but the extension to include side chains is straightforward (Moult & James, 1986).

We envisage a procedure in which poor regions of the current model are automatically identified then replaced by the systematic search procedure. Following a round of such replacement, conventional refinement would be carried out. This would be followed by further rounds of systematic search and refinement until no further rebuilding occurs. The occasional failure to select a conformation within the convergence radius of the refinement would not be a serious obstacle since the general improvement of the phases would increase the power of the method in succeeding rounds. Thus, systematic search offers an alternative approach to extending the convergence radius of refinement, beyond even that offered by MD refinement.

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Molecular Reorientation in an Electric Field as Studied by Single-Crystal X-ray Diffraction

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Abstract

The molecular reorientation induced by an external electric field has been determined for the first time in order to obtain a microscopic understanding of the interaction between crystals and electric fields. Changes in scattering intensity are found when an electric field is applied parallel to the polar axis of a non-linear optical crystal of 2-methyl-4-nitroaniline (MNA), which has large piezoelectric constants [Paturle, Graafsma, Sheu, Coppens & Becker (1991). *Phys. Rev. B*, **43**, 14683-14691]. The effect has been analyzed in terms of a change in cell parameters, a molecular rotation of $0.45(5)\times10^{-2\circ}$ about an axis nearly parallel to the electric field and a molecular translation of $0.19(3)\times10^{-3}$ Å along the *b* axis. Since

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the orientation of the molecular dipole moment vector is unaffected, the piezoelectric contribution to the permittivity for this electric field direction is small. As expected, the centrosymmetric crystals of *p*-nitroaniline and *p*-nitropyridine *N*-oxide have no first-order converse piezoelectric effect and show no measurable change in X-ray scattering intensity under the influence of an external electric field of $2.2 \times 10^6\,\mathrm{V\,m^{-1}}$. For the non-centrosymmetric crystals of 3-methyl-4-nitropyridine *N*-oxide, the effect is small, in agreement with the small value of the piezoelectric constants.

Introduction

The study of the influence of an external electric field on crystals has been largely limited to macroscopic effects. With the development of more powerful synchrotron X-ray beams, it has become feasible to study such effects at the atomic level, opening the way to a better understanding of properties like piezoelectricity, the electrooptic effect and ionic conductivity. Recent publications on the influence of an external electric field on crystalline structures (Fujimoto, 1982; Ståhl, Kvick & Abrahams, 1990; Graafsma, Majewski, Cahen & Coppens, 1991) have been concerned with ionic compounds. We report here the response of the crystals of four monocyclic aromatic organic compounds to the application of an external electric field. The effect of the field on the unit-cell dimensions of 4-methyl-2-nitroaniline (MNA) (the converse piezoelectric effect) has been described in an earlier publication (Paturle, Graafsma, Sheu, Coppens & Becker, 1991).

Theory

The various responses of a crystal to an electric field are illustrated in Fig. 1 (Nye, 1957). Although from a theoretical point there is no preference for the conditions under which the various effects are measured, in practice the crystal is kept at constant temperature and constant stress (instead of constant entropy and strain). The induced strain, through the converse piezoelectric effect, and the induced electric displacement, through the permittivity, involve a redistribution of the electron density which corresponds to a finite change in the X-ray scattering intensities.

Strain

In an atomic or ionic crystal, in which rigid polyatomic units are absent, a homogeneous deformation can be described as having two components (Born & Huang, 1954). The displacement of a particle k in unit cell m may be written as

$$u^i(k, m) = u^i(k) + \sum_j U^i_j x^j(k, m) \tag{1}$$

where $\mathbf{u}(k)$ is a displacement vector identical for all atoms k in different unit cells, U^i_j are the elements of a deformation tensor and $\mathbf{x}(k, m)$ is the position vector of particle k in unit cell m with respect to a *fixed* origin. The second term on the right-hand side of (1) gives rise to a change in cell parameters and correspondingly to a change in crystal shape. It describes an elastic deformation of the crystal and is referred to as the *elastic* or *external* strain. The first term does not involve a cell deformation, since the displacements of atoms of the same kind are the same for all unit cells, irrespective of their distance from the fixed origin. The term represents the displacements of each of the atoms within the deformed unit cell, and is referred to as the *internal* strain.

In the case of an ionic or atomic solid, external strain does not affect the contravariant components $x^i(k, m)$ of the position vectors of the atoms when referred to the new basis, *i.e.* an elastic deformation of the crystal does not change the fractional coordinates of the atoms. In this case the exponent in the structure-factor equation

$$F_{\mathbf{H}} = \sum_j f_j \exp\{2\pi i \sum_k (h_{jk} x^k_j)\} T_j \tag{2}$$

is invariant and $F_{\mathbf{H}}$ changes only through small changes in atomic scattering factors f_j, *via* the change in $(\sin\theta)/\lambda$, and possible changes in the temperature factors T_j.

