A	D···A	D–H	H···A	D–H···A
O9	H6	O10	2.815(8)	0.93(7)	2.00(7)	145.0(5)
O10	H1	O11	2.850(9)	0.88(7)	2.01(7)	161.4(7)
O10	H2	O1	2.761(6)	0.82(7)	1.96(7)	168.4(7)
O11	H3	O5	2.786(6)	0.87(7)	1.97(7)	155.3(6)
O11	H4	O2	2.896(6)	0.87(7)	2.13(7)	146.6(6)
N1	H7	O1	2.719(6)	0.88(5)	1.87(6)	162.4(4)
N1	H8	O5	2.841(6)	0.91(5)	1.95(6)	163.3(4)
N1	H9	O9	2.863(7)	1.02(5)	1.85(6)	174.1(4)
N2	H10	O1	2.792(6)	0.91(5)	1.90(6)	168.3(5)
N2	H11	O5	2.797(6)	0.82(5)	1.99(6)	167.1(5)
O9	H5	O6	3.106(8)	0.86(7)	2.38(7)	141.2(5)
O9	H5	O7	3.108(8)	0.86(7)	2.26(7)	162.9(7)

a great homogeneity of hydrogen bond distances is observed in this structure (Table 4).

The structure of crystal (II) built-up from the optically pure cation *trans*-(1*R*,2*R*)-diammoniocyclohexane shows remarkable similarities with that of the racemic crystal (I). The alignment of the anionic chromophores (Fig. 4) is likewise directed by two pairs of H-bonds originating from the ammonium groups grafted on adjacent carbon atoms C5, C6. The anion planes are parallel and the angle between the charge transfer axes N3–O1, N4–O5 is about 10.1°. The anions are aligned as well as in the structure of racemic crystal. O4 and O8 atoms of the respective methoxy groups are not involved in H-contacts. Three water molecules self aggregated through H-contacts are also connected to oxygen atoms of the CO and nitro groups. A three-centre H-bond O9–H30···O6,O7 is established between a water molecule and a nitro group. The homogeneity of H-bond distances, *i.e.* equivalence in energy, is the main feature of this packing as it is that of racemic crystal (Table 6). The crystal anisotropy is also noteworthy.

The structure of crystal (III) could not be solved accurately because of its instability at ambient conditions. It has been solved with a weighted reliability factor $R_w = 6.9\%$ using 1885 reflections and refining 331 parameters does not establish the precise location of hydrogen atoms of water molecules. The crystal structure should be reinvestigated at low temperature. However the quasi-perfect alignment of chromophores is seen without ambiguity in a *P*1 structure with the cell parameters: $a = 6.971(3)$, $b = 8.289(1)$, $c = 11.971(3)$ Å, $\alpha = 110.04(2)°$, $\beta = 95.46(3)°$, $\gamma = 100.61(2)°$, $Z = 1$.

The structure of crystal (IV) is strictly described with a $P2_1$ symmetry, which reflects the presence of the chiral cation (*R*)-2-methylpiperazinium. However if we scrutinise the atomic coordinates or Fig. 6 pseudo centres of symmetry are evidenced. The chromophore anions are connected to the (*R*)-2-methylpiperazinium through two short hydrogen bonds involving O3 and O7 atoms of CO groups (Table 8). These atoms are also hydrogen acceptors from water molecules so linking the anion layers. The oxygen atoms of the methoxy groups O4, O8 are involved in long hydrogen bonds: it was not the case in the previous structures. The pseudo-centrosymmetric arrangement of anions can be estimated through the angle between the charge transfer axes N2–O7, N1–O3 close to 177°. It would be 180° in an ideal centrosymmetric structure $P2_1/m$. This situation cancels the SHG signal of this crystal. Actually the opposite and symmetrical location of NH_2^+ groups in the cation and their ability to form strong hydrogen bonds control the anchorage of anions and water molecules onto it. The methyl group, linked to the chiral atom C16 with a weak stericity, unable to form strong H-bonds, cannot hinder the symmetric anchorage of anions onto the cation. This structure reveals once more the importance of the local symmetry and bond strengths to the packing symmetry of chromophores.

