until nitrogen evolution ceased (8 hours). The reaction mixture was cooled, diluted with water, and the hydrocarbon was steam distilled. The combined distillates were extracted with pure pentane. The combined pentane solutions were washed and dried, and the pentane was removed by fractional distillation. After distillation the hydrocarbon had b.p. 196.5°, $n^{25}D$ 1.4744, d^{25} 0.8940, yield 2.3 g. (70%). Gas phase chromatography showed the compound was substantially better than 99% pure; reported[8] $n^{20}D$ 1.4761, d^{20} 0.8833.

Anal. Calcd. for C_9H_{16}: C, 87.10; H, 12.90. Found: C, 86.83; H, 12.66.

trans-1,2-Bis-(hydroxymethyl)-cyclopentane (IIIb).—Diester IIb was reduced with lithium aluminum hydride to the diol, b.p. 128–130° (2.5 mm.), $n^{26}D$ 1.4773 (reported[13] b.p. 147° (11 mm.), $n^{22}D$ 1.4760).

trans-1,2-Bis-(bromomethyl)-cyclopentane (IVb).—Diol IIIb was converted to the dibromide in a manner similar to that described for the preparation of IVa; yield 66%, b.p. 75–77° (1.3 mm.), $n^{25}D$ 1.5336.

Anal. Calcd. for $C_7H_{12}Br_2$: C, 32.83; H, 4.72. Found: C, 32.88; H, 4.63.

trans-1,2-Bis-(cyanomethyl)-cyclopentane (Vb) was prepared from dibromide IVb as described for the preparation of Va from IVa; yield 65%, b.p. 120–121° (0.75 mm.), $n^{24.5}D$ 1.4708.

Anal. Calcd. for $C_9H_{12}N_2$: C, 72.94; H, 8.16. Found: C, 72.75; H, 7.86.

trans-1,2-Bis-(carbethoxymethyl)-cyclopentane (VIb).—Nitrile Vb was converted to the ester as described for the conversion of Va to Via. The yield was 65%, b.p. 99–118° (0.8–1.7 mm.), $n^{25}D$ 1.4477.

Anal. Calcd. for $C_{13}H_{22}O_4$: C, 64.44; H, 9.16. Found: C, 64.42; H, 8.87.

trans-1,2-Bis-(β-cyanoethyl)-cyclopentane (IXb).—Diester VIb was reduced to the diol with lithium aluminum hydride as described for the preparation of VIIa; the crude product was converted to the dinitrile as described for the preparation of IXa. The dinitrile was distilled; b.p. 147–148° (0.75 mm.), $n^{25}D$ 1.4715, over-all yield 40%.

Anal. Calcd. for $C_{11}H_{16}N_2$: C, 74.95; H, 9.15. Found: C, 74.70; H, 9.35.

trans-Bicyclo[5.3.0]decanone-4 (Xb).—The cyclization of IXb, the hydrolysis and the decarboxylation all paralleled the conversion of IXa to Xa. The semicarbazone of Xb was isolated in 48% yield, m.p. 170–175° (reported[15] m.p. 178°).

trans-Bicyclo[5.3.0]decane (XIb).—The hydrocarbon was prepared from the ketone Xb as described for preparation of the *cis* isomer XIa; b.p. 190.5° (746 mm.), $n^{25}D$ 1.4717, d^{25} 0.8816; reported[8] $n^{20}D$ 1.4751, d^{20}_4 0.8794. Gas chromatography showed the hydrocarbon was better than 99% pure.

Anal. Calcd. for $C_{10}H_{18}$: C, 86.99; H, 13.12. Found: C, 86.71; H, 13.42.

Equilibration Studies.—A 100-mg. sample of the hydrocarbon to be equilibrated together with 20 mg. of 10% palladium-on-carbon was sealed in a tube with a total volume of about 0.2 ml. or less. The tube was heated in an iron pipe in a furnace at the desired temperature ±1.5°. At the end of the heating period, the equilibration was quenched by plunging the iron pipe into an ice-bath. The catalyst was centrifuged to the bottom, the tube was opened and the sample was withdrawn.

Vapor phase chromatography on the following columns failed to separate the isomeric perhydroazulenes: squalene on florex; tricresyl phosphate, silicone grease, tricyanoethylation product of glycerol and γ-methyl-γ-nitropimelonitrile, all on firebrick. The analysis was therefore carried out by the infrared method. Synthetic mixtures could be analyzed to ±1% by using bands at 10.14 μ (*cis*) and 11.05 μ (*trans*). The data are summarized in Table I.

