J. Am. Chem. Soc. **1987**, *109*, 7797-7803

shifts indicate that the NH···O interactions described here are weak interactions in comparison with amide bonds. Cooperative effects arising from the conjugated nature of the hydrogen-bonded chains may contribute an additional stabilizing force to these chains.[24] Nevertheless, the most important factor that determines these packing patterns is not the strength of the hydrogen bonds but their ability to organize molecules into aggregates. The strength of the hydrogen bond contributes to the stability of the crystals but does not influence the aggregate pattern of hydrogen-bonded molecules. Our analyses suggest that the orienting process precedes crystal nucleation and that polar aggregates formed in solution are preserved throughout the crystal growth process.

The use of the NH···ONO interaction for predicting crystal packing modes is derived primarily from the statistical distribution of hydrogen-bond geometries of known nitroaniline structures. The role of steric hindrance, conjugation, dipolar interactions, and solvent effects are implicit in the data, but further analyses are needed before these specific factors can be used as reliable predictors.

Listed below are features common to the crystal structures of compounds in Tables I and II that can be used as synthetic guidelines for preparing new solid-state structures based on nitroanilines.

1. All amino protons will form close contacts with nitro groups. These contacts may be intra- or intermolecular.
2. At least one intermolecular NH···O hydrogen bond should form.
3. The geometry of most NH···O hydrogen-bond patterns will be that of an inside three-center interaction.
4. Polar chain structures will form when nitro and amino groups are meta or para to one another.
5. Centric dimers may form when nitro and amino groups are ortho to one another.
6. Points 1–5 are valid even when strongly hydrogen-bonding functional groups such as carboxylic acids and amides are present in a nitroaniline compound.

The structures of compounds **33–40**, which are isographic with nitroanilines, show that hydrogen-bond rules developed for nitroanilines can be used to analyze and predict hydrogen-bond patterns of related compounds.

For nonlinear optical applications, one would like to design crystal structures that have predictable molecular orientations and that do not have inversion centers. The work presented here has shown how hydrogen bonds can be used to form acentric polymeric chains of molecules. Often these chains will pack about proper symmetry elements or glide planes to give acentric crystals. The challenge remains to find a way to control the packing patterns of these chains by molecular design or by crystal growth methods.

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Registry No. 1, 100-15-2; **2**, 100-01-6; **3**, 99-52-5; **6**, 99-09-2; **7**, 88-74-4; **10**, 1214-32-0; **12**, 97-02-9; **28**, 99-30-9.

Supplementary Material Available: Cambridge Crystallographic Data Base search for nitroaniline analogues and tables of temperature factors, inter- and intramolecular bond lengths, and angles and esd's for *N*-methyl-*p*-nitroaniline (**1**) (35 pages); table of observed and calculated structure factors for **1** (3 pages). Ordering information is given on any current masthead page.

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Mesomorphic State of Cyclotetradecane

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Abstract: Cyclotetradecane shows a thermal transition 7 K below the melting point. The high-temperature crystal phase is characterized by high molecular mobility and easy deformation. Thermal analysis, MAS ^{13}C NMR with high-power proton decoupling, X-ray diffraction, and birefringence experiments have been performed and are discussed with respect to the onset of molecular motion and molecular disorder. The NMR experiments clearly show the onset of a conformational interconversion process well below the transition, while the positional, orientational, and conformational order are largely preserved. The same applies to some extent even within the high-temperature crystal phase. It is thus shown that molecular dynamics must be strictly differentiated from molecular and crystal disorder. Disordering of molecules with low symmetry such as cyclotetradecane is shown to result in rather large transition entropies, even when the molecular motions are jumplike and involve only minor disorder in the crystal. The concepts of liquid crystal, plastic crystal, and condis-crystal are discussed with regard to the classification of the mesomorphic character of the high-temperature crystal phase of cyclotetradecane. It is classified as a molecule that shows a mesophase with partial orientational disorder and high conformational mobility.

Many nonpolar, flexible-chain molecules undergo transitions from the fully ordered crystal to a phase of intermediate order and mobility. These include *n*-alkanes,[1] cycloalkanes,[2] poly(ethylene),[3] *trans*-1,4-poly(butadiene),[4] poly(tetrafluoroethylene),[5] poly(diethylsiloxane),[6] poly(*p*-xylylene),[7] and the polyphosphazenes.[8] In contrast to plastic crystals, these molecules

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are not close to spherical and cannot rotate isotropically as an entire unit; and in contrast to liquid crystals, they do not possess a rigid mesogen that maintains some orientational order, and they do not show translational mobility. In the mesomorphic state, these long-chain molecules are usually packed in a hexagonal or pseudohexagonal crystal with positional and orientational order largely preserved. The conformational order is, however, lost, contributing significantly to the increase in entropy at the transition. The flexible nature of the molecules permits at the same time maintenance of positional and orientational order. To differentiate from both liquid crystals formed by molecules with rigid motifs and plastic crystals formed by small molecules of close to spherical shape, Wunderlich and Grebowicz[9] labeled the mesomorphic phases of such flexible molecules CONDIS-crystals. The term condis-crystal is an abbreviation for CONformationally DISordered crystal.

During the last 30 years it was shown, mainly through solid-state NMR, that rather large-scale rotational and translational motion is possible in crystals. For example, such large motifs as benzene or cyclohexane can jump in the plane of the molecule by 60 and 120°, respectively, and even show diffusional jumps to neighboring lattice sites. Since the initial and final states of such motion are of indentical symmetry within the crystal and the lifetime in the intermediate state is negligible, such motion does not contribute significantly to the disorder (entropy). It is also difficult to detect such motion by the long time average measured by X-ray diffraction or by infrared or Raman spectroscopy, for which the instantaneous concentration of the intermediate species is too low. In this paper we will show that large-scale conformational mobility may also exist in crystals and cause little or no change in order. With the example of cyclotetradecane it will be illustrated that conformational dynamics does not have to lead to conformational disorder.

