germanium and tin polymers become progressively larger. Since the transport properties of MPcI$_x$ compounds are largely ligand-dominated and relatively insensitive to M,[3,3c,21] it appears reasonable to relate a significant portion of the conductivity trend in the $\{[M(Pc)O]I_x\}_n$ series to differences in the plane-plane separation.

Further studies of these and other linked metallomacrocycle systems are in progress.[22]

Acknowledgments. This work was generously supported by the Office of Naval Research and by the NSF-MRL program through the Materials Research Center of Northwestern University (Grant DMR76-80847). We thank Professor Malcolm Kenney for helpful comments.

References and Notes

(1) For reviews of low-dimensional conductive materials see: (a) Devreese, J. T.; Evrard, V. E.; Van Doren, V. E. Eds. "Highly Conducting One-Dimensional Solids"; Plenum: New York, 1979. (b) Torrance, J. B. *Acc. Chem. Res.* **1979**, *12*, 79–86. (c) Miller, J. S.; Epstein, A. J., Eds. *Ann. N.Y. Acad. Sci.* **1978**, 313. (d) Keller, H. J., Ed. "Chemistry and Physics of One-Dimensional Metals"; Plenum: New York, 1977. (e) Miller, J. S.; Epstein, A. J. *Prog. Inorg. Chem.* **1976**, *20*, 1–151. (f) Keller, H. J., Ed. "Low Dimensional Cooperative Phenomena"; Plenum: New York, 1975. (g) Soos, Z. G.; Klein, D. J. In "Molecular Associations", Foster, R., Ed.; Academic: New York, 1975; Chapter 1.

(2) (a) Marks, T. J. *Ann. N.Y. Acad. Sci.* **1978**, 594–616. (b) Cowie, M. A.; Gleizes, A.; Grynkewich, G. W.; Kalina, D. W.; McClure, M. S.; Scaringe, R. P.; Teitelbaum, R. C.; Ruby, S. L.; Ibers, J. A.; Kannewurf, C. R.; Marks, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 2921–2936. (c) Brown, L. D.; Kalina, D. W.; McClure, M. S.; Ruby, S. L.; Schultz, S.; Ibers, J. A.; Kannewurf, C. R.; Marks, T. J. *Ibid.* **1979**, *101*, 2937–2947. (d) Lin, L.-S.; Wang, J. C.; Kannewurf, C. R.; Marks, T. J., submitted for publication.

(3) (a) Schramm, C. S.; Stojakovic, D. R.; Hoffman, B. M.; Marks, T. J. *Science* **1978**, *200*, 47–48. (b) Petersen, J. L.; Schramm, C. S.; Stojakovic, D. R.; Hoffman, B. M.; Marks, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 286–288. (c) Schramm, C. S.; Scaringe, R. P.; Stojakovic, D. R.; Hoffman, B. M.; Ibers, J. A.; Marks, T. J., submitted for publication. (d) Phillips, T. E.; Hoffman, B. M. *Ibid.* **1977**, *99*, 7734–7736.

(4) (a) Endres, H.; Keller, H. J.; Lehaman, R.; van de Sand, H.; Dong, V.; Poveda, A. *Ann. N.Y. Acad. Sci.* **1978**, 633–650, and references therein. (b) Miller, J. S.; Griffiths, C. H. *J. Am. Chem. Soc.*, **1977**, *99*, 749–755.