TABLE I

DATA FOR THE REACTION *cis*- ⇄ *trans*-DECAHYDROAZULENE

T, °K.	Starting isomer	% trans/% cis	K_e
494	*trans*	59.4/37.8	1.71
511	*cis*	59.6/36.3	1.67
532	*cis*	55.6/36.9	1.507
	trans	56.8/37.5	1.515
548	*cis*	57.5/36.8	1.563
	trans	58.1/38.1	1.525
576	*cis*	53.4/35.6	1.500
	trans	56.9/37.8	1.505

[CONTRIBUTION FROM THE LYMAN LABORATORY, HARVARD UNIVERSITY, CAMBRIDGE 38, MASS.]

The Nuclear Magnetic Resonance Spectra of the 10-Methyldecalols-2

BY J. I. MUSHER

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The high-resolution n.m.r. spectra of the four isomers of 10-methyldecalol-2 were studied. The data show that the ring configuration greatly affects the resonance position of the angular methyl hydrogens and that there is also a smaller effect due to the hydroxyl group being either *cis* or *trans* to the methyl group. Comparisons are made with similar data in the literature. In addition, the spectra from the 2-hydrogens are discussed and a method of identification for molecules of unknown hydroxyl conformation is examined.

The high-resolution n.m.r. spectra of the four possible isomers of 10-methyldecalol-2 were obtained at 60 Mc./s. Single recordings of these spectra are reproduced in Fig. 1. The samples were dissolved in degassed CS_2 and the usual spinning technique was employed. Frequency shifts were measured relative to internal hexamethyldisiloxane and the data are presented so that a positive shift from the standard signifies that the peak lies to *low* field.[1] The peak separations were calibrated by the use of audio sidebands from a variable frequency oscillator whose frequency was monitored by a cycle counter. The field was swept upfield and downfield on alternate calibrations in order to minimize the effect due to drift. Four calibrations were made for each spectrum and the standard deviations for the peak positions relative to the standard were less than 0.2 c./s. or 0.003 p.p.m. for the methyl peaks and less than 0.5 c./s. or 0.008 p.p.m. for the 2-hydrogen peaks.

Angular Methyl Groups.—The chemical shifts in p.p.m. to low field relative to internal hexamethyldisiloxane for the methyl groups in the four isomers of 10-methyldecalol-2 are listed in Table I along with data from the literature for 10-methyl-*cis*-decalin[2] and five steroid molecules[2,3] approximately

(1) The reversal of sign from the usual convention is so chosen to avoid the continual repetition of minus signs.

(2) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp. 291–292.

(3) J. N. Shoolery and M. T. Rogers, *J. Am. Chem. Soc.*, **80**, 5121 (1958).

