Homoallylic Coupling in 1,4-Dihydronaphthalenes

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The Birch reduction of 5-acenaphthoic acid using lithium in ammonia affords a high yield of *cis*-2a.5-dihydro-5-acenaphthoic acid as the sole isolated product whereas reduction with sodium gives a mixture of the *cis*- and *trans*-isomers. The ^1H n.m.r. spectrum of the *cis*-dihydro-acid exhibits the largest homoallylic coupling constant yet seen in a 1.4-dihydronaphthalene ring system (*ca.* 8 Hz), a result which is consistent with considerable puckering expected for the dihydrobenzene ring in this strained system. This result is compared with that observed in 4-methyl-1.4-dihydronaphthoic acid.

INDO CALCULATIONS [1] indicate that homoallylic coupling can be quite large when the interacting nuclei are suitably oriented. This prediction has been borne out experimentally particularly in the ^1H n.m.r. spectra of 1,4-dihydrobenzenes † and related systems.[2] In the case of 1,4-dihydrobenzenes (I) there are two equivalent interaction pathways available, one through each of the double bonds, with a consequent doubling of the observed homoallylic splitting. The experimental coupling constants have been used to probe the geometry of the unconstrained 1,4-dihydrobenzene ring, it being concluded that this is essentially planar.[2] In order to examine the dependence of the homoallylic coupling on the ring geometry it is necessary to incorporate the 1,4-dihydrobenzene ring into a rigid polycyclic structure. It has been found [3] that *cis*-3a,6-dihydroindane-6-carboxylic acid (II) has $J_{5,7a}$ 11.4 Hz. Models of this compound suggest that the C–H bonds of interest are essentially parallel and oriented to offer maximal overlap of the σ-electrons with the p-orbitals of the double bonds, and that the ring has a degree of puckering $\alpha = 140°$.‡ This coupling constant is close to the maximum predicted for J_{cis} by the theoretical calculations and should be compared with the value of 8.6 Hz § observed [4] in 1,4-dihydrobenzoic acid itself, and with *ca.* 6 Hz found [2] in two of its 2,6-disubstituted derivatives. In the tetrahydroparacyclophane system (III) a large homoallylic coupling has been observed [5] in the dihydrobenzoic acid ring, which has been assigned to $J_{1,4\text{-}cis}$. However, as this system is somewhat flexible, it is difficult to assess accurately the degree of puckering which the carboxydihydrobenzene ring might have.

In the case of the 1,4-dihydronaphthalenes and 9,10-dihydroanthracenes the observed couplings are much smaller. For example, in 1,4-dihydronaphthoic acid (IV) the observed values are J_{cis} 3.84 and J_{trans} 4.36 Hz (but see ref. 2 concerning these assignments). It is not clear whether this ring system is nearly planar, or whether the observed coupling results from the rapid equilibration of two unequally populated boat conformations, as shown in (IV).[2] If the latter is true then, whilst J_{trans} should be essentially unaffected by the position of equilibrium, the observed J_{cis} will be the population-weighted average of large pseudoaxial–pseudoaxial ($J_{\psi ax/\psi ax}$) and a small pseudoequatorial–pseudoequatorial ($J_{\psi eq/\psi eq}$) coupling. For unsubstituted 9,10-dihydroanthracene (V), the long-range pseudoaxial–pseudoaxial coupling has been estimated [2] at 4.8 Hz. Crystallographic data suggest that this ring is highly puckered in the solid state (α *ca.* 145°),[6] and for such a situation J_{cis} is predicted to be 10.4 Hz in a 1,4-dihydrobenzene ring. Reducing this value by a factor of 2/3 to allow for the reduced π-bond order leads to a predicted value of 6.9 Hz for the pseudoaxial–pseudoaxial coupling in (V), somewhat higher than the observed value. It was therefore of interest to prepare a rigid structure in which homoallylic coupling through an aromatic ring could be studied. Models suggest that 2a,5-dihydro-5-acenaphthoic acid (VI) should be puckered

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† Though strictly cyclohexa-1,4-dienes the dihydrobenzene numbering will be used here to avoid confusion in comparisons with the dihydronaphthalenes *etc.*

‡ The angle α here is that between the two planes defined by C(1)–C(2)–C(3)–C(4) and C(1)–C(6)–C(5)–C(4) in (I).

