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Polymorphism of Crystalline Cyclooctanone and Cyclononanone[†][‡]

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Abstract—The polymorphism of crystalline cyclooctanone and cyclononanone has been investigated using X-ray diffraction, nuclear magnetic resonance spectroscopy and differential thermal analysis. Both compounds undergo phase transitions below room temperature; the crystalline phases stable at room temperature are highly disordered and are isostructural with corresponding phases of several widely differing compounds, including cyclooctane, cycloheptatriene, β-fluorine and γ-oxygen.

1. Introduction

Molecular solids which undergo one or more crystallographic transformations often exhibit abnormally low entropies of fusion and anomalously high melting points. In the modifications stable just below the melting points the crystals are often of relatively high symmetry, soft and volatile, and are generally referred to as "plastic crystals".[1] At lower temperatures they may undergo one or more solid phase transformations to crystal systems of lower symmetry. In many instances the entropies of these transitions are considerably greater than the corresponding entropies of fusion. Dielectric and specific heat anomalies also characterize these transitions.

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In general, crystals manifest "plastic" behavior if distinguishable molecular orientations in the solid do not differ appreciably in potential energy (i.e., if these differences are small compared to kT). Pauling[2] has shown that the onset of free molecular rotation in the crystals could account for the specific heat anomalies which accompany these transitions. Modifications of this viewpoint have been developed in terms of hindered molecular rotation[3] and of static orientational disorder in the crystal.[4]

The possibility of free molecular rotation in the solid may be checked by comparing the unit cell dimensions of the plastic crystals with the volume requirements of freely rotating molecules.[5] These indicate that free rotation in the solid must be very rare, a view supported by simple considerations of the probable magnitudes of intermolecular forces.

Both cyclooctanone and cyclononanone have abnormally low entropies of fusion[6] and it appeared likely that they are disordered or plastic near their melting points. In this paper we report the results of a study of the crystalline forms of these compounds over a wide range of temperature.

2. Experimental

X-Ray Diffraction

Standard low-temperature X-ray diffraction single-crystal and powder techniques using nickel-filtered CuKα radiation were employed. X-ray powder measurements were made at a number of temperatures to establish ranges of stability of the various phases.

Coefficients of linear thermal expansion for Phase I† were calculated from single-crystal counter data over the temperature range −60° to +25°C (Fig. 1). These single crystals invariably shattered as they were cooled through the transition regions; investigation of the low-temperature phases was therefore restricted to powder photographs.

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† In accordance with the most widely accepted convention, we designate the solid phase formed by cooling from the melt as Phase I; other phases, stable at progressively lower temperatures, are designated as Phase II, Phase III, etc.

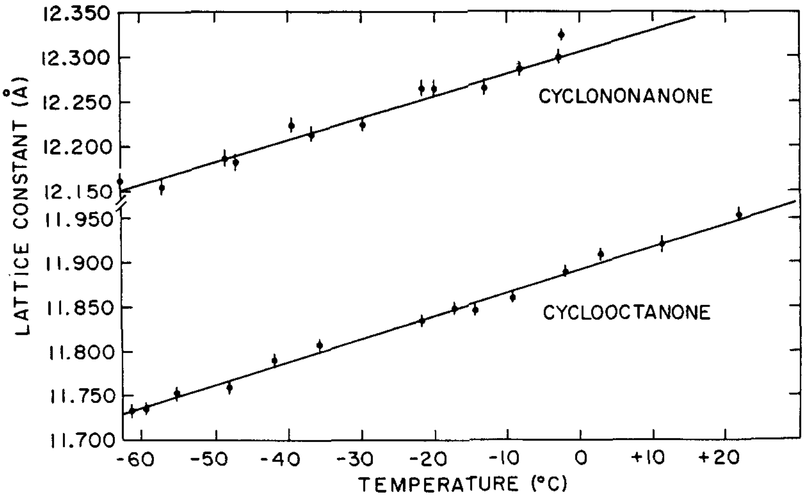

Figure 1. Linear thermal expansion of cyclooctanone and cyclononanone.

NUCLEAR MAGNETIC RESONANCE (N.M.R.)

