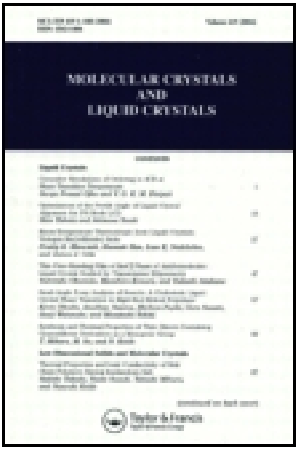

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Nonlinear Optical Crystals Designed with 4-Nitrophenolate Chromophores: An Engineering Route using a Multidipolar Chromophore, 3-Hydroxy-2,4,6-Trinitrophenolate

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Nonlinear Optical Crystals Designed with 4-Nitrophenolate Chromophores: an Engineering Route using a Multidipolar Chromophore, 3-Hydroxy-2,4,6-Trinitrophenolate

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4-Nitrophenol derivatives are interesting chromophores for nonlinear optics (NLO), being typical donor-acceptor system connected by π conjugation. Due to the presence of the acidic phenolic proton, they also readily form salts with suitably selected organic and metallic bases. The so-formed 4-nitrophenolates have increased molecular hyperpolarizabilities (β). The phenolate and nitro oxygens are strong hydrogen bond acceptors and the nitro group has a tendency to coordinate with metal centers. This opens up two different engineering routes to build NLO materials from these chromophores: (a) organic-organic and (b) metal-organic salts. This paper reviews the crystal packing and nonlinear optical (NLO) efficiency in nitrophenolate crystals engineered through these routes and presents the crystal structure of a new NLO efficient organic-organic salt, 1-hydroxy-4-methylpyridinium 3-hydroxy-2,4,6-trinitrophenolate ($P2_1$). In this crystal both the multidipolar anion and dipolar cation are NLO chromophores. The anions form herringbone mediated chain with intra and intermolecular O-H····O hydrogen bonds and the cations are attached to them through strong O-H····O^- hydrogen bonds.

Keywords: organic NLO materials; crystal engineering; non-centrosymmetry; herringbone motif

INTRODUCTION

Organic nonlinear optical materials continue to attract attention driven by the ever increasing demands in the field of optical signal processing, communication, computing and data storage [1]. Organic materials offer various advantages over conventional inorganic NLO materials: these includes high nonlinearities, fast response time, facile modification of molecular properties through precise synthetic methods, high optical damage threshold [2]. However, most of the efficient NLO chromophores have an increased tendency to pack in an antiparallel manner, thus eliminating the macroscopic susceptibility ($\chi^{(2)}$) [3]. Moreover, the molecular crystals often have low thermal and mechanical stabilities which limits their practical application in the device fabrication. To obtain efficient macroscopic NLO effects in a single crystal, one needs to incorporate the NLO chromophores in an optimized non-centrosymmetric assembly. Ideally, the chromophores should self-assemble in a non-centrosymmetric structure in such a way that the molecular nonlinearities (β) are added up so as to result in high macroscopic tensor components of $\chi^{(2)}$ [4]. Several problems concerning the overall quality of this class of materials remain to be fully solved, and more research is needed to improve their optical as well as mechanical properties. This has triggered the intensive research in the field of molecular and crystal engineering for efficient NLO materials, making use of the understanding of intermolecular interactions in the design of new crystals with the desired properties [5].

Various strategies have been proposed to answer the problem of getting non-centrosymmetric packing. These include meta substitution [6], introducing chiral centers [7], vanishing dipole moment [8], using noncovalent interactions, inclusion compounds [9] etc. Meredith first proposed the use of ionic interactions to override the deleterious dipolar interactions [10] and Marder et al [11] have reported that the ionic crystals have greater tendency to form non-centrosymmetric packing than do neutral dipolar entities. Hydrogen bonds are strong, directive and predictable [12] and their combination with ionic interactions may further favour the non-centrosymmetry [13]. Various molecular candidates: cationic, neutral and anionic chromophores have been tried as efficient NLO chromophores: (a) 2-amino-5-nitropyridinium ($2A5NP^+$), 2-amino-3-nitropyridinium ($2A3NP^+$) - cationic chromophores which have been extensively used to engineer NLO crystals with inorganic polymeric anions [14], (b) 4-nitropyridine-1-oxide [15], 3-methyl-4-nitropyridine-1-oxide [16] – neutral chromophores forming coordination complexes with transition metal halides and (c) nitrophenolates – anionic chromophores forming salts with inorganic and organic bases. 4-nitrophenol derivatives are interesting candidates, as they are typical one dimensional (1D) donor-acceptor π system and the presence of phenolic OH favours the formation of salts with various organic and inorganic bases. The conjugated base, phenolate thus formed have increased molecular hyperpolarizability because of the better electron donating character of phenolate O^- (Hammett coefficient σ = -0.81) than that of phenolic OH (Hammett coefficient σ = -0.38). This has been further confirmed by the β calculations (Table 1). The phenolate and nitro oxygens are efficient hydrogen bond acceptors, also the nitro group has a tendency to form coordination bonds with metal centers, opening two different crystal engineering routes: organic-organic and metal-organic salts. We now review the main structural features of NLO efficient crystals built with 4-nitrophenolate dipolar chromophores and present a new engineering route based on the packing of a multidipolar anionic chromophore: 3-hydroxy-2,4,6-trinitrophenolate.

