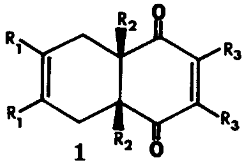
Tetrahedron Letters,Vol.22,No.48,pp 4779-4782,1981 0040-4039/81/484779-04$02.00/0
Printed in Great Britain

THE CONFORMATIONAL ANALYSIS OF TETRAHYDRONAPHTHOQUINONES USING HIGH RESOLUTION SOLID STATE ^{13}C NMR SPECTROSCOPY

C.A. McDowell, A. Naito, John R. Scheffer* and Yiu-Fai Wong
Department of Chemistry, University of British Columbia
2075 Wesbrook Mall, Vancouver, B.C., Canada V6T 1W5

Abstract. The proton-decoupled ^{13}C NMR spectra of five conformationally mobile cis-tetrahydronaphthoquinone derivatives were obtained in solution ($CDCl_3$) and in the solid state (cross polarization, magic angle spinning). The major difference between the results in the two media is that in solution the spectra consist of a series of well separated two carbon atom singlets whereas in the solid state, the singlets are replaced by doublets, with separations ranging from 0.4 to 9.3 ppm. This difference is interpreted as being due to rapid equilibrium between enantiomeric conformers in solution resulting in an average plane of symmetry. In the solid state the static spectrum of the asymmetric conformer is observed, the doublets arising because of the chemical shift differences between two conformationally distinct carbon atoms. The magnitude of the solid state doublet separations can be used to make tentative conformationa assignments.

One of our major research goals over the past several years has been the development of structure-reactivity relationships for unimolecular photorearrangements of organic molecules in the solid state.[1] Wherever possible, the structural features of the substrates to be photolyzed are determined by X-ray crystallography. Not infrequently, however, this approach was not successful because our substrates simply do not form single crystals suitable for X-ray diffraction analysis. For this reason we have embarked on a program of investigating the structures of these compounds in the solid state by ^{13}C NMR spectroscopy. Using the techniques of cross-polarization, proton-decoupling and magic angle spinning, it is now possible to obtain solid state ^{13}C NMR spectra which approach, in sensitivity and resolution, those determined in solution.[2] The NMR technique, while providing less information than X-ray crystallography, does have several advantages. These include reduced time and cost factors as well as the elimination of the requirement for single crystals since the NMR measurements can be carried out on powdered, polycrystalline samples. In addition, the NMR method provides information on the magnetic and stereoelectronic properties of nuclei which is lacking in X-ray crystallography. In this communication we outline our results with the cis-4a,5,8,8a-tetrahydro-1,4-naphthoquinones **1a** - **1e** whose solid state photochemistry we have previously reported.[3] Of these five substrates, only **1c** and **1e** could be analyzed successfully by X-ray crystallography.[4]



1

(a) $R_1=CH_3$, $R_2=R_3=H$
(b) $R_1=R_2=H$, $R_3=CH_3$
(c) $R_1=R_3=CH_3$, $R_2=H$
(d) $R_2=R_3=CH_3$, $R_1=H$
(e) $R_1=R_2=R_3=CH_3$

Figure 1 illustrates some typical spectra. Part A shows the fully decoupled solid state ^{13}C spectrum of compound 1d. Below it (part B) is shown the fully decoupled solution ($CDCl_3$) spectrum of the same material, and in part C we see the single frequency off-resonance decoupled (SFORD) spectrum, also in solution. The SFORD technique permits observation of the coupling between a given carbon atom and its attached hydrogen atoms and serves as an aid in assigning the resonances. The chemical shift and splitting pattern data derived from these spectra are summarized in Table I. Also included in Table I are the analogous data from the other four tetrahydronaphthoquinone substrates.

