coupling to ^{53}Cr, which we observe for $\mathbf{1}^{-\cdot}$, C(p_π)–Cr(ns) spin polarization is to be inferred.

Turning to the g factors, it is noted that, as in the case of aromatic radicals,[22] for $\mathbf{1}^{-\cdot}$ the relation $g_\perp > g_\parallel$ applies. However, contrary to aromatic radicals, for the complex radical anion $\mathbf{1}^{-\cdot}$ $g_\perp$ rather than $g_\parallel$ approaches the free-spin value. Furthermore, $\Delta g = |g_\parallel - g_\perp|$ is considerably larger for $\mathbf{1}^{-\cdot}$ ($\Delta g = 0.022$) as compared to aromatic radicals ($\Delta g = 0.0005$). The larger g anisotropy Δg does not contradict the proposed π-ligand character of the singly occupied MO of $\mathbf{1}^{-\cdot}$ since it is via the contribution of the central metal atom to other MO's, which are connected to the singly occupied MO via spin orbit coupling and which may contain a higher metal contribution, that chromium can influence the magnitude of Δg. In view of the uncertainty about the nature of the distortion and the lack of a quantitative energy level scheme, attempts to interpret the numerical values of $g_\parallel$ and $g_\perp$ would be premature. However, a comparison of $\mathbf{1}^{-\cdot}$ with the isoelectronic iron complex $\mathbf{3}^{+\cdot}$ ($g_x = 2.086$, $g_y = 1.996$, $g_z = 1.865$[16]) seems appropriate. For both species, the g values display the same trend,[23] yet Δg is larger for $\mathbf{3}^{+\cdot}$ than for $\mathbf{1}^{-\cdot}$. This may be traced to larger metal contribution to the MO's of $\mathbf{3}^{+\cdot}$,[24] as compared to corresponding orbitals of $\mathbf{1}^{-\cdot}$.

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[22] (a) Theory: Stone, A. J. *J. Mol. Phys.* **1963**, *6*, 509–515; **1964**, *7*, 311–316. (b) Experiment: Volland, W. V.; Vincow, G.; *J. Phys. Chem.* **1969**, *73*, 1147–1149.

[23] In the spectrum of $\mathbf{1}^{-\cdot}$ in rigid solution, the inequivalence of g_x and g_y is not resolved.

[24] Michaud, P.; Mariot, J.-P.; Varret, F.; Astruc, D. *J. Chem. Soc., Chem. Commun.* **1982**, 1383. Rajasekharan, M. V.; Giezynski, S.; Ammeter, J. H.; Oswald, N.; Michand, P.; Hamon, J. R.; Astruc, D. *J. Am. Chem. Soc.* **1982**, *104*, 2400–2407.

Simple Method for Determination of Spin Coupling Networks in NMR Spectroscopy

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Investigations of molecules in liquids by NMR have relied to a considerable extent on the information present in spin–spin couplings. The couplings can contain information that is useful for conformational and structural analysis. To be able to utilize the information present in the couplings, the relevant signals must be observable and a determination of the coupling network—which nuclei are coupled to which—be made. While in some favorable cases the coupling network can be determined by inspection of the NMR data, in many instances there is either insufficient resolution or the connectivities are not obvious.

When the NMR spectrum is at least partially resolved assignments of which nuclei are coupled to which, neighbor spins, can be determined via selective decoupling or chemical shift correlation experiments.[1] Correlations between nuclei that are not coupled to one another but do share a common coupling partner, remote spins, can be performed via relay transfer[2] or multiple-quantum experiments.[3] For AX spin systems a procedure based on double-quantum filtering can be useful in the absence of resolution of either signal.[4] Each of these experimental approaches has distinct advantages and disadvantages and will not be discussed further.

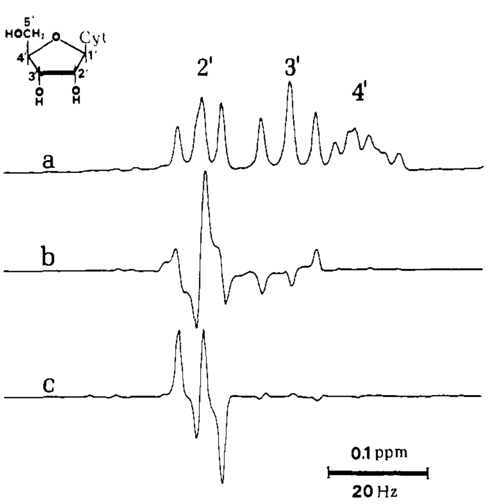

Figure 1. Normal proton spectrum of the 2′-, 3′-, and 4′-protons of cytidine (a), whose structure is also given. Fourier transform of the difference between the free induction decays obtained with and without selective decoupling of the 1′-proton during t_m followed by double-quantum filtering (b).[9] Fourier transform of the difference between the free induction decays obtained with and without selective saturation of the 1′-proton prior to double-quantum filtering.[9]

Multiple-quantum filters have been shown to be a useful technique for selective detection of nuclei with a particular number of coupling partners.[5] For example, experiments have been performed to detect only those protons coupled to two other protons.[5] Selective multiple-quantum filtering is also possible and allows determination of coupling networks in one-dimensional NMR experiments. The fundamental idea is to alter the generation of multiple-quantum coherence by means of selective irradiation of a single spin. The difference spectrum constructed by subtracting the spectrum obtained with selective irradiation from that obtained without allows direct identification of the coupling network to which the irradiated spin belongs.

