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"Inclusion Tuning of Nonlinear Optical Materials:
SHG of Organic Guests in Molecular Sieve Hosts."

by

S. D. Cox, T. E. Gier, G. D. Stucky and #J. Bierlein

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Abstract:

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SHG of Organic Guests in Molecular Sieve Hosts**

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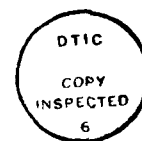
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Key Words: Inclusion, Nonlinear Optical Materials, Molecular Sieves.

Compound Key Words: ALPO-5, *p*-Nitroaniline, 2-Methyl-*p*-nitroaniline.

Abstract

The use of inclusion for the development of new nonlinear optical materials is reviewed and a study of the relative intensities of second harmonic generation (SHG) in sorbate complexes of *p*-nitroaniline (NA)_λ^{and} 2-methyl-*p*-nitroaniline (MNA)_λ in molecular sieve hosts is presented. An SHG signal ten times larger than that of any previously reported organic or organometallic inclusion complex is observed. NA in ALPO-5 complexes gave a maximum SHG of 630 (relative to quartz) at 13 wt. % NA. Pure NA has no SHG signal. With MNA in ALPO-5 (13 wt. %) the SHG signal is equal to that of the ALPO-5 host. X-ray powder diffraction and spectroscopic techniques were used to characterize the inclusion nanocomposites. Hydrogen bonding is found to play an important role in SHG production for NA.



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1. Introduction

Nonlinear optical properties are determined by the bulk hyperpolarizability tensor, a quantity which, in the second order case (ie. second harmonic generation, SHG) is very sensitive to symmetry restrictions[1]. For a material to exhibit SHG it must have a noncentrosymmetric crystal structure. This single restriction dominates any search for new materials for SHG applications. In solid state inorganic chemistry the search is for families of compositional types with acentric crystal structures, the KTP family, for example[2-6]. In molecular chemistry the effort is to align molecules so that a net bulk dipole results.

Oudar and Zyss[7,8] have thoroughly treated the structural dependence of nonlinear optical properties. The bulk second order hyperpolarizability of a crystal of known structure was calculated from known molecular hyperpolarizabilities using a summation scheme that included factors taking into account the orientation of molecules in the unit cell and the relevant crystal point group. This treatment allows the calculation of bulk nonlinear properties based on experimentally determined molecular hyperpolarizability tensor coefficients or the reverse process to obtain molecular information from bulk measurements. Most important from our vantage point was the calculation of the optimum molecular orientation for any crystal point group symmetry. These optimal structures show second order nonlinear hyperpolarizabilities 2.5 to 3.5 times greater than the real crystal structures.

Inclusion chemistry is ideally suited to accomplish this type of molecular alignment and optimization by careful size and shape matching of host and guest. The first reports of inclusion chemistry as a method of generating nonlinear optical materials, were in 1984, by Tomaru, *et. al* [9,10]. They showed that *p*-nitroaniline and closely related organic guests exhibited SHG (64 times quartz) in the presence of beta-cyclodextrin. Yang and Eaton showed shortly thereafter that this was indeed due to inclusion[11] and expanded the field[12] to other hosts (thiourea, tris(*o*-

thymotide), and deoxycholic acid) and organometallic guests, mainly of the arylmetaltricarboxyl type.

Our recent work[13] is the first to use inorganic hosts with organic guests. Inorganic hosts appropriate for consideration in nonlinear optical applications include the molecular sieves and layered materials. Host materials must be transparent in at least part of the optical region (UV to IR) and must be available in a form usable in optical devices, normally thin films or single crystals. Molecular sieves are difficult to obtain as large single crystals, but progress is being made, especially with technologically important materials. Numerous reports have appeared on ZSM-5 (an important petroleum cracking catalyst) crystals in the 0.1 to 0.8mm range.[14]

The wide variety of pore structure, size, shape and charge density available in the molecular sieves makes them attractive. One dimensional pore structures are particularly promising for the alignment processes required. Size and shape variability will allow the host to be matched to the guest so that a chosen orientation in the host pore can be achieved. Variation in charge density on the host framework allows matching of polarity between host and guest. A highly polar or charged guest requires a more highly charged host framework than a hydrophobic guest.

Inorganic hosts have the advantages of rigidity as well as thermal and chemical stability over organic hosts. Molecular organic hosts such as urea or thiourea[15] form channels built around the included guests. The diameter of the channel depends on the size of the guest so the orientation of the guest cannot be predicted. With a rigid inorganic host the guest orientation will be the lowest energy configuration. This simple rigid-body host guest interaction is amenable to computer simulation which can enhance predictive powers.

Acentric hosts may be important for the production of SHG. Guest molecules in a centrosymmetric host can cause a structural rearrangement in the host to give a noncentrosymmetric inclusion material. Our initial studies[13] have not yet revealed a case where this happens for molecular sieves. So far, only acentric hosts have given positive SHG results. The only acentric molecular sieves available to our knowledge are ALPO-5[16] (space group $P6cc$), ALPO-11[17],

VPI-5[18], Sodalite and Offretite[19].