(5) For discussions of the structural chemistry of low-dimensional materials see: (a) Kistenmacher, T. J. *Ann. N.Y. Acad. Sci.* **1978**, 333–342. (b) Megtert, S.; Pouget, J. P.; Comes, R. *Ibid.* **1978**, 234–243. (c) Stucky, G. D.; Schultz, A. J.; Williams, J. M. *Annu. Rev. Mater. Sci.* **1977**, *7*, 301–339. (d) Bespalov, B. P.; Titov, V. V. *Russ. Chem. Rev.* **1975**, *44*, 1091–1108. (e) Dahm, D. J.; Horn, P.; Johnson, G. R.; Miles, M. G.; Wilson, J. D. *J. Cryst. Mol. Struct.* **1975**, *5*, 27–34. (f) Herbstein, F. H. *Perspect. Struct. Chem.* **1971**, *IV*, 166–395. For other approaches to controlling stacking, see: (g) Torrance, J. B.; Mayerle, J. J.; Lee, Y. K.; Bechgaard, K. *J. Am. Chem. Soc.* **1979**, *101*, 4747–4748. (h) Kuznesof, P. M.; Wynne, K. J.; Nohr, R. S.; Kenney, M. E. *J. Chem. Soc., Chem. Commun.*, in press.

(6) (a) Joyner, R. D.; Kenney, M. E. *Inorg. Chem.* **1960**, *82*, 5790–5796. (b) Joyner, R. D.; Kenney, M. E. *Ibid.* **1962**, *1*, 717–718. (c) Kroenke, W. J.; Kenney, M. E. *Ibid.* **1964**, *3*, 251–254. (d) Esposito, J. N.; Sutton, L. E.; Kenney, M. E. *Ibid.* **1967**, *6*, 1116–1120.

(7) Davison, J. B.; Wynne, K. J. *Macromolecules* **1978**, *11*, 186–191.

(8) (a) Schoch, K. F., Jr.; Marks, T. J.; Kundalkar, B. R.; Lin, L.-S.; Teitelbaum, R. C. *Bull. Am. Phys. Soc.* **1979**, *24*, 326. (b) Schoch, K. F., Jr.; Marks, T. J., manuscript in preparation.

(9) (a) Meyer, G.; Wöhrle, D. *Makromol. Chem.* **1974**, *175*, 714–728. (b) Meyer, G.; Hartmann, M.; Wöhrle, D. *Ibid.* **1975**, *176*, 1919–1927.

(10) Stoichiometries were determined by C, H, N, and I elemental analyses.

(11) (a) Teitelbaum, R. C.; Ruby, S. L.; Marks, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3215–3217. (b) Teitelbaum, R. C.; Ruby, S. L.; Marks, T. J. *Ibid.*, in press. (c) Marks, T. J.; Webster, D. F.; Ruby, S. L.; Schultz, S. *J. Chem. Soc., Chem. Commun.* **1976**, 444–445. (d) Kalina, D. W.; Stojakovic, D. R.; Teitelbaum, R. C.; Marks, T. J., manuscript in preparation.

(12) (a) Seeger, K. "Semiconductor Physics"; Springer-Verlag: New York, 1973; pp 483–487. (b) Cahen, D.; Hahn, J. R.; Anderson, J. R. *Rev. Sci. Instrum.* **1973**, *44*, 1567–1568. (c) Van der Pauw, L. J. *Philips Res. Rep.* **1958**, *13*, 1–9; *Philips Tech. Rev.* **1958**, *20*, 220–224.

(13) (a) Chiang, C. K.; Druy, M. A.; Gau, S. C.; Heeger, A. J.; Louis, E. J.; MacDiarmid, A. G.; Park, Y. W.; Shirakawa, H. *J. Am. Chem. Soc.* **1978**, *100*, 1013–1015. (b) Chiang, C. K.; Park, Y. W.; Heeger, A. J.; Shirakawa, H.; Louis, E. J.; MacDiarmid, A. G. *J. Chem. Phys.* **1978**, *69*, 5098–5104.

(14) (a) Scott, J. C.; Kulick, J. D.; Street, G. B. *Solid State Commun.* **1978**, *28*, 723–727. (b) Bloch, A. N.; Carruthers, T. F.; Poehler, T. O.; Cowan, D. O. *Ann. N.Y. Acad. Sci.* **1978**, 47–85. (c) Heeger, A. J. *Ibid.* **1978**, 87–135. (d) Scott, J. C.; Garito, A. F.; Heeger, A. J. *Phys. Rev. B* **1974**, *10*, 3131–3139.