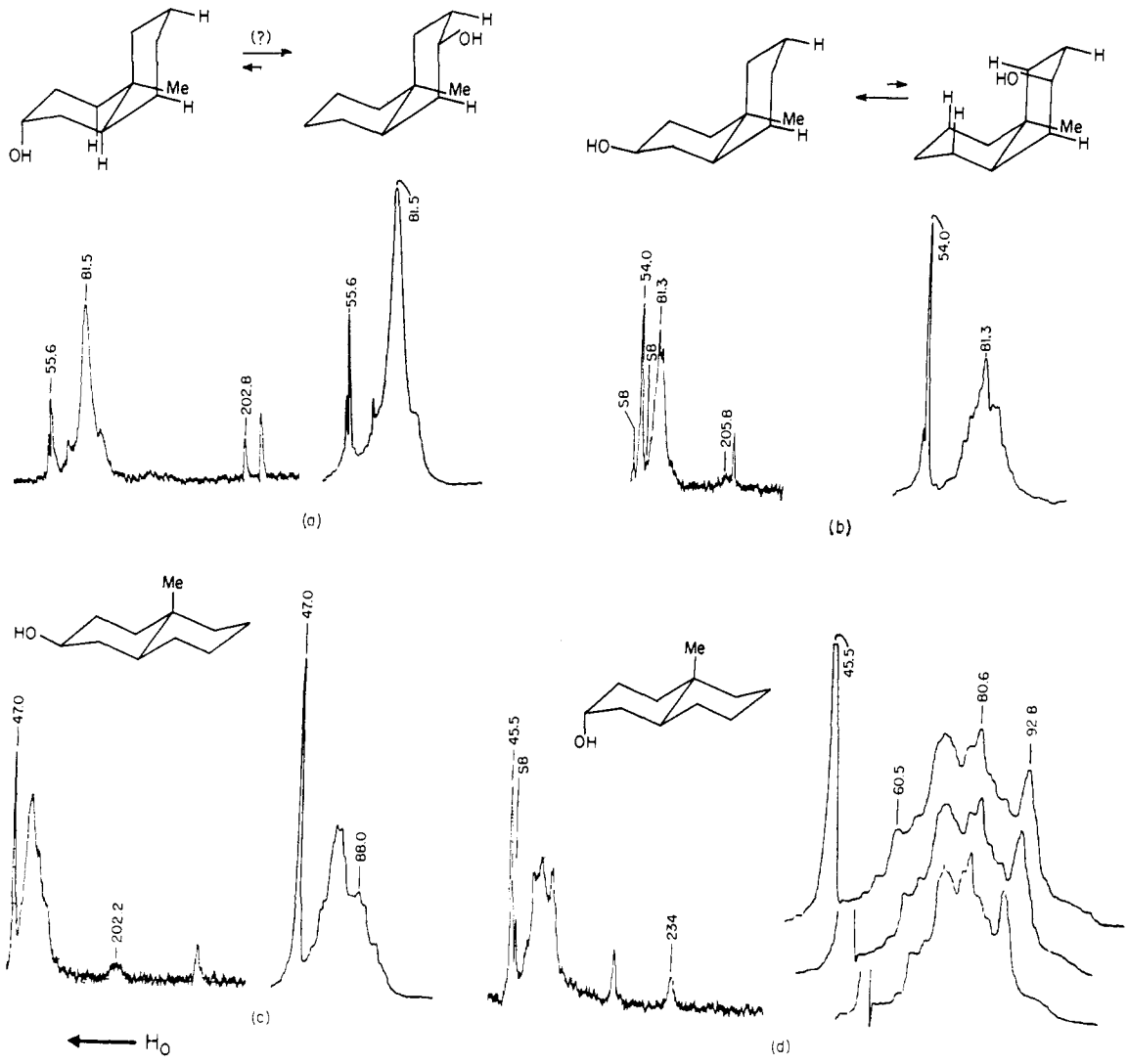

Fig. 1.—Conformations and reproductions of individual 60 Mc./s. n.m.r. spectra of the isomeric 10-methyldecalols-2: (a) 10-methyl-*cis*-decal-*cis*-2-ol, (b) 10-methyl-*cis*-decal-*trans*-2-ol, (c) 10-methyl-*trans*-decal-*cis*-2-ol and (d) 10-methyl-*trans*-decal-*trans*-2-ol. Peak positions are reported in c./s. relative to internal hexamethyldisiloxane and serve as approximate scale factors. They do not, however, refer to the individual spectra reproduced but rather to the average over a number of spectra as indicated in the text. Detailed data are reported in the tables.

The spectra on the left for each isomer show the entire absorption taken at a single power level and at a fast sweep rate on a Varian recorder. However, for determinations of specific peak positions the individual parts of the spectra were examined at appropriate power levels and sweep rates and calibrated separately. The right-hand spectra for each isomer show the methyl and ring-hydrogen absorptions taken at a slower sweep rate on a Texas Instrument Co. recorder. Several spectra of (d) run at slightly different sweep rates are shown in order to indicate the reproducibility of the overlapping multiplet structure. All spectra are reduced from the originals by a common scale factor.

referred to the same standard.[4] The assignment of peaks to the methyl groups on the 10- and 13-carbon atoms for the two androstane-3-ol-17-one isomers[3] have been reversed from their original assignments for reasons to be discussed below.

From the data on the 10-methyldecalols-2 we see that the angular methyl peak for a *trans*-decalol lies 0.142 p.p.m. to high field from the position for the corresponding *cis*-decalol and that when the 2-hydroxyl group is *cis* to the methyl group the methyl peak will occur at 0.026 p.p.m. to low field from its position when the two substituents are *trans*.[5]

It is not in general possible to compare chemical shift data from n.m.r. spectra taken in different solvents with different concentrations and with different referencing. Thus the chemical shift is a poor parameter to be uniquely related to a func-

(4) Considering 7.65 and 6.325 p.p.m. as the chemical shift differences between our standard, hexamethyldisiloxane, and chloroform and external benzene, respectively.

(5) The same effect (0.024 p.p.m.) is observed in the *cis*- and *trans*-4-methylcyclohexanols,[6] although here the methyl group is principally equatorial in both isomers while the methyl group is axial to the hydroxyl-containing ring in the *trans*-decalols and in one of the *cis*-decalols and is equatorial to the hydroxyl-containing ring in the other *cis*-decalol. The relative distances and angles are not, therefore, the same in all these examples.

(6) J. I. Musher, unpublished data.

tional group within a specific molecule. However in solvents, which are neither aromatic nor associating such as through hydrogen bonds, the chemical shift referred to the same internal standard is practically invariable. It is also possible when such solvents are employed to correlate within a few c./s. the line positions of many internal standards such as cyclohexane, chloroform and hexamethyldisiloxane; and the same can be done for external standards although under more stringent conditions. Also when the compounds involved are very similar, and do not associate intermolecularly, the effects of different concentrations will be relatively insignificant. But what is most important is that under most conditions, although again only in the proper solvents, small *differences* in chemical shifts are to a great degree completely independent of all three experimental variables: solvent, standardization and concentration. Thus, as long as we recognize the limitations of our correlations and place the greatest weight on data taken under the same experimental conditions, we can compare the above data on the 10-methyldecalols-2 with the data of Pople, *et al.*,[2] and Shoolery and Rogers[3] as listed in Table I.

