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Cohesive Energies in Polar Organic Liquids. 3. Cyclic Ketones

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Densities and vapor pressures over a range of temperatures have been measured for several cyclic alkanes and ketones. The former have been fitted to power series; the latter, to Antoine and Cox equations. Overall averages for $\Delta p/p$ are 3 \times 10⁻⁴ and 2 \times 10⁻⁴, respectively, for the vapor pressure equations. Evaluation of the contributions of orientation, induction, and dispersion energies to total cohesion leads to results similar to those for the linear 2ketones. The dipole in the cyclic ketones from C₄ through C7 is more effective in attractive interactions than that in the 2-ketones. However, in C₈, C₁₁, and C₁₂ rings, the dipole loses increasing amounts of effectiveness in attracting its neighbors, and the last one behaves as though 75% of its "polarity" has disappeared. A temperature change of 40° has very little effect on the polar interactions In the cyclic ketones.

Previous papers in this series (11, 12) have produced estimates of the contributions of orientation (dipole-dipole), induction (dipole-induced dipole), and dispersion (nonpolar) attractive energies to total cohesion in liquid n-alkyl nitriles, 2ketones, and 1-chloroalkanes. In order to investigate the role of molecular geometry in determining these energies, we have applied our method to cyclic alkanes from C₅ to C₁₂ and cyclic ketones from C₄ to C₁₂. In effect, we have repeated the work on the 2-ketones (12) after tying the ends of the molecules together. For an explanation of the method, the earlier papers should be consulted (11, 12).

Experimental Section

Vapor pressures were measured for the C₈, C₁₀, and C₁₂ cyclic alkanes and the C_4 , C_5 , C_7 , C_8 , C_{11} , and C_{12} cyclic ketones with the comparative ebulliometric apparatus already described (10). For cycloheptane the same boiler was used, but pressures were read on a thermostated mercury manometer; for the C10 alkane and both of the C12 compounds, data were extended below the accessible range of the comparative technique using a DC 704 oil manometer (11).

Density and thermal expansion data were obtained for the C7, C₈, C₁₀, and C₁₂ cyclic alkanes, and for the C₄, C₇, C₈, C₁₁, and C_{12} cyclic ketones using the dilatometer already described (19).

The compounds were obtained from Chemical Samples Company, except for the C₁₁ ketone, which was made from the C_{12} ketone following the method of Garbisch (5), and the C_{10} alkane, which was obtained from Pfaltz and Bauer. Compounds which were not at least 99.9% pure by gas chromatography were distilled to this minimum purity (by GLC) on a spinning band column, except the C₄ ketone, which was 99.0% pure. The single impurity had a retention time of 0.055 relative to the main peak on a DEGS column at 75 °C.

Results

The vapor pressure data were fitted to both Antoine (for convenient usage within the range of data) and Cox (for more reliable extrapolation to lower temperatures) equations (10). The constants with their standard deviations are presented in Tables I and II; the data upon which they are based are in Table III. The temperature of the water equilibrium (t_w) is included for those data obtained by comparative ebulliometry.

In order to increase the reliability of vaporization enthalpies calculated at temperatures below the range of the present data, the combined oil manometer and comparative ebulliometric data were fitted to the same Cox equation. Weighting of the comparative data was the same as previously described (10), with the standard deviation in temperature taken as 0.001 K. The manometer data were assigned equal weights, with the standard deviation in pressure taken as 0.0003 cmHg. Results of the initial data fitting showed a small systematic discrepancy between the two sets of data. Subsequent analysis of the procedure used to calibrate the oil manometer against a mercury manometer indicated that the precision of both sets of data was slightly greater than that of the calibration.

Consequently the oil manometer data were adjusted by minimizing the squares of the residuals of the combined data fit with respect to a constant factor, x, which multiplied the measured oil manometer pressures. The values of x obtained for cyclodecane, cyclododecane, and cyclododecanone were 0.9990, 0.9997, and 1.0034. The last figure is least meaningful, since the manometer thermostat was unstable during these measurements, decreasing the precision of the oil data for cyclododecanone (see Tables I and II). For another compound for which similar data were obtained, x = 0.9996. These results imply that our oil manometer calibrations lead to results that are

Compound	Temp range, °C	A	B	C	T _{bp} , K	$10^4 \left(\frac{\Delta \rho}{\rho}\right)_{\rm av}$
Cycloheptane	63-122	5,856830 ± 0,00156	1333.780 ± 0.970	216.6438 ± 0.1124	391.963	1.5
Cyclooctane	100-161	5.861786 ± 0.00183	1438,455 ± 1.249	210.1844 ± 0.1478	424.298	1.1
Cyclodecane (oil)	70–113	5.981257 ± 0.01300	1679.005 ± 7.924	207.5574 ± 0.719		1.2
(ebull.)	131-216	5.879877 ± 0.00090	1613.793 ± 0.674	201.1804 ± 0.0781	475.512	0.9
Cyclododecane						
(oil)	105-148	5.902318 ± 0.01410	1759.266 ± 9.145	193.1014 ± 0.842		3.5
(ebull.)	167-256	5.854541 ± 0.00095	1715.015 ± 0.758	187.5560 ± 0.0878	517.183	2.5
Cyclobutanone	44-107	6.122770 ± 0.00135	1359.414 ± 0.803	222.3942 ± 0.0878	371.982	4.2
Cyclopentanone	66-142	6.069071 ± 0.00103	1450.044 ± 0.660	215.6663 ± 0.0726	403.700	0.7
Cycloheptanone	100-191	6.007327 ± 0.00068	1592.290 ± 0.478	205.4597 ± 0.0528	453.559	1.0
Cyclooctanone	121-211	5.987174 ± 0.00158	1648.08 ± 1.17	199.907 ± 0.131	474.590	3.1
Cycloundecanone	176-227	6.438738 ± 0.00421	2216.96 ± 3.62	229.351 ± 0.352	530.2 <i>b</i>	6.8
Cyclododecanone						
(oil)	135-177	6.331940 ± 0.01608	2145.9 ± 11.9	207.73 ± 1.02		12.5
(ebull.)	185-291	5.987360 ± 0.00067	1898.240 ± 0.572	185.7390 ± 0.0636	549.658	5.5

