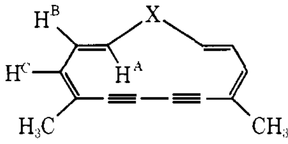
treatment with 2 mol equiv of **3** at this temperature yielded a mixture of **6**, **11**, and the di-cis stereoisomer[9a] (*m/e* 214; main λ_{max} (ether) 337 nm). Coupling of this mixture essentially as before gave 2.9% (based on **2** and **3**) of the stable di-trans thia[13]annulene **14**[9b] (yellow needles;[10] *m/e* 212; λ_{max} (ether) 295 (ϵ 37,200), ~305 sh (33,900), ~380 sh nm (3700)) and 2.2% of the unstable cis,trans isomer **20**[9b] (yellow oil; *m/e* 212; λ_{max} (ether) 238 (ϵ 19,100), 295 nm (9100); ^{1}H nmr (CDCl$_3$, 60 MHz), τ 2.92 d (J = 15 Hz, H^A), 3.48 d (J = 10 Hz, H$^{A'}$), 2.7-4.4 m (other olefinic), 8.10 s, 8.25 s (CH$_3$, CH$_3$')).

Oxidation of **14** with excess *m*-chloroperbenzoic acid in CH$_2$Cl$_2$ at 20° for 2 hr led to 83% of the sulfone **15**[9a] (very pale yellow needles;[10] *m/e* 244; λ_{max} (ether) 265 (ϵ 14,800), ~279 sh (12,000), ~312 sh (5600), 331 nm (5900)). Similar oxidation of **20** at 20° for 1 hr gave 82% of the sulfone **21**[9a] (yellow needles;[10] *m/e* 244; λ_{max} (ether) 252 (ϵ 9400), 262 (9700), ~275 sh (8500), ~315 sh (2700), ~335 sh nm (2300); ^{1}H nmr (CDCl$_3$, 60 MHz), τ 2.80 dd (J = 10, 15 Hz, H^B), 2.97 d (J = 15 Hz, H^A), 3.45 d (J = 11 Hz, H$^{A'}$), 3.53 m (H^C, H$^{C'}$), 3.95 dd (J = 11, 12 Hz, H$^{B'}$), 8.05 s, 8.07 s (CH$_3$, CH$_3$')). Oxidation of **14** with only ~1 mole equiv of *m*-chloroperbenzoic acid in CH$_2$Cl$_2$ at 0° for 1.5 hr yielded 78% of the sulfoxide **16**[9a] (very pale yellow needles;[10] *m/e* 228; λ_{max} (ether) 263 (ϵ 16,800), 332 nm (4100)).[11]

The ^{1}H nmr spectra of the di-trans heteroannulenes **13–16**, as well as of the related alcohol **17**[12a] and ketone **18**,[12b] are presented in Table I. The differences in chemical shift on passing from the acyclic models **5–7**[13,14] and **8–9**[12] to the corresponding cyclic compounds are also given in Table I. The best ring current probe for the annulenes is provided by the "fixed" outer H^C and especially the CH$_3$ resonances. Compared with the shift differences of these bands in the atropic alcohol **17** (−0.41, −0.06), the sulfone **15** (−0.56, −0.08) is clearly also atropic,[15] the oxide **13** (−0.60, −0.15) is at most weakly diatropic, the sulfide **14** (−0.93, −0.37) is definitely diatropic, and the ketone **18** (+0.17, +0.28) is paratropic.

That both the H^A and H^B resonances in the ^{1}H nmr spectrum of the diatropic sulfide **14** have shifted to higher field as compared to the acyclic model can be explained by contribution of the rotamer **22** and/or **23** with internal H^A and external H^B, since in a diatropic molecule the shielding effect on an inner proton far exceeds the deshielding effect on an outer proton. Such rotation could indeed be demonstrated for **14** (but not for **13** or **15**) by low-temperature ^{1}H nmr experiments, coalescence of the H^A and H^B resonances each occurring at *ca.* −90°.[16] Cyclization affects the H^B more than the H^A resonances in **13**, **14**, and **18**, while the reverse is true for **15** and **17**. We therefore assume that the conformations indicated for **13**, **14**, and **18** (with both H^B internal) are the main contributors to the structures of these compounds but that conformations of type **22** (with both H^A internal) are the main contributors to **15** and **17**.[17] This assumption is supported by the fact that $J_{B,C}$ = ~9.5 Hz in **13**, **14**, and **18**, but only 5 Hz in **15**, **16**, and **17**.[18] The unusually high field H^A resonances in **15**, **16**, and **17** are presumably due to the anisotropy of the acetylenes, and it appears that such anisotropy can cause either an upfield or a downfield shift, depending on the exact dispositions of the groups.[19]



