tivity in the NaY/pyrolyzed PAN samples is not suprising because the polymer is encapsulated completely within the insulating zeolite, and no external polymer coats the zeolite crystal surfaces. The conductivity of the pyrolyzed PAN extracted from the zeolite is almost identical with that of bulk PAN pyrolyzed at 530 °C, and 5 orders of magnitude smaller than that of the bulk sample pyrolyzed at 650 °C. In contrast to the bulk polymer, pyrolysis treatment conditions above about 600 °C have little effect on the resulting conductivity of the intrazeolite samples. The same conductivity value of about 2×10^{-5} S cm^{-1} is obtained for extracted pyrolyzed PAN, pyrolyzed at different temperatures, atmospheres, and times. It can be concluded that the spatial limitations within the zeolite channels prevent the formation of more extended, graphitized structures with higher conductivity.

Conclusions

Poly(acrylonitrile) was synthesized in the channel systems of NaY and Na-mordenite zeolites and pyrolyzed to yield a conducting material. Before pyrolysis, the intrazeolite polymer has a random configuration as in the bulk, and extends through a significant part of the NaY zeolite crystals, while polymerization in the one-dimensional channels of mordenite produces much shorter chains. Upon pyrolysis, conjugated ladder polymers are formed which show conductivities in the semiconductor regime when extracted from the zeolite hosts. A striking feature of these pyrolyzed polymer inclusions is the strong limiting effect of the zeolite structure on the degree of ring closure and graphitization. As expected from the channel dimensions, complete graphitization with formation of extended sheetlike structures is not possible in the zeolite; instead, the pyrolysis reactions are limited to the ladder structures formed in the bulk at lower temperature. Future work will explore the effect of larger pore sizes on polymerization and graphitization of acrylonitrile inclusions and their associated electronic conductivity. These systems are promising candidates for low-field conductivity at nanometer scale dimensions.

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Induction of Noncentrosymmetry by Polar Hydrogen-Bonded Chains in Nitroaniline Crystals

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The role of polar hydrogen-bonded nitroaniline chains in inducing noncentrosymmetry in bulk nitroanilines is explored here using correlations between the presence of such motifs and the occurrence of noncentrosymmetric space groups among all known nitroaniline crystal structures. Our results show a significant bias for compounds with polar nitroaniline motifs to have noncentrosymmetric structures (46% of 24 structures) compared to the frequency with which achiral molecules in general form noncentrosymmetric crystal structures (11%). Thus, the special role that nitroanilines have played in the field of organic nonlinear optical materials may be attributed not just to their normally large hyperpolarizabilities but also to the fact that this class of molecules has an unusually high tendency to form noncentrosymmetric crystals.

Introduction

We are seeking to understand what features of noncentrosymmetric crystal structures are controllable and what features correlate with the absence of centers of symmetry, a necessary constraint for second-order nonlinear optical materials. The problem is that controlling any feature of a crystal packing pattern is a formidable task. This task would be much simpler if the mechanisms of organic crystal nucleation and propagation were better understood, especially at the molecular level. From our recent work on the use of hydrogen bonds to control cocrystal formation,[1] we have begun to view the crystal growth process as one that involves a preassembly step whereby hydrogen-bonded sets of molecules form in solution.[2] These aggregates are thought to then nucleate crystal growth while retaining their hydrogen-bond connectivity patterns. Our previous analysis of nitroaniline crystal structures, showing the presence of recurring polar hydrogen-bonded nitroaniline chains, is consistent with the idea that the nitroaniline chains themselves, rather than individual molecules, are the prenucleation sites for crystal growth.[3] With this perspective in mind and with the realization that nitroaniline chains are necessarily noncentrosymmetric,[3] we questioned whether these chains could be inducing nitroaniline compounds to grow as noncentrosymmetric crystals. In other words, despite the favorable hyperpolarizability properties of nitroanilines, are they better than normal candidates for nonlinear optical uses because they are more likely than usual to be noncentrosymmetric? This question is addressed here using data retrieved from the Cambridge Structural Da-

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[1] Etter, M. C. *J. Phys. Chem.* 1991, *95*, 4601.