 $4 \log \rho$ (cmHg) = A - (B/(C + t)). To convert to k Pa, add 0.124903 to A. b Extrapolation beyond range of data.

Table II. Cox Constants^a

Compound	а	$-b \times 10^3$	$c \times 10^{6}$	$ au_{\mathrm{bp}}, \kappa$	$\left(\frac{\Delta\rho}{\rho}\right)_{\rm av}$
Cycloheptane	0.878453 ± 0.00470	0.916539 ± 0.0266	0.965009 ± 0.0376	391.9627 ± 0.00065	1.2
Cyclooctane	0.869777 ± 0.00580	0.775348 ± 0.0295	0.716695 ± 0.0374	424.3005 ± 0.00079	0.8
Cyclodecane					
(oil and ebull.)	0.872681 ± 0.00060	0.685094 ± 0.0030	0.559036 ± 0.0036	475.5157 ± 0.00055	1.1
(ebull.)	0.879382 ± 0.00223	0.715710 ± 0.0103	0.593876 ± 0.0119	475.5166 ± 0.00064	0.7
Cyclododecane					
(oil and ebull.)	0.857472 ± 0.00077	0.520908 ± 0.0035	0.334716 ± 0.0040	517.1828 ± 0.00064	2.2
(ebull.)	0.834753 ± 0.00244	0.422577 ± 0.0104	0.228592 ± 0.0111	517.1777 ± 0.00067	1.6
Cyclobutanone	0.957579 ± 0.00327	1.314504 ± 0.0194	1.607447 ± 0.0287	371.9908 ± 0.00062	2.8
Cyclopentanone	0.852771 ± 0.00222	0.632301 ± 0.0122	0.559267 ± 0.0166	403.6997 ± 0.00062	0.4
Cycloheptanone	0.881515 ± 0.00135	0.704324 ± 0.0067	0.601850 ± 0.0083	453.5605 ± 0.00052	1.0
Cyclooctanone	0.908211 ± 0.00442	0.786187 ± 0.0206	0.672676 ± 0.0240	474.5893 ± 0.00083	3.0
Cycloundecanone	0.072880 ± 0.0145	-2.89769 ± 0.0064	-3.35869 ± 0.0072	531.392 ± 0.026	1.3
Cyclododecanone					
(oil and ebull.)	0.928773 ± 0.00063	0.746605 ± 0.0027	0.565434 ± 0.0028	549.6659 ± 0.00059	8.1
(ebuli.)	0.976283 ± 0.00138	0.938904 ± 0.0056	0.759318 ± 0.0057	549.6748 ± 0.00060	2.5

 $a \log \rho$ (atm) = $A'(1 - (T_{bp}/T))$, where $\log A' = (a + bT + cT^2)$. T_{bp} was treated as a parameter in fitting the data. To convert atm to k Pa, multiply by 101.325.

too high by 0.03-0.1%. The data upon which the relevant constants in Tables I and II are based include adjustment of the oil data by the factor *x*.

The cycloundecanone sample used for vapor pressure measurement decomposed measurably as temperature increased. It is difficult to say at which point the decomposition invalidates an enthalpy of vaporization derived from the data. Successive fits of the data were made, each time excluding the highest temperature, and the magnitude of the residuals as well as their apparent randomness were examined. Inclusion of the seven lowest temperature points yields residuals in line with the other data, but results in an upper temperature about 30° below the boiling point (see Tables I and II).

The density data were fitted to quadratic or cubic equations in temperature; constants are presented in Table IV; original data, in Table V. The dilatometric method used for measuring thermal expansion (19) requires the density of mercury as a function of temperature. For the more precise work herein, the difference in the density of mercury expressed relative to the IPTS-48 or IPTS-68 scale is significant. We adjusted the data of Beattie et al. (7) to the latter scale using quadratic expressions over 40° temperature ranges from 0 to 160 °C for use in this work.

Densities of cyclopentane and cyclohexane were taken from Timmermans (17); those for cyclopentanone and cyclohexanone, from Vogel (18). In general, extrapolation of the density data was required, but due to their slight variation with temperature, no significant error in the cohesive energy plots results. Vapor pressure of cyclohexanone was taken from Meyer and Hotz (10).

Discussion

Table VI compares densities and boiling points measured in the present work with literature values. The only serious discrepancies involving recent work arise in the comparison with values quoted by Wolf (20, 21). His boiling points were determined by an approximate method. Vapor pressures were measured using an isoteniscope, but in no case did values exceed 10 cmHg. Furthermore, there are differences of up to 0.8 cmHg between our vapor pressure values in the temperature ranges wherein the data overlap.