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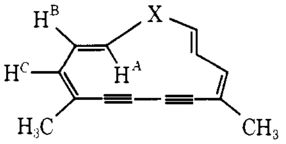

23

Comparison of the ^{1}H nmr spectra of the cis,trans isomers **19–21** with those of the corresponding acyclic models **10–12**[13,14] shows these heteroannulenes to be atropic, and they are presumably less planar than the di-trans compounds.

Acknowledgment. We thank the Science Research Council for financial support.

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(1) Unsaturated Macrocyclic Compounds. CX. For part CIX, see K. Yamamoto and F. Sondheimer, *Tetrahedron*, **30**, 4229 (1974).
(2) A. G. Anastassiou and J. H. Gebrian, *Tetrahedron Lett.*, 825 (1970).
(3) G. Schröder, G. Frank, H. Röttele, and J. F. M. Oth, *Angew. Chem.*, **86**, 237 (1974).
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(7) See K. Dimroth, H. Follmann, and G. Pohl, *Chem. Ber.*, **99**, 642 (1966).
(8) E. R. H. Jones and B. C. L. Weedon, *J. Chem. Soc.*, 937 (1946); I. Heilbron, E. R. H. Jones, and M. Julia, *ibid.*, 1430 (1949).
(9) Isolated by chromatography on (a) Al$_2$O$_3$ (Woelm, act III); (b) SiO$_2$ (Woelm, act III).
(10) The compound decomposed on attempted melting point determination.
(11) Initially, bis(cyclohexene)-annelated derivatives of **13–15** and **19–21** were synthesized, using 2-ethynyl-1-cyclohexene-1-carboxaldehyde instead of **3** in the initial step (P. J. Beeby, R. L. Wife, and F. Sondheimer, unpublished experiments). These polycyclic substances showed similar properties to those of the corresponding monocyclic annulenes but proved to be more stable.
(12) (a) R. L. Wife and F. Sondheimer, unpublished experiments; (b) J. Ojima and F. Sondheimer, unpublished experiments.
(13) The acyclic sulfones **7** and **12** were prepared from the corresponding sulfides essentially as described for the cyclic sulfones **15** and **21**.
(14) Unequivocal ^{1}H nmr assignments to the various protons of **5–7** and **10–12** involved, *inter alia*, the preparation of the corresponding deuterio derivatives (D instead of H^B) by use of **4** (from **3** by reduction with LiAlD$_4$ and then oxidation with MnO$_2$) instead of **3** in the first step.
(15) The sulfoxide **16** is also atropic, since its ^{1}H nmr spectrum closely resembles that of the sulfone **15**.
(16) The coalescence temperature is considerably lower than that of related conformationally mobile diatropic bisdehydro[14]annulenes, where the individual conformers could be observed at low temperature (R. T. Weavers and F. Sondheimer, *Angew. Chem.*, **86**, 165 (1974)).
(17) X-Ray crystallographic analyses of **14** and **15** are now in progress, in order to determine their conformation in the solid state. Preliminary results indicate that the sulfone **15** exists as conformer **22** (C. C. Chiang and I. C. Paul, private communication).
(18) The very low value of $J_{B,C}$ in **15**, **16**, and **17** suggests that these substances exist entirely as conformation **22**, but variable temperature ^{1}H nmr experiments with **15** (−110 to +150°) gave no further information.
(19) See J. A. Pople and K. G. Untch, *J. Amer. Chem. Soc.*, **88**, 4811 (1966); K. G. Untch and D. C. Wysocki, *ibid.*, **89**, 6386 (1967); H. A. Staab and R. Bader, *Chem. Ber.*, **103**, 1157 (1970); P. J. Beeby and F. Sondheimer, *J. Amer. Chem. Soc.*, **94**, 2128 (1972); *Angew. Chem.*, **85**, 404 (1973); J. M. Brown and F. Sondheimer, *ibid.*, **86**, 348 (1974).

