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Conformation of the Cycloalkanes $C_{14}H_{28}$, $C_{16}H_{32}$, and $C_{22}H_{44}$ in the Liquid and High-Temperature Crystalline Phases by Vibrational Spectroscopy

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Abstract: This paper reports a conformational analysis, by means of vibrational spectroscopy, of the conformationally disordered phases [that is, the liquid and high-temperature crystalline (mesomorphic) phases] of c-$C_{14}H_{28}$, c-$C_{16}H_{32}$, and c-$C_{22}H_{44}$. From the observed spectra, the concentration of the lowest energy conformer in the liquid state has been estimated along with the concentration ratios of certain short sequences of trans and gauche bonds. The experimentally derived values of the concentrations are compared with calculated values derived from various sets of conformers whose calculated strain energies have been previously reported in the literature. Good agreement was found for c-$C_{14}H_{28}$. However, for c-$C_{16}H_{32}$ the calculated concentration of the lowest energy conformer is significantly higher than is found experimentally and, in addition, there are some serious differences between the observed and calculated values of the concentrations of the conformational sequences. The most important factor contributing to the discrepancies between the measured and calculated conformational statistics is probably the force field used in the strain energy calculations. For c-$C_{22}H_{44}$, a relatively flexible ring, the experimentally measured concentrations are in reasonable agreement with values derived from a set of diamond-lattice conformers. The distribution of conformers in the high-temperature crystalline phase of all three cycloalkanes is similar to, but somewhat narrower than, that found for the liquid. In the case of c-$C_{14}H_{28}$, for which a measurement is possible, the concentration of the lowest energy (rectangular) conformer in the high-temperature crystalline phase is estimated to be about 70 ± 10%, a value somewhat higher than the 60 ± 10% estimated for the liquid. For c-$C_{22}H_{44}$, the concentration of gauche bonds is used to characterize the liquid and the high-temperature crystalline phases. In terms of the average number of gauche bonds per ring, the high-temperature phase of c-$C_{22}H_{44}$ is found to lie closer to the liquid than to the low-temperature phase.

I. Introduction

We report here on the conformational structure of some intermediate size cycloalkanes in physical states characterized by disorder. In particular, we have studied c-$C_{14}H_{28}$, c-$C_{16}H_{32}$, and c-$C_{22}H_{44}$. These belong to a class of intermediate size cycloalkanes that tend to have conformational structures that are basically different from those of the much more extensively studied small, highly strained cycloalkanes.[1] These larger cycloalkanes tend to have collapsed rather than annular structures and can assume conformations that, again in contrast to the smaller rings, often involve CC bond conformations near those characterized as "trans" or "gauche" in unconstrained, open chains.

Infrared and Raman spectroscopy are the principal techniques that we have used in this study. Our methods are similar to those

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(1) Eliel, E. L.; Allinger, N.; Angyal, S. J.; Morrison, G. A. *Conformational Analysis*; Interscience: New York, 1965. Strauss, H. L. *Annu. Rev. Phys. Chem.* **1983**, *34*, 301-328.

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we have used earlier in measuring conformational disorder in the various crystalline phases of the odd-numbered *n*-alkanes.[2-4] In fact, the present work can be considered an extension of our *n*-alkane investigation, undertaken with a similar purpose, namely, to characterize disorder in complex chain systems that are relevant to polymer and biological systems. We note, however, that our understanding of the structure of the disordered phases of the cycloalkanes begins at a low level relative to that which we enjoyed prior to embarking on our study of the *n*-alkanes. In addition, the spectroscopy of the cycloalkanes is more complex.

The work presented here focuses primarily on the conformer distribution in the liquid state, about which surprisingly little is known. Our work demonstrates that the rings assume many different low-energy conformations. However, it is difficult to determine the distribution of these conformations theoretically because the calculated values of the energies of the conformers are extremely sensitive to the details of the assumed force field. It is also difficult to determine the distribution experimentally because the conformers and hence their spectra tend to be similar and complex. Consequently, an analysis of the spectra of the liquid with the aim of sorting out individual conformers is extremely difficult. On the other hand, we can make quantitative measurements on the distribution of short sequences of CC bonds in specific conformations. The results of these latter measurements will be compared with the predictions from theory.

A number of efforts to estimate the conformer distributions through the calculation of relative strain energies by minimization techniques have been reported in the literature. In the cases of c-$C_{14}H_{28}$ and c-$C_{16}H_{32}$, a sizable number of the low-energy conformers have been found and their relative energies estimated. As will be presently shown, the calculated energy differences between conformers are consistent with our spectroscopic results for c-$C_{14}H_{28}$ but not for c-$C_{16}H_{32}$.

The distribution of conformers observed for the liquid state serves as a reference against which to compare the mesomorphic phase. The latter is an especially interesting crystalline phase that we will refer to here as the high-temperature (HT) phase. In the phase transition from the low-temperature (LT) crystalline phase to the high-temperature crystalline phase, a transition that is characteristic only of cycloalkanes of intermediate size, the cycloalkane rings change from a state of conformational homogeneity to one of conformational inhomogeneity;[5] that is, the crystalline cycloalkanes are transformed from a highly ordered phase to a highly disordered phase. The degree of disorder that characterizes the HT crystal is in fact remarkably high, as may be inferred from the large value of the enthalpy change associated with the solid–solid transition, a value that is two to four times that observed for melting. The solid–solid phase transition for the cycloalkanes may be contrasted with a similar type of solid–solid transition that intermediate size, odd-numbered crystalline *n*-alkanes such as *n*-$C_{23}H_{48}$ can undergo. For this *n*-alkane, the enthalpy change in going from the ordered (orthorhombic) phase to the disordered (rotator) phase is only about 40% that of melting.[3,6]

The nature of the solid–solid transition for the cycloalkanes and the structure and dynamics of the HT crystalline phase have been the subject of a number of recent studies. Those that are particularly relevant to the present study are the infrared and Raman measurements reported by Grossman and his co-workers[7-9] and the magic angle spinning (MAS) ^{13}C NMR measurements reported by Moller and his co-workers.[5,10,11]

Table I. Summary of the Bands Used To Analyze Conformation

mode type	spectrum	approx freq, cm^{-1}	conformation measured	ref
CH_2 wagging	IR	1368	gtg′ and gtg	14
		1352	gg	14
		1300–1280	gtg′ and gtg	14
CD_2 rocking in $(CH_2)_mCD_2(CH_2)_{m'}$	IR	658–667	gg	17
		643–649	gt	15,16
		617–620	tt	15, 16
D-LAM	Raman	250–200	$p(t)^a$	18, 21

$^a p(t)$ is the trans bond probability.

II. Experimental Methods

All infrared spectra were measured with an evacuatable Nicolet Model 8000 FTIR spectrometer. The resolution used was 1 cm^{-1}.

Sample temperatures were controlled by the following methods. In the temperature range from 7 to 273 K, the samples were cooled with the use of a CTI Model 21 closed-cycle helium cryocooler equipped with a heater and temperature controller. For higher temperatures, 273–373 K, the sample was placed in a copper-block housing through which thermostated water or alcohol was circulated. In this case, sample temperatures could be regulated to ±0.02 K with an estimated accuracy of ±0.10 K.[3]

Raman spectra were measured with Spex 1401 and 1403 spectrometers and with a standard 90° scattering geometry and a resolution of 2 cm^{-1}. The excitation was with the argon ion 514.5-nm line. Sample temperatures were controlled by blowing cooled or heated nitrogen over the sample.

The transition temperatures and enthalpies were kindly measured for us by Dr. Richard Twaddell of E. I. du Pont de Nemours using a differential scanning calorimeter (DuPont Instruments 1090 Thermal Analyzer).

The sample of c-$C_{14}H_{28}$ was obtained from Wiley Organics and was recrystallized from an alcohol solution to a purity better than 99.6% as measured by mass spectroscopy. The samples of c-$C_{16}H_{32}$ and c-$C_{22}H_{44}$ were synthesized from the cyclic ketone by reduction with Zn dust and hydrochloric acid. Recrystallization led to purities better than 99.8%.

The samples of cyclohexadecane-*1,1*-d_2 and cyclodocosane-*1,1*-d_2 were synthesized in the same way from the appropriate cyclic ketone. The synthesis will be summarized for cyclodocosane-*1,1*-d_2. The starting material was 10-undecynoic acid, which was esterified to give methyl 10-undecynoate and then converted by oxidative coupling[12] and hydrogenation to dimethyl docosandioate. This product was purified and converted to cyclodocosanone by acyloin coupling in the presence of trimethylsilyl chloride.[13] Finally, cyclodocosane-*1,1*-d_2 was prepared from cyclodocosanone by reduction to the monodeuteriocarbinol with $LiAlD_4$. This alcohol was converted to the tosylate, which was reduced to the hydrocarbon with lithium triethylborodeuteride. The final product had a purity better than 99% and an isotopic purity of 97–98%. The principal isotopic impurity was the molecule with a CHD group in the place of the CD_2 group.

III. Methods of Analysis

A. Spectroscopic Methods. The infrared and Raman bands that are useful for determining conformational structure are listed in Table I and will be discussed briefly here.

1. Methylene Wagging Modes. These bands, which are unique to the infrared spectra of disordered polymethylene chains, are associated with specific kinds of short conformational sequences.[14] The three wagging bands that are observed in the spectra of the disordered cycloalkanes are near 1368, 1352, and 1300 cm^{-1}. Those at 1368 and 1300 cm^{-1} are associated only with both gtg′ and gtg sequences. The band at 1350 cm^{-1} is associated only with the gg sequence. We note that all three bands are broad, indicating that the modes associated with them may not be entirely localized in the conformational sequence and that there are some variations in the dihedral angles that define the sequence.

The intensity of the wagging bands can be used as a quantitative measure of the relative concentration of the conformational sequences. The bands near 1352 and 1368 cm^{-1} are the best defined

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(2) Snyder, R. G.; Maroncelli, M.; Qi, S. P.; Strauss, H. L. *Science* **1981**, *214*, 188–190.

(3) Maroncelli, M.; Qi, S. P.; Strauss, H. L.; Snyder, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 6237.

(4) Maroncelli, M.; Strauss, H. L.; Snyder, R. G. *J. Chem. Phys.* **1985**, *82*, 2811.

(5) Drotloff, H.; Emeis, D.; Waldron, R. F.; Moller, M. *Polymer*, in press.

(6) Broadhurst, M. G. *J. Res. Natl. Bur. Stand., Sect. A* **1962**, *66*, 241.

(7) Grossmann, H.-P.; Arnold, R.; Burkle, K. R. *Polym. Bull.* **1980**, *3*, 135–142.

