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CALIXARENES 9

CONFORMATIONAL ISOMERS OF THE ETHERS AND ESTERS OF CALIX[4]ARENES

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Abstract—Calix[4]arene (**1A**), *p*-t-butylcalix[4]arene (**1B**), and *p*-allylcalix[4]arene (**1C**) have been converted to various derivatives, including the methyl, ethyl, allyl, benzyl and trimethylsilyl ethers and the acetates. Although the parent calixarenes exist preferentially in the cone conformation, they are conformationally flexible and at room temperature interconvert at a rate of *ca* 100 sec^{-1}. All but the methyl ethers, on the other hand, are conformationally rigid at room temperature. The preferred conformations in most cases are the cone and partial cone, depending on the derivative formed (i.e. methyl and ethyl ethers favor the partial cone; benzyl and trimethylsilyl ethers favor the cone). In the cases of the allyl ethers and the acetates the *p*-substituents appear to influence the conformational outcome (i.e. **1A** and **1B** form the allyl ethers in the partial cone and cone conformation, respectively; **1A** and **1B** form the acetates in the 1,3-alternate and partial cone conformation, respectively). The conformationally rigid calixarene derivatives in the cone and partial cone conformations belong to the small group of *synthetic* compounds that contain a permanent cavity (a "changeless calix") whose dimensions are large enough to encapsulate other molecules.

Calixarenes, which are [1_n]metacyclophanes comprising phenolic and methylene units,[1] are conformationally flexible compounds. The smallest of the known calixarenes are the cyclic tetramers, designated as calix[4]arenes (**1**), for which four "up-down" conformations can be specified, *viz* cone (all "up"), partial cone (three "up" and one "down"), 1,2-alternate (two "up" and two "down"), and 1,3-alternate (two "up" and two "down"), as illustrated in Fig. 1. Dynamic ^{1}H NMR measurements of several calix[4]arenes[2-4] have shown that they exist preferentially in the cone conformation but are conformationally mobile at room temperature, interconverting at a rate of *ca* 100 sec^{-1}. The conformational mobility increases as the size of the calixarene increases, and the calix[5]arene, for example, has been shown to have a coalescence point in the dynamic ^{1}H NMR at a considerably lower temperature than that of the calix[4]arenes.[5] Surprisingly, the calix[8]arenes show dynamic ^{1}H NMR characteristics that are almost identical with those of the calix[4]arenes in non H-bonding solvents;[4] this similarity disappears in pyridine solution, however, indicating that the conformational rigidity of the calix[8]arene is due primarily to intramolecular H-bonding. Space-filling molecular models of the calix[4]arenes indicate that in addition to intramolecular H-bond interactions, non-bonded steric hindrance must also play a part in determining the degree of conformational rigidity in these compounds. When a transformation between conformations occurs, an aryl group rotates around the C-2/C-6 axis in a direction that brings the OH groups *through the center* of the macrocyclic ring. While the OH groups experience only a

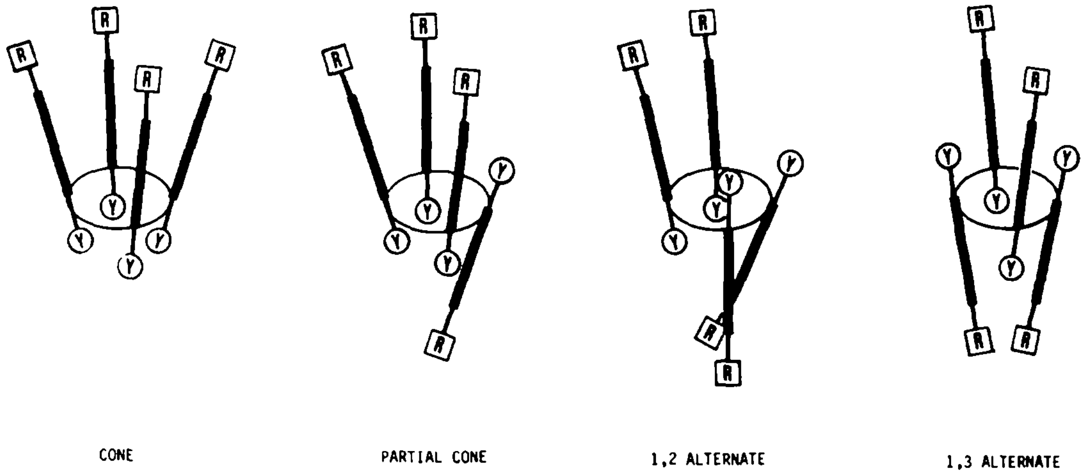
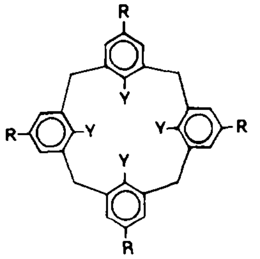


Fig. 1. Conformations of the calix[4]arenes.

modest degree of interference in this process, larger groups would be expected to experience greater interference. The tetra-ethers and tetra-esters of the calix[4]arenes, in fact, are so much less conformationally mobile than the parent compound that in most cases they are frozen into a single conformation at room temperature. Which conformation is preferred when derivatization occurs is the question dealt with in this paper.

NMR spectral characteristics of the conformers of the calix[4]*arenes*. Using *p*-t-butylcalix[4]arene as a specific example, Table 1 shows the ^1H NMR and ^{13}C NMR spectral patterns that would be expected to be observed for each of the four conformers. Inspection of the table suggests that the ^1H NMR spectrum will generally be a better conformational probe than the ^{13}C NMR spectrum, because each of the four conformers displays a distinctively different pattern. On occasion, however, the ^{13}C NMR spectra can provide very useful corroboratory information. Most of the ^1H NMR spectra were obtained on a 100 MHz instrument, although in a few cases, as noted, spectra on a 360 MHz instrument are reported. In all instances spectra were obtained at several temperatures, although only where significant changes occurred are they displayed in this paper. Cycling experiments were performed to show that no decomposition or other irreversible changes occur either upon heating or cooling the samples used in the NMR analyses.

Methyl ethers of calix[4]*arenes* (**2**). The tetraalkyl ethers of the calix[4]arenes can be obtained in good yield by treatment of a DMF–THF solution of the calixarene with NaH followed by the alkyl halide. The tetramethyl ethers of calix[4]arene (**1A**) and *p*-t-butylcalix[4]arene (**2B**) show ^1H NMR spectra which, like those of the parent calixarenes, are temperature dependent. The patterns displayed at −30°, as shown in Fig. 2, are best interpreted in terms of a partial cone conformation. Thus, the three prominent singlets in the approximate ratio of 1:2:1 in the upfield region of the spectrum of the t-Bu compound **2B** and the three singlets arising from the OMe hydrogens in both **2A** and **2B** are compatible only with a partial cone conformation. The methylene resonances for **2A** and **2B** in the partial cone conformation could be expected to appear as a 5–8 line pattern. Although these patterns are not completely clear, an almost completely resolved 7-line pattern can be discerned for **2A** and at least four of these resonances can be discerned for **2B**. In the spectra of **2A** and **2B** there is an additional resonance upfield from the other OMe resonances (δ 3.02 for **2A** and δ 2.0 for **2B**) which is tentatively assigned to a conformation in which the OMe group of the "down" aryl ring is "inside" the calix provided by the partial cone; in this environment it experiences an upfield shift due to the proximate phenyl rings that define the wall of the calix. Thus, it is postulated that at −30° the prevailing conformation is the partial cone which exists in an "inside" and "outside" conformation with respect to one of the OMe groups, as



Compound No	R	Y
1A	H	OH
1B	t-Bu	OH
1C	$CH_2CH{=}CH_2$	OH
2A	H	OCH_3
2B	t-Bu	OCH_3
3A	H	OC_2H_5
3B	t-Bu	OC_2H_5
4A	H	$OCH_2CH{=}CH_2$
4B	t-Bu	$OCH_2CH{=}CH_2$
5A	H	$OCH_2C_6H_5$
5B	t-Bu	$OCH_2C_6H_5$
6A	H	$OSi(CH_3)_3$
6B	t-Bu	$OCH_2C_6H_5$
6C	$CH_2CH{=}CH_2$	$OSi(CH_3)_3$
7A	H	$OCOCH_3$
7B	t-Bu	$OCOCH_3$

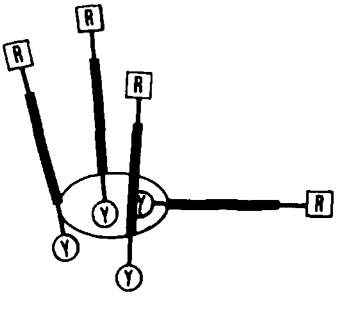
Table 1. ^1H NMR and ^{13}C NMR spectral patterns for the conformers of *p*-t-butylcalix[4]arene

	^1H NMR			^{13}C NMR			
Conformation	ArH	CH_2	$C(CH_3)_3$	Ar	CH_2	Ç$(CH_3)_3$	C(ÇH_3)
Cone	One singlet	One pair of doublets (J = 12 Hz)	One singlet	4	1	1	1
Partial cone	Two singlets and two doublets *or* four singlets (ratio 1:1:1:1)	Two pairs of doublets (J = 12 Hz) (ratio 1:1) or one pair of doublets (J = 12 Hz) and one singlet (ratio 1:1)*	Three singlets (ratio 1:2:1)	12	2	3	3
1,2-Alternate	Two singlets (ratio 1:1)	One singlet and two doublets (J = 12 Hz) (ratio 1:1)	One singlet	4	2	1	1
1,3-Alternate	One singlet	One singlet	One singlet	4	1	1	1

*The two equivalent methylene groups contain hydrogens in almost identical environments. Whether a 5-line or an 8-line pattern is observed will depend on whether or not there is a chemical shift difference between these hydrogens.

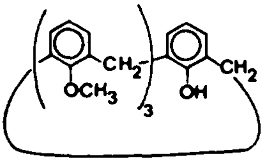
illustrated schematically in Fig. 3. This also provides an explanation for the fourth resonance in the upfield region of **2B** which could arise from the t-Bu group opposite the OMe group that is "inside" the calix; different chemical shifts for this t-Bu group would be expected for the "inside" and "outside" forms of **2B**.

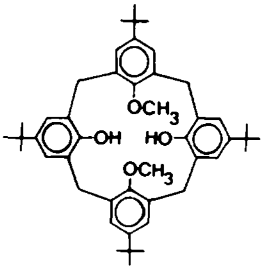
Although space filling molecular models of **2A** and **2B** suggest that these compounds should be conformationally rigid, the temperature dependence of the ^{1}H NMR spectra suggest otherwise. As illustrated in Fig. 2, when the temperature is raised above − 30° the spectra become less well resolved; the methylene and OMe resonances collapse to a broad singlet at *ca* 50° and then sharpen to a pair of narrow singlets at 120°. Because all four of the possible conformers will give single line resonances if the interconversion is rapid on the NMR time scale, it cannot be determined which conformer predominates at the higher temperatures. It is apparent, though, that the tetramethyl ethers of the calix[4]arenes are only moderately less conformationally mobile than the parent compounds, once again illustrating the fact that hard, space filling molecular models tend to overestimate the barriers to conformational changes.



"FLATTENED" PARTIAL CONE

When dimethyl sulfate is used as the methylating agent in the presence of BaO and $Ba(OH)_2 \cdot 8H_2O$ in DMF solution, a trimethyl ether of calix[4]arene (**8**) is produced. It appears to be conformationally less flexible than the corresponding tetramethyl ether (**2A**), for the room temperature ^{1}H NMR spectrum (Fig. 4) shows a set of well-resolved resonances in the 3–4 ppm region, *viz* two sharp singlets in the ratio of 1:2 for the OMe hydrogens and 7 or more additional lines arising from the methylene protons in doublet or doublet patterns. However, a choice between the cone and partial cone conformations cannot be made; as a result of the reduced symmetry of the molecule, both would be expected to show two OMe resonances and two pairs of doublet methylene resonances. The resonance from the OH proton of **8** appears at δ 5.65 ppm, the upfield position commensurate with its proximity to the aryl rings of the calix. It exchanges its proton much less readily than do the OH groups of **1A**, also commensurate with the OH group of **8** being buried in the calix. The stretching band in the IR spectrum of **8** appears at 3450 cm^{-1}, a considerably shorter wave length than observed for **1A**[6] but, nevertheless, indicative of intramolecular H-bonding. To accommodate these spectral characteristics it is suggested that **8** exists in a "flattened" partial cone conformation, as schematically illustrated above.