Recently we reported on high-resolution, solid-state ^{13}C NMR and DSC measurements of cycloalkanes $(CH_2)_n$, with n = 12-16, 24, 36, 48, 72, and 96.[2] Three types of compounds were distinguished in this series of cycloalkanes with respect to their thermal behavior. Molecules with 12-24 carbon atoms show a thermal transition well below the melting point. Molecules with 36 and 48 carbon atoms have no such transition. Finally, the cycloalkanes with 72 and with 96 carbons may crystallize as different polymorphs, the chain packing of which depends on whether the crystals are grown from solution or the melt. A thermal transition was found only for the melt-crystallized modification. In the present paper we will discuss an example of the first group, the low-temperature transition of cyclotetradecane.

The low-temperature transition of cyclotetradecane is observed about 7 K below the transition to the isotropic melt and exhibits a transition entropy nearly twice as large as the entropy change to the isotropic melt.[2] This transition is thus classified as a disordering transition, and its transition temperature is labeled T_{tr}. The final transition to the isotropic phase is called T_m. Overall melting occurs thus in two steps. Cyclotetradecane is a highly flexible molecule. However, while several conformations coexist in the liquid state of larger rings, cyclotetradecane, like cyclododecane,[11] is considered to be conformationally homogeneous at ambient temperature and below. IR spectra of the high-temperature crystal phase and the melt do not show new bands when compared with that of the low-temperature crystal phase.[10] X-ray diffraction experiments at 116 K reveal a rectangular diamond-lattice conformation $(g^+g^+ag^-g^-aa)_2$ for the solid-state structure.[12] Solution ^{1}H and ^{13}C NMR spectra below 173 K show a fast-exchange–slow-exchange transition for the ring atom sites, which is consistent with the $(g^+g^+ag^-g^-aa)_2$ conformation.[13] The energy barrier calculated from NMR line-shape analysis is 29 kJ/mol.[14] Also, force-field calculations yield $(g^+g^+ag^-g^-aa)_2$ as the most stable conformation.[14-16] Higher energy conformations are intermediates for the conformational interconversion process between the $(ggaggaa)_2$ sites, but their abundance is negligible in terms of the Boltzmann distribution.[14,17] Since these results indicate only a minor contribution from conformational disordering to the transition entropy, it is unlikely that the onset of orientational disorder alone can account for the transition entropy. The molecular structure in the mesomorphic state is not yet known, and the type of molecular motion is also not fully understood. To obtain a more detailed picture, we will compare in this paper the results of state ^{13}C NMR, X-ray diffraction, and thermoanalytical investigations.

Experimental Section

Cyclotetradecane was prepared by a Tiffeneau–Demjanov ring-insertion reaction.[18] In an inert-gas atmosphere of dry nitrogen, trimethylsilyl cyanide (3 g) and a catalytic amount of zinc iodide were added to a diethyl ether solution (45 mL, absolute) of cyclotridecanone (5 g). The mixture was stirred for 20 h at room temperature and afterward slowly added to a suspension of excess $LiAlH_4$ (4.6 g) in diethyl ether (230 mL, absolute). After the resultant mixture was refluxed for 20 h, unreacted $LiAlH_4$ was destroyed by the addition of ice–water. Acetic acid (30%, 570 mL) was added to dissolve the aluminum hydroxide precipitate. Sodium nitrite (4.6 g) was then added and the solution allowed to stand overnight. The crude cyclotetradecanone $C_{14}H_{26}O$ (4.6 g) was isolated by extracting the reaction mixture with pentane. The pentane extract was then washed with aqueous sodium carbonate and the solvent removed on a rotary evaporator. The cyclotetradecanone was purified by converting it to the semicarbazone, recrystallizing the semicarbazone twice from ethanol, and regenerating the pure ketone (1.4 g) by acidolysis. Finally, the purified cyclotetradecanone was reduced to the alkane by a Huang–Minlon reduction with hydrazine hydrate (2 g) and potassium hydroxide (2 g) in diethylene glycol (45 mL). The product (400 mg) was recrystallized twice from ethanol/water and then sublimed at reduced pressure (1 mbar), yielding 250 mg of cyclotetradecane: purity (GC) >99.9%; mp 56.2 °C (lit.[10] mp 56 °C).

DSC data were determined with a Perkin-Elmer Model DSC-7 using three heating rates. The temperature of the onset of the transition was extrapolated to a heating rate of zero in order to approach the equilibrium transition temperature. The instrument was calibrated with high-purity cyclohexane, gallium, and indium standards. Temperature accuracy was better than ±0.3 K. Transition enthalpies, as determined by numerical integration of the transition peaks, show variations of less than 5%. The transition entropies were calculated assuming equilibrium; i.e., $\Delta H = T\Delta S$.

High-resolution, solid-state ^{13}C NMR spectra were recorded at 75.47 MHz on a Bruker CXP 300 spectrometer. A Bruker double-bearing MAS probe that was modified for variable-temperature experiments was used. The end caps of the rotor (Al_2O_3 cylinders, o.d. 7 mm) were made from Macor (Corning Glass). Line narrowing was achieved by high-power decoupling and magic-angle sample spinning. Spinning speeds were set at 2200-3000 Hz. Two different pulse sequences were used to generate the spectra. The usual spin-lock cross-polarization sequence was applied for spectra of the rigid molecules in the low-temperature state[19]

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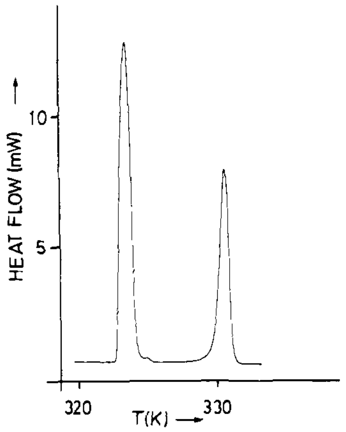

Figure 1. DSC trace of cyclotetradecane (heating rate 5 K/min).