$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Cycloh	eptane ^b	Cv	clooctane			Cyclod	decane <i>c</i>		Cyclodecane	
	t	p	t	p	tw		t	p	t	ρ	tw
66.329 15.360 108.375 22.200 66.800 79.148 113.335 138.431 134.28 57.546 60.300 77.77 21.155 118.13 30.689 75.564 87.571 1.5984 142.307 17.5244 65.372 66.324 33.364 133.455 55.868 91.619 99.384 3.2443 154.448 22.238 66.841 106.462 55.550 149.031 71.945 98.487 105.270 4.1114 166.55 30.645 76.543 121.661 82.132 160.911 96.955 106.902 173.139 37.032 81.282 121.681 82.132 160.911 96.955 106.302 173.139 37.032 81.282 132.892 1.747 71.2837 72.807 12.823 113.286 62.965 98.481 132.820 1.448 167.668 106.535 52.820 202.444 70.311 100.365 132.820 1.747 71.2537 12.847 71.935 131.746 71.8455 108.917 133.672 20.777	63.030	12 235	100 133	16 842	62 592	, 7	0.614	0.8819	131.861	10.818	53,171
0.77, 72 21,135 112,813 30,869 76,564 87,571 119,889 142,370 152,224 66,397 96,324 33,364 139,435 55,888 91,619 99,3384 3,2636 147,637 17,924 66,397 10,6462 53,550 149,013 71,948 88,727 104,418 112,817 5,5013 165,365 30,844 76,548 121,661 82,122 160,911 96,955 106,902 173,139 37,032 81,022 121,618 82,177 16,636 52,820 202,490 76,210 100,076 120,890 1.992 173,737 12,823 56,733 210,044 90,274 104,895 132,962 1,74,101 197,000 24,137 1,74,01 197,000 24,137 143,0164 5,712 30,264 31,306 76,501 10,556 6,770 42,656 120,490 1,922 15,203 10,556 6,770 42,656 10,536 10,791	68 929	15 360	108 375	22 200	68 800	. ,) 7	9 1 4 8	1 3 3 3 4	138 431	13 428	57.696
65.702 27.867 127.569 40.061 22.966 94.398 22.836 147.637 17.924 63.942 96.324 33.343 55.886 91.619 99.384 32.443 154.848 22.238 66.841 106.462 53.550 149.031 71.945 95.487 105.270 4.1114 160.755 26.373 72.807 121.681 82.132 160.911 96.955 106.902 173.139 37.032 81.082 123.520 1.448 167.663 10.636 52.820 202.490 70.210 100.056 132.052 13.778 12.832 56.733 210.044 50.211 100.0563 132.622 31.74 182.571 15.631 62.318 216.374 103.455 108.455 133.727 21.83.772 13.83 85.703 120.5484 31.305 76.901 Cyclobutanone 122.492 62.336 61.70 22.55 65.70 42.635 61.70 233.133 65.708 95.909 71.16 100.553 6.370 42.636 61.791 <t< td=""><td>77 747</td><td>21 195</td><td>118.813</td><td>30.869</td><td>76 564</td><td>,, , 8</td><td>7.571</td><td>1.9589</td><td>142.370</td><td>15.224</td><td>60.390</td></t<>	77 747	21 195	118.813	30.869	76 564	,, , 8	7.571	1.9589	142.370	15.224	60.390
56.322 39.364 139.425 55.888 91.619 99.384 3.2443 154.848 22.228 66.841 117.547 73.409 157.386 88.727 104.418 112.817 5.501 160.750 26.377 72.807 117.547 73.409 157.386 88.727 104.418 112.817 5.5013 166.365 20.3845 77.847 121.681 82.127 16.636 52.820 173.193 37.032 81.022 120.890 1.992 173.787 12.832 56.733 210.044 90.274 104.89 122.622 3.174 182.727 16.634 93.433 94.403 12.374 132.662 1.740 197.900 25.413 71.935 Cyclobutanome 72.42.656 231.74 182.727 16.314 103.745 110.430 12.337 55.904 143.018 5.571 20.584 93.105 100.556 6.70 42.656 231.81 50.91 105.575 <t< td=""><td>85.702</td><td>27.881</td><td>127.569</td><td>40.061</td><td>82.996</td><td>9</td><td>4.398</td><td>2.6356</td><td>5 147.637</td><td>17.924</td><td>63.972</td></t<>	85.702	27.881	127.569	40.061	82.996	9	4.398	2.6356	5 147.637	17.924	63.972
$ \frac{16}{16} \frac{2}{62} \frac{53}{50} \frac{149}{61} \frac{31}{61} \frac{71}{548} \frac{92}{548} \frac{105}{270} \frac{4.1114}{116} \frac{160.755}{6.365} \frac{26.373}{30.48} \frac{72.807}{6.543} \frac{72.807}{173.139} \frac{72.807}{7.032} \frac{81.022}{173.139} \frac{73.032}{7.032} \frac{81.022}{100.076} \frac{173.139}{120.890} \frac{73.032}{120.890} \frac{85.466}{120.890} \frac{73.02}{120.890} \frac{120.890}{120.890} \frac{73.42}{120.890} \frac{120.890}{120.890} \frac{73.42}{120.890} \frac{73.42}{120.890} \frac{120.890}{120.890} \frac{73.42}{120.890} \frac{120.890}{120.890} \frac{73.42}{120.890} \frac{120.890}{120.890} \frac{73.42}{120.890} \frac{120.890}{120.890} \frac{73.42}{120.890} \frac{120.890}{120.890} \frac{73.42}{120.890} \frac{120.890}{120.890} \frac{73.42}{120.890} 73.$	96.324	39.364	139.435	55.888	91.619	9	9.384	3.2443	154.848	22.238	68.841
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	106.462	53,550	149.031	71.945	98.487	10	5.270	4.1114	160.755	26.373	72.807
121.681 82.132 160.911 96.955 106.902 173.139 37.032 81.022 Cyclododesare* Cyclododesare 186.644 52.321 85.865 r r r r r st.846 113.296 1.448 167.668 10.636 52.820 202.490 76.210 100.076 133.722 3.958 185.958 20.277 66.736 213.720 38.083 81.720 r c/r r	117.547	73.409	157.388	88.727	104.418	3 11	2.817	5.5013	3 166.365	30.845	76.543
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	121.681	82.132	160.911	96.955	106.902	2			173.139	37.032	81.022