(8) Grossmann, H.-P. *Polym. Bull.* **1981**, *5*, 137–144.

(9) Grossmann, H.-P.; Bolstler, H. *Polym. Bull.* **1981**, *5*, 175–177.

(10) Moller, M.; Grosnki, W.; Cantow, H.-J.; Hocker, H. *J. Am. Chem. Soc.* **1984**, *106*, 5093.

(11) Drotloff, H.; Rotter, H.; Emeis, D.; Moller, M. *J. Am. Chem. Soc.* **1987**, *109*, 7797–7803.

(12) Campbell, I. D.; Eglinton, G. *Org. Synth.* **1965**, *45*, 39.

(13) Ruhlman, K. *Synthesis* **1971**, 236–253.

(14) Snyder, R. G. *J. Chem. Phys.* **1967**, *47*, 1316–1360.

pair, and we have used the ratio of their integrated intensities as a measure of the ratio of the probability for the occurrence of gg sequences to the sum of the probabilities for gtg′ and gtg sequences. However, for the 1368-cm^{-1} band there is a complication that arises because the intrinsic intensity of the mode associated with gtg′ differs to an unknown extent from that associated with the gtg mode. However, for the cycloalkane rings that we consider here, the concentration of the gtg sequence is much greater than that for gtg′. Thus, to a good approximation

$$p(\mathrm{gg})/p(\mathrm{gtg}) = A[I(1352)/I(1368)] \qquad (1)$$

where $p(\mathrm{gg})$ and $p(\mathrm{gtg})$ stand for the probability of the indicated sequence and where I represents the intensity of the indicated infrared band. The constant A has a value of 1.2. This value was determined from the infrared spectrum of liquid c-$C_{14}H_{28}$, since the probability ratio, gg to gtg, can be accurately estimated for this ring (see section IV.C. below).

We note that eq (1) is not valid for the open chains because in this case $p(\mathrm{gtg}') \cong p(\mathrm{gtg})$. Consequently, the ratio $I(1352)/I(1368)$ cannot be used to compare the conformational statistics of the cycloalkanes with those of the *n*-alkanes.

2. Isotopically Isolated CD_2-Rocking Bands. These bands are associated with tt, gt, and gg pairs and appear in the infrared spectra of polymethylene chains containing CD_2 groups that are separated from each other by CH_2 groups. The bands near 620 and 645 cm^{-1} represent tt and gt pairs, respectively, and have been well characterized.[15,16] Recently, a third band, near 665 cm^{-1}, has been identified with the gg pair.[17] The relative intensities of these bands are good measures of the relative concentrations of pair sequences. A prerequisite to the use of the method is that we know $A(\zeta\eta)$ in the expression

$$p(\zeta\eta)/p(\mathrm{tt}) = A(\zeta\eta)[I(\zeta\eta)/I(\mathrm{tt})] \qquad (2)$$

where p and I represent respectively the second-order probabilities and the infrared intensities of the bands associated with the pairs $\zeta\eta$ and tt. The values of $A(\mathrm{gt})$ and $A(\mathrm{gg})$ can be obtained from the intensities of the CD_2 bands in the spectrum of the LT crystalline phase of cyclohexadecane-*1,1*-d_2, which is comprised of conformationally ordered rings. These rings are square and have tt, gt, and gg pairs that occur in the ratio 4:8:4. We have found that $A(\mathrm{gt}) = 1.06 \pm 0.03$ and $A(\mathrm{gg}) = 1.10 \pm 0.03$.[17] For comparison, a value of $A(\mathrm{gt})$ of 1.00 ± 0.07 has been previously determined from measurements on CD_2-substituted *n*-alkanes.[16]

3. The D-LAM Band. The low-frequency isotropic Raman spectrum of the conformationally disordered polymethylene chain displays a broad band between 300 and 200 cm^{-1} that is made up of the individual bands from the many conformers that constitute the sample.[18,19] The frequency of this band, known as the D-LAM band, is dependent on the concentration of trans bonds, $p(\mathrm{t})$. This dependence forms the basis of a method to determine $p(\mathrm{t})$. The method has been used to determine $p(\mathrm{t})$ in semicrystalline linear[20] and branched[21] polyethylenes.

We have used the D-LAM to estimate $p(\mathrm{t})$ only in the case of c-$C_{22}H_{44}$ for the following reason. In general, LAM bands of the polymethylene chain can be analyzed only in two limits—for chains in the all-trans conformation (LAM-k bands) and for an assembly of chains in statistically random conformations (D-LAM bands). Liquid c-$C_{22}H_{44}$ has a sufficient number of conformations to provide a D-LAM band from which we can estimate $p(\mathrm{t})$. However, this is not the case for c-$C_{14}H_{28}$ and c-$C_{16}H_{32}$, which have too few conformations to provide a simple D-LAM band.

B. Calculated Energies of Cycloalkane Conformers. The result of our spectroscopic measurements on the conformations of the cycloalkanes will be compared with the results from theory. The theoretical results are derived from the calculated energy differences between the members of a particular set of conformers that have been identified as having the lowest energies. One such set of conformer structures and energies is that compiled by Dale.[22] The members of this set will be referred to as EM-D conformers, and they include both c-$C_{14}H_{28}$ and c-$C_{16}H_{32}$. In Dale's calculation, an *n*-butane-like potential for the torsional angle about a CC bond was used. The CC bond lengths and CCC bond angles were not adjusted. A scheme for selecting likely ring conformations was used that involved the transferability of certain short, low-energy sequences of trans and gauche bonds to form initial structures. The strain or steric energies computed by Dale are probably too high, however. For use here, we have reduced the values of the energies by $^5/_8$, because the potential energy function that was assumed for torsion around a CC bond is such that the gauche position is 0.8 kcal/mol higher than the trans position, whereas a value near 0.5 kcal/mol is now thought to be more likely.[23,24] The strain energies may also be too high because the structures were not fully minimized and only the torsional angles were allowed to vary.

A second source of estimated values of the conformer energies comes from a tabulation of diamond-lattice (DL) conformers derived by Mattice and Snyder.[25] This set consists of all the non-self-intersecting conformers whose carbon skeletons can be traced out on a diamond lattice. The energies associated with the DL conformers have been estimated by assigning an energy difference of 0.5 kcal/mol between trans and gauche bonds and 2.0 kcal/mol for the gauche gauche-prime (gg′) pair. The results are given in detail in ref 25 for the even-numbered cycloalkanes C_6 through C_{22}.

For c-$C_{14}H_{28}$ and c-$C_{16}H_{32}$, we have combined the lowest energy conformers from both the EM-D and DL sets to approximate these cycloalkane systems in the liquid state. The lowest energy EM-D conformers have CC bonds that are nearly trans or gauche, and some of these conformers are close to a DL conformation. However, there remains considerable uncertainty concerning the relative energies of the EM-D and DL forms since the potential energy functions for the two sets are quite different. We will comment later on some instances where the EM-D conformer corresponds to a DL chain that is nearly but not quite closed. Finally, we note that the DL set is complete in itself, while the EM-D set is, of course, not. However, neither set contains all possible low-energy conformations, and therefore we have in some instances combined the sets to obtain better estimates of the conformational statistics.

A very recent set of EM conformers is that of Saunders, who has developed a stochastic search method for exploring molecular mechanics energy surfaces and has applied the method to the cycloalkanes.[26,27] The method involves inducing random (small) changes to each coordinate of each atom of the molecule and minimizing the energy of the resultant structure. If a new conformation is found, it is refined with the use of the Allinger MM2 force field.[28]

Application of this method to c-$C_{14}H_{28}$ has yielded a much larger and mostly different set of conformers than that reported by Dale[22] for this cycloalkane. Professor Saunders has kindly provided us with the steric energies and structures of these conformers, which we will refer to as the EM-S conformers. In addition, he has also provided us with a set of conformers for

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(15) Snyder, R. G.; Poore, M. W. *Macromolecules* **1973**, *6*, 708–715.

(16) Maroncelli, M.; Strauss, H. L.; Snyder, R. G. *J. Phys. Chem.* **1985**, *89*, 4390–4395.

(17) Shannon, V. L.; Strauss, H. L.; Snyder, R. G.; Elliger, C. A. *J. Phys. Chem.*, to be submitted.

(18) Snyder, R. G. *J. Chem. Phys.* **1982**, *76*, 3921–3927.

(19) Snyder, R. G.; Strauss, H. L. *J. Chem. Phys.* **1987**, *87*, 3779–3788.

(20) Snyder, R. G.; Schlotter, N. E.; Alamo, R.; Mandelkern, L. *Macromolecules* **1986**, *19*, 621–626.

(21) Mandelkern, L.; Alamo, R.; Mattice, W. L.; Snyder, R. G. *Macromolecules* **1986**, *19*, 2404–2408.

(22) Dale, J. *Acta Scand.* **1973**, *27*, 1115–1129.

(23) Scherer, J. R.; Snyder, R. G. *J. Chem. Phys.* **1980**, *72*, 5798–808. Kint, S.; Scherer, J. R.; Snyder, R. G. *J. Chem. Phys.* **1980**, *73*, 2599–2602.

(24) Abe, A.; Jernigan, R. L.; Flory, P. J. *J. Am. Chem. Soc.* **1966**, *88*, 631.

(25) Mattice, W. L.; Snyder, R. G. *Macromolecules* **1988**, *21*, 2452–2456.

(26) Saunders, M.; Jarret, R. M. *J. Comput. Chem.* **1986**, *7*, 578–588.

(27) Saunders, M. *J. Am. Chem. Soc.* **1987**, *109*, 3150–3152.

(28) Saunders, M. Private communication.

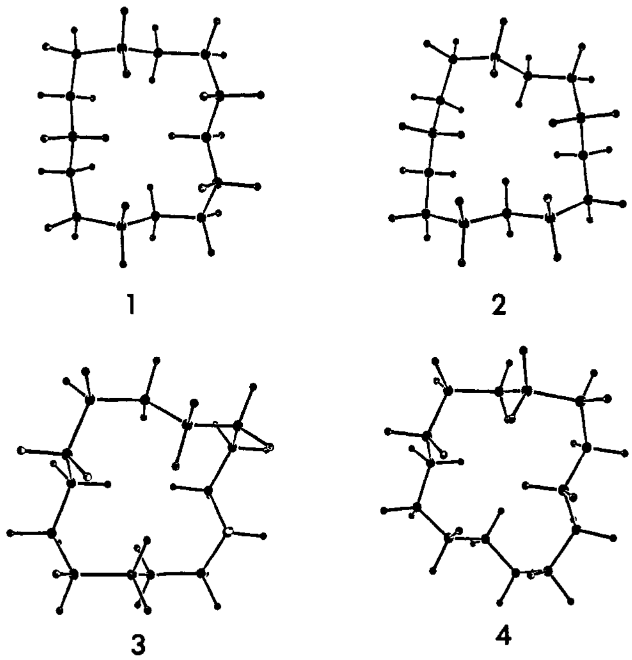

Figure 1. The five lowest energy EM-S conformers of c-$C_{14}H_{28}$. The conformers are ordered in terms of increasing strain energy and correspond to those listed in Table IV. Conformers **1** and **2** are the [3434] and [3344] forms. [These drawings were kindly furnished by M. Saunders.[28]]

c-$C_{16}H_{32}$. The interpretation of our experimental results includes reference to these new results.