The most striking feature of the fully decoupled spectra is that *chemically equivalent carbons appear as singlets in solution and as doublets in the solid state.* The only exceptions to this are the R_3 methyl group resonances in compounds 1b - 1e which appear as singlets in both media. We interpret the results as follows: In the solid state, it has been established by X-ray crystallography[4] that compounds 1c and 1e adopt the twisted conformation 1' (or 1") shown on the next page. This conformation lacks a plane of symmetry, and because ring inversion is prevented by the restraints present in the crystal lattice, one sees a separate NMR resonance for each individual carbon atom. The doublets observed in the solid state thus arise from the slight environmental differences experienced by nominally equivalent carbons.[5] In solution, on the other hand, equilibration

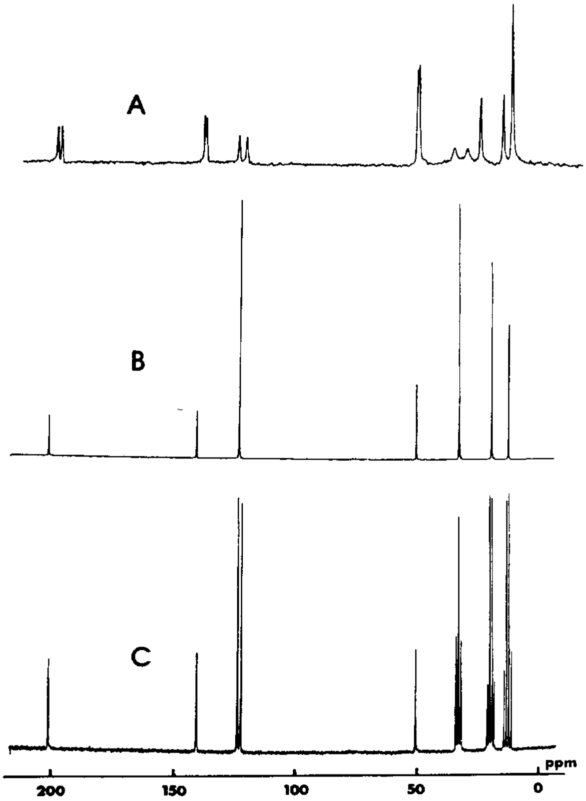


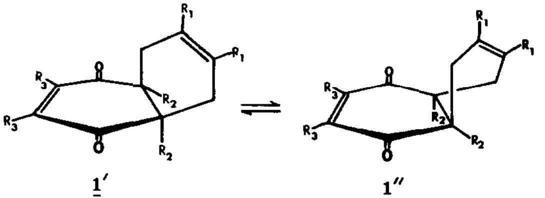
Figure 1. ^{13}C NMR spectra of compound 3d. (A) fully decoupled solid state spectrum; (B) fully decoupled solution spectrum; (C) SFORD solution spectrum.

Table I. ^{13}C NMR Chemical Shift Data for Tetrahydronaphthoquinones 1a - 1e[a]

Carbon Atom	1a solution	1a solid	1b solution	1b solid	1c solution	1c solid	1d solution	1d solid	1e solution	1e solid
R_3 R_3			12.92(q)	12.8	12.88(q)	14.2	12.98(q)	12.8	12.93(q)	13.8
C(2) C(3)	139.34(d)	141.9 137.0	143.87	145.9 142.3	143.87	146.3 142.3	141.57	142.5 141.7	141.61	141.9 140.9
C(1) C(4)	200.08	201.9 200.7	199.72	201.7 199.7	200.01	201.3 199.9	202.72	203.9 202.3	203.00	202.9 201.8
C(4a) C(8a)	47.09(d)	47.6 46.4	46.07(d)	47.0 45.8	46.87(d)	48.0 45.8	51.10	52.1 51.5	51.71	52.9 52.5
R_2 R_2							19.95(q)	25.8 16.5	19.91(q)	22.4 17.0
C(5) C(8)	30.50(t)	31.4 30.0	24.53(t)	27.6 23.9	30.89(t)	32.8 31.2	33.42(t)	36.7 31.0	39.84(t)	42.8 35.9
C(6) C(7)	123.36	126.3 122.6	124.56(d)	126.1 124.7	123.37	124.5 123.2	124.13(d)	126.5 123.2	122.78	124.1 122.8
R_1 R_1	18.81(q)	20.9 18.5			18.81(q)	20.1 18.5			18.63(q)	20.0 19.0

[a] The solid state spectra were obtained at room temperature on a Bruker CXP-200 FT NMR spectrometer and the solution spectra were measured at the same temperature on a Bruker WH-400 FT instrument. The chemical shifts are given in ppm relative to TMS. The solution splitting patterns refer only to the SFORD measurements; all other resonances appear as singlets.

between the enantiomeric conformers 1' and 1" is rapid on the NMR time scale resulting in a time-averaged singlet for carbon atoms which are equivalent with respect to the average plane of symmetry.