(15) Susceptibilities are expressed per mole of $[M(Pc)O]I_x$ subunits. Studies have been performed to 77 K; detailed experiments at lower temperatures as a function of dopant level will be reported in the future. Small increases in the paramagnetism at temperatures below 100 K are tentatively attributed to impurities.

(16) Kroenke, W. J.; Sutton, L. E.; Joyner, R. D.; Kenney, M. E. *Inorg. Chem.* **1963**, *2*, 1064–1065.

(17) Swift, D. R. Ph.D. Thesis, Case Western Reserve University, 1970.

(18) Shannon, R. D. *Acta. Crystallogr., Sect. A* **1976**, *32*, 751–767.

(19) The known PcSi-O-SiPc distance[17] can be obtained by adjusting the tabulated[18] six-coordinate Si(IV) ionic radius to the unique phthalocyanine environment (subtracting 0.088 Å). A similar process for Ge(IV) and Sn(IV) yields calculated PcM-O-MPc distances of 3.58 and 3.90 Å, respectively. Since four- and six-coordinate radii for Si(IV), Ge(IV), and Sn(IV) differ for each element by 0.14 Å, this is a physically reasonable approximation.

(20) Glidewell, C.; Liles, D. C. *J. Chem. Soc., Chem. Commun.* **1979**, 93–94, and references therein. Glidewell, C.; Liles, D. C. *J. Organomet. Chem.*, **1979**, *174*, 275–279, and references therein.

(21) (a) Stojakovic, D. R. Ph.D. Thesis, Northwestern University, Aug 1977. (b) Schramm, C. S. Ph.D. Thesis, Northwestern University, March 1979.

(22) Dirk, C. W.; Lin, L.-S.; Schoch, K. F., Jr.; Marks, T. J., research in progress.

(23) Camille and Henry Dreyfus Teacher-Scholar.

Karl F. Schoch, Jr., Bhagyashree R. Kundalkar
Tobin J. Marks*[23]
Department of Chemistry and the Materials Research Center
Northwestern University, Evanston, Illinois 60201

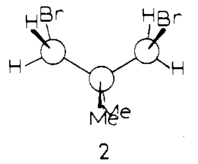
Received May 3, 1979

1,3-Dipolar Interactions in Acyclic Systems. NMR Evidence for a Strong Conformational Preference in 1,3-Dibromo-2,2-dimethylpropane

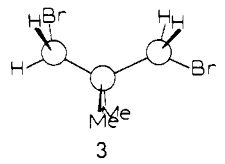
Sir:

Over the past several years, variable-temperature or "dynamic" NMR (DNMR) spectroscopy[1] has been used extensively to probe conformational preferences involving polar *vicinal* substituents in simple and moderately complex *acyclic* systems.[1-3] However, there is only a small amount of information available regarding *1,3 interactions* between two polar substituents in simple acyclic molecules,[4] although analogous data is available for the more constrained cyclic systems.[5] This report concerns an ^{1}H DNMR study of 1,3-dibromo-2,2-dimethylpropane and evidence for a strong preference for one molecular geometry.

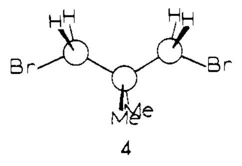
A previous ^{1}H DNMR study of neopentyl bromide[6] in our laboratory suggested that the barrier to rotation about the C(1)-C(2) and C(2)-C(3) bonds of 1,3-dibromo-2,2-dimethylpropane (**1**) should be high enough to be detectable by the DNMR method. The ^{1}H DNMR spectrum (270 MHz) of **1** (2% v/v in CBrF$_3$) at 170 K shows a singlet at δ 3.39 (CH$_2$Br) and singlet at 1.19 (CMe$_2$). At lower temperatures (Figure 1), *no changes* are observed for the CMe$_2$ resonance, but the CH$_2$Br singlet broadens and is separated into *one* AB spectrum (δ_A 3.61, δ_B 3.19 ($J_{AB} = -10.2$ Hz)) at 121 K (Figure 1). Assuming essential staggering along all of the carbon-carbon bonds of **1**, four reasonable molecular geometries exist (**2**, **3**, **4**, **5**). However, the spectrum of **1** at 121 K (Figure 1) is consistent only with **2**. In **2** (C_2 symmetry), the *gem*-dimethyl groups are equivalent and will give a singlet