The action of ethereal diazomethane on **1B** produces a dimethyl ether of *p*-t-butylcalix[4]arene (**9**) which also appears to be conformationally less flexible than the corresponding tetramethyl ether (**2B**). As shown in Fig. 5, the ^{1}H NMR spectrum of **9** shows a pair of sharp upfield singlets at δ 0.92 and 1.30 ppm in a 1:1 ratio arising from the t-Bu hydrogens, a pair of symmetrical doublets at δ 4.27 and 3.30 ppm arising from the methylene hydrogens, a sharp singlet at δ 3.90 ppm arising from the OMe hydrogens, and two downfield envelopes in a 1:1 ratio arising from the aryl hydrogens. To accommodate this NMR pattern and also to explain why only a dimethyl ether forms, it is postulated that **9** exists in a distorted cone or a flattened 1,3-alternate conformation in which the OMe groups, located on alternate aryl moieties, have the "inside" conformation. This places them *over* the OH groups, protecting the OH groups from reaction; it also brings the t-Bu groups on the phenyl rings carrying the OMe groups close to one another and pushes the t-Bu groups on the phenyl rings carrying the OH groups away from one another. The t-Bu groups that are forced toward each other should experience an upfield shift due to the proximity of the transannular phenyl rings, as reflected by the resonance at δ 0.92 ppm. The OH stretching band at 3450 cm^{-1} in the IR indicates a modest degree of intramolecular H-bonding.[6]

Ethyl ethers of calix[4]*arenes* (**3**). The tetraethyl ethers of **1A** and **1B**, prepared by the action of NaH and ethyl iodide in DMF–THF solution, give room temperature ^{1}H NMR spectra (Fig. 6) containing well resolved resonances in accord with a partial cone conformation. Particularly evident are the three sets of triplets from the Me hydrogens of the OEt groups in both **3A** and **3B** and three singlets from the t-Bu groups in **3B**. The highest field triplet is assigned to the OEt group of the "down" aryl moiety in which the OEt group assumes the "inside" conformation and experiences an upfield shift from the proximate aryl rings of the partial cone. The ^{13}C NMR spectrum, also, is in complete accord with a partial cone conformation, containing 12 downfield resonances arising from the aryl carbons, three midfield resonances arising from the methylene carbons of the OEt groups, and 8 upfield resonances arising from the Me carbons of the OEt groups (3 lines), the Me carbons of the t-Bu groups (2 lines) and the methylene carbons of the calix (3 lines). Clearly, the tetraethyl ethers are conformationally less flexible than the tetramethyl ethers, although there remains some temperature dependence of the NMR patterns; at 50° the ^{1}H NMR spectrum of **3A** shows a coalescence of the two downfield triplets into one triplet, while the upfield triplet assigned to the "inside" OEt group remains unaffected. It is postulated that this is due not to "up–down" conformational inversions but to more subtle flexing motions that are not yet well understood.

Allyl ethers of calix[4]*arenes* (**4**). The tetraallyl ether

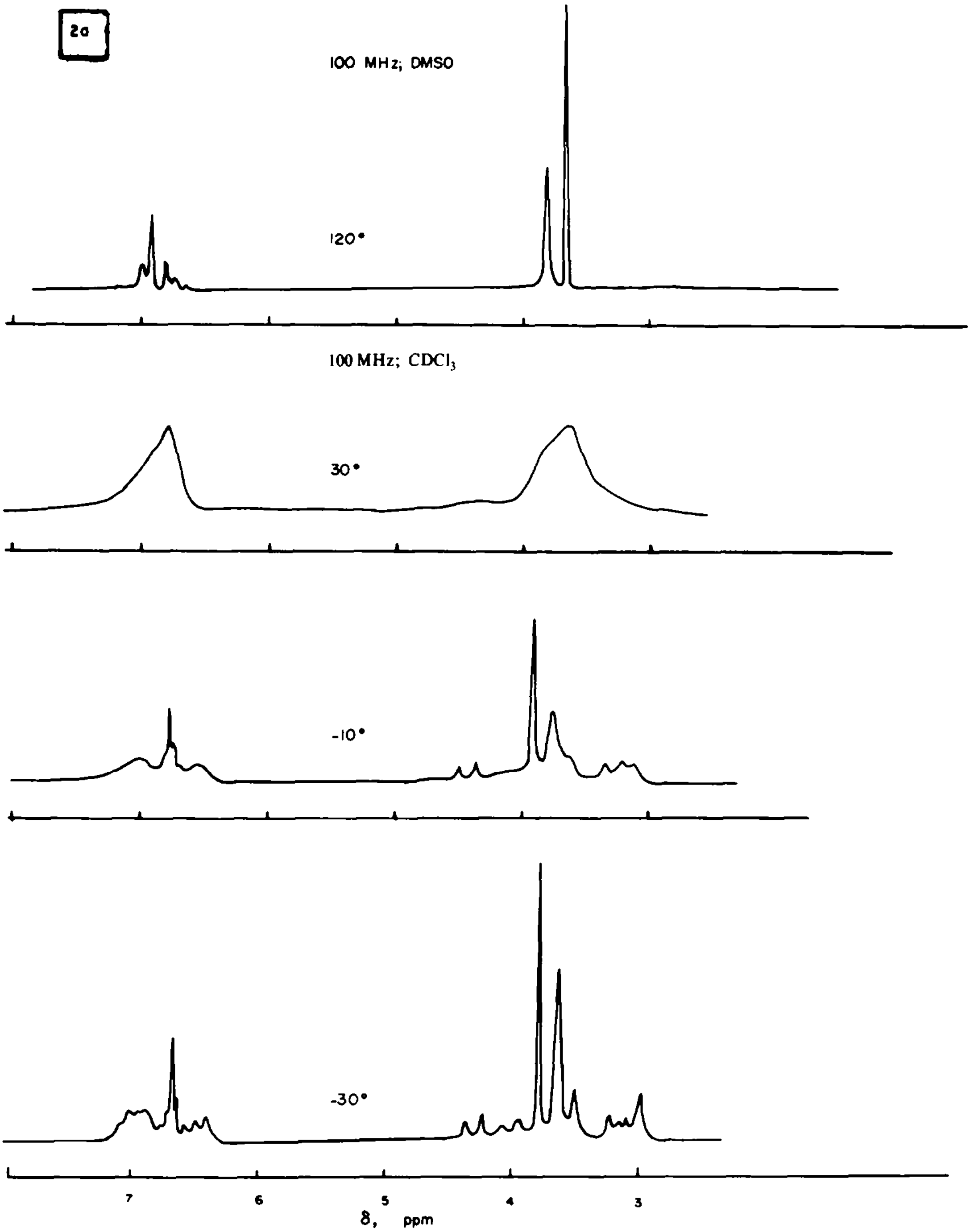


Fig. 2(a).

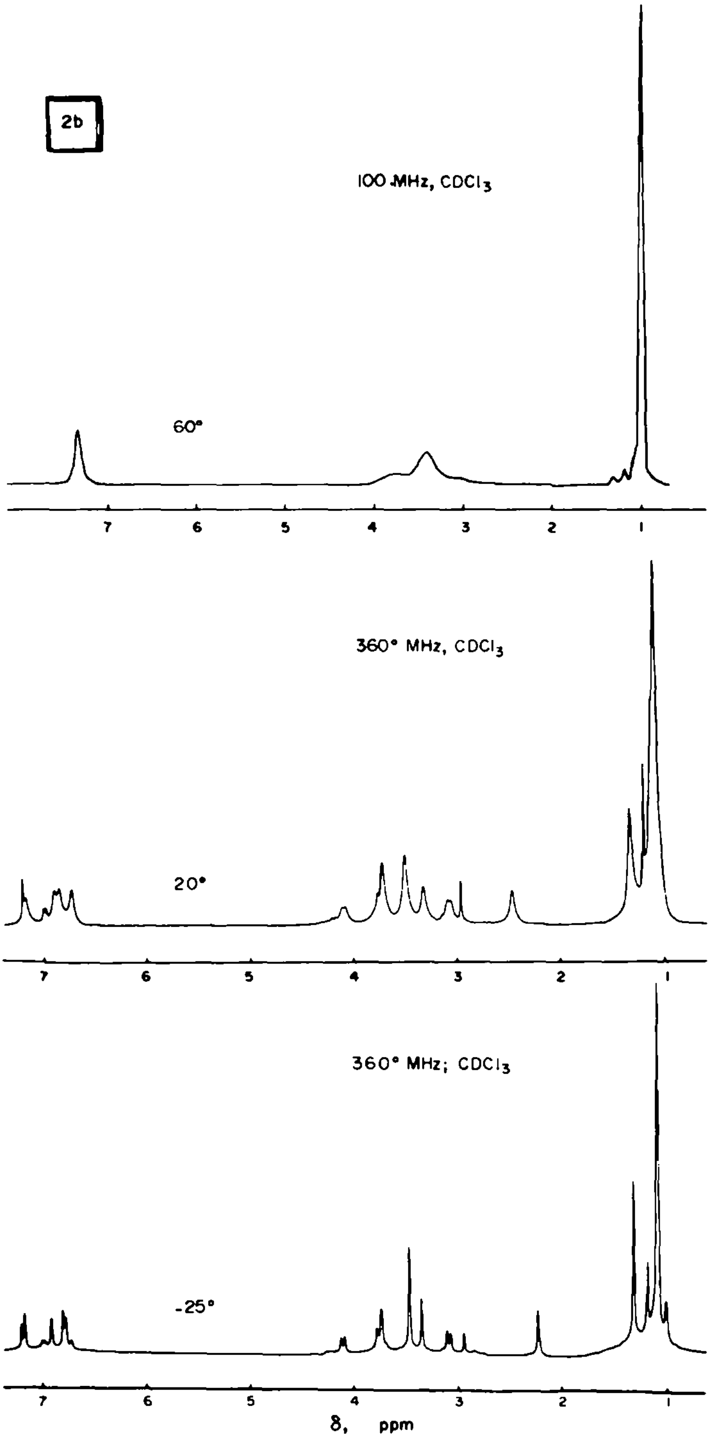


Fig. 2(b). ^{1}H NMR spectra of the tetramethyl ether of calix[4]arene (**2A**) and the tetramethyl ether of *p*-t-butylcalix[4]arene (**2B**).

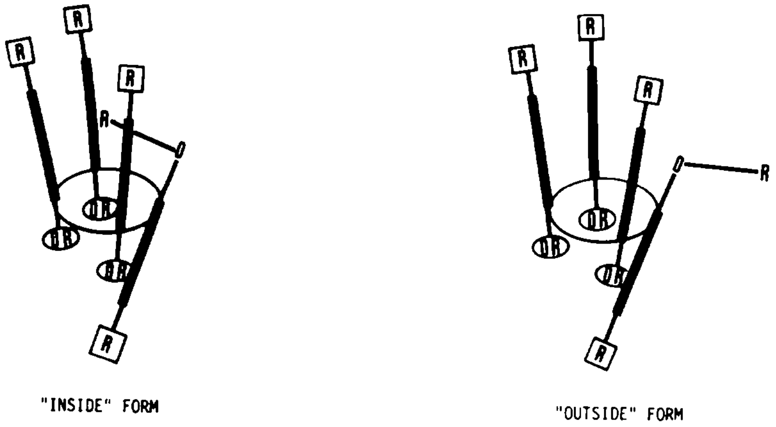


Fig. 3. "Inside" and "outside" forms of partial cone conformation.

