concentration within the range of concentrations from 0.8 × 10^{-4} to 6 × 10^{-3} *M* (observed on dibenzofuran and dibenzothiophene). The diffusion currents were corrected for the residual current and were found to be reproducible within 5% of their mean value.

Electron Spin Resonance Spectra. These were measured on a modified Microspin X-band spectrometer at room temperature. The radicals were generated within the cavity by electrolysis at mercury pool cathode, the anode and cathode compartments being separated by a Grade 3 fritted glass disk. The solvent and supporting electrolyte were the same as those employed in the polarographic measurements.

Ultraviolet Spectroscopy. The ultraviolet absorption spectra were determined in spectral grade 95% ethanol using a Cary Model 11 spectrophotometer.

Proton Magnetic Resonance Spectroscopy. Configurational Stability of Neohexyl(3,3-dimethylbutyl) Organometallic Compounds[1]

Michal Witanowski and John D. Roberts

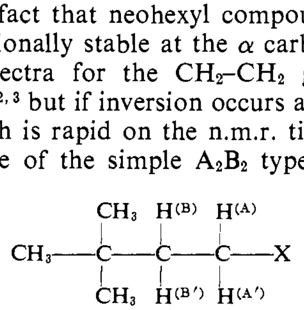
Contribution No. 3251 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California.

Received September 27, 1965

Abstract: The proton resonance spectra of dilute ether solutions of neohexyl(3,3-dimethylbutyl) organometallic compounds have been investigated as a function of temperature as a means of determining their configurational stabilities. Neohexyllithium, dineohexylmagnesium (free from magnesium chloride), and dineohexylzinc appear to undergo the inversion of configuration at the α-methylene groups at various temperatures. The activation energies for inversion are approximately 15, 20, and 26 kcal. for the lithium, magnesium, and zinc compounds, respectively. Inversion appears to be a first-order process for the lithium and magnesium compounds. This fact and the general dependence of the inversion rate on the nature of the metal suggest a dissociation–recombination mechanism (SE1). Trineohexylaluminum and dineohexylmercury were found to be configurationally stable up to 150–160°. The chemical shifts of the CH_2–CH_2 groupings in these organometallic compounds can be correlated with the electronegativity of the metal atoms.

In an extension of previous work[2] on the configurational stability of primary Grignard reagents, we have studied other kinds of organometallic compounds and also carried out a more detailed investigation of dineohexylmagnesium prepared free of magnesium halides.

The *modus operandi* was the same as before, being based on the fact that neohexyl compounds (I) which are configurationally stable at the α carbon show proton n.m.r. spectra for the CH_2–CH_2 groups of the AA′BB′ type,[2,3] but if inversion occurs at the α carbon at a rate which is rapid on the n.m.r. time scale, then the spectra are of the simple A_2B_2 type. In general, the AA′BB′ spectrum presented by these compounds when the configurations are stable may be relatively easily analyzed, a particular advantage is the symmetry of the spectrum, which permits a complete analysis even if the A (or B) part is hidden under the solvent resonances. The procedure used for obtaining rate constants for inversion of configuration from line shapes was the same as before.[2b]



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{H^{(B)}}{\underset{H^{(B')}}{C}}-\overset{H^{(A)}}{\underset{H^{(A')}}{C}}-X$$

I, X = Li, Mg, Zn, Al, and Hg

Results and Discussion

The proton resonance spectra at 60 Mc.p.s. of ether solutions of neohexyllithium (−18°), dineohexylmagnesium (30°), dineohexylzinc (30°), trineohexylaluminum (30°), and dineohexylmercury (30°) show typical AA′BB′ patterns for the methylene resonances (Figures 1–5). For the first four compounds, the β-methylene signals are partly obscured by the methyl peaks of ether, while with dineohexylmercury, the α-methylene signal is partially hidden. Reducing the temperature to −35° does not introduce any observable changes in these spectra.