Inclusion guests for SHG are molecules with conjugated π electron systems with attached donor and acceptor groups which lead to one (e.g. in *p*-nitroaniline) or two (e.g. in 2,4-dinitro-*p*-nitroaniline) dimensional charge transfer, a process known to enhance nonlinear optical properties. Size and shape can be varied by alkylation on nitrogen or on the aromatic ring which leaves the electronic system unaffected. Cutoff wavelengths can be shifted into the UV by using pyrimidine for the aromatic substrate or toward the red with stilbene or related extended conjugated systems. Only a few of these organics with favorable molecular nonlinear optical properties have the required noncentrosymmetric structure to show an SHG signal. This allows comparison between guests which show and do not show SHG as pure organics.

Hydrogen bonding plays an important role in determining molecular orientation in many organic crystals of interest for SHG[20-22]. A particularly ubiquitous molecular arrangement is a chain of molecules with their dipoles pointing all in the same direction[20] (See Figure 3). If such chains are maintained in an inclusion complex, the possibility of favorable bulk alignment is obvious. Hydrogen bonding of the guest to the host framework may often dominate and could be used to advantage.

The systems we have studied in our initial work are various molecular sieves and organic guests *p*-nitroaniline (NA, SHG=0) and 2-methyl-*p*-nitroaniline (MNA, SHG=375[23]). Emphasis has been on the molecular sieve ALPO-5 which has a neutral framework composed of alternating AlO_4 and PO_4 tetrahedra linked by oxygen bridges forming an array of one-dimensional 12-ring channels[16]. Preliminary results of this work have been published[13]. We report here a more extensive characterization of the ALPO-5 system.

2. Experimental

2.1 Synthesis

Samples were prepared using a vapor-phase loading method. Desired portions of predried

molecular sieve and NA or MNA (purified by sublimation followed by recrystallization from 95% ethanol) are weighed into an ampoule fitted with a vacuum stopcock. This step is done in a dry atmosphere. The stopcock is closed off, connected to a vacuum line, the ampoule evacuated to oil pump vacuum, and closed off again. The sample is thoroughly mixed and heated to 100°C overnight.

2.2 Characterization

SHG measurements were made as described by Dougherty and Kurtz[24]. The values quoted are in reference to quartz samples. X-ray powder diffraction patterns were obtained open to air using a Scintag PADX theta-theta diffractometer, Cu K-alpha radiation, and associated software running on a Microvax II computer. Infrared spectra were obtained on a Digilab FTS-60 FTIR spectrometer with a Spectra Tech diffuse reflectance attachment and a home made inert atmosphere cell with KBr windows. ^{31}P MAS and CP-MAS NMR spectra were obtained on a General Electric GN-300 spectrometer with Chemagnetics probe, ca. 3 kHz spinning speed, 100 microsec. CP contact time. Molecular graphics and modeling were done with Chemx, developed and distributed by Chemical Design, Ltd., Oxford, England.

3. Results and Discussion

NA and MNA samples in ALPO-5 are all bright yellow, the color being nearly independent of loading. The guest molecules are strongly adsorbed. Heating to 100°C under dynamic vacuum does not result in any weight loss except when excess organic, not included within the molecular sieve pores is present. This happens between 15 and 20 percent for both guests. Exposure to ambient air does not cause displacement of the guest from the ALPO-5 pores according to X-ray powder diffraction.

SHG results as a function of loading are shown overlaid with unit cell volume in Figure 1 for NA and Figure 2 for MNA. The unit cell volumes increase regularly with loading in both

cases. This is as expected since the included organic exerts pressure on the inside of the pores. The highest loading level in each case shows external crystalline organic in the X-ray diffraction pattern. SHG results are strikingly different. NA shows an onset of SHG at around 3%. SHG then rises sharply to a maximum of 630 at 13%. The reduced SHG at the highest loading is due to dilution with external NA which has an SHG of zero. Thus the SHG of NA is turned on by inclusion into ALPO-5. MNA shows just the opposite effect. The SHG at 13% MNA is 0.66, about the same as the ALPO-5 host alone. Only when external crystalline MNA is present does the SHG increase sharply. The SHG of MNA is turned off by inclusion.

The onset of SHG at about ³4% for NA in ALPO-5 and the switching of SHG on for NA and off for MNA are the main points of interest. The onset phenomenon observed in NA in ALPO-5 could be rationalized in terms of a packing density argument. At low loadings the guest molecules are independent and can distribute randomly within the pores. At a particular loading the packing density is such that the molecules start to interact, lose their randomness and the nonlinear effect turns on. The guest molecules may also tend to cluster at all loading levels, but the argument can proceed in a similar manner. If clustering occurs guest molecules will see similar chemical environments, a combination of the framework and other guest molecules, at both low and high packing densities. If clustering does not occur, at low loadings guest molecules will be exposed only to the framework, so whether or not clustering occurs could be determined spectroscopically.