In the case of a molecular crystal consisting of molecules which behave as rigid bodies under the influence of the deformation, the displacement of a particle k belonging to a molecule l in unit cell m may be written as

$$u^i(k, l, m) = u^i(k) + \sum_j U^i_j x^j(l, m) \tag{3}$$

where $\mathbf{x}(l, m)$ is the position vector of the center of

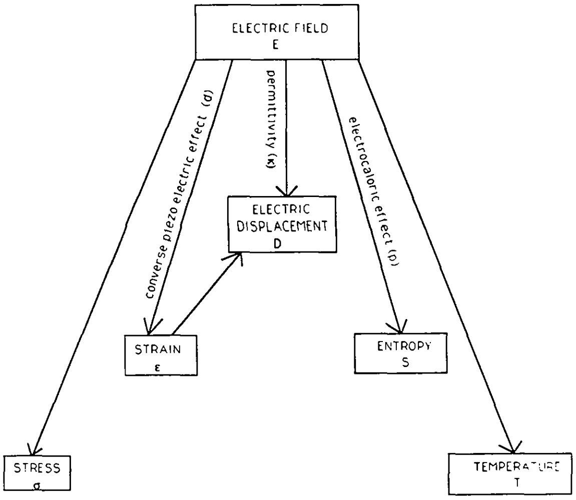

Fig. 1. Various responses of a crystal to an external electric field as described by Nye (1957).

mass of molecule l in unit cell m. The translation vectors $\mathbf{u}(k)$ are now restricted by the molecule being a rigid body. In this case $\mathbf{u}(k)$ is not linear with the deformation, but results from the combination of a molecular translation $\mathbf{T}(l)$ and rotation $\mathbf{R}(l)$, which both are to first approximation linear with the deformation. Equation (3) shows that, for molecular crystals, external strain does not change the contravariant components of the *centers of mass* of the molecules when referred to the new basis. But the contravariant components of the individual *atoms* will change, thus leading to an additional change in the structure factor.

Born & Huang (1954) explain the internal strain as being a reaction to the external strain such as to minimize the energy density. This assignment of cause and result is somewhat arbitrary in the case of strains induced through the converse piezoelectric effect, in which the response of the crystal originates from the electric forces applied to the atomic or molecular entities in the solid.

Electric displacement

When an electric field $\mathbf{E}$ across a crystal at constant temperature is changed by $\mathrm{d}\mathbf{E}$, a change in electric displacement $\mathrm{d}\mathbf{D}$ is induced *via* separate paths (Nye, 1957; Fig. 1). The linear effects can be described by the following equation (in which all the sub- and superscripts are omitted for clarity):

$$\begin{aligned}\mathrm{d}\mathbf{D} = \kappa\,\mathrm{d}\mathbf{E} &= (\partial\mathbf{D}/\partial\mathbf{E})\mathrm{d}\mathbf{E} + (\partial\mathbf{D}/\partial\varepsilon)(\partial\varepsilon/\partial\mathbf{E})\,\mathrm{d}\mathbf{E}\\ &\equiv \kappa_p\,\mathrm{d}\mathbf{E} + \mathbf{ed}\,\mathrm{d}\mathbf{E}, \qquad (4)\end{aligned}$$

where $\mathbf{d}$ is the piezoelectric tensor and $\mathbf{e}$ is the tensor relating strain and electric displacement. The primary effect corresponds to the first term of the right-hand side of (4) and involves the primary permittivity κ_p, the secondary effect, represented by the second term, is due to the converse piezoelectric effect and induced strains.

If the permittivity is measured on a clamped crystal which cannot deform, the strain ε is constant and the secondary effect is absent. Alternatively, if it is measured on a crystal which is free to deform, the stress σ is constant and both the primary and secondary effect are present. The corresponding permittivities are known as the clamped and free isothermal permittivity respectively.

For a clamped molecular crystal, where only the primary effect is present, it is reasonable to assume that the polarization due to molecular reorientation is greatly if not completely suppressed (external and internal strain is absent). So what is left is only the contribution from the polarization of the molecules. Therefore the difference between the polarization of a free and clamped molecular crystal is the polarization due to molecular reorientation, including both a cell deformation (external strain) and an internal reorientation (internal strain), and constitutes the piezoelectric contribution to the permittivity.

