Tetrahedron Letters No. 16, pp 1359 - 1362, 1978. Pergamon Press. Printed in Great Britain.

RESTRICTED ROTATION IN DIPHENYLMETHYL ANIONS. ^1H AND $^{13}C[^1H]$ DNMR EVIDENCE FOR DIFFERENT RATES OF ROTATION IN THE LITHIUM SALT OF THE 4-DEUTERIO-4'-METHYLDIPHENYLMETHYL ANION

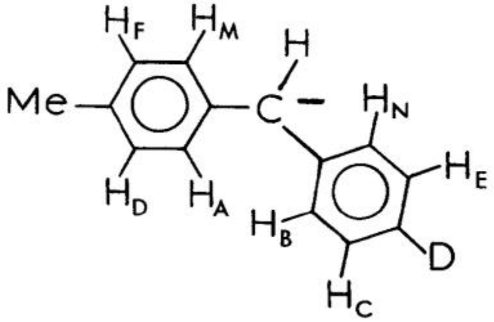
C. Hackett Bushweller*, John S. Sturges, Michael Cipullo, Steven Hoogasian, Mona W. Gabriel, Shelton Bank*

Department of Chemistry and the Institute of Biomolecular Stereodynamics, State University of New York, Albany, New York 12222 USA

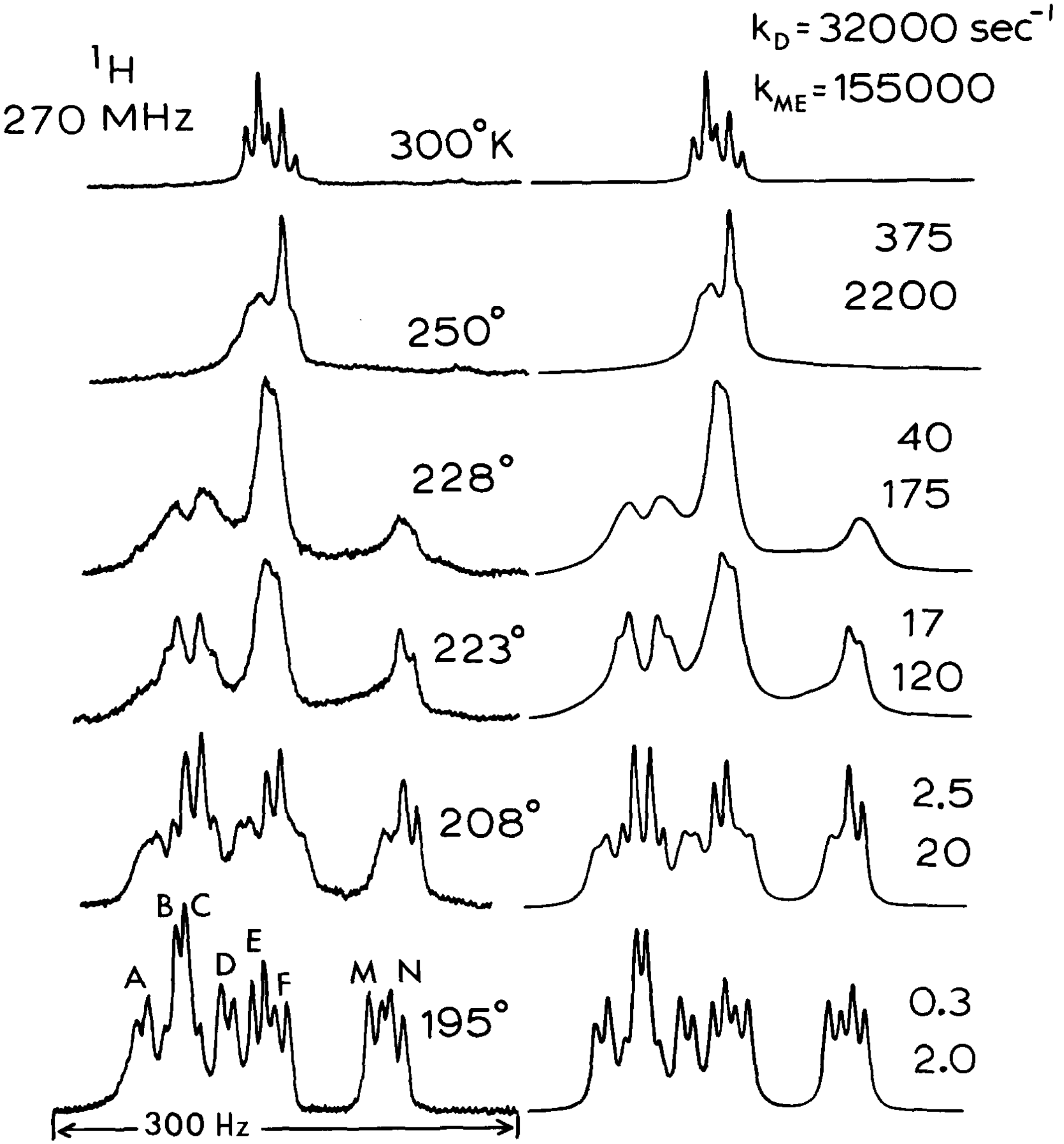
(Received in USA 22 November 1977; received in UK for publication 6 March 1978)