The n.m.r. spectrum of cyclooctanone† was investigated over the temperature range −120° to +25°C (Fig. 2). Measurements of the first derivative curve were made on a Varian V-4502 EPR Spectrometer equipped with a V-4201 RF NMR Conversion Unit. The sweep time was calibrated with the proton field meter by measuring the frequency at two fields.

The sample was sealed under vacuum and was cooled by blowing cold gas across it; temperatures were measured with a thermocouple placed adjacent to the sample.

DIFFERENTIAL THERMAL ANALYSIS (DTA)

A 32.5 mg sample of cyclooctanone was examined over the temperature range −125° to +100°C, using a duPont 900 Differential Thermal Analyzer with cooling jacket. Two exothermic and

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† Cyclooctanone is more readily available than cyclononanone. For this reason our investigation of cyclononanone was confined to the X-ray study which showed that it is isostructural with cyclooctanone. Both compounds were obtained from K and K Laboratories, Inc. Plainview, New York 11803 and were used without any further purification.

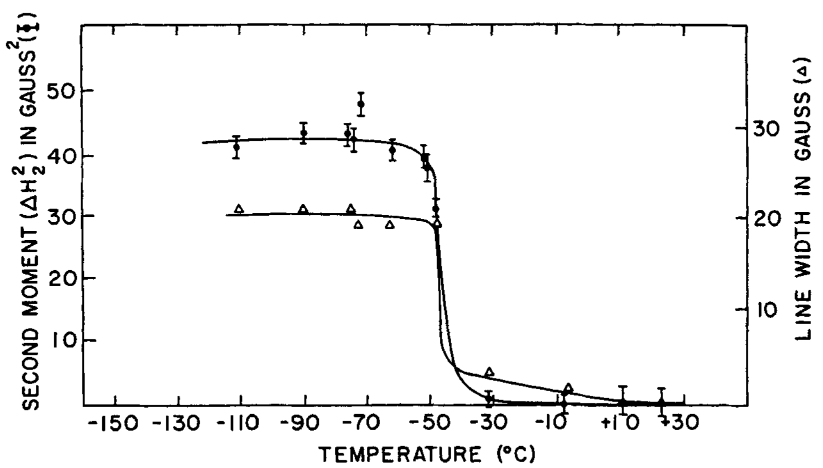

Figure 2. Second moment and line width of cyclooctanone.

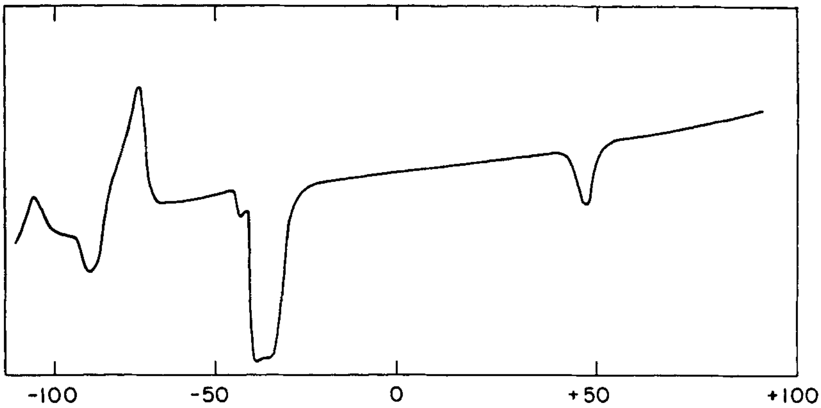

Figure 3. DTA thermogram of cyclooctanone.

three endothermic peaks were observed at temperatures below the melting point (Fig. 3). Similar results were obtained using a Perkin-Elmer Differential Scanning Calorimeter (DSC-1B).

3. Results

The X-ray, n.m.r. and DTA results all indicate that cyclooctanone forms three distinct crystalline phases in the temperature range investigated: Phase I is stable between the melting point and $-42 \pm 2°C$, Phase II between -42 and $-90 \pm 2°C$ and Phase III is stable below $-90°C$. Some difficulty was encountered in establishing the range of stability of Phase I. No transition was observed when the high-temperature modification was cooled until temperatures between $-90°$ and $-105°C$ were reached at which point it transformed directly to Phase III. When the specimen was warmed to a temperature above $-90°C$ it transformed to Phase II which is stable up to $-42°C$. The DTA thermogram (Fig. 3) reveals that the transition from Phase III to Phase II is accompanied by a large exothermic peak indicating extensive recrystallization.