The permittivity tensor κ in (4) is related to the dielectric susceptibility tensor χ and the relative permittivity tensor $\mathbf{K} \equiv \kappa/\kappa_0$ *via*

$$\kappa = \kappa_0(I + \chi) = \kappa_0\mathbf{K},$$

where κ_0 is the permittivity of vacuum ($8.854 \times 10^{-12}\,\mathrm{C}^2\,\mathrm{N}^{-1}\,\mathrm{m}^{-2}$) and I is the unit tensor. For the principal axes of the relative permittivity tensor,

$$n_i = K_i^{1/2},$$

the n_i's being the principal refractive indices of the medium.

Effect on X-ray scattering

For a free crystal a total of four different contributions to the change in scattering intensity due to the external electric field may be distinguished:

(1) a change in cell parameters, resulting in a change in atomic scattering power, and a change in atomic coordinates for crystals containing rigid molecules or groups;

(2) an additional change in positional parameters due to internal strain;

(3) a change in thermal parameters;

(4) a change in electron density due to molecular polarization.

For the fields that could be used in the present study, the effect of molecular polarization on the X-ray scattering is expected to be too small to be measured. The polarization of 2-methyl-4-nitroaniline, for example, can be calculated with the theoretical *ab initio* polarizabilities (Dupuis, 1990). The linear polarizability $\alpha_{zz} = 2.48 \times 10^{-39}\,\mathrm{C\,m^2\,V^{-1}}$ (z being along the long axis of the molecule) gives, for a field of $3.9 \times 10^6\,\mathrm{V\,m^{-1}}$ parallel to this axis, a change in molecular dipole moment of 9.7×10^{-33} C m or 2.9×10^{-3}debye, below our present experimental sensitivity. For comparison, values for the permanent dipole moment of 2-methyl-4-nitroaniline range from 6.2 to 8.65 debye [experimental: 6.2 debye (Deshpande, Shashidbar & Suryanarayana, 1981); theoretical: 8.2 debye (Dupuis, 1990) (extended basis set HF); 8.65 debye (Paturle, 1990) (6−31G basis set, HF)]. The first-order non-linear polarizability $\beta_{zzz} = 4.37 \times 10^{-52}\,\mathrm{C\,m^3\,V^{-2}}$ gives, with the same field, a change of only 6.6×10^{-39} C m or 2.0×10^{-9} debye.

A number of solids were selected for this first study. 2-Methyl-4-nitroaniline (MNA) is non-centrosymmetric and has a large piezoelectric effect (Paturle *et al.* 1991). Preliminary studies show a measurable change in scattering intensity when a crystal of MNA is exposed to an external electric field (Paturle, Graafsma, Boviatsis, LeGrand, Restori, Coppens, Kvick & Wing, 1989). To eliminate the intensity effect of the cell-parameter change, the centrosymmetric analog nitroaniline (NA), for which the cell parameters will be invariant, was chosen for comparison. A value of 6.5 debye has been reported for the dipole moment of NA (Lutskii, Kondratenko, Granzhan & Obukhova, 1967). The molecules 3-methyl-*p*-nitropyridine *N*-oxide (POM) and *p*-nitropyridine *N*-oxide (PNPNO) form a similar pair, but have only small molecular dipole moments. They were therefore expected to show a smaller molecular reorientation in an external electric field. Both MNA and POM are organic solids with large higher-order polarizabilities and are of importance as non-linear optical materials.

Experimental

Data collection and data reduction

To measure the change in intensity upon application of the field we use the three-step-modulation method (Fig. 2), developed by Paturle *et al.* (1989) as a modification of earlier modulation methods (Godefroy, 1963; Fujimoto, 1982). The electric field is varied in three steps (field 'up', field 'down' and zero field) with a frequency of approximately 50 Hz. The output of the detector is synchronously gated to three different counting chains, such that three different reflection profiles, corresponding to each of the three states of the electric field, are recorded in one single scan. This 'synchronous modulation-demodulation technique' measures relative changes in intensity, expressed as response ratios η:

$$\eta_{\pm 0} = \Delta I_{\pm}/I_0 = (I_{\pm} - I_0)/I_0 \qquad (5)$$

where I_+, I_- and I_0 refer to the intensity with field up, down or zero respectively. The response ratio η_{+-} is the relative difference between field-up and field-down scattering, equal to $\eta_{+0} - \eta_{-0}$. Since the three intensities I_+, I_-, I_0 are measured at very small time intervals, virtually all experimental errors cancel in the response-ratio calculations, thus allowing the measurement of very small intensity changes (<0.05%), as well as small positional shifts of the reflection resulting from the change in cell parameters (Paturle *et al.*, 1991). The theory of error propagation gives for the counting-statistical error in the response ratio

$$\begin{aligned}\sigma^2(\eta_{+0}) &= \sigma^2[(I_+ - I_0)/I_0] \\ &= (1/I_0^2)\sigma^2(I_+) + (I_+^2/I_0^4)\sigma^2(I_0) \\ &= (I_+/I_0^2) + (I_+^2/I_0^3) \qquad (6)\end{aligned}$$

or, since the changes are small,

$$\sigma^2(\eta_{+0}) = 2/I_0. \qquad (7)$$

It follows that for an intensity change of the order of 0.1%, 5×10^7 counts are required to achieve an accuracy of 10%. Since the deadtime of an NaI scintillation detector greatly limits its count rate, a period of a few hours to one day is needed to collect one reflection, even with highly intense sources. The strategy outlined below was followed to achieve maximum efficiency.

