Hysteresislike Behavior in Meta-Nitroaniline Crystals

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In this paper we report, for the first time, an experimentally observed hysteresislike variation of lattice parameter of the organic crystal 2-nitro aniline (mNA) under the influence of an externally applied dc electric field. Calculations have been made to determine whether the main features of the hysteresislike behavior can be explained in terms of the geometrical distortions of isolated mNA molecules or are dominated by molecular interactions. The results show that the main features of the nonlinearity can be explained in terms of changes in the acceptor-donor properties of isolated mNA molecules.

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The potential for the exploitation of the exceptionally large second-order polarizabilities (first hyperpolarizabilities) of some organic crystals are extensive because of the almost endless variations in chemical structure. Also, the magnitude of this effect can be modified through molecular engineering. Molecular engineering, in this context, is the procedure whereby the molecular structure is refined by chemical synthesis to produce the desired combination of linear optical, nonlinear optical, and other physical and chemical properties in a given phase for a particular application [1]. The nonlinear responses of crystals have their origins in the (fairly predictable) molecular nonlinearities [2], but the crystal structure and intermolecular interactions in the crystal may also play a crucial part in determining the nature of the produced effects.

Large high quality noncentrosymmetric single crystals have been grown at the University of Strathclyde [3] in recent years, mainly with the aim of exploiting their nonlinear optical properties, particularly for second-harmonic generation (SHG) and signal modulation via the linear electro-optic effect. The crystals, by virtue of their highly polar, anisotropic structures, might also be expected to exhibit substantial piezoelectric and, in some cases, pyroelectric effects. These responses are related to a range of interesting phenomena, including the optoacoustic and photorefractive effects. Recent studies of one such material, 2-nitro aniline, by the x-ray multiple diffraction technique using synchrotron radiation have allowed the determination of some components of its piezoelectric tensor [4].

X-ray diffraction techniques provide the optimum tool for studying subtle changes in lattice geometry of nonlinear optical materials when subjected to external stimuli, such as an applied electric field. Such approaches when coupled with the use of synchrotron radiation enable, in principle, dynamical diffraction measurements. Thus, the effects associated with lattice relaxation at low frequencies can be isolated from the remaining high frequency electronic processes, which are, in principle, calculable from the SHG susceptibilities.

2-nitro aniline (mNA) [5] organic crystal is one of a large group of meta disubstituted benzenes, which have been investigated for their potential as electro-optic materials [6,7]. Crystallizing in the orthorhombic system with point group mm2, mNA has four molecules per unit cell and lattice parameters $a = 6.501$ Å, $b = 19.330$ Å, and $c = 5.082$ Å. The molecule is essentially planar, with the dipole moment directed from N_1 in the amino group towards N_2 in the nitro group. The polar axis of the material is **c**, [001] as shown in Fig. 1.

The experimental samples, $20 \times 10 \times 2{-}5$ mm^3, were prepared by cleaving slices from large high quality mNA single crystals which had been first cut using a solvent saw to minimize induced damage. Sample faces were polished with solvent to ensure the required degree of flatness and parallelism of the faces.

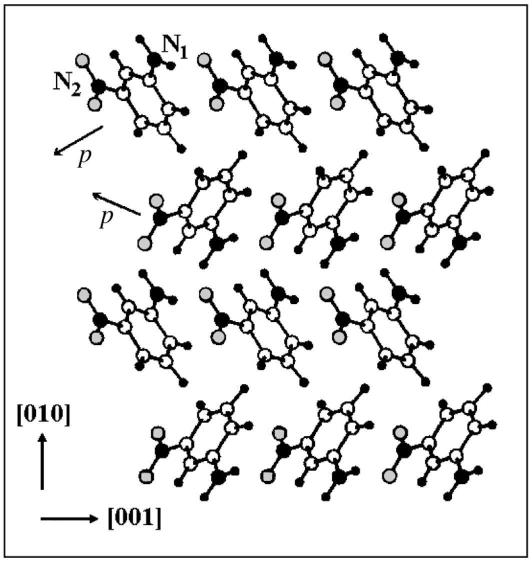

FIG. 1. Projection of the mNA structure on the (100) plane. The electric field was applied in the [001] direction and the strain was observed in the [010] direction. The molecular dipole momentum is directed from the N_1 in the amino to the N_2 in the nitro group and is indicated by **p**.