The analysis of the spectra was carried out in the usual way[4]; the notation for the couplings in I being $K = J_{AA'} + J_{BB'}$, $L = J_{AB} - J_{AB'}$, $M = J_{AA'} - J_{BB'}$, $N = J_{AB} + J_{AB'}$. Six transitions of the AA′ (or BB′) part of the AA′BB′ system are independent of *K*; two of them immediately give *N* and, in combination with their symmetrical counterparts in BB′, the chemical shift. The remaining four, together with their counterparts in BB′, give *L*, *M*, and the chemical shift, thus providing a check on the assignments. The final values of the spectral parameters were chosen on the basis of comparisons with theoretical spectra, plotted by a computer for several values of *K*. The results are summarized in Table I, along with values of the

---

[1] Supported in part by the National Science Foundation and the Office of Naval Research.

[2] (a) G. M. Whitesides, F. Kaplan, and J. D. Roberts, *J. Am. Chem. Soc.*, **85**, 2167 (1963); (b) G. M. Whitesides, M. Witanowski, and J. D. Roberts, *ibid.*, **87**, 2854 (1965).

[3] The spectra closely approximate AA′XX′ when the chemical shift difference is large.

[4] See, for example, K. B. Wiberg and B. J. Nist, "Interpretation of N.M.R. Spectra," W. A. Benjamin, Inc., New York, N. Y., 1962, pp. 309–317.

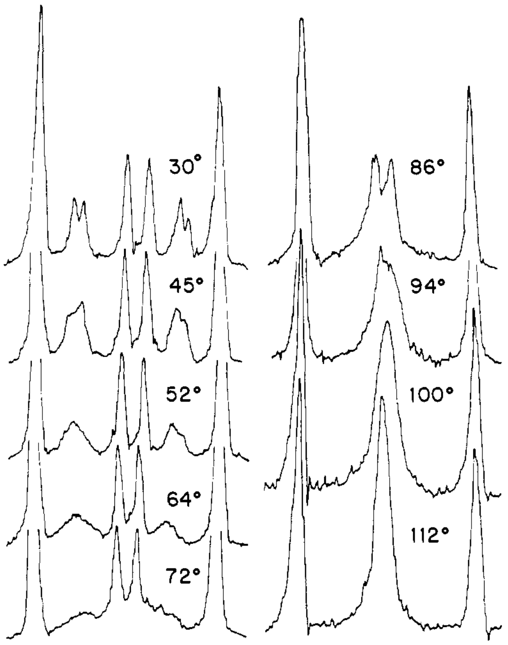


Figure 1. Proton resonance of the α-methylene group of dineohexylmagnesium at 60 Mc.p.s. (5 mole % ether solution).

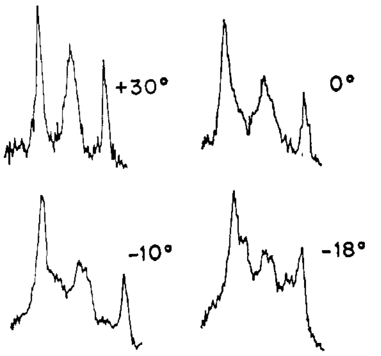


Figure 2. Proton resonance of the α-methylene group of neohexyllithium at 60 Mc.p.s. (5 mole % ether solution).

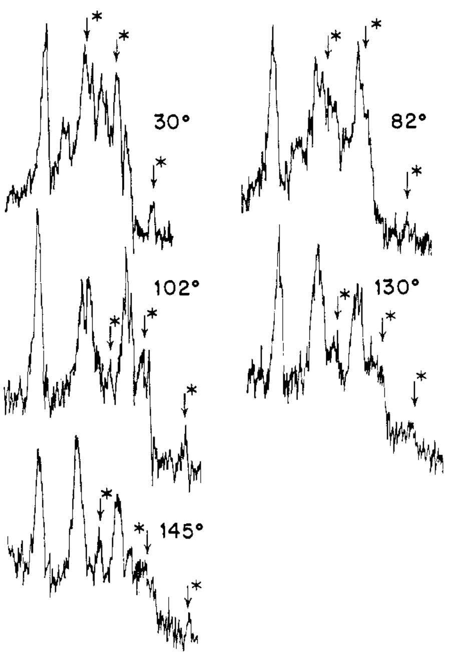


Figure 3. Proton resonance of the α-methylene group of dineohexylzinc at 60 Mc.p.s. (1 mole % ether solution). The peaks marked with asterisks are the ^{13}C satellite peaks of the diethyl ether methyl groups.