§ For a discussion of this value see ref. 2.

[1] M. Barfield and S. Sternhell, *J. Amer. Chem. Soc.*, 1972, **94**, 1905.

[2] M. C. Grossel and M. J. Perkins, *J.C.S. Perkin II*, 1975, 1544 and references therein.

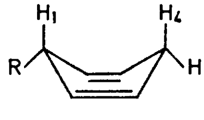
[3] G. H. Whitham and S. G. Davies, personal communication. We are grateful for permission to cite these results.

[4] J. L. Marshall, K. C. Erickson, and T. K. Folsom, *J. Org. Chem.*, 1970, **35**, 2038.

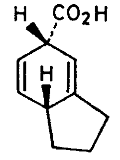
[5] J. L. Marshall and B.-H. Song, *J. Org. Chem.*, 1975, **40**, 1942.

[6] W. G. Ferrier and J. Iball, *Chem. and Ind.*, 1954, 1296.

to a similar extent to the dihydroindanecarboxylic acid (II), and in this system coupling will be through one double bond and one aromatic ring rather than two double bonds [see (VII)].



(I)



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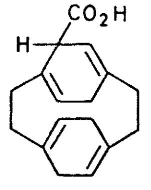

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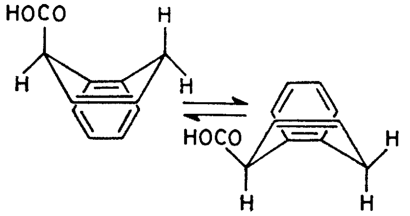
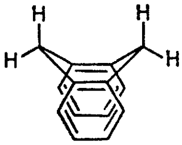
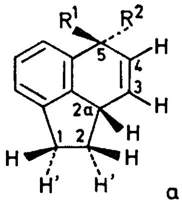


(IV)

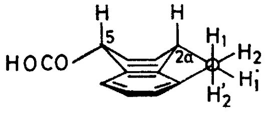


(V)

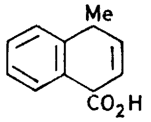


(VI)

a; R^1=H,R^2=CO_2H
b; R^1=Me,R^2=CO_2H
c; R^1=CO_2H,R^2=H
d; R^1=CO_2H,R^2=Me



(VII)



(VIII)

RESULTS AND DISCUSSION

The Birch reduction of 5-acenaphthoic acid using lithium and ammonia and quenching the anion formed with ammonium chloride afforded a single product, the 90 MHz ^1H n.m.r. spectrum of which was consistent with 2a,5-dihydro-5-acenaphthoic acid (VIa). The lowest field non-olefinic absorption at τ 5.63 appeared as a broadened doublet (J 8.4 Hz), which sharpened on decoupling of the vinyl protons consistent with its assignment to the proton on C-5. Irradiation of this absorption affected both the vinylic absorptions and that of the other low-field aliphatic multiplet at τ 6.56. This latter was therefore assigned to 2a-H which resonates downfield from those of the alkyl bridge since it is both allylic and benzylic. At 270 MHz the spectrum simplified sufficiently for first-order analysis. The parameters obtained were used to simulate both the 90 and 270 MHz spectra, and are presented in the Table.

Reduction with lithium in ammonia followed by quenching with methyl iodide produced a single crystalline carboxylic acid, the ^1H n.m.r. spectrum of which now lacked the absorption at τ 5.63 (5-H) but contained a singlet at τ 8.60 (3-H) assigned to a methyl group α to the carboxy-function. The remainder of the spectrum above τ 5 was found to be virtually identical with that obtained from the dihydro-acid (VIa) upon decoupling 5-H. From this result this compound has been assigned the structure (VIb).