[2] Etter, M. C.; MacDonald, J. C.; Wanke, R. A. *J. Phys. Org. Chem.*, in press.

[3] Panunto, T. W.; Urbańczyk-Lipkowska, Z.; Johnson, R.; Etter, M. C. *J. Am. Chem. Soc.* 1987, *109*, 7786.

Table I. CSD Data Sets[a]

	search algorithms					
	1[b]	2[c]	3[d]	4[e]	5[f]	6[g]
1. initial hits	46	82	22	20	35	22
2. additional functional H-bonding groups	4	6	1	5	1	1
3. multiple reports	7	7	3	1	1	1
4. 1° + 3°,2° + 3°	0	0	0	0	2	8
5. *R* factors between 11% and 16%[h]	0	2	0	2	0	0
6. total entries[i]	35	67	18	12	31	12

[a] Details of search algorithms are given in the supplementary material. [b] Entries containing the names nitro and aniline. [c] Entries from the chemical class anilines, and containing the nitro group fragment. [d] Molecules containing the nitrobenzene fragment and a primary (1°) aniline group. [e] Molecules containing the nitrobenzene fragment and a secondary (2°) aniline group. [f] Molecules containing the nitrobenzene fragment and a type I tertiary (3°) aniline group, Ph—N<. [g] Molecules containing the nitrobenzene fragment and a type II tertiary (3°) aniline group, Ph—N=. [h] Original crystal structure papers were consulted and each structure was examined to ascertain whether it should be included in the data set. Details of the assessment are given in the supplementary material. [i] The total entries are obtained by subtracting lines 2–5 from line 1.

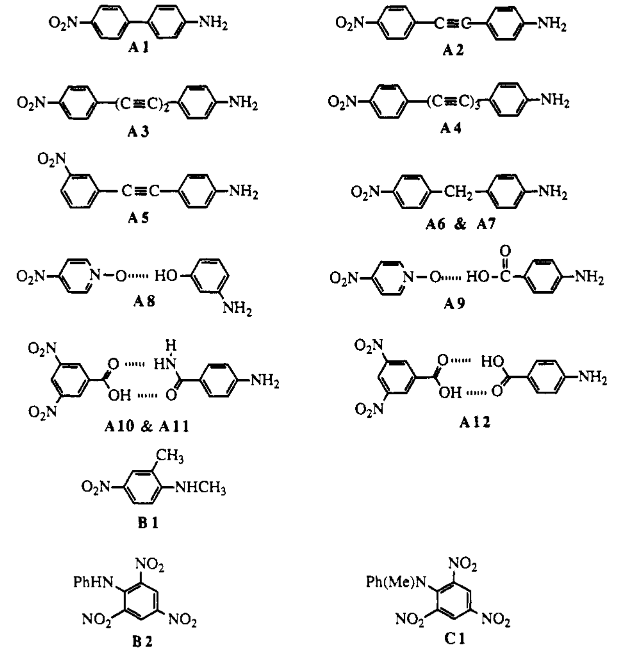

Figure 1. Structural formulae and codes used for nitroaniline analogs and cocrystals from sources other than CSD.

tabase and from other recently reported nitroaniline crystal structures.

Experimental Section

The Cambridge Structural Database (CSD)[4] was used to search for crystal structures of molecules with nitroaniline groups. To produce the most comprehensive data base, six different search algorithms were run and compared. In each search, crystal structures containing molecular complexes and solvated compounds were excluded. Entries containing the metals, residues, or functional groups listed here were also excluded: first- and second-row metals, lanthanide and actinide series metals, charged residues, hydroxyl and carbonyl groups, cyclic C–N and C–S compounds, and N–N, O–O, P–N, N=N, and P=N.