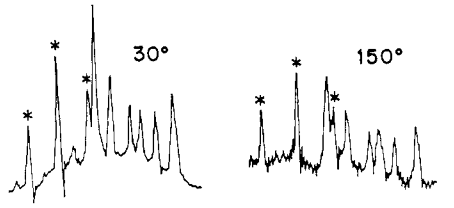


Figure 4. Proton resonance of the α-methylene group of trineohexylaluminum at 60 Mc.p.s. (1 mole % ether solution). The peaks marked with asterisks are the ^{13}C satellite peaks of the diethyl ether methyl groups.

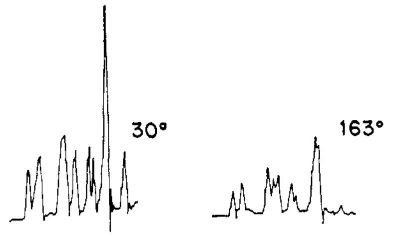


Figure 5. Proton resonance signal of the β-methylene group of dineohexylmercury at 60 Mc.p.s. (15 mole % ether solution).

electronegativities of the metals according to Pauling[5a] and Haissinsky.[5b]

There are some points of interest in the general trends of chemical shifts and coupling constants shown in Table I. The chemical shifts of both methylene groups move essentially linearly upfield with decreasing electronegativity of the metal. This means that the important factor for the chemical shifts is the electron density at the methylene groups and anisotropic effects are small. The vicinal coupling constants between the methylene protons of the system show a pronounced dependence on the nature of the metal, the *gauche* constant (J_{AB}) generally increasing and the *trans* constant ($J_{AB'}$) generally decreasing with increasing electronegativity. The opposite trends in the *gauche* and the *trans* couplings may be in fact solely due to electronegativity effects or might possibly result in whole, or part, from changes in the populations of the various conformations. The importance of differences in conformation seems likely to be small because the largest metal atoms are also the ones which have J_{AB} and $J_{AB'}$ most nearly equal. In any case, the results are of obvious interest to the problem of finding an expression correlating the averaged vicinal coupling constant in substituted ethanes with the electronegativity of substituents.[6]

The geminal coupling constants cannot be calculated very accurately from the spectra except for dineohexylmercury (Table I). However, the values of $M = J_{AA'} - J_{BB'}$ are more reliable (±0.1 c.p.s.) and they are similar (1.1 to 1.4 c.p.s.) in all of the spectra with

---

(5) (a) L. Pauling, *J. Am. Chem. Soc.*, **54**, 3570 (1932); (b) M. Haissinsky, *J. Phys. Radium*, 7, 7 (1946); see also E. G. Rochow, D. T. Hurd, and R. N. Lewis, "The Chemistry of Organometallic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 17.

(6) C. N. Banwell and N. Sheppard, *Discussions Faraday Soc.*, 34 (1962), and references therein.

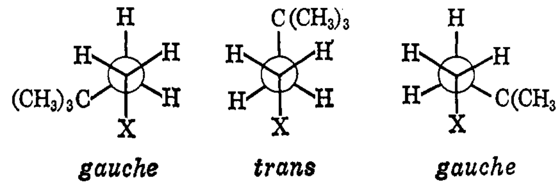
Table I. Proton Resonance Spectra (60 Mc.p.s.) of Neohexylorganometallic Compounds (I)

Compound [R = $(CH_3)_3CCH_2CH_2$]		RLi	R_2Mg	R_2Zn	R_3Al	R_2Hg
Concn. in diethyl ether (mole %)		10–5	6–1	1	1	15–5
Temp., °C.		−18	30	30	30	30
Chemical shifts	$\Delta\nu$ (c.p.s.)[a]	145.6	124.1	80.2	87.0	34.2
	δ_A (p.p.m.)	−1.08	−0.68	+0.15	−0.20	+1.01
	δ_B (p.p.m.)	1.35	1.39	1.47	1.25	1.58
Coupling constants c.p.s.[b]	J_{AB}	3.5	4.0	4.7	3.9	5.1
	$J_{AB'}$	15.5	14.2	13.3	14.2	11.8
	$J_{AA'}$	−12.1	−12.5	−12.4	−13.4	−12.5
	$J_{BB'}$	−13.5	−13.4	−13.6	−13.4	−13.6
Electronegativity of metal		1.0	1.2	1.5	1.5	1.9