Non-linear optical efficiency

The structures built with the chromophore 2-methoxy-4-nitrophenolate associated to different chiral cations show without ambiguity that *trans*- and *cis*-1,2-diammoniocyclohexane are able to induce a quasi perfect alignment of chromophores. In crystal (I) of *Cc* symmetry the chromophore orientation is

Table 5 Intramolecular distances for crystal (II), $C_{20}H_{34}O_{11}N_4$

Distances/Å (esd's in parentheses)

O1	C7	1.297(2)	C1	C2	1.516(3)
O2	N3	1.230(2)	C1	C6	1.524(2)
O3	N3	1.227(2)	C2	C3	1.510(4)
O4	C12	1.368(2)	C3	C4	1.516(3)
O4	C13	1.422(3)	C4	C5	1.529(3)
O5	C14	1.307(2)	C5	C6	1.526(2)
O6	N4	1.232(3)	C7	C8	1.400(2)
O7	N4	1.217(3)	C7	C12	1.429(2)
O8	C19	1.368(2)	C8	C9	1.376(3)
O8	C20	1.423(2)	C9	C10	1.379(3)
O9	H29	0.84(3)	C10	C11	1.399(3)
O9	H30	0.84(4)	C11	C12	1.372(3)
O10	H31	0.92(4)	N2	C6	1.499(2)
O10	H32	0.83(4)	N2	H14	0.86(2)
O11	H33	0.89(4)	N2	H15	0.87(3)
O11	H34	0.78(3)	N2	H16	0.90(3)
N1	C5	1.491(2)	N3	C10	1.436(2)
N1	H11	0.86(2)	N4	C17	1.434(2)
N1	H12	0.90(2)	C14	C15	1.400(2)
N1	H13	0.90(2)	C14	C19	1.429(2)
C15	C16	1.376(3)	C16	C17	1.379(3)
C17	C18	1.399(3)	C18	C19	1.369(3)

Intramolecular bond angles (°)

C12	O4	C13	117.3(2)	O3	N3	O2	122.4(2)
C19	O8	C20	117.8(2)	C2	C1	C6	111.0(2)
C3	C2	C1	110.3(2)	C2	C3	C4	110.5(2)
O3	N3	C10	119.0(2)	O2	N3	C10	118.6(2)
O7	N4	O6	121.4(2)	C3	C4	C5	113.0(2)
O7	N4	C17	119.8(2)	O6	N4	C17	118.7(2)
N1	C5	C6	110.6(1)	N1	C5	C4	107.4(1)
C6	C5	C4	111.5(1)	N2	C6	C1	108.0(1)
N2	C6	C5	111.3(1)	O5	C14	C15	122.6(2)
C1	C6	C5	111.5(1)	O5	C14	C19	120.4(1)
O1	C7	C8	121.8(2)	C15	C14	C19	117.1(1)
O1	C7	C12	121.1(1)	C8	C7	C12	117.1(1)
C16	C15	C14	121.8(2)	C9	C8	C7	122.4(2)
C15	C16	C17	119.3(2)	C16	C17	C18	121.6(2)
C8	C9	C10	118.6(2)	C16	C17	N4	119.2(2)
C9	C10	C11	121.8(1)	C18	C17	N4	119.1(2)
C9	C10	N3	119.0(2)	C11	C10	N3	119.1(2)
C19	C18	C17	118.7(2)	O8	C19	C18	125.1(2)
C12	C11	C10	118.9(2)	O8	C19	C14	113.4(1)
O4	C12	C11	125.2(2)	C18	C19	C14	121.5(2)
O4	C12	C7	113.6(1)	C11	C12	C7	121.1(1)

Table 6 Hydrogen bonds for crystal (II), $C_{20}H_{34}O_{11}N_4$

D······H······A			D···A	D–H	H···A	D–H···A
O9	H29	O11	2.779(3)	0.84(4)	1.95(4)	167.5(3)
O10	H31	O5	2.775(3)	0.92(4)	1.86(4)	171.3(3)
O10	H32	O2	2.865(2)	0.82(4)	2.05(4)	167.5(3)
O11	H33	O10	2.774(3)	0.89(4)	1.90(4)	165.9(3)
O11	H34	O1	2.780(3)	0.78(4)	2.02(4)	166.5(3)
N1	H11	O5	2.819(2)	0.86(2)	1.98(2)	163.1(2)
N1	H12	O9	2.871(3)	0.90(2)	1.99(3)	164.7(2)
N1	H13	O1	2.690(2)	0.90(3)	1.82(3)	161.7(2)
N2	H14	O1	2.820(2)	0.86(3)	1.97(3)	165.9(2)
N2	H16	O5	2.797(2)	0.90(2)	1.90(3)	177.8(2)
O9	H30	O7	3.125(3)	0.84(4)	2.29(4)	113.7(3)
O9	H30	O6	3.169(3)	0.84(4)	2.16(4)	135.1(3)

not favourable to a high value of macroscopic hyperpolarisabilities $\chi^{(2)}$ if we consider a description of tensorial properties following the oriented gas model.[18] The optimal orientation of charge transfer axes of chromophores with respect to the *b* axis should be 35(26)° in point group *m*. For the two chromophore sub-networks the angles are respectively (N3–O1,*b*) = 87(4)° and (N4–O5,*b*) = 84°, far from the optimal angle. Such a situation is more favourable to high values of linear electrooptical coefficients of the r_{ij} tensor in the direction of alignment. The case of crystal (II) of *P*1 symmetry is distinct.