Table I. Thermal Transition Parameters of Cyclotetradecane

T_{tr}, K	ΔH_{tr}, kJ/mol	ΔS_{tr}, J/K·mol	T_m, K	ΔH_m, kJ/mol	ΔS_m, J/K·mol
322.0[a]	16.5	51.25	329.3	9.3	28.2
324.1[b]	17.2	53.0	329.1	7.95	24.2

[a] All data from this work. [b] All data from ref 10.

using a 3-μs, 90° pulse followed by a mixing time of 1–5 ms and acquisition time of 30–150 ms. The delay time between the pulse experiments was 10–100 s. Below 250 K, even ^{1}H T_1 times were exorbitantly long. In order to obtain fast relaxation, the sample was heated to room temperature after each pulse and cooled down again. The spectra of the mobile molecules in the melt and in the mesomorphic state were obtained without cross polarization. A simple 90° carbon pulse was applied in combination with high-power proton decoupling. Delay times long enough to assure complete relaxation were allowed between the pulses. The ^{13}C signals arising from undisturbed Boltzmann equilibrium populations have intensities that quantitatively represent the relative amounts of carbons. In CP spectra, true relative intensities are obtained when the cross-polarization times (T_{CH}) are short enough to allow the ^{13}C nuclei to equilibrate with the proton system and when the shortest proton rotating frame relaxation time is long compared with the mixing time.[20] These conditions are well satisfied for the rigid molecules at low temperatures, such that the signal intensities of the low-temperature spectra represent the relative populations of the different carbon sites. Chemical shifts were determined by comparison with the methylene signal of crystalline linear poly(ethylene), which was set at 32.81 ppm relative to TMS[21] and considered to be temperature independent. Temperature was measured by a thermocouple next to the spinning rotor and was less accurate (±3 K) than the DSC measurements. The original temperature readings, given in Figure 3, may therefore disagree slightly with the DSC data. However, the indicated state (mesomorphic or melt) could be checked independently.

X-ray diffraction powder patterns were recorded with a Simon-Guinier camera, Enraf-Nonius FR 533, by the moving-film technique (3 mm/h) in the temperature range 293–325 K. The well-characterized low-temperature modification of cyclotetradecane[12] was used as a standard.

Optical micrographs were recorded and analyzed under crossed polarizers with a Leitz Ortholux II POL BK microscope equipped with a Mettler FP82 hot stage and a FP 80 central processor.

Results and Discussion

Thermal Analysis. Figure 1 shows the DSC trace of cyclotetradecane at 5 K/min. The thermal transition is 7 K below the transition to the isotropic state at 329.3 K. Beginning with the low-temperature phase, we will denote the three phases as A, B, and C. Thus, A represents the fully ordered crystal, B represents the mesophase, and C represents the isotropic melt. Table I lists the transition temperatures and the corresponding enthalpy and entropy changes. Data from this work and that reported previously by Borgen and Dale[10] are listed. Although the transition temperatures agree well, there are slight differences in ΔH and ΔS. Because of the lack of information concerning sample purity in the previous study, our discussion is based on the present data, which are mean values of up to five measurements.

As revealed by the sharp peak in the DSC trace, the low-temperature transition T_{tr} represents a disordering process of high cooperativity.[22] Optical microscopy clearly shows that phase B is an anisotropic solid. Thus, the mesomorphic state of cyclotetradecane differs strongly from the mesomorphic states of the smaller cycloalkanes. From cyclobutane to cyclononane, the mesomorphic phases are optically isotropic. At their disordering transition the small rings become orientationally mobile (plastic crystals), and body- or face-centered cubic lattices result. The transition entropy of 35–40 J/K·mol accounts for full orientational disordering. Conformational mobility develops gradually in the plastic crystalline state and is similar to the behavior in the liquid state.[23] The final entropy change to the isotropic state, ΔS_m = 3–9 J/K·mol, shows the value expected for the remaining positional disordering. In contrast, the entropy change to the isotropic state of cyclotetradecane is too large to be accounted for solely by positional disordering. About 19 J/K·mol of the entropy of fusion, ΔS = 28.2 J/K·mol, has to be explained by orientational disordering. This is about 50% of the change in entropy observed for small cycloalkanes at the transition to the plastic crystalline state. Consequently, the molecules must lose only part of their orientational order at the transition to the B phase. One may assume thus that in the B phase the molecules can undergo only jumplike reorientational motions and not full reorientation. Because of the low symmetry of the molecular structure, two-site jumps would, for example, result in considerable disorder without complete loss of orientational order. Such a process could account for the partitioning of the entropy of fusion between the two transitions. In addition, it has to be considered that the occurrence of conformations other than $(g^+g^+ag^-g^-aa)_2$ could also contribute considerably to the entropy change at the T_{tr} low-temperature transition.

Optical Microscopy. Optical micrographs under crossed polarizers of cyclotetradecane in phases A and B are shown in Figure 2. The anisotropic nature of the sample is clearly evident from the birefringence. When the sample is crystallized from the melt, large areas of homogeneous orientation are seen (Figure 2a). On cooling through the low-temperature transition, these areas break up and small crystallites form (Figure 2b). Raising the sample temperature again to that of the mesophase does not result in an immediate re-forming of large crystals. A substantial change in birefringence and further breaking up of the microcrystallites indicate a significant change in crystal density (Figure 2c). However, after annealing the sample for several hours above T_{tr}, large homogenous areas are slowly re-formed through Ostwald ripening (Figure 2d). Obviously there must be considerable mobility and diffusion in the mesophase. Hence, optical microscopy offers not only evidence of a change in crystal structure but also some idea about the dynamic character of the mesomorphic state.

^{13}C NMR Spectra. Figure 3 presents the high-resolution solid-state ^{13}C NMR spectra of cyclotetradecane at various temperatures for phases A, B, and C. The spectrum of the melt was also recorded by the MAS technique to allow direct comparison with the crystal spectra.