The switching phenomenon cannot be rationalized without detailed structural information beyond saying that the added methyl group on MNA must restrict its orientation in the ALPO-5 channels in ways which prohibit the type of alignment needed for SHG.

To investigate the above points we first looked at hydrogen bonding effects. The crystal structures of NA[25] and MNA[26] both show chains of molecules held together by hydrogen bonds between amino hydrogens and nitro oxygens, shown in Figure 3 for NA. A comparison of the IR N-H bands in the pure and the included organic should show if the chain structure has been disturbed by inclusion. Figures 4 and 5 show the SHG data overlaid with IR N-H band shifts for

NA and MNA respectively. There is an obvious parallel trend. For NA at low loadings there is a +40 cm^{-1} shift from the pure, solid organic value. NA in chloroform solution has the same N-H band position, so that essentially all hydrogen bonding is lost. Hydrogen bonding to framework oxygen atoms is not present at the lowest loading. The N-H band position shifts rapidly with increasing loading. A shoulder appears at 3%, indicated by two data points arranged vertically, and is gone by 5%. Just as SHG appears, the N-H band position levels out at an intermediate value. In the samples which show SHG there is weak hydrogen bonding. MNA shows no such increase in hydrogen bonding at low loading levels in accordance with the SHG results. The conclusion is that weak intermolecular hydrogen bonding plays an important role in SHG production for NA.

Preliminary MAS and CP-MAS ^{31}P NMR data on NA in ALPO-5 (Table) shows a distinct difference between 15% and 3% NA samples. Cross polarization allows detection of not only those phosphorus atoms near hydrogen atoms but all phosphorus atoms in any ALPO-5 particle with a significant number of hydrogen atoms because of dipole coupling between the 100% abundant phosphorus nuclei. In pure dry ALPO-5 only a very weak signal is present as expected, probably due to an impurity. 3% NA has a signal at -30.25 ppm and 15% NA has a signal at $\times$ -30.39 ppm. This shows that the NA hydrogens are close enough to framework phosphorus atoms for cross polarization to occur. Single pulse spectra showing the total phosphorus signal exhibit a $\times$ -0.5 ppm shift going from pure ALPO-5 to 15% NA and perhaps more significantly, a change in line shape from a broad, Gaussian shape in pure ALPO-5 and 3% NA to a narrower, Lorentzian shape in 15% NA. This is shown in Figure 6. Thus 3% NA and pure ALPO-5 have very similar NMR spectra and SHG signals.

Without complete structural information, no full explanation of these results is possible. Modeling based on chemical knowledge can be an aid in thinking about possible structures. IR data show that structural fragments present in the pure organic which involve hydrogen bonding are disrupted at least partially in the inclusion complex. This is confirmed by modelling. If a chain of NA molecules as shown in Figure 3 is forced into an ALPO-5 channel, many interatomic distances

are less than van der Waals, see Figure 7. This chain would fit easily if stretched or straightened out moderately. An orientation with the aromatic plane perpendicular to the ALPO-5 channel was our initial choice because Reitveld analysis of high-resolution X-ray powder data indicated a ring of electron density perpendicular to the channel. The data has not refined properly, so this indication is in doubt. Modeling shows that a NA molecule does not fit exactly perpendicular to the ALPO-5 channel. Figure 8 shows two orientations of NA with reasonable van der Waals contacts with the ALPO-5 channel. The angle these molecules make with the channel axis is approximately 60° very close to the optimal angle Oudar and Zyss[8] determined for the ALPO-5 point group (54.74° for 6mm). Monte Carlo calculations to explore organic clusters and packing and additional structural characterization are now being carried out.

4. Conclusion

Inclusion chemistry is a promising avenue for the development of new *nonlinear optical* materials. A large number of promising untried host-guest combinations exist. In the example discussed above, an onset of SHG is observed and hydrogen bonding appears to be important. Future studies of single crystal structure and phase matchability in the NA/ALPO-5 system will be pursued.

5. Acknowledgement

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Figure Captions

Figure 1. *p*-Nitroaniline in ALPO-5. Loading level (weight % *p*-nitroaniline) versus relative SHG intensity (*) and unit cell volume in Å³ (o).

Figure 2. 2-Methyl-*p*-nitroaniline in ALPO-5. Loading level (weight % 2-methyl-*p*-nitroaniline) versus relative SHG intensity (*) and unit cell volume in Å³ (o).

Figure 3. Chain of *p*-nitroaniline molecules as it occurs in the *p*-nitroaniline crystal structure. Hydrogen bonds are indicated as heavy dashed lines.

Figure 4. *p*-Nitroaniline in ALPO-5. Loading level (weight % *p*-nitroaniline) versus relative SHG intensity (*) and IR N-H band shift (cm⁻¹) (o). The N-H band shift is obtained by subtracting the average position of the two major N-H bands in NA (in KBr) from the corresponding average position in the inclusion material.