1′ 1″

From the data in Table I, this interpretatio can be concluded to be general for the five tetrahydronaphthoquinones investigated. Several other inferences can also be drawn from the data. First, the variation in chemical shift observed for a given carbon atom in compounds 1a - 1e is qualitatively explicable in terms of the α, β and γ effects of the methyl substituents.[6] Secondly, for a given carbon atom in a given molecule, $\delta_{solution}$ differs slightly from δ_{solid}. This is shown by the chemical shifts of the R_3 methyl singlets in the two media which vary by as much as 1.3 ppm (compound 1c). This is also indicated by the fact that, in general, $\delta_{solution}$ does not occur at the midpoint of the corresponding solid state doublet. Finally, we point out that the magnitude of the solid state doublet separation (Δδ) can be used to obtain structural information. From Table I, the doublet separation reaches a maximum for the R_2 methyl groups in compounds 1d and 1e (Δδ = 9.3 and 5.4 ppm respectively) and also for the C(5)/C(8) carbon atoms in the same compounds (Δδ = 5.7 and 6.9 ppm). It seems likely that these are the result of upfield steric compression shifts[7] of the more hindered carbons. We thus tentatively assign the upfield portion of these doublets to the methyl group which is axial with respect to the cyclohexene ring and to the allylic methylene group with which it forms a gauche-butane interaction. This assignment is supported by the fact that when the R_2 methyl groups of compounds **1d** and **1e** are absent (i.e., substrates **1b** and **1c** respectively), the C(5)/C(8) chemical shift differences are much reduced ($\Delta\delta$ = 3.7 ppm for **1b** and 1.6 ppm for **1c**).

The technique of high resolution solid state ^{13}C NMR spectroscopy both complements and extends the scope of NMR methods which have been applied to problems in conformational analysis. Coupled with precise X-ray crystallographic data, it also holds great potential for the development of improved theories which relate conformation and stereochemistry to ^{13}C chemical shifts. Work on this aspect of the problem as well as extensions to other conformationally mobile systems is in progress.

Acknowledgement. We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

1. J.R. Scheffer, Acc. Chem. Res., 13, 283 (1980) and references cited therein. For more recent work, see Z.Q. Jiang, J.R. Scheffer, A.S. Secco and J. Trotter, Tetrahedron Lett., 891 (1981).

2. (a) R.W. Vaughan, Ann. Rev. Phys. Chem., 29, 397 (1978); (b) J. Jonas and H.S. Gutowsky, ibid., 31, 1 (1980).

3. J.R. Scheffer and A.A. Dzakpasu, J. Am. Chem. Soc., 100, 2163 (1978).

4. Compound **1c**: S.E.V. Phillips and J. Trotter, Acta Crystallogr., Sect. B, 32, 3095 (1976); Compound **1e**: S.E.V. Phillips and J. Trotter, ibid., 32, 3088 (1976).

5. Alternative explanations, such as the occurrence of more than one conformer per unit cell or other crystal packing effects, are ruled out, at least in the case of compounds **1c** and **1e**, by the crystal structure data. The R_3 methyl groups experience a very similar environment in **1'** and hence give rise to a fortuitous two carbon atom singlet in the solid state.

6. J.W. Cooper, "Spectroscopic Techniques for Organic Chemists," John Wiley and Sons, New York, N.Y., 1980, Ch. 6.

7. (a) D.M. Grant and V.V. Cheney, J. Am. Chem. Soc., 89, 5315 (1967); (b) D.K. Dalling and D.M. Grant, ibid., 89, 6612 (1967); (c) J.B. Grutzner, M. Jautelat, J.B. Dence, R.A. Smith and J.D. Roberts, ibid., 92, 7107 (1970); (d) G.C. Levy and G.L. Nelson, ibid., 94, 4897 (1972); (e) D.K. Dalling, K.H. Ladner, D.M. Grant and W.R. Woolfenden, ibid., 99, 7142 (1977).

(Received in USA 16 June 1981)