The spectrum of phase A at 175 K was recorded under conditions in which the relative intensities of the signals represent the relative populations of carbons in conformationally different sites of the molecule. Six sharp resonances are observed. The line width is about 15 Hz(!). The intensity ratios are 1:1:2:1:1:1 in the direction of increasing field. Chemical shifts depend on the torsional angles, due to the so-called gauche and vicinal–gauche effects.[24] In order to assign solid-state MAS ^{13}C NMR spectra, the rotational isomeric states of two adjacent bonds on either side of the carbon atom in question must be considered.[25] The cy-

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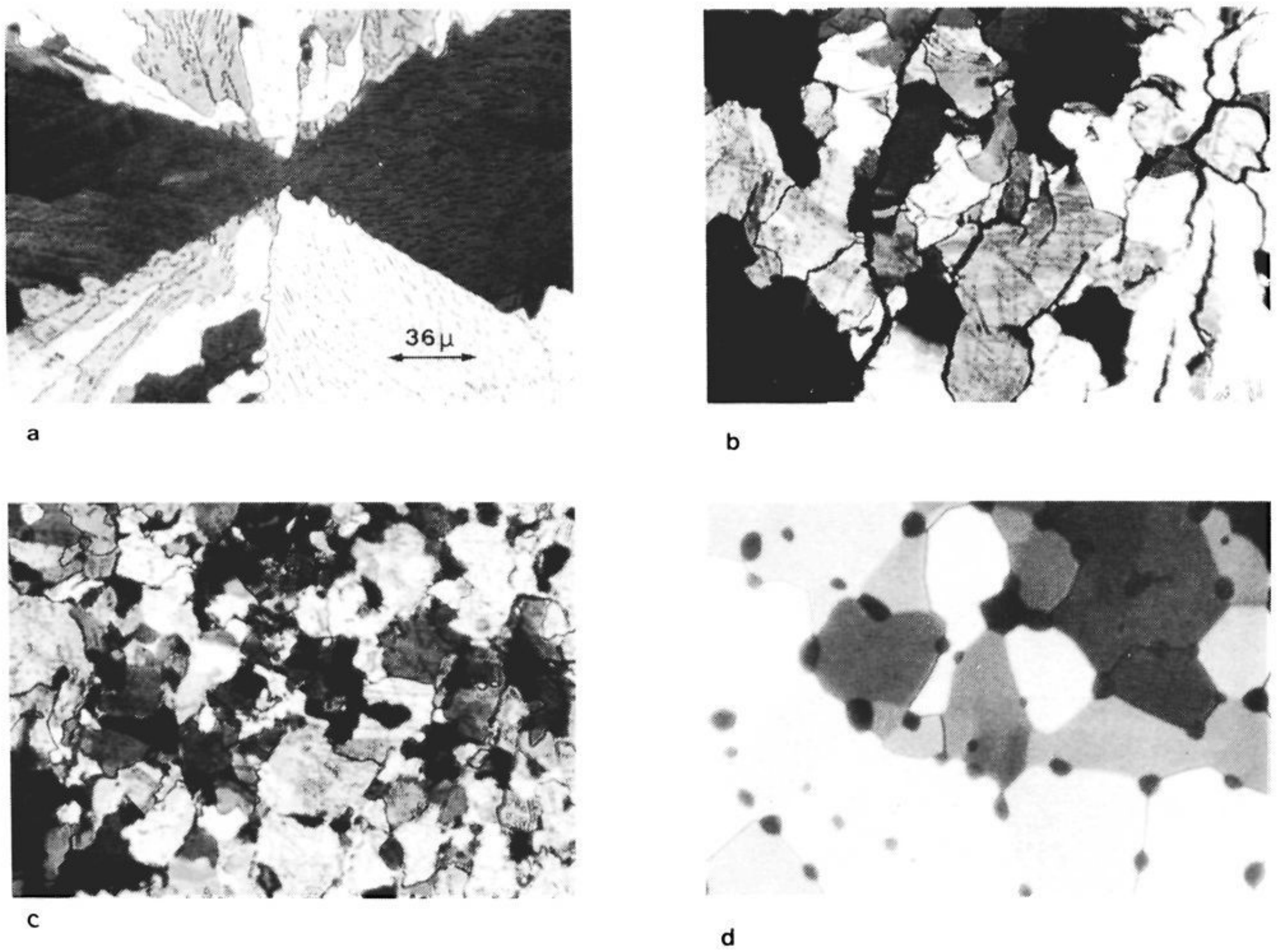

Figure 2. Optical micrographs of cyclotetradecane: (a) phase B, sample isothermically crystallized from the melt at 325 K; (b) phase A at 318 K; (c) phase B at 323 K, after slow heating from phase A; (d) phase B at 323 K, after 14 h annealing.