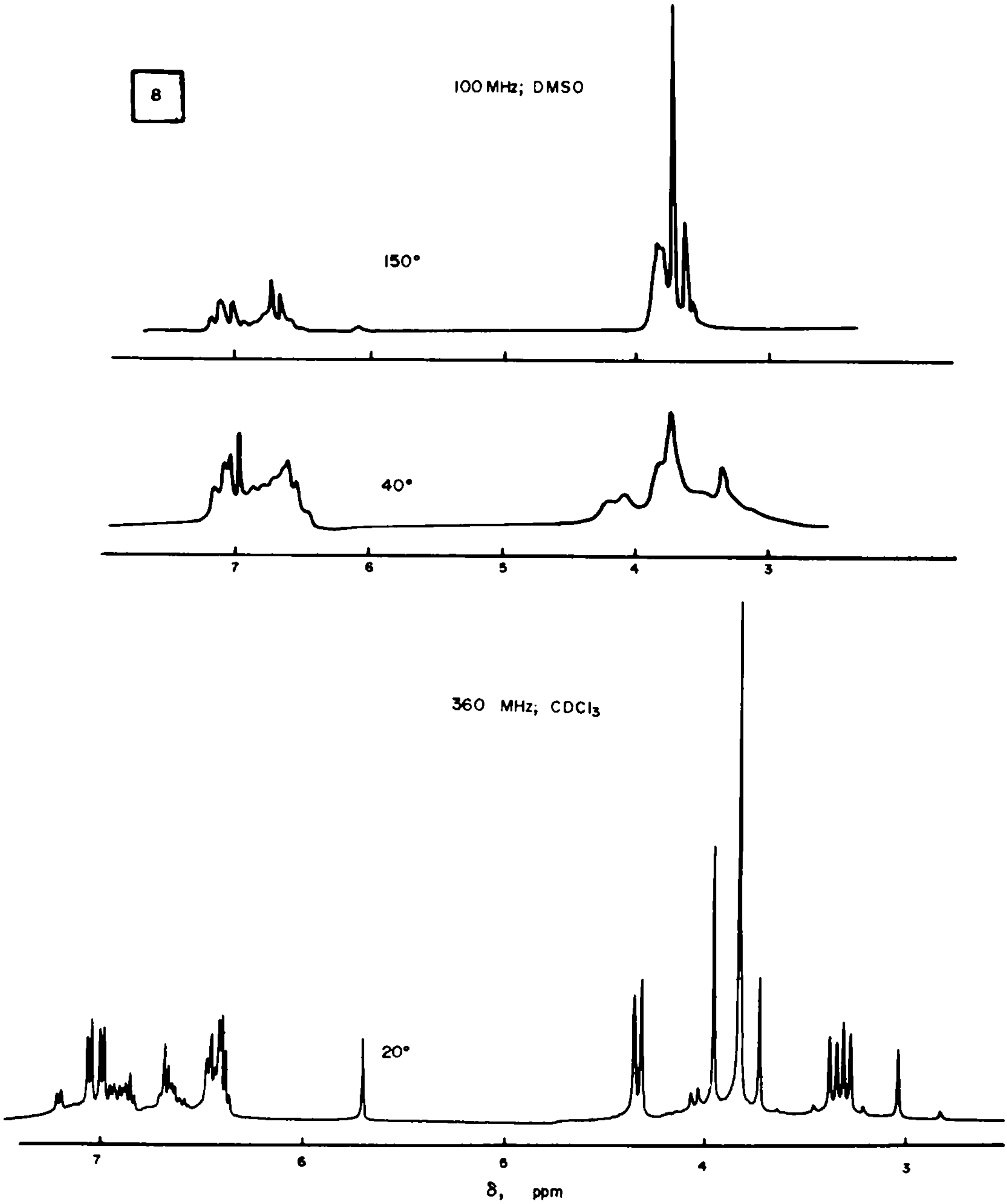


Fig. 4. ^{1}H NMR spectrum of the trimethyl ether of calix[4]arene (8).

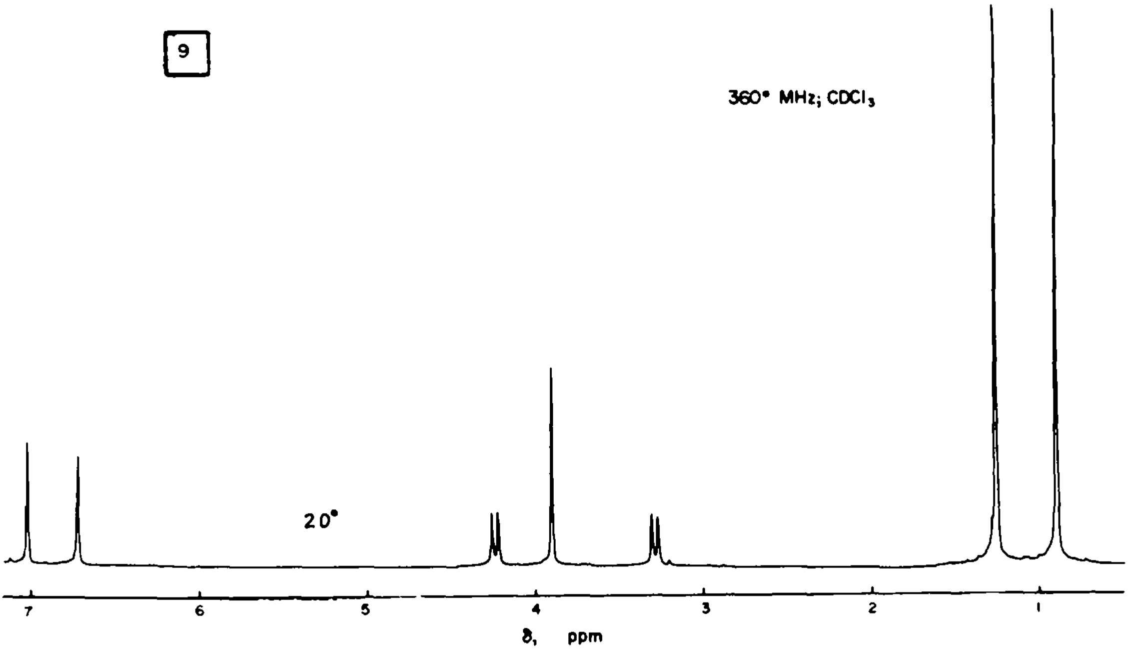


Fig. 5. ^{1}H NMR spectrum of the dimethyl ether of *p*-t-butylcalix[4]arene (**9**).

of calix[4]arene (**4A**) is of special interest because of the synthetic utility that it affords.[7] The ^{1}H NMR spectrum of **4A** (Fig. 7) shows a rather complex pattern in the δ 3–5 ppm region as the result of overlapping resonances from the methylene groups of the calixarene ring and the allyl ether functions, the latter split by spin–spin coupling with the vinyl hydrogens. A 360 MHz spectrum of **4A** was also obtained as an aid in interpreting the pattern, but its complexity is such that only tentative individual assignments can be made. However, the overall pattern is commensurate with a partial cone conformation for **4A**, probably as a mixture of "inside" and "outside" forms. The spectrum in DMSO at 150° is somewhat different from that in $CDCl_3$ at lower temperature, but it remains commensurate with a cone conformation.

Because the methyl ethers **2A** and **2B**, the ethyl ethers **3A** and **3B**, and the allyl ether **4A** all favor the partial cone conformation, the allyl ether **4B** prepared from **1B** by the action of NaH and allyl bromide in DMF–THF was expected to do likewise. However, its 360 MHz ^{1}H NMR spectrum shows a sharp downfield singlet for the aryl hydrogens, a multiplet at δ 6.44 ppm and a pair of doublets at δ 5.26 and δ 5.19 ppm for the vinyl hydrogens, a pair of doublets at δ 4.39 and δ 3.13 for the calixarene methylene groups, and an upfield singlet for the t-Bu groups (Fig. 8). Only the cone conformation is compatible with this pattern. That the tetraaryl ethers of **4A** and **4B** exists in different conformations is further substantiated by their ^{13}C NMR spectra. That of **4B** is very simple, showing only 6 lines in the downfield region (four from the aryl carbons and two from the vinyl carbons), a single line at midfield (from the OCH_2 carbon), and two lines in the upfield region (a strong line from the t-Bu methyl carbons and a weak line from the methylene carbons of the calix), as expected for the cone conformation. The ^{13}C NMR of **4A**, on the other hand, is much more complex, showing 20 lines in the downfield region (12 from the aryl carbons and 8 from the vinyl carbons),[8] four lines at midfield (from the OCH_2 carbons), and three lines in the upfield region (from the methylene carbons) as expected for a partial cone conformation.

Benzyl ethers of calix[4]*arenes* (**5**). Like the allyl ether of **1B**, the benzyl ether **5B** also displays a ^{1}H NMR spectrum that is commensurate only with a cone conformation, showing a pair of narrow envelopes in the aryl region arising from the aryl groups of the calixarene and benzyl moieties, a sharp singlet at δ 4.85 ppm arising from the methylene hydrogens of the benzyl group, a pair of doublets (δ 4.16 and 2.9 ppm) arising from the methylene hydrogens of the calixarene, and an upfield singlet arising from the t-Bu hydrogens (Fig. 9). The pattern remains unchanged up to temperatures as high as 150°. Similarly, the tetrabenzyl ether of calix[4]arene (**5A**) displays a ^{1}H NMR spectrum that indicates the compound to be in a cone conformation. Thus, **1A** and **1B** behave differently upon allyl ether formation but identically upon benzyl ether formation.

Attempts to prepare the tetrabenzyl ether of **1C** have yielded only an oil which is indicated by TLC and NMR analyses to be a mixture of materials. When benzyl tosylate is substituted for benzyl bromide as the benzylating agent, a dibenzyl ether (**10**) is obtained as a crystalline solid. Its ^{1}H NMR spectrum (Fig. 10) shows a pair of doublets (δ 4.26 and 3.28 ppm) arising from the four equivalent methylene groups of the calixarene ring, a pair of doublets (δ 3.20 and 3.14 ppm) arising from two pairs of non-equivalent methylene groups of the allyl moieties, multiplet patterns at δ 5.0 and 5.78 ppm arising from the vinyl hydrogens, sharp singlets at δ 6.70 and 6.84 ppm arising from the aryl hydrogens of the calixarene, and a multiplet at δ 7.2–7.8 arising from the aryl hydrogens of the benzyl group. This pattern is commensurate with either a distorted cone or a flattened 1,3-alternate conformation, as suggested for the dimethyl ether (**9**) of **1B**.

Trimethylsilyl ethers of calix[4]*arenes* (**6**). The tetrakistrimethylsilyl ethers of the calix[4]arenes proved

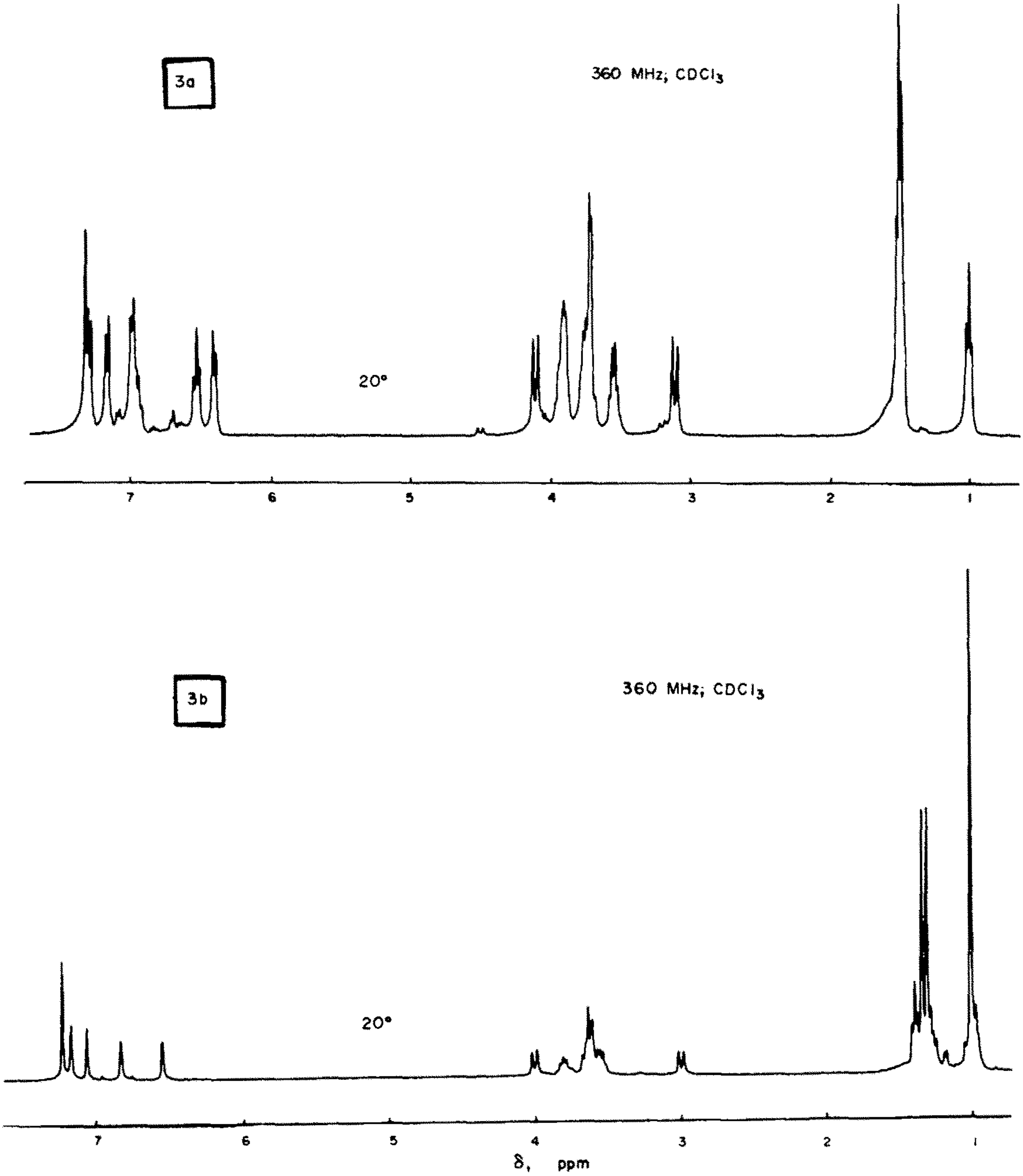
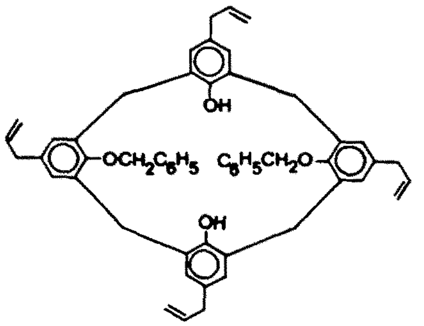