A reflection is scanned repeatedly with scan times of about 10 min, using a modified version of the standard diffractometer control package *ZACK* (Restori, 1988). The scans are summed and analyzed in real time by a program *COZAK*, which calculates both the shift of the reflection and the three different response ratios. The measurements are continued until the accumulated response ratio has converged to a constant value. Fig. 3 shows the evolution of the response ratio η_{+-} for a typical reflection as more scans are recorded.

The change in Bragg angles may be determined by averaging of the shifts of the reflection at positive and negative θ. The piezoelectric elements can be derived from the Bragg-angle shifts $\Delta\theta_r$ using the Barsch (1976) equation:

$$\begin{aligned}\Delta\theta_r &= -\tan\theta_r \sum_{i=1}^{3}\sum_{j=1}^{3} h_{r,i}h_{r,j}\varepsilon_{ij} \\ &= -E\tan\theta_r \sum_{k=1}^{3}\sum_{i=1}^{3}\sum_{j=1}^{3} e_k h_{r,i}h_{r,j}d_{kij} \qquad (8)\end{aligned}$$

where ε_{ij} is the *ij*th component of the strain tensor ε, d_{kij} the *kij*th component of the piezoelectric tensor **d** and the e_k's and the $h_{r,i}$'s are the direction cosines of the electric field (of magnitude E) and the diffraction vector $\mathbf{h}_r$ respectively. Alternatively, the

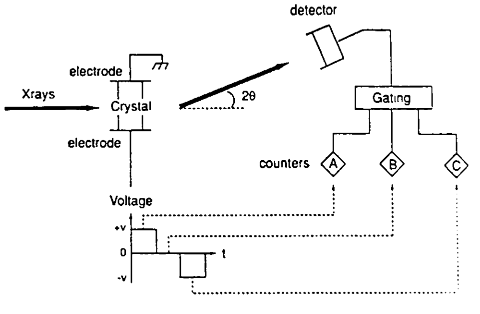

Fig. 2. Schematic drawing of the three-step modulation method.

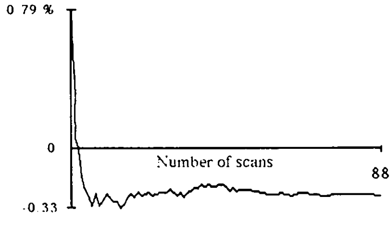

Fig. 3. Evolution of the accumulated response ratio η_{+-} as a function of the number of scans recorded.

piezoelectric elements can be derived by determination of the complete strain tensor, including a rigid rotation of the lattice, from the change in direction of the scattering vectors relative to a laboratory-based coordinate system (Graafsma, 1992).

To place the intensity changes on an absolute scale, the relative changes were multiplied by $|F_c|^2$ (Paturle *et al.*, 1989), where F_c is the calculated structure factor obtained from the known structure, according to

$$\Delta F^2_{+-} = \eta_{+-} F^2_c. \tag{9}$$

Analogous expressions were used for η_{+0} and η_{-0}. The resulting ΔF^2 values are the input for the least-squares refinement using a program *TLSBMOL*, in which, to account for the converse piezoelectric effect, different sets of cell parameters are used in the intensity calculation for the two states of the field. Because of the small number of experimental data a rigid-body model was used for the molecule. The use of this model is justified by the rigidity of the molecule relative to the softness of the intermolecular interactions. However, the use of a more flexible segmented-body model in subsequent more extended studies is envisioned.

To optimize the use of instrument time preliminary refinements were made with data obtained as the experiment proceeded, in order to identify reflections with a maximum intensity effect.

Sample preparation

p-Nitroaniline (*NA*). Large good-quality crystals were obtained in four days by slow cooling of a hot aqueous solution. A crystal of 0.50 × 0.60 × 0.60 mm, showing sharp extinction under a polarizing microscope, was selected and mounted with the field along the [101] direction, which is parallel to the long molecular axis (Trueblood, Goldish & Donohue, 1961). A voltage of 1.1×10^3 V was applied over 0.5 mm giving a field of 2.2×10^6 V m^{-1}.