C. Designation of Conformers. The cycloalkane rings that we consider here have sufficient flexibility that the conformation of the CC bonds can usually be identified with trans (t) or gauche (g and g′) states. This makes it possible to describe the lower energy conformers in terms of the conformation of the individual CC bonds. When possible, however, we will use the more compact designation of Dale,[22] which can be applied to conformers that are rectangular or nearly rectangular. This system will be explained by an example. The low-energy conformation of c-$C_{14}H_{28}$, which is conformer **1** in Figure 1, is designated in terms of bond conformations as ggtggtttg′g′tg′g′ttt. In Dale's system the designation is [3434], where the numbers in brackets indicate the number of CC bonds between corner carbon atoms.

The low-energy rectangular conformation is the one normally assumed by large cycloalkanes in their low-temperature crystalline phase. We note that the rectangular conformer is a DL conformer only if the number of carbon atoms in the ring equals $4m + 2$, where m is an integer. Rings larger than c-$C_{16}H_{32}$ that do not satisfy this requirement nevertheless also assume a rectangular conformation so as to enable the trans chains to pack efficiently. In these cases, the extra strain energy is dispersed over many bonds and is therefore small. We note that for the larger rings, c-$C_{22}H_{44}$, for example,[25] the rectangular conformer is *not* the lowest energy conformer if intermolecular factors are ignored.

It will be convenient to summarize here the abbreviations we have introduced and will continue to use: LT, low temperature; HT, high temperature; DL, diamond-lattice; EM, energy minimized; EM-D and EM-S refer to the EM conformers reported by Dale[22] and by Saunders,[28] respectively; t, trans bond; and g and g′, gauche bonds of opposite handedness. Also for future reference, the transition temperatures and enthalpies for c-$C_{14}H_{28}$, c-$C_{16}H_{32}$, and c-$C_{22}H_{44}$ are listed in Table II.

IV. Cyclotetradecane

A. Background. The rings in the LT ordered phase of c-$C_{14}H_{28}$ have the rectangular [3434] conformation.[29] Increasing the temperature results in a solid–solid phase transition at 322 K in which the ordered LT crystalline phase is converted to a disordered HT crystalline phase. The HT phase persists up to the melting point at 329 K. We note that the temperature range over which the HT phase of c-$C_{14}H_{28}$ exists (7 K) is much smaller than that for c-$C_{16}H_{32}$ (57 K) and c-$C_{22}H_{44}$ (21 K).

Table II. Transition Temperatures (K) and Enthalpies (kJ/mol) for the Solid–Solid and Melting Transitions of the Cycloalkanes $C_{14}H_{28}$, $C_{16}H_{32}$, and $C_{22}H_{44}$

	T_t	T_m	$\Delta H_t{}^d$	$\Delta H_m{}^d$
c-$C_{14}H_{28}$	322[a]	329[a]	16.3	9.3
c-$C_{16}H_{32}$	273[b]	330[b]	22.6	8.4
c-$C_{22}H_{44}$	299[c]	320[c]	39.7	10.2

[a] Reference 11. [b] Reference 30. [c] Reference 37. [d] This work.

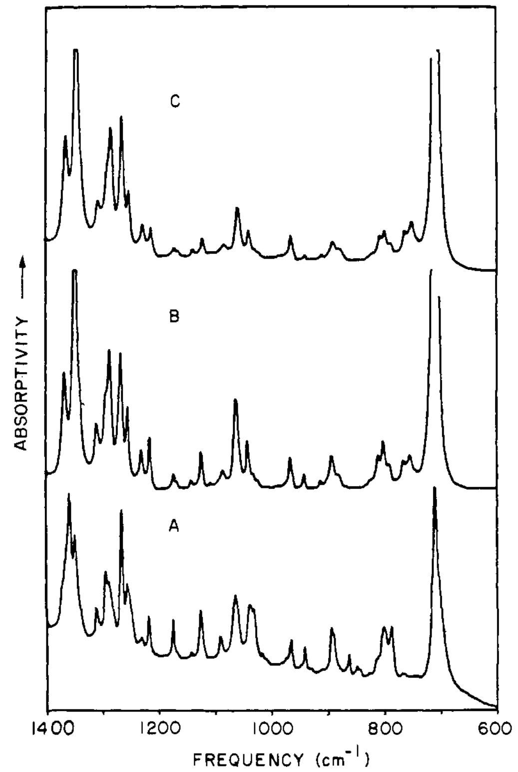

Figure 2. Infrared spectra of c-$C_{14}H_{28}$: (A) low-temperature crystalline phase (313 K); (B) high-temperature crystalline phase (320 K); (C) liquid (343 K).

The solid–solid transition of c-$C_{14}H_{28}$ was detected by Billeter and Gunthard[30] from changes in the infrared spectra. The authors concluded that the relative abundances of the different conformers present in the HT solid and in the liquid are approximately the same. These spectra were later re-interpreted by Borgan and Dale[31] to indicate that the rings remain in the [3434] conformation in all three phases, a conclusion contrary to our own.

B. Infrared Spectra and Estimated Conformational Disorder. Infrared spectra of c-$C_{14}H_{28}$ in the 1400–600-cm^{-1} region are shown in Figure 2 for the LT (313 K) and HT phases (320 K) and for the liquid (343 K). In going from the LT crystal to the HT crystal, the infrared spectrum undergoes major changes. In the region 1400–1250 cm^{-1}, the relative intensities of the bands in the LT and HT spectra are quite different, and below 1250 cm^{-1}, many new, well-defined bands are apparent in the HT-phase spectrum. In fact, there are so many new features that the bands associated with the [3434] conformer become difficult to identify.

We interpret these changes to indicate that there is an appreciable concentration of conformers in the HT phase other than the [3434] form. Borgan and Dale[31] proposed that the new features in the HT spectrum could be accounted for in terms of

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(29) Groth, P. *Acta Chem. Scand., Part A* **1976**, *30*, 155.

(30) Billeter, E.; Gunthard, H. H. *Helv. Chim. Acta* **1958**, *41*, 338.

(31) Borgan, G.; Dale, J. *Chem. Commun.* **1970**, 1340.

Table III. A Set of Low-Energy Conformers of c-$C_{14}H_{28}$ Comprised of EM-D and DL Forms

	type[a]	conformer[b]	rel wt	E,[c] kcal/mol	concn, % 300 K	concn, % 343 K
1	DL+EM	ggtggttg'g'tg'g'tt or [3434]	1	0	79.7	72.7
2	DL	ggtggtgggtgg'tt	4	2.5	4.8	7.4
3	DL	ttgttg'gttg'ttgg'	1	3.0	0.5	0.9
4[d]	EM	ggtggttg'g'ttggt or [3344]	2	1.44	14.2	17.6
5[d]	EM	ggtggtggtttggt or [3335]	4	3.63	0.7	1.4

[a] The diamond lattice (DL) conformers are from ref 25 and the energy minimized (EM-D) conformers are from ref 22. [b] In the DL set, t, g, and g' refer to dihedral angles 180, 60, −60°. In the EM-D set, there are significant variations from these values. [c] The strain energies of the EM-D forms reported in ref 22 have been reduced by $^5/_8$. See text. [d] Conformers **4** and **5**, if drawn on a diamond lattice, have respectively end-to-end distances of 1.63 and 2.83 in units of bond length.

a breakdown in selection rules owing to high-amplitude skeletal motion. While highly anharmonic modes could modify the spectrum, it is likely that any new bands that result will be weak and broad, a description that does not at all apply to the new bands that are observed.

We have made a rough measurement of the concentration of the [3434] conformer in the HT solid phase. The estimate is based on the infrared intensities of the two bands near 800 cm^{-1} which belong to the [3434] conformer and two bands near 760 cm^{-1} which belong to other conformers (Figure 2B). The spectrum of the HT phase contains both pairs of bands. These bands are all methylene rocking modes, as has been demonstrated by normal coordinate calculations on *n*-alkanes[14] and on c-$C_{14}H_{28}$ itself.[32] From these calculations we know that rocking-mode bands that have similar frequencies (800 and 760 cm^{-1}) are associated with modes that are similar in character, and hence their intensities can be used as an approximate measure of the conformer concentrations.

On this basis we estimate that about 70 ± 10% of the c-$C_{14}H_{28}$ conformers in the HT phase have the [3434] conformation. However, this estimate may be on the high side, since it is based on the assumption that the 800-cm^{-1} band belongs entirely to the [3434] conformer, while in fact it is apparent that conformers other than [3434] are contributing to the intensity of this band.

The spectrum of liquid c-$C_{14}H_{28}$ at 343 K is very similar to that of the spectrum of the HT solid. This indicates that the conformers present in the liquid are probably the same as those in the HT phase and that the main difference between the two phases is in the conformer concentration. A semiquantitative comparison can be made for the [3434] conformer. Using the same method used for the HT phase, we find that for the liquid phase about 60 ± 10% of the conformers have the [3434] conformation. Again, as indicated above for the HT solid, this estimate is probably on the high side. These estimates of the concentration of the [3434] conformer in the HT and liquid phase of c-$C_{14}H_{28}$ are supported by recent Raman measurements that will be published separately.[33]

Finally, we note that the infrared intensity ratio $I(1352)/I(1368)$, which is a measure of $p(gg)/p(gtg)$, is virtually unchanged in going from the HT phase to the liquid. The reason for the constancy of the ratio will be discussed in the next section.