Fig. 6. ^{1}H NMR spectra of the tetraethyl ether of calix[4]arene (**3A**) and the tetraethyl ether of *p*-t-butylcalix[4]arene (**3B**).

to be considerably more difficult to make than those of the previously reported calix[6]arenes and calix[8]arenes,[1] requiring the very reactive N,O-bis(trimethylsilyl)acetamide[9] as the silylating agent. Attempts to obtain a pure trimethylsilyl derivative of calix[4]arene (**1A**) have not yet been successful. The products obtained from **1B** and **1C** are high melting, crystalline solids which show room temperature ^{1}H NMR spectra very much like those of the benzyl ethers, as shown in Fig. 11. The mixed calixarene, *p*-phenyl-*p*-t-butylcalix[4]arene (**11**)[10] yields a crystalline tetrakistrimethylsilyl derivative whose ^{1}H NMR spectrum (Fig. 11) has four singlets



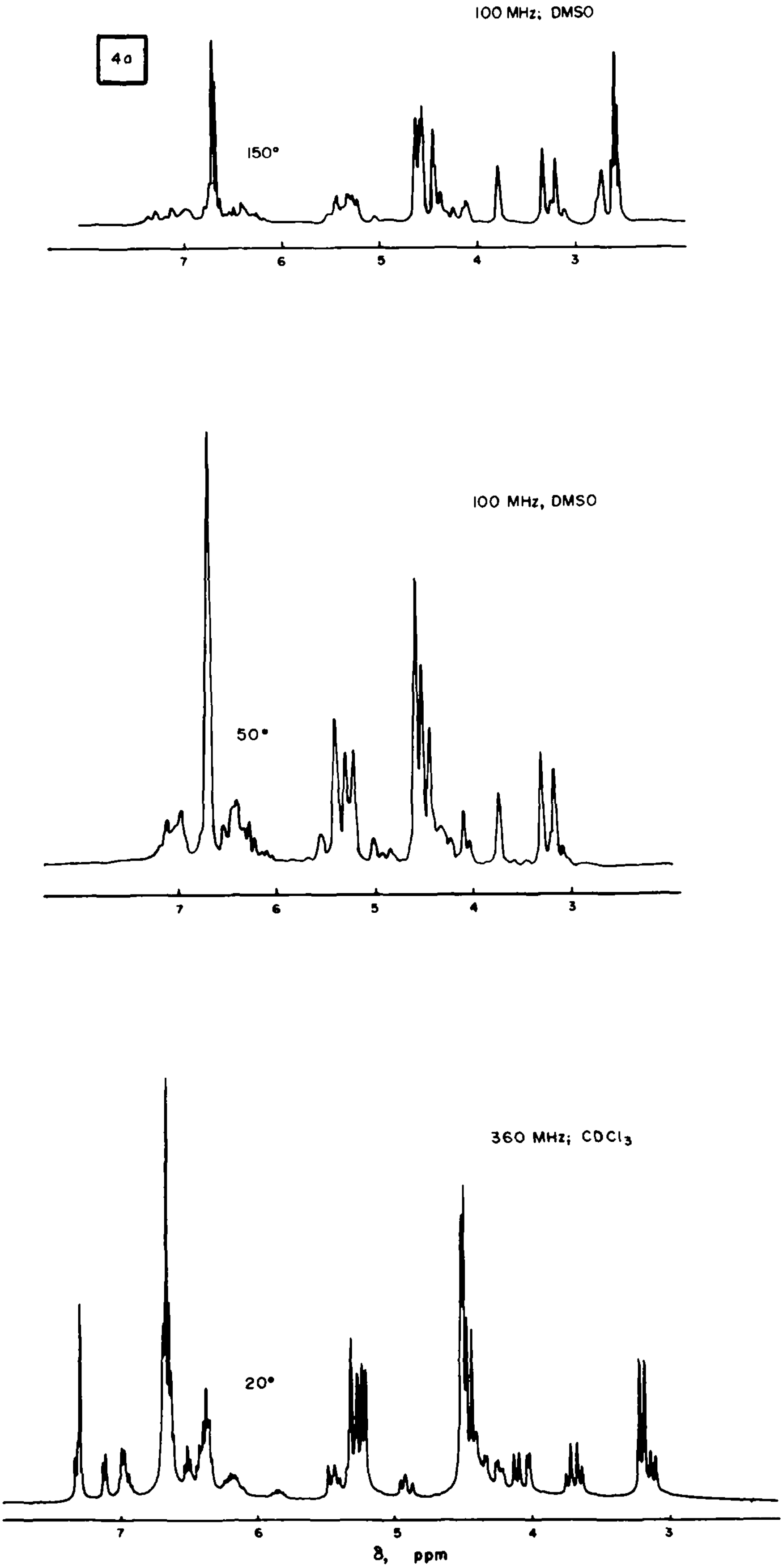


Fig. 7. ^{1}H NMR spectrum of the tetraallyl ether of calix[4]arene (4A).

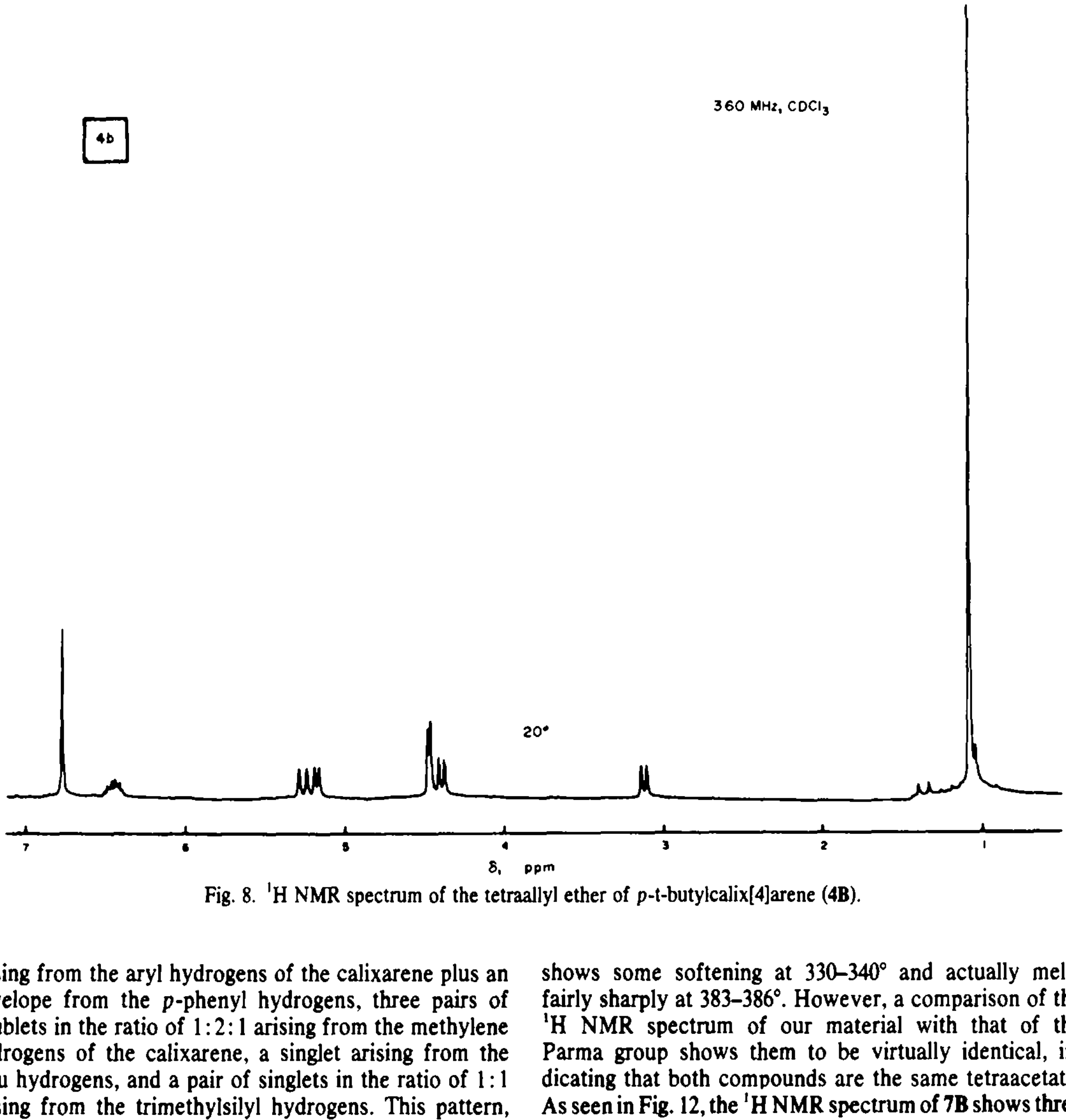
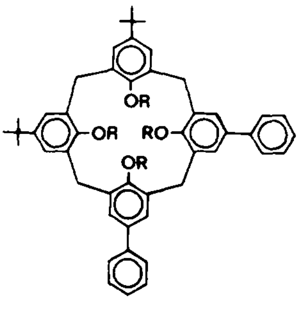


Fig. 8. ^{1}H NMR spectrum of the tetraallyl ether of *p*-t-butylcalix[4]arene (**4B**).

arising from the aryl hydrogens of the calixarene plus an envelope from the *p*-phenyl hydrogens, three pairs of doublets in the ratio of 1:2:1 arising from the methylene hydrogens of the calixarene, a singlet arising from the t-Bu hydrogens, and a pair of singlets in the ratio of 1:1 arising from the trimethylsilyl hydrogens. This pattern, also, is commensurate with a cone conformation.

Acetates of calix[4]*arenes* (**7**). Treatment of **1A** with acetic anhydride and *p*-toluenesulfonic acid yields a tetraacetate (**7A**) whose ^{1}H NMR spectrum (Fig. 12) shows only three sharp singlets (δ 7.00, 3.71, 1.53 in a 3:2:3 ratio) and whose ^{13}C NMR spectrum shows single resonances for the CO and Me carbons of the acetoxyl group and the methylene carbons of the calix along with four lines for the aryl carbons. Only the 1,3-alternate conformation is commensurate with these spectral data.