[a] The reported values of the chemical shifts are believed to be accurate to ±0.3 c.p.s. [b] The coupling constants are believed to be accurate to ±0.3 c.p.s. for the geminal couplings and those for neohexyllithium; ±0.1 c.p.s. for the remaining coupling constants; and ±0.1 c.p.s. for $M = J_{AA} - J_{BB}$.

the exception of that of trineohexylaluminum where $M = 0$. This is in accord with a steric effect in the aluminum compound because, if repulsions between the three branched groups are large enough to cause the H–C–H angle of one CH_2 group to change by 1° relative to the angle at the other CH_2 group, this could cause a decrease in M by 1 c.p.s.[7]

The values of the vicinal coupling constants indicate that all of the organometallics studied exist predominantly in the *trans* conformation.[2b]



Increasing the temperature of the solutions of neohexyllithium, dineohexylmagnesium, and dineohexylzinc results in a gradual change from the AA'BB' type of spectrum to the A_2B_2 one for the CH_2–CH_2 system of the neohexyl group (Figures 1–3). These changes result from averaging of the vicinal coupling constants and have two distinctive features: first, that the value of N remains constant (within about 0.3 c.p.s.) throughout the whole range of temperature, and second, that the four peaks corresponding to the so-called "antisymmetric quartet" in either half of the spectrum (AA' or BB') coalesce first. That N remains constant and the form of change of the spectra is only consistent with *inversion of the configuration* at the α carbon. Should the averaging of the vicinal coupling constants result from internal rotation, the value of N should decrease significantly since $^3/_2N + {}^1/_2L$ is independent of the population of rotational isomers[8] and L changes from negative values for the *trans* conformation to 0 at fast rotation. It would correspond to the change in N from 19.0 to 14.3 c.p.s. for neohexyllithium, from 18.2 to 14.7 c.p.s. for dineohexylmagnesium, and from 18.0 to 15.1 c.p.s. for dineohexylzinc. Furthermore, the changes in the central part of the multiplet would have occurred in a different way in the case of internal rotation; the central peaks would coalesce first.[2b] Theoretical spectra for neohexyl systems undergoing inversion as a function of τ were given earlier.[2b] Comparison of these with the experimental spectra for the lithium, magnesium, and zinc compounds (Figures 1–3) afford approximate rates of inversion as a function of temperature, and these rates are summarized in Table II. The values are approximate to the degree that the theoretical spectra were calculated for AA'XX' systems, not AA'BB' systems.

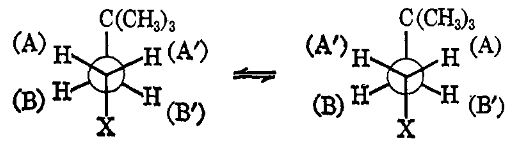


Table II. Inversion Rates of Neohexylorganometallic Compounds

RLi		R_2Mg		R_2Zn	
Temp., °C.	τ, sec.	Temp., °C.	τ, sec.	Temp., °C.	τ, sec.
−18	1.0	45	1	80	0.6
−10	0.3	52	0.5	102	0.06
0	0.1	64	0.4	130	0.006
30	0.01	72	0.1	145	0.002
		86	0.06		
		94	0.016		
		100	0.010		
		112	0.006		

The rate of inversion of dineohexylmagnesium at 112° was studied as a function of concentration in the range 1–6 mole %. The temperature was chosen to be one where the spectrum appears as a triplet with a broadened center line and the relative heights of the peaks are sensitive to even small changes in the rate of inversion. No change in inversion rate was observed for dineohexylmagnesium in the range of concentrations used. Similarly, a twofold dilution of neohexyllithium solution at 30° gave no observable differences in relative peak heights. The results suggest that inversion with these compounds is *unimolecular*, and of the SE1 type.[2b] The alternative is that the organometallic compounds are essentially completely associated to dimers, trimers,

---

(7) H. S. Gutowsky, M. Karplus, and D. M. Grant, *J. Chem. Phys.*, 31, 1278 (1959).

(8) R. J. Abraham and K. G. R. Pachler, *Mol. Phys.*, 7, 165 (1964).