Table II. Nitroaniline Analogs and Cocrystals from Sources Other Than CSD

compound code[a]	space group	classification	ref
A1	$Pca21$	1°	*b*
A2	$Pbcn$	1°	*b*
A3	$P2_1/c$	1°	*b*
A4	$P2_1/c$	1°	*b*
A5	$P\bar{4}2_1c$	1°	*c*
A6	$P1$	1°	*d*
A7	An	1°	*d*
A8	Cc	1°	*e*
A9	$P2_12_12_1$	1°	*f*
A10	$P2_1/c$	1°	*g*
A11	$P2_1/n$	1°	*g*
A12	$Fdd2$	1°	*g*
B1	$Pna2_1$	2°	*h*
B2	$P2_1/n$	2°	*i*
C1	$P2_1/c$	3°	*i*

[a] Structural formulae corresponding to these codes are given in Figure 1. [b] Graham, E. M.; Miskowski, V. W.; Perry, J. W.; Coulter, D. R.; Stiegman, A. E.; Schaefer, W. P.; Marsh, R. E. *J. Am. Chem. Soc.* **1989**, *11*, 8771. [c] Stiegman, A. E., personal communication. [d] Wnek, G. E., personal communication. [e] Lechat, J. R.; de A. Santos, R. H.; Bueno, W. A. *Acta Crystallogr. Sect. B* **1981**, *37*, 1468. [f] Lechat, J. R., personal communication. [g] Etter, M. C.; Frankenbach, G. M. *Chem. Mater.* **1989**, *1*, 10. [h] Twieg, R. J., IBM, personal communication. [i] Forlani, L.; Battaglia, L. P.; Corradi, A. B.; Pelosi, G. J. *Cryst. Spectrosc.* **1990**, *20*, 499.

The results of the searches are given in Table I. The number of initial hits obtained from each of the six algorithms is listed on line 1. The chemical structure of each entry was examined and compounds containing additional H-bonding functional groups besides nitro or aniline, listed on line 2, were excluded. The excluded structures included free radicals, nitroso, sulfonyl, or heterocyclic-containing compounds. Occasionally multiple entries were found for the same polymorph (line 3). Compounds with primary and secondary aniline groups in addition to the desired tertiary anilines were removed in searches 5 and 6 (line 4). For structures with *R* factors between 11% and 16%, each individual crystal structure paper was read in detail and independent decisions were made about whether to retain the structure in the analysis. On this basis two structures were removed from searches 2 and 4 (line 5). (Details of the analyses are included in the supplementary material.) The final number of retrieved structures for each search algorithm is given on the last line of Table I.

Fifteen additional nitroaniline analogs and cocrystals, taken from unpublished data from our laboratory, from private communications with other authors, or from recently published structures not yet included in the database, are shown in Table II. Upon collecting all the data sets, unique data for 32 primary anilines, 16 secondary anilines, and 44 tertiary anilines were obtained. The compounds corresponding to these sets and their bibliographic citations are given in the Supplementary Material.

In Table III, the distribution of noncentrosymmetric structures among these three nitroaniline classes is given. Sets I–III are comprehensive sets with compounds containing any number of nitro or aniline groups. Sets IV–VI contain molecules with only single $-NO_2$ and $-NH_2$ or $-NO_2$ and $-NH$ groups. Sets II and V include compounds with any kind of intermolecular hydrogen bonds,[5] while III and VI specifically contain hydrogen-bonded chains. Sets III and VI give the frequency of occurrence of noncentrosymmetric space groups among the nitroaniline sets containing polar hydrogen-bonded nitroaniline chains. The best set to use to test whether hydrogen-bond chains bias the formation of noncentrosymmetry in three-dimensional crystal structures is set VI, where 46% of the compounds are noncentrosymmetric. Molecules in this set have only a single nitro and a single amino group and the hydrogen-bond motif is a polar chain. There are no competing nitro or aniline groups to impose additional hydrogen-bonding constraints on this system, as for set III.