TABLE I
ANGULAR METHYL CHEMICAL SHIFTS[a]

Compound	$\delta_{10\text{-methyl}}$	$\delta_{13\text{-methyl}}$
10-Methyl-*cis*-decal-*cis*-2-ol	0.927	
10-Methyl-*cis*-decal-*trans*-2-ol	.900	
10-Methyl-*trans*-decal-*cis*-2-ol	.784	
10-Methyl-*trans*-decal-*trans*-2-ol	.758	
10-Methyl-*cis*-decalin[2]	.87	
Androstane[2] (A/B *trans*)	.75	0.65
Etiocholane[2] (A/B *cis*)	.87	.65
Androstane-3α-ol-17-one[3]	.75	.80
Androstane-3β-ol-17-one[3]	.775	.80
Etiocholane-3α-ol-17-one[3]	.85	.75

[a] Chemicals shifts, δ, are given in p.p.m. to *low* field relative to internal hexamethyldisiloxane. Shifts from refs. 2 and 3 have been referred to the same standard. (It is assumed that there is a misprint in ref. 2 and that chloroform is meant as the standard and not benzene.)

Pople, *et al.*, find the 10-methyl peak to be 0.12 p.p.m. to lower field in etiocholane—a steroid whose A/B rings are *cis* linked—from its position in androstane—the same steroid except that its A/B rings are *trans* linked—and this is close to the value of 0.142 p.p.m. observed for the 10-methyldecalols-2. This correlation serves to justify better the assignment of the 10- and the 13-methyl peaks in these steroids instead of on the basis of the position of the methyl peak in 10-methyl-*cis*-decalin. It is only fortuitous that the 10-methyl groups in 10-methyl-*cis*-decalin and etiocholane exhibit identical chemical shifts, since in general the addition of the C and D rings to the decalin would be expected to affect the shift of the 10-methyl group.[7] In assigning the peaks in these steroids it would have been desirable to examine the spectrum of 10-methyl-*trans*-decalin and compare methyl peaks from the pair of steroids with those from the *pair* of decalins thus eliminating the effect, expected to be almost identical in both steroids, of the added C and D rings. The assignment of the peaks in the steroids might be further justified by the constancy of the 13-methyl peaks for both A/B structures—the changing of which is a relatively distant phenomenon—yet the same change in structure in the androstane–etiocholane-3α-ol-17-one pair does cause a shift of the 13-methyl peak by 0.05 p.p.m.

Shoolery and Rogers[3] find that in general a 13-methyl peak will appear to high field from a 10-methyl peak and they assign these peaks throughout the steroids they have studied on this basis. From such assignments in the case of the androstane-3-ol-17-ones and etiocholane-3α-ol-17-one these authors conclude that the type of A/B ring linkage does not significantly affect the position of resonance of the 10-methyl group. However in these molecules the 17-ketone considerably deshields the 13-methyl group—as does the hydroxyl group in *trans*-2-methylcyclohexanol whose methyl peak is 0.112 p.p.m. to low field from that of methylcyclohexane[6]—so that the peaks from the 10- and 13-methyl groups almost overlap. In fact, they actually do cross for the two androstane derivatives, an observation which is justified by the data from the 10-methyldecalols-2. If we therefore reassign the peaks for the androstane-3α- and 3β-ol-17-ones as is done in Table I we find that the isomer with the α-OH and the *cis*-A/B ring linkage has its 10-methyl peak 0.10 p.p.m. to high field from that of the isomer with the α-OH but with the *trans*-A/B ring linkage. This is of the same order as the 0.142 and 0.12 found above. Furthermore, the shift of 0.025 p.p.m. to low field in androstane-3β-ol-17-one for the peak of the 10-methyl group *cis* to the 3-OH from its position in androstane-3α-ol-17-one where the 10-methyl group is *trans* to the 3-OH, compares favorably with the values of 0.027 and 0.028 from the 10-methyldecalols-2. Shoolery and Rogers note that there is a shift of only 0.025 p.p.m. to high field for the 10-methyl peak going from the *cis*-A/B linkage in pregnane-3,11,20-trione to the *trans*-A/B linkage in its allo isomer. Most probably the deshielding effect of the 3- and 11-ketones which is about 0.30 p.p.m. serves to obscure what would be the smaller effect due to the changing of the A/B ring linkage. Incidentally, it is rather surprising that in this pair of isomers the peaks from the methyl groups on the 13- and 20-carbons are each shifted by 0.05 p.p.m. by the relatively distant change of the A/B ring linkage. This is identical with the occurrence mentioned above in the pair androstane-3α-ol-17-one–etiocholane-3α-ol-17-one, and makes the constancy of such peak positions as in the pair androstane–etiocholane the exception rather than the rule.