In an earlier paper[1] we reported the synthesis of two acetates of **1B**, one melting at 247–250° and assigned a triacetate structure and one melting at 383–386° and assigned a tetraacetate structure (**7B**), isolated as a 1:1 complex with acetic acid. When the present paper was being written our attention was called to a parallel study[11] of the conformations of some calixarenes in which particular attention is given to **7B**, isolated as the 1:1 complex with acetic acid and stated to have a m.p. of 320°. Because of the disparity in m.ps we have reinvestigated our preparation and find that after a single recrystallization of the crude product a material is obtained which softens extensively at 322° but does not actually melt at that temperature. After several additional recrystallizations a material is obtained which shows some softening at 330–340° and actually melts fairly sharply at 383–386°. However, a comparison of the ^{1}H NMR spectrum of our material with that of the Parma group shows them to be virtually identical, indicating that both compounds are the same tetraacetate. As seen in Fig. 12, the ^{1}H NMR spectrum of **7B** shows three singlets near δ 1.3 ppm in a 2:1:1 ratio arising from the t-Bu hydrogens and a second set of three singlets near δ 2.3 ppm in a 2:1:1 ratio arising from the OAc hydrogens, along with another singlet arising from the Me hydrogens of acetic acid. In agreement with the Italian group, we interpret this pattern as being commensurate with a partial cone conformation. Conclusive proof is cited in a footnote in Ref. 11 which states that an X-ray crystallographic analysis of the acetic acid complex of **7B** has been carried out and that it shows a partial cone conformation.



11 (R = H)
12 (R = $Si(CH_3)_3$)
13 (R = $COCH_3$)

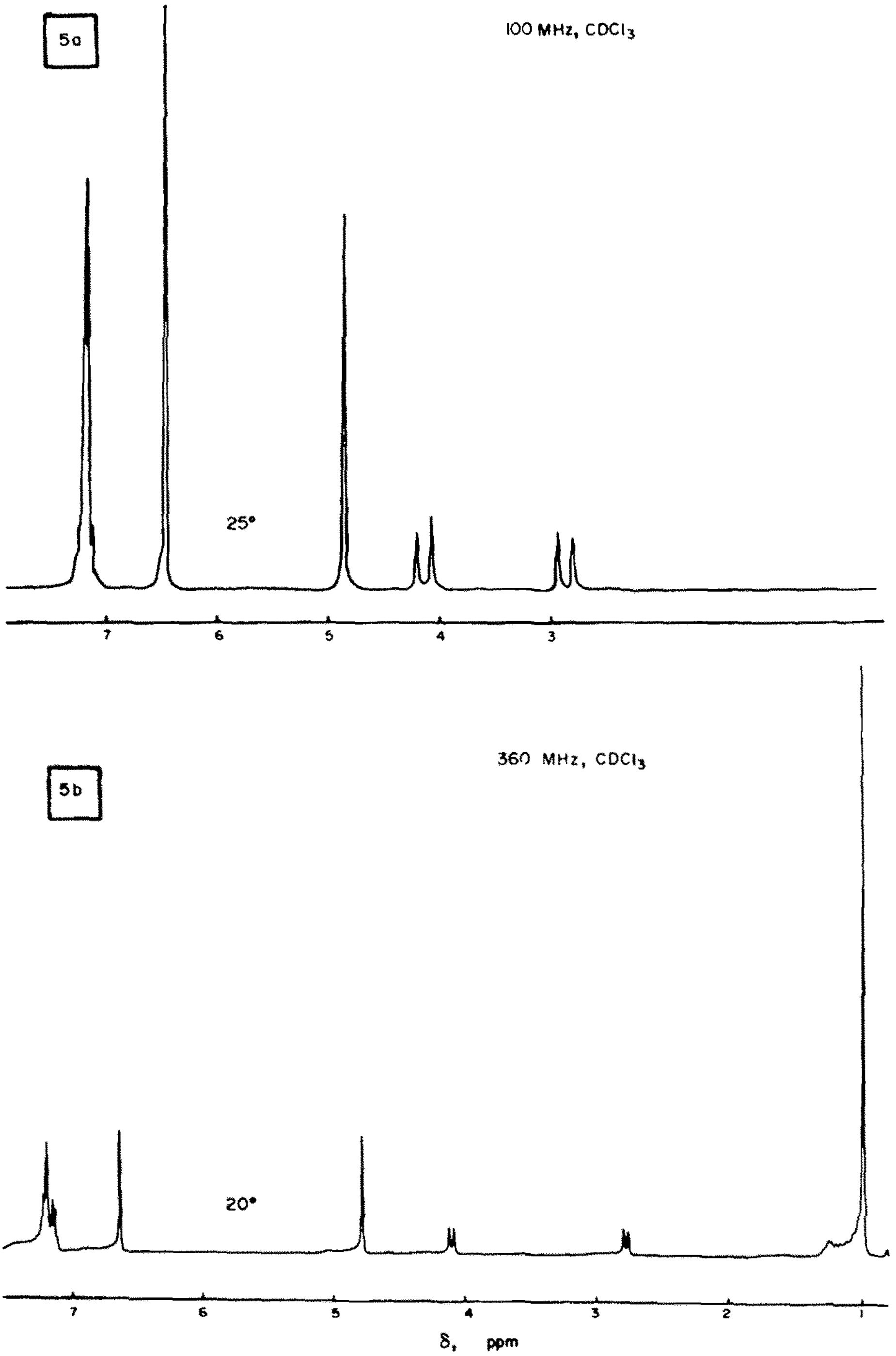


Fig. 9. ^{1}H NMR spectra of the tetrabenzyl ether of calix[4]arene (**5A**) and the tetrabenzyl ether of *p*-t-butylcalix[4]arene (**5B**).

Three tetraacetates of di-*p*-phenyl–di-*p*-t-butylcalix[4]arene (**13**) have been previously reported.[10] The ^{1}H NMR patterns that would be expected for the six conformational isomers of **13** (i.e. one cone, two partial cones, two 1,2-alternates, and one 1,3-alternate) are shown in Table 2. As shown in Fig. 13, isomer-A of **13** possesses a spectrum commensurate with a 1,3-alternate conformation, and isomer-C possesses a spectrum commensurate with a partial cone conformation. Because of the closeness of the lines arising from the two t-Bu groups in isomer-C it is postulated that it is in the partial cone conformation in which both of the t-Bu moieties are in the "up" position. The proximate *p*-phenyl moiety, then, must be postulated to exert a diamagnetic anisotropic shielding effect that shifts the t-Bu resonance upfield to almost the same extent. The assignment of the conformation of isomer-B is equivocal. The cone and 1,3-alternate conformations are clearly ruled out, and the pattern is slightly too complex for the 1,2-alternate. Therefore, the partial cone conformation is

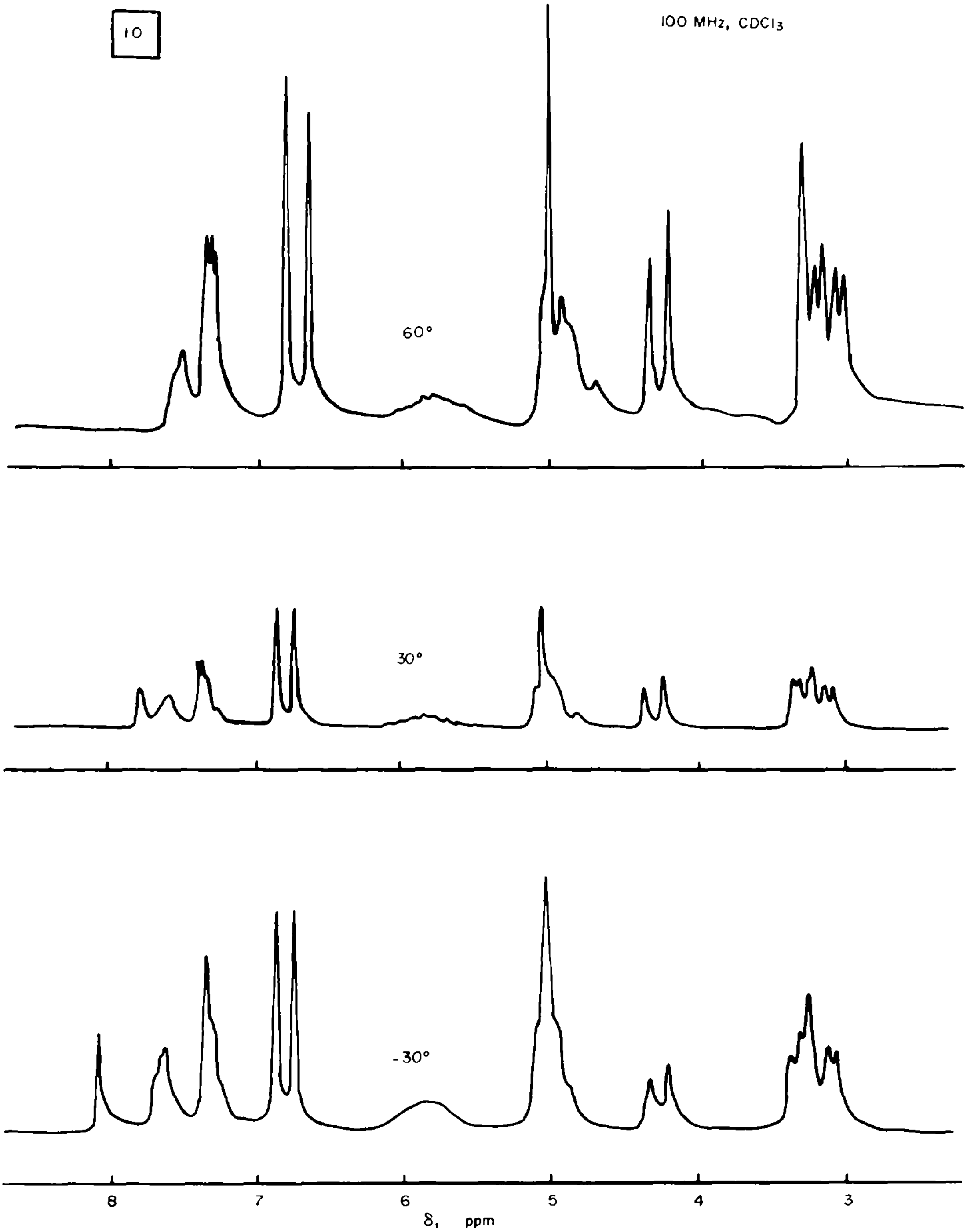


Fig. 10. ^{1}H NMR spectra of the dibenzyl ether of *p*-allylcalix[4]arene (**10**).

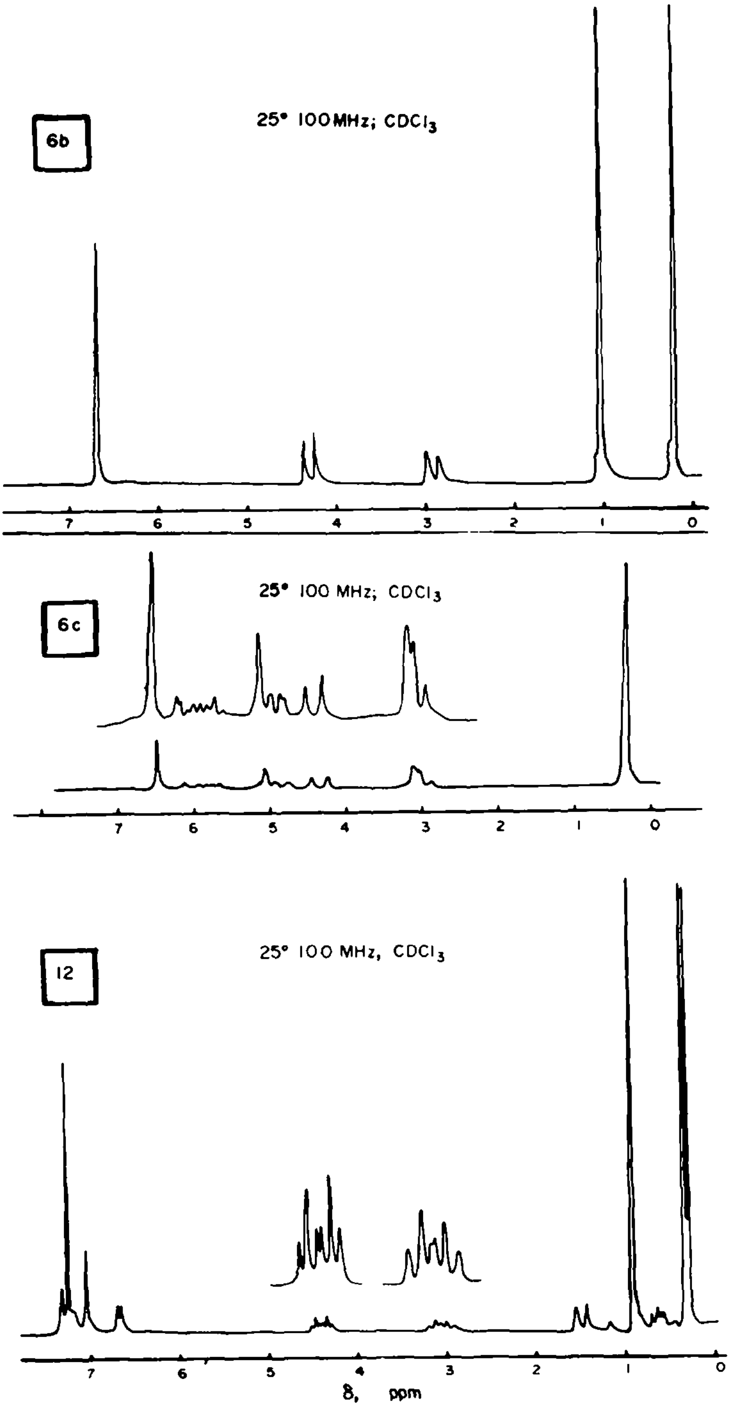


Fig. 11. ¹H NMR spectra of the tetrakistrimethylsilyl ether of *p*-t-butylcalix[4]arene (**6B**), tetrakistrimethylsilyl ether of *p*-allylcalix[4]arene (**6C**), and tetrakistrimethylsilyl ether of di-*p*-phenyl–di-*p*-t-butylcalix[4]arene (**12**).