Richard L. Wife, Franz Sondheimer*
Chemistry Department, University College
London WC1H OAJ, England
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Synthesis of Bisdehydrooxa- and -thia[15]annulenes, Conjugated 15-Membered Heterocycles[1]

Sir:

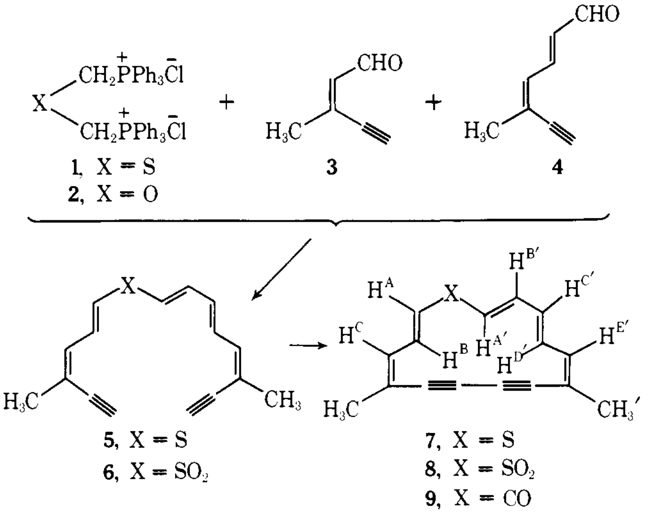
The preparation of potentially diatropic ("aromatic") bisdehydrooxa- and -thia[13]annulenes, described in the preceding publication,[1] encouraged us to study the synthesis of potentially paratropic ("antiaromatic") bisdehydrohetero[15]annulenes by similar methods. We now report the synthesis of the bisdehydrothia[15]annulenes **7** and **18**, as

Table I. ^1H Nmr Parameters of **7–9** and **18–19** at 100 MHz in $CDCl_3$ (τ Values; Internal Standard, TMS; J Values in Hz in parentheses)

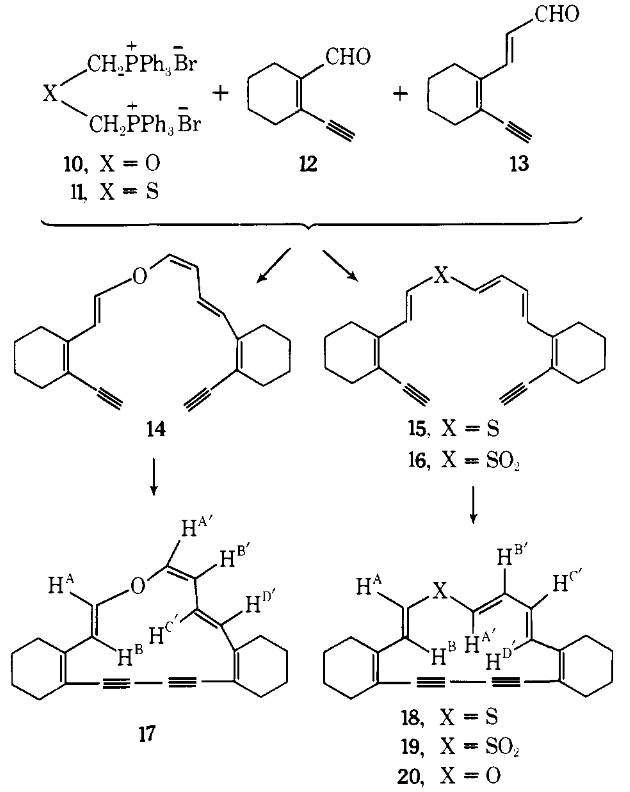
	Inner H			Outer H					
Compd	H^B	$H^{A'}$	$H^{D'}$	H^C	H^A	$H^{B'}$	$H^{C'}$	$H^{E'}$	CH_3, CH_3' or allylic CH_2
7, S	0.79 dd (11, 15)	1.09 d (14)	1.07 dd (14, 14)	← 3.55–4.2 m →					8.39 s, 8.43 s
8, SO_2	← 2.3–3.6 m →								8.03 s, 8.05 s
9, CO	4.24 dd (11, 16)	4.43 d (15)	4.60 dd (11, 15)	← 2.35–3.5 m →					7.82 s, 7.87 s
18, S[a]	1.10 d (15)	1.88 d (15)	1.65 d (15)	—	4.00 d (15)	3.34 dd[b]	3.76 dd[b]	—	8.0 m
19, SO_2[c]	~2.6	~3.5	~3.5	—	~3.5	~2.6	~3.5	—	7.75 m

[a] The assignments are based on decoupling and nuclear Overhauser experiments (irradiation at τ 8.0). [b] J = 7.5, 15 Hz. [c] The bands were unresolved due to accidental equivalence. Individual assignments are based on $Eu(fod)_3$ shifts.

