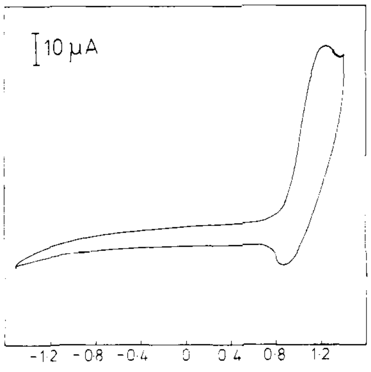
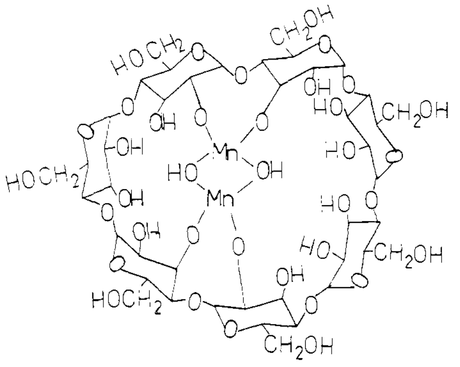


Figure 2. Cyclic voltammogram of 2 mM Mn–β-CD complex in DMF and 0.1 M tetrabutylammonium perchlorate (scan rate 100 mV s^{-1}).

coupling of the Mn spins. This could be fostered readily by the bis(μ-hydroxo)-bridged structure I. The bis(μ-hydroxo)structure



I

results in an uncharged complex, which is consistent with the conductivity data. EPR at 4.2 K revealed only a weak signal at $g' = 4$, which is presumably due to a small Mn(IV) impurity.

In order to establish which side of the β-CD ligand the Mn coordinates to, we treated the complex with 1 equiv of terephthaloyl chloride, which selectively esterifies the primary hydroxy groups.[10] This resulted in a "capped"-β-CD product that retained the original manganese. This experiment conclusively shows that it is the secondary hydroxyls of β-CD that coordinate both Mn ions. Cyclic voltammetry of the compound in DMF showed a quasi-reversible two-electron oxidation wave with a peak potential of +1.28 V (vs. aqueous SCE). The corresponding reduction wave has a peak potential of +0.81 V (Figure 2). The two-electron oxidation process was confirmed by use of an internal standard of ferrocene and also by constant potential electrolysis of the compound at 1.3 V (vs. SCE). The latter did not give rise to the mixed-valence Mn(III)–Mn(IV) product (assayed for spectrophotometrically) expected for a one-electron oxidation of Mn(III)–Mn(III) species. The Mn(IV) species so obtained was unstable, and at room temperature it decomposed within a few hours. This instability may be due to oxidation of the ligand. No evidence for reduction to the Mn(II) state was observed out to potentials of −1.5 V (vs. SCE). This indicates that the usually unstable Mn(III) oxidation state is stabilized considerably by coordination of β-CD in preference to the Mn(II) state.

Reaction of the compound with various oxidizing agents has been investigated. The compound in 80:20 DMF–H$_2$O (was not oxidized by excess potassium ferricyanide ($E_0 \simeq 0.44$ V). On treatment with 2 equiv of Ce(IV) ($E_0 \simeq 1.4$ V), the 482-nm band was bleached. One equivalent produced only partial bleaching, with no evidence again for the intervalence transition for a Mn(III)–Mn(IV) oxidation state. Evidently a two-electron oxidation to the (IV,IV) state is preferred, with eventual decomposition of ligand or water over hours, at least in aqueous DMF and Me$_2$SO.

Acknowledgment. This work was supported by a grant from the U.S. Department of Energy/Solar Energy Research Institute (DE-FG02-80CS84003) and by an award from the Chicago Community Trust/Searle Scholars Program (G.C.D.).