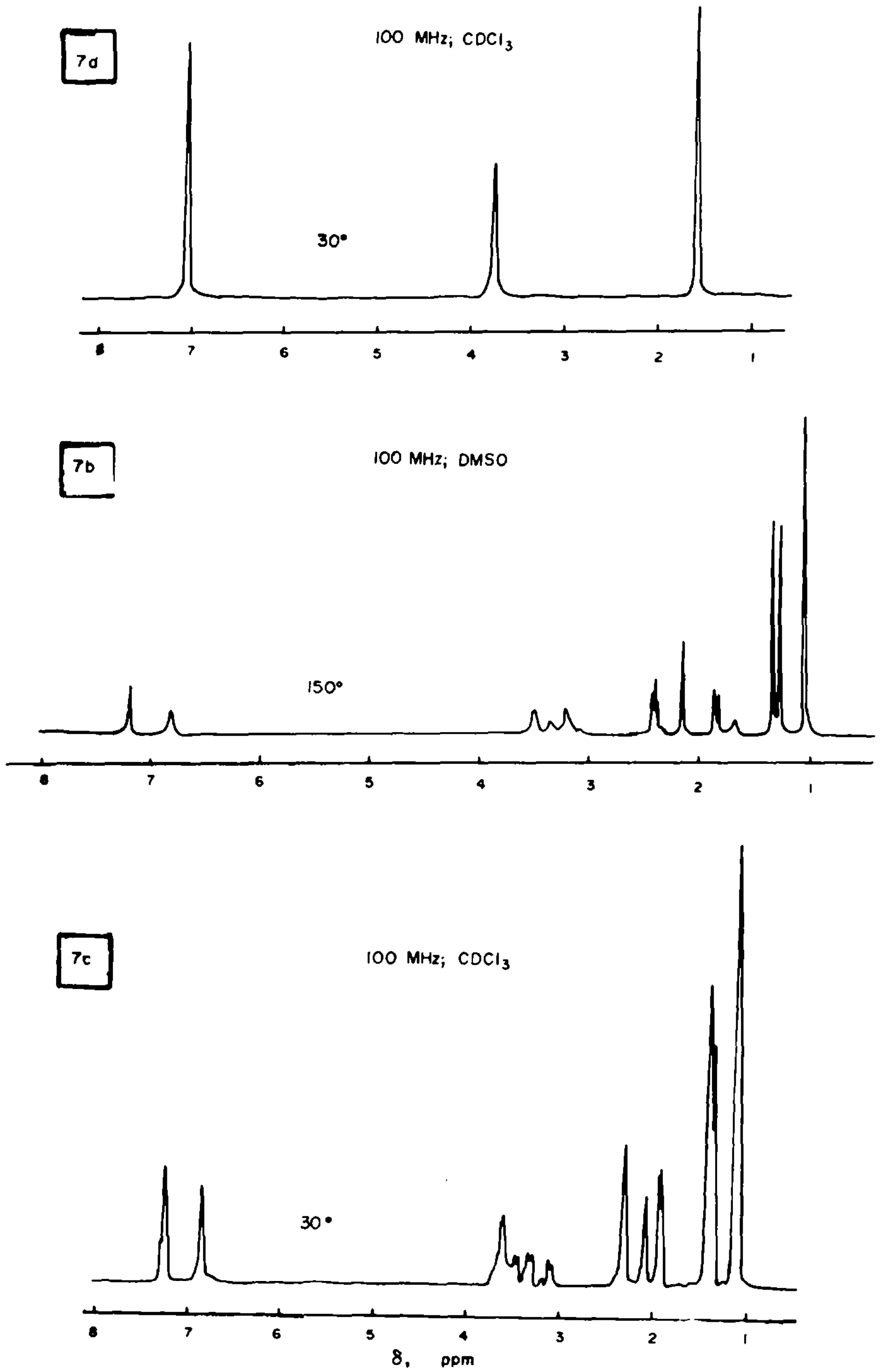


Fig. 12. ^{1}H NMR spectra of the tetraacetate of calix[4]arene (**7A**) and the tetraacetate of *p*-t-butylcalix[4]arene (**7B**).

assigned, and it is postulated that it is the one in which the two *p*-phenyl moieties are in the "up" position.

DISCUSSION

Compounds containing what have been termed "enforced cavities"[12] large enough to engulf other molecules are well represented by natural products, of which the enzymes and cyclodextrins are typical examples. However, they are rare among unnatural compounds obtainable by laboratory synthesis, and prior to the present work the only *synthetic* compounds with "enforced cavities" as large as those in the cyclodextrins are the recently reported spherands.[12] The parent calixarenes do not qualify for inclusion in this elite group, because at room temperature they are conformationally mobile though at any instant in time they are most often in the cone conformation. But, as illustrated by the examples in the present paper, most of the ethers and esters of the calixarenes are conformationally rigid at room temperature and many possess either a circum-

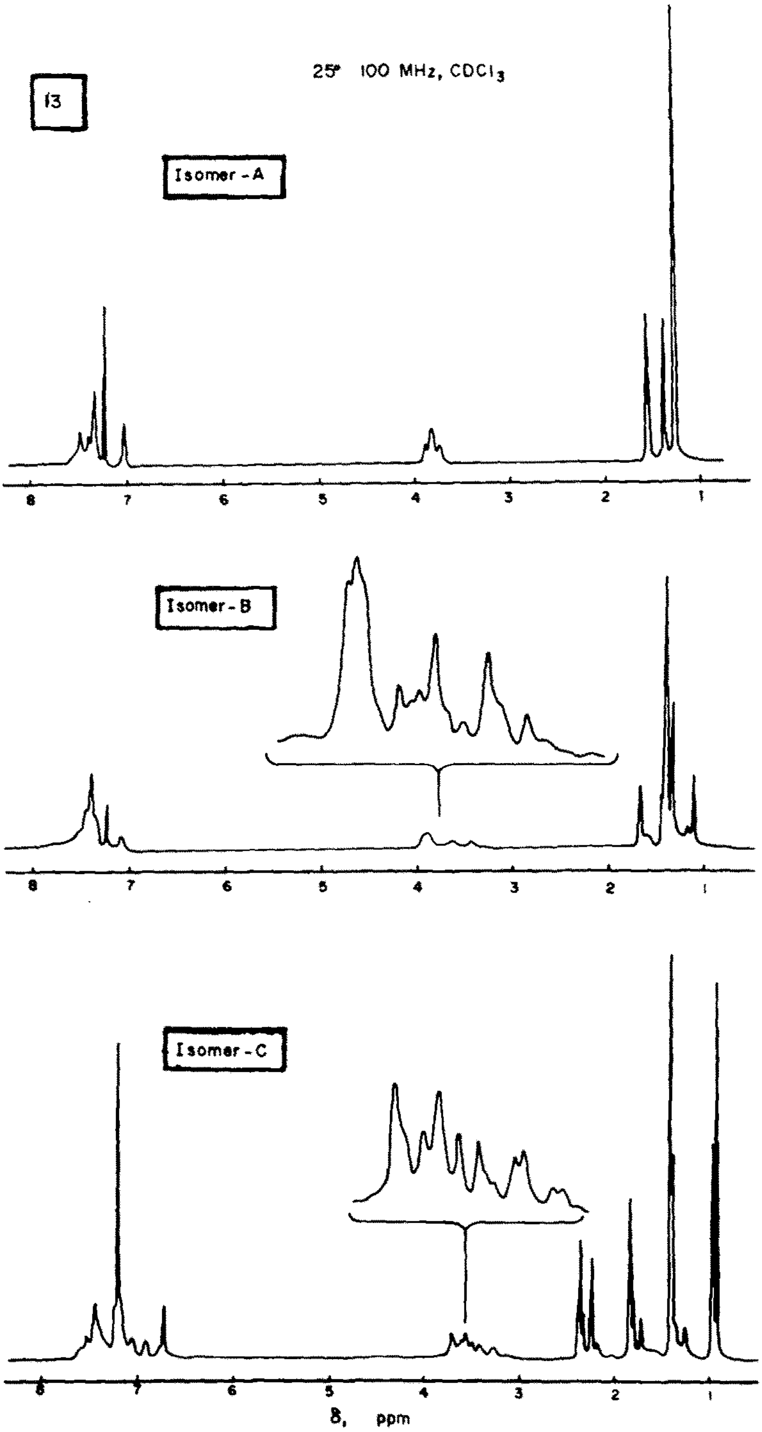
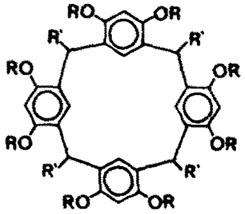


Fig. 13. ^{1}H NMR spectra of the tetraacetates of di-*p*-phenyl-di-*p*-t-butylcalix[4]arene (13).

ferentially enclosed cavity (i.e. the cone conformation) or a cavity with a circumferential "entrance" (i.e. the partial cone conformation). Thus, these conformers join the ranks of compounds containing large "enforced cavities" or, as we choose to call them, "changeless calixes".



14 (R = H)
15 (R = CH_3CO or C_3H_7CO)

The discovery that the ethers and esters of calixarenes **1A**, **1B** and **1C** exist, in most cases, either in the partial cone or cone conformation came as a surprise in view of literature precedents. Resorcinol condenses with some aldehydes under acid-catalyzed conditions to form calix[4]arenes of structure **14**.[13] The octa-esters (**15**) of several of these have been studied both by ^1H NMR spectroscopy[14] and by X-ray crystallography,[15] and it has been shown that the preferred conformations are a 1,3-alternate array in which two of the phenyl rings are coplanar and the other two are parallel, in one case in a face-to-face fashion and in the other case an "up–down" fashion.[16] Another study which seemed to indicate the probability of obtaining the 1,3-alternate conformation upon derivatization was a dynamic ^1H NMR study of *p*-octylcalixarene and its acetate.[3] Whereas the low temperature ^1H NMR spectrum of the calixarene itself showed a pair of doublets arising from the methylene hydrogens, the corresponding acetate showed only a singlet regardless of the temperature. On the assumption that the *p*-octylcalixarene was a cyclic tetramer this behavior was interpreted in terms of a 1,3-alternate conformation for the acetate. However, it is now thought[4] that the calixarene used in this study was probably a cyclic octamer rather than a cyclic tetramer; thus, the singlet methylene resonance for the calixarene acetate was the result of conformational *flexibility*, not conformational rigidity. But, until this was established during the course of the present work, the literature precedents appeared to be strong; if our first derivatization experiment had been the preparation of the tetraacetate of calix[4]arene (which exists in the 1,3-alternate conformation) we would probably have generalized from this one experiment and concluded that the 1,3-alternate conformation is likely in all cases. As the present work shows, this is not the case, and the 1,3-alternate conformation seems to be the exception rather than the rule. Why this is true, however, is not yet clear. The conformational outcome upon derivatization, as shown in Table 3, is not solely a function of the *p*-substituent (i.e. both **1A** and **1B** give the methyl and ethyl ethers in partial cone conformation, and **1B** and **1C** both give trimethylsilyl ethers in the cone conformation). Nor is it solely a function of the derivative being formed (i.e. **1A** gives the allyl ether in the partial cone conformation, but **1B** gives the allyl ether in the cone conformation; **1A** gives the acetate in the 1,3-alternate conformation, but **1B** gives the acetate in the partial cone conformation). The ease of derivative formation, *per se*, does not seem to be a critical factor (i.e. the readily formed benzyl ethers and the reluctantly formed trimethylsilyl ethers both appear to prefer the cone conformation). Reaction conditions have been shown to have an effect on the *structure* of the product formed (i.e. the methyl ethers via methyl iodide, dimethyl sulfate and diazomethane; the benzyl ethers via benzyl bromide and benzyl tosylate) but no discernible influence on the conformational preference. Work on this problem is continuing in an effort to discover the critical factors that determine the conformational outcome in the hope that predictive correlations can be established.