It was noted also that Phase I can be retained even below $-105°C$ if cooled with sufficient speed.

X-RAY DIFFRACTION MEASUREMENTS

Crystal data are listed in Table 1; powder data in Tables 2 and 3. The high-temperature modifications of both compounds are cubic with 8 molecules per unit cell. Reflections of type *hhl* with *l* odd were not detected, indicating that the space group is either Pm3n or P$\bar{4}$3n. The former is centrosymmetric; the latter refers to an acentric cell. The absence of a positive piezoelectric effect when single crystals were investigated at 25°C indicated that Pm3n is the most probable space group.

The point symmetry of molecules in the eight-fold positions of Pm3n is 32. Neither cyclooctanone or cyclononanone possesses intrinsic molecular symmetry of this type. It is therefore evident that the effective point symmetries of the molecules must be enhanced by substantial disorder in Phase I. The very rapid decrease of diffraction intensities with increasing Bragg angles lends support to these assumptions.

It was not possible to carry out a meaningful analysis of the X-ray powder data of Phase II because of the difficulties mentioned above.

Table 1 Crystal Data: Cyclooctanone and Cyclononanone

	Cyclooctanone	Cyclononanone	
Formula	$C_8H_{14}O$	$C_9H_{16}O$	
Melting point (°C)	42	28	
Entropy of melting (eu)[a]	2.0	1.5	
Data obtained at:	25°C	−105°C	15°C
Phase	I	III	I
Crystal system	Cubic	Monoclinic	Cubic
Lattice constants (Å)	11.97 ± 0.02	$a = 11.37$, $b = 11.61$, $c = 11.69$, $\beta = 95.10°$	12.33 ± 0.05
Space group	Pm3n	—	Pm3n
Molecules/unit cell	8	8	8
Volume/molecule ($Å^3$)	214	192	234
Density (X-ray) (g/cc)	0.979	1.091	0.995
Coefficient of linear thermal expansion (−60 to +25°C)	$2.18 \pm 0.02 \times 10^{-4}$		$1.94 \pm 0.02 \times 10^{-4}$

[a] From Ref. 6.

TABLE 2 Powder Diffraction Measurements: Cyclooctanone and Cyclononanone, Phase I

		$d_{(hkl)}$ (in Å)	
Relative intensity	*hkl*	Cyclooctanone (25°C)	Cyclononanone (−47°C)
75	200	6.0	6.1
100	210	5.4	5.5
90	211	4.9	5.0
20	220	4.23	4.33
10	310	3.79	3.86
5	222	3.45	3.51
20	320	3.31	3.40
40	321	3.20	3.27
30	400	2.99	3.05
20	410	2.90	2.96
10	411 330	2.82	—
10	420	2.67	2.73
15	421	2.61	2.67
10	332	2.55	—
5	520	2.22	—

We were able to index the diffraction pattern of Phase III on the basis of a monoclinic unit cell with marked dimensional similarity to the cubic unit cell of Phase I (Table 3).

N.M.R. DATA

A sharp decrease in the line width and second moment of cyclooctanone was observed when the temperature was raised above −48 ± 5°C (Fig. 2). The extremely small second moment and the very narrow line width are characteristic of plastic crystals[7] and indicate extensive molecular motion in this temperature region.

Between −48° and −90°C a single broad peak was observed. Below −90°C the line pattern exhibits a splitting characteristic of molecules containing rigid methylene groups.[8] The temperature at which splitting is observed corresponds to that of the crystallographic Phase II–III transition. The analysis of the line shape