NA crystallizes in space group $P2_1/n$ (Trueblood *et al.*, 1961). Cell parameters, determined from 24 reflections with $32 < 2\theta < 42°$ using a Rigaku rotating-anode generator and Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å), are: $a = 12.346\,(1)$, $b = 6.0430\,(7)$, $c = 8.5988\,(9)$ Å, $\beta = 91.52(1)°$.

p-Nitropyridine N-oxide (*PNPNO*). Crystals were grown by slow evaporation of a 50% acetone/50% ligroin solution. Large good-quality crystals were obtained in four days. A crystal of 0.55 × 0.60 × 0.75 mm, showing sharp extinction under a polarizing microscope, was mounted with the field parallel to the *b* axis. A voltage of 1.3×10^3 V was applied over 0.55 mm, giving a field of 2.4×10^6 V m^{-1}. PNPNO has the space group *Pnma* (Eichhorn, 1956; Wang, Blessing, Ross & Coppens, 1976). Cell parameters determined from 24 reflections with $24 < 2\theta < 29°$, using a Rigaku rotating-anode generator, a Huber four-circle diffractometer and Mo $K\alpha$ radiation, are: $a = 12.531\,(2)$, $b = 6.0078\,(5)$, $c = 7.891\,(1)$ Å.

3-*Methyl*-4-*nitropyridine N-oxide* (*POM*). Crystals were grown by slow evaporation of an acetonitrile solution (Shiro, Yamakawa & Kubota, 1976). Large good-quality crystals were obtained in a few days. Two crystals with good optical quality and sharp extinction under a polarizing microscope were selected for study. Crystal 1 had dimensions 0.35 × 0.70 × 1.0 mm and was mounted with the electric field parallel to the *b* axis. A voltage of 2.9×10^3 V was applied over 1.00 mm to give a field of 2.9×10^6 Vm^{-1}. Crystal 2 had dimensions 0.75 × 0.88 × 1.3 mm and was mounted with the field parallel to the *c* axis. This time a voltage of 2.9×10^3 V was applied over 1.3 mm to give a field of 2.2×10^6 V m^{-1}. POM crystallizes in space group $P2_12_12_1$ (Shiro *et al.*, 1976). Cell parameters determined from 24 reflections with $25 < 2\theta < 35°$, using a Rigaku rotating-anode generator and Mo $K\alpha$ radiation are: $a = 21.492\,(8)$, $b = 6.145\,(1)$, $c = 5.169\,(2)$ Å.

The intensity measurements on both samples were made at the SUNY X3 beamline at Brookhaven National Laboratory, using a focused beam with wavelength $\lambda = 1.500$ Å.

2-*Methyl*-4-*nitroaniline* (*MNA*). MNA crystals were grown using the thermal-gradient vapor growth technique (Levine, Bethea, Thurmond, Lynch & Bernstein, 1979). Crystals showing sharp extinction under a polarizing microscope were selected to be cut to give faces perpendicular to the polar axis, which is nearly parallel to $2\mathbf{a} + \mathbf{c}$ (Paturle *et al.*, 1989). A crystal with size 0.40 × 0.50 × 0.75 mm was mounted with the field parallel to the polar axis. A voltage of 2.9×10^3 V was applied over 0.75 mm, giving a field of 3.9×10^6 V m^{-1}. MNA crystallizes in space group *Ia* (equivalent to *Cc*) and has cell parameters: $a = 8.223(2)$, $b = 11.6199\,(9)$, $c = 7.588\,(2)$ Å, $\beta =$

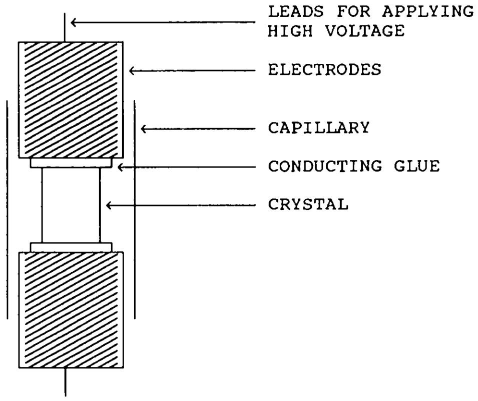

Fig. 4. Schematic drawing of the method of crystal mounting.

94.17 (3)° (Paturle *et al.*, 1989). Symmetry arguments show that a field along $2\mathbf{a}+\mathbf{c}$ can induce changes in a, b, c and β (Nye, 1957). Previous measurements of the piezoelectric tensor (Paturle *et al.*, 1991) showed MNA to be strongly piezoelectric. The intensity changes were measured with synchrotron radiation at the SUNY X3 beamline at Brookhaven National Laboratory using a focused beam of wavelength $\lambda = 1.380$ Å.