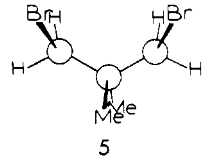
2



3



4



5

0002-7863/79/1501-7073$01.00/0

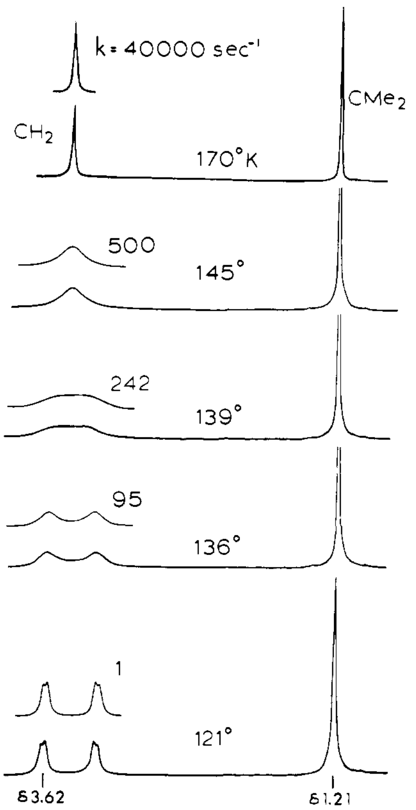


Figure 1. The ^1H DNMR spectra (270 MHz) of 1,3-dibromo-2,2-dimethylpropane (**1**, 2% v/v in $CBrF_3$) at various temperatures. Computed spectra using an AB to BA exchange model for the CH_2Br resonance are illustrated above the experimental spectra (k is the first-order rate constant for AB to BA exchange).

while the two methylene groups will give rise to the same AB spectrum as observed. The two protons on a given methylene group of **2** are indeed nonequivalent. Conformer **3** (C_1 symmetry) will show a doublet for CMe_2 and two different AB spectra for CH_2Br; **4** (C_{2v} symmetry) will give singlets for both CMe_2 and CH_2Br groups; **5** (C_s symmetry) will give a doublet for CMe_2 and one AB spectrum for the CH_2Br groups. Based on the observed ^1H NMR chemical-shift difference between the different methyl groups of neopentyl bromide at 105 K (0.10 ppm),[6] it would be anticipated that various methyl protons signals due to conformers **3**, **4**, or **5** would indeed be sufficiently shifted from that due to **2** to be detectable. In addition, the width at half-height of the methyl protons signal for **1** at 121 K (7.0 Hz; see Figure 1) is essentially identical with that for the tetramethylsilane reference signal. This speaks for no DNMR effect for the methyl groups of **1** and for magnetic equivalence of the methyl protons of **1** which is of course consistent with the symmetry of **2**.

It is interesting to note that, within the limits of NMR detection, **2** is the *only* conformer observed. Conformers **3** and **4** are more or less reasonable on steric grounds but are not observed. The geometry **5** is intuitively less stable than **2**, **3**, and **4**. The essentially parallel C-Br bonds in **5** lead to a significant dipole moment and substantial repulsions between the two proximate bromine atoms. The increased stability of **2** compared with that of **3** or **4** may result from optimized electrostatic *attractions*[5] between the respective oppositely charged monopoles of the two C-Br bond moments. These results for **1** are qualitatively consistent with IR data for 1,3-dibromopropane which indicate a preference in the *crystal* for a geometry which is analogous to **2**.[4a] However, the IR data for 1,3-dibromopropane in *solution* reveal the presence of geometries which are analogous to **2**, **3**, and **4** but not **5**.[4a] The strong preference for conformer **2** is also analogous to the preference for the gauche-gauche conformation in dimethoxymethane.[7]