Cyclobdecane Cyclobdecane 136.644 52.321 98.862 r p t p t p s 98.862 94.813 113.296 1.4.48 167.668 10.636 52.820 202.490 76.210 100.076 138.722 3.787 12.822 56.733 210.044 90.274 104.394 133.720 3.986 189.592 20.77 66.736 Culture Culture p fw 133.720 3.8063 81.720 t p fw 231.530 57.834 92.510 73.75 18.430 12.375 94.843 95.908 231.530 57.834 92.510 75.63 73.33 12.2792 14.330 12.375 91.833 11.332 55.908 146.73 10.532 52.619 66.698 8.586 48.485 137.533 23.175 69.71 44.673 10.232 52.619 66.698 8.586 48.4845 137.533 23.106									179.932	44.201	85.486
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Cyclode	odecan e ¢	Cycl	ododecane	2				186.644	52.321	89.862
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	t	p	t	p	tw				194.295	62.985	94.818
120 800 132 662 132 662 133 672 148.088 5.571 128 32 148.088 5.571 128 32 148.088 5.571 210.44 205.087 205.0894 213.510 205.0894 213.510 213.520 120.5894 31.306 76.901 210.344 205.087 76.901 02.74 216.344 103.455 108.877 148.088 5.571 5.571 205.894 213.530 57.834 92.519 92.519 100.553 6.370 6.370 42.655 6.370 120.345 42.656 6.370 122.792 42.337 143.307 6.426 6.580 101.975 7.845 118.430 48.103 123.37 6.390 59.098 122.792 14.339 122.792 14.339 59.098 126.482 16.235 6.179 61.79 7.845 126.482 6.235 16.79 7.97 8.456 48.180 10.532 52.619 6.6598 66.698 8.586 48.485 5.127 137.533 7.140.804 23.75 6.9791 28.066 7.4279 60.429 20.640 66.696 6.48.83 17.536 63.487 7.168 16.617 6.299 143.800 7.636 3.844 160.152 7.766 7.38.246 12.236 6.667 8.989 115.252 143.807 7.168 16.01.22 48.667 7.090 170.822 59.653 13.297 7.077 7.080.16 5.044 7.013.299 7.043 16.73 7.044 18.544 7.014.371 18.700 7.777 7.050.16 7.077 7.050.16 7.077 7.050.16 7.077 7.050.16 7.077 7.050.16 7.077 7.050.16 7.077 7.000 18.544 7.010.799 7.016.17 7.000 18.544 7.017 7.000 18.544 7.010.799 7.016.16 7.027 7.027 7.027 7.027 7.027 7.027 7.027 7.027 7.027 7.027 7.027 7.027 7.027 7.027 7.027 7.027 7.027 7.020.16 7.077 7.00 7.016 7.09 7.016 7.09 7.016	113.296	1.448	167.668	10.636	52.820)			202.490	76.210	100.076
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	120.890	1.992	173.787	12.832	56.733	3			210.044	90.274	104.894
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	132.662	3.174	182.577	16.631	62.318	3			216.344	103.455	108.877
	138.722	3.985	189,589	20.277	66.736	5					
148.088 5.571 205.894 31.306 76.901 Cyclobertanone 231.530 57.834 92.519 100.563 6.370 42.650 231.830 65.080 97.116 107.977 8.455 48.180 247.201 81.231 101.875 118.430 12.337 55.90.98 255.604 96.497 106.830 126.442 16.235 61.79 246.731 10.532 52.619 66.698 8.586 48.483 137.533 20.617 69.79 44.673 10.532 52.619 66.698 8.586 48.485 137.533 20.667 74.279 5.327 16.517 62.168 80.908 15.127 60.252 143.791 28.066 74.279 72.011 31.299 76.896 101.748 31.676 77.644 85.987 75.647 140.804 12.787 75.44 72.011 31.299 76.896 101.748 31.676 77.647 98.9561 06.193.81 177.	143.517	4.740	197.900	25.413	71.935	5					
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	148.088	5.571	205.894	31.306	76.901				С	ycloheptanone	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $			213.720	38.083	81.720)			t	p	tw
$\begin{array}{c c c c c c c c c c c c c c c c c c c $			231.530	57.834	92.519)			100.563	6.370	42.656
$\begin{array}{c c c c c c c c c c c c c c c c c c c $			239.183	68.508	97.116	5			107.977	8.455	48.180
$\begin{array}{c c c c c c c c c c c c c c c c c c c $			247.201	81.231	101.875	5			118.430	12.337	55.904
$\begin{array}{c c c c c c c c c c c c c c c c c c c $			255,604	96.497	106.830)			122.792	14.339	59.098
Cyclobultanone Cyclobultanone 129.634 18.013 64.082 t p tw t p fw 133.354 20.311 66.775 44.673 10.532 52.619 66.698 8.586 48.485 137.533 23.175 69.721 48.311 12.328 55.890 74.991 12.026 55.370 140.804 25.632 72.137 60.429 20.240 66.696 80.908 15.127 60.4252 143.791 28.066 74.279 60.429 20.240 66.896 101.748 31.678 77.188 160.152 44.896 85.886 63.540 46.680 86.89 115.252 48.667 87.969 170.823 59.653 93.350 102.436 84.699 103.065 136.104 88.494 104.321 187.207 89.561 104.677 107.047 9.661 162.104 142.402 104.574 109.155 104.670 100.755 107.74					_				126.482	16.235	61.791
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		Cyclobutanor	ne		Cyc	opentan	ione		129.634	18.013	64.082
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	t	p	t_{W}	t		p		t_{W}	133.354	20.311	66.775
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	44.673	10.532	52.619	66.6	98	8.586		48.485	137.533	23.175	69.791
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	48.311	12.328	55.890	74.9	91	12.026		55.370	140.804	25.632	72.137
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	55.327	16.517	62.168	80.9	08	15.127		60.252	143.791	28.066	74.279