TABLE 3 Powder Data Cyclooctanone, Phase III (at −105°C)

d	Relative intensity	hkl	($1/d^2 \times 10^4$) obs.	($1/d^2 \times 10^4$) calc.
8.50	M	$10\bar{1}$	138	138
7.77	W	101	166	165
5.82	S	020 002	294	297 295
5.19	VS	021 012 120	372	371 369 375
4.78	W	$21\bar{1}$ $12\bar{1}$	437	433 435
4.55	VS	211	482	487
4.23	M	$20\bar{2}$	559	553
3.88	W	030 202 003	664	668 661 664
3.66	W	031 130	746	742 746
3.34	M	$20\bar{3}$ 311	894	895 891
3.15	S	$13\bar{2}$	1010	1014
3.08	M	203	1053	1057
2.99	M	321	1120	1114
2.90	M+	040 $22\bar{3}$	1189	1187 1192
2.76	W	104 $31\bar{3}$	1315	1313 1318
2.69	W	$20\bar{4}$ 322 401	1380	1385 1375 1376
2.60	M	331 042	1485	1485 1482
2.36	M−	$31\bar{4}$	1791	1795

shows that the peak-to-peak distance corresponds to $\Delta H = 7.05$ G (H is the field strength in gauss, G). The hydrogen-to-hydrogen distance in the methylene group was calculated using the expression

$$\Delta H = \frac{3}{2} g\beta \frac{1}{r_{12}^3}$$

where r_{12} is the hydrogen-to-hydrogen distance, g is the gyromagnetic ratio, β is the nuclear magneton and $(3/2)g\beta$ equals 42.31. The calculated value of r_{12} is 1.82 Å which compares favorably with the 1.78 Å H–H distance calculated on the basis of a C–H distance of 1.09 Å and a H–C–H angle of 109.5°.

DTA MEASUREMENTS

The endothermic minima (Fig. 3) are consistent with the information obtained from X-ray diffraction and n.m.r. studies. The entropies of the two transitions were obtained by comparing the areas of the corresponding endotherms with that of the fusion endotherm. Using the reported entropy of fusion of 2.0 e.u.,[6] we found $\Delta S_{\text{I-II}} = 17$ e.u. and $\Delta S_{\text{II-III}} = 4$ e.u.

The significance of the two large exothermic peaks is not completely understood; similar phenomena have been attributed to pre-transition effects such as recrystallization[9] or nucleation of a new phase.[10, 11]

4. Discussion

It is possible to estimate the approximate size and shape of cyclooctanone from known interatomic distances and angles. These indicate that the smallest possible diameter which can reasonably be assigned to the pseudospherical molecule is 8.0 Å. The volume requirements of freely rotating molecules of this size exceed by far the 214 Å^3/molecule available in the cubic unit cell and appear to rule out the possibility of free, uncoupled molecular rotation in the solid.

A surprisingly large number of molecules of widely different shapes and composition have been reported to crystallize in the cubic space group Pm3n, all with eight molecules per unit cell and with evidence of considerable disorder in the crystal. These include in addition to cyclooctanone and cyclononanone, cyclooctane,[12] cycloheptatriene,[13] γ-O_2[14] and β-F_2[14, 15] (Fig. 4). It appears likely that additional members of this group will be uncovered as more X-ray studies are carried out. It is difficult at this stage to

