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Proton Spin-Lattice Relaxation in Meta-Carborane

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ground state of the exciplex (or the CT complex). This will render these vibrations exceptionally good accepting modes for the nonradiative decay process. Deuteration of the methyl group reduces the frequencies of these modes (especially the stretching mode), leading to a decrease in Franck–Condon factors for the radiationless process.

The large deuterium isotope effect observed here suggests that it is the changes in the methyl C–H stretching force constants which is largely responsible for the observed isotope effect on k_{nr}. This finding supports the conclusions of MO calculations[8] that hyperconjugative interaction weakens the methyl C–H bonds. The present result also supports the oft-held view[9] that methyl hyperconjugation is much more important in molecular cations than in their neutral precursors.

[1]For a review on deuterium effect on k_{nr}, see B. R. Henry and W. Siebrand, in *Organic Molecular Photophysics*, edited by J. B. Birks (Wiley–Interscience, London, 1973), Vol. 1, p. 153.
[2]T. E. Martin and A. H. Kalantar, Chem. Phys. Lett. 4, 23 (1969); N. G. Kilmer and J. D. Spangler, J. Chem. Phys. 54, 604 (1971).
[3]R. Li and E. C. Lim (unpublished results).
[4]S. Nagakura, in *Excited States*, edited by E. C. Lim (Academic, New York, 1975), Vol. 2, p. 321.
[5]J. Prochorow, S. Okajima, and E. C. Lim, Chem. Phys. Lett. 66, 590 (1979).
[6]S. Okajima and E. C. Lim, Chem. Phys. Lett. 70, 283 (1980).
[7]I. Deperasinska, J. Prochorow, and A. Sobolewski, Chem. Phys. 32, 257 (1978).
[8]A. Pross, L. Radom, and N. V. Riggs, J. Am. Chem. Soc. 102, 2253 (1980) and references therein.
[9]See, for example, R. Hoffmann, L. Radom, J. A. Pople, P. V. R. Schleyer, W. J. Hehre, and L. Salem, J. Am. Chem. Soc. 94, 6221 (1972).

Proton spin–lattice relaxation in *meta*-carborane

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In a recent work[1] the temperature dependence of the proton spin–lattice relaxation time T_1, was investigated in *ortho*- and *para*-carborane between 170 and 310 K and between 210 and 320 K, respectively. We have completed the present phase of the study by measuring T_1 at 30 MHz in *meta*-carborane between 171 and 303 K. The experimental technique is discussed in Ref. 1 and schematic diagrams of the three isomers of carborane can also be found in Ref. 1.

The experimental results for *meta*-carborane are shown in Fig. 1. There is a first order phase transition at about 276 K. The dashed curve below 220 K ($10^3 T^{-1}$ > 4.5) in Fig. 1, shows a linear least squares fit of the data in this region and yields an activation energy of 25 kJ/mol. The region on the high temperature side of the T_1 minimum in the low temperature phase cannot be fitted to a straight line because the transition occurs before the short correlation time limit in the low temperature phase is reached. We show a dashed line corresponding to an activation energy of 40 kJ/mol in order to compare the results in *meta*-carborane with those of the other two isomers (Table II of Ref. 1).

The details in the vicinity of the phase transition are shown in Fig. 2. Nonexponential relaxation is indicated by vertical dashed lines and is indicative of both phases being present. (This is discussed more fully in the previous work.[1]) Although only the short time T_1 or the long time T_1 was measured in most cases, for three runs both time constants were measured and these are indicated by pairs of data points connected by the verti-

cal dashed lines. The lengths of the other five vertical dashed lines in Fig. 2 have no significance. Taking the transition temperature as the midpoint of the coexistence range, on increasing the temperature, the transition oc-
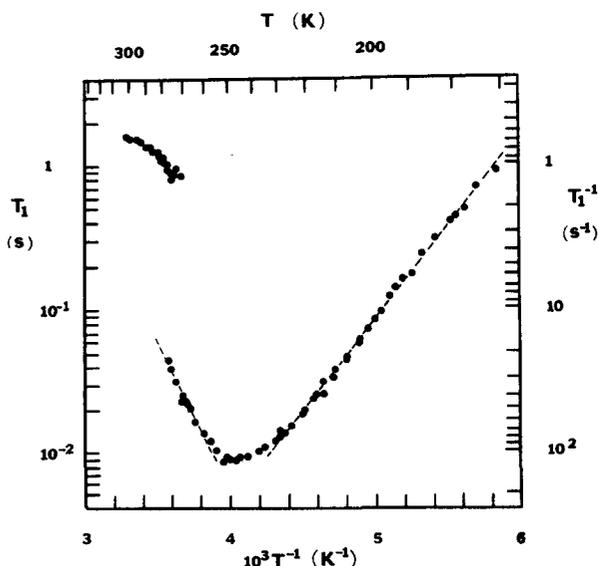