All samples were mounted between two polished platinum electrodes using conductive adhesive as shown in Fig. 4.

Results

Twelve reflections of NA, distributed over reciprocal space, were measured. None showed a significant (<0.05%) change in intensity with the applied electric field. Similarly, no change could be detected for 15 reflections of PNPNO. Neither of the two compounds showed a significant θ shift ($<10^{-4}$°) of the reflections, in agreement with the centrosymmetric nature of the crystals.

For the orthorhombic POM crystals (space group $P2_12_12_1$) the piezoelectric tensor has only three nonzero elements, d_{14}, d_{25} and d_{36} (Nye, 1957). This means that fields along **a**, **b** or **c**, will only induce changes in α, β or γ, respectively. From the two different settings with the field parallel to **b** and **c**, we obtain respectively:

$$d_{25} = \pm 5.7(4)\ \mathrm{pC\ N^{-1}}$$

$$d_{36} = \pm 2.6(3)\ \mathrm{pC\ N^{-1}}.$$

Since the absolute direction of the field is not known, the sign of the elements are undetermined (Paturle *et al.*, 1991). The ambiguity can be resolved by determining the crystal polarity, either by measuring sensitive Bijvoet pairs (Le Page, Gabe & Gainsford, 1990) or by using other physical properties such as the pyroelectric response (Ståhl *et al.*, 1990). We note that accurate integrated intensities are difficult to obtain for large crystals mounted between electrodes.

On the first sample with **E** parallel to **b** the intensity changes for a total of 17 reflections were measured. Thirteen of these showed no change in intensity larger than 3σ; the other four appeared to show some effect, but it could not be reproducibly established. On the second sample with **E** parallel to **c**, 36 reflections were measured, of these only three showed a definite change in intensity larger than 3σ, the largest relative change being 0.12%. Although the results indicate that a molecular reorientation takes place, the effect is too small to allow detailed study. In space group $P2_12_12_1$ the applied electric field always destroys symmetry elements and therefore increases the number of molecules in the asymmetric unit, further complicating the refinement. For example, a field parallel to **b** changes β and transforms the orthorhombic space group $P2_12_12_1$, with one molecule in the asymmetric unit, into the monoclinic space group $P2_1$, having two molecules in the asymmetric unit.

Table 1. *Observed changes in cell parameters between field up (+) and field down (−) for 2-methyl-4-nitroaniline (MNA), $E = 3.9\times10^6$ V m^{-1} parallel to* $2\mathbf{a}+\mathbf{c}$

Numbers in parentheses are e.s.d.'s.

Δa	0.000625 (23) Å
Δb	0.000222 (45) Å
Δc	−0.000012 (111) Å
$\Delta\beta$	−0.003761 (665) °

Table 2. *Observed and calculated changes in intensity between field up (+) and field down (−) for 2-methyl-4-nitroaniline (MNA), $E = 3.9\times10^6$ V m^{-1} parallel to* $2\mathbf{a}+\mathbf{c}$

The last column gives the e.s.d.'s of the obsrved changes.

h	k	l	F^2	ΔF^2_{+-} observed	ΔF^2_{+-} calculated	$\sigma(\Delta F^2_{+-})$ observed
7	−1	0	841.2378	−0.7773	−0.6917	0.1626
8	0	−2	591.6570	−0.3686	−0.4870	0.0911
1	−9	2	479.2991	−0.3827	−0.3224	0.0792
1	1	2	1620.2879	0.7430	1.0909	0.2173
−7	2	−1	787.6611	0.6635	0.5997	0.1239
6	2	2	476.4048	−0.6514	−0.5811	0.1337
5	2	3	518.9785	−1.3270	−1.1310	0.0976
4	4	0	692.2108	0.4255	0.4256	0.1242
3	3	2	1095.9079	0.7274	0.7396	0.1232
5	−3	0	389.6202	−0.5905	−0.4078	0.0946
7	−2	−1	175.1546	−0.2591	−0.2943	0.0382
6	−3	1	201.8246	−0.3409	−0.3721	0.0456
7	1	2	81.5012	0.3187	0.4262	0.0513
6	1	1	217.5389	−0.4626	−0.4603	0.0612
5	−3	4	121.8949	−0.2274	−0.2439	0.0629

For MNA the effect of the field is much more pronounced. Of 19 unique reflections (29 reflections measured), 15 showed a relative change larger than 3σ, the largest being 0.39%. The effect was symmetric in the field direction ($\eta_{+0} = -\eta_{-0}$) and the agreement between Friedel pairs and the reproducibility were good.