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Solution Structure of Thianthrene: Dihedral Angle between the Benzene Rings Determined from the Analysis of NMR Spectra in Nematic Phase

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Thianthrene is a typical example of the tricyclic compounds that have a "butterfly structure" folded along one of the principal molecular axes. The folded angle, i.e., the dihedral angle between the two benzene rings, has been repeatedly studied by several methods in different states.[1-6] This angle was first determined to be 128° from X-ray analysis with crystals[1,2] and later to be 131.4° from the electron diffraction study in gaseous state.[3] As for the solution structure of this molecule, on the other hand, values between 140 ± 10 and 144 ± 8° have been suggested from the dipole moment[4,5] and Kerr constant[4] measurements. Recent study on the molecular optical anisotropy similarly suggested the angle of 142°.[6] These studies all supported evidence that the dihedral angle is opened in solution, or otherwise the values in solution might be misleading. However, to make sure of the fact, it is necessary to determine the dihedral angle unambiguously in solution by means of a more direct and unequivocal procedure. For this purpose, NMR spectroscopy using liquid–crystal solvents[7] is quite useful. In the present communication we have analyzed the ^{1}H NMR spectra of thianthrene in a nematic-phase (Merck ZLI1167) mixture of three cyanocyclohexanes and determined the molecular structure in solution. The thus-derived solution structure of the molecule has led to a dihedral angle of 141.6±0.2°, and dependence of the angle on the molecular state of investigation has been proved.

The ordered spectra are analyzed by a modified LAOCN3 program extended to 9-spin system,[8] by using published values[9] of the indirect coupling constants. Direct coupling constants were processed to the program SHAPE[10] after extension from the original 7-spin system. The spectrum of 0.1 M (M = mol dm^{-3}) thianthrene dissolved in ZLI1167 was taken with a Hitachi R-900M FT NMR spectrometer operating at 90 MHz, the probe temperature being held constant at 34.1 °C. The experimental and simulated spectra are depicted in Figure 1, where 224 lines were used for the simulation. Deviation between the observed and the simulated lines is 1.6 Hz at its maximum and 0.43 Hz in the rms value, the latter being smaller than the NMR computer resolution. Analysis of the ordered NMR spectrum is summarized in Table I, and the structural as well as order parameters are cited in Table II. Large amplitude vibration of the "butterfly motion"

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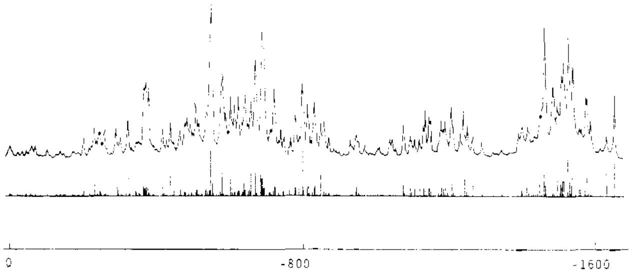


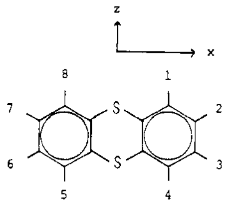
Figure 1. ^{1}H NMR spectra of thianthrene in nematic solution of ZLI1167. Only high-field half is shown.

Table I. NMR Spectral Parameters of Thianthrene in Nematic Solution of ZLI1167[a]

direct couplings	$D_{26} = 14.73 \pm 0.05$
$D_{12} = 565.98 \pm 0.02$[b]	$D_{27} = 16.90 \pm 0.04$
$D_{13} = 96.60 \pm 0.02$	chemical shift
$D_{14} = 58.87 \pm 0.04$	$\nu_1 - \nu_2 = 20.84 \pm 0.08$
$D_{15} = 29.09 \pm 0.04$	indirect coupling[c]
$D_{16} = 22.20 \pm 0.03$	$J_{12} = 7.71$
$D_{17} = 33.06 \pm 0.03$	$J_{13} = 1.63$
$D_{18} = 101.58 \pm 0.04$	$J_{14} = 0.11$
$D_{23} = 456.89 \pm 0.04$	$J_{23} = 7.54$

[a] In units of hertz at 90 MHz. [b] Probable errors. [c] Cited from ref 9.

Table II. Structural Parameters and Order Parameters of Thianthrene



bond length, Å	$r_{23} = 2.482$[a]
$r_{12} = 2.536 \pm 0.003$	$r_{26} = 9.654 \pm 0.014$
$r_{13} = 4.316 \pm 0.002$	$r_{27} = 9.329 \pm 0.015$
$r_{14} = 4.913 \pm 0.001$	order parameter:
$r_{15} = 7.104 \pm 0.007$	$S_{xx} = -0.11429 \pm 0.00055$
$r_{16} = 8.154 \pm 0.010$	$S_{zz} = -0.05818 \pm 0.00001$
$r_{17} = 7.369 \pm 0.011$	rms dev, Hz: $\sigma^b = 0.06$
$r_{18} = 5.131 \pm 0.009$	angle, deg: $\theta^c = 141.6 \pm 0.2$