C. Estimates of Conformational Statistics. As indicated above, we have found that c-$C_{14}H_{28}$ in the liquid state near 340 K is comprised of a variety of different conformers. The most stable of these, the [3434] form, accounts for about 60% of the rings. This result is at odds with most earlier work. The calculations of Dale, for example, lead to the conclusion that the liquid should consist almost entirely of the [3434] conformer.[22] The presence of essentially only the [3434] conformer in both the HT and liquid phases is assumed in a recent ^{13}C NMR study of c-$C_{14}H_{28}$.[11]

The experimentally determined value of about 60% for the concentration of the [3434] in the liquid is supported by calculations based on two sets of conformers that will now be described. The first set, which is listed in Table III, consists of a combination of those DL conformers[25] and EM-D conformers[22] that have calculated strain energies that are less than 4.0 kcal/mol relative to the [3434] conformer. (As explained in section III.B, the energies of the EM-D conformers have been reduced from the values reported by Dale.) For this set, about 73% of the rings are computed to be in the [3434] conformation at 343 K, the temperature at which the spectroscopic measurements were made. This calculated value is in reasonable agreement with the estimate of 60 ± 10% obtained from the infrared spectrum of the liquid.

Table IV. The Five Lowest Energy EM-S Conformers of c-$C_{14}H_{28}$[a]

	conformer[b]	rel wt	E,[c] kcal/mol	concn, % 300 K	concn, % 343 K
1	ggtggttg'g'tg'g'tt or [3434]	1	0	54.6	43.8
2	ggtggttg'g'ttggt	2	1.08	17.8	17.8
3	gggtggtgggtggt	2	1.47	9.4	10.2
4	gtggttg'ggtggtg	4	2.16	5.9	7.4
5	tggtgggtgg'tg'g't	4	2.42	3.8	5.1

[a] The conformation and the relative strain energies were computed by Saunders.[26,27] [b] The dihedral angles associated with t, g, and g' vary significantly from 180, 60, and −60°. [c] Reference 28.

Table V. Calculated Concentrations, for c-$C_{14}H_{28}$, of Short Conformational Sequences for [3434] by Itself and for the Two Sets of Conformers Defined in Tables III and IV

sequence (i)	[3434] conformer alone n(i)	[3434] conformer alone p(i)	5-member set[a] n(i)[b]	DL+EM-D at 343 K p(i)[c]	11-member set[d] n(i)	EM-S at 343 K p(i)
t	6	0.429	5.96	0.426	5.64	0.403
tt	2	0.143	1.94	0.139	1.65	0.118
gt	8	0.571	8.00	0.571	7.97	0.569
gg	4	0.286	3.96	0.283	4.15	0.296
gg'	0	0	0.09	0.001	0.23	0.016
gtg	2	0.143	2.07	0.148	2.33	0.166
gtg'	0	0	0	0	0	0

[a] This set is defined in Table III. [b] Average number of sequences per conformer over all conformers. [c] Probability [$p(i) = n(i)/14$]. [d] The first 5 members are listed in Table IV.

A second, much larger set of conformers leads to similar agreement with experiment. This set consists of 99 (EM-S) conformers found by Saunders.[27,28] The four lowest energy conformers of this set are illustrated in Figure 1, and the first five are listed in Table IV along with their relative energies and their concentrations calculated for 300 and 343 K. We note that, at 343 K, the concentration of the [3434] conformer is computed to be 44%.

The agreement between the experimental and theoretical values of the concentration of the lowest energy conformer represents only a first step, since there remain large uncertainties about the identity and concentrations of all the other conformers that make up the liquid. The magnitude of the problem becomes apparent when the two sets of conformers, each of which gives reasonable values for the [3434] concentration, are compared. Only *two* conformers, [3434] and [3344], are found to be common to these two sets, which are listed in Tables III and IV. Clearly, much more work will be needed to clarify the conformer distribution in the liquid.

We end this section by noting that the spectral analysis of the distribution of conformers is particularly difficult in the case of c-$C_{14}H_{28}$. This is because the concentrations of those kinds of short conformational sequences that are experimentally accessible

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(32) Shannon, V. L.; Strauss, H. L.; Snyder, R. G. To be published.
(33) Kim, Y.; Strauss, H. L.; Snyder, R. G. To be published.

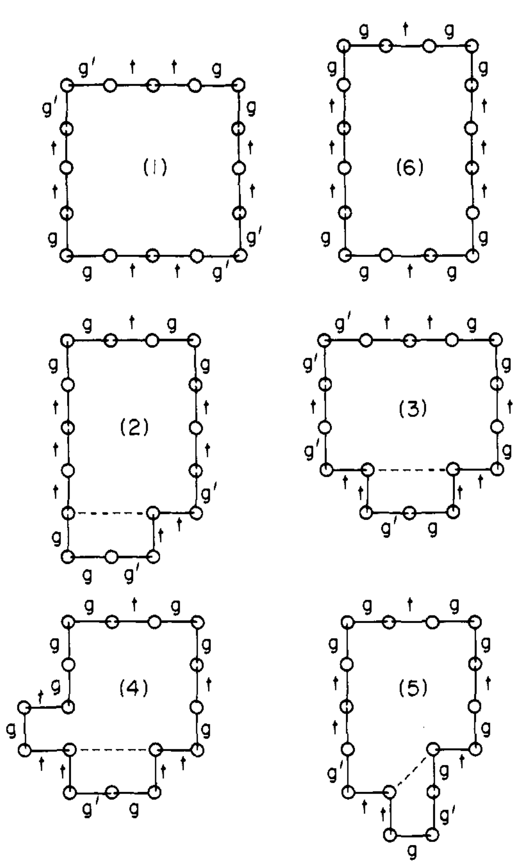

Figure 3. Conformers of c-$C_{16}H_{32}$. All are diamond-lattice conformers except **6**. Conformer **1** is the most stable, followed by **6**. Pentane interactions are indicated by a dashed line. The numbers refer to the conformer numbers listed in Table VII.

to us are insensitive to the distribution of conformers in the liquid and HT phases. The insensitivity results from the fact that for c-$C_{14}H_{28}$, the concentrations of these sequences are nearly the same for each of the individual conformers, as may be seen from Table V. This makes it difficult to distinguish between the HT and liquid phases: The observed value of the $p(\mathrm{gg})/p(\mathrm{gtg})$ ratio is observed to be essentially the same for both phases. Likewise, the concentration of gauche bonds, which can be determined through ^{13}C NMR chemical-shift measurements, is also essentially the same.[11] However, in spite of these observations we know from their infrared spectra that the HT and liquid phases do not have the same distribution of conformers.

V. Cyclohexadecane

A. Background. The rings in the LT ordered phase of c-$C_{16}H_{32}$ assume the highly symmetric [4444] DL conformation shown in Figure 3.[32] This conformation is predicted by strain-energy calculations to be the lowest energy form,[28,34,35] a prediction that is supported by the ^{13}C NMR results of Anet and Cheng.[35] The LT phase is transformed at 273 K into a HT disordered crystalline phase, which in turn is transformed to the liquid phase at 330 K.

The conformational distribution of the rings in the liquid has been discussed in connection with the interpretation of infrared and ^{13}C NMR measurements, but there is no consensus. Billeter and Gunthard[30] measured the infrared spectra of c-$C_{16}H_{32}$ in the crystalline and liquid phases and observed the solid–solid phase transition. These spectra led Borgen and Dale[31] to conclude later that cyclohexadecane is conformationally inhomogeneous in the HT solid phase and in the melt, in keeping with the earlier calculations of Dale.[22] From an energy minimization calculation, Anet and Cheng[35] computed an energy difference of 1.9 kcal/mol between the square [4444] DL conformer, which their calculations indicate is the most stable form, and the rectangular [3535] conformer, which is the next most stable form, and concluded that in the liquid phase at room temperature at least 70% of the rings are in the [4444] conformation. They suggested that the breadth of the bands in the infrared spectra was the result of high-amplitude, low-frequency librational modes. More recently, Allinger et al.[34] reported a calculated value of about 3.4 kcal/mol for the energy difference between the [4444] and [3535] conformers. According to their result, nearly all of the rings in the liquid phase should be in the [4444] conformation.

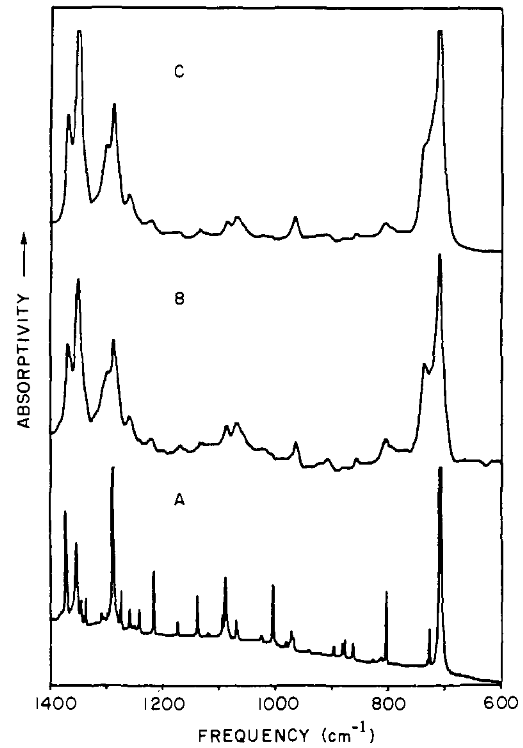

Figure 4. Infrared spectra of c-$C_{16}H_{32}$: (A) low-temperature crystalline phase (7 K); (B) high-temperature crystalline phase (298 K); (C) liquid (343 K).

Our spectroscopic measurements indicate a quite different distribution from those reported in these earlier studies.

B. Infrared Spectra. 1. Cyclohexadecane. The infrared spectra of c-$C_{16}H_{32}$ in the LT solid phase at 7 K, in the HT phase near 295 K, and in the liquid phase at 343 K are shown in Figure 4. The spectrum of the LT solid phase, which is discussed in ref 32, is relatively simple because the [4444] conformer has a high symmetry, point group D_{2d}.

The LT to HT solid–solid transition changes the simple, well-defined spectrum of the LT phase to a spectrum with new bands and no sharp detail. The changes are much more profound than those observed in the case of c-$C_{14}H_{28}$ and indicate that the degree of disorder in the HT solid phase of c-$C_{16}H_{32}$ is greater than in the HT phase of c-$C_{14}H_{28}$.

The transition from the HT phase of c-$C_{16}H_{32}$ to the liquid is accompanied by further band broadening and further changes in band intensities. The intensity ratio of the bands at 1352 and 1368 cm^{-1} (which are associated with gg and gtg'+gtg sequences, respectively) undergoes a small change from 2.0 to 2.4. If the very small contribution of gtg' to the 1368-cm^{-1} band is ignored, the value of $p(\mathrm{gg})/p(\mathrm{gtg})$ changes from 2.4 to 2.9. However, part or all of this change may be attributable to the temperature difference (ΔT = 45 K) between the samples.