Diphenylmethyl anions are stable hydrocarbon anions due to charge delocalization into the two aromatic rings.[1a] The resultant π-bonding across the benzylic carbon-phenyl bond leads to restricted phenyl rotation.[1b] Indeed, it might be expected that the electron-donor properties of para substituents on the phenyl rings would affect the respective exocyclic π-bond orders and thus the respective barriers to phenyl rotation. This report concerns ^1H and $^{13}C[^1H]$ DNMR evidence for differential rates of phenyl rotation for the two rings of the 4-deuterio-4'-methyldiphenylmethyl anion (**1**).

Examination of the ^1H DNMR spectrum (270 MHz) of the lithium salt of **1** (0.4M in THF) at 300°K (Figure 1) shows two different overlapping spectra each of which has apparent AB characteristics consistent with the presence of two different rings. The two low-field doublets of each respective phenyl spectrum are superimposed while the low-field line of the highest field doublet overlaps with the high field line of the next lower field doublet. At lower temperatures, the spectrum undergoes a series of complex changes and is sharpened at 195°K into overlapping ADFM and BCEN spectra as labeled in Figure 1 and determined from complete ^1H DNMR line shape analysis.[2] The spectrum at 195°K (Figure 1) is clearly consistent with the observation of four different protons on each ring and rotation of both rings being static on the DNMR time scale in the delocalized anion (see **2**). At temperatures



2



¹H
270 MHz
300°K
250°
228°
223°
208°
195°
A
B C
D
E
F
M N
300 Hz
k_D = 32000 sec⁻¹
k_ME = 155000
375
2200
40
175
17
120
2.5
20
0.3
2.0

Figure 1

above 195°K, complete DNMR line shape analyses reveal an interesting dynamical situation in 1. Perusal of the DNMR spectra (Figure 1) at 208°K or 223°K illustrates the situation. It is clear at 208°K or 223°K that the ADFM spectrum is substantially more collapsed than the BCEN spectrum due to the onset of a rate process which is becoming rapid on the DNMR time scale. Indeed, a complete DNMR line shape analysis at 208°K reveals the rate constant for exchange of the ADFM system to an MFDA system is 20 sec^{-1} and that for the BCEN to NECB exchange is 2.5 sec^{-1}. Phenyl rotation will exchange H_A with H_M, H_F with H_D, H_B with H_N, and H_C with H_E (see 2). The important observation is that one ring is rotating faster than the other. This observation is very nicely consistent with the electron-donating property of methyl leading to reduced π-bonding of the methylated ring to the benzylic carbon of 1 and a reduced barrier to 4-methylphenyl rotation as compared to 4-deuteriophenyl rotation.[3] Thus, these observations for 1 provide unequivocal evidence for differential rates of rotation in an unsymmetrical 4,4'-disubstituted diphenylmethyl anion.