Scheme I



Scheme II



well as of the bisdehydrooxa[15]annulene **17**. The thia compounds **7** and **18** proved to be paratropic and these are the first nonbridged heteroannulenes to show this type of ring current effect.[2]

Treatment of **1**[3] in ether with 2 mole equiv of n-C_4H_9Li at 20° led to the corresponding bis ylid, which was allowed to react with a mixture of **3**[4] and **4**[5] (1 mole equiv each) at this temperature for 1 hr (Scheme I). Chromatography of the complex mixture on Al_2O_3 (Woelm, act III, then Merck GF_{254}) gave 4.5% of **5** and its stereoisomers (*m/e* 240; main λ_{max} (ether) 348 nm). Coupling of this unstable and inseparable mixture with $Cu(OAc)_2$ in pyridine at 50° for ~1 hr yielded 9% of **7**, isolated by chromatography on Al_2O_3 (Merck GF_{254}) and then on Kieselgel (Merck GF_{254}, short column[6]). The very unstable dimethylbisdehydrothia[15]annulene **7** formed red needles:[7] *m/e* 238; λ_{max} (ether) 288 (ϵ 45,800), ~315 sh (19,200), ~345 sh nm (12,300). Oxidation of **7** with excess *m*-chloroperbenzoic acid in CH_2Cl_2 at 0° for 2 hr, and chromatography on SiO_2 (Woelm, act III), afforded 77% of the sulfone **8** as rather unstable pale yellow crystals:[7] *m/e* 270; λ_{max} (ether) 246 sh (ϵ 16,800), 258 (21,900), 286 (27,100), ~365 sh nm (2800).

The oxygen analog of **7** could not be prepared similarly from **2**,[3] **3**, and **4**. Experiments designed to prepare the potentially more stable[8] annelated bisdehydrooxa[15]annulene **20** led instead to the mono-cis stereoisomer **17**. Wittig reaction of **10**[3] (1 mole equiv) with **12**[9] and **13**[5,10] (1 mole equiv each) in DMF in the presence of ethanolic LiOEt (2 mole equiv) at 70° for ~1 hr and rapid chromatography on Al_2O_3 (Woelm, act III) gave 65% of a mixture containing **14** (Scheme II). This very unstable material was then coupled directly with $Cu(OAc)_2$ in pyridine at 60° for ~1 hr. Chromatography on SiO_2 (Woelm, act II) and then on silicic acid (Mallinckrodt) yielded 3.5% of the extremely unstable mono-cis bisdehydrooxa[15]annulene **17** as a yellow oil: *m/e* 302; λ_{max} (ether) 275 nm (broad), with absorption >400 nm; ^1H nmr ($CDCl_3$, 60 MHz), τ 2.84 dd (J = 11, 17 Hz, $H^{C'}$), 3.00 d (J = 13 Hz, H^A), 3.70 d (J = 17 Hz, $H^{D'}$), 3.80 d (J = 6.5 Hz, $H^{A'}$), 4.38 d, br (J = 13 Hz, H^B), 4.40 dd (J = 6.5, 11 Hz, $H^{B'}$), 7.8 m (allylic CH_2), 8.35 m (nonallylic CH_2).

On the other hand, replacement of **10** by **11**[3] in the above-described reaction sequence led to the "all-trans" annelated bisdehydrothia[15]annulene **18** in 1.3% over-all yield as relatively stable red needles: mp 140–142°; *m/e* 318; λ_{max} (ether) 290 (ϵ 37,200), ~325 sh (8400), 395 nm (1700). Oxidation of **18** with excess *m*-chloroperbenzoic acid in CH_2Cl_2 at 20° for 2 hr, and isolation as for **8**, gave 75% of the sulfone **19** as light yellow crystals:[7] *m/e* 350; λ_{max} (ether) 249 (ϵ 22,100), 263 (24,000), 288 (21,800), 374 nm (4600).