2. Cyclohexadecane-*1,1*-d_2. The relative intensities of the CD_2 rocking bands in the infrared spectra of the LT, HT, and liquid phases of cyclohexadecane-*1,1*-d_2 were measured to determine the relative concentrations of tt, gt, and gg pairs. Representative spectra are shown in Figure 5. In going from the LT to the HT phase, there is a significant change in relative intensities, and an increase in bandwidths. The latter changes will be discussed below

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[34] Allinger, N. L.; Gorden, B.; Profeta, S., Jr. *Tetrahedron* **1980**, *36*, 859–864.

[35] Anet, F. A. L.; Cheng, A. K. *J. Am. Chem. Soc.* **1975**, *97*, 2420–2424.

Table VI. Measured Values of Some Second-Order Probability Ratios Evaluated from the CD_2 Rocking Mode Intensities of Cyclohexadecane-*1,1*-d_2

		ratio[a]	
phase	temp, K	p(gt)/p(tt)	p(gg)/p(tt)
LT	270	(2.0)[b]	(1.0)[b]
HT	275	3.9	0.8_5
	280	4.0	1.1_5
	295	4.4	1.2
	305	4.8_5	1.3
	325	3.8_5	0.7_5
melt	340	4.6	0.5_5

[a] Estimated errors for p(gt)/p(tt) and p(gg)/p(tt) are ±0.2 and ±0.1, respectively. The errors are based on the estimated errors in the curve-fitting results. [b] These values, which are appropriate to the [4444] conformer, were assumed in order to evaluate the A_r in eq 2. See Section III.A.2.

in section VI.B.2. In going from the HT phase to the liquid phase, however, there is little additional change.

Curve-fitting procedures were used to obtain the relative intensities of the CD_2 bands for the LT, HT, and liquid phases. The observed spectra of the HT and liquid phases can be closely approximated if bands at 618, 645, 655, and 666 cm^{-1} are used. The bands at 618, 645, and 666 cm^{-1} are clearly associated with tt, gt, and gg pairs. The band at 655 cm^{-1}, which must be included for a good fit, is less intense, amounting to 2–6% and 8–9% of the total intensity of all four bands for the HT phase and the liquid phase, respectively. It is likely that the 655-cm^{-1} band represents a *gg* pair in a *gggt* sequence. Table VI summarizes the CD_2 intensity data.

C. Conformation. 1. An Upper Limit to the Concentration of the [4444] Conformer in the Liquid. The general complexity of the infrared spectrum argues strongly against earlier calculations that imply that the liquid phase of cyclohexadecane consists primarily of the square [4444] conformer.[34,35] The spectrum of the [4444] conformer is shown in Figure 4A. It is important to note that none of the bands of the [4444] conformer are in evidence in the spectrum of the liquid (Figure 4C). An upper limit to the concentration of the [4444] conformer in the liquid can be established by comparing the spectrum of the LT phase with that of the liquid. We conclude that not more than about 15% of the square conformer can exist in the liquid at 343 K, because, if the concentration of the [4444] conformer was greater than this value, its bands could be detected in the spectrum of the liquid.

Additional experimental evidence that favors a low concentration of the [4444] conformer in the liquid comes from the measured value of the concentration ratio p(gg)/p(gtg). This ratio is significant because it is extremely sensitive to the presence of conformers other than [4444]. The sensitivity comes about because the [4444] conformer is nearly unique among the low-energy conformers, which are listed in Tables VII and VIII, in that it has no gtg sequence. (Conformer **9** in Table VII and **5** and **10** in Table VIII have no gtg sequences. However, the concentrations of these conformers are expected to be very low.) Consequently, if the concentration of the [4444] conformer approaches 100%, the ratio approaches an infinite value.

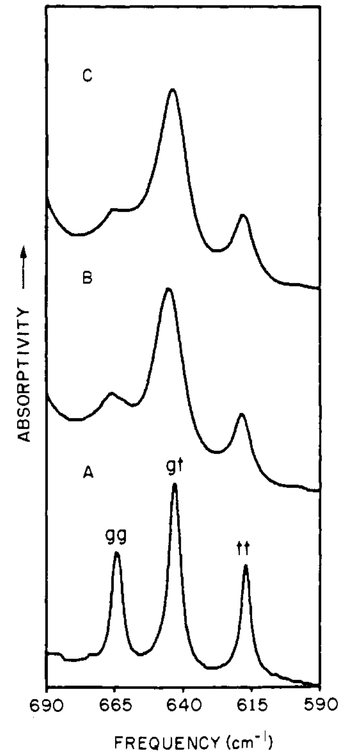

Figure 5. Infrared spectra of cyclohexadecane-*1,1*-d_2 in the CD_2 rocking mode region: (A) low-temperature crystalline phase (270 K); (B) high-temperature crystalline phase (303 K); (C) liquid (343 K).

The observed value of p(gg)/p(gtg) for the liquid at 340 K is 2.3. This value is very much smaller than the values calculated on the basis of the strain energies reported in ref 34 and 35. The computed value of p(gg)/p(gtg) for a two-conformer set made up of the [4444] and [3535] forms, whose energy difference is calculated in ref 34 to be 3.4 kcal/mol, is 143. Reference 35 reports a smaller energy difference, 1.9 kcal/mol, between these forms. However, unless additional conformers are included, the ratio p(gg)/p(gtg) is calculated to be 17, a value approximately 7.5 times that observed. Clearly, models that are based on the existence of only these two conformers are unrealistic.

2. Multiconformer Representation of the Liquid. We have considered four different sets of conformers of c-$C_{16}H_{32}$ as al-

Table VII. Lowest Energy DL and EM-D Conformers of c-$C_{16}H_{32}$

						concentration,[d] %					
						T = 300 K			T = 350 K		
	conformer type[a]	conformation[b]	rel wt	ΔE,[c] kcal/mol		DL	EM-D	DL+EM-D	DL	EM-D	DL+EM-D
1	DL+EM-D	ggttg′g′ttggttg′g′tt or [4444]	1	0		56	48	35	41	38	22
2	DL	ggtggtttggg′ttg′tt	8	2.0		15		10	18		10
3	DL	ggttg′g′tg′ttg′gttgt	4	2.0		8		5	9		5
4	DL	gggtgttg′gttgtggt	8	2.5		7		4	9		5
5	DL	gg′g′tgtggtggttg′tt	8	2.5		7		4	9		5
6[e]	EM-D	ggtggtttggtggttt or [3535]	2	0.75			28	20		26	15
7	EM-D	ggtggttg′g′ttggttt or [3445]	8	2.00			13	10		17	10
8	EM-D	ggtggttg′g′tttg′g′tt or [3454]	4	2.12			6	4		7	4
9	EM-D	ggg′g′tttg′g′ttggttt or [2545]	4	2.25			4	3		6	3
					$\sum$ =	92	99	94	86	94	79

[a] DL = diamond lattice (ref 25). EM-D = energy minimized (ref 22). [b] In the DL set, t, g, and g′ refer to dihedral angles 180°, 60°, and −60°. In the EM-D set, there are significant variations around these values. [c] Energies of the EM-D forms reported in ref 22 have been reduced by a factor of $^5/_8$. See text. [d] The calculated concentrations are based on larger sets of conformers than those listed here. See text. [e] Conformer **6** drawn on a diamond lattice has an end-to-end distance of 2.31 in units of bond length. Similarly, conformers **7**–**9** all have end-to-end distances of 1.61 in the same units.

Table VIII. The 11 Lowest Energy EM–S Conformers of c-$C_{16}H_{32}$[a]

	conformer[b]	rel wt	E,[c] kcal/mol	conc, % 300 K	conc, % 350 K
1	ggttg′g′ttggttg′g′tt [4444]	1	0	62.1	46.6
2	ggtggttg′g′tttg′g′tt [3454]	4	2.09	7.4	9.2
3	gttg′g′ttggtggtttg	8	2.38	9.2	12.2
4	gtggttgtggttg′ttg	8	2.39	9.0	12.0
5	g′g′ttggttg′gttg′gtt	4	2.95	1.2	2.7
6	g′ggtttggtgggtgtt	8	3.1	2.7	4.3
7	gtttggg′ttg′tg′g′ttg	8	3.1	2.6	4.2
8	ggtg′tg′g′ttggtggtg	8	3.30	2.0	3.2
9	ggtggtttggtggttt [3535]	2	3.41	0.4	0.7
10	tg′g′ttggttg′ttgg′tt	8	3.47	1.5	2.5
11	ggtgggtggtgtg′g′tt	8	3.48	1.4	2.5

[a] The conformation and the relative strain energies were computed by Saunders.[26,27] [b] The dihedral angles associated with t, g, and g′ vary significantly from 180, 60, and −60°. [c] Reference 28.

ternative bases for computing the conformational statistics of the liquid. These consist of the following: (a) the 9 lowest energy EM-D conformers of the total of 12 found by Dale;[22] (b) all DL conformers reported in ref 25; (c) a combination of the above EM-D and DL sets; and (d) the 11 EM-S conformers found by Saunders.[27,28]

The five lowest energy conformers of sets a and b above are described in Table VII; those of set d are described in Table VIII. As noted in section III.B, the energies associated with the DL conformers are based on the generally accepted values of E_g and E_{gg}, which are used in the rotational isomeric state model. The strain energies used here for the EM-D rings have been reduced from Dale's values as indicated earlier. The method employed to derive the EM-S set is briefly described in section III.B.

The lowest energy conformer in all sets is the [4444] form. Its calculated concentration at 350 K assumes values ranging from 47% for the EM-S set to 22% for the combined EM-D+DL set. This range of values is in keeping with our spectroscopic finding that the liquid does not consist primarily of the [4444] conformer. However, the calculated values are significantly higher than the experimentally determined upper limit of 15%.

The calculated and observed values of the relative probabilities of conformational sequences in the liquid phase are found to agree within a factor of about 2, and in a few cases the agreement is significantly better. The values are listed in Table IX for the four sets.

A disturbing measure of our present understanding is found in the fact that there is little correspondence between the various sets of conformers that have been derived for c-$C_{16}H_{32}$. Excluding the [4444] conformer, which is for all sets the lowest energy form, we find in comparing the 9 EM-D+DL conformers with the 11 EM-S conformers (listed in Tables VII and VIII) that there are only two conformers, [3535] and [3454], that are common to both sets. Even then, their energies relative to those of the other conformers in each set are quite different. The [3535] conformer has the second lowest strain energy in the EM-D set but ranks among the highest in the EM-S list. The reverse is true for the [3454] conformer.

A similar situation has already been noted for c-$C_{14}H_{28}$.

