Photo-CIDNP Studies on Calixarenes and Bridged Calixarenes

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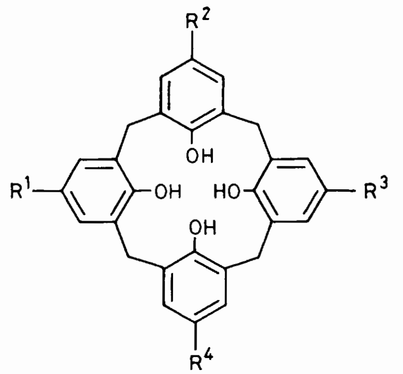
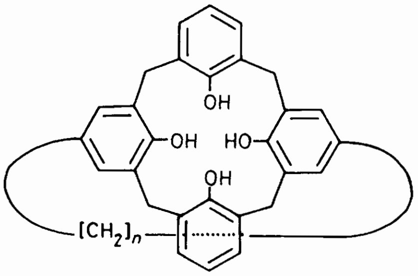
A comparison of the photo-CIDNP spectra of calix(4)arenes (**1**) and bridged calix(4)arenes (**2**) shows that a certain degree of flexibility is necessary for a rapid intramolecular hydrogen transfer from the hydroxy groups of phenolic units to adjacent phenoxyl radical units.

Recently we reported a pronounced selectivity in the photo-CIDNP spectra of oligonuclear phenolic compounds.[1] Only the most heavily substituted phenolic rings showed CIDNP effects, and these results were explained by a mechanism involving very rapid hydrogen atom transfers between neighbouring phenol and phenoxyl units. After H abstraction,



(1a) R^1 = R^2 = Me , R^3 = R^4 = H
(1b) R^1 = R^3 = Me , R^2 = R^4 = H



(2a) n = 6
(2b) n = 8
(2c) n = 12
(2d) n = 16

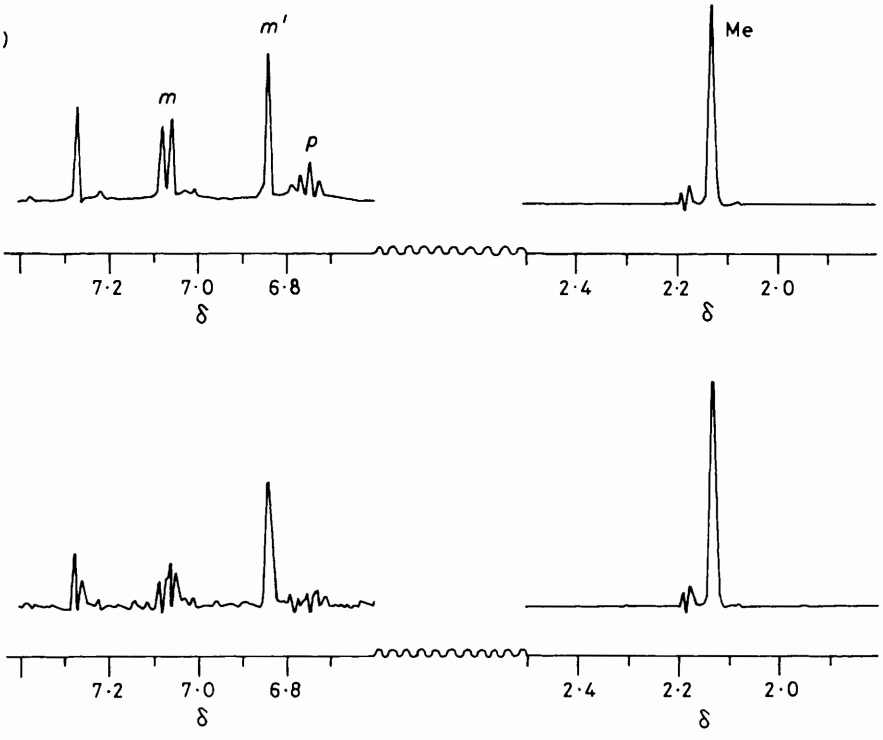


Figure 1. 360 MHz ^{1}H n.m.r. spectrum (a) and photo-CIDNP difference spectrum (b) of calixarene (**1b**).