The ^1H nmr spectra of the bisdehydrothia[15]annulenes **7** and **18**, the sulfones **8** and **19**, as well as of the related ketone **9**[11] are given in Table I. The spectra of **7** and **18** do not indicate any conformational mobility, in contrast to bisdehydrothia[13]-[1] and -[17]annulenes.[12] The sulfones **8** and **19** are atropic, as is evident from the similarity of the olefinic and of the methyl or allylic methylene proton chemical shifts to those anticipated for the "open" compounds **6** and **16** from appropriate models.[1,12] The sulfides **7** and **18** are clearly paratropic, since the inner olefinic protons resonate at considerably lower field than those of the atropic sulfones **8** and **19**, while the outer olefinic and methyl or allylic methylene protons resonate at higher field.[13] By comparison, the inner olefinic protons in the spectrum of the diatropic ketone **9** resonate at higher field than those of the sulfone **8**, while the outer methyl protons resonate at lower field.

The ^{1}H nmr spectrum of the mono-cis bisdehydrooxa[15]annulene **17** shows that it is atropic; models suggest that **17**, unlike the "all-trans" bisdehydrohetero[15]annulenes, cannot be planar.

The electronic spectra of carbocyclic annulenes and dehydroannulenes have been shown to alternate, the main maxima of $(4n + 2)$ π-electron systems being at higher wavelength than those of $4n$ systems.[14] The electronic spectra of "all-trans" bisdehydrothiaannulenes appear to exhibit the same alternation, in both the dimethyl series ([13] 295 nm,[1] [15] 288 nm, [17] 322 nm[12]) and the biscyclohexene annelated series ([13] 300 nm,[15] [15] 290 nm, [17] 324 nm[10,16]).

It is also of interest that the dimethylbisdehydrothia[15]annulene **7** is much less stable than either the "all-trans" 13-[1] or 17-membered[12] homolog, which may reflect the antiaromaticity of the 15-membered heterocycle.

Acknowledgment. We thank the Science Research Council for financial support.

References and Notes

(1) Unsaturated Macrocyclic Compounds. CXI. For part CX, see R. L. Wife and F. Sondheimer, *J. Amer. Chem. Soc.*, preceding paper.

(2) For syntheses of paratropic bridged heteroannulenes, see H. Ogawa, M. Kubo, and H. Saikachi, *Tetrahedron Lett.*, 4859 (1971) (dioxido-bridged oxa[15]annulene); P. J. Beeby and F. Sondheimer, *Angew. Chem.*, **85**, 406 (1973) (methylene-bridged bisdehydroaza[19]annulene).

(3) See K. Dimroth, H. Follmann, and G. Pohl, *Chem. Ber.*, **99**, 642 (1966).

(4) E. R. H. Jones and B. C. L. Weedon, *J. Chem. Soc.*, 937 (1946); I. Heilbron, E. R. H. Jones, and M. Julia, *ibid.*, 1430 (1949).

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(6) See B. J. Hunt and W. Rigby, *Chem. Ind. (London)*, 1868 (1967).

(7) The compound decomposed on attempted melting point determination.

(8) See ref 1, footnote 11.

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(10) R. H. McGirk and F. Sondheimer, *Angew. Chem.*, **84**, 897 (1972).

(11) J. Ojima and F. Sondheimer, unpublished experiments.

(12) R. L. Wife and F. Sondheimer, *Tetrahedron Lett.*, in press.

(13) The annelated sulfide **18** appears to be appreciably less paratropic than the monocyclic compound **7**, as indicated by the relative chemical shifts of the inner protons. This cyclohexene-annelation effect has already been observed in diatropic bisdehydro[14]annulenes (R. T. Weavers and F. Sondheimer, *Angew. Chem.*, **86**, 165 (1974)) and is presumably due to steric interaction in the fused compounds, reducing their planarity.

(14) See P. J. Garratt and K. Grohmann in "Houben-Weyl, Methoden der Organischen Chemie," Vol V, Part 1d, Georg Thieme Verlag, Stuttgart, 1972, pp 533–535.

(15) P. J. Beeby and F. Sondheimer, unpublished data.

(16) R. H. McGirk and F. Sondheimer, unpublished data.