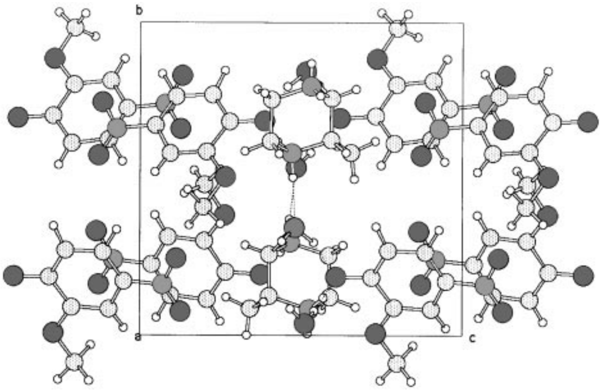

Fig. 6 View along the *a* direction of the complete packing in crystal (IV).

Table 7 Intramolecular distances in crystal (IV), $C_{19}H_{30}O_{10}N_4$

Distances/Å (esd's in parentheses)

O1	N1	1.215(5)	C1	C2	1.426(4)
O2	N1	1.239(4)	C1	C6	1.395(4)
O3	C1	1.314(3)	C2	C3	1.376(4)
O4	C2	1.356(3)	C3	C4	1.401(5)
O4	C7	1.430(4)	C4	C5	1.372(5)
O5	N2	1.228(5)	C5	C6	1.375(5)
O6	N2	1.240(5)	C8	C9	1.418(5)
O7	C8	1.307(3)	C8	C13	1.421(4)
O8	C13	1.379(4)	C9	C10	1.380(5)
O8	C14	1.418(5)	C10	C11	1.379(5)
N1	C4	1.451(3)	C11	C12	1.388(5)
N2	C11	1.435(4)	C12	C13	1.375(4)
N3	C15	1.474(5)	C15	C16	1.511(5)
N3	C18	1.482(4)	C16	C19	1.511(4)
N4	C16	1.504(3)	C17	C18	1.510(5)
N4	C17	1.494(4)			
O9	H21	0.85(5)	O9	H22	1.06(5)
O10	H24	0.85(5)	O10	H25	0.95(5)
N3	H13	0.83(4)	N3	H14	0.83(5)
N4	H15	1.07(4)	N4	H16	0.88(5)

Bond angles (°)

C2	O4	C7	117.2(2)	C4	C5	C6	118.5(3)
C13	O8	C14	116.5(2)	C5	C6	C1	122.3(3)
O1	N1	O2	122.2(3)	O7	C8	C9	122.8(3)
O1	N1	C4	120.7(3)	O7	C8	C13	120.5(3)
O2	N1	C4	117.0(4)	C9	C8	C13	116.7(3)
O5	N2	O6	122.2(3)	C10	C9	C8	121.3(3)
O5	N2	C11	118.9(4)	C11	C10	C9	119.3(3)
O6	N2	C11	118.9(3)	C10	C11	C12	122.0(3)
C15	N3	C18	111.5(2)	C10	C11	N2	119.5(3)
C17	N4	C16	111.9(2)	C12	C11	N2	118.5(4)
O3	C1	C6	123.2(3)	C13	C12	C11	118.5(3)
O3	C1	C2	119.5(3)	C12	C13	O8	124.3(3)
C6	C1	C2	117.3(2)	C12	C13	C8	122.1(3)
O4	C2	C3	124.5(3)	O8	C13	C8	113.5(2)
O4	C2	C1	114.1(2)	N3	C15	C16	111.5(3)
C3	C2	C1	121.3(3)	N4	C16	C19	108.9(2)
C2	C3	C4	118.0(3)	N4	C16	C15	108.6(2)
C5	C4	C3	122.5(3)	C19	C16	C15	112.2(3)
C5	C4	N1	120.4(3)	N4	C17	C18	109.7(3)
C3	C4	N1	117.0(3)	N3	C18	C17	110.2(3)

Applying the same interpretation by using the oriented gas model[18] only a non-linear macroscopic coefficient of tensor $\chi^{(2)}$ does not vanish $b_{xxx} = \beta_{xxx}$, x being the direction of crystal coinciding with the direction of molecular charge transfer *x* in the chromophore. However two sub-networks of chromophores have to be considered in this case with an orientation difference: (N3–O1, N4–O5) = 10(1)°. Then the macroscopic coefficient b_{xxx} will result from the contribution of molecular hyperpolarisabilities of the two sub-networks $\beta_{xxx}(1)$ and $\beta_{xxx}(2)$. In the case of *P*1 symmetry we can observe simul-