Figure 5. 2-Methyl-*p*-nitroaniline in ALPO-5. Loading level (weight % 2-methyl-*p*-nitroaniline) versus relative SHG intensity (*) and IR N-H band shift (cm⁻¹) (o). The N-H band shift is obtained as in Figure 4.

Figure 6. Single pulse ³¹P MAS NMR of dry ALPO-5 (broad line) and 15% NA in ALPO-5 (narrow line).

Figure 7. Chain of NA molecules from Figure 3 within a channel of ALPO-5. Short (<2 Å) internuclear contacts are shown as heavy lines. Two of the contacts are less than 1.5 Å.

Figure 8. Two possible positions for NA in the ALPO-5 channel. Internuclear distances are greater than $3\text{\AA}$ for NA nitro oxygen atoms and greater than about $2\text{\AA}$ for NA amino hydrogen atoms.

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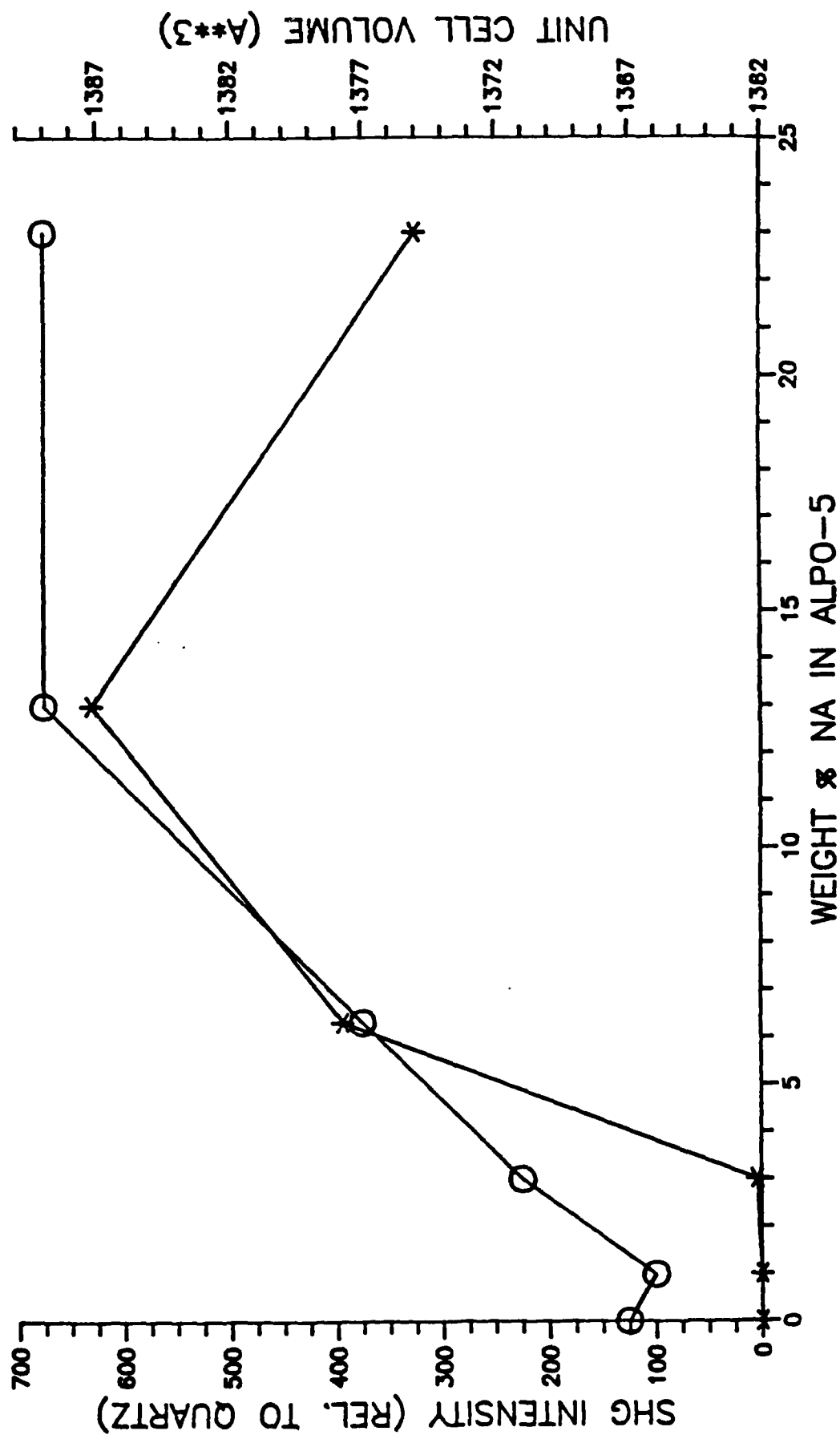
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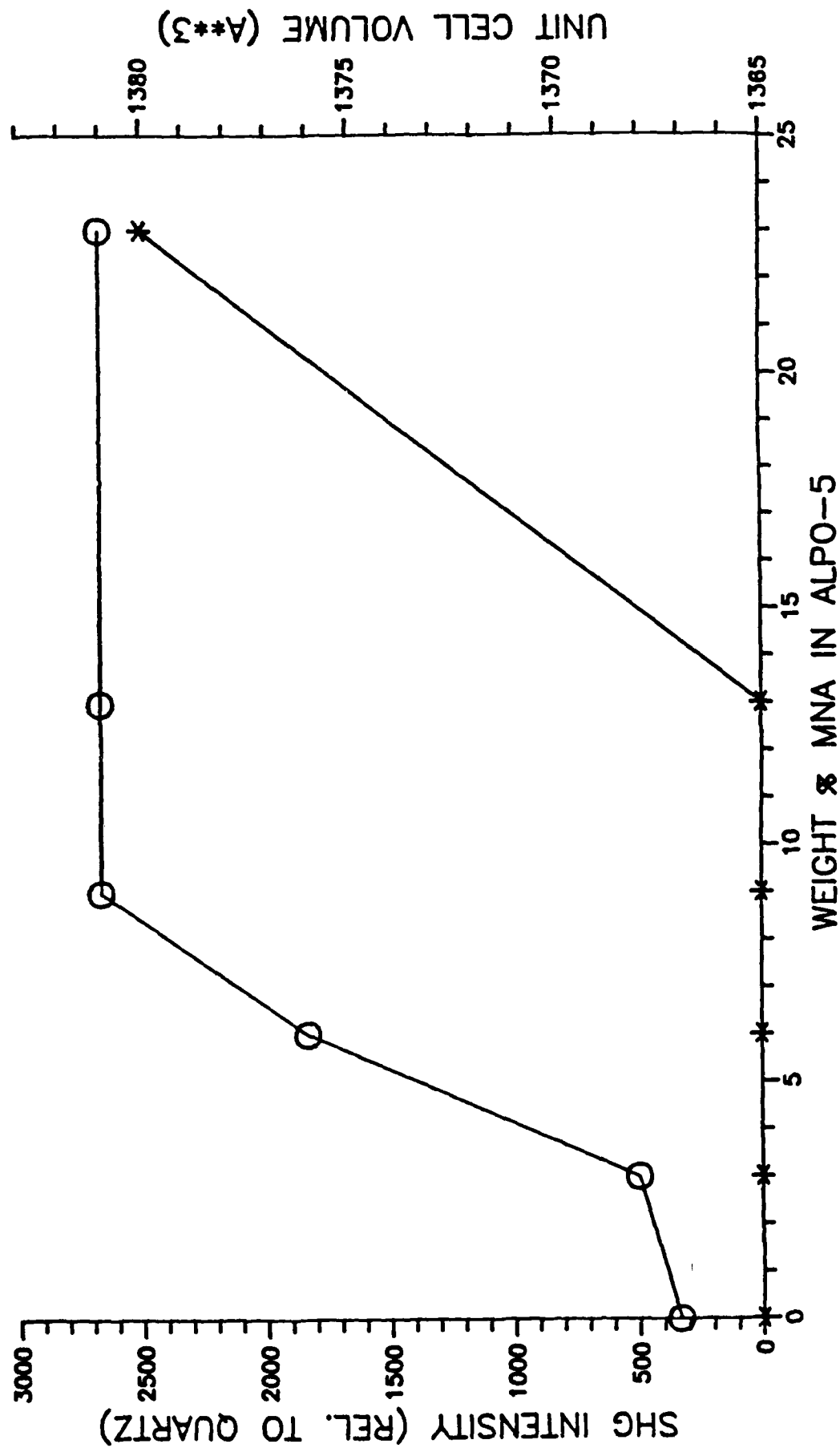
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P-NITROANILINE IN ALPO-5 SHG AND UNIT CELL VOLUME