TABLE 1: Calculated values of molecular hyperpolarizabilities (β_{XXX}).

S.No	Chromophores	β_{XXX} ($x10^{-30}$ esu) neutral	anion
1.	4-nitrophenol	5.2	18.2
2.	3-methyl 4-nitrophenol	5.3	17.4
3.	2-methoxy 4-nitrophenol	6.0	20.2

*assuming the OH (O^-) → NO_2 CT axis oriented along x direction

RESULTS

The salt of 3-hydroxy-2,4,6-trinitro phenolate anion was obtained with 1-hydroxy-4-methylpyridinium cation and details are given in experimental section. The starting composition was 1 :2 mixture of 2,4,6-trinitroresorcinol (TNR) and 4-methylpyridine-1-oxide (4MPO), because we anticipated a double proton transfer from TNR, but the crystals contain in fact a 1:1 mixture as confirmed by elemental analysis. Pale yellow needle crystals and small amount of prismatic crystals were obtained, and were separated manually. The melting points are 145.1°C and 144.3°C respectively for needles and prisms.

The X-ray structure analyses showed that the prismatic crystals are P1 (a = 12.0663 Å, b = 14.6706 Å, c = 9.0986 Å, α = 90.58°, β = 98.00°, γ = 66.31°, V = 1455.4 Å^3, Z = 4) with a pseudocenter of symmetry. They do not show NLO activity when observed by the Kurtz and Perry second harmonic generation (SHG) powder test [17] with a Nd^{3+}:YAG laser (λ = 1.064 μm). The needles crystallize in $P2_1$ space group (crystal data summarized in Table 2) and are NLO efficient with the SHG activity equivalent to that of 3-methyl-4-nitropyridine-1-oxide (POM) [8].

TABLE 2: Crystallographic data of 1-hydroxy-4-methylpyridinium 3-hydroxy-2,4,6-trinitrophenolate.

Empirical formula	$C_{12}H_{10}N_4O_9$	Z	2
Formula weight	354.23	V/Å^3	717.9(2)
Crystal system	monoclinic	D_{calc}/Mg m^{-3}	1.638
Space group	$P2_1$	R (R_w)	4.47 (4.95)
A/Å	11.745(2)	Ref. collected	5602
B/Å	4.9142(7)	unique data	3376
C/Å	12.744(2)	Data with I>3σ(I)	1841
α/°	90	no. of parameters	233
β/°	102.556(12)	Diffractometer	Nonius – CAD4
γ/°	90		

DISCUSSION

(a) Non-centrosymmetric Organic-Organic Salts Based on 4-Nitrophenolates

The presence of phenolic OH, and the strong hydrogen bonding accepting ability of phenolate and nitro oxygens facilitate the route of constructing organic-organic salts with possibly increased cohesion due to multiple hydrogen bond network and ionic interactions with suitable counter ions. This route has been exploited by various groups to engineer NLO crystals. We have reported the quasi polar alignment of the chromophores, 2-methoxy -4-nitrophenolates (also called 4-nitroguiacol – 4NGA) in a matrix formed by 1,2-diammoniocyclohexane (DACH) counter ion, directed by the strong N^+-H···O^- hydrogen bonding (Figure 1) [18]. The polar packing pattern in the 1 :2 DACH-4NGA ionic crystal is robust in this class of crystal whether the counter ion is trans (1R,2R)-(-), racemic trans 1,2-(±), or cis 1,2 DACH. This clearly indicates that the non-centrosymmetric polar alignment is not only due to the chiral center but also to the presence of adjacent proton accepting sites in the base and the formation of strong N^{+}-H···O^{-} hydrogen bonds. The water inclusion could not be avoided in these crystals as the water molecules fill the space between the cations and also provide hydrogen bonding network between them. This quasi perfect polar alignment of 4NGA chromophores is not favorable for a high value of the macroscopic hyperpolarizabilities $\chi^{(2)}$ if we consider a description of tensorial properties following the oriented gas model. However it is interesting for electrooptic applications. The SHG efficiency of these crystals are equivalent to