Richard L. Wife, Philip J. Beeby, Franz Sondheimer*
Chemistry Department, University College
London WC1H OAJ, England

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Conformational Analysis by Spin Transmission into Rotating Alkyl Groups

Sir:

Unpaired spin density transmitted from a nickel atom into an organic ligand represents a very small electronic perturbation but may nevertheless be used as a sensitive tool to determine dihedral angles. We synthesized new pseudo-tetrahedral[1] complexes, **1**, and measured their isotropic shifts,[2] $\Delta H_i/H$, in 1,2-dideuterio-1,1,2,2-tetrachloroethane relative to the free ligands. We find it more practical to use a differently defined isotropic shift, ϑ_i in eq 1,

$$\vartheta_i = \frac{\Delta H_i}{H}\,\frac{T}{298°\text{K}} = -\rho_i{}^{\text{H}}60{,}400 \text{ ppm} \qquad (1)$$

which is reduced to 298°K. ϑ_i will depend exclusively on the spin population $\rho_i{}^{\text{H}}$ transferred to a proton i if the Bloembergen-McConnell equation[2] applies to **1**.[3] Curie-type $(1/T)$ behavior is expected[1] for ΔH_i of **1**.[4] Therefore, ϑ_i should not depend on the temperature. Figure 1 demonstrates this for five types of protons in a typical example, **1c**. Only ϑ_i of the two equivalent β-hydrogens drifts strongly downfield with increasing temperature. We assume that this "abnormal" temperature dependence originates in modulation of the spin density by rotation about the $C^{\alpha}C^{c}$ bond of **1**.

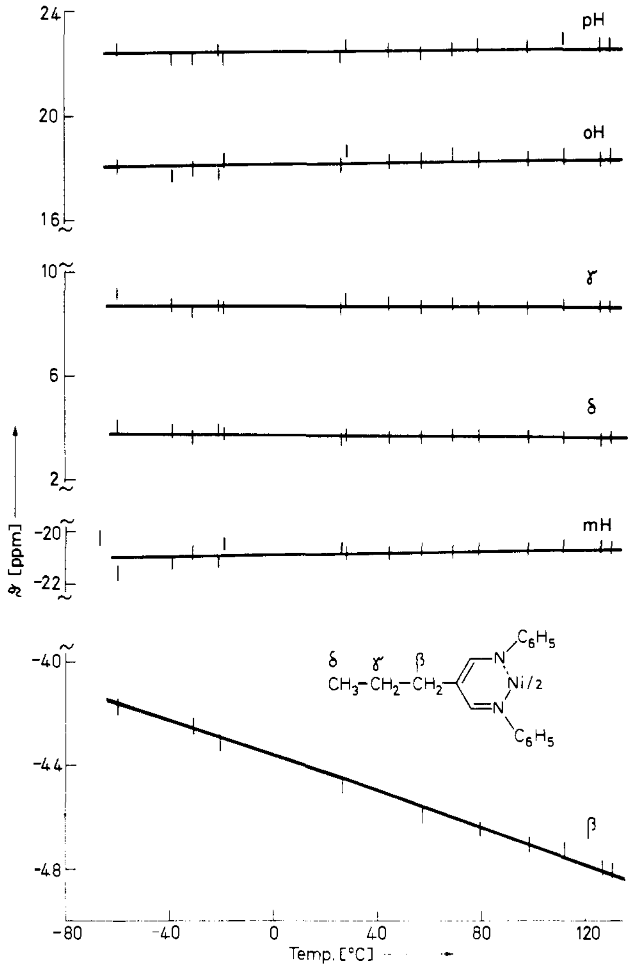
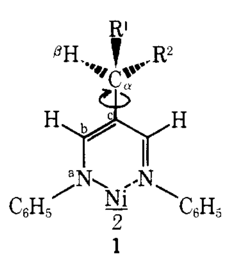


Figure 1. Isotropic reduced shifts ϑ of **1c** as a function of temperature.



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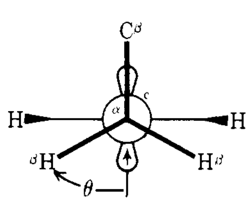

2

The 2p orbital at C^c carries positive spin density.[1a,d,5] Spin transmission into the $C^{\alpha}H^{\beta}$ bond depends on the $\cos^2$ of the dihedral angle θ between this bond and the axis of the