3. The High-Temperature Phase. The experimentally measured values of the probability ratios of pairs of short conformer sequences are found to be similar for the HT and liquid phases (Tables VI and IX). In one case, there is a marked difference between the two phases. This is in the value of the $p(gg)/p(tt)$ ratio, which is significantly larger for the HT phase than for the liquid. The higher value for the HT phase may reflect a higher concentration of the [4444] conformer in this phase.

There is a puzzling temperature effect associated with the HT phase that is manifest in the temperature dependence of the observed ratios $p(gt)/p(tt)$ and $p(gg)/p(tt)$, or equivalently, in the intensity ratios used to determine them. Both of these ratios (Table VI) initially increase with increasing temperature but then decrease as the melting point is approached. The magnitude of the changes and the reversal in their sign are remarkable. We have no explanation for this phenomenon. However, we note that for the HT crystalline phase of the *n*-alkanes there is also an anomalously large temperature dependent phenomenon. This is associated with intrinsic infrared intensities and is intimately related to the high coefficient of thermal expansion of the HT-phase unit cell.[36] This suggests that the HT-phase cycloalkane behavior may also be occurring in conjunction with a large thermal expansion of the unit cell.

Table IX. Calculated and Observed Conformational Statistics for c-$C_{16}H_{32}$

	set[a]	no. of con-formers	concn of [4444], %	p(gt)/p(tt)	p(gg)/p(tt)	p(gg)/p(gtg)
calcd (350 K)	EM-D	5	38	1.9	1.0	4.6
	DL	5	41	2.3	0.86	3.0
	EM-D+DL	9	22	2.2	1.0	3.1
	EM-S	11	47	2.2	1.0	5.3
obsd	Liq (343 K)		<15	4.6	0.5	2.9
	HT (275 K)		<15	3.9	0.8	2.4
	HT (325 K)		<15	3.8	0.8	2.4

[a] The conformers in the EM-D and DL sets are listed in Table VII and those for EM-S in Table VIII.

VI. Cyclodocosane

A. Background. Cyclodocosane is the largest and most complex cycloalkane considered here. We are unaware of any earlier studies on c-$C_{22}H_{44}$. However, the phase behavior of c-$C_{24}H_{48}$, which has been investigated by Grossmann[7-9] and Moller[10,37,38] and their collaborators, is quite similar to that of c-$C_{22}H_{44}$.

From an infrared analysis,[32] we have shown that c-$C_{22}H_{44}$ in the LT solid has the rectangular DL [3838] conformation analogous to the [3434] conformer c-$C_{14}H_{28}$ depicted in Figure 1. An X-ray determination of the structure of c-$C_{22}H_{44}$ has apparently not yet been carried out. However, X-ray structures have been determined for c-$C_{24}H_{48}$ and c-$C_{26}H_{52}$,[39] and the ring conformations are found to be rectangular.

The ordered LT crystalline phase of c-$C_{22}H_{44}$ is transformed at 298 K into the disordered HT crystalline phase, which in turn becomes a liquid at 325 K. These transition temperatures are similar to those for c-$C_{24}H_{48}$, which are respectively 299 and 320 K.[37]

We have confirmed the crystalline nature of the HT phase of c-$C_{22}H_{44}$ from X-ray diffraction and optical measurements. The X-ray powder pattern of the HT solid shows a reflection pattern characteristic of a crystalline material, albeit the lines tend to be diffuse. The pattern is similar to that obtained by Grossman et al.[8] for c-$C_{24}H_{48}$. Further evidence of crystallinity is the birefringence of thin films of the HT phase of c-$C_{22}H_{44}$ which was observed with a polarizing microscope.

B. Vibrational Spectra. 1. Infrared Spectra of c-$C_{22}H_{44}$. Figure 6 shows infrared spectra of the LT and HT crystalline phases and of the liquid. The solid phases were measured 1 K below and 1 K above the solid–solid phase transition, and the liquid phase was measured 3 K above the melting temperature. The spectrum of the HT solid is essentially devoid of all the detail observed in the LT spectrum. The spectrum of the liquid is very similar to that of the HT solid except that the bands of the liquid are broader.

We were unable to observe any evidence of dichroism in the infrared spectrum of the HT phase, although the film measured was known to be preferentially oriented. The situation contrasts with that for the LT phase of c-$C_{22}H_{44}$, where large dichroic effects can be observed.[32] The HT phase is therefore essentially isotropic insofar as infrared transition moments are concerned.

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(36) Snyder, R. G.; Maroncelli, M.; Strauss, H. L.; Hallmark, V. M. *J. Phys. Chem.* **1986**, *90*, 5623–5630.

(37) Kruger, J. K.; Albers, J.; Moller, M.; Cantow, H.-J. *Polym. Bull.* **1981**, *5*, 131.

(38) Moller, M.; Cantow, H.-J.; Kruger, J. K.; Hocker, H. *Polym. Bull.* **1981**, *5*, 125.

(39) Groth, P. *Acta Chem. Scand., Part A* **1979**, *33*, 199.

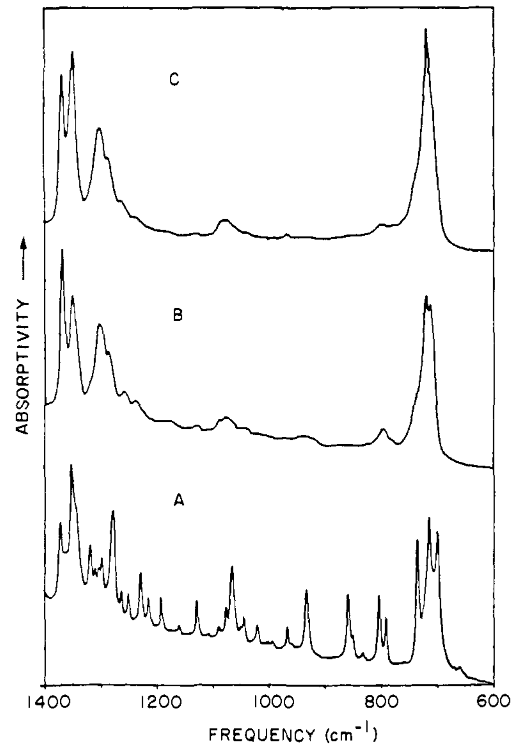

Figure 6. Infrared spectra of c-$C_{22}H_{44}$: (A) low-temperature crystalline phase (297 K); (B) high-temperature crystalline phase (299 K); (C) liquid (333 K).

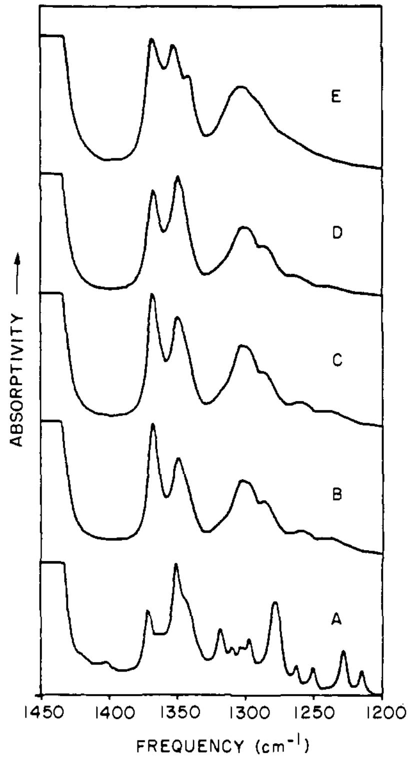

Figure 7. Infrared spectra of c-$C_{22}H_{44}$ and *n*-$CD_3(CH_2)_{20}CD_3$ in the methylene wagging-mode region. Spectra of c-$C_{22}H_{44}$: (A) low-temperature crystalline phase (297 K); (B) high-temperature crystalline phase (299 K); (C) high-temperature crystalline phase (322 K); (D) liquid (333 K); (E) liquid phase (333 K) of *n*-$CD_3(CH_2)_{20}CD_3$.

Figure 7 shows the methylene wagging region of the spectrum of the LT and HT phases and of the liquid. For comparison, the methylene wagging region of the spectrum of the *n*-alkane *n*-$CD_3(CH_2)_{20}CD_3$ in the liquid phase at 333 K has been included.

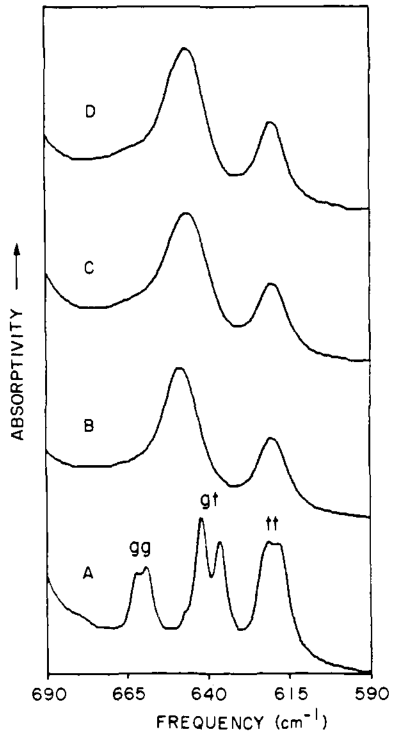

Figure 8. Infrared spectra of cyclodocosane-*1,1*-d_2 in the CD_2 rocking-mode region: (A) low-temperature crystalline phase (297 K); (B) high-temperature crystalline phase (302 K); (C) liquid phase (333 K); (D) dissolved in *n*-hexane (295 K).

2. Infrared Spectra of Cyclodocosane-*1,1*-d_2. The relative intensities of the CD_2 rocking-mode bands of the cyclodocosane ring containing a single CD_2 group were measured in order to estimate the relative concentrations of tt, gt, and gg pairs. The relevant region of the infrared spectrum is shown in Figure 8 for both crystalline phases, the liquid, and an *n*-hexane solution.

The tt, gt, and gg bands appear as doublets in the spectrum of the LT phase. We have found that this phase may have one or the other of two kinds of infrared spectra. One of these is the spectrum shown in Figure 8. The other kind of spectrum shows the tt, gt, and gg bands as single bands. Presumably the two spectra are associated with two different crystal forms of cyclodocosane. We speculate that one form involves [3838] rings that are exactly rectangular so that the four corners are equivalent and that the other form involves rings that are slightly distorted rectangles, that is, parallelograms, so that there are two pairs of equivalent corners. The latter crystal form would give rise to band doubling. This possibility is discussed further in ref 32.

