Conversion of 4-anisyl-5-methyl-1,3-dioxane (III) *to 1-anisyl-2-methyl-1,3-diacetoxypropane* (Ia *and* Ib). A mixture of 40 g. (0.19 mole) III and 300 ml. glacial acetic acid was refluxed for 16 hr., after which time there was observed a deposit of paraformaldehyde in the reflux condenser. Removal of acetic acid *in vacuo* followed by fractional distillation gave two fractions. Fraction A, 30 g., 130–148° (1 mm.), consisted amost entirely of III. Fraction B, 11 g. 121–125° (0.08 mm.), n^{24} 1.4976, consisted entirely of the diacetate mixture. An infrared determination showed it to consist of 25% Ia and 75% Ib.

Equilibration of 1-anisyl-2-methyl-1,3-diacetoxypropane (Ia). A mixture of 1.0 g. of Ia and 25 ml. of glacial acetic acid was refluxed a total of 19 hr. The mixture was neutralized with aqueous sodium bicarbonate solution and extracted with ether. The ether extract was dried over magnesium sulfate and the solvent removed *in vacuo*. The remaining oil crystallized on standing. The mixture, when analyzed by infrared, contained 25% Ia and 75% Ib. On decreasing the refluxing time to 6 hr. the mixture consisted of 34% Ia and 66% Ib.

Conversion of 1-Anisyl-2-methyl-1,3-diol (IIa *and* IIb) *to 4-Anisyl-5-methyl-1,3-dioxane* (III). When subjected to the following conditions, both pure IIa and pure IIb afforded III. One gram of glycol on 30 ml. of 37% formaldehyde was heated on a steam bath for 24 hr. After extraction with ether, drying with magnesium sulfate, and removal of ether, the residual oil was found to be identical to the *m*-dioxane (III) obtained by the method of Beets.[7]

Infrared spectral procedure. The infrared spectra of diols IIa and IIb were determined in spectroquality carbon tetrachloride solution in the OH stretching region, 3200–3800 cm.$^{-1}$ A Perkin-Elmer Model 21 spectrophotometer was employed. The compounds were studied at 0.025*M* and 0.05*M* using a 0.5-mm. path length, and at 0.005*M* using a 1 cm. path length. Assignments are considered to be accurate to ±5 cm.$^{-1}$ for sharp bands.

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Conformational Analysis. XXIII. The 4-Cyclohepten-1-one System[1]

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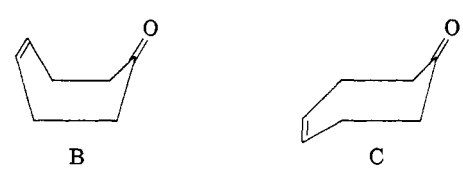
The conformation of the 4-cyclohepten-1-one system was investigated by studying the dipole moments of three compounds, 5,6,8,9-tetrahydro-7*H*-cycloheptabenzen-7-one (I), bicyclo[5.4.0]undecan-4-one (II), and 6,7,8,9-tetrahydro-5*H*-cycloheptabenzene (III). It was concluded that an equilibrium mixture of chair and boat forms existed in which the former predominated to the extent of about 92%. This result was interpreted as being primarily due to van der Waals repulsion forces which destabilize the boat form.

While the six-membered ring system has been studied intensively from the conformational viewpoint,[2] relatively little is known about the seven-membered ring. Some detailed calculations have been carried out regarding the geometry of cycloheptane,[3–5] some more approximate ones regarding cycloheptene[5] and cycloheptanone,[4] and there is a variety of evidence available[6] which indicates the flexibility of the ring. The reason for the contrast in our knowledge regarding six- and seven-membered rings is that while simple cyclohexane derivatives exist as a mixture of two chair forms separated by a large energy barrier, the corresponding cycloheptane exists (in general) as a mixture of fourteen chair forms and a similar number of boat forms, separated for the most part by small barriers.