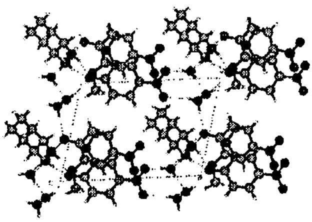


FIGURE 1: Quasi polar arrangement of 4NGA anions in the matrix of trans (1R,2R)-(-) diammoniocyclohexyl cations.

that of POM, even though the cyclohexyl non-chromophoric part occupies almost half the volume of the cell thus diluting the concentration of the NLO chromophores. To avoid this drawback, ionic crystals have to be engineered in such a way that both cation and anion are NLO chromophores and such an approach has already been reported in the literature. Huang et al [13a] have reported the non-centrosymmetric salts of 4NGA with 4-dimethylaminopyridine and 4-pyrrolidinylpyridine and observed a SHG activity of twice that of urea. We have reported NLO efficient salts formed between 4-nitrophenol and 4-dimethylaminopyridine and observed the calculated β increase of 2-3 times in the cation and anion upon proton transfer [13b].

In recent times, molecular engineering has widened its scope to encompass 2D and 3D multipolar chromophores involving multiple charge transfer pathways [19], which may avoid the drawback of dipolar interactions, and also increase the chances of multiple hydrogen bonding networks and hence crystal cohesion. Cationic chromophores like $2A5NP^{+}$ and $2A3NP^{+}$ are some examples of multidipolar chromophores already reported. In this context, we extended our studies to get ionic crystals of 4-nitrophenolate based multidipolar NLO chromophores.

1-Hydroxy-4-methylpyridinium 3-hydroxy-2,4,6-trinitrophenolate

1-hydroxy-4-methylpyridinium 3-hydroxy-2,4,6-trinitrophenolate is an organic-organic salt with multidipolar anion and dipolar cation. The basicity of 4MPO is not sufficient enough to remove both the phenolic protons of TNR and thus a 1:1 crystal results. The two polymorphs, needles and prisms are obtained in the same batch revealing that the problem of polymorphism is of particular importance in application oriented crystal engineering. Conditions are being stabilized to exclusively obtain NLO efficient needle type crystals.

Structural description and NLO activity

The structure analysis of needle crystals confirms that the proton is transferred from one of the phenolic OH of TNR to oxygen of 4MPO. The OH protons were isotropically refined. There exists a very strong hydrogen bond between these two oxygens ($O\text{-}H\cdots O^-$: d = 1.576 Å, D = 2.520 Å and θ = 166.6°) and the hydrogen donating ability of the OH is enhanced by the N^+ of pyridinium to which it is attached. The phenolic OH is involved in strong intramolecular hydrogen bonding ($O\text{-}H\cdots O$: d = 1.870 Å, D = 2.604 Å and θ = 138.9°) with the nitro group which is para to the phenolate oxygen and also in intermolecular hydrogen bonding ($O\text{-}H\cdots O$: d = 2.233 Å, D = 2.862 Å, θ = 127.6°) with the nitro group para to the phenolate oxygen of another molecule. These two intra and intermolecular hydrogen bonds form a chain with herringbone arrangement of the anion along the **b** axis with the 2_1 symmetry (Figure 2a). A quasi tetrahedral arrangement is built with two cations and two anions (Figure 2b). All the possible hydrogen bond donors and acceptors are involved in hydrogen bonding (Table 3) and thus increase the crystal cohesion, revealed in the higher melting point (145°C).

The two long charge transfer (CT) axes ($O^- \rightarrow NO_2$(para) and $OH \rightarrow NO_2$(para)) make respectively an angle of 72.69° and 71.56° with respect to the crystallographic **b** axis. The cation is also having a CT axis ($CH_3 \rightarrow N^+$) which makes an angle of 59.9° with the crystallographic **b** axis. As a rough simplification, if we consider these three CT axes as *independent 1D dipolar entities*, then these angles are

TABLE 3: Hydrogen bonds in 1-hydroxy-4-methylpyridinium 3-hydroxy-2,4,6-trinitrophenolate.