The electric field was generated by a variable voltage, low current, dc power supply and was applied along the polar **c**-axis of the material. Electrical contacts were established through conductive sponges kindly provided by the SGL Carbon Group, Meitingen, Germany. These sponges are placed between metal plates and the larger sample faces serve to establish a uniform electric field within the crystal. The sponge also avoided the development of mechanical strain in the sample due to physical contact.

The x-ray beam was incident on the narrower sample face, allowing the simultaneous measurement of rocking curves and of other x-ray experiments such as multiple diffraction (Renninger scan). The peak shifts for the primary diffraction $0k0$ rocking curves were obtained by measuring the change in the corresponding Bragg angle (θ) [4]:

$$\frac{\Delta b}{b} = \frac{\Delta d}{d} = -\cot\theta^{0k0}\Delta\theta^{0k0}. \tag{1}$$

Rocking curves were measured using a SIEMENS P4 single crystal diffractometer equipped with encoders to ensure step sizes in the omega axis smaller than 1 mdeg. The synchrotron measurements were performed on the high resolution diffractometer station (16.3) [8] at the Daresbury Laboratory, Warrington, UK, which allows step sizes of 0.0002°. The wavelengths used throughout the experiments were 1.3922 Å (Cu K_β—conventional radiation) and 1.4878 Å (synchrotron radiation). The accuracy of the experimental equipment was checked by measuring several rocking curves for mNA in the absence of the electric field and by determining the d_{22} piezoelectric coefficient of lithium niobate [4]. Furthermore, during all measurements, the full width at half maximum of the $0k0$ diffraction peaks was determined as a function of E_z and no variation was observed, indicating the uniformity of the electric field within the samples.

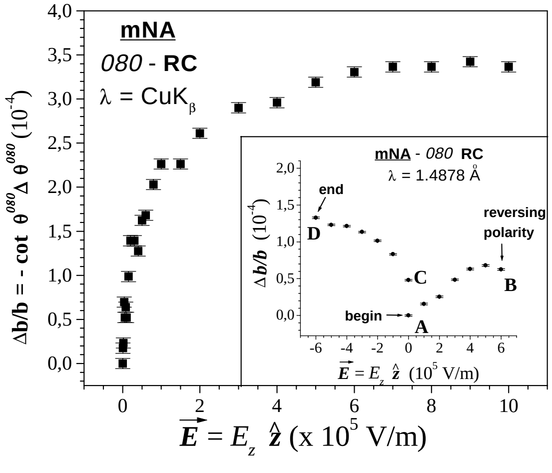

FIG. 2. Strain $(\Delta b/b)$ as a function of E ($0 \rightarrow 1 \times 10^6$ V/m). We show in the inset the strain $(\Delta b/b)$ as a function of E ($0 \rightarrow 1 \times 10^6$ V/m $\rightarrow 0$, half-cycle) using synchrotron radiation ($\lambda = 1.4878$ Å). See text for discussion.

In Fig. 2 we show changes in the lattice parameter $(\Delta b/b)$ as a function of the electrical field strength. From the figure we can clearly observe two distinct linear regimes (at low and high E values, respectively). This is the first time that a ferroelectric behavior for mNA crystals is observed; only piezoelectric results had been reported before [4]. In the inset of Fig. 2 we show the results from synchrotron experiments using different mNA samples with the same 080 as the primary reflection plane. As can be seen from the inset, a memory effect is clearly visible (points A, B, and C) as also a linear regime for high E values (0.1 to 0.5 MV/m), consistent with the results shown in Fig. 2.

In order to further analyze this phenomenon, measurements were carried out over a complete electric field cycle. The field was increased from zero to 1.0×10^6 V/m and then decreased back to zero. It was then reversed in polarity from zero to -1.0×10^6 V/m and returned to zero again to complete the whole E-cycle. The rocking curve was measured at each E value and the maximum peak was used to define the lattice strain in the **b** direction [$\Delta b/b$, Eq. (1)]. This procedure allowed us to determine the existence of phase transitions and/or memory effects.