(7) For example, the chemical shift of the methyl peak in methylcyclohexane is shifted 0.076 p.p.m. to low field by the addition of a *trans*-4-methyl group in *trans*-1,4-dimethylcyclohexane.[5]

(8) *Cf.* Our comments above on the possible error introduced to these correlations by virtue of the fact that they were not all taken at the same concentration. Since peak separations were reproducible to 1 c./s. in these steroids,[3] the maximum probable error should be 0.5 c./s. or 0.013 p.p.m. and we consider no differences smaller than 1 c./s. or 0.025 p.p.m. Dr. J. Shoolery (private communication) has expressed reservations about drawing conclusions from his chemical shifts of only 1–2 c./s. While we recognize that such shifts are near the limit of experimental significance, we feel that the conclusions here drawn are valid and reasonable.

TABLE II

60 MC./S. RING HYDROGEN DATA[a]

Compound, 10-Methyl-	Chemical shifts in c./s.
cis-Decal-*cis*-2-ol	53.8!, 68.5!, 81.5 (58.1, 92.6)
cis-Decal-*trans*-2-ol	53.3!, 81.3, 87.6, (58.0, 71.6, 74.5, 77.0, 79.1, 85.0)
trans-Decal-*cis*-2-ol	72.7, 88.0 (56.0, 61.7, 64.6, 69.5, 78.0, 83.5, 90.6, 99.3, 103.5)
trans-Decal-*trans*-2-ol	71.6, 80.6, 92.8, (55.8, 60.5, 64.5, 77.9, 84.0, 87.5)

[a] Chemical shifts are given to *low* field relative to internal hexamethyldisiloxane. Subsidiary peaks are indicated in parentheses and peaks marked by exclamation points (!) are discussed in the text.

Ring Hydrogens.—The spectra from the 15 ring hydrogens in the two *trans*-decalols show the same wide envelope of absorption previously reported and attributed to the rigidity of structure.[9] The *cis–cis* isomer shows the comparatively sharp resonance peak generally attributed to rapid ring inversion between energetically identical conformers as in cyclohexane and *cis*-decalin, while the *cis-trans* isomer shows a somewhat broader spectrum—although not approaching the breadth of the spectra in the *trans* isomers—and a very definite multiplicity of peaks. Table II lists the data for the ring hydrogen spectra where the subsidiary peaks are indicated in parentheses and the unusual peaks in the region of angular methyl peaks mentioned below are indicated with exclamation points. From the principal peaks an idea can be obtained of the spectral breadths involved.

The two conformers for the *cis* isomers are shown in Fig. 1. From the 2-hydrogen spectra (below) we can show that each of these isomers is principally in the conformer with the OH group equatorial. We would certainly expect this in the *cis–trans* isomer because of the 1,3-interaction involved when the OH is axial. but are more surprised to find it so in the *cis–cis* isomer where the difference in energy between conformers might be small. However, because of the 2-hydrogen spectrum the sharp peak for the *cis–cis* isomer cannot be attributed to inversion between energetically identical conformers, but is either due to very small differences in chemical shift between the hydrogens around the ring[10] or to whatever phenomenon causes the unusually sharp 2-hydrogen resonance for this isomer (see below).

The two 10-methyl-*cis*-decalols-2 also show additional field dependent spectral peaks in the region of the angular methyl peaks. In 10-methyl-*cis*-decal-*trans*-2-ol there is a sharp peak at 0.89 p.p.m. of intensity about one-tenth that of the methyl and in 10-methyl-*cis*-decal-*cis*-2-ol there is a pair of sharp peaks at 0.898 and 1.140 p.p.m. each of intensity about one-third that of the methyl peak. Such peaks have not been observed in other decalols nor in the steroids in the literature and no explanation is proposed for their existence.

Hydrogens Adjacent to Hydroxyl Groups.—The chemical shifts of the 2-hydrogens (on the ring carbon containing the OH group) for the four decalols are given in Table III along with their full width at half-height (half-width or $W_{1/2}$). Lemieux, *et al.*,[15] have given a discussion of such resonance peaks based on the 4-*t*-butylcyclohexanols and their acetates and the data presented here along with much other unpublished data[6] and those on the chemical shifts in steroids of Shoolery and Rogers[3] are in agreement with and serve to generalize further their findings.[16]

TABLE III

2-HYDROGEN DATA[a]

Compound, 10-Methyl-	δ	$W_{1/2}$	H-conformation
cis-Decal-*cis*-2-ol	3.38	2.5	Axial
cis-Decal-*trans*-2-ol	3.43	21.0	Axial
trans-Decal-*cis*-2-ol	3.37	19.5	Axial
trans-Decal-*trans*-2-ol	3.90	6.7	Equat.