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(4) (a) Allen, F. H.; Bellard, S.; Brice, M. D.; Cartwright, B. A.; Doubleday, A.; Higgs, H.; Hummerlink-Peters, B. G.; Kennard, O.; Motherwell, W. D.; Rodgers, J. R.; Watson, D. G. *Acta Crystallogr., Sect. B* **1979**, *35*, 2331. (b) Allen, F. H.; Kennard, O.; Taylor, R. *Acc. Chem. Res.* **1983**, *16*, 146. (c) Cambridge Structural Database; Cambridge Crystallographic Data Centre, University Chemical Library: Cambridge, England, Version 4.3, update June 1990.

(5) The presence of hydrogen bonds was inferred by consideration of bond lengths, angles, and motif patterns, as described in detail in ref 3.

Table III. Analysis of the Distribution of Noncentrosymmetric Structures and the Role of Hydrogen Bonds for 1°, 2°, and 3° Nitroanilines (NA) from Tables I and II

set	analyses	1° NA	2° NA	1° + 2° NA	3° NA
I–III (All Nitroaniline Compounds, Regardless of the Multiplicity of $-NO_2$ and/or $-NH_2$, $-NH$ Substituents)					
I	no. of total entries	32	16	48	44
	no. with noncentrosym SG	13	3	16	9
	% noncentrosym	40.6	18.8	33.3	20.0
II	no. of entries with intermolecular H bonds	31	14	45	0
	no. with noncentrosym SG	13	3	16	0
	% noncentrosym	42.0	21.4	35.6	0
III	no. of entries with H-bonded chains	29	7	36	0
	no. with noncentrosym SG	13	1	14	0
	% noncentrosym	44.8	14.3	38.9	0
IV VI Are Subsets of I–III Where Only Single $-NO_2$ and $-NH_2$ or $-NO_2$ and $-NH$ Are Present in the Molecule Substituents					
IV	no. of entries	20	8	28	0
	no. with noncentrosym SG	10	1	11	0
	% noncentrosym	50.0	12.5	39.3	0
V	no. of entries with intermolecular H bonds	20	6	26	0
	no. with noncentrosym SG	10	1	11	0
	% noncentrosym	50.0	16.7	42.3	0
VI	no. of entries with H-bonded chains	18	6	24	0
	no. with noncentrosym SG	10	1	11	0
	% noncentrosym	55.6	16.7	45.8	0

Results

Primary nitroanilines, with a single $-NH_2$ and a single $-NO_2$ group, all form polar hydrogen-bonded chains and have a significantly higher tendency (56%, set VI, column 1) to pack in noncentrosymmetric space groups than do tertiary anilines (20%, set I, column 4), where hydrogen bonds are not possible. Even though the data are limited, the bias is evident even in the broader class of nitroanilines where multiple nitro or amino groups are involved in complex hydrogen-bonded patterns. In these cases, 42% of the nitroanilines occur in noncentrosymmetric space groups (set II, column 1). For nitroanilines of all types, with polar hydrogen-bonded chains in their packing patterns, 45% had noncentrosymmetric crystal structures (set III, column 1). Even though the secondary aniline data sets are too small to be convincing, preferences of these anilines for noncentrosymmetric crystal structures seem about the same or slightly less than those of tertiary anilines.

Discussion

Curtin and Paul demonstrated that crystal structures of meta-substituted compounds are more likely to be noncentrosymmetric than other organic compounds.[6] A reasonable rationale for this phenomenon is that noncentrosymmetric molecules induce noncentrosymmetricity in developing crystal nucleation sites. If molecules aggregate in solution into noncentrosymmetric aggregates and if these aggregates then assemble into nucleation sites, induction of noncentrosymmetry, analogous to the process proposed by Curtin and Paul, could in principle occur. We tested this hypothesis by using data from the CSD and from other recently available crystal structures. Various sets of nitroaniline structures were analyzed for the frequency of occurrence of noncentrosymmetric space groups and compared to the comparable frequencies for non-nitroaniline structures.