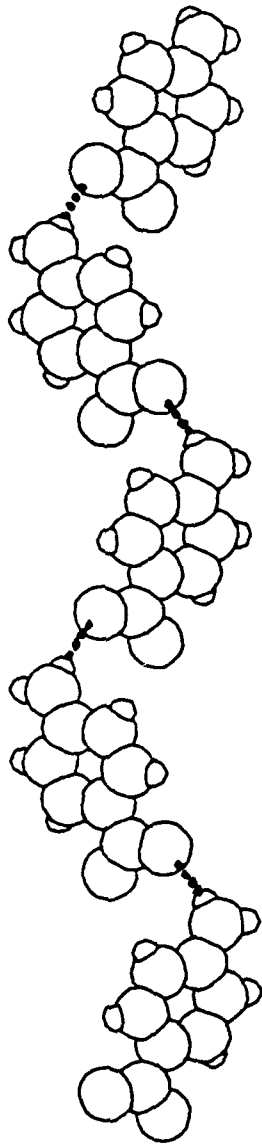
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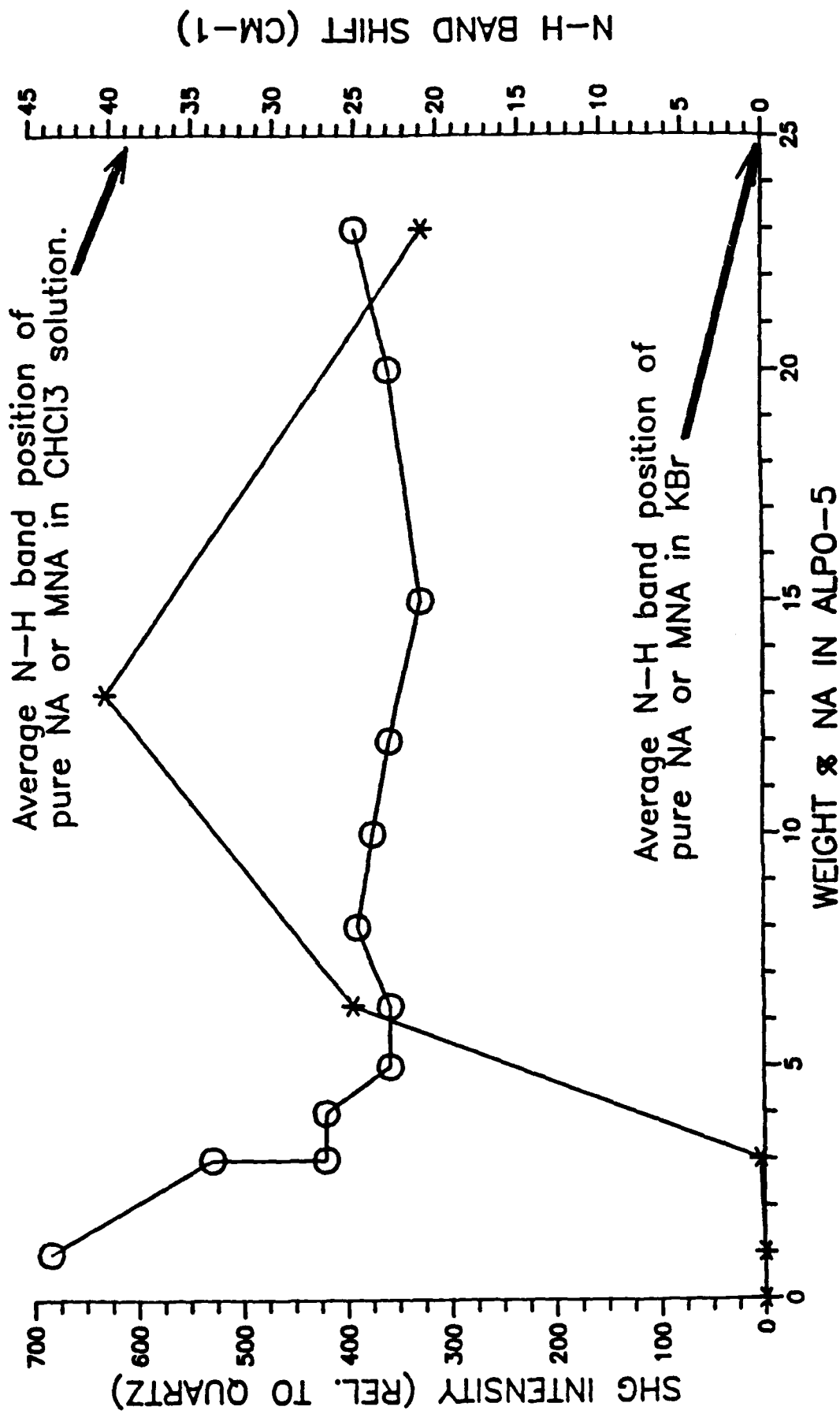