Chemical shifts and coupling constants in the 2a,5-dihydro-5-acenaphthoic acid system (VI)

(a) Chemical shift (τ)	(VIa)†	(VIb)‡
ν_1	6.98	7.02
$\nu_{1'}$	7.15	7.20
ν_2	7.55	7.53
$\nu_{2'}$	8.25	8.35
ν_{2a}	6.56	6.53
ν_3	3.73	3.91
ν_4	3.95	3.95
ν_5	5.61	

(b) Coupling constants (Hz)			
$J_{1.1'}$	−15.3	$J_{2.2a}$	7.08
$J_{1.2}$	7.08	$J_{2'\ 2a}$	11.59
$J_{1.2'}$	11.29	$J_{2a.3}$	1.80
$J_{1,2a}$	0.0	$J_{2a.4}$	−3.22
$J_{1'.2}$	0.0	$J_{2a.5}$	8.46
$J_{1'.2'}$	7.75	$J_{3.4}$	10.17
$J_{1',2a}$	0.0	$J_{3,5}$	−3.09
$J_{2.2'}$	−11.59	$J_{4.5}$	1.93

† In $CDCl_3$. The spectrum of (VIb) showed essentially identical chemical shifts for the appropriate protons in this solvent. ‡ In $(CD_3)_2CO$.

The large 2a,5-coupling observed in (VIa) must reflect a diaxial interaction across the dihydronaphthalene ring since 2a-H is of necessity pseudoaxial, and pseudoaxial–pseudoequatorial couplings would not be expected to be of this size even in a planar dihydronaphthalene (or even dihydrobenzene) ring for which geometry the *trans*-coupling should reach a maximum. From the close similarity of the spectra of (VIa and b) the 5-methylated acid was also assigned *cis*-stereochemistry. Irradiation of the 5-methyl group produced a surprisingly small[7] (4%) but reproducible nuclear Overhauser enhancement on the signal due to 2a-H.

Further evidence for the highly puckered nature of the dihydronaphthalene ring in (VI) is obtained from the vicinal and allylic couplings. Marshall and his co-workers[8] have reported vicinal couplings of 2.44 and 4.60 Hz respectively, for the pseudoaxial and pseudo-equatorial protons on C-4 in 1,4-dihydronaphthoic acid. The analogous vicinal couplings in the dihydroacenaphthoic acids (VI) are <2 Hz, a result consistent with a large dihedral angle between the interacting protons and hence indicative of a high degree of puckering in the dihydrobenzene ring.

Barfield[9] has calculated the angular dependence of allylic couplings. We have used these data to estimate the dependence of such coupling in the cyclohexadiene

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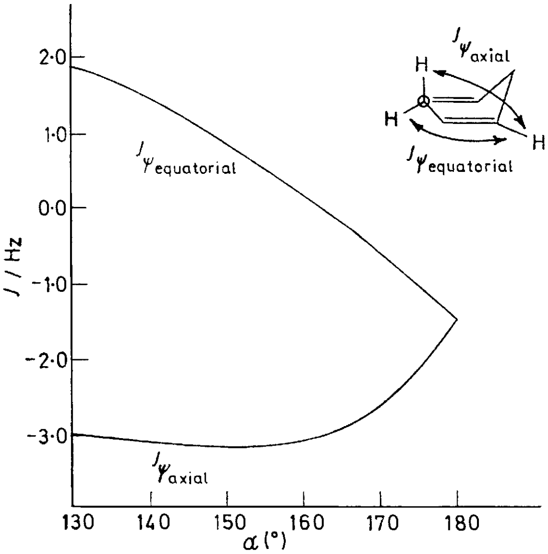
[7] R. A. Bell and J. K. Saunders, *Canad. J. Chem.*, 1970, **48**, 1114. Models suggest a separation of *ca.* 2.8 Å for which an effect of up to 10% might be expected.

[8] J. L. Marshall and T. K. Folsom, *J. Org. Chem.*, 1971, **36**, 2011.

[9] M. Barfield, *J. Amer. Chem. Soc.*, 1971, **93**, 1066.