No polarization of *para* protons is found. *m* and *p* indicate *meta* and *para* protons in the unsubstituted phenol rings, while *m'* indicates *meta* protons in the *para*-substituted rings.

reshuffling of H atoms takes place rapidly (on the CIDNP time-scale) to form the most stable phenoxyl radical. Here we present some photo-CIDNP results on cyclic oligomers, the calixarenes (**1**) and the bridged calixarenes (**2**), which provide some insight into the conditions necessary for rapid intramolecular H atom transfer.

^{1}H Photo-CIDNP spectra of phenols taken with flavin as the photo-excited dye are characterized by a strong emission effect for *ortho*- and *para*-protons and weakly enhanced absorption for the *meta*-protons. When methyl or methylene groups are present at *ortho* or *para* positions, these protons show strong positive enhancements. The effect has found use in the study of proteins, where it serves as an accessibility probe for tyrosine units.[2,3] In the case of *ortho*-methylene bridged oligophenols, however, the observed selectivity is not due to differences in accessibility of the OH groups, but rather to H atom transfers and it was suggested that these were favoured by pre-existing hydrogen bonds.[1]

In calix(4)arenes these intramolecular hydrogen bonds between neighbouring hydroxy groups are known to be present. *X*-Ray analysis has revealed several examples[4] in which the molecules exist in the so-called cone conformation.[5] O–O distances of 2.67 Å were found, for instance, for t-butyl calix(4)arene. Temperature dependent ^{1}H n.m.r. spectra have shown a rapid interconversion of the two opposite but equivalent cone conformations.[6] During this conformational inversion the hydroxy groups have to pass through the annulus.

Photo-CIDNP experiments with the calixarenes (**1a**) and (**1b**), which are partially substituted by methyl groups in *para*-positions,† show a polarization only for the *p*-cresol units, not for the unsubstituted phenol units. As an example, Figure 1 shows the ^{1}H n.m.r. and photo-CIDNP difference spectra of (**1b**). These results are in complete agreement with analogous observations for linear oligomers[1] and show that all the radicals formed by hydrogen abstraction from a phenol unit are rearranged before recombination to more stable radicals with the radical position at one of the *p*-cresol units.

In compounds (**2**)† the cone conformation of calix(4)arenes is fixed by an aliphatic chain, connecting two opposite phenolic units,[7] as has been confirmed by *X*-ray analysis for two compounds with $n = 8$[8] and more recently for compounds with $n = 6$ and $n = 16$.[9] O–O distances of 2.62—2.72 Å are found for $n = 8$ [compound (**2b**)], which are comparable to those of calix(4)arenes. However, photo-CIDNP spectra of (**2a**) and (**2b**) show polarization for both kinds of phenolic units, not only for the *para*-alkyl substituted units. This indicates that all hydroxy groups can be abstracted with a similar probability by the excited dye, but also suggests that a closer contact between the hydroxy groups is necessary for a rapid rearrangement on the CIDNP time scale. Such a closer contact, which implies O–O distances momentarily $<$*ca.* 2.6 Å, is obviously impossible in the rigid compounds (**2a**) and (**2b**). As the chain length, *n*, increases, the calixarene part of the molecules becomes more and more flexible. This increasing flexibility leads to stronger intramolecular hydrogen bonds, as indicated by decreasing values for ν_{OH} in the i.r. spectra and by a downfield shift of the OH signals in the ^{1}H n.m.r. spectra. A further consequence is that the polarization of the unsubstituted phenol units decreases, as demonstrated by the decreasing intensity of the emissive triplet of the *para*-protons (see Figure 2), owing to rapid H atom transfer. For $n = 16$ (**2d**), the rearrangement to the most stable radical occurs nearly as quickly as in the unbridged calixarenes (**1**).

