

considering compressibility from a molecular viewpoint. At low pressures molecules fit loosely together with a considerable amount of free space between them. The amount of free space depends upon the molecular shape and how well the molecules pack together. At low pressures the major part of the compressibility arises from crowding the molecules together, thus restricting any free rotation around C—C bonds. As higher pressures are approached this source of compressibility gradually disappears and the remaining compressibility probably is determined largely by the intermolecular repulsive forces. Since the only atoms in the compounds studied were hydrogen and carbon

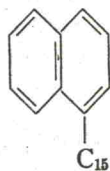
 TABLE VIII. Compressibility (bar)⁻¹

P (bars)	135°C		
	PSU 174	PSU 87	PSU 528
Atmospheric	9.14×10 ⁻⁵	11.8×10 ⁻⁵	18.3×10 ⁻⁵
3446	2.02	2.13	2.28
6891		1.18	1.21

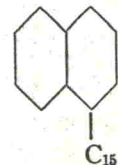
it is not surprising that the ultimate compressibilities approach the same value for all compounds studied.

Effect of Structure on Compression

To examine the effect of molecular structure on volume behavior the compression was plotted against pressure. Compression, which is defined as the change in volume per unit initial volume, was determined by dividing the fully corrected changes in specific volume by the atmospheric pressure value of the volume. In Fig. 3 the compressions of PSU 174



and 175



at 135°C are shown. The data at 135°C were selected to give the widest possible pressure range for the compression study. The comparative results at 135°C are in no way unique. PSU 174 and 175 differ in structure in that 174 consists of a naphthyl group with an attached chain of 15 carbon atoms whereas 175 is made up of a decalyl group with the same attached chain. The decalyl group proved to be the more com-

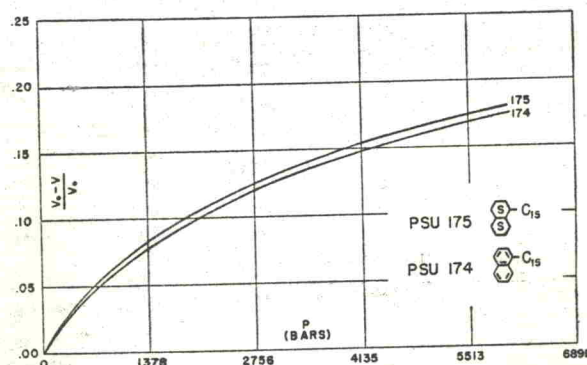


FIG. 3. Compression $(v_0 - v)/v_0$ versus pressure for 1- α -naphthylpentadecane (PSU 174) and 1- α -decalylpentadecane (PSU 175) at 135°C.

pressible of the two structures. Although the difference in compression between these two compounds is small, less than 1% at 5500 bars and 135°C, the data consistently show PSU 175 to be the more compressible.

In Fig. 4 are shown the compressions of five more hydrocarbons with molecular structure such that the effect on compression of changing from straight chain groups to one or two cyclohexyl groups or one or two phenyl groups is revealed. A structural change from a straight chain to a cyclohexyl group decreases the compression, and a change from two straight chain groups to two cyclohexyl groups further reduces the value of the compression. The same sort of behavior is displayed in changing from straight chain groups to phenyl groups. Comparison of the data for PSU 88 and 87 and PSU 18 and 19 shows that the cyclohexyl compounds are more compressible than the corresponding benzenoid compounds. Again these differences are small but they occur without exception over the whole pressure and temperature range.

Figure 5 shows, first of all, the effect of increasing the length of straight chains in normal paraffins is to decrease the compression. Also shown in Fig. 5 for comparison purposes are compression data on two other

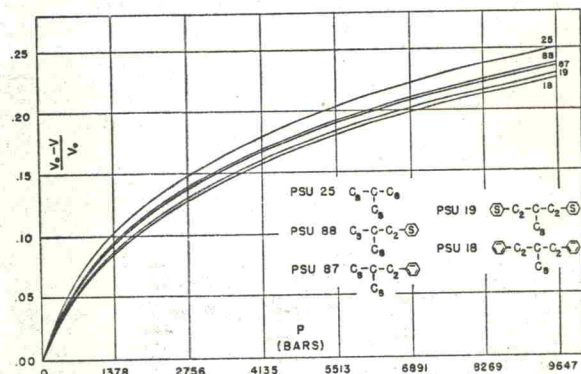


FIG. 4. Compression $(v_0 - v)/v_0$ versus pressure for 9-*n*-octylheptadecane (PSU 25), 9-(2-phenylethyl)heptadecane (PSU 87), 1-phenyl-3-(2-phenylethyl)heptadecane (PSU 18), 9-(2-cyclohexylethyl)heptadecane (PSU 88), and 1-cyclohexyl-3-(2-cyclohexylethyl)heptadecane (PSU 19), at 135°C.