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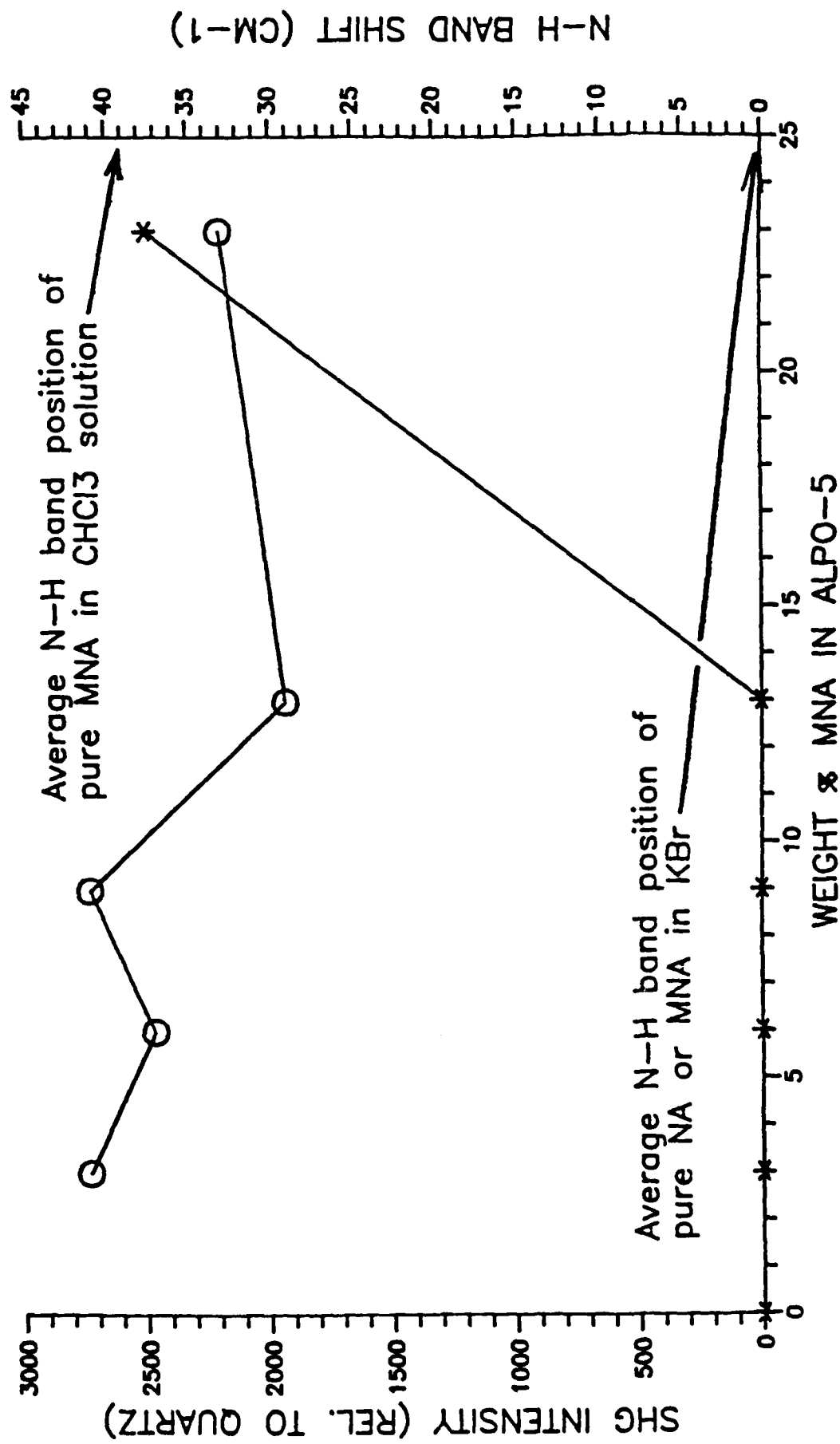