One form of this technique is the identification of all of the neighbors of a particular spin. To obtain this information selective saturation of spin A is performed prior to double-quantum filtering. The saturation of A decreases the net generation of double-quantum coherence between A and each of its neighbors. The difference spectrum constructed between the spectrum obtained with and without saturation of A will contain signals only from spin A and its neighbors.[6] The multiplet patterns of the neighbor spins will correspond to the difference between the subspectra associated with the two polarizations of spin A.[7] The procedure for simulating such difference spectra has been discussed previously in the context of heteronuclear two-dimensional spectroscopy.[8]

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[1] Benn, R.; Gunther, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 350–380 is a recent review.

[2] (a) Eich, G.; Bodenhausen, G.; Ernst, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 3731–3732. (b) Bolton, P. H.; Bodenhausen, G. *Chem. Phys. Lett.* **1982**, *48*, 139–144. (c) Bolton, P. H. *J. Magn. Reson.* **1982**, *48*, 336–340.

[3] Braunschweiler, L.; Bodenhausen, G.; Ernst, R. R. *Mol. Phys.* **1983**, *48*, 535–560.

[4] Hore, P. J.; Zuiderweg, E. R. P.; Nicolay, K.; Dijkstra, K.; Kaptein, R. *J. Am. Chem. Soc.* **1982**, *104*, 4286–4288.

[5] Sørensen, O. W.; Levitt, M. H.; Ernst, R. R. *J. Magn. Reson.* **1983**, *55*, 104–113.

[6] In the presence of strong coupling of either the A spin or one of its neighbors additional signals may be observed. The multiplet pattern of the A spin in the difference spectrum also contains useful information but is not discussed since it is assumed that the A signals are resolved.

[7] The multiplet pattern that will be observed when degenerate nuclei are irradiated can be predicted in the limit of weak coupling by treating the system as AA′X. Selective saturation of the A and A′ spins leads to a difference spectrum corresponding to the difference between the subspectra associated with A and A′ being $\alpha\alpha$ and $\beta\beta$. Similar rules can be developed for other spin systems.

[8] (a) Bolton, P. H. *J. Magn. Reson.* **1981**, *45*, 239–253. (b) Bolton, P. H.; Bodenhausen, G. *J. Am. Chem. Soc.* **1979**, *101*, 1080–1084.

0002-7863/84/1506-4299$01.50/0

This neighbor spin detection scheme has been applied to cytidine with irradiation of the 1′-proton and typical results are shown in part c of Figure 1. The up–down pattern of the signals allows direct determination of both $J_{1',2'}$ and $J_{2',3'}$. The pulse sequence used is 90°–t_m/2–180°–t_m/2–90°–90°–acquisition. The phases of the first two 90° pulses are cycled through $X,Y,-X,-Y$ and the last 90° through $X,-X$ to give double-quantum filtering.[5] The phase of the 180° pulse is Y.

A variation on the scheme is to apply a decoupling field to spin A during the time used for generation of multiple-quantum coherence. When this occurs the efficiency of generation of multiple-quantum coherence between neighbor and remote spins may be altered. For a weakly coupled AMX spin system and for double-quantum filtering the maximum percentage effect occurs when $t_m = {}^1/_2 J_{AM}$.[10] This approach has been applied to cytidine with the result shown in part b of the figure. Selective decouploing of the 1′-proton allows detection of the remote 3′-proton. The remote proton multiplet structure corresponds to the difference between the subspectra associated with the two polarizations of the neighbor proton giving an up–down pattern.[11] In general, the phases of the signals from different spins will not be the same.[12] This combination of selective irradiation and multiple-quantum filtering is reminiscent of a one-dimensional approach to allow heteronuclear detection of remote protons.[13]

The use of multiple-quantum filtering is not essential, and analogous procedures based on the simple pulse sequence 90°–t_m–90°–acquisition with the phase of the first pulse being X and the second pulse cycled through $X,Y,-X,-Y$ have been demonstrated. This approach does not necessarily give the up–down multiple pattern needed for spectral analysis but is adequate for determination of the chemical shifts of neighbor and remote nuclei.

A one-dimensional version of relayed coherence transfer has been proposed which utilizes a selective 90° pulse at the beginning of the experiment.[2a] This approach requires the use of two delay times as well as phase coherence between the selective 90° pulse and the other pulses and is not as versatile or as easy to implement as the selective irradiation methods proposed here.