Table 2. ^1H NMR spectral patterns for the conformers of di-*p*-phenyl-di-t-butylcalix[4]arene (**13**)

Conformation	CH_2	$CH_3C\begin{smallmatrix}/\!\!/O\\ \backslash\\ O\end{smallmatrix}$	$C(CH_3)_3$
Cone	12 lines	2 lines	1 line
Partial cone†	6–16 lines‡	4 lines	2 lines
1,2-Alternate†	6–16 lines‡	2 lines	1 line
1,3-Alternate	3 lines in a ratio of 1:2:1§	2 lines	1 line

†Two different conformers are possible, but the predicted ^1H NMR resonance patterns are identical.

‡The number of lines will depend on the degree of similarity of the chemical environments of the two methylene hydrogens.

§In *p*-t-butylcalix[4]arene (see Table 1) the methylene hydrogens in the 1,3-alternate conformation are in identical chemical environments. In **12** they are in almost, but not precisely, identical chemical environments, the only difference being the identity of the substituent in the *p*-position of the phenyl ring (i.e. phenyl and t-Bu). Thus, although three sets of quartets would be predicted in theory, a 1:2:1 triplet pattern is considered more likely.

Table 3. Conformations of ethers and esters of calixarenes **1A**, **1B**, **1C** and **11**

p-Substituent	OR Group	Compound No.	Conformation
H	OMe	**2A**	Partial cone
t-Bu	OMe	**2B**	Partial cone
H	OEt	**3A**	Partial cone
t-Bu	OEt	**3B**	Partial cone
H	$OCH_2CH{=}CH_2$	**4A**	Partial cone
t-Bu	$OCH_2CH{=}CH_2$	**4B**	Cone
H	$OCH_2C_6H_5$	**5A**	Cone
t-Bu	$OCH_2C_6H_5$	**5B**	Cone
t-Bu	$OSiMe_3$	**6B**	Cone
$CH_2CH{=}CH_2$	$OSIMe_3$	**6C**	Cone
C_6H_5/t-Bu	$OSiMe_3$	**12**	Cone
H	OCOMe	**7A**	1,3-Alternate
t-Bu	OCOMe	**7B**	Partial cone
C_6H_5/t-Bu	OCOMe	**13**	1,3-Alternate + partial cone

EXPERIMENTAL[17]

M.ps of all compounds were taken in sealed and evacuated capillary tubes on a Mel-Temp apparatus (Laboratory Devices, Cambridge, MA) using 500°C thermometer calibrated against a thermocouple (accuracy ± 1°). IR spectra were determined on a Perkin–Elmer 283B spectrometer. ^1H NMR spectra were recorded on a Hitachi–Perkin–Elmer R-24B spectrometer, a JEOL FX-100 spectrometer, or a Brucker WH-360 spectrometer.[17] ^{13}C NMR were recorded on the JEOL FX-100 instrument. Chemical shifts are reported as δ values in parts per million relative to TMS (δ 0.0) as an internal standard. Mass spectra were obtained on a Varian MAT 311A instrument. Microanalyses were carried out by Industrial Testing Laboratories, St. Lois, MO. TLC analyses were carried out on silica gel plates (adsorbant thickness 250 μm), using $CHCl_3$ (3 parts)/hexane (4 parts) as the eluting agent.

25,26,27,28-*Tetramethoxycalix*[4]*arene* (**2A**). Following directions[18] a 1.04 g sample of **1A** was dissolved in 50 mL THF containing 5 mL DMF and treated with 1.0 g NaH followed by 10 g MeI. The mixture was refluxed 1 hr, the THF was removed by evaporation, and the residue was partitioned between water and $CHCl_3$. The $CHCl_3$ extract was washed with water, dried, and evaporated, and the residue was recrystallized from n-BuOH to give 0.82 g (70%) of **2A** as white needles: m.p. 234–235°; ^{1}H NMR ($CDCl_3$) δ 6.65 (br s, 12, ArH), 4.2–3.0 ppm (m, 20, CH_2 and CH_3O); mass spectrum (EI, 90 eV), *m/e* 480 (100%), 481 (33%) for M and M + 1. (Found: C, 80.00; H, 6.72. Calc. for $C_{32}H_{32}O_4$: C, 79.97; H, 6.71%).

5,11,17,23 - *Tetra* - t - *butyl* - 25,26,27,28 - *tetramethoxycalix*[4]*arene* (**2B**). A 5.0 g sample of **1B** in 25 ml THF and 2.5 mL DMF was treated with 0.5 g NaH and 5 mL MeI. The mixture was refluxed 1 hr, the THF was evaporated, and the residue was treated with 100 mL water. The white ppt was collected by filtration and recrystallized from $CHCl_3$–MeOH to give **2B** as colorless, elongated blades: m.p. 226.5–228°; ^{1}H NMR ($CDCl_3$) δ 6.6 (br s, 8, ArH), 4.2–2.9 (m, 20, CH_2 and CH_3O), 1.30 and 1.24 ppm (s, 36, $C(CH_3)_3$). (Found: C, 81.37; H, 9.14. Calc. for $C_{48}H_{64}O_4$: C, 81.82; H, 9.09%).

25,26,27,28-*Tetraethoxycalix*[4]*arene* (**3A**). A 1.0 g sample of **1A** in 50 mL THF and 5 mL DMF was treated with 1.0 g NaH followed by 19.5 g EtI as described to give 0.75 g (60%) of **3A** as colorless needles after recrystallization from $CHCl_3$–MeOH: m.p. 315.5–317°; ^{1}H NMR ($CDCl_3$) δ 7.2–6.3 (12 lines, 12, ArH), 4.1–3.1 (15 lines, 16, ArC$\underline{H}_2$Ar and $CH_3C\underline{H}_2O$), 1.44 (t, 6, J = 9 Hz, $C\underline{H}_3CH_2O$), 1.37 (t, 3, J = 7.2 Hz, $C\underline{H}_3CH_2O$), 0.94 ppm (t, 3, J = 7.0 Hz, $C\underline{H}_3CH_2O$); mass spectrum (EI, 90 eV), *m/e* 536 (100%), 537 (31%) (M and M + 1). (Found: C, 80.36; H, 7.49. Calc. for $C_{96}H_{40}O_4$: C, 80.56; H, 7.51%).

5,11,17,23 - *Tetra* - t - *butyl* - 25,26,27,28 - *tetraethoxycalix*[4]*arene* (**3B**). A 0.50 g sample of **1B** in 25 mL THF and 5 mL DMF was treated with 0.5 g NaH followed by 10 g EtI as described to give **3B** as colorless plates after recrystallization from i-PrOH: m.p. 261–262°; ^{1}H NMR ($CDCl_3$) δ 7.2–6.5 (m, 8, ArH), 3.96 (d, 2, J = 12 Hz, ArC$\underline{H}_2$Ar), 3.85–3.40 (m, 12, ArC$\underline{H}_2$Ar as a singlet at 3.63 and $OC\underline{H}_2CH_3$), 2.95 (d, 2, J = 12 Hz, ArC$\underline{H}_2$Ar), 1.52–1.0 ppm (11 lines, 48, $OCH_2C\underline{H}_3$ and $C(CH_3)_3$); ^{13}C NMR ($CDCl_3$) δ 153.5 (Ar), 143.3 (Ar), 142.8 (Ar), 136.0 (Ar), 133.1 (Ar), 132.7 (Ar), 131.9 (Ar), 127.8 (Ar), 126.0 (Ar), 125.3 (Ar), 125.1 (Ar), 69.3 ($O\underline{C}H_2CH_3$), 68.3 ($O\underline{C}H_2CH_3$), 66.9 ($O\underline{C}H_2CH_3$), 38.8 (Ar$\underline{C}H_2$Ar), {33.7, 31.7, 31.4, 30.1, 16.6 and 16.1 ppm} ($OCH_2\underline{C}H_3$ and $C(\underline{C}H_3)_3$). (Found: C, 81.74; H, 9.73. Calc. for $C_{52}H_{72}O_4$: C, 82.10; H, 9.47%).

25,26,27,28-*Tetraallyloxycalix*[4]*arene* (**4A**. A 1.07 g sample of **1A** in 50 mL THF and 5 ml DMF was treated with 1.0 g NaH and 14 g allyl bromide as described for **2A**, and 1.09 g (74%) of **4A** was obtained as colorless needles after recrystallization from 95% EtOH: m.p. 184–185°; ^{1}H NMR ($CDCl_3$) δ 7.2–6.5 (m, 16, ArH and HC=), 5.3–4.9 (m, 8, H_2C=), 4.4–3.0 ppm (m, 16, $C\underline{H}_2C$= and ArC$\underline{H}_2$Ar); ^{13}C NMR ($CDCl_3$) δ 155.9, 137.2, 135.5, 135.2, 134.7, 134.2, 133.9, 133.2, 132.1, 130.8, 129.8, 128.8, 128.4, 128.1, 122.3, 121.7, 116.9, 115.1 (these 20 lines assigned to Ar and C=C), 75.8, 75.0, 73.8, 72.5 (these 4 lines assigned to $\underline{C}H_2C$=C), 36.1 (Ar$\underline{C}H_2$Ar), 31.2 ppm (Ar$\underline{C}H_2$Ar); mass spectrum (EI, 90 eV), *m/e* 584 (100%), 585 (37%) (M and M + 1). (Found: C, 82.43; H, 6.97. Calc. for $C_{40}H_{40}O_4$: C, 82.16: H, 6.90%).

5,11,17,23 - *Tetra* - t - *butyl* - 25,26,27,28 - *tetraallyloxycalix*[4]*arene* ((**4B**) was prepared as described for **2A** and obtained in 75% yield, m.p. 186–187°. An analytical sample was produced as colorless needles after recrystallization from $CHCl_3$/MeOH: m.p. 188–189°; ^{1}H NMR ($CDCl_3$) δ 6.77 (s, 8, ArH), 6.44 (m, 4, HC=), 5.26 (d, 4, H_2C=), 5.19 (d, 4, H_2C=), 4.44 (d, 8, J = 7 Hz, $C\underline{H}_2CH{=}CH_2$), 4.39 (d, 4, J = 12 Hz, ArC$\underline{H}_2$Ar), 3.13 (d, 4, J = 12 Hz, ArC$\underline{H}_2$Ar), 1.08 ppm (s, 36, $C(CH_3)_3$); ^{13}C NMR ($CDCl_3$) δ 153.2, 144.5, 136.3, 134.0, 124.9, 116.3 (these 6 lines assigned to Ar and C=C), 75.7 ($\underline{C}H_2C$=C), 33.8 (Ar$\underline{C}H_2$Ar), 31.4 ppm ($C(\underline{C}H_3)_3$). (Found: C, 81.82; H, 8.87. Calc. for $C_{56}H_{72}O_4 \cdot CH_3OH$: C, 81.42; H, 9.05%).

25,26,27,28-*Tetrabenzyloxycalix*[4]*arene* (**5A**). A 1.0 g sample of **1A** was dissolved in 50 mL THF and 5 mL DMF and treated with 1.0 g NaH followed by 9.1 g benzyl chloride. The mixture was refluxed for 1 hr and then worked up to give 0.70 g (37%) of **5A** as white needles after recrystallization from glacial HOAc: m.p. 135–136°; ^{1}H NMR ($CDCl_3$) δ 7.25–7.20 (m, 20, ArH), 6.54 (s, 12, ArH), 4.93 (s, 8, $OC\underline{H}_2$Ar), 4.23 (d, 4, J = 13 Hz, ArC$\underline{H}_2$Ar), 2.96 ppm (d, 4, J = 13 Hz, ArC$\underline{H}_2$Ar). (Found: C, 86.20; H, 6.19. Calc. for $C_{56}H_{48}O_4$: C, 85.68; H, 6.16%).