In the present work the goal was to determine the exact conformation of a seven-membered ring. The 4-cyclohepten-1-one system has been examined for a number of reasons, the two most important being that the double bond puts a rigidity into the system which reduces the number of possible conformations to two, and it presents a system in which we may gain some idea of the correctness of earlier assumptions made regarding the van der Waals' repulsion between the π electrons of sp^2 hybridized carbons.[7]

Examination of scale models showed that the compound has only two conformations (energy minima), which will be called the boat (B) and the chair (C). Because of the easier availability of the compounds, the benzenoid derivative (I) of the



B C

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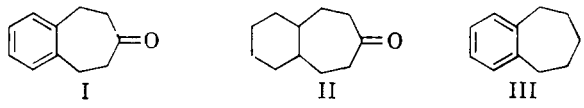

I II III

system was actually studied. The dipole moments of II and III were measured and found to have the values 3.08 ± 0.03 and 0.63 ± 0.09 D, respectively. These values were used for the moments of the individual dipoles of I. Dreiding scale models were then constructed for the two conformations of I, and the angles between the dipoles were measured. They were found to have the values 59° for the boat (B) and 170° for the chair (C). Using these angles, together with the group moments, the dipole moments of B and C were calculated to be 3.44 ± 0.06 and 2.46 ± 0.11 D, respectively.

The observed moment for I was 2.55 ± 0.03 D. From Equation (1) where μ_B and N_B are re-

$$\mu^2 = N_B\mu_B^2 + N_C\mu_C^2 \quad (1)$$

spectively the moment and the mole fraction of B and μ_C and N_C have the corresponding meaning with respect of C, the conformational composition of the mixture was calculated. It was found that 92% of the compound existed as the chair, and the remainder as the boat form.

The accuracy to which the moment of the hydrocarbon was determined is the limiting factor in determining the accuracy of the results. The actual experimental error in the polarization measurements was no more than 0.02 D, but because of the small moment, the atomic polarization introduces a sizable uncertainty. A value of 2 cc. has been assigned arbitrarily to this quantity, which amounts to about 5% of the electronic polarization. Values of 1% to 8% are typical for hydrocarbons,[8] so the error in the atomic polarization is taken as ±2 cc. While this procedure is somewhat arbitrary, the estimate of the probable error is regarded as generous, and it is expected that the final results are likely to be better than indicated by the probable errors.

Because of the uncertainty introduced by the atomic polarization, there is considerable uncertainty in the chair-boat equilibrium. The most probable value is 92% chair form, corresponding to an energy difference of 1.4 kcal./mole. The limits of uncertainty are such that the amount of chair form may be anywhere from 82–100%, and the energy difference is therefore greater than 0.91 kcal./mole, but no upper limit can be set.

The close inspection of Dreiding scale models of the two conformers B and C was made in an effort to obtain a theoretical basis for the observed result. It was found that the ethane type rotational barrier[4] did not make any significant contribution to the equilibrium, since the conformers have the same dihedral angles.

To simplify the calculation of the equilibrium constant, two assumptions were made. The first of these was that the ratio of the partition functions for the two conformers was unity. Such an approximation is known to be a good one if the conformations have the same symmetry properties.[9] The second assumption was that the calculations made can neglect the interaction of the two dipoles and solvation effects. Solvation of a dipole lowers its energy, and since the moments are different for the two conformations, solvation will shift the equilibrium. This effect has been studied in detail in a number of cases.[10] Since the difference in the dipole moments of the two conformations is not very large, and since the moments are rather far separated, these effects should be small enough to neglect.