As before, the changes in this spectral region are greatest in going from the LT phase to the HT phase. In the HT phase, the gg and gt bands observed for the LT phase have merged into one band. Further changes in the spectrum in going to the liquid phase are relatively small. The gt+gg band undergoes a small downward shift in frequency (~2 cm^{-1}) and some increased broadening. There is very little difference between the spectrum of the liquid and that of the solution.

There are significant differences between the spectra of cyclohexadecane-*1,1*-d_2 and cyclodocosane-*1,1*-d_2 in the widths of the CD_2 bands. The half-widths of the CD_2 bands for these cycloalkanes in their HT solid and liquid states are given in Table X. For comparison, this table also includes the CD_2-band half-widths for two *n*-alkanes in the liquid state that have CD_2 groups at the middle of their chains. The *n*-alkanes are *n*-heneicosane-*11,11*-d_2 and *n*-pentatriacontane-*18,18*-d_2.

The width of the gt band is always greater than that of the tt band. It has been shown elsewhere that this is primarily due to the greater sensitivity of the frequency of the gt rocking mode to variations in the CCCC dihedral angles associated with the CC bonds adjoining the CD_2 group.[15]

In general, the widths of the CD_2 bands associated with the HT phase of cycloalkanes are somewhat smaller than those for

Table X. The Observed Widths (fwhh in cm^{-1}) of the CD_2 Rocking Mode Bands in the Infrared Spectra of c-C_{16} and c-C_{22} in the HT and Liquid Phases and of n-C_{21} and n-C_{35} in the Liquid Phase[a]

	cycloalkanes				n-alkanes	
	C_{16}		C_{22}		C_{21}	C_{35}
	HT (303 K)	Liq (343 K)	HT (302 K)	Liq (333 K)	Liq (318 K)	Liq (352 K)
tt	7.5	8.8	9.9	10.0	9	9
gt	11.9	12.2	13.9	15.0	14.5	13.5

[a] For the n-alkanes, the CD_2 group is in the middle of the chain. (The resolution used in the measurements was 1 cm^{-1}.)

Table XI. Measured Values of Some Second-Order Probability Ratios Evaluated from the CD_2 Rocking Mode Intensities of Cyclodocosane-*1,1*-d_2

		ratios		
phase	temp, K	p(gt+gg)/p(tt)[a]	p(gt)/p(tt)[c]	p(gg)/p(tt)[c]
LT	297	(1.20)[b]		
HT	302	2.35	2.2	0.14
	322	2.49		
melt	333	2.94	2.4	0.5
soln[d]	296	2.76	2.3	0.5

[a] Estimated errors of about ±0.05 are based on the estimated errors in the curve fitting. [b] This value, which is appropriate to the [3838] conformer, was assumed in order to evaluate A_r in eq 2. See section III.A.2. [c] Estimated error ±0.1. [d] In n-hexane.

the liquid phase, an observation that is consistent with the HT phase being less fluid than the liquid and being comprised of a narrower distribution of conformers. We note also that the widths associated with c-C_{16} are smaller than those of c-C_{22} and the n-alkanes, an observation that is consistent with the more severe constraints inherent to c-C_{16} rings relative to those for c-C_{22} rings and open chains.

The relative intensities of the bands at 622 and 649 (or 647) cm^{-1} were used to obtain the ratio p(tg+gg)/p(tt). The values are listed in Table XI. The gg band, which is found near 660 cm^{-1}, was separated from the gt+gg band with the use of curve-fitting procedures. The ratios p(gg)/p(tt) and p(gt)/p(tt) are included in Table XI, although their accuracy is significantly less than that of the other ratios listed.

3. Raman Spectra of c-$C_{22}H_{44}$. The low-frequency region of these spectra is shown in Figure 9. No information on polarization was obtained from these spectra for the following reason. Although the sample of the HT solid appeared clear except for some weak striations, the polarization of the exciting radiation proved to be scrambled by the sample, so that it was not possible to make polarization measurements for this phase. Therefore, to facilitate comparison of the spectra of the HT and liquid phase, no polarization analyzer was used in either case.

In general, the differences between the Raman spectra of the various phases tend to mirror those found in the infrared spectra. Thus, the Raman spectrum of the HT solid differs from that of the LT solid in being much more diffuse; the Raman spectrum of the liquid is similar to, but more diffuse than, that of the HT solid. On the other hand, the Raman spectra differ from the infrared spectra in being more sensitive to conformation.

The D-LAM band, which appears at frequencies near 200 cm^{-1}, is of special interest because its frequency is related to the concentration of trans bonds. (See section III.A.3.) The intensity-weighted frequency of the D-LAM band for the HT phase (~315 K) is about 215 cm^{-1} and for the liquid (~340 K) about 230 cm^{-1}. From the relation between p(t) and ν(D-LAM) reported in ref 21, the values of p(t) for the HT and liquid phases are found to be 0.56 and 0.50, respectively.

C. Conformation. 1. The Liquid Phase. c-$C_{22}H_{44}$ is sufficiently flexible and large that it is reasonable to expect that a description of the conformational makeup of the liquid could be based on a set of DL conformers. This proves to be the case. The DL set, which consists of about 2.78 × 10^6 conformers, is described in ref 25. In Table XII are listed some relevant conformational statistics for c-$C_{22}H_{44}$ based on the DL set. The same statistics for an infinite polymethylene chain are also included.[40] A comparison of the closed and open chains shows that even though c-$C_{22}H_{44}$ is a relatively large ring, the effect of the cyclic constraint on its conformational statistics is still significant. We note, however, that, as shown in ref 25, the effect of the cyclic constraint is significant only because the trans and gauche bonds have significantly different statistical weights. Otherwise, the effect of the cyclic constraint would be negligible.

The gross alteration of the vibrational spectrum of c-$C_{22}H_{44}$ in going from the LT crystalline phase to the liquid phase is understandable in terms of the DL set, since this transition changes the [3838] conformer concentration from 100% to a value calculated to be about 1%. There are, in fact, many other conformers in the liquid that are more abundant than the [3838] conformer.[25]

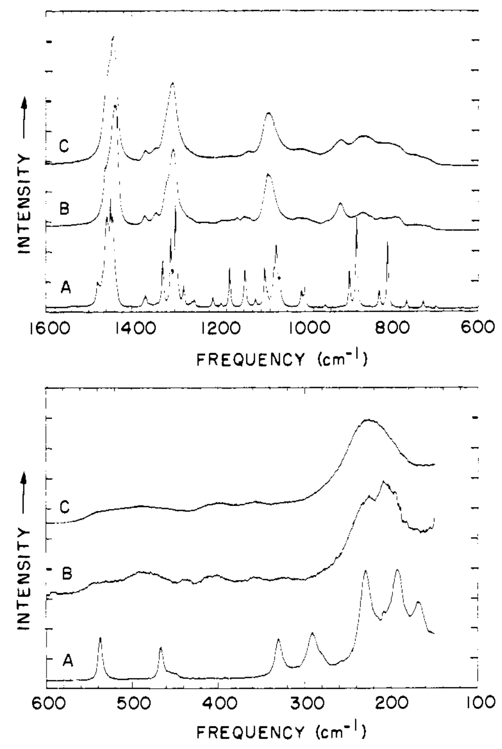

Figure 9. Raman spectra (unpolarized) of c-$C_{22}H_{44}$: (A) low-temperature crystalline phase (~270 K); (B) high-temperature crystalline phase (~310 K); (C) liquid (~340 K).

Table XII. Summary of Calculated and Observed Values of Some Conformational Statistics for Cyclodocosane in Various Phases[e]

	C_∞	c-$C_{22}H_{44}$			
	calcd[a] (300 K)	calcd[b] (300 K)	liq (340 K)	obsd HT (295 K)	LT[c]
p(t)	0.64	0.59	0.50	0.56	0.64
Δn_g[d]				1.3	1.8
p(gt+gg)/p(tt)	1.80	2.40	2.94	2.35	2.67
p(gt)/p(tt)	1.38	1.98	~2.4	~2.2	0.57
p(gg)/p(tt)	0.25	0.43	~0.5	~0.14	0.57
p(gg)/p(gtg+gtg')	0.87	1.26	2.3	1.5	2.0

[a] Based on the rotational isomeric state model with E_g and $E_{gg'}$ equal to 0.5 and 2.0 kcal/mol.[24] [b] Based on the set of DL conformers.[25] [c] Based on the [3838] conformer. [d] Δn_g is the change in the number of gauche bonds. [e] Calculated values for the infinite chain C_∞ are included for comparison.

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[40] Flory, P. J. *Statistical Mechanics of Chain Molecules*; Interscience: New York, 1969; pp 73–80.

The conformational disorder for c-$C_{22}H_{44}$ in the liquid state is comparable to that of the liquid phase of an *n*-alkane of a similar molecular weight. For example, we have observed that the infrared and Raman spectra of liquid c-$C_{22}H_{44}$ are quite similar to the corresponding spectra of $CD_3(CH_2)_{20}CD_3$. This may be seen in part in Figure 7.

Overall, the agreement between the calculated and observed conformational statistics for liquid c-$C_{22}H_{44}$ is better than that found for c-$C_{16}H_{32}$, for which statistics derived from the CD_2-substituted ring are also available. The distribution of conformers calculated for c-$C_{22}H_{44}$ is broad, in keeping with the diffuse character of the infrared and Raman spectra. In addition, there is reasonable agreement between the calculated and observed values of $p(\mathrm{pt}+\mathrm{gg})/p(\mathrm{tt})$ and $p(\mathrm{gg})/p(\mathrm{tt})$ as shown in Table XII.

Some significant discrepancies still remain, however. The value of the first-order probability $p(\mathrm{t})$ for c-C_{22} in the LT solid is 0.64 since each ring has eight gauche bonds. The observed and calculated values of $p(\mathrm{t})$ for the liquid are significantly different, being 0.50 and 0.59, respectively. These values correspond to 11 gauche-bonds/ring (determined experimentally) and 9 gauche-bonds/ring (calculated from the DL set). In the latter case, the 40 K difference between the temperature of the sample and the temperature assumed in the calculation accounts for only about 0.2 gauche bonds of the observed difference of two gauche bonds.

There is also a large discrepancy between the observed and calculated values of the $p(\mathrm{gg})/p(\mathrm{gtg'}+\mathrm{gtg})$ ratio. The value of this ratio for the rings in the LT form is 2.0. That observed for the liquid is about 2.3, a value that is about twice the value calculated for the DL set of conformers. The large difference between the observed and calculated values calls for a comment on the accuracy of the experimental value.

Equation 1, from which the observed value was obtained, assumes that the gtg′ sequence is absent, and, indeed, the DL statistics for c-$C_{22}H_{44}$ show a concentration ratio for gtg:gtg′ of about 4:1. Thus, the relative concentration of gtg′ is still low enough to avoid a serious error. (As an aside, we note that the errors in the calculated values of the higher order probabilities will in general tend to be greater than those for the lower order probabilities.)