These two applications indicate some of the utility of combining selective irradiation with multiple-quantum filtering. While the cases presented here utilize only double-quantum filters, weakly coupled spin systems, and homonuclear examples,[14] many variations are possible. The main limitation on the basic approach is that of having *a* resolved signal from which to begin the determination of a coupling network. For the determination of a few coupling networks at high resolution the combination of selective irradiation with multiple-quantum filtering is much less demanding of spectrometer time than two-dimensional methods.

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(9) The pulse sequence used for the experiments is 90°–t_m/2–180°–t_m/2–90°–90°–acquisition with the phases of the pulses cycled for selective detection of double-quantum coherence. The delay time t_m was 0.1 s for the results shown in Figure 1. The free induction decay obtained with selective irradiation of the 1′-proton was substracted from the one obtained with far off-resonance irradiation and the resulting difference Fourier transformed. The experiments were performed using a Varian XL-200 spectrometer on a 50 mM sample of cytidine which was in 95% deuterated water. A 1-s equilibration delay was used, and the selective saturation was performed over 0.4-s.

(10) To predict the absolute intensities of the remote proton signals one need compare the efficiency of generation of MX double-quantum coherence in the presence and absence of coupling of M to A using the rules presented elsewhere.[3]

(11) In the presence of strong coupling of the irradiated neighbor or remote spins additional signals may be observed.

(12) As discussed in ref 5, the phases of the signals in multiple-quantum filtered spectra for spin systems other than AX are generally not the same.

(13) Bolton, P. H. *J. Magn. Reson.* **1982**, *46*, 91–97.

(14) A heteronuclear experiment can consist of selective irradiation of a heteronucleus during t_m and no 180° pulse. The difference spectrum then consists of either those protons that are neighbors to the heteronucleus or both the neighbors and remote protons depending on the choice of t_m. Selective decoupling of the heteronucleus can be applied during acquisition in both experiments if desired. This approach has been applied to selective decoupling of ^{31}P for oligonucleotide–drug complexes and will be presented elsewhere.[15]

(15) Bolton, P. H.; Gerlt, J. A., manuscript in preparation.

Thermolysis of 7,8-Dioxabicyclo[4.2.2]deca-2,4,9-trienes. An Unusual Decomposition Mode of Endoperoxides

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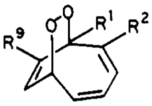
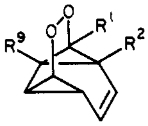
With only few exceptions, the thermolysis of endoperoxides leads to decomposition products derived from initial cleavage of the peroxide bond.[1] Presently we describe a hitherto unprecedented decomposition mode in the case of the endoperoxide of cyclooctatetraene **1a** and derivatives. Instead of affording the expected diepoxides **4a** and **5a**, facile intramolecular cycloaddition led to the isomeric endoperoxide **2a**, which on allowed (4 + 2) retrocyclization generated the intermediary, labile dialdehyde **3a**. Depending on the reaction conditions, the major final products of the latter were 4-(hydroxymethyl)benzaldehyde, terephthalaldehyde, benzaldehyde, or benzene. The product distributions of the solution and gas-phase thermolyses are summarized in Table I.



1a, $R^1 = R^2 = R^9 = H$
b, $R^1 = OMe$; $R^2 = R^9 = H$
c, $R^1 = R^2 = H$; $R^9 = OMe$
d, $R^1 = R^2 = H$; $R^9 = Ph$
e, $R^1 = Me$; $R^2 = R^9 = H$
f, $R^1 = R^9 = H$; $R^2 = Me$



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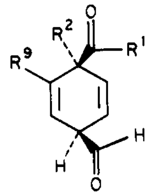

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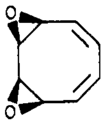

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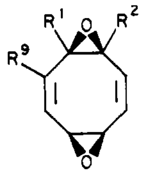

5

The endoperoxides **1** were prepared via tetraphenylporphine (TPP)-photosensitized oxygenation[2] of the respective cyclooctatetraene. The experimental details are described elsewhere.[3] While the photochemical and the cobalt–tetraphenylporphine complex catalyzed reactions of these endoperoxides afforded exclusively the diepoxides **5**, the thermal decomposition did not produce even traces of the diepoxides **4** and **5**. The fact that in the liquid-phase thermolysis of the endoperoxide **1a** in acetonitrile the main product was the 4-(hydroxymethyl)benzaldehyde (Table I, entry 1) provided the first clue that the dialdehyde **3a** could have served as a potential intermediate.

This mechanistic supposition was made plausible through the following experiments. In CCl_4 at 130 °C endoperoxide **1a** gave

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† Research participant in the science teachers program.

‡ Doctoral Dissertation, University of Würzburg, July 1984.

(1) Saito, I.; Nittala, S. S. "The Chemistry of Peroxides"; Patai, S., Ed.; Wiley: New York, 1983; pp 311–374.

(2) Adam, W.; Klug, G. *Tetrahedron Lett.* **1982**, *23*, 3155.

(3) Adam, W.; Klug, G.; Peters, E.-M.; Peters, K.; von Schnering, H. G. *Tetrahedron*, in press.

0002-7863/84/1506-4300$01.50/0