Table IV. Space Group Frequencies (%; Total Number of Crystal Structures in Parentheses)

space group	1° and 2° nitroaniline structures[a] (48)	all-organic structures[b] (29 059)	mono C=O- or CN-containing structures[c] (93)
	Common Centrosymmetric Space Groups		
$P2_1/c$	52.1	36.0	39.8
$P\bar{1}$	8.3	13.7	11.8
$C2/c$	4.2	6.6	3.2
	Common Noncentrosymmetric Space Groups		
$P2_12_12_1$	6.2	11.6	18.3
Cc	6.2	1.0	NA[d]
Pc	4.2	0.4	NA
$Pna2_1$	4.2	1.8	NA
$Pca2_1$	4.2	0.8	NA
$P2_1$			2.2
other centrosymmetric and noncentrosymmetric space groups	10.4	28.1	24.7

[a] Present work. [b] Mighell, A. D. *Acta Crystallogr., Sect. A* **1983**, *39*, 737. [c] From ref 9. [d] Data not available.

For primary and secondary nitroanilines containing hydrogen-bonded chains of molecules, 46% of the structures with only single nitro and amino groups (set VI, column 3), had noncentrosymmetric crystal structures. When all primary and secondary nitroanilines were considered including those with multiple nitro and/or amino groups, 39% of the compounds had noncentrosymmetric crystal structures (set III, column 3).

These numbers are to be compared with the frequency with which all organic molecules adopt noncentrosymmetric crystal structures. In our sets of structures with hydrogen-bonded chains, none are noncentrosymmetric by virtue of chiral centers in the molecules. Using the recently determined figure that 27% of organic crystal structures are noncentrosymmetric, and about 60% of those contain resolved enantiomers,[7] then only about 11% of achiral organic molecules from noncentrosymmetric structures,[8] as compared to 46% of achiral nitroanilines with hydrogen-bonded chains found from our data.

It is also interesting to compare space group frequencies for primary and secondary nitroanilines with those of all other organic compounds (Table IV). In both classes, $P2_1/c$ is the most common space group. The nitroanilines, however, show a disproportionate preference for the four polar space groups (Cc, Pc, $Pna2_1$, $Pca2_1$) as compared to all-organic structures, where $P2_12_12_1$ is the preferred noncentrosymmetric structure. Although there are only 48 structures in the nitroaniline set, the trend for hydrogen-bonding molecules to form polar structures is consistent with our hypothesis that hydrogen-bonded chains may direct crystal nucleation and thereby induce noncentrosymmetry in the final three-dimensional crystal packing patterns.

These analyses have been based on consideration of hydrogen bonds as the only relevant intermolecular interactions occurring in crystal structures of organic com-

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(6) Curtin, D. Y.; Paul, I. C. *Chem. Rev.* **1981**, *81*, 525.

(7) Allen, F. H.; Galloy, J.; Smith, J. M. personal communication. From 43 000 structures, 5000 were organic compounds in a Sohncke space group and had no disorder. Of these 5000 structures, 874 had no chiral atoms.

(8) Since 40% of the noncentrosymmetric crystal structures contain achiral molecules and since the noncentrosymmetric structures constitute 27% of all known crystal structures, then the achiral noncentrosymmetric crystal structures constitute 27% × 0.40, or 11%, of the total data base.

pounds. This situation is certainly not the case. Other strong interactions that could be influencing nitroaniline packing patterns are charge transfer interactions and dipole–dipole interactions. No systematic structural analyses of the effects of charge transfer on the packing of nitroanilines has been reported, but two groups have analyzed the role of dipole–dipole interactions on the packing of polar molecules in organic crystals.[9,10] These studies are important here since most nitroanilines are also polar molecules. Interestingly, our analyses show that 20% of tertiary nitroanilines, where hydrogen bonds are not present to compete with dipole–dipole interactions, form noncentrosymmetric structures. This percentage is very close to that found by Gavezzotti for his prototype dipolar molecules (monosubstituted carbonyl and nitrile compounds) for which about 20% are found in $P2_12_12_1$ and $P2_1$ noncentrosymmetric space groups[9] (Table IV). An interesting future project would be to carry out a dipole moment/space group correlation on the sets of nitroaniline structures presented here to see if the dipolar contribution to noncentrosymmetry can be separated from the hydrogen-bond contributions.