The refinement of the intensity data required, in addition to the change in cell parameters listed in Table 1, the introduction of the effect of internal strain. Since the field is in the mirror plane, the symmetry is not lowered by the deformation and the asymmetric unit of the deformed crystal contains only one molecule. As Ia is a polar space group, the x and z coordinates of one atom have to be fixed in the refinement. This results in a total of four parameters in the rigid-body refinement: the molecular rotations around three perpendicular axes and one translation. In Table 2 both the observed and calculated changes between field up (+) and field down (−) are given for the 15 reflections for which the effect is larger than 3σ. The reflections with an effect smaller than 3σ were not used in the refinement. The results of the refinement on the three different sets of data, η_{+0}, η_{-0} and η_{+-}, are given in Table 3,

Table 3. *Results of refinement of the data of* 2-*methyl*-4-*nitroaniline* (*MNA*), $E = 3.9\times10^6$ $V\,m^{-1}$ *parallel to* $2\mathbf{a}+\mathbf{c}$

Numbers in parentheses are e.s.d.'s.

Rotation		
η_{+0}	$0.27\,(6) = 10^{-2\circ}$	$1.6\mathbf{a}+1.0\mathbf{c}$
η_{-0}	$0.23\,(5)\times10^{-2\circ}$	$-1.3\mathbf{a}-1.0\mathbf{c}$
η_{+-}	$0.45\,(5)\times10^{-2\circ}$	$1.4\mathbf{a}+1.0\mathbf{c}$
Translation		
η_{+0}	$0.12\,(2)\times10^{-3}$ Å	along **b**
η_{-0}	$-0.09\,(3)\times10^{-3}$ Å	along **b**
η_{+-}	$0.19\,(3)\times10^{-3}$ Å	along **b**

where the three rotations have been reduced to the direction and magnitude of the rotation vector. For the η_{+-} data the agreement factor R, defined as $\sum|\Delta I^{\rm calc}-\Delta I^{\rm obs}|/\sum|\Delta I^{\rm obs}|$, equals 16.1%, $wR = \sum w|\Delta I^{\rm calc}-\Delta I^{\rm obs}|/\sum w|\Delta I^{\rm obs}| = 17.8\%$, GOF = 1.32.

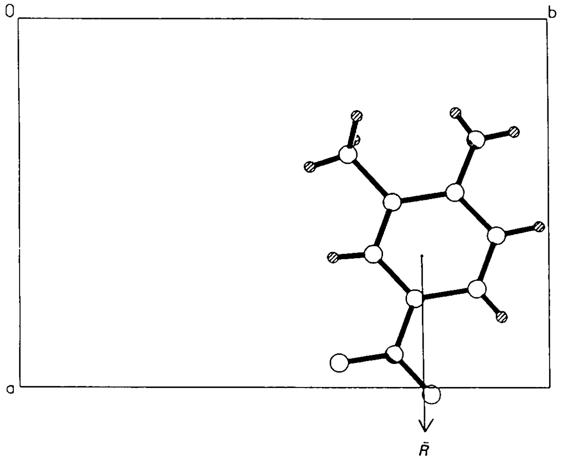

Fig. 5. Orthogonal projection of the MNA molecule and the axis of rotation due to the applied field onto the *ab* plane.

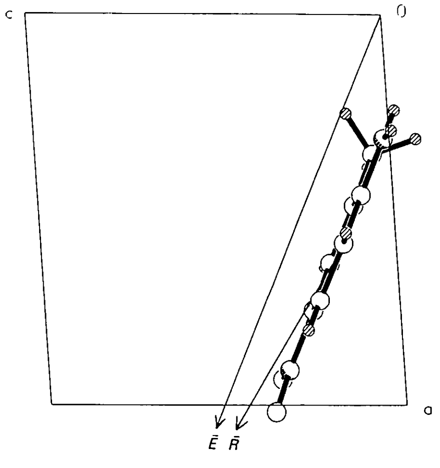

Fig. 6. Orthogonal projection of the MNA molecule and the axis of rotation due to the applied field onto the *ac* plane.

Table 3 shows that both the rotation and the translation reverse with the field, indicating a linear behavior. This is in agreement with the observation that the relative change in intensity reverses sign when the field direction is reversed. The linearity is also found in the observed θ shift of the reflections (Paturle *et al.*, 1991). The axis of molecular rotation $1.4\mathbf{a}+\mathbf{c}$ is close to the long axis of the molecule, as shown in Fig. 5, and nearly parallel to the applied electric field, as seen from Fig. 6.

