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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 2-ketones. The dipole in the cyclic ketones from C<sub>4</sub> through C<sub>7</sub> is more effective in attractive interactions than that in the 2-ketones. However, in C<sub>8</sub>, C<sub>11</sub>, and C<sub>12</sub> 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, 2-ketones, 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 C<sub>5</sub> to C<sub>12</sub> and cyclic ketones from C<sub>4</sub> to C<sub>12</sub>. 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 C<sub>8</sub>, C<sub>10</sub>, and C<sub>12</sub> cyclic alkanes and the C<sub>4</sub>, C<sub>5</sub>, C<sub>7</sub>, C<sub>8</sub>, C<sub>11</sub>, and C<sub>12</sub> 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 C<sub>10</sub> alkane and both of the C<sub>12</sub> 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 C<sub>7</sub>, C<sub>8</sub>, C<sub>10</sub>, and C<sub>12</sub> cyclic alkanes, and for the C<sub>4</sub>, C<sub>7</sub>, C<sub>8</sub>, C<sub>11</sub>, and C<sub>12</sub> cyclic ketones using the dilatometer already described (19).

The compounds were obtained from Chemical Samples Company, except for the C<sub>11</sub> ketone, which was made from the C<sub>12</sub> ketone following the method of Garbisch (5), and the C<sub>10</sub> 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 C<sub>4</sub> 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 cyclo-decane, 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 cyclo-dodecanone (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

Table I. Antoine Constants<sup>a</sup>

Compound	Temp range, °C	A	B	C	T <sub>bp</sub> , K	10 <sup>4</sup> $\left(\frac{\Delta p}{p}\right)_{av}$
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 <sup>b</sup>	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

<sup>a</sup> Log *p* (cmHg) = *A* - (*B*/(*C* + *t*)). To convert to *k*Pa, add 0.124903 to *A*. <sup>b</sup> Extrapolation beyond range of data.

Table II. Cox Constants<sup>a</sup>

Compound	<i>a</i>	- <i>b</i> × 10 <sup>3</sup>	<i>c</i> × 10 <sup>6</sup>	T <sub>bp</sub> , K	10 <sup>4</sup> $\left(\frac{\Delta p}{p}\right)_{av}$
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
(ebull.)	0.976283 ± 0.00138	0.938904 ± 0.0056	0.759318 ± 0.0057	549.6748 ± 0.00060	2.5

<sup>a</sup> Log *p* (atm) = *A*'(1 - (T<sub>bp</sub>/T)), where log *A*' = (*a* + *b*T + *c*T<sup>2</sup>). T<sub>bp</sub> 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. (1) 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.



**Table IV. Fit of Density Data to  $\rho = a + bt + ct^2 + dt^3$** 

Compound	Temp range, °C	<i>a</i>	$-b \times 10^3$	$c \times 10^6$	$-d \times 10^8$	Av dev $\times 10^4$
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.

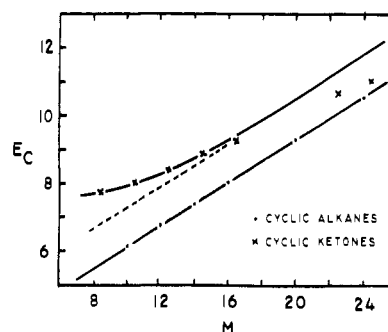
**Table V. Density Data**

<i>t</i>	$\rho$	<i>t</i>	$\rho$	<i>t</i>	$\rho$
Cycloheptane		Cyclooctane		Cyclodecane	
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
Cyclododecane		Cyclobutanone		Cycloheptanone	
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		
Cyclooctanone		Cycloundecanone		Cyclododecanone	
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		