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	60.429	20.240	66.696	84.8	53	17.536		63.487	148.511	32.278	77.644
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	65.997	25.069	71.617	96.2	:99	26.362		72.796	154.447	38.300	81.862
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	72.011	31.299	76.896	101.7	48	31.678		77.188	160.152	44.896	85.886
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	77.667	38.246	81.827	108.0	96	38.933		82.273	165.408	51.749	89.573
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	83.540	46.680	86.889	115.2	52	48.667		87.969	170.823	59.653	93.350
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	89.461	56.658	91.971	122.3	59	60.166		93.581	177.552	70.777	98.016
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	95.541	68.659	97.177	129.3	16	73.424		99.036	181.544	78.170	100.790
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	102.436	84.699	103.065	136.1	04	88.494		104.321	187.207	89.596	104.677
$\begin{tabular}{ c c c c c c c c c c c } \hline Cycloundecanone & Cyc$	107.047	96.955	106.969	142.4	02	104.574		109.195	191.461	99.017	107.585
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		Cyclooctar	0000			Cvr	lounde	ecanone		Cvclodod	ecanone c
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	+	cycloocial	10110		+	Cyc	nouniae 0	scanone	t	t	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	121 790	7 7 2 2 7	45 3	N 257	175 967		بم م ع	21	50 1 32	135 610	1 205
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	127.780	9.061	40.	557	185 900		12.5	69	56 296	142 358	1 594
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	127.774	12342	49.0	14	105.900		16.7	Q1	62 529	149 216	2 093
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	130.724	12.342	55.5	514 011	202 700		20.3	51	66 828	155 377	2.033
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	143.072	20.163	66.6	510	210 935		25.3	41	71 868	159 796	3 115
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	152.028	20.103	71 4	599	210.333		31.5		77.090	165 274	3 797
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	167 145	23.030	76.0	967	213.444		38.3	79	81 913	170 526	4 548
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	174 009	31.350	21 4	507	227.337		30.5	/ 5	01.515	177 143	5 709
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	192 208	47 328	87 (535 545						177.145	0.705
$\begin{array}{c ccccc} 197.010 & 68.327 & 52.747 & t & p & t_w \\ 197.010 & 68.394 & 97.071 & t & p & t_w \\ 205.017 & 82.623 & 102.357 & 185.130 & 7.390 & 45.525 \\ 210.909 & 94.300 & 106.159 & 191.954 & 9.148 & 49.755 \\ & 204.870 & 13.425 & 57.691 \\ & 209.438 & 15.273 & 60.460 \\ & 214.759 & 17.694 & 63.686 \\ & 223.265 & 22.203 & 68.804 \\ & 229.738 & 26.232 & 72.679 \\ & 230.169 & 26.523 & 72.940 \\ & 239.059 & 32.993 & 78.177 \\ & 247.113 & 39.981 & 82.939 \\ & 255.432 & 48.354 & 87.800 \\ & 264.524 & 59.050 & 93.077 \\ & 273.224 & 70.973 & 98.092 \\ & 282.375 & 85.606 & 103.368 \\ & 290.759 & 100.895 & 108.137 \end{array}$	102.290	47.320	07.2	24J 747		C)	clodor	decanone			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	190.516	20.327	92.	747	•	دى	n Ciouot		+		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	205 017	82622	1023	257	185 130		73	an	'w 45525		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	205.017	02.023	102.3	557	101.052		0.1	<i>3</i> 0 <i>1</i> 0	40.755		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	210.909	94.300	106	159	204 970		12 /	40 25	49.755 57.691		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$					204.0/0		15.4	72	57.091		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$					209.436		10.2	04	62.686		
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$					214./05		22.0	03	68 804		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$					223.203		26.2	32	72 6 7 9		
239.059 239.059 247.113 247.113 247.113 247.12 2					229.730	, 	20.2	23	72.940		
247.113 39.981 82.939 255.432 48.354 87.800 264.524 59.050 93.077 273.224 70.973 98.092 282.375 85.606 103.368 290.759 100.895 108.137					230,105	1	320.0	93	78 177		
255.432 255.432 264.524 264.524 273.224 273.224 282.375 260.501 261.551 261.551 282.354 85.606 103.368 290.759 100.895 108.137					247 112		30 0	81	82,939		
264.524 59.050 93.077 273.224 70.973 98.092 282.375 85.606 103.368 290.759 100.895 108.137					255 432		29.9 48 २	54	87.800		
273.224 70.973 98.092 282.375 85.606 103.368 290.759 100.895 108.137					264 524		-0.0 59 A	50	93 077		
282.375 85.606 103.368 290.759 100.895 108.137					273 224		70 9	73	98,092		
290.759 100.895 108.137					282.375		85.6	06	103.368		
					290.759	•	100.8	95	108.137		