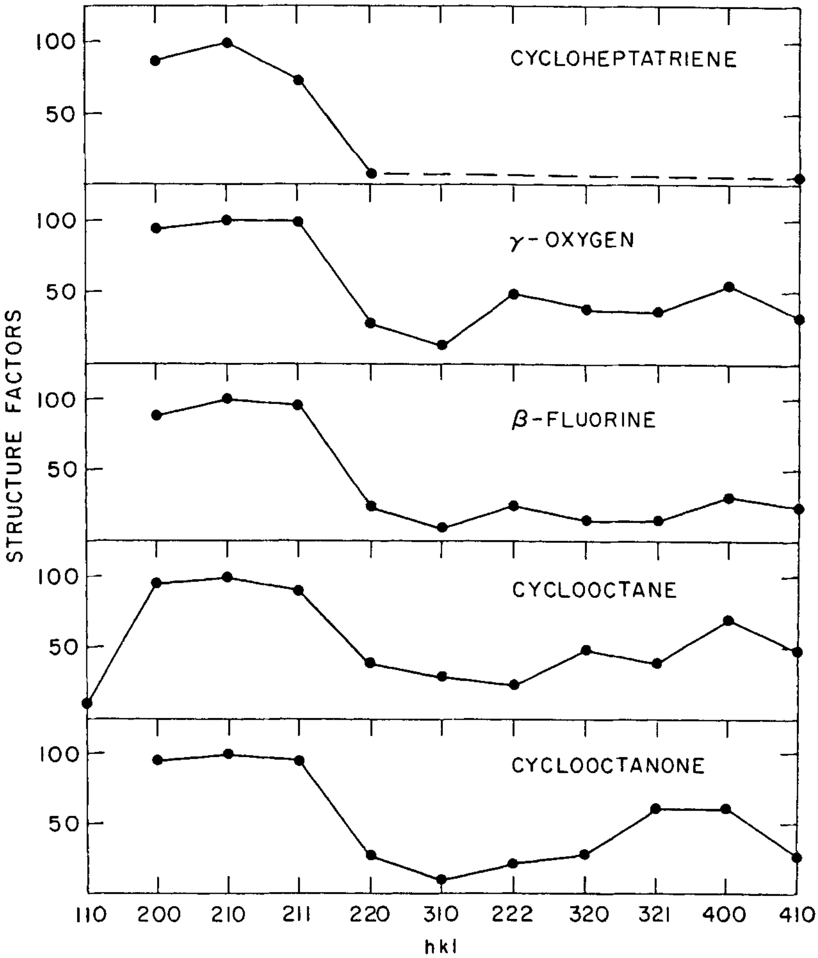

Figure 4. Comparison of the magnitudes of the observed structure factors of isostructural disordered phases (normalized on the basis of $F_{210} = 100$).

establish reasons for the stability of this structure in these disordered phases. Sands and Day[12] assumed that six of the eight molecules per unit cell of cyclooctane are present in cylindrically disordered form in one set of six-fold positions and the other two molecules are spherically disordered in two-fold positions.

Calculations of structure factors for cyclooctanone based on this model yielded physically unreasonable temperature factors (e.g. 80 Å^2) and relatively poor agreement with observed data.

A detailed analysis of the molecular disorder of β-F_2 has been published by Jordan, Streib and Lipscomb.[15] Least-squares analysis of a number of disordered models were carried out; the best fit was obtained with two spherically disordered molecules at 0,0,0 and $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ and six cylindrically disordered molecules statistically arranged in the general 48-fold positions of space group Pm3n. The temperature factors varied from 6 to 14 Å^2.

There seems to be little point to efforts to establish details of the structural arrangement in these disordered phases, when relatively large molecules are involved, on the basis of the X-ray data alone. The number of observed reflections is unavoidably small and, with sufficient ingenuity, it is always possible to postulate models which will result in fair agreement between observed and calculated data. Unfortunately the number of variable parameters is then dangerously close to, or may even exceed, the number of available experimental measurements.

The importance of supplementing X-ray techniques by other methods in the investigation of plastic crystals is illustrated by our difficulties in establishing the low-temperature border of Phase I of cyclooctanone (at −42°C). Both the X-ray and n.m.r. results indicated extensive molecular reorientation in Phase I. However, at lower temperatures the effects of supercooling led to ambiguities in the interpretation of the X-ray data. The n.m.r. measurements, which were satisfactorily reversible and reproducible throughout the temperature range investigated, indicated clearly that the molecules cease to undergo rapid reorientation below −42°C although extensive motion of the methylene hydrogen atoms persists down to −90°C.

The broadening of the n.m.r. line below −42°C could not, by itself, be taken as unambiguous evidence of a phase transition. In neopentane n.m.r. line broadening occurs 65° above the transition temperature.[16–18] However, the observation of broadening of the n.m.r. line below −42°C did lead us to investigate this temperature region more closely by DTA methods. The DTA findings indicated clearly that the crystalline phase which was stable between −42 and −90°C could only be formed by warming Phase III. Subsequent X-ray diffraction studies verified the existence of this phase.†

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† Burer and Gunthard[19] reported that an investigation of the infrared spectra down to −180°C showed no phase transition for cyclooctanone but did show a transition for cyclononanone at −30°. The reasons for the discrepancies between their results and ours are not clear. One possible explanation is that their rate of cooling was too rapid to allow the formation of the low-temperature forms of cyclooctanone.

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