These results show that the photo-CIDNP effect provides a sensitive tool to monitor rapid H atom transfer reactions between phenol-phenoxy units, that take place on a time-scale of about 10^{-10}—10^{-9} s. Further measurements with selected linear and cyclic oligomers are in progress to define better the conformational requirements for these reactions.

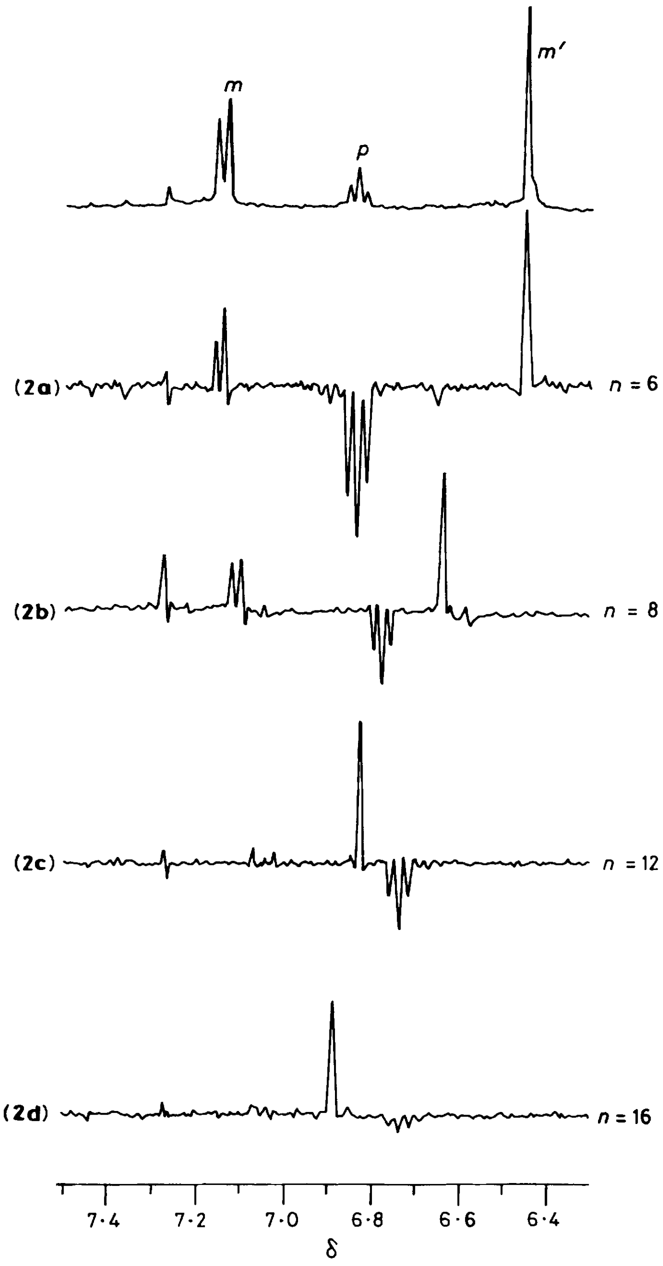


Figure 2. Photo-CIDNP difference spectra of bridged calixarenes (**2a**)—(**2d**) in the aromatic region.

The intensity of the emissive triplet for the *para* protons decreases with increasing number of methylene groups (*n*) in the aliphatic bridge. For comparison, the 360 MHz ^{1}H n.m.r. spectrum of (**2a**) is shown above.

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† Calixarenes (**1**) were synthesized by debutylation of well known precursors[10] as described in the literature.[11] The bridged calixarenes were obtained by dehalogenation,[12] (**2b**), or by debutylation, (**2a**), (**2c**), (**2d**), of compounds prepared similar to the examples already published.[7,8]

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