^{*a*} t in °C, *p* in cmHg, t_w is temperature of water equilibrium. ^{*b*} Pressure measured with mercury manometer. ^{*c*} Pressure measured with oil manometer.

Table III. Vapor Pressure Data^a

Table IV. Fit of Density Data to $\rho = a + bt + ct^{2}$

0	Temp range,		1.03			Av dev
Compound	-0	а	$-b \times 10^{3}$	c × 10°	$-d \times 10^{\circ}$	× 104
Cycloheptane	16-114	0.82841	0.85984	0.06038	0.2042	0.03
Cyclooctane	29-129	0.85280	0.82487	0.22566	0.1931	0.07
Cyclodecane	21-131	0.87428	0.79862	0.62498	0.2339	0.07
Cyclododecane	66-133	0.8656	0.4961	-0.8247	0	2.
Cyclobutanone	20-89	0.9557	1.0207	-0.6970	0	2.
Cycloheptanone	24-100	0.9680	0.8729	0.6034	0.3859	0.4
Cyclooctanone	43-138	0.9658	0.8103	-0.0287	0	2.
Cycloundecanone	28-138	0.96787	0.7360	0.03982	0	0.7
Cyclododecanone	70-142	0.9551	0.6369	-0.2234	0	5.

	Density Data	Table V. I	ensity	/ Data
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t	ρ	t	ρ	t	ρ
Cyclob	neptane	Cyclo	octane	Cyclo	decane
16.078	0.81459	29.091	0.82895	21.673	0.85723
28.400	0.80400	45.775	0.81533	34.571	0.84733
45.135	0.78954	64.562	0.79995	49.133	0.83627
60.370	0.77627	76.472	0.79020	66.244	0.82342
75.990	0.76252	90.589	0.77849	79.409	0.81363
90.309	0.74975	110.339	0.76194	93.731	0.80299
103.813	0.73752	128.737	0.74623	112.007	0.78938
114.290	0.72788			131.267	0.77492
Cyclod	odecane	Cyclob	utanone	Cyclohe	ptanone
66.153	0.8294	20.342	0.9340	24.194	0.9472
73.366	0.8246	28.364	0.9272	36.346	0.9369
83.656	0.8185	36.164	0.9179	49.652	0.9256
92.866	0.8123	45.018	0.9082	64.319	0.9134
102.662	0.8058	52.616	0.9004	76.192	0.9032
112.486	0.8000	59.324	0.8925	89.259	0.8922
123.656	0.7915	68.872	0.8819	100.289	0.8826
133.346	0.7848	74.882	0.8753		
		83.043	0.8662		
		89.152	0.8593		
Cyclood	tanone	Cycloun	decanone	Cyclodo	decanone
43.546	0.9301	28.498	0.9470	70.314	0.9091
55.926	0.9201	37.251	0.9406	81.494	0.9018
65.000	0.9128	52.607	0.9292	92.376	0.8944
73.320	0.9061	65.690	0.9196	101.464	0.8882
82.845	0.8986	79.349	0.9097	110.595	0.8820
96.911	0.8874	93.039	0.8997	119.708	0.8756
110.058	0.8766	109.756	0.8878	129.410	0.8690
123.152	0.8657	123.825	0.8774	142.170	0.8600
137.967	0.8533	138.571	0.8665		



Figure 1. Cohesive energy (kcal/mol) vs. M, the effective number of CH bonds in the molecule. The reference state is n-hexane at 0 °C.

However, using our Cox parameters and the compressibility factors quoted by Wolf (20), we calculate standard heats of vaporization at 25 °C that are in good agreement with those produced with isoteniscope data (Table VII). Only the values for the 8- and 12-membered rings lie outside the quoted experimental error. Our cycloundecanone data are unreliable, involving too great an extrapolation. The rather large differences for cyclooctanone and cyclododecanone are real, we think, and not entirely the result of extrapolation. The isoteniscope data for these compounds were 10 and 20% lower, respectively, in value than our data in the same temperature ranges.

A cohesive energy plot is presented in Figure 1. The first important observation is the linearity of the cyclic alkane data. (A straight line reproduces the experimental points within $\pm 0.4\%$.) Thus here, as in the case of the linear alkanes, each successive CH₂ group contributes the same amount to total

Table VI. Comparison of Data with Literature

Compound	$\rho(t)$	$ ho^{ m lit.}$	τ_{bp}	$ au_{bp}^{lit.}$
Cycloheptane	0.8112 (20)	0.8109 <i>b</i>	391.965	391.960 <i>h</i>
Cyclooctane	0.8323 (25)	0.8320 <i>c</i>	424.327	424.321 <i>h</i>
Cyclodecane	0.8585 (20)	0.8581 <i>d</i>	475.517	473.7 <i>d</i>
Cyclododecane	0.855 (20)4	0.861 <i>°</i>	517.178	
Cyclobutanone	0.9297 (25)	0.94 2 f	371.991	372.9 <i>i</i>
Cyclopentanone	_ ` `	_	403.700	403.65. <i>b</i> 403.8 <i>i</i>
Cycloheptanone	0.9508 (20)	0.9498	453.561	453.8 453.0 ⁱ
Cyclooctanone	0.945 (25) ^a	0.95 2 f	474.589	478.7 <i>i</i>
Cycloundecanone	0.953 (20)	0.955 <i>f</i>	531.4 <i>ª</i>	520.3 <i>i</i>
Cyclododecanone	0.942 (20)	0.956 <i>f</i>	549.675	538.3 <i>i</i>