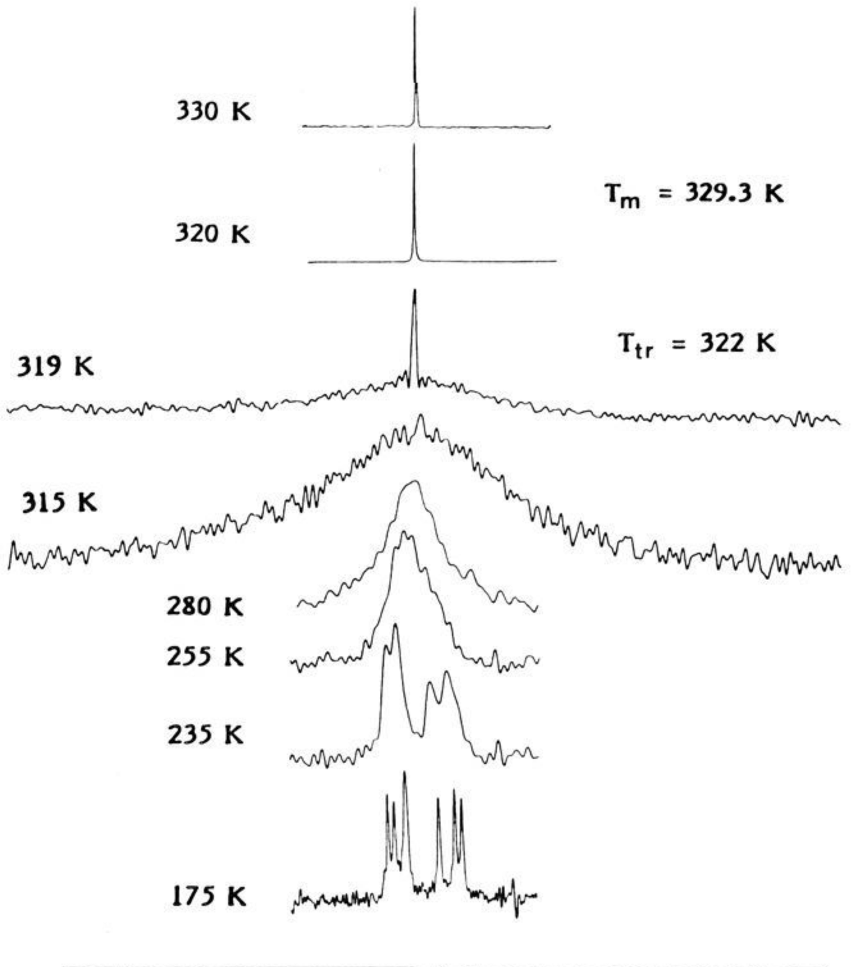

Figure 3. CP-MAS ^{13}C NMR spectra of cyclotetradecane. Temperatures represent direct readings. Transition temperatures as determined by DSC are given for comparison.

clotetradecane spectrum at 175 K is in agreement with the molecular structure revealed by X-ray diffraction.[12] The rectangular $(g^+g^+ag^-g^-aa)_2$ conformation is shown in Figure 4. Four different sites are defined by the sequences of dihedral angles: *ggag*, *agga*, *aagg*, and *gaag*. A relative intensity ratio of 2:2:2:1 would be expected. The spectrum has been assigned as given in Figure 4,

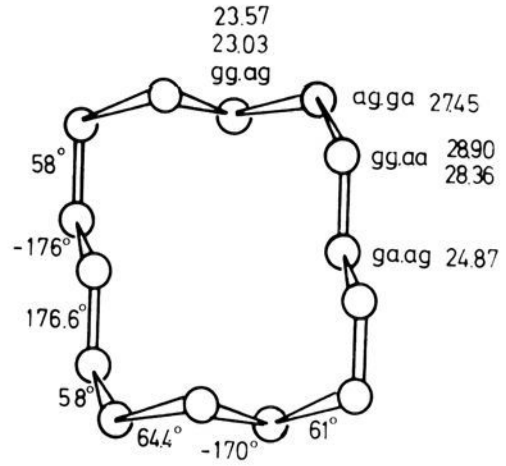

Figure 4. Assignment of phase A solid-state ^{13}C NMR spectra of cyclotetradecane (dihedral angles as given in ref 12).

Table II. Chemical Shifts of Cyclododecane, Cyclotetradecane, and Cyclohexadecane in the Solid State and in Solution (ppm Against TMS)

	$C_{12}H_{24}$		$C_{14}H_{28}$		$C_{16}H_{32}$
	solid[a]	solute[b]	solid[a]	solute[b]	solute[c]
ga·gg	23.58	21.80	23.57 23.03	21.30	
ga·ag			24.87	23.30	22.80
ag·ga	27.91	26.60	27.45	26.20	26.80
gg·aa			28.90 28.76	26.80	27.00

[a] Data from this work. [b] Data from ref 14. [c] Data from ref 13.

assuming that the *ggag* sequence given above results in the resonances at 23.52 and 23.03 ppm and that the *ggaa* sequence results in the resonances at 28.90 and 28.36 ppm. The splitting of these signals can be explained either by small distortions of bond or dihedral angles or by intermolecular packing effects. Similar splittings have been observed in the MAS ^{13}C NMR spectra of almost all well-crystallized cycloalkanes. This assignment is consistent with the solid-state spectra of cyclododecane[25] and cyclotetraeicosane,[25] as well as with the low-temperature solution spectra of cyclododecane,[14] cyclotetradecane,[14] and cyclohexadecane.[13] As mentioned above, Anet et al.[13,14] were able to observe the solution spectra of $C_{12}H_{24}$, $C_{14}H_{28}$, and $C_{16}H_{32}$ at temperatures low enough that the exchange of the carbons between

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Table III. Chemical Shift of Cyclotetradecane in the Melt, the Mesophase, and the Fully Ordered Crystal (ppm)

	melt		mesophase		crystal[a]
δ	26.77		26.37		26.23
$\Delta\delta^b$		0.4		0.14	

[a] Calculated average for the signals. [b] Chemical shift difference for two subsequent phases.

the different conformational sites was slow. Discrete signals corresponding to different sites were therefore resolved, and the signals of cyclotetradecane were assigned to the same $(g^+g^+ag^-g^-aa)_2$ conformation shown in Figure 4.[14] For comparison, the spectral assignments of different cycloalkanes in solution and in the solid state are listed in Table II. Clearly, carbons in the center of the same torsional angle sequence result in equivalent chemical shifts. Remarkably, the solid-state spectrum of $C_{14}H_{28}$ is better resolved than the solution spectrum. The novel techniques used in solid-state NMR can yield spectra of nearly comparable, and in special cases, even superior quality to solution spectra.

On increasing the temperature, the six sharp resonances broaden and finally converge to one broad signal. Line broadening is expected when the rate of conformational interconversion increases, since the carbon atoms are exchanged between the different conformational sites. However, the observed line width in the spectrum at 313 K ($\Delta\nu$ = 1800 Hz) far exceeds the width of the initial low-temperature spectrum. This extreme broadening is not due to coalescence but rather results from interference of the proton decoupling field and the molecular motion. When the frequency of molecular motion is similar to the frequency of the ^{1}H decoupling field, decoupling becomes ineffective and the line width may increase considerably.[26,27] As the molecular motion changes with temperature, the line width goes through a maximum. Such a maximum in line width corresponds to a T_2 minimum.[28] However, without quantitative simulation of the contribution of different motional processes to T_2 we cannot conclude whether the observed T_2 minimum is a result of conformational interconversion, of an additional motional process such as free or jumplike rotations about the axis perpendicular to the plane of the ring, or from a combination of both.