Discussion

The absence of a measurable intensity change in centrosymmetric structures, combined with the fact that the effects are symmetric with respect to the field direction in non-centrosymmetric crystals, shows second-order structural changes to be negligible.

In the case of MNA we had anticipated a rotation of the molecule such as to line up the dipole moment with the direction of the applied field, as the dipole moment makes an angle of 19.5 (2)° with the polar axis, and thus with the applied electric field. This would imply rotation around an axis perpendicular to the applied field, with the atoms moving *within* the plane of the molecule. The observed rotation around an axis close to the applied field direction and in the molecular plane corresponds to atomic displacements in the direction of easiest motion perpendicular to the plane of the molecule. If we consider the molecular reorientation as a response to the external strain, the rotation in the softest direction is less surprising.

Following the concept of internal strain being induced by external strain (Born & Huang, 1954), we may consider the translations of the molecules relative to each other, and the corresponding change in cell dimensions, as the primary effect and the rotation of the molecules as the secondary response. The absence of molecular reorientation in the centrosymmetric compounds, where the change in cell dimensions is symmetry forbidden, supports this interpretation.

Our results indicate that for MNA the piezoelectric contribution to the permittivity is small. The polarization resulting from the deformation of the unit cell (external strain) is, for a field of $3.9\times10^6\,\mathrm{V\,m^{-1}}$ parallel to the polar axis, only 3.7×10^{-7} debye Å^{-3}, corresponding to a susceptibility $\chi = 0.04$ or a relative permittivity $K = 1.04$. The polarization due to the additional molecular rotation (internal strain) is also very small, since there is no rotation around an axis perpendicular to the polar axis. The absence of a molecular rotation about an axis perpendicular to the applied electric field could in principle be verified by measuring the clamped and free permittivities.

Levine *et al.* (1979) found one of the principal axes of the permittivity tensor to be nearly parallel to the polar axis. Thus, for a field parallel to the polar axis, the induced dipole moment and therefore the electric displacement are parallel to the applied field. Since the clamped permittivity is very difficult to measure, one can take the permittivity at high frequency, where the molecules cannot follow the rapidly changing field, as an approximate value for the clamped permittivity at zero frequency. The refractive index in the direction of the polar axis at a wavelength $\lambda = 0.6328\ \mu\text{m}$ was measured to be $n = 2.0\,(1)$ (Levine *et al.*, 1979), which corresponds to a relative permittivity $n^2 = K = 4.0$.

A small rotation of the molecule around an axis perpendicular to the polar axis, so that the large molecular dipole lines up with the applied field, would result in a large piezoelectric contribution to the permittivity. For instance a rotation over an angle of 0.002° would, with a molecular dipole moment of 8.65 debye, give a polarization of 0.32×10^{-4} debye Å^{-3}. For a field of $3.9 \times 10^6\ \text{V m}^{-1}$, this corresponds to a susceptibility $\chi = 3.1$ or a relative permittivity $K = 4.1$ in the direction of the polar axis. Thus a small molecular rotation over an angle perpendicular to the polar axis would give a relatively large piezoelectric contribution to the permittivity.

Nye (1957) states that a typical difference between the two permittivities is of the order of 1% of the primary effect. This may not necessarily be true for molecular crystals with large piezoelectric coefficients. However, for MNA the small contribution to the permittivity from the polarization due to external strain, relative to the total value derived from the refractive index, indicates Nye's statement to be qualitatively valid in this case.

Although the piezoelectric contribution to the permittivity is small, the piezoelectric contribution to the non-linear electrooptic effect may still be sizeable. As pointed out earlier (Paturle *et al.*, 1991), the interpretation of the large electrooptic effect in MNA as being electronic in nature (Lipscomb, Garito & Narang, 1981) might need reconsideration for fields parallel to the polar axis. Since, as shown here, fields in this direction give rise to large external as well as internal strains, the piezoelectric contribution to the electrooptic effect (the piezooptic effect) might not be negligible relative to the electronic effect.

Further development of the method

The successful refinement of the observed changes in MNA in terms of a molecular reorientation confirms the theoretical prediction that the molecular polarizations are too small to be measured with the fields applied. However, if the field strength can be increased by a factor of 20, the polarization of the MNA molecule due to the linear polarizability would be about 0.1 debye, which appears measurable with present capabilities. With the large field more reflections would show a significant intensity change, thus opening the way to a more complete structure refinement.

The main limitation to increasing the field strength is electrical discharge through the air. To overcome this problem we are experimenting with MNA crystals mounted in a transformer-oil-filled capillary (see Fig. 4). Preliminary results are in agreement with those reported above. We are currently testing the use of a much faster plastic scintillator detector to eliminate deadtime limitations in the synchrotron experiments and developing electronics capable of switching larger fields.

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