^{*a*} Beyond range of data. ^{*b*} Reference 1. ^{*c*} Reference 2. ^{*d*} Reference 16. ^{*e*} Reference 13. ^{*f*} Reference 9. ^{*s*} Reference 18. ^{*h*} Reference 4. ^{*i*} Reference 21.

Table VII. Comparison of Standard Enthalpies of Vaporization at 25 $^\circ\text{C}$

Compound	Present work	Wolf ^a
Cyclobutanone	9.11	9.14 ± 0.10
Cyclopentanone	10.07	10.19 ± 0.10
Cyclohexanone ^b	10.81	10.73 ± 0.15
Cycloheptanone	11.89	11.84 ± 0.15
Cyclooctanone	12.89	11.59 ± 0.15
Cyclododecanone	16.18	15.65 ± 0.15

^a Reference 21. ^b Reference 10.

Table VIII. Comparison of Cohesive Energy Contributions in Cyclic and 2-Ketones

No. of	Ed	isp ^a	Eorient		
Carbons	Cyclic	2-Ketone	Cyclic	2-Ketone	
3	(5.0) ^b	5.0		0.8	
4	5.7	5.9	0.9	0.4	
5	6.3	6.8	0.6	0.3	
6	6.9	7.6	0.3	0.3	
7	7.6	8.5	0.1	0.3	

^{*a*} Values given in kilocalories per mole. ^{*b*} Extrapolated value.

cohesion. It should be noted, however, that the contribution is considerably less in the present case: 0.64 vs. 0.88 kcal/mol of CH₂ groups for the linear alkanes. Apparently that portion of each CH₂ group which faces toward the inside of the cyclic molecule is not available for intermolecular attraction. It is probably not correct to use the ratio of these figures as representative of the fraction of each CH₂ group which is exposed to neighboring molecules, however, since the average intermolecular distances may not be equal for the cyclic and linear alkanes, even though we have assigned equal volumes per CH_2 group to both series. The considerably higher heats of combustion of cyclic alkanes (excepting only C₆) than linear homologues (7) indicate that the average distance between methylene groups in the same ring is smaller than that between methylene groups in adjacent linear alkanes. Thus our method probably results in having the cyclic molecules at slightly greater distances than linear ones when assigning the same volume per CH₂ group to both series, accounting at least in part for the smaller slope of the cyclic alkane line.

It may be worth noting that the considerable difference in chemical energy of cyclic homologues (7) has no apparent effect on the cohesive energy of these molecules in the liquid state. Cyclohexane exhibits zero strain energy, while cyclodecane exhibits more than 13 kcal/mol, yet they fall on the same straight line of cohesive energy vs. ring size.

The reference state in Figure 1 is *n*-hexane at 0 °C, as in our earlier studies. In order to put cyclohexane into this state, i.e., with 19.08 ml/CH₂ group, its temperature must be raised to 52 °C. This is additional indication that the intermolecular distance is greater for cyclic than for linear molecules under these conditions. As a consequence, the vapor pressures of the cyclic homologues are higher than the linear ones, and sufficient nonideality of the vapor exists to require estimation of compressibility factors for inclusion in the estimation of energies of vaporization from vapor pressures via the Clapeyron equation. Z = PV/RT was estimated using the simple relationship Z = 1 - 0.05P (atm). For the "hexane O" state, values of Z varied from 0.98 to 0.96 for both the cyclic alkanes and ketones.

The next important feature of Figure 1 is the failure of the ketone energies to approach a line parallel to that for the al-

kanes. The data for C₄ through C₇ display behavior exactly analogous to that of the linear polar molecules studied previously (*11, 12*), and are displaced upward from the alkane line by very nearly the same amount as the 2-ketones. However, C₈, C₁₁, and C₁₂ lie progressively closer to the alkane line, the cyclodode-canone exhibiting a cohesive energy only 0.3 kcal/mol greater than it would if it had zero dipole moment. This is in contrast to a difference of 1.1 kcal/mol between the linear C₁₂ ketone and its nonpolar counterpart (*12*).

It might be argued that there is a smooth gradation in the cyclic ketone plot, with the C_7 point slightly high due to experimental error, and that postulating a break between the C_7 and C_8 is not justified. In order to minimize the error for the C_7 ketone, we measured half again as many data points for this one as for the other ketones. Furthermore, using the elements of the variance–covariance matrices, we have calculated the standard deviations of the heats of vaporization derived from the vapor pressure data, and find the greatest standard deviation to be less than 5 cal/mol.

The probable explanation for the unexpected behavior of the larger cyclic ketones lies in their ability to exist in conformations in which the carbonyl group is shielded from its neighbors. Models indicate that such shielding is virtually nonexistent in cycloheptanone, but becomes possible for larger rings, increasing in likelihood with ring size.