D-H···A	D-H (Å)	H···A (d, Å)	D···A (D, Å)	D-H···A (θ, °)
O_2-H_1···O_5 (intra)	0.887	1.870	2.604	138.9
O_2-H_1···O_5 (inter)	0.887	2.233	2.862	127.6
O_2-H_1···N_2 (intra)	0.887	2.501	2.932	110.5
O_9-H_3···O_1'	0.961	1.576	2.520	166.6
C_5-H_2···O_8	1.077	2.539	3.565	159.0
C_7-H_4···O_1'	1.079	2.617	3.310	121.4
C_7-H_4···O_7	1.079	2.287	3.273	151.2
C_7-H_4···O_8	1.079	2.698	3.285	113.7
C_7-H_4···N_3	1.079	2.606	3.503	140.1
C_8-H_5···O_6	1.078	2.613	3.629	156.9
C_8-H_5···O_8	1.078	2.610	3.248	117.3
C_{10}-H_6···O_3	1.071	2.508	3.255	125.9
C_{10}-H_6···O_4	1.071	2.793	3.455	120.0
C_{11}-H_7···O_3	1.070	2.733	3.343	116.0
C_{11}-H_7···O_1'	1.070	2.544	3.609	173.3
C_{12}-H_8···O_6	1.079	2.843	3.748	141.5
C_{12}-H_9···O_2	1.084	2.388	3.405	155.6
C_{12}-H_8···O_5	1.084	2.854	3.633	128.8
C_{12}-H_{10}···O_4	1.067	2.471	3.441	150.6

close to the ideal angle of 54.74° in an optimal 1D chromophoric arrangement for the point group 2, and respectively 70.5, 74.0 and 97.5% of theoretically possible NLO efficiencies could be recovered for

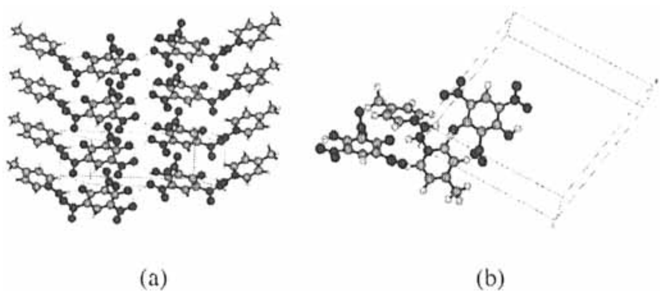


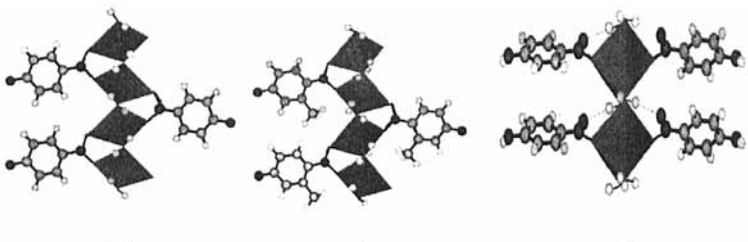
FIGURE 2: Herringbone motif (a) and quasi tetrahedral motif (b) in 1-hydroxy-4-methylpyridinium 3-hydroxy-2,4,6-trinitrophenolate

such chromophore orientations [4]. However the situation is complicated, as there would be interactions between the independent dipolar axes, and also there exists some other CT axes, like O→NO_2(ortho) in the anion.

(b) Non-centrosymmetric Metal 4-Nitrophenolate Salts

The nitro group of nitrophenolate chromophores is an efficient metal ligand, always involved in the formation of the coordination polyhedra which induce a herringbone arrangement of chromophores. Five non-centrosymmetric crystals of metal 4-nitrophenolate without other organic residues are known so far. Among them only the following four crystals have herringbone arrangement of the nitrophenolate suitable for SHG activity: sodium 4-nitrophenolate dihydrate (Na4NP - Ima2) [20], sodium 3-methyl-4-nitrophenolate dihydrate (Na3M4NP – Cc) [21], sodium 4-nitrophenolate 4-nitrophenol dihydrate (Na4NP·4NP - C2) [22] and magnesium 4-nitrophenolate dihydrate (Mg4NP - C2) [23]. We will discuss about the crystal packing and NLO efficiency of these four crystals in the light of nitro-metal coordination and hydrogen bonding.