The DNMR behavior observed for the CH_2Br groups of **1** can be simulated using a simple AB to BA exchange model (Figure 1). The preliminary activation parameters for exchange are $\Delta H^{\ddagger} = 6.2 \pm 0.6$ kcal/mol, $\Delta S^{\ddagger} = -1 \pm 3$ eu, and $\Delta G^{\ddagger} = 6.4 \pm 0.2$ kcal/mol at 139 K. The process detected by the DNMR method involves conversion of **2** into its enantiomeric form which of course involves rotation about two carbon-carbon bonds. The nature of the DNMR data in Figure 1 does not allow a distinction between a concerted double rotation or stepwise separate rotations.

Thus, it is apparent that the ^1H DNMR method will be useful in probing the effects of 1,3 interactions in relatively simple molecular systems and a systematic evaluation of steric, electronic, and solvent effects is planned.

Acknowledgment. We are grateful to the National Science Foundation for Grant No. CHE78-21161. We acknowledge 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 and Notes

(1) L. M. Jackman and F. A. Cotton, Eds., ''Dynamic Nuclear Magnetic Resonance Spectroscopy'', Academic Press, New York, 1975.
(2) W. J. Orville-Thomas, Ed., ''Internal Rotation in Molecules,'', Wiley, New York, 1974.
(3) For recent papers, see F. A. L. Anet and I. Yavari, *J. Am. Chem. Soc.*, **99,** 6752 (1977); C. Y. Wang and C. H. Bushweller, *ibid.*, **99,** 313 (1977), and references therein.
(4) (a) J. Thorbjornsrud, O. H. Ellestad, P. Klaboe, and T. Torgrimsen, *J. Mol. Struct.*, **15,** 61 (1973). (b) See also G. A. Crowder, *Spectrochim. Acta, Part A*, **33,** 721 (1977); M. A. Cochran, A. S. Gilbert, J. Greer, and R. A. Pethrick, *Spectrochim. Acta, Part A*, **32,** 859 (1976).
(5) R. Schrooten, F. Borremans, and M. Anteunis, *Spectrochim. Acta, Part A*, **34,** 297 (1978); F. Borremans and M. Anteunis, *Bull. Soc. Chim. Belg.*, **85,** 681 (1976); M. Kaloustian, N. Dennis, S. Mager, S. A. Evans, F. Alcudia, and E. L. Eliel, *J. Am. Chem. Soc.*, **98,** 956 (1976); E. L. Eliel, D. Kandasamy, and R. C. Sechrest, *J. Org. Chem.*, **42,** 1533 (1977). See also F. R. Jensen and C. H. Bushweller, *Adv. Alicycl. Chem.*, **3**, 139 (1971).
(6) C. H. Bushweller, S. Hoogasian, W. G. Anderson, and L. J. Letendre, *J. Chem. Soc., Chem. Commun.*, 152 (1975).
(7) T. Uchida, Y. Kurita, and M. Kubo, *J. Polym. Sci.*, **19,** 365 (1956).

C. Hackett Bushweller,* Michael R. Whalon
Stephen H. Fleischman, Christopher D. Rithner
Department of Chemistry, University of Vermont
Burlington, Vermont 05405

John S. Sturges
Department of Chemistry, State University of New York
Albany, New York 12222

Received June 15, 1979

Nuclear Magnetic Resonance Studies of the Effects of Pressure on the Heme Environmental Structure of Hemoproteins

Sir:

The effect of pressure on the physicochemical properties of hemoproteins has been the subject of considerable investigation in recent years.[1] These studies have been dealt with changes in the functional properties, the thermodynamic properties associated with the binding of ligands, and the denaturation of the protein. Visible and Soret spectra were used to follow the changes of the heme crevice structure of hemoproteins when these molecules were subjected to high hydrostatic pressures.[1-5] We report here the effect of pressure on the ^1H, NMR spectra of metmyoglobin, methemoglobin, and their

0002-7863/79/1501-7074$01.00/0