system upon ring puckering in a manner similar to that previously reported for homoallylic interaction.[2] The results are presented in the Figure. It will be seen that for a highly puckered ring (α *ca.* 140—150°) the allylic coupling of a pseudoaxial proton should be *ca.* −3 Hz, in good agreement with the values presented in the Table ($J_{2a,4}$ and $J_{3,5}$). In dihydroindane (II) a value of 3 Hz has also been observed for $J_{4,6}$ (sign undetermined).[3] Allylic couplings of 0.8 Hz have been observed in the spectra of 1,4-dihydro-2,6-dimethoxybenzoic acid and 1,4-dihydro-2,6-bis(trideuteriomethyl)benzoic acid.[2] Other evidence has been presented for the approximate planarity of the dihydrobenzene ring in these compounds, and the allylic coupling reported is consistent with a value of α = *ca.* 173°. Attempted epimerisation to, perhaps, a mixture of the pseudoaxial and pseudoequatorial dihydro-acids (VIa and c) using KOBu^t–DMSO was unsuccessful, a mixture of the aromatised acid and a compound tentatively assigned (n.m.r.) as a double-bond positional isomer being obtained. However, when sodium was used in place of lithium in these reductions the reaction was found to be no longer stereospecific; a result which has been observed previously and ascribed to decreased association of the metal counter-ion.[10] Reductive methylation, like reduction, was also no longer stereospecific with sodium, approximately equal amounts of the inseparable *cis*- and *trans*-isomers being obtained as a slowly solidifying oil. Confirmation that the product contained two isomers, and the approximate assessment of the proportions in which they were formed was obtained from the n.m.r. spectrum of the derived mixture of methyl esters, the spectrum of which exhibited two pairs of signals for both the ester and alkyl methyl signals of approximately equal intensity. The signals due to 5-H in the mixture of acids obtained upon reduction without methylation were found to be sufficiently different at 90 MHz to allow an estimate of the composition of this mixture as well, the *cis*-isomer (VIa) comprising *ca.* 50% of the product. This also confirmed the high stereospecificity of the lithium reduction (estimated by n.m.r. to be >95%).



Allylic coupling in 1,4-cyclohexadienes (for α see text)

As a model for the 2a,5-dihydro-5-acenaphthoic acid system, 4-methyl-1-naphthoic acid was also reduced with lithium in ammonia to 1,4-dihydro-4-methyl-1-naphthoic acid (VIII). The ^{1}H n.m.r. spectrum of the product indicated that it was a mixture of two isomers. Irradiation of the vinyl protons simplified the signal assigned to 1-H into a pair of doublets (J 4.67 and 3.63 Hz), that with larger coupling constant being of slightly lower intensity. These spectra may be interpreted in terms of a mixture of unequal proportions of *cis*- and *trans*-isomers and shows that the stereospecificity of the reduction of 5-acenaphthoic acid must derive from the steric requirements of the polycyclic structure rather than from electronic factors arising from the substitution pattern of the naphthalene nucleus. The couplings observed are similar to those reported[11] for 1,4-dihydro-1-naphthoic acid itself (J_{cis} 3.84, J_{trans} 4.36 Hz). The increase in the larger and decrease in the smaller value may reflect a slightly greater puckering of (VIII) resulting from steric interaction between the methyl group and the C-5 aromatic proton, but the failure to separate these isomers prevented an unambiguous assignment of the geometries and also measurement of allylic and vicinal couplings. In particular it is not reasonable to assume that the *cis*- and *trans*-isomers should be puckered to the same extent.

Conclusions.—The 2a,5-dihydroacenaphthene system (VI) seems to approach the optimum for homoallylic coupling in 1,4-dihydronaphthalenes, the observed pseudoaxial–pseudoaxial coupling constant being the largest yet reported for such compounds. It is interesting that this value is *ca.* 2/3 that observed in the dihydroindane (II) in which both π-bonds through which coupling is taking place are olefinic. Indeed models suggest that the dihydrobenzene ring in (VI) is more highly puckered even than that in (II). This comparison would appear to demonstrate that the magnitude of the expected coupling cannot simply be equated to π-bond order since the predicted value would then be *ca.* 10 Hz, but that the contribution to coupling through the aromatic system is *ca.* 1/2 that through the olefinic system, a point of some theoretical interest.

We are currently trying to obtain a crystal structure for (VI) which should provide an accurate geometry for this relatively rigid system. We are also exploring other polycyclic systems in which the dihydrobenzene ring is held in rigid conformations.*

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* *Note added in proof:* The relationship used both here and in ref. 2 relating the angle α to the parameter θ, used by Barfield[1,9] to define the relative orientation of the coupled protons is that derived by D. J. Atkinson and M. J. Perkins, *Tetrahedron Letters*, 1969, 2335.

[10] R. Lapouyade, P. Labandibar, and H. Bouas-Laurent, *Tetrahedron Letters*, 1971, 979.