The results of these measurements are shown in Fig. 3. A clear nonlinear response of the sample was observed over the whole cycle. At the end of the cycle ($E = 0$) the peak returned to its initial angular position. This is the first experimentally observed hysteresislike behavior for mNA crystals. As we have dynamic memory effects, the absolute values indicated in Figs. 2 and 3 depend on time exposure. In order to compare the data from these figures only their relative values are meaningful. In the inset of Fig. 3 we show these relative variations for the linear regime. The angular coefficients are very similar, as expected. These

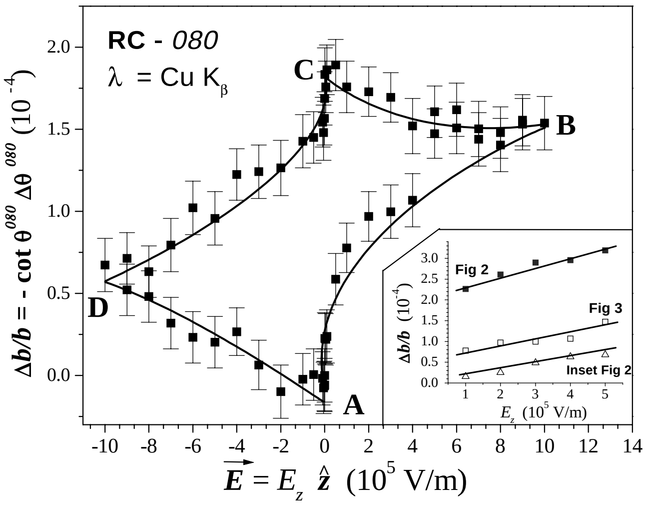

FIG. 3. Strain $(\Delta b/b)$ as a function of E ($0 \rightarrow 1 \times 10^6$ V/m $\rightarrow 0 \rightarrow -1 \times 10^6$ V/m $\rightarrow 0$, complete cycle). Radiation: Cu K_β ($\lambda = 1.3922$ Å). We show in the inset the relative variation of $\Delta b/b$ from the following: Fig. 2 (inset) and Fig. 3 (through 0.1 to 0.5 MV/m). See text for discussion.

variations are in agreement with previous work [4] (insets of Figs. 2 and 3).

The behavior of the $\Delta b/b$ shown in Fig. 3 as E approaches zero can be explained in terms of the asymmetry of potential for charge transfer (instead of a phase transition [9]), favoring it when E is positive, and resisting it when E is negative.

No phase transition was detected but a memory effect was clearly observed. After removing the electric field from the sample, a period of typically 10 hours was required before the sample returned to its initial structural state.

mNA presents a very simple structure (Fig. 1) with a linear alignment of molecules. This simplifies the theoretical analysis since this particular alignment allows us to estimate the effect of molecular interactions from calculations on isolated molecules. As the molecules are essentially planar with the dipole moment directed from N_1 in the amino group towards N_2 in the nitro group, we carried out calculations applying an external electric field in the appropriate directions and studied the elastic molecular deformations of isolated structures. On this basis we investigated whether the main feature of the hysteresis-like behavior can be explained in terms of these molecular deformations.

The calculations were carried out using the well-known semiempirical method AM1 (Austin method one) [10], with a modified code which allows the introduction of an external field into the Hamiltonian. The details of the methodology have been discussed elsewhere [11]. In spite of their simplicity, semiempirical and even simpler topological methods have been proved to be efficient tools for the investigation of the electronic structure of organic materials [12–15].

The geometrical optimizations were performed as a function of the electric field strength applied along the direction connecting the nitrogen atom in the amino group (donor group) to the adjacent carbon atom, which is the natural choice in donor-acceptor molecules.

Exploring the symmetry properties of mNA crystals we can qualitatively express lattice crystal change dimensions in terms of the geometric bond-length changes of isolated mNA molecules. Our results show that the major distortions are in the N1-C1 and N2-C3 bond lengths, the bond lengths of the acceptor-donor groups. These changes can be linked to the charge population since they have the same qualitative behavior [11,16]. The option to use charge population analysis (instead of bond-length deformations) is based on the fact that it is an intrinsic property of the molecular structure and is very easy to visualize. The use of bond-length deformations would require geometric corrections (projections over the plane) for each value of the electric field, a very tedious process that does not add any helpful information to our qualitative analysis.

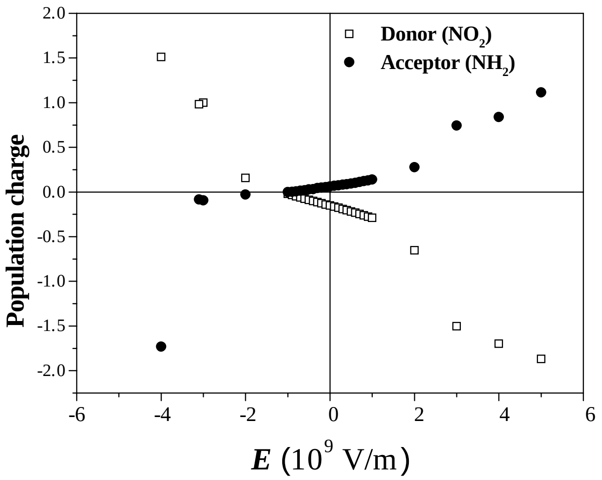

FIG. 4. Charge population in the acceptor (NH_2) and donor groups (NO_2) as a function of the strength of the applied electric field E. See text for discussion.