To check the possibility that the conformational equilibrium of liquid c-$C_{22}H_{44}$ might be affected by dissolution in an open-chain hydrocarbon solvent, we measured $p(\mathrm{gt}+\mathrm{gg})/p(\mathrm{tt})$ for cyclodocosane-*1,1*-d_2 dissolved in *n*-hexane. Within experimental error, the value of this ratio was found to be essentially the same as that for the neat liquid. The measured values for the solution at 295 K and the neat liquid at 332 K were 2.8 and 2.9, respectively, with the experimental error being about 0.1 (see Table XI).

2. The HT Solid Phase. The degree of conformational disorder in the HT phase of c-$C_{22}H_{44}$ is intermediate between that of the LT and liquid phases. In terms of the number of gauche bonds, we find experimentally that while the HT phase is between the liquid and LT phases, it is closer to the liquid. In going through the LT to HT transition, there is an increase of about 2 gauche bonds per ring, while the HT to liquid transition yields one additional gauche bond. Our spectroscopic results (Table XII) are supported by ^{13}C NMR data indicating that both for c-$C_{24}H_{48}$[38] and for c-$C_{22}H_{44}$,[41] the LT to HT transition is accompanied by an increase of about 2 gauche bonds. Grossmann[8] inferred a similar gauche-bond increase for this transition from his IR measurements on c-$C_{24}H_{48}$, although he did not report an additional increase upon melting.

The placement of the HT phase of c-$C_{22}H_{44}$ nearer the liquid than the LT phase in terms of conformational disorder is qualitatively consistent with other vibrational spectroscopic evidence. For example, the low-frequency Raman spectrum of the HT solid phase is quite similar to that of the liquid, but it differs from the liquid mainly by exhibiting weak broad bands at frequencies that tend to correspond to those of the most intense bands for the LT phase (Figure 9).

VII. Summary

Conformational disorder in the liquid phase and in the high-temperature crystalline phase of c-$C_{14}H_{28}$, c-$C_{16}H_{32}$, and c-$C_{22}H_{44}$ has been studied with the use of infrared and Raman spectroscopy. The spectroscopic measurements have led to estimates of the concentrations of the more stable conformers and estimates of probabilities and probability ratios for the occurrence of a variety of short conformational sequences. The measured values have been compared with various calculated values based on the theoretically derived energy differences between conformers that have been reported in the literature.

For c-$C_{14}H_{28}$, our spectroscopic measurements indicate a distribution of conformers that is much broader than those that follow from most of the earlier energy minimization calculations. For example, the concentration of the lowest energy conformer (the rectangular form) derived from the strain energy calculations of Dale[22] is around 99%, while the value estimated from our measurements is 60 ± 10%.

Recently, however, two new computationally determined sets of c-$C_{14}H_{28}$ conformers have been reported, and these lead to estimates of the concentration of the lowest energy conformer that are in quite good agreement with the observed value. One of the new sets consists of all the diamond lattice conformers, complete sets of which have been derived by Mattice and Snyder for the cycloalkanes $n = 6$ through 22.[25] The second new set of c-$C_{14}H_{28}$ conformers is comprised of energy minimized rings. This set is much larger than that of Dale,[22] which up to now was the largest available. The new set was derived by Saunders[27,28] using a stochastic technique to search conformer space.

The analysis of c-$C_{16}H_{32}$ conformers has so far given somewhat less satisfactory results than that for c-$C_{14}H_{28}$. Earlier energy calculations based on small sets of conformers have indicated that the concentration of the lowest energy, square conformer is high, at least 70% in the liquid at 350 K.[34,35] However, our spectroscopic measurements indicate that the concentration of this conformer in the liquid at 350 K is much smaller, less than 15%.

A number of larger sets of c-$C_{16}H_{32}$ have been explored in an attempt to reduce the discrepancy between the observed and calculated concentrations of the square conformer in the liquid. These sets involve both diamond-lattice and energy-minimized forms and lead to concentrations of the square conformer that range from 47 to 22%. The calculated values are improvements over earlier results, but there is still a serious disagreement with the experimental value. We note that most of the improvement is attributable to the use of sets that are comprised of a greater variety of conformers.

For c-$C_{16}H_{32}$, we have measured, using the isolated-CD_2 technique and certain conformationally characteristic infrared bands, the relative concentrations of short conformational sequences. In this case also, the agreement between the calculated and observed concentrations tends to be mediocre.

It appears that, in order to calculate more accurate conformational statistics, improved force fields are needed. As we have noted, there are very large differences in the calculated values of the strain energies obtained with the use of different force fields. This is clearly manifest for c-$C_{14}H_{28}$ and c-$C_{16}H_{32}$ in the strikingly poor correspondence between the sets of their conformers derived by Dale[22] and the sets derived by Saunders.[27,28]

A second factor of importance is the completeness of the conformer set. The searching method developed by Saunders[26,27] represents a significant advance in this area. For our purposes, the set of 99 c-$C_{14}H_{28}$ conformers that he derived is essentially complete. For c-$C_{16}H_{32}$, Saunders derived a set consisting of 11 conformers, which did not lead to better agreement with experiment than other sets we tried. It remains to be seen whether a larger set of conformers will improve matters for this cycloalkane. However, we think not, since the large difference between the calculated and observed values of the concentration of the lowest energy conformer indicates that the problem is in the force field.

c-$C_{22}H_{44}$ is much more flexible than the smaller rings, and therefore the liquid state of this cycloalkane can be represented to a good first approximation by a set of diamond-lattice con-

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(41) Drotloff, H. Dissertation, Albert-Ludwigs-Universitat Freiburg, 1987.

formers. This set consists of about 2.78×10^6 conformers, the most abundant having a concentration of about 5%.[25] However, the rectangular conformer, which constitutes the low-temperature crystalline phase, is calculated to have a concentration of only about 1% in the liquid at 350 K. The set of diamond-lattice structures accounts for the fact that the spectrum of the liquid shows no evidence of individual conformers. In addition, the values of the probability ratios calculated on the basis of this set are in reasonably good agreement with the values obtained experimentally.

The distribution of conformers in the high-temperature crystalline mesomorphic phase was found to resemble that of the liquid for the three cycloalkanes we investigated. However, relative to the liquid, the distribution in the high-temperature solid appears to favor the lowest energy conformers. The lowest energy form [3434] of c-$C_{14}H_{28}$ can be identified in the infrared spectra of both phases. For this cycloalkane, the high-temperature phase was estimated to contain about 70 ± 10% [3434] in contrast to 60 ± 10% for the liquid phase.

The vibrational spectra of c-$C_{16}H_{32}$ and c-$C_{22}H_{44}$ indicate that the conformer distribution in the high-temperature phase greatly resembles that of the liquid phase. However, there are significant differences between the two phases in the values of the ratios of the concentrations of short conformational sequences.

In the case of c-$C_{22}H_{44}$, the low-temperature, high-temperature, and liquid phases can be characterized in terms of their gauche bond content. The rings in the low-temperature phase each have 8 gauche bonds. The transition to the high-temperature phase results in an average increase of about 2 gauche bonds. The transition to the liquid adds about 1 more gauche bond. In these terms, the high-temperature phase is seen to be very much closer to the liquid than to the low-temperature phase.

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Registry No. c-$C_{16}H_{32}$, 295-65-8; c-$C_{22}H_{44}$, 296-86-6; c-$C_{14}H_{28}$, 295-17-0; cyclohexadecane-*1,1*-d_2, 118655-69-9; cyclodocosane-*1,1*-d_2, 118681-72-4; cyclodocosanone, 59358-81-5; cyclohexadecanone, 2550-52-9.

Spectroscopic Observation and Geometry Assignment of the Minimum Energy Conformations of Methoxy-Substituted Benzenes

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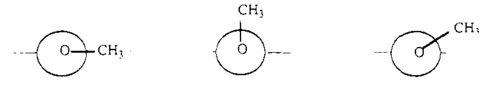
Abstract: Optical spectroscopic data are presented for methoxybenzene, the three methoxytoluenes, 1-ethyl-4-methoxybenzene, and 1,2- and 1,3-dimethoxybenzene cooled and isolated in a supersonic jet expansion. Each unique stable conformation of the sterically unencumbered-methoxybenzenes displays a unique and assignable spectrum; the interpretation of these spectra leads to the assignment of specific molecular geometries for each system. The minimum energy conformation of the methoxy group with respect to the ring is shown to be a planar conformation in which the methoxy group lies in the plane of the ring. The potential barrier for rotation of the ring methyl group in the methoxytoluenes is characterized from observed transitions between methyl group rotational levels which accompany the electronic transition. The meta isomer exhibits a large barrier to methyl rotation in S_1 ($V_3 \sim 520$ cm^{-1}) whereas the methyl group in the ortho and para isomers is nearly freely rotating ($V_3 \leq 50$ cm^{-1}). The dimethoxybenzenes exhibit spectral features due to torsions of the methoxy groups. Substantial barriers to methoxy group rotation ($V_1 = 500$ cm^{-1}, $V_3 = 100$ cm^{-1} for ortho, V_1 and $V_3 \sim 2000$–5000 cm^{-1} for meta) are established; again the torsional barrier appears to be highest for the meta or 3-position on the ring. The presence of cross kinetic and potential terms between methoxy groups is further suggested for the ortho isomer.

I. Introduction

The conformational preference of aromatic methyl ethers is a topic of significant current and fundamental interest.[2-12] While the geometrical differences among various possible conformations of this substituent are large (see Chart I), the experimental de-

Chart I. Possible Conformations of Aromatic Methyl Ethers



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(2) Kruse, L. I.; DeBrosse, C. W.; Kruse, C. H. *J. Am. Chem. Soc.* **1985**, *107*, 5435.

(3) (a) Hummel, W.; Huml, K.; Bürgi, H.-B. *Helv. Chim. Acta* **1988**, *71*, 1291 and references cited therein; (b) Nyburg, S. C.; Faerman, C. H. *J. Mol. Struct.* **1986**, *140*, 347.

(4) Schaefer, T.; Salman, S. R.; Wildman, T. A.; Penner, G. H. *Can. J. Chem.* **1985**, *63*, 782.

(5) Jardon, P. W.; Vickery, E. H.; Pahler, L. F.; Pourahmady, N.; Mains, G. J.; Eisenbraun, E. J. *J. Org. Chem.* **1984**, *49*, 2130.

0002-7863/89/1511-1958$01.50/0