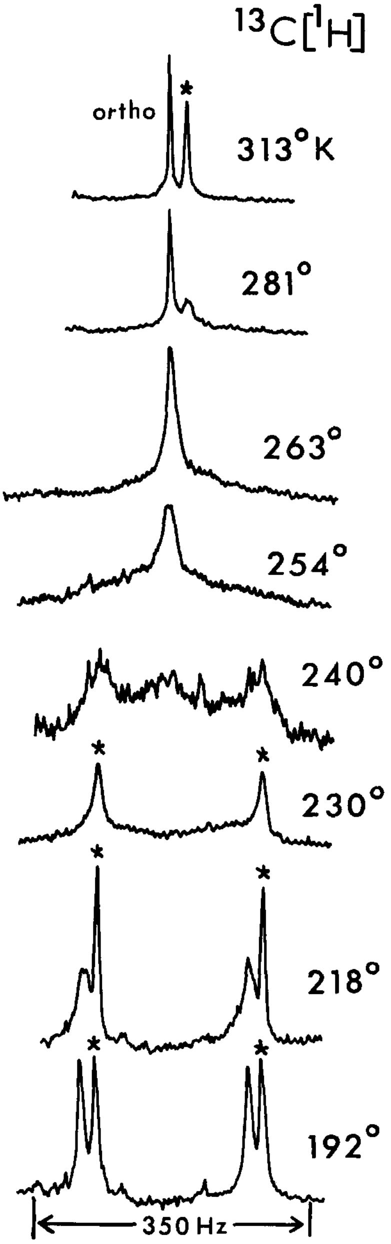


Figure 2

The phenomenon of differential rates of rotation is also illustrated very effectively in the $^{13}C[^1H]$ DNMR spectra of 1 (Figure 2). Examination of the $^{13}C[^1H]$ FT DNMR spectrum (22.64 MHz) of 1 (~0.4M in THF) at 313°K reveals two different ortho carbon resonances at δ117.7 and 116.9 (TMS reference) consistent with the presence of two different rings. The singlet nature of both signals suggests that the ortho carbons are being rotationally averaged at a rate which is fast on the DNMR time scale. At lower temperatures, the spectrum undergoes exchange broadening and the singlet indicated by the asterisk at 313°K is sharpened into two singlets (indicated by asterisks) at 192°K which are separated by 9.30 ppm. The other singlet resonance at 313°K separates into two singlets at 192°K separated by 9.35 ppm. It is obvious from an examination of the $^{13}C[^1H]$ DNMR spectrum of 1 at 218°K that the rate process associated with the asterisked peaks is slow on the DNMR time scale while the other pair of singlets is subject to exchange broadening, i.e., one ring is rotating faster than the other. Such DNMR spectral behavior is consistent with the asterisked peaks being assigned to the ortho carbons of the 4-deuteriophenyl group which is rotating at a *slower* rate than the 4-methylphenyl ring.[3] A complete DNMR line shape analysis at 254°K revealed the rate of rotation of the deuteriated ring to be 500 sec^{-1} and that for the methylated ring to be 3000 sec^{-1} in good agreement with the ^{1}H DNMR data (Figure 1). The activation parameters for 4-deuteriophenyl rotation are $\Delta H^{\ddagger} = 12.1 \pm 0.4$ kcal/mole, $\Delta S^{\ddagger} = 1.9 \pm 1.0$ gibbs, $\Delta G^{\ddagger} = 11.7 \pm 0.1$ kcal/mole at 223°K, and for 4'-methylphenyl rotation $\Delta H^{\ddagger} = 11.2 \pm 0.4$ kcal/mole, $\Delta S^{\ddagger} = 1.8 \pm 1.0$ gibbs, and $\Delta G^{\ddagger} = 10.8 \pm 0.1$ kcal/mole at 223°K.

These observations for 1 reveal a clear cut differential substituent effect on the rate of rotation in an unsymmetrical 4,4'-disubstituted diphenylmethyl anion. We are pursuing work aimed at an incisive depiction of the origin of the substituent effect in terms of intrinsic substituent electron-donor properties, solvation, and ion-pairing phenomena.

Acknowledgement: CHB is grateful for support from the National Science Foundation, Sloan Foundation, and Dreyfus Foundation. We wish to acknowledge the support of the Southern New England High Field NMR Facility made possible by a grant from Biotechnology Resources Program of the National Institutes of Health (RR-798).

REFERENCES

(1) (a) J. Smid in "Ions and Ion Pairs in Organic Reactions," Vol. 1, M.Szwarz, Ed., Wiley-Interscience, New York, 1972; (b) D.H. O'Brien, R. Russell, and A. J. Hart, *J. Am. Chem. Soc.*, *98*, 7427 (1976) and references therein.

(2) Our DNMR computer program is a local substantially modified version of DNMR3 by D. A. Kleier and G. Binsch, *J. Magn. Reson.*, *3*, 146 (1970). Our modifications are described in C. H. Bushweller, G. Bhat, L. J. Letendre, J. A. Brunelle, H. S. Bilofsky, H. Ruben, D. H. Templeton, and A. Zalkin, *J. Am. Chem. Soc.*, *97*, 65 (1975). The spectrum is simulated accurately using $\delta_{A}6.63$ (TMS reference), $\delta_{D}6.43$, $\delta_{F}6.30$, $\delta_{M}6.08$; $^{3}J_{AD} = 8.0$ Hz, $^{5}J_{AF} = 0.0$, $^{4}J_{AM} = 1.1$, $^{4}J_{DF} = 1.1$, $^{5}J_{DM} = 0.0$, $^{3}J_{FM} = 8.2$ *and* $\delta_{B}6.56$, $\delta_{C}6.52$, $\delta_{E}6.36$, $\delta_{N}6.03$; $^{3}J_{BC} = 8.0$ Hz, $^{5}J_{BE} = 0.0$, $^{4}J_{BN} = 1.1$, $^{4}J_{CE} = 1.1$, $^{5}J_{CN} = 0.0$, $^{3}J_{EN} = 8.2$.

(3) Assignments of the ADFM and BCEN spectra to the respective rings of 1 (see 2) is consistent with substituent effects on the ^{1}H NMR spectra of symmetrical 4,4'-disubstituted diphenylmethyl anions examined in our laboratory. Assignments made for the ^{13}C DNMR spectra of 1 herein are also consistent with the general effect of a 4-methyl group on the ortho ^{13}C NMR chemical shifts of diphenylmethyl anions.