5,11,17,23 - *Tetra* - t - *butyl* - 25,26,27,28 - *tetrabenzyloxycalix*[4]*arene* (**5B**) prepared as described for **2A** and obtained in 65% yield. An analytical sample was produced as colorless needles after recrystallization from $CHCl_3$/MeOH: m.p. 230–231°; ^{1}H NMR ($CDCl_3$) δ 7.20 (s, 20, ArH), 6.68 (s, 8, ArH), 4.85 (s, 8, $OC\underline{H}_2$Ar), 4.16 (d, 4, J = 13 Hz, ArC$\underline{H}_2$Ar), 2.90 (d, 4, J = 13 Hz, ArC$\underline{H}_2$Ar), 1.08 ppm (s, 36, $C(CH_3)_3C$). (Found: C, 85.76; H, 8.07. Calc. for $C_{72}H_{80}O_4$: C, 85.71; H, 7.94%).

5,11,17,23 - *Tetra* - t - *butyl* - 25,26,27,28 - *tetrakistrimethylsilyloxycalix*[4]*arene* (**6B**). A 0.2 g sample of **1B** was dissolved in 10 mL MeCN, treated with 1.5 mL N,O-tris(trimethylsilyl)acetamide,[9] and heated at reflux for 16 hr under N_2. The product that precipitated upon cooling the mixture was removed by filtration and recrystallized from $CHCl_3$–MeOH to give 0.27 g (92%) of colorless, elongated blades: m.p. 338° (softening at 315–320°); ^{1}H NMR ($CDCl_3$) δ 6.80 (s, 8, ArH), 4.45 (d, 4, J = 12 Hz, ArC$\underline{H}_2$Ar), 3.00 (d, 4, J = 12 Hz, ArC$\underline{H}_2$Ar), 1.18 (s, 36, $C(CH_3)_3$), 0.35 ppm (s, 36, $Si)CH_3)_3$). (Found: C, 71.51; H, 9.47. Calc. for $C_{56}H_{88}O_4Si_4$: C, 71.79; H, 9.40%).

5,11,17,23 - *Tetraallyl* - 25,26,27,28 - *tetrakistrimethylsilyloxycalix*[4]*arene* (**6C**) was prepared as described and obtained in 77% yield. An analytical sample was produced as colorless needles after recrystallization from MeOH/H_2O: m.p. 173–181°; ^{1}H NMR ($CDCl_3$) δ 6.43 (s, 8, ArH), 6.05–5.43 (m, 4, HC=), 5.13 (br s, 4, H_2C=), 4.93–4.63 (m, 4, H_2C=), 4.31 (d, 4, J = 12 Hz, ArC$\underline{H}_2$Ar), 3.12 (br s, 8, $C\underline{H}_2CH{=}CH_2$), 3.02 (d, 4, J = 12 Hz, ArC$\underline{H}_2$Ar), 0.26 ppm (s, 36, $Si(CH_3)_3$). (Found: C, 71.49; H, 8.45. Calc. for $C_{52}H_{72}O_4Si_4$: C, 71.50; H, 8.31%).

25,26,27,28-*Tetraacetoxycalix*[4]*arene* (**7A**). A 0.50 g sample of **1A** was dissolved in 25 ml Ac_2O, treated with a small amount of *p*-toluenesulfonic acid, and refluxed for 18 hr. The cooled mixture was poured into 150 mL water containing 1 mL conc H_2SO_4, stirred for 3 hr, and extracted with $CHCl_3$. The $CHCl_3$ extract was washed, dried, and evaporated to give 0.51 g (73%) of a white powder which was recrystallized from benzene to give 0.36 g (51%) of small, colorless rhomboids which collapse to a white powder upon drying: m.p. 399–402° (dec); ^{1}H NMR ($CDCl_3$) δ 7.01 (s, 12, ArH), 3.72 (s, 8, CH_2), 1.53 ppm (s, 12, CH_3CO); ^{13}C NMR ($CDCl_3$) δ 167.8 (C=O), 148.2 (Ar), 133.0 (Ar), 129.0 (Ar), 125.3 (Ar), 37.4 (CH_3), 28.3 ppm (Ar$\underline{C}H_2$Ar). (Found: C, 72.90; H, 5.40. Calc. for $C_{36}H_{32}O_8$: C, 72.97; H, 5.41%).

5,11,17,23 - *Tetra* - t - *butyl* - 25,26,27,28 - *tetraacetoxycalix*[4]*arene* (**7B**). As described,[1] a 1.5 g sample of **1B** was treated with 37 mL Ac_2O and 2 drops conc H_2SO_4. The mixture was heated under reflux for 2 hr, poured into 300 mL ice water, and the ppt was collected by filtration as 1.1 g of a brown solid. After one crecystallization from AcOH a material was obtained that softened at 322° (the m.p. reported by Ungaro *et al.* is 320° (dec)) but did not melt at that temp. After several more recrystallizations from AcOH a material was obtained that was pure by TLC analysis, that softened about 330–340°, and that melted at 383–386°.

25,26,27 - *Trimethoxy* - 28 - *hydroxycalix*[4]*arene* (**8**). A 1.14 g sample of **1A** in 25 mL DMF was treated with 1.81 g BaO, 1.94 g $Ba(OH)_2 \cdot 8H_2O$, and 6.67 g Me_2SO_4. After the mixture had been stirred for 15 hr at room temp, 5 mL conc NH_4OH was added followed by 25 mL water. The product was extracted into $CHCl_3$, and the $CHCl_3$ was washed with water, dried over Na_2SO_4, and evaporated. The residue was recrystallized from $CHCl_3$–MeOH to give 0.76 g (60%) of **8** as colorless needles: m.p. 212.5–214.5°; IR (KBr) 3450 cm^{-1} (OH stretching); ^{1}H NMR ($CDCl_3$) δ 7.2–6.4 (m, 12, ArH), 5.65 (s, 4, OH), 4.3–3.0 (m, 17, ArC$\underline{H}_2$Ar and CH_3O) with singlet and shoulder at 3.20 ppm; mass spectrum (EI, 90 eV) 466 (100%), 467 (31%) (M and M + 1). (Found: C, 79.86; H, 6.48. Calc. for $C_{31}H_{30}O_4$: C, 79.80; H, 6.48%).

5,11,17,23 - *Tetra* - t - *butyl* - 25,27 - *dimethoxy* - 26,28 - *dihydroxycalix*[4]*arene* (**9**). A 1.0 g sample of **1B** was suspended in 250 mL ether, cooled in a dry ice–acetone bath, and treated with an ether soln of diazomethane prepared from 16 g N,N′ - dimethyl - N,N′ - dinitrosoterephthalamide.[20] The mixture was allowed to warm to room temp and was stirred for 48 hr, by which time all of the starting material had gone into soln. The excess diazomethane was decomposed by the addition of 1 N HCl, and the ether layer was separated, dried over Na_2SO_4, and evaporated to dryness. The residue was triturated with petroleum ether (b.p. 35–60°) left a white crystaltine solid which was crystallized from $CHCl_3$–MeOH to give colorless rhombs; IR (KBr) 3450 cm^{-1} (OH stretching); ^1H NMR ($CDCl_3$) δ 7.02 (s, 4, ArH), 6.72 (s, 4, ArH), 4.27 (d, 4, J = 13 Hz, CH_2), 3.90 (3, 6, CH_3O), 3.30 (d, 4, J = 13 Hz, CH_2), 1.30 (s, 18, $C(CH_3)_3$), 0.92 ppm (3, 18, $C(CH_3)_3$); ^{13}C NMR ($CDCl_3$) δ 123.5 (Ar), 123.0 (Ar), 120.9 (Ar), 117.6 (Ar), 112.7 (Ar), 110.0 (Ar), 108.5 (Ar), 108.3 (Ar), 69.5 (CH_3O), 29.4 ($\underline{C}(CH_3)_3$); 28.7 ($C(\underline{C}H_3)_3$), 28.5 ($Ar\underline{C}H_2Ar$), 28.3 ppm ($C(\underline{C}H_3)_3$). (Found: C, 81.81; H, 9.09. Calc for $C_{46}H_{60}O_4$: C, 81.66; H, 8.87%).

5,11,17,23 - *Tetraallyl* - 25,27 - *dibenzyloxy* - 26,28 - *dihydroxycalix*[4]*arene* (**10**). Following the procedure of Dewick[21] for benzylation, a 0.212 g (0.36 mmol) sample of **1C** in 25 ml dry acetone was treated with 0.403 g (1.64 mmol) benzyl tosylate[22] and refluxed for 2 hr with stirring. The crude product obtained from the mixture was recrystallized from $CHCl_3$–MeOH to give 0.203 g (73%) of colorless, fine needles: m.p. 171–172.5°; ^1H NMR ($CDCl_3$) δ 7.8–7.3 (m, 10, benzyl ArH), 6.88 (s, 4, ArH), 6.71 (s, 4, ArH), 6.0–5.6 (m, 4, HC=), 5.12–4.68 (m, 12, H_2C= and $C_6H_5C\underline{H}_2$), 4.26 (d, 4, $ArC\underline{H}_2Ar$), 3.36–2.92 ppm (m, 14, $ArC\underline{H}_2Ar$, $C\underline{H}_2CH{=}CH_2$ and OH). (Found: C, 83.67; H, 6.68. Calc. for $C_{54}H_{52}O_4 \cdot 1/2CH_3OH$: C, 83.84; H, 6.92%).

5,11 - *Di* - *phenyl* - 17,23 - *di* - t - *butyl* - 25,26,27,28 - *tetrakistrimethylsilyloxycalix*[4]*arene* (**12**) was prepared as described above for **6B** and obtained as colorless crystals after recrystallization from 95% EtOH: m.p. 275–276° (softening at 262°); ^1H NMR ($CDCl_3$) δ 7.3–6.6 (m, 18, ArH), 4.4–4.22 (m, 4, $ArC\underline{H}_2Ar$), 3.2–2.8 (m, 4, $ArC\underline{H}_2Ar$), 0.83 (s, 18, $C(CH_3)_3$), 0.24 (s, 18, $Si(CH_3)_3$), 0.21 ppm (s, 18, $Si(CH_3)_3$). (Found: C, 73.23; H, 8.43. Calc. for $C_{60}H_{80}O_4Si_4 \cdot 1/2C_2H_5OH$: C, 73.20; H, 8.38%).

5,11 - *Diphenyl* - 17,23 - *di* - t - *butyl* - 25,26,27,28 - *tetraacetoxycalix*[4]*arene* (**13**) was prepared by the procedure described and as reported.[10] The crude product was separated into three isomers: Isomer-A, m.p. 314–316°; Isomer-B, m.p. 335° (with shrinking at 252° and color change at 260°); Isomer-C, m.p. 293–295° with shrinking at 286°.

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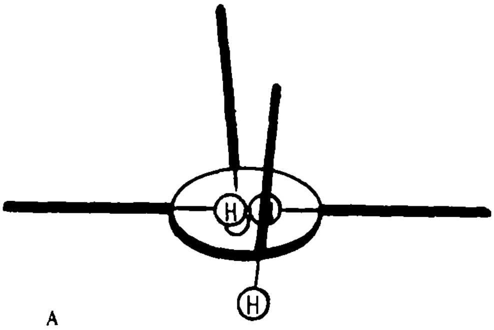
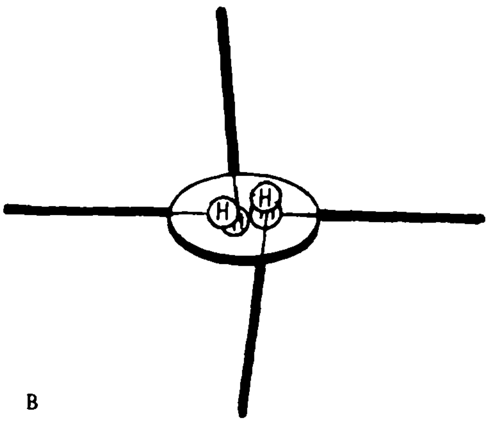


A



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