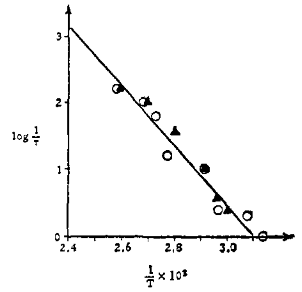


Figure 6. Arrhenius plot for inversion in dineohexylmagnesium ($Mg[CH_2CH_2C(CH_3)_3]_2$). O represents data from the present research using dineohexylmagnesium prepared from the mercury compound, while ▲ represents data from dineohexylmagnesium made by dioxane treatment of the Grignard reagent[2b]; ΔE = 20 ± 2 kcal./mole; $A = 10^{13\pm1.5}$ sec.$^{-1}$.

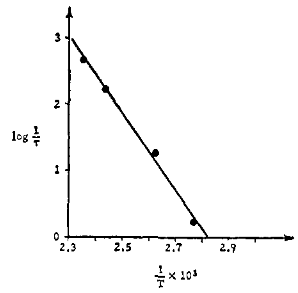


Figure 8. Arrhenius plot for inversion in dineohexylzinc ($Zn[CH_2CH_2C(CH_3)_3]_2$) ΔE = 26 ± 2 kcal./mole, $A = 10^{16\pm1.5}$ sec.$^{-1}$.

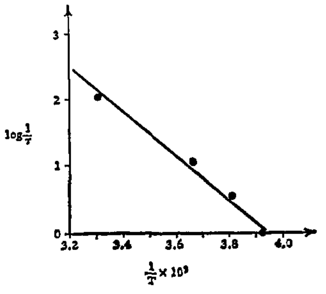


Figure 7. Arrhenius plot for inversion in neohexyllithium ($LiCH_2CH_2C(CH_3)_3$); ΔE = 15 ± 2 kcal./mole, $A = 10^{13\pm1.5}$ sec.$^{-1}$.

etc., with no appreciable change in composition over the concentration range studied. Inversion could then involve unimolecular reactions of the association complexes. Such association is, of course, well established for lithium compounds.[9] The situation with dialkylmagnesiums is less clear, although diethylmagnesium is reported to be monomeric in dioxane.[10]

The AA′BB′ spectra of trineohexylaluminum (Figure 4) and dineohexylmercury (Figure 5) in ether show only small changes in their spectra over the investigated ranges of temperature (30–150 and 30–163°, respectively). These substances are therefore assumed to be configurationally stable in ether.

The inversion rates for the lithium, magnesium, and zinc compounds (Table II) gave reasonably linear Arrhenius plots (Figures 6–8), from which the values of activation energy (E_a) may be obtained with accuracy of ±2 kcal./mole (Figures 6–8). Dineohexylmagnesium from dineohexylmercury was found to give essentially identical results as dineohexylmagnesium obtained by dioxane precipitation from the corresponding Grignard reagent[2b] (see Figure 6). Clearly, there is no significant effect of trace amounts of magnesium halides or dineohexylmercury on the inversion rates.

The activation energy for inversion generally increases with increasing electronegativity of the metal in the carbon–metal bond except that zinc and aluminum, which have the same electronegativity in the Pauling–Haissinsky scale,[5] differ appreciably in stability of configuration of their neohexyl derivatives. What is not clear here is whether the zinc compound is abnormally reactive or the aluminum compound abnormally unreactive. Steric hindrance to solvation in the bulky aluminum compound is a possible complicating factor. Indication of some kind of abnormality in trineohexylaluminum is provided by the fact that the n.m.r. spectral parameters for its CH_2 groups do not follow the rather smooth trends of the other organometallics as a function of electronegativity (see Table I).

Experimental Section

Dineohexylmercury was prepared by boiling an ethereal solution of neohexylmagnesium chloride from 10 g. of neohexyl chloride and 2.3 g. of Grignard-grade magnesium turnings in 100 ml. of anhydrous ether in a dry nitrogen atmosphere for 16 hr. in a micro-Soxhlet apparatus with 12 g. of mercuric chloride in the thimble. The mixture was then poured into an equal volume of 5% aqueous ammonium chloride solution and shaken in a separatory funnel for 1 hr. The aqueous layer was extracted with ether, the combined extracts were dried overnight with anhydrous sodium sulfate, the ether was removed by distillation, and the residue was distilled in a microapparatus under vacuum-reduced pressure. The principal fraction had a boiling point of 98° (0.6 mm.) and amounted to 11 g. The product was an almost colorless oil and gave a negative chloride test and an AA′BB′ n.m.r. spectrum plus a single peak, corresponding to the methyl groups.