[11] J. L. Marshall, A. M. Ihrig, and P. N. Jenkins, *J. Org. Chem.*, 1972, **37**, 1863.

EXPERIMENTAL

2a,5-*Dihydroacenaphthoic Acid* (VIa).—Lithium metal (0.021 g, 3.0 mmol) was added under nitrogen to a stirred solution of 5-acenaphthoic acid (0.25 g, 1.2 mmol) in dry ether (25 ml) and liquid ammonia (100 ml). After stirring for 10 min, the reaction was quenched at *ca.* −40° by the addition of excess of solid ammonium chloride and the ammonia allowed to evaporate. Work-up in the usual way [2] gave cis-2a,5-*dihydroacenaphthoic acid* (VIa) (0.21 g, 85%) as a crystalline solid which recrystallised from benzene as prisms, m.p. 158—162° (decomp.), $\nu_{max.}$($CHCl_3$) 3 500—2 400 (CO_2H) and 1 710 cm^{-1} (C=O), τ ($CDCl_3$) −0.5br (1 H, s, CO_2H), 2.82 (3 H, s, ArH), 3.73br (2 H, d, *J* 11 Hz), 3.95br (2 H, d, *J* 11 Hz), 5.63 (1 H, d, *J* 8.4 Hz), 6.56 (1 H, m), 7.08 (2 H, m), 7.55 (1 H, m), and 8.25 (1 H, m) (Found: C, 77.8; H, 6.15. $C_{13}H_{12}O_2$ requires C, 78.0; H, 6.05%).

When sodium (2.5 mol. equiv.) was used in place of lithium metal, an inseparable mixture of *cis-* and *trans-*2a,5-dihydroacenaphthoic acids was obtained as an oil (87%), $\nu_{max.}$($CHCl_3$) 3 500—2 400 (CO_2H) and 1 710 cm^{-1} (C=O), τ [$(CD_3)_2CO$] −0.20br (1 H, CO_2H), 2.95 (3 H, m, ArH), 3.93 (2 H, m, CH=CH), 5.70 (1 H, m, *trans*-C*H*CO_2H), 5.81br (1 H, d, *J* 8.4 Hz, *cis*-C*H*CO_2H), 6.30 (1 H, m, *trans*-CHC=C), 6.52 (1 H, m, *cis*-CHC=C), 6.56 (1 H, m), 7.08 (2 H, m), 7.55 (1 H, m), and 8.25 (1 H, m).

Treatment of 2a,5-dihydroacenaphthoic acid in DMSO under nitrogen with potassium t-butoxide for 24 h at 20° gave, after work-up, an inseparable 1 : 4 mixture of 5-acenaphthoic acid and 2a,3-dihydroacenaphthoic acid as a solid. The structure of the latter compound was assigned from spectral data, $\nu_{max.}$(KBr) 3 500—2 400 (CO_2H), 1 660br (C=O), 1 600, and 1 570 cm^{-1} (conjugated C=C), τ [$(CD_3)_2CO$] 2.25 (1 H, t, *J* 4 Hz, ArH), 2.85 (3 H, m, ArH and vinyl proton), 7.06 and 7.17 (2 × 1 H, d, *J* 4 Hz, CH_2C=), and 6.63—8.50 (5 H, m, alkyl protons).

5-*Methyl*-2a,5-*dihydroacenaphthoic Acid* (VIb).—5-Acenaphthoic acid (2.2 g, 10 mmol) in dry ether (50 ml) and liquid ammonia (300 ml) was reacted with lithium metal (0.17 g, 25 mmol) as described above. Excess methyl iodide in dry ether was added dropwise at −40° and the ammonia allowed to evaporate. Work-up gave cis-5-*methyl*-2a,5-*dihydroacenaphthoic acid* (VIb) (2.28 g, 83%) as a solid. Crystallisation from benzene gave chunky needles, m.p. 175—178° (decomp.), $\nu_{max.}$($CHCl_3$) 3 500—2 400 (CO_2H) and 1 710 cm^{-1} (C=O), τ [$(CD_3)_2CO$] 2.90 (3 H, s, ArH), 3.93 (2 H, m, CH=CH), 6.53 (1 H, m, 2a-H), 7.13 (2 H, m), 7.55 (1 H, m), 8.35 (1 H, m), and 8.60 (3 H, s, CH_3) (Found: C, 78.1; H, 6.6. $C_{14}H_{14}O_2$ requires C, 78.5; H, 6.6%).