[a] Chemical shifts, δ, are given in p.p.m. to *low* field relative to internal hexamethyldisiloxane. Half-widths, $W_{1/2}$, are given in c./s.

(9) J. I. Musher and R. E. Richards, *Proc. Chem. Soc.*, 230 (1958), and ref. 2, p. 399.

(10) It must be remembered that a sharp resonance for a molecule inverting between energetically equivalent conformers requires that *all* ring hydrogens be in the time-average magnetically equivalent (see J. S. Waugh and F. W. Dobbs, *J. Chem. Phys.*, **31**, 1253 (1959), for a discussion of magnetic equivalence)—a condition only truly fulfilled in the unsubstituted saturated single ring structures: cyclohexane, cyclopentane, etc. In fact, it is only fortuitous that the spectrum for *cis*-decalin shows a single peak, for even in the time-average for which there is no distinction between axial and equatorial hydrogens there are still three types of hydrogens—at the bridgehead, α to the bridgehead and β to the bridgehead—which might all be magnetically different each giving a peak of its own and spin–spin coupling with the others. In *cis*-hydrindane,[11] for example, there are two peaks of equal intensity, one of which corresponds to the methylene hydrogens of the 6-membered ring and the other of which corresponds to the methylene hydrogens of the 5-membered ring *and* the two bridgehead hydrogens. These tertiary hydrogens are then magnetically different from the other hydrogens on the six-membered ring unlike the case of *cis*-decalin. Similarly,[12] the inverting *cis*-1,2- and *cis*-1,4-dimethylcyclohexanes happen to show a sharp ring hydrogen resonance, but the inverting *trans*-1,3-dimethylcyclohexane shows a two-peaked structure, one peak of which might be due to the pair of hydrogens at the 2-position "sandwiched" between the two methyl groups. Thus a spectrum of several peaks does not preclude the possibility of ring inversion, but also a single-peaked sharp spectrum does not necessarily imply ring inversion. The latter statement would be true were all the hydrogens in the rigid molecule magnetically non-equivalent, a condition which is not generally valid. The prevalent belief is that even if all the axial hydrogens around the ring have the same magnetic shielding, σ_A, and all the equatorial hydrogens around the ring have the same magnetic shielding, σ_E, σ_A will be significantly greater than σ_E thus making all the hydrogens magnetically non-equivalent as in cyclohexane itself.[13] An instance in which this is not the case has recently been examined[14] and thus care must be taken when this postulate is employed. Therefore, only when a spectrum is decidedly broadened at low temperatures or narrowed at high temperatures (due to equalizing the equilibrium ratio of the two conformers) can any conclusions be drawn about ring inversion and hence the energy barriers. In the instance that *all* the hydrogens around the ring are magnetically equivalent in the rigid conformers the ring spectrum will appear sharp at all temperatures and no conclusions as regards inversion will ever be possible from the n.m.r.

(11) "A Catalogue of the Nuclear Magnetic Resonance Spectra of Hydrogen in Hydrocarbons and their Derivatives," N. F. Chamberlain, Editor, Humble Oil and Refining Co., Baytown, Texas, 1958, p. 30.

(12) J. I. Musher, *Spectrochim. Acta*, **16**, 835 (1960).

(13) F. R. Jensen, D. S. Noyce, C. S. Sederholm and A. J. Berlin, *J. Am. Chem. Soc.*, **82**, 1256 (1960).

(14) J. I. Musher, *J. Chem. Phys.*, in press.

(15) R. U. Lemieux, R. K. Kullnig, H. J. Bernstein and W. G. Schneider, *J. Am. Chem. Soc.*, **80**, 6098 (1958).

(16) There is a significant disagreement: Lemieux, *et al.*, show only a 0.12 p.p.m. shift to low field for the equatorial 1-hydrogen in *cis*-4-*t*-butylcyclohexanol relative to the axial 1-hydrogen in *trans*-4-*t*-butylcyclohexanol. Apparently they have inverted the assignment of the hydrogen and the hydroxyl peaks in the *cis* isomer thus obscuring the first aspect of these spectra discussed below. At our suggestion Prof. Lemieux has re-examined this spectrum (*J. Am. Chem. Soc.*, Erratum

The two aspects of the spectra involved are the chemical shifts and the half-widths of the hydrogen peaks. In the methylcyclohexanols[6] an axial hydrogen adiacent to an (equatorial) hydroxyl lies between 2.92 and 3.50 p.p.m. and an equatorial hydrogen adjacent to an (axial) hydroxyl lies between 3.68 and 4.10 p.p.m. The difference in the chemical shifts for such hydrogens for any pair of isomers differing only in the orientation of the hydroxyl group are in the range 0.4–0.7 p.p.m. with the equatorial hydrogen appearing to lower field. The 2-hydrogen peaks from the 10-methyl-*trans*-decalols-2 are at 3.37 p.p.m. for the axial hydrogen and 3.90 p.p.m. for the equatorial hydrogen with a difference of 0.53 p.p.m., all within the aforementioned ranges. The two *cis*-decalol isomers have their 2-hydrogen peaks at 3.38 and 3.43 p.p.m. which indicates that most probably they are both principally in the conformation with the hydroxyl group equatorial.