In Fig. 4 we present the results of the calculations for the charge populations over the acceptor (NH_2) and donor (NO_2) groups. At low E values we observe linear variations with similar angular coefficients (in module) for both donor and acceptor groups. This behavior is qualitatively similar to that experimentally observed (see Fig. 2). For high E values the variation is nonlinear and differs for donor and acceptor groups. These distinct changes are related to different types of geometrical distortions: simple elongation of the bond lengths (donor) and elongation followed by torsional changes (acceptor).

This results in a macroscopic memory effect since the relaxation times will have different time scales. Also, as the facility for charge transfer is related to the hardness of the molecular structures (strain/stress) [9], we expect an inverse steeper dependence of charge population and $\Delta b/b$ with the electric field, exactly the experimentally observed behavior.

Thus the theoretical results explain qualitatively the main features experimentally observed, namely, the nonlinear behavior, the different regimes for the positive and negative electric fields, and the memory effects. Although it is expected that molecular interactions will be very important in defining the macroscopic behavior of mNA crystals, the above results strongly suggest that the observed features can be directly associated with changes in the donor-acceptor properties of isolated molecules.

In summary, we report the first experimentally observed (from x-ray and synchrotron experiments) hysteresislike behavior and ferroelectric signature of mNA crystals. Theoretical analysis explained qualitatively this behavior in terms of changes in the donor-acceptor properties of mNA molecules. If confirmed by other techniques the ferroelectricity would open up interesting new perspectives to the potential application of this class of organic crystals.

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[1] *Nonlinear Optical Properties of Organic Molecules and Crystals*, edited by D. S. Chemla and J. Zyss (Academic Press, Orlando, FL, 1987), Vol. 1.
[2] D. Pugh and J. O. Morley, in Ref. [1], Vol. 1, pp. 192–225.
[3] R. T. Bailey, F. R. Cruickshank, D. Pugh, and J. N. Sherwood, Acta Crystallogr. Sect. A **47**, 145 (1991).
[4] L. H. Avanci, L. P. Cardoso, S. E. Girdwood, D. Pugh, J. N. Sherwood, and K. J. Roberts, Phys. Rev. Lett. **81**, 5426 (1998).
[5] A. C. Skapski and J. L. Stevenson, J. Chem. Soc. Perkin Trans. **2**, 1197 (1973).
[6] J. G. Bergman and G. R. Crane, J. Chem. Phys. **66**, 3803 (1977).
[7] A. Carenco, J. Jerphagnon, and A. Perigaud, J. Chem. Phys. **66**, 3806 (1977).
[8] S. P. Collins, R. J. Cernik, C. C. Tang, N. W. Harris, M. C. Miller, and G. Oszlanyi, J. Synchrotron Radiat. **S5**, 1263 (1998).
[9] J.-C. Toledano and P. Toledano, *The Landau Theory of Phase Transitions* (World Scientific, Singapore, 1987), and references therein.
[10] M. S. Dewar, E. G. Zoebisch, E. F. Healy, and J. J. P. Stewart, J. Am. Chem. Soc. **107**, 3902 (1985).
[11] S. O. Dantas, M. C. Santos, and D. S. Galvão, Chem. Phys. Lett. **256**, 207 (1996).
[12] D. S. Galvão, D. A. dos Santos, B. Laks, C. P. de Melo, and M. J. Caldas, Phys. Rev. Lett. **63**, 786 (1989); **65**, 527 (1990).
[13] Z. G. Soos, S. Ramasesha, and D. S. Galvão, Phys. Rev. Lett. **71**, 1609 (1993).
[14] R. H. Baughman and D. S. Galvão, Nature (London) **365**, 735 (1993).
[15] P. M. V. B. Barone, A. Camilo, and D. S. Galvão, Phys. Rev. Lett. **77**, 1186 (1996).
[16] M. Pickholz and M. C. dos Santos, J. Mol. Struct.: THEOCHEM **432**, 89 (1998).