In Na4NP, the edged shared polymeric chain of NaO_6 octahedra is formed by four water molecules constituting the basal plane and two 4-nitrophenolate chromophores in the axial positions (Figure 3a). The adjacent polymeric chains are connected by four strong phenolate oxygen-water hydrogen bonds on the other side (O-H···O⁻: d = 1.761



(a) (b) (c)

FIGURE 3: Herringbone arrangement of 4-nitrophenolate chromophore in Na4NP (a), Na3M4NP (b) and Na4NP·4NP* (c), (* The phenolic hydrogen in (c) is having an occupancy of 0.5).

and 1.801 Å, D = 2.800 and 2.789 Å, θ = 178.4° and 172.3°). The two oxygens of nitro group are attached to two adjacent metal center in the polymeric chain with the O-Na coordination bong lengths of 2.664 Å and 2.329 Å and thus distort the octahedra axially ((NO_2)O···Na···O(NO_2) = 170.7°). No significant distortion in the basal plane is seen. The bi-coordination of nitro group with different coordination bond lengths and the strong hydrogen bonding of the phenolate oxygen play crucial role in distorting the octahedral polymeric chain and hence in forming herringbone arrangement of the chromophores. The angle between the CT axis of the chromophore and the crystallographic **b** axis is 78.7°. For an optimized structure of dipolar chromophores in the point group mm2, this angle should be 54.74°. With this chromophore packing only 49% of the theoretically possible NLO efficiency could be recovered [4].

The packing pattern in Na3M4NP (Figure 3b) is similar to that of Na4NP. The methyl group in Na3M4NP, provides weak hydrogen bonds with the nitro oxygen (C-H···O: d = 2.606 Å , D = 3.225 Å and θ = 122.6°) which influences the herringbone arrangement in the polymeric chain. These interactions favour the axial distortion of the octahedra (((NO_2)O···Na···O(NO_2)) = 165.1°), which is pronounced when compared to Na4NP. The nitro group is coordinated to two adjacent metal center through the two oxygens (2.508 Å and 2.378 Å) and the phenolate oxygen is involved in strong hydrogen bonding and holds the octahedral polymeric chains together as in the case of Na4NP. The distortion of octahedra makes an angle θ = 10.7° (the angle between the molecular CT axis and the **b** axis perpendicular to the mirror **c**) and for an optimized arrangement of chromophores in the point group m, it should be 35.26° [4]. Thus only about 47 % of the theoretically possible NLO efficiency has been recovered in the crystals [21].

Na4NP$^-$4NP (Figure 3c) and Mg4NP are isotypic (space group C2) except that the unique proton shared by two chromophores in Na4NP$^-$ 4NP which balances the charge difference between Mg^{2+} and Na^+. In these crystals only one nitro oxygen is involved in coordination with metal and the other is involved in strong hydrogen bonding with water (O-H···O: d = 2.069 Å and 2.003 Å, D = 2.854 Å and 2.785 Å and θ = 165.3° and 159.9° respectively for Na4NP$^-$4NP and Mg4NP). The charge on magnesium prevents a close approach and hence the bi-coordination of nitro group whereas in Na4NP$^-$4NP the unique proton may be responsible for the single coordination of nitro group, eliminating the formation of multiple hydrogen bonds between the phenolate oxygen and water as in the cases of Na4NP and Na3M4NP. In Na4NP$^-$4NP, the phenolate oxygens for two chromophores share the unique proton with the O···O distance of 2.477 Å and also interact with water through hydrogen bonding (O-H···O$^-$: d = 1.951 Å, D = 2.786 Å,

θ = 168.9°). In Mg4NP, the phenolate oxygen is involved in hydrogen bonding with water (O-H···O⁻: d = 1.815 Å, D = 2.785 Å, θ = 159.9°). In these two crystals, because of the single coordination of nitro group, the octahedral distortion is slight ((NO_2)O···Metal···O(NO_2) = 173.8° and 174.6° respectively for Na4NP·4NP and Mg4NP). However a slight twisting of the chromophores occurs due to hydrogen bonds formed between the free nitro oxygen and phenolate oxygen with water on the same side, which makes the herringbone arrangement of the chromophores. The angles (θ) of CT axes with respect to crystallographic **b** axis are 86.39° and 86.42° respectively for Na4NP·4NP and Mg4NP. The NLO efficiency is calculated as $\cos\theta\sin^2\theta$ = 0.0625 i.e., 16% of the theoretically possible efficiency (0.3849 for ideally oriented chromophores in the point group 2, with θ = 54.74°) [4] can be recovered for this chromophore orientation.