In the *cis*- and *trans*-4-*t*-butylcyclohexanols and their acetates, Lemieux, *et al.*, found half-widths of 7 c./s. for the equatorial 1-hydrogens and 22 c./s. for the axial 1-hydrogens. For the 10-methyl-*trans*-decalols-2 the half-widths are 6.7 and 19.5 c./s. for the equatorial and axial hydrogens, respectively, in agreement with these observations as are also the data on the methylcyclohexanols.[6] Thus, given a single isomer, which is either rigid or has an energetically favorable conformer, containing a secondary hydroxyl group of unknown conformation, it should be possible to assign this conformation uniquely on the basis of either the half-width of the tertiary hydrogen peak or its chemical shift. If the other isomer is also available its spectrum will provide added justification for this assignment. Similar assignments are possible for hydrogens adjacent to acetoxy groups,[15] halides,[17] carboxylic acids[6] and most probably ethynyl groups.

The half-width of the 2-hydrogen peak in 10-methyl-*cis*-decal-*trans*-2-ol is 21 c./s., but that of the 2-hydrogen peak in 10-methyl-*cis*-decal-*cis*-2-ol is 2.5 c./s. The former is what we would expect for an axial hydrogen—that both of these decalols should be principally in the conformer with the OH equatorial was mentioned above—but the latter is smaller than we would expect for *either* conformation. Thus in some way, the spin–spin coupling between the 2-hydrogen and the 1- and 3-hydrogens is averaged out by the ring inversion to less than it would be in either of the two rigid conformations and far less than the 20 c./s. expected on the basis of the chemical shift data. There is at present no explanation for this highly unusual phenomenon.

It is instructive to examine for a moment further the data of Lemieux, *et al.* They have determined the axial–axial coupling constant, $J_{aa} = 9.0$ c./s. in $1\alpha,3\alpha$-dimethoxy-2β-acetoxycyclohexane, and the axial–equatorial coupling constant, $J_{ae} = 2.6$ c./s. and the apparent $J_{aa} = 6.4$ c./s. in $1\alpha,3\beta$-dimethoxy-2α-acetoxycyclohexane. The ring hydrogen spectrum of this latter molecule is a single relatively sharp peak as compared with the broad spectrum of the other isomer which probably indicates ring inversion as discussed above. (The spectrum of cyclohexyl acetate at 40 Mc./s. shows the same sharp peak.)[6] However the two conformers are not energetically identical since the doublet character of the OCH_3 lines indicates that the time in each conformation is not the same. We therefore explain the small apparent J_{aa} as the time-weighted average of the two couplings $J_{aa} \rightleftarrows J_{ee}$, and, were both couplings known, the equilibrium ratio between the two conformers could, in principle, be determined. For example, as is currently the practice, let it be assumed that $J_{ee} = J_{ae} = J_{gauche}$.[18] Given the above data and assuming that the true value of J_{aa} does not differ markedly for the two isomers, we determine that $1\alpha,3\beta$-dimethoxy-2α-acetoxycyclohexane spends 60% of its time in the conformation with the acetoxy group equatorial. This implies that the ΔE between the two conformers—which only differ by the orientation of the acetoxy group—is 0.3 kcal./mole. Were the peak positions of the 2-hydrogen or the OCH_3 group in the respective axial and equatorial positions known, the equilibrium ratio could be independently determined and thus justify or not the assumptions made about the coupling constants. Again, temperature studies are necessary for a proper determination of both the coupling constants and the ΔE involved.

Now, based on these coupling constants, an estimate can be given of the maximum full-line width expected for the resonances from the axial and equatorial hydrogens adjacent to hydroxyl groups assuming that they are each coupled with 2 axial and 2 equatorial hydrogens three bonds away. For the equatorial hydrogens this will be 10.4 c./s. with seven-eighths of the total intensity within 5.2 c./s. and for the axial hydrogens this will be 23.2 c./s. with seven-eighths intensity within 18 c./s. These, of course, do show the proper relationship between breadths of spectral peaks due to equatorial and axial hydrogens as noted by Lemieux, *et al.*[15] However what would be the half-widths of such predicted spectra are decidedly smaller than the half-widths observed. We have observed[14] the coupling constants $J_{aa} = 12.35$ c./s. and $J_{ea} = 4.25$ c./s., using which the above calculations predict peaks of seven-eighths total intensity within 8.5 c./s. and 24.7 c./s. for equatorial and axial hydrogens, respectively, in much closer agreement with experiment.