**Table VI. Comparison of Data with Literature**

Compound	$\rho(t)$	$\rho^{lit.}$	$T_{bp}$	$T_{bp}^{lit.}$
Cycloheptane	0.8112 (20)	0.8109 <sup>b</sup>	391.965	391.960 <sup>h</sup>
Cyclooctane	0.8323 (25)	0.8320 <sup>c</sup>	424.327	424.321 <sup>h</sup>
Cyclodecane	0.8585 (20)	0.8581 <sup>d</sup>	475.517	473.7 <sup>d</sup>
Cyclododecane	0.855 (20) <sup>a</sup>	0.861 <sup>e</sup>	517.178	
Cyclobutanone	0.9297 (25)	0.942 <sup>f</sup>	371.991	372.9 <sup>i</sup>
Cyclopentanone	—	—	403.700	403.65, <sup>b</sup> 403.8 <sup>i</sup>
Cycloheptanone	0.9508 (20)	0.949 <sup>g</sup>	453.561	453, <sup>g</sup> 453.0 <sup>i</sup>
Cyclooctanone	0.945 (25) <sup>a</sup>	0.952 <sup>f</sup>	474.589	478.7 <sup>i</sup>
Cycloundecanone	0.953 (20)	0.955 <sup>f</sup>	531.4 <sup>a</sup>	520.3 <sup>i</sup>
Cyclododecanone	0.942 (20)	0.956 <sup>f</sup>	549.675	538.3 <sup>i</sup>

<sup>a</sup> Beyond range of data. <sup>b</sup> Reference 1. <sup>c</sup> Reference 2. <sup>d</sup> Reference 16. <sup>e</sup> Reference 13. <sup>f</sup> Reference 9. <sup>g</sup> Reference 18. <sup>h</sup> Reference 4. <sup>i</sup> Reference 21.


**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  $\text{CH}_2$  group contributes the same amount to total

**Table VII. Comparison of Standard Enthalpies of Vaporization at 25 °C**

Compound	Present work	Wolf <sup>a</sup>
Cyclobutanone	9.11	9.14 ± 0.10
Cyclopentanone	10.07	10.19 ± 0.10
Cyclohexanone <sup>b</sup>	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

<sup>a</sup> Reference 21. <sup>b</sup> Reference 10.

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

No. of Carbons	$E_{\text{disp}}^a$		$E_{\text{orient}}$	
	Cyclic	2-Ketone	Cyclic	2-Ketone
3	(5.0) <sup>b</sup>	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

<sup>a</sup> Values given in kilocalories per mole. <sup>b</sup> 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 CH<sub>2</sub> groups for the linear alkanes. Apparently that portion of each CH<sub>2</sub> 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 CH<sub>2</sub> 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<sub>2</sub> group to both series. The considerably higher heats of combustion of cyclic alkanes (excepting only C<sub>8</sub>) 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 CH<sub>2</sub> 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 cyclododecane 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/CH<sub>2</sub> 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 C<sub>4</sub> through C<sub>7</sub> 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, C<sub>8</sub>, C<sub>11</sub>, and C<sub>12</sub> lie progressively closer to the alkane line, the cyclododecanone 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 C<sub>12</sub> ketone and its nonpolar counterpart (12).

It might be argued that there is a smooth gradation in the cyclic ketone plot, with the C<sub>7</sub> point slightly high due to experimental error, and that postulating a break between the C<sub>7</sub> and C<sub>8</sub> is not justified. In order to minimize the error for the C<sub>7</sub> 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<sub>4</sub> through C<sub>7</sub> cyclic ketones.

If we assume that the very close similarity in behavior between the 2-ketones and the cyclic ketones up to C<sub>7</sub> 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<sub>8</sub>, C<sub>11</sub>, and C<sub>12</sub> 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<sub>4</sub> to C<sub>7</sub> 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 diminution in dipole moment with carbon number than do the linear ketones (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.

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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  $\rho$  (g/cm<sup>3</sup>) =  $a + bT$  (°K). The experimental technique and errors involved in the measurements are discussed.

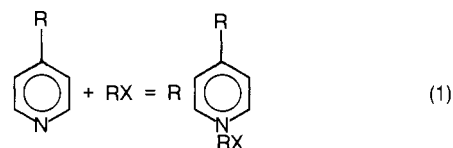
Fused pyridinium salts are useful as electrolytes in high temperature batteries and as solvents for both synthetic and structural studies. Mixtures of pyridinium salts are potentially useful as energy storage media to be used in conjunction with solar heating and air conditioning units. These salts are 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), *N*-methylpyridinium 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 pycnometer 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  $V_{\text{liq}} = a + b$  (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.