[a] Assumed from ref 3. [b] Root-mean-square deviation between observed and recalculated direct couplings. [c] Dihedral angle between the two benzene rings.

is not included in the present communication, considering the high inversion barrier for the molecules, i.e., ~25 kJ/mol.[12] The dihedral angle is 141.6 ± 0.2° and evidently differs from those in the gaseous and crystalline states. This angle is also being tested in a liquid-crystal of carboxylic acid (140.2 ± 0.2°) in a detailed study of this solvent dependency now under way. In conclusion, the significant dependency of the angle on the environment of the molecule has been revealed.

r_{12}/r_{23} is 1.022 ± 0.001, and r_{12} is shown to be longer than r_{23} in the benzene ring. This tendency is also observable in the recently reported case of dibenzo-*p*-dioxin.[11] These facts support a distorted hexagon for the ring protons, although the gas electron diffraction study of thianthrene[3] has failed to detect such distortion.

Acknowledgment. H.F. is grateful to Professor P. Diehl (Basel University) for making the program SHAPE available to him.

Registry No. Thianthrene, 92-85-3.

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Formation of 1,2-Oxathietanes and Their Formal [$_\sigma2_s$ + $_\sigma2_a$] Cycloreversion during the Stereoelectronically Controlled Aqueous Decomposition of Sulfoxide-Substituted Nitrosoureas

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Ambient-temperature aqueous decomposition of nitrosoureas and nitrosourethanes provides a convenient source of alkanediazohydroxides[1-3] to explore neighboring group effects on incipient carbenium ions. We have exploited this approach in the controlled aqueous decomposition of certain nitrosourea sulfoxides that leads to the hitherto elusive 1,2-oxathietanes, which are inter alia subject to formal [$_\sigma2_s$ + $_\sigma2_a$] cycloreversion or rearrangement. 1-[2-[(2-Chloroethyl)sulfinyl]ethyl]-3-cyclohexyl-1-nitrosourea (**1a**)[4] was allowed to decompose in aqueous potassium phosphate buffer pH 7.0 at 37 °C. The volatile products that were detected and identified by GC and GC-MS were formaldehyde, thioformaldehyde hydrate, and vinyl chloride.[5] The nonvolatile products that were isolated and identified were cyclohexyl isocyanate and dicyclohexylurea. The results are in accord with the decomposition pathway outlined in Scheme I.

The initial step involves a rotation about the N-N bond followed by hydration of the amide carbonyl group.[2,3] Subsequent stereoelectronically controlled collapse of the tetrahedral intermediate **2**[2,3] in which the hetero atom lone pairs are aligned antiperiplanar to the breaking CO–N$_1$ bond[6] releases the alkane diazohydroxide **3** and the isocyanate. Participation of the sulfoxide oxygen at the demand of the incipient cationic center in the diazohydroxide forms 1,2-oxathietane **4**. The latter eliminates vinyl chloride to give the parent 1,2-oxathietane **5**, which is then subject to cycloreversion (formally of the type [$_\sigma2_s$ + $_\sigma2_a$][7] or possibly a stepwise diradical pathway) to formaldehyde and thioformaldehyde, the latter of which is identified as the hydrate.

The alternative pathway to the carbonyl products via the thiirane *S*-oxides **6** and **7** may be eliminated since 1-[2-[(2-chloroethyl)sulfinyl]ethyl-*2*-d_2]-3-cyclohexyl-1-nitrosourea (**1b**)[8] affords formaldehyde and thioformaldehyde-d_2 hydrate with no label scrambling, although it is conceivable that **7** may give rise to **9** (which see). The aqueous decomposition of 1-[2-[(2-chloroethyl)sulfinyl]-1,1-dimethylethyl]-3-cyclohexyl-1-nitrosourea (**1c**)[9] afforded acetone, thioformaldehyde hydrate, vinyl chloride, cyclohexyl isocyanate, and dicyclohexylurea. The relative yields of the cycloreversion products from 1,2-oxathietane **4c** are increased compared with **4a**, in qualitative agreement with the easier ring closure as a result of the buttressing effects of the geminal methyl groups.[10] Similar aqueous decomposition of 1-[2-[(2-chloroethyl)sulfinyl-^{18}*O*]-1,1-dimethylethyl]-3-cyclohexyl-1-nitrosourea (**1a**-^{18}*O*)[11] afforded acetone-^{18}*O* and thioformaldehyde

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