Careful inspection of the spectra reveals that the two different dynamic effects—the coalescence due to conformational interconversion and the motional modulation of the ^{1}H decoupling—are well separated on the temperature scale. Line broadening below 255 K can clearly be related to the slow-exchange–fast-exchange transition of conformational interconversion, while the T_2-minimum process is apparently negligible below 280 K. In case the conformational interconversion process reaches rates of 10^4–10^5 Hz, it will also result in motional modulation of the ^{1}H decoupling. Thus, both dynamic effects, coalescence and T_2 minimum, could be caused by the same conformational interconversion process. A quantitative evaluation of the dynamics by computer simulation is in progress but is beyond the scope of the present paper.

Most important, the spectra clearly indicate the onset of motion below the temperature of the phase transition. The fact that no additional thermal effect is observed below T_{tr} (322 K) shows that this motion does not result in disordering.

Once the phase transition at 322 K is reached, a sudden narrowing of the spectrum to a sharp line ($\Delta\nu$ = 16 Hz) is observed. All carbon atoms become magnetically equivalent within the time scale of the NMR experiment as given by the total width of the low-temperature spectrum (900 Hz). However, as seen by infrared experiments, the conformation of cyclotetradecane molecules does not change at the solid–solid transition, nor at the melt transition. That is, the infrared spectrum,[10] which is sensitive to conformational changes, changes little at the transition temperature. Raman spectroscopy also confirms that the same conformation exists in both phases.[29] This is in good agreement with the chemical shift of the mesophase signal. As shown in Table III, the mesophase signal has the same chemical shift as the melt signal and differs only slightly from the weight average value calculated for the A-phase resonances. These small differences may be due solely to differences in molecular packing and cannot be regarded as an indication of conformational changes, which are known to give rise to more significant shift variations.

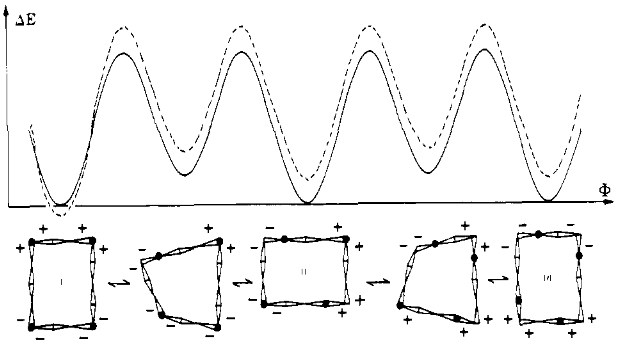

Figure 5. Energy profile and conformational interconversion path of cyclotetradecane: solid line, isolated or dissolved molecule (cf. ref 17); dotted line, suggested changes due to intermolecular interactions in the crystal.

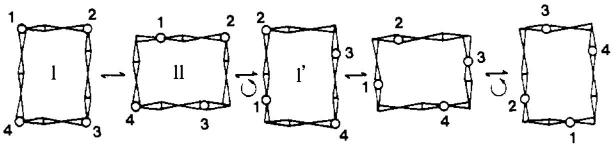

Figure 6. Combined pseudorotation (a) and jump reorientation (b) of cyclotetradecane.

The observation of a slow-exchange–fast-exchange transition due to conformational interconversion is not in contradiction with the evidence that the cyclotetradecane molecules do not change their overall conformation. The collapse of the low-temperature NMR spectrum to a single resonance can be explained by a process in which the different carbon atoms in the $(g^+g^+ag^-g^-aa)_2$ conformation are exchanged in a manner similar to the interconversion of cyclohexane from one chair conformation to another chair conformation (pseudorotation). In the case of cyclotetradecane, the carbon atoms are switched between the *ggag*, *agga*, *ggaa*, and *gaag* sites. Dale investigated such processes for cyclotetradecane by force-field calculations.[15,17] The resulting pseudorotation interconversion path is shown schematically by the solid line in Figure 5 according to ref 17. The repeated passage from one conformational minimum to another results in an exchange of the ring atoms between different topological sites. By four successive conformational changes all ring atoms are moved to an adjacent site of the molecule. Anet[13] explained the coalescence of solution spectrum resonances by the same process and reported an energy barrier of 29.3 kJ/mol from line-shape analysis. Force-field calculations yield 33.5 kJ/mol. This value is somewhat lower than that obtained by Dale[15] by a simpler approach.

The pseudorotation shown in Figure 5 could also give by itself a satisfying and consistent explanation of the signal coalescence of the topomeric carbons observed within the mesophase. Within this process the corners of the rectangular-shaped molecule must, however, travel around the ring. With respect to the crystal lattice this would correspond to a fourteen-site, jumplike reorientation. Such pure pseudorotation would then result in considerable orientational disorder within the plane of the molecule. This is not observed for phase A. To bring all experimental facts in agreement, two explanations may be considered for the observed coalescence of the MAS ^{13}C NMR signals in phase A. In the first explanation, the energy levels of the different conformations would change because of the additional packing energy in the crystal as indicated schematically in Figure 5 by the dotted line. Energy levels of conformations that are not oriented consistent with the

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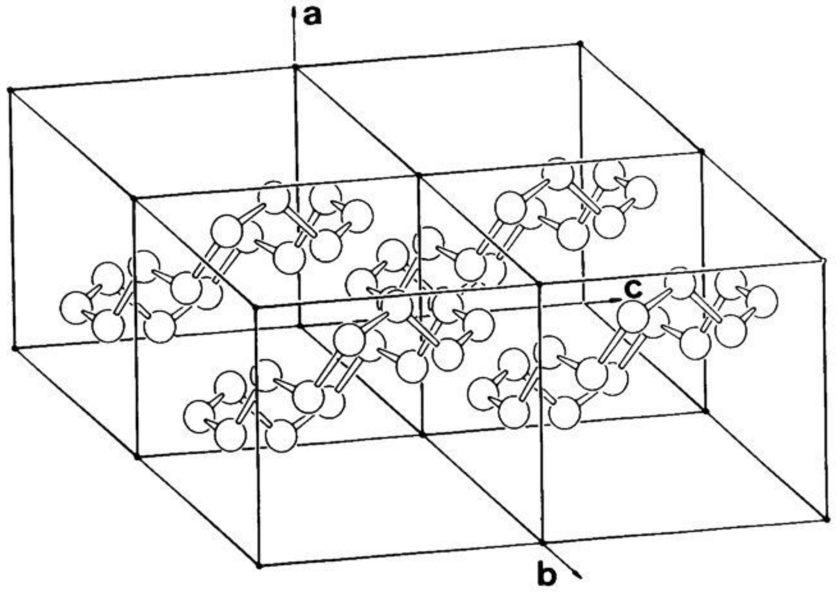

Figure 7. Crystal structure of cyclotetradecane at 116 K, according to ref 12.