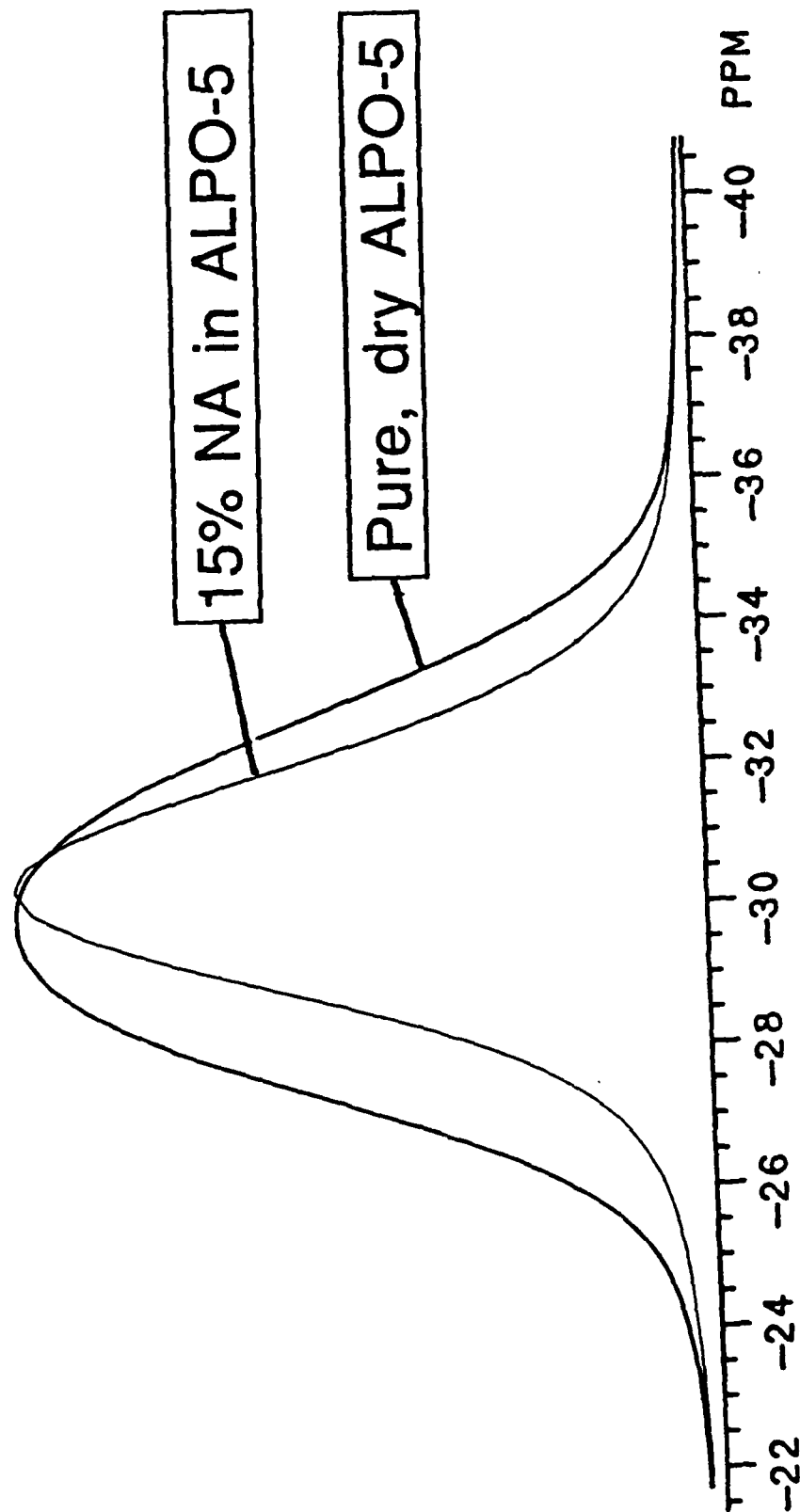
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P-NITROANILINE IN ALPO-5 SHG AND N-H BAND SHIFT