It was noted that an appreciable van der Waals' repulsion between the carbons of the double bond and the carbonyl carbon was to be expected in the boat, but not in the chair form. Pauncz and Ginsburg[5] predicted the boat form of cycloheptene would be of lower energy than the chair, but they neglected the analogous van der Waals' interaction.[11] For cycloheptenone an estimate of the energy in question was arrived at in the following way. It has been shown[12] that an approximate van der Waals' energy can be calculated for any pair of atoms in terms of two parameters, α and ϵ. The first of these parameters is equal to the ratio of the actual distance between atomic centers (2.7 Å in B) to the sum of the van der Waals' radii (1.70 + 1.70[13] = 3.40 Å for the two carbon atoms) and is equal to 0.79 for B. The second parameter is a measure of the amount of energy required to bring the atoms in question together (107 cal./mole for carbon atoms[13]). From these quantities and Hill's equation it is found here that $U/\epsilon = 8.5$, so $U = 0.91 \pm 0.30$ kcal./mole. Since two such repulsions exist in B, the total repulsion energy is 1.8 ± 0.6 kcal./mole.

The equilibrium constant between the two conformers was calculated from the equation, $-\Delta F^\circ = RT\ln K$, where ΔF° is taken as equal to U. These calculations revealed that the equilibrium mixture should contain from 89 to 98% of C at 25°. This value is in agreement with the experimental value of 92 ± 10% observed for compound I.

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(9) For example see C. W. Beckett, K. S. Pitzer, and R. Spitzer, *J. Am. Chem. Soc.*, 69, 2488 (1947).

(10) For example J. Allinger and N. L. Allinger, *Tetrahedron*, 2, 64 (1958).

(11) Pauncz and Ginsburg considered only the hydrogen-hydrogen interactions and concluded the boat form of cycloheptene was of lower energy than the chair by 0.67 kcal./mole. A van der Waals' calculation as outlined in this paper gave a repulsion energy between the double bond carbons and the near hydrogen at the "prow" of the boat of 4.6 kcal./mole. This value is so large that all things considered, it seems safe to predict the chair will be the stable form of cycloheptene.

(12) T. L. Hill, *J. Chem. Phys.*, 16, 399 (1948).

(13) Unpublished determination of the authors.

EXPERIMENTAL

5,6,8,9-Tetrahydro-7H-cycloheptabenzen-7-one (I). The condensation of phthaldehyde[14] and diethyl acetonedicarboxylate[15] was carried out by the method of Tarbell and Wargotz[16] and gave diethyl 7-oxo-7*H*-cycloheptabenzene-6,8-dicarboxylate (IV) in 56% yield, m.p. 96–96.5° (reported m.p. 96–97°). Reduction of this compound by the method of Tarbell and Wargotz, except using a palladium on carbon catalyst, gave the tetrahydro derivative of IV (V) in 98% yield, m.p. 89–101° (reported,[16] m.p. 99–102°).

A mixture of 25.53 g. (0.079 mole) of V, 50 ml. of ethanol, and 300 ml. of 30% sulfuric acid was heated under reflux for 36 hr. After this time evolution of carbon dioxide had ceased, and a two-phase mixture was obtained. The ethanol which was formed during the reaction was removed by distillation until the product began to steam distill. Steam distillation was continued until 2.5 l. of distillate had been collected. After the distillate had been saturated with sodium sulfate it was extracted continuously with ether for 12 hr. The ether extract obtained was dried over sodium sulfate and the solvent was removed. The colorless product was recrystallized from 35–42° petroleum ether and then from purified *n*-pentane. The yield of final pure product was 12.0 g. (91.5%), m.p. 43–43.8° (lit.[17,18] 41–42, 42–43°).

Bicyclo[5.4.0]undecan-4-ol (VI). Ten grams of I was hydrogenated at atmospheric pressure and room temperature in 200 ml. of glacial acetic acid with 1 g. of platinum oxide. The catalyst was removed by filtration and the solvent was evaporated. The residue was heated under reflux for 1 hr. in 100 ml. of 50% ethanol containing 5 g. of potassium hydroxide. The solution was diluted with water and extracted with ether. The extracts were dried, the solvent was removed and the product was distilled, b.p. 115–117° (5 mm.), wt. 8.27 g. (79.5%) $n^{25}D$ 1.5030.

Anal. Calcd. for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.26; H, 11.73.