Evidence for the existence of "O-out" and "O-in" conformations in cyclic ketones with from 8 to 12 or 13 carbon atoms was cited shortly after methods for their synthesis became available many years ago (13, 14). Though an intramolecular "hydrogen bridge" was thought to be responsible at least in part for the "O-in" conformation, it seems more likely that some relief of hydrogen atom repulsion occurs when the carbonyl group positions itself more nearly perpendicular to the plane of the ring than parallel with it. Whatever the reason, in such a conformation the ability of the carbonyl dipole to influence neighboring molecules is certainly decreased relative to the "O-out" conformations characteristic of the C_4 through C_7 cyclic ketones.

If we assume that the very close similarity in behavior between the 2-ketones and the cyclic ketones up to C_7 would extend to higher members were it not for the existence of "O-in" conformations for the latter, we can use our results to obtain estimates of the relative amounts of "O-in" and "O-out" conformations for the C_8 , C_{11} , and C_{12} cyclic ketones. It must be appreciated, however, that there are in all likelihood several conformations consistent with what we refer to as "O-in" and "O-out" (*15*), making the estimates crude ones. The results are (compound (% "O-in")): cyclooctanone (13), cycloundecanone (50), cyclododecanone (75).

Extrapolation of the curve produced by the cyclic ketones from C_4 to C_7 leads to induction energies of 1.2-1.3 kcal/mol, slightly but significantly higher than the value 1.1 kcal/mol characteristic of the linear ketones (2, 3). The values of orientation and dispersion energies taken from Figure 1 are given in Table VIII, and compared with those for the 2-ketones.

The orientation energies for the four- and five-membered cyclic ketones are greater than even those for the next smaller 2-ketones. This is probably the result of two factors: the dipole moments of the cyclics are greater than their linear counterparts (e.g., cyclobutanone, 3.1 D; 2-butanone, 2.5 D), and the near planarity of the rings may promote the alignment of their dipoles.

The more rapid drop-off of orientation energy with carbon number for the cyclics is probably a reflection of having them at greater distances than the 2-ketones, as discussed earlier, though they do display a slightly greater dimunition in dipole moment with carbon number than do the linear ketones ($\boldsymbol{6}$).

In order to estimate the effect of temperature on our conclusions, the entire analysis was carried out using a reference state 40° cooler for *n*-hexane. The ketone curve lies 0.1 kcal/ mol higher relative to the alkane curve as a result. That is, at the

lower temperatures, the dipole makes a measurably larger contribution to total cohesion. Because the change is so small, however, it is impossible to say whether it is due to an increase in orientation or induction energy, or both. Except for the unlikely situation that they are changing in opposite senses, we can accept this as direct experimental evidence that temperature effects on dipolar interactions in pure liquids involving moments of 2-3 D are slight.

Acknowledgments

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The Density of Fused Pyridinium Salts

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The densities of seven fused pyridinium salts were measured as a function of temperature using a modified Lipkin bicapillary pycnometer. The results for each salt may be expressed by an equation of the form ρ (g/cm³) = a + bT (°K). The experimental technique and errors involved in the measurements are discussed.

Fused pyridinium salts are useful as electrolytes in high temperature batteries and as solvents for both synthetic and structural studies. Mixtures of pyridinium salts are potentially useful as energy storage media to be used in conjunction with solar heating and air conditioning units. These salts are low melting, and in their molten state are noncorrosive to Pyrex, stable over a relatively wide temperature range, and accessible to study by NMR techniques as well as by more conventional means.

The measurement of the change in density of eight of these fused pyridinium salts as a function of temperature was undertaken to provide information for use in structural studies and those energy related applications where these salts may be important.

Experimental Section

The salts studied were pyridinium chloride (I), N-methylpyridinium chloride (II), 4-methylpyridinium chloride (III), 4-methyl-N-methylpyridinium chloride (IV), pyridinium bromide (V), Nmethylpyridinium bromide (VI), 4-methylpyridinium bromide (VII), and 4-methyl-N-methylpyridinium bromide (VIII). They are shown in Figure 1.

All of the salts were synthesized in basically the same way using a technique first described by Rozdhestvenskii and Brode (5) and modified by Newman et al. (3). The syntheses can all be summarized by eq 1.



The purity of each salt was ascertained by C, H, N analyses, ir spectrum, and melting point. All salts used contained less than 1% impurities.

The density of the molten salts was measured using a modified Lipkin bicapillary arm pyconometer shown in Figure 2 (2). The pycnometer was calibrated with water at 25 °C in such a way that the volume of the liquid could be given by an equation of the form $V_{\text{lig}} = a + b$ (capillary reading).

To measure density as a function of temperature, the solid salts were each placed in the large reservoir on the left side of the pycnometer which was closed with a one-hole Teflon stopper connected to a filled drying tube. The filled pycnometer was placed in a constant temperature bath slightly above the melting point of the salt and as the salt melted a slight vacuum was applied to the right side of the pycnometer through another filled drying tube. This technique facilitated the filling of the capillary region of the pycnometer with molten salt. The temperature was increased in 10° increments and allowed to equilibrate for 10 min at each temperature before a volume reading was made. This procedure was followed until a predetermined upper temperature limit was reached. The temperature was then decreased first 5° and then in 10° increments until the salt froze. A volume reading was taken at each temperature after the system had equilibrated. The weight of the salt was determined as follows. Excess salt that adhered to the reservoirs was removed and the pycnometer together with the remaining frozen salt weighed. Next the salt was remelted and poured from the pycnometer. The pycnometer was then thoroughly cleaned and reweighed.