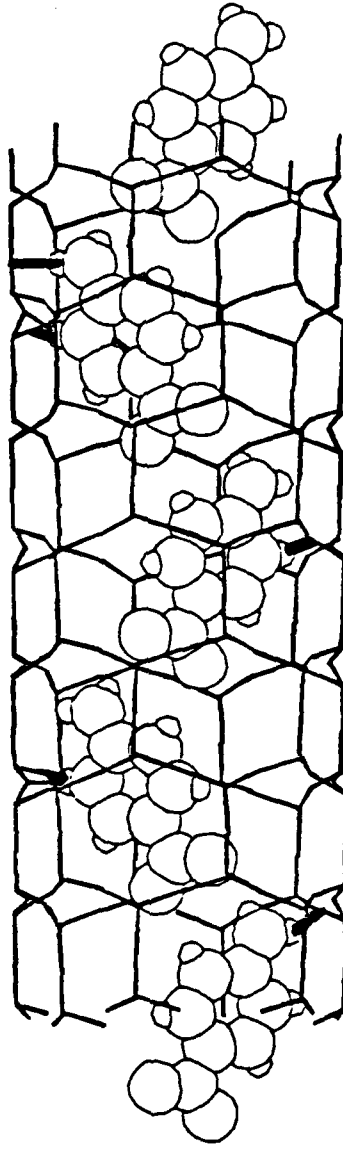
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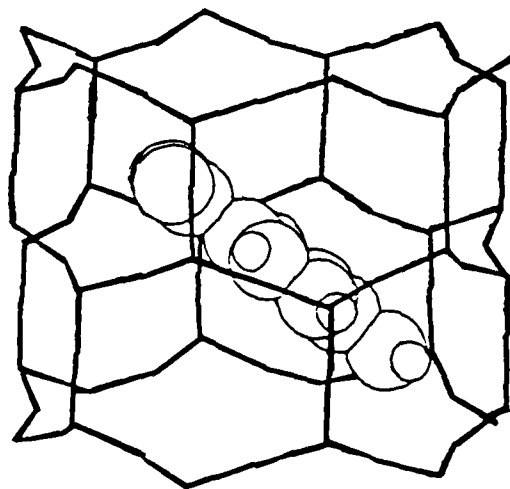
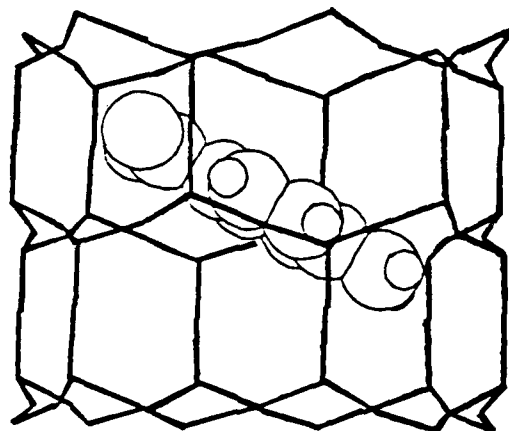


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