Table 8 Hydrogen bonds for crystal (IV), $C_{19}H_{30}O_{10}N_4$

D······	H······	A	D···A	D–H	H···A	D–H···A
O9	H21	O7	2.857(4)	0.85(5)	2.01(5)	169.7(4)
O9	H22	O3	2.691(3)	1.06(5)	1.66(5)	162.4(4)
O10	H24	O7	2.683(3)	0.85(5)	1.83(5)	174.7(5)
O10	H25	O3	2.883(4)	0.95(4)	1.95(5)	166.8(4)
N3	H13	O7	2.698(4)	0.83(4)	1.87(4)	177.0(4)
N3	H14	O10	2.727(4)	0.83(5)	1.90(5)	171.8(4)
N4	H15	O3	2.727(4)	1.07(4)	1.67(4)	166.9(3)
N4	H16	O9	2.724(4)	0.88(4)	1.86(4)	165.6(3)
N3	H13	O8	2.923(3)	0.83(4)	2.52(4)	110.7(3)
N4	H15	O4	2.914(3)	1.07(4)	2.35(4)	111.5(3)

taneously an optimal value of b_{xxx} coupled with an optimal value of linear electrooptical coefficient r_{ii} in the alignment direction. Phase-matching conditions could be realised with this $P1$ triclinic crystal. Moreover the chromophores comprise only 48.8% for crystal (I) and 49.24% for crystal (II) of the total unit cell volume and the rest are non-chromophoric cation and water molecules, which also disfavours the nonlinear efficiency of the crystal. Crystal (IV) shows poor SHG efficiency because of the near antiparallel arrangement of the two 2-methoxy-4-nitrophenolates, which is directed by the two symmetrically located proton acceptor sites in methylpiperazinium. The signal of second harmonic generation $I_{2\omega}$ observed for powder samples of crystals (I), (II), dehydrated crystal (III) and crystal (IV) can be correlated quantitatively with the signals of urea and 3-methyl-4-nitropyridine-1-oxide[19] (POM) standards in the same experimental conditions, illuminated by a Nd^{3+} : YAG laser at 1.064 μm.

$I_{2\omega}$ (urea) $<$ $I_{2\omega}$ (crystal (IV)) $<$ $I_{2\omega}$ (crystal (I)) $\approx$ $I_{2\omega}$ (crystal (II)) $\approx$ $I_{2\omega}$ (crystal (III)-dehydrated) $\approx$ $I_{2\omega}$ (POM).

Very few structures built with organic chromophores exhibit a pure one-dimensional arrangement: the merocyanine dye 2,4-dihydroxybenzaldehyde with $P1$ symmetry,[6c] 4-hydroxy-*N*-methylstilbazolium 4-toluenesulfonate ($P1$),[20] 4,4′-dimethylaminocyanobiphenyl ($P2_1$).[21] The 2-amino-5-nitropyridinium hydrogen L-tartrate with $P2_1$ symmetry displays a quasi-perfect polar orientation of chromophore cations.[22,4b,c] Since the quasi-perfect alignment of 2-methoxy-4-nitrophenolate entities in crystals (I), (II) and (III) is mainly controlled by the two adjacent chiral centres able to form strong H-bonds on the same side of the cation, it could be suggested: (a) to extend this engineering route to other 4-nitrophenol derivatives in order to generalise the design, (b) to replace the base *cis*-1,2- or *trans*-1,2-diaminocyclohexane by enantiomers with the same adjacent chiral centres but having a weaker steric hindrance. The capture of three water molecules which participate in the crystal packing in structures (I)–(III) but weaken the crystal stability is the main drawback, limiting a possible further application of these materials. This engineering route is however very attractive for chromophore alignment.

Conclusion

A perfect or quasi-perfect alignment of chromophores is required in order to reach optimal electrooptical properties. Crystal packing with $P1$ symmetry is rarely encountered and if the same chromophores are located as two independent crystallographic motifs (or more) the chances of aligning the two sub-networks of chromophores are reduced. The crystals referenced in the previous paragraph and the present crystals built with the 2-methoxy-4-nitrophenolate anion show a chromophore alignment directed by hydrogen bonds. Other engineering routes have already been proposed to realise the alignment of organic entities. Such alignment is very probably imperfect. The perhydrotriphenylene inclusion compounds in which the honeycomb architecture of the molecular host induces an organisation of polar chains of chromophores in the channels of crystal structure are noteworthy.[23] Another example would be the alignment of 4-nitroaniline molecules in aluminophosphate molecular sieves having one-dimensional channel structures: AlPO4–5, AlPO4–11.[24] In these composite materials the polar arrangement of 4-nitroaniline molecules has been evidenced[24a,b] and controlled through reliable second harmonic generation experiments.[24c]

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Paper 9/02498K