Bicyclo[5.4.0]undecan-4-one (II). A solution of 6.52 g. of VI in 125 ml. of redistilled acetone was titrated with 5.23 ml. of Jones[19] reagent. The mixture was filtered to remove the inorganic salts and the solvent was evaporated. After 50 ml. of water had been added to the liquid residue, the mixture was extracted with ether. The ether layer was dried and the ether was evaporated. The liquid residue was dissolved in 80 ml. of 80% ethanol and 6 g. of semicarbazide hydrochloride and 9 g. of sodium acetate were added. The mixture was shaken well, placed briefly into a beaker of water at 80°, and was allowed to cool to room temperature. After 3 hr. the white powdery semicarbazone was collected, washed with water, and recrystallized five times from absolute alcohol. The crystalline semicarbazone was collected, yield 10 g., m.p. 235° (d).

Anal. Calcd. for $C_{12}H_{21}N_3O$: C, 64.52; H, 9.48. Found: C, 64.35; H, 9.67.

A 10% hydrochloric acid solution containing 5.00 g. of the semicarbazone was heated under reflux for 2 hr. The liberated ketone was extracted with ether, and the extracts were dried, the solvent was removed and the product was distilled, b.p. 121.5–122° (8 mm.), $n^{25}D$ 1.4969.

Anal. Calcd. for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.19; H, 10.68.

6,7,8,9-Tetrahydro-5H-cycloheptabenzene (III). Benzsuberone (6,7,8,9-tetrahydro-5*H*-cycloheptabenzen-5-one)[20] was reduced to the hydrocarbon by the Huang-Minlon method following essentially the procedure of Cogneant.[21] The product had b.p. 72° (4 mm.), $n^{20}D$ 1.5400 (reported, b.p. 101° (15 mm.), $n^{16}D$ 1.5495.

TABLE I. DIPOLE MOMENT DATA
(Benzene solution, 25°)

N_2	d_{12}	ϵ_{12}
5,6,8,9-Tetrahydro-7*H*-cycloheptabenzen-7-one (I)		
0.00000000	0.873133	2.2712
0.00113352	0.873593	2.2819
0.00227254	0.873999	2.2924
0.00283742	0.874228	2.2979
0.00444513	0.874740	2.3124
α = 9.278	β = 0.363	ϵ_1 = 2.2713
d_1 = 0.87316	$P_{2\infty}$ = 180.00	$P_e + P_a$ = 47.37 cc.
μ = 2.55 ± 0.03 D		
Bicyclo[5.4.0]undecan-4-one (II)		
0.00000000	0.873458	2.2715
0.00143541	0.873594	2.2914
0.00316078	0.874063	2.3136
0.00491837	0.874693	2.3365
0.00596259	0.874750	2.3501
α = 13.140	β = 0.250	ϵ = 2.2719
d_1 = 0.87334	$P_{2\infty}$ = 242.2	$P_e + P_a$ = 48.73 cc.
μ = 3.08 ± 0.03 D		
6,7,8,9-Tetrahydro-5*H*-cycloheptabenzene (III)		
0.00000000	0.873226	2.2718
0.0041987	0.873870	2.2750
0.0130935	0.875201	2.2826
0.0162687	0.875661	2.2853
0.0198679	—	2.2879
0.0251041	0.876969	2.2926
α = 0.8288	β = 0.149	ϵ = 2.2717
d_1 = 0.87324	$P_{2\infty}$ = 57.50	$P_e + P_a$ = 49.40 cc.
μ = 0.63 ± 0.09 D		

Dipole moments. The dipole moments were determined by measuring the dielectric constants and densities of solutions of the compound at various mole fractions in benzene at 25° using the apparatus previously described.[22] The molar refractivities were obtained from the data of Vogel.[23] Atomic polarization was neglected except for III where 2 cc. was added to the molar refractivity. The calculations were made following essentially the procedure of Halverstadt and Kumler[24] using an IBM 650 computer as described earlier.[25] The data are summarized in Table I.

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