The crystal structure of sodium 3-nitrophenolate dihydrate (Na3NP – $P2_1/n$) [24] is similar to that of Na4NP. The bi-coordination of nitro oxygens with nearly equal coordination bond lengths (2.633 Å and 2.566 Å) leads to only a little axial distortion ((NO_2)O···Na···O(NO_2) = 178.6°). Moreover, the adjacent polymeric chains are oriented in an antiparallel manner. This may be due to the 1,3 positions of the functional groups (phenolate and nitro) and the preference for close packing. If we compare this with the centrosymmetric structures of potassium 4-nitrophenolate (K4NP - $P2_1/c$) [25], and potassium 2-chloro-4-nitrophenolate (K2Cl4NP – $P2_1/c$) [25] the importance of the coordination mode of NO_2 and the resulting polyhedron distortion and the hydrogen bonding of phenolate oxygen is revealed. In these crystals, the crystal structures consist of sheets (K4NP) and chains (K2Cl4NP) of face shared metal polyhedra formed by eight coordinated potassium ions. The sheets/chains are connected by strong coordination of both nitro and phenolate oxygens, unlike the non-centrosymmetric metal phenolates where the phenolate oxygen is involved in hydrogen bonding. This eliminates the herringbone arrangement of the chromophores, excluding the possibility of NLO activity.

CONCLUSIONS

Ionic crystals engineered using multidipolar 4-nitrophenolate based anions appear to be a promising lead to build thermally stable NLO crystals because of multiple hydrogen bond networks. The

4-nitrophenols having another nitro group at the position ortho to OH are known to form chains with herringbone arrangement of 4-nitrophenols through O-H···O and C-H···O hydrogen bonds, as seen in the crystal structures of 2,4-dinitrophenol [26], 2,4,6-trinitro-1,3,5-benzenetriol [27], 2,4,6-trinitro-3,5-dichlorophenol [28], 2,4-dinitro-6-chlorophenol [29]. The robustness of this hydrogen bonding pattern has been utilized to design herringbone arrangement of chromophores in organic-organic crystal.

The axial distortion of NaO_6 octahedra chains in Na4NP and Na3M4NP is induced by the nitro group which can coordinate to two adjacent metal centers. The 3D packing of these polymeric chains is a staggered organization maintained by a network of strong hydrogen bonding between water molecules and phenolate oxygens of adjacent chains, which strengthen and stabilize the distorted octahedra and hence the herringbone motif of the chromophores. In Na4NP·4NP and Mg4NP, the NaO_6 and MgO_6 octahedra are less distorted due to the single coordination of nitro group in forming coordination sphere. This weak distortion of octahedra induces a slight shift towards the centrosymmetry and thus a lesser NLO activity than for the previous crystals. By comparing these crystal structures with those of centrosymmetric metal-nitrophenolates, the following conclusions may be drawn: (a) The bi-coordination of nitro group with unequal coordination bond length is necessary for efficient distortion of the metal coordination sphere and (b) The phenolate oxygen should involve in strong hydrogen bonding with the water of adjacent polymeric chain.

Experimental Section

The salt of 3-hydroxy-2,4,6-trinitro phenolate was obtained with 1-hydroxy-4-methylpyridinium cation by mixing 1:2 molar solutions of 2,4,6-trinitroresorcinol (TNR) and 4-methylpyridine-1-oxide (4MPO) in acetonitrile medium. The slow evaporation of the mixture gave pale yellow needle and prismatic crystals. Crystal structures of these two polymorphs were determined using an Enraf-Nonius CAD-4 four-circle diffractometer with MoKα radiation. Diffracted intensities were corrected for Lorentz and polarization factors. No absorption correction was applied due to favorable crystal geometry and low absorption coefficient in each case. The space groups were confirmed by the diffraction limiting conditions: needle crystal, only 0k0 with $k = 2n$, symmetry $P2_1$; prismatic crystal, hkl without conditions, symmetry P1. The structures were solved by direct methods using SIR 92 program

[30]. Full matrix least-squares refinements were performed on F with teXsan software [31]. Scattering factors for neutral atoms and f', Δf', f'', Δf'' were taken from *International Tables for X-ray Crystallography* [32].

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the Cambridge Crystallographic Data Centre and can be obtained on request at CCDC, Union Road, Cambridge CB2 IEZ, England. (CCDC 136028)

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