to **80**, 6099 (1958); **82**, 6427 (1960)). We have examined these isomers in CCl_4 solution and find chemical shifts of 3.987 p.p.m. and 3.457 p.p.m. and half-widths of 7.3 c./s. and 18.5 c./s. for the *cis*- and *trans*-4-*t*-butylcyclohexanol, respectively. In principle, when long-range intramolecular effects are unimportant, the comparison of the position of the 1-hydrogen peak in cyclohexanol with these data should provide the energy difference between an axial and an equatorial hydroxyl group. The chemical shift of the 1-hydrogen of cyclohexanol in CCl_4 solution is 3.457 p.p.m. ($W_{1/2} = 18.2$ c./s.) which accidentally is exactly the same as that of *trans*-4-*t*-butylcyclohexanol (although the standard deviation of these shifts is 0.008 p.p.m.). This would imply that the molecule were in the conformer with the hydroxyl group equatorial 100% of the time in contradiction to all expectation. Thus apparently the 4-*t*-butyl group does exert considerable effect on the 1-hydrogen resonance and conclusions based on this type of analysis must be made with caution. (The analytical consequences of this will be published soon by the author.)

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Molecular Complexes of Pyromellitic Dianhydride[1]

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The ability of pyromellitic dianhydride to form molecular complexes is demonstrated for a large number of compounds. Both solid and solution complexes are formed, although the former have more rigorous steric requirements than the latter. Using binary mixtures of the C_8-aromatic hydrocarbons, competitive experiments were performed to determine relative stabilities of their solid complexes. The phenomenon of solid complex formation limits is discussed. Quantitative data, thermodynamic and spectral, are given for the solution complexes of a family of substituted benzenes. These data are compared with other series of complexes and several correlations are drawn. The free energies of formation indicate that pyromellitic dianhydride is among the strongest acceptor molecules known in complex formation.

Introduction

The first molecular complexes, aromatic hydrocarbons with picric acid, were discovered in 1858,[2] and a large number of similar complexes have been discovered since.[3,4] Only a single reference[5] is known to complexes with pyromellitic dianhydride (abbreviated PMDA, the anhydride of 1,2,4,5-benzenetetracarboxylic acid). That work described PMDA complexes with four compounds: tetralin, anisole, veratrol and hydroquinone dimethyl ether. PMDA, in fact, complexes with a wide variety of aromatic hydrocarbons, heteroaromatic compounds, and even some non-aromatic materials. These complexes are of the charge transfer type[6] in which PMDA serves as the electron acceptor or π-acid and a large number of organic materials can serve as the electron donor or π-base.

Discussion

PMDA is sparingly soluble in most organic liquids. However, when solid PMDA is mixed with a suitable electron donor, the solid increases in volume strikingly, changes color from white to yellow, orange or red, and becomes warm. If the solid is collected, it is observed that it has gained more weight than is expected by simple mechanical wetting of the crystals. However, most of the solid complexes are not stable in the absence of excess hydrocarbon. These are the qualitative observations accompanying complexing of PMDA with many compounds. The complex formation can be verified by ultraviolet absorption spectra of the colored solutions. These complexes, both the solids and the solutions, have a 1:1 ratio of the donor and acceptor molecules. This was determined for the solids by weight gain and for the solutions by studying the effect of dilution on the extinction coefficient.

Information obtained on the formation and stability of solid complexes, on the qualitative aspects of solution complexes, and on thermodynamic and spectral data of solution complexes will be discussed in turn.

Solid Complexes.—The formation of solid complexes appears to have important steric as well as electronic demands. Benzene and all the methyl-substituted benzenes up to durene were shown to form solid complexes. On the other hand, none of the following materials form solid complexes at room temperature: ethylbenzene, cumene, *t*-butylbenzene, *o*- and *p*-ethyltoluene, and a mixture of diisopropylbenzenes. The fact that compounds containing these electron-donating substituents do not undergo solid complex formation must mean that the steric requirements are severe. It is possible that the solid complexes are graphite-like with the aromatic compounds in the space between planes. Calculations of closest approach to form such a sandwich structure show that ethyl-substituted compounds should be much less stable than methyl substituted.[7] Both chlorobenzene and *o*-dichlorobenzene fail to form solid complexes, but apparently for electronic reasons since chloro groups are about the same size as methyls. It is interesting to note that at 0° *o*-ethyltoluene, chlorobenzene and *o*-dichlorobenzene form weak complexes.

The relative stabilities of several complexes were determined by competitive experiments. In these experiments a pair of aromatic compounds was mixed with an insufficient amount of PMDA. The mother liquor was separated from the solid complex and examined to determine the new ratio of the aromatic pair. Assuming that the compound suffering the greater depletion formed the more stable complex, in one series the following order was found: durene > *o*-xylene > pseudocumene > mesitylene.

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