When sodium (2.5 mol. equiv.) was used in place of lithium metal, a mixture of *cis-* and *trans-*5-methyl-2a,5-dihydroacenaphthoic acids was obtained as a solidifying oil (85%). For the purpose of determining the proportions of isomers, the methyl esters were prepared by treatment with excess of diazomethane at 0°, and obtained as an oil (100%), $\nu_{max.}$ (film) 1 730 (C=O) and 1 250 cm^{-1} (ester C–O), τ ($CDCl_3$) 2.91 (3 H, m, ArH), 3.94 (2 H, m, CH=CH), 6.30 (3 H, s, OCH_3), 6.32 (3 H, s, OCH_3), 6.53 (1 H, m), 7.13 (2 H, m), 7.55 (1 H, m), 8.35 (1 H, m), 8.50 (3 H, s, CH_3), and 8.52 (3 H, s, CH_3).

4-*Methyl*-1,4-*dihydro*-1-*naphthoic Acid* (VIII).—4-Methyl-1-naphthoic acid (2.0 g, 11.5 mmol) was reacted with lithium metal (0.33 g, 48 mmol) and the solution quenched with ammonium chloride to give 4-*methyl*-1,4-*dihydro*-1-*naphthoic acid* (2.0 g, 90%) as a gummy solid which was crystallised from benzene–light petroleum (b.p. 60—80°) at 0°, m.p. 110—120°, $\nu_{max.}$ 3 500—2 400 (CO_2H) and 1 700 cm^{-1} (C=O), τ ($CDCl_3$) 0.04br (1 H, s, OH), 2.77 (4 H, m, ArH), 4.05 (2 H, m, CH=CH), 5.6br (1 H, t, *J* 4 Hz, C*H*CO_2H), 6.52 (1 H, m, C*H*Me), and 8.66 (3 H, d, *J* 8 Hz, CH_3) (Found: C, 76.6; H, 6.4. $C_{12}H_{12}O_2$ requires C, 76.55; H, 6.45%).

Spectral Simulation.—The 90 and 270 MHz spectra were calculated using the program NMRCAL supplied with a Nicolet B-NC 12 computer attached to a Bruker HFX90 spectrometer. This program will calculate problems containing a maximum of six spins. However, the system of interest (VI) contains eight protons but decoupling experiments verified that there was negligible coupling between 3-, 4-, and 5-H and those of the alkyl bridge formed by C-1 and C-2. The problem therefore conveniently divided into two parts: (i) the system 1-, 1′-, 2-, 2′, and 2a-H and (ii) the homoallyl system 2a-, 3-, 4-, and 5-H.

Couplings within system (i) were readily measured from the 270 MHz spectra of (VIa and b). The 1-protons, being benzylic, were assigned to lower field than the 2-protons, and as models indicated that 1′-H was virtually orthogonal to 2-H, individual assignments could be made. It is interesting, but perhaps not surprising, that the homoallylic couplings between 1- or 1′-H and 2a-H appear to be very small (<0.5 Hz).

Calculations using these parameters were found to satisfactorily simulate both the 270 and 90 MHz spectra of (VIa and b) with the exception of the absorption due to 2a-H which is further coupled to spin system (ii). The spectra of (VIa and b) had a slight solvent dependence and the Table therefore includes chemical shift values for both the $CDCl_3$ and $(CD_3)_2CO$ spectra.

A similar procedure was followed for the analysis of spin system (ii), selective decoupling of 2a-H and 5-H aiding the assignment of couplings to 3- and 4-H.

^1H *N.m.r. Spectra.*—The 270 MHz spectra were recorded on the Oxford enzyme group 270 MHz spectrometer in the Department of Biochemistry, University of Oxford. Resolution enhancement by the method of convolution difference [12] was used to aid accurate measurement of the coupling constants. Double resonance experiments and 90 MHz spectra were recorded on a Perkin-Elmer R32 instrument.

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[12] I. D. Campbell, C. M. Dobson, R. J. P. Williams, and A. V. Xavier, *J. Magnetic Resonance*, 1973, **11**, 172.