FIG. 1. Spin–lattice relaxation time T_1 vs temperature T in *meta*-carborane. The experimental results are indicated by closed circles and the dashed lines are discussed in the text. The details in the region of the phase transition are shown in Fig. 2.
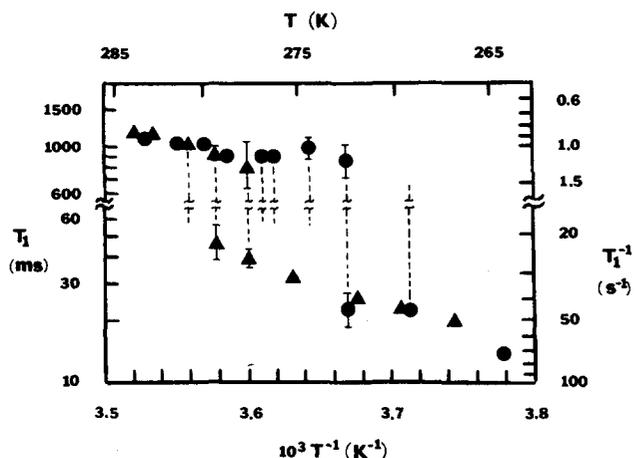
FIG. 2. Spin–lattice relaxation time T_1 vs temperature T in the vicinity of the phase transition in *meta*-carborane. Note that one decade is omitted on the abscissa between the T_1 values in the two phases. The circles and triangles denote decreasing and increasing temperature, respectively. The vertical dashed lines indicate nonexponential relaxation which is discussed further in the text.

FIG. 3. A summary of the temperature dependence of the spin–lattice relaxation times T_1, in the carboranes. The solid line corresponds to *ortho*-carborane, the long dashes correspond to *meta*-carborane and the short dashes correspond to *para*-carborane. The results for the *ortho* and *para* isomers are taken from Fig. 2 of Ref. 1 and the results for the *meta* isomer are taken from Fig. 1 of this work. Note that *ortho*- and *meta*-carborane experience one phase transition whereas *para*-carborane experiences two transitions.

curs at 279.3 ± 2.8 K and on decreasing the temperature it occurs at 272.5 ± 3.9 K. The coexistence ranges are 5.5 ± 2.3 K and 10.9 ± 3.4 K on increasing and decreasing the temperature, respectively, and the hysteresis range is 6.8 ± 5.7 K. The origin of the uncertainties is discussed in the previous work.[1] These temperatures for *meta*-carborane can be compared with those for the *ortho* and *para* isomers (Table I in Ref. 1).

The temperature dependence of T_1 in the three isomers of carborane is summarized in Fig. 3. The *ortho*[1] and *meta* isomers undergo one phase transition in the temperature region studied whereas the *para* isomer[1] undergoes two transitions. The present experiments in *meta*-carborane tend to support the conjectures put forth in the previous work[1] in that the high temperature phase transition in *meta*-carborane occurs at a temperature between that found for the other two isomers and at low temperatures, *meta*-carborane behaves like *ortho*-carborane and not like *para*-carborane, particularly with respect to the lack of a second phase transition. The origin of the difference between the T_1 vs T curves for *ortho*- and *para*-carborane is discussed in detail in the
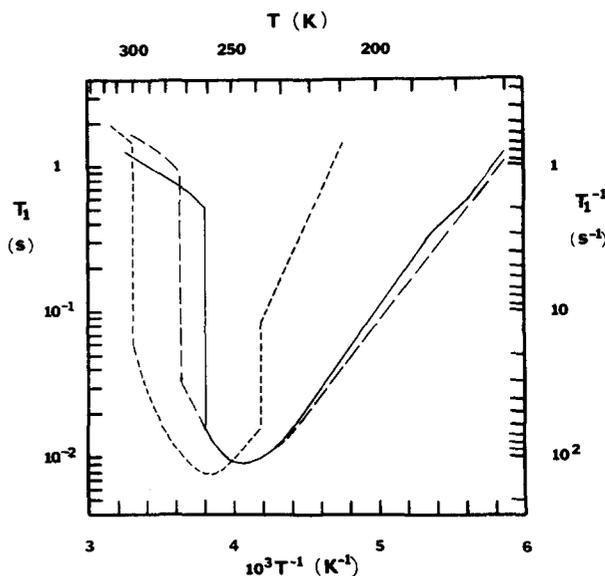
previous work[1] and is based on the fact that the *ortho* (and *meta*) isomers have a relatively large molecular electric dipole moment whereas *para*-carborane has none.

There are important problems which still require investigation in the carborane system and these are discussed in the previous work.[1]

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[1] P. A. Beckmann and A. J. Leffler, J. Chem. Phys. 72, 4600 (1980).

Spin-orbit coupling and Λ-doubling in LiO

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Theoretical calculations of molecular spectroscopic properties have reached a stage where in some instances they challenge experimental determinations. This is

true even in the accurate radio frequency region since parameters are derived by fitting observed transitions using formulas which necessitate assumptions about

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