Conclusion

We have found that while achiral organic molecules in general have an 11% chance of forming noncentrosymmetric crystal structures, achiral nitroanilines that have single $-NO_2$ and $-NH_2$ (or $-NH$) groups and that form hydrogen-bonded chains have a 46% chance of forming noncentrosymmetric structures. We interpret this high incidence of noncentrosymmetric structures in this class of compounds as an indication that noncentrosymmetric hydrogen-bonded aggregates induce noncentrosymmetryity during crystal nucleation. If this interpretation is correct, it implies that choosing molecules with hydrogen-bonding groups that drive molecules to aggregate into chains are useful for improving one's chances of obtaining noncentrosymmetric crystal structures, even for achiral molecules.

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Supplementary Material Available: Structures with R factors between 11% and 16%, CSD search algorithms, and the search results with Refcodes and bibliographic citations (13 pages). Ordering information is given on any current masthead page.

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[9] Gavezzotti, A. *J. Phys. Chem.* **1990**, *94*, 4319.

[10] Whitesell, J. K.; Davis, R. E.; Saunders, L. L.; Wilson, R. J.; Feagins, J. P. *J. Am. Chem. Soc.* **1991**, *113*, 3267.

Fluorescence Anisotropy as a Probe of Molecular Mobility in a Plasticized Poly(vinyl chloride) Membrane

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Steady-state fluorescence anistropy is shown to monitor the mobility of a small molecule in a plasticized polymer membrane and yields information about the microviscosity in the membrane. The technique was applied to a valinomycin based neutral-carrier K^+ ion-selective electrode and a relationship was derived expressing the bulk resistance of the membrane in terms of the microviscosity. The bulk resistance was then measured by ac impedance and shown to correlate with the microviscosity verifying the derived relationship. The instrumentation is described, including a discussion of the anisotropy calculation for measurement from a planar membrane held at a fixed angle in the light path. The results of experiments carried out on the valinomycin electrode suggest that the K^+–valinomycin complex is the mobile, charge-carrying species in the membrane.

Introduction

The study of ionic conduction in neutral-carrier ion-selective electrodes has relied primarily on ac impedance to measure electrical resistance through the bulk of the membrane. This information is important for understanding the identity of the charge-carrying species and the mechanism of charge movement. It would be useful to monitor the membrane parameters that may impinge on the charge conduction using a method independent of the electrical performance. One parameter crucial to the movement of an ion or ion complex would be the viscosity. Plasticized polymer membranes are descendants of the "liquid membranes" and are frequently visualized as a liquid supported by an inert polymer matrix. The plasticized membrane is not obviously viscous, the microviscosity is not easily measured, and the relationship between microviscosity and ion conduction has not been clearly established. It is the purpose of this study to demonstrate a method for measuring the membrane microviscosity and show that it is related to ion movement, as measured by ac impedance, and that it can be used to gain greater insight into the mechanism of charge conduction.

Neutral-carrier ion-selective electrodes use plasticized polymer membranes as the ion-selective element. The hydrophobic membrane blocks the movement of ions but can be made electrically conductive by doping it with a mobile ion carrier. These neutral carriers, so named because they are themselves electrically neutral, such as valinomycin or corwn ether, can facilitate transport of ions from an aqueous phase into the organic membrane thus imparting permselectivity to the membrane. Valinomycin is a cyclododecadepsipeptide antibiotic which forms a cage

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