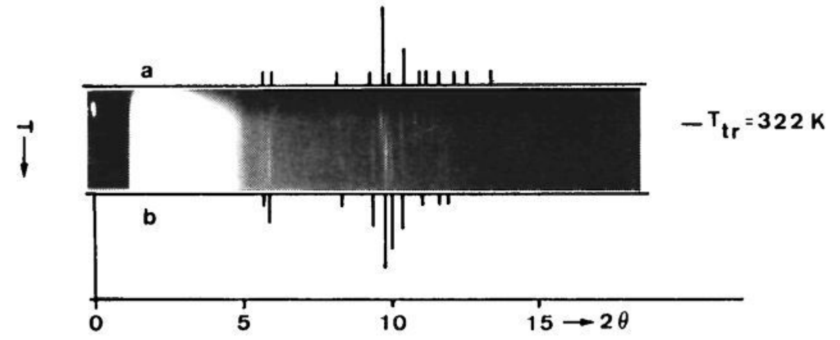

Figure 8. Temperature dependence of the powder pattern of cyclotetradecane. Transition temperature as determined by DSC.

low-energy crystal packing are raised. Thus, unsuitable $(g^+g^+ag^-g^-aa)_2$ conformations become intermediate states of low population as required by the Boltzmann distribution. The molecules would still be able to undergo conformational interconversions, but the arrangement within the lattice would not change significantly. In the second explanation, the disordering due to the pseudorotation would be canceled by a real rotational jump in the opposite direction. This is shown schematically in Figure 6. As a consequence, no orientational disorder would result. At the present, one cannot distinguish between the two mechanisms. In addition to considering the results from these complementary experiments, quantitative evaluation of the dynamics is required to present a conclusive and consistent picture.

X-ray Diffraction. According to Groth,[12] the crystals of cyclotetradecane in phase A are triclinic, with unit cell dimensions $a = 0.534$ nm, $b = 0.804$ nm, and $c = 0.8424$ nm and angles $\alpha = 64.4°$, $\beta = 89.5°$, and $\gamma = 82.0°$. The space group is $P\bar{1}$, with 1 molecule per unit cell (Figure 7). No information on the crystal packing of phase B has been reported. Figure 8 shows the temperature dependence of the powder pattern of cyclotetradecane. The transition from phase A to phase B can be easily recognized. Above T_{tr}, the diffraction pattern is consistent with a monoclinic lattice. No *hkl* assignment of higher symmetry is possible.[30] The resulting unit cell is described by $a = 0.5567$ (6) nm, $b = 0.8416$ (6) nm, $c = 1.6343$ (25) nm, and $\beta = 110.531$ (12)°.[31] The space group is $P2_1/c$ with $Z = 2$. The calculated volume is 0.7120 (1) nm^3. Thus, the transition results in an 11% volume increase. Assuming that the atomic coordinates transform analogous to the unit cell, the powder diagram can be simulated by means of the computer program LAZY PULVERIX.[32] As shown in Table IV, the calculated powder diagram agrees satisfactorily with the experiment.

Table IV. Powder Diagram of $C_{14}H_{28}$ at 325 K

	d		intensity	
h,k,l	obsd	calcd	obsd[a]	calcd[b]
0,0,2	0.7655	0.76588	vw	28.9
0,1,1	0.7369	0.73699	m	173.2
0,1,2		0.56617		7.8
1,0,−2		0.5252		240.4
1,0,0		0.5210		46.4
1,1,−1	0.4643	0.46408	m	68.2
1,1,−2	0.4436	0.44543	vs	1000.0
1,1,0		0.44286		409.0
0,1,3	0.4360	0.43641	s	497.3
0,2,0	0.4207	0.42035	m	92.0
0,2,1		0.40536		9.8
1,1,−3		0.39875		20.7
1,1,1	0.3948	0.39508	w	155.0
0,0,4		0.38294		52.8
1,0,−4		0.37861		58.1
1,0,2	0.3743	0.37392	m	0.6
3,0,2	0.3690	0.3685	m	210.2

[a] vw, very weak; w, weak; m, medium; s, strong; vs, very strong. [b] Normalized to 1000 for the strongest reflection.

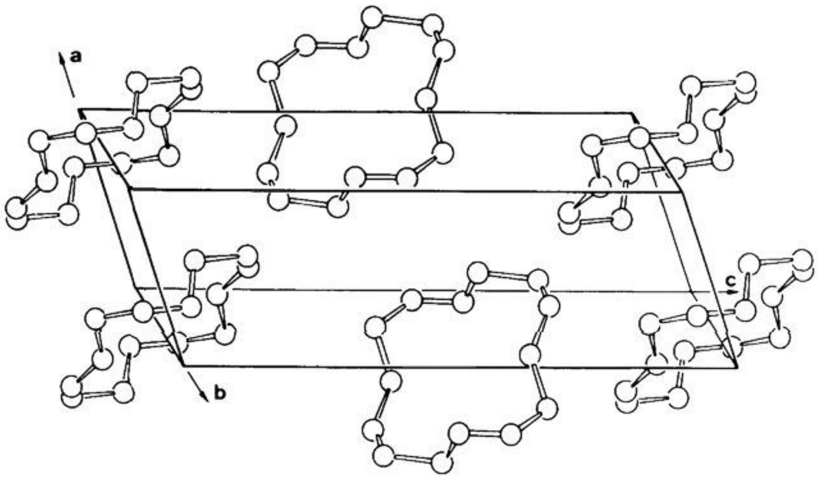

Figure 9. Possible crystal arrangement of cyclotetradecane at 325 K. The long-range orientational order suggested represents an oversimplified view of the arrangement of the molecules. Molelcular mobility may superimpose dynamic orientational disorder.

The change in the lattice can be understood by the following geometrical considerations:

$$a \overset{\sim}{\rightarrow} a' \qquad b - c \overset{\sim}{\rightarrow} b' \qquad b + c - a \overset{\sim}{\rightarrow} c'$$

A body-centered lattice would be expected from this transition in which, according to group theory, the unit cell transformation would be described as follows.

$$P\bar{1} \xrightarrow{e(2)} I\bar{1} \xrightarrow{t(2)} I^2/a(C^2/c)$$

Because the powder diagram indicates that cyclotetradecane exists in a primitive lattice with a $P2_1/c$ space group in phase B, it can be concluded that the molecules are not only displaced but are also turned against each other. Figure 9 shows an arrangement consistent with a $P2_1/c$ space group, with ring planes inclined with respect to each other. However, a transition between such regular arrangements would not be in accord with the large change in entropy observed. An arrangement in which the molecules occupy discrete, different orientational sites with respect to the axis perpendicular to the ring plane and to one or both the axes parallel to the ring plane would still result in an acceptable crystal packing. However, because of the low symmetry of the cyclotetradecane structure, the disorder would be rather high. The transition from the fully ordered crystal into such a partially orientationally disordered state could account for the large change in entropy. The observed X-ray patterns would not exclude the dynamic nature of orientational disorder.

Conclusions

In summary, three major points have been clarified by the present experiments:

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(1) In the low-temperature phase A, the molecular arrangement is highly ordered. A crystal lattice with long-range order in terms of position, orientation, and conformation is observed. However, rather complex molecular motions occur. The coalescence of CP/MAS NMR resonances below 200 K indicates a interconversion process between identical conformations that, however, leads to an exchange of the carbons between the different sites in the ring structure. A pseudorotationlike motion, similar to that of cyclotetradecane molecules in solution is proposed. Additional jumplike reorientations of the molecules as a whole may superimpose the conformational interconversion to restore the crystalline order. At temperatures above the coalescence of the NMR spectrum, substantial line broadening of the NMR resonances occurs, which is due to motional modulation of the dipolar C–H decoupling. At that temperature the molecular motion has reached a correlation time comparable with the inverse of the decoupling field frequency, i.e., 10^5 Hz. The T_2 minimum may be either due to the same conformational interconversion or to the onset of an additional motion like a whole-body rotation. All motions do not result in disorder that would affect the entropy.

(2) At the transition to the mesophase B, the symmetry of the lattice increases but still remains low (monoclinic). There is a considerable decrease in the density. The transition appears by thermal analysis as an order–disorder transition of high cooperativity. Sudden narrowing of the MAS NMR resonance indicates a sharp increase of the rate of the molecular motion observed at low temperature, or more likely, the onset of an additional type of molecular motion. The molecules remain, however, conformationally largely homogeneous. Also, recent ^{2}H NMR experiments show two steps for the onset of motion.[33] The first is the conformational interconversion process below the solid–solid transition and the second most probably a whole-body rotation, starting at the solid–solid transition. Consistent with the known crystal lattice, a jumplike reorientation between different orientational positions acceptable by the crystal, caused by conformational mobility, is proposed. This could explain the rather drastic change in molecular packing and the high entropy of transition and at the same time is consistent with the observed high long-range positional, orientational, and conformational order. The low degree of molecular symmetry results thus in rather large transition entropies, even though the molecular motions are jumplike and lead to disordering between only few different sites with identical molecular conformation.

The third point follows from the first two and relates to the classification of mesophases discussed in the beginning.

(3) Although the thermotropic formation of mesomorphic states on heating results from onset of larger scale molecular motion, molecular dynamics alone may not always also produce disorder. Considerable and complex motions, such as the ring inversions, can occur in a fully ordered crystal, provided the crystalline order is not changed. Conformational interconversion in the A polymorph of cyclotetradecane does not result in conformational disorder. At the transition to the B polymorph conformational mobility causes dynamic orientational disordering, but again no substantial conformational disorder. The transition is linked to the changes in the crystal lattice that, in turn, increase the molecular mobility. The orientational disordering is not diffuse, but discrete and jumplike. In this way, the crystal-lattice symmetry remains low and the anisotropy high. Although conformational disorder is not the main characteristic feature of this mesophase, conformational mobility is certainly the driving force for its formation.

Because of the positional order, the mesophase of cyclotetradecane (polymorph B) does not fit into the concept of liquid crystals. It also does not fit fully into the definition of a plastic crystal due to its rather high orientational order. But since the molecules are also not significantly disordered conformationally, the condis concept may also not apply. Cyclotetradecane represents an intermediate case. It demonstrates the need to discuss not only positional, orientational, and conformational order, but also the positional, orientational, and conformational dynamics. Ordered crystals may be dynamically mobile in one or several of the types of motion. Cyclotetradecane is an example of a molecule that displays a mesophase with partial orientational disorder and high conformational mobility.

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Registry No. Cyclotetradecane, 295-17-0.

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Photochemistry of 3- and 4-Nitrophenyl Azides: Detection and Characterization of Reactive Intermediates

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Abstract: Irradiation of nitro-substituted aromatic azides initiates a complex series of chemical reactions that lead to different products depending on the details of the experiment. There is evidence that four reactive intermediates participate in product-determining reactions. These are the singlet nitrene, the triplet nitrene, the triplet azide, and the ring-expanded dehydroazepine. The chemical and physical properties of each of these species is modified by the nitro substituent. The reactivity of the singlet nitrene with nucleophilic amines is increased, the lifetime of the dehydroazepine is shortened, and the triplet nitrene becomes a powerful single-electron acceptor. Nitro-substituted aromatic azides are widely used in photolabeling experiments. The findings of this study suggest that they may be inappropriate choices as photolabeling agents in many circumstances.

Systematic investigation of the photochemistry of aromatic azides began in 1951[1] and has endured to the present time.[2] The continuous high level of interest in these reactions for more than 35 years is a result of both their challenging, enigmatic nature and the importance of their practical applications.[3,4] A major objective of this inquisition has been the identification and

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