Dineohexylmagnesium was prepared in a 5-mm. glass tube in a dry nitrogen atmosphere inside of a glove bag. In the tube was placed about 5 cm. of Grignard-grade magnesium turnings (washed with dry ether and dried at 130° for 2 hr.) and sufficient dineohexylmercury to cover the turnings. The tube was degassed, sealed under reduced pressure, and heated in an oil bath at 150° for 3 days. The product was a white solid, deposited on the excess of magnesium, neither melting nor decomposing to at least 240°. The tube was opened under dry nitrogen in a glove bag, the contents was extracted with small amount of anhydrous ether, and the extract was filtered through a small Schott funnel (a Teflon plug was used to force the solution gently through the filter) and collected in an n.m.r. tube filled with dry nitrogen. The n.m.r. tube was cooled in liquid nitrogen, evacuated, and sealed.

Trineohexylaluminum was prepared by a similar procedure employing aluminum powder which had been dried in a small tube under reduced pressure at 200° for 15 min. The transmetalation was carried out at 180° for 4 days. The product was a gelatinous solid, melting at about 60° which appeared from its n.m.r. spectrum to be free of dineohexylmercury.

Neohexyllithium was obtained similarly, using lithium cut into small pieces under dry nitrogen. The sealed tube was warmed to

---

(9) G. Wittig, F. J. Meyer, and G. Lange, *Ann.*, **57**, 167 (1951); T. V. Talalaeva, A. N. Radinov, and K. A. Koheshkov, *Dokl. Akad. Nauk SSSR*, **154**, 174 (1964); T. L. Brown, D. W. Kickenhoof, and D. A. Bafus, *J. Am. Chem. Soc.*, **84**, 1371 (1962); also L. Seitz and T. L. Brown, paper in press. We are indebted to Professor T. L. Brown for sending us a copy of the latter paper in advance of publication.

(10) W. Strohmeier, K. Hümpfner, K. Miltenberger, and F. Seifert, *Z. Elektrochem.*, **63**, 537 (1959).

50° for 20 min., then left at room temperature for 3 days. The product was a white powder which decomposed without melting at temperatures above 100°.

Dineohexylzinc was prepared in the same way from dineohexylmercury and zinc turnings at 150° for 3 days.

Proton resonance spectra were taken at 60 Mc.p.s. using Varian A-60 and HR-60 spectrometers, using low radiofrequency power (about 0.02 mgauss) in combination with a 0.5-c.p.s./sec. sweep rate and a 4–5-c.p.s. filter band width. The spectra were calibrated by the side-band method as well as with the aid of the ^{13}C satellites of the methyl resonance of the diethyl ether used as solvent. The temperature of the sample in the radiofrequency probe was measured to an estimated accuracy of ±2° with a copper–constantan thermocouple.

Nuclear Magnetic Resonance Spectroscopy. Analysis of the Proton Spectrum of 7,7-Dicyanonorcaradiene[1]

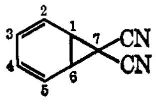
Camille Ganter and John D. Roberts

Contribution No. 3307 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California.

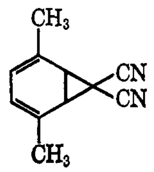
Received September 27, 1965

Abstract: Complete analysis of the six-spin proton high-resolution n.m.r. spectrum of 7,7-dicyanonorcaradiene (I) at room temperature has been achieved at 60 and 100 Mc.p.s. Only one set of parameters with all of the couplings having a positive sign gave good agreement between observed and calculated resonance lines at both frequencies.

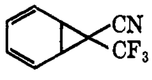
The existence of simple norcaradiene derivatives has recently been demonstrated by Ciganek.[2] The adducts of dicyanocarbene to benzene and *p*-xylene exist in the norcaradiene form. Earlier efforts to obtain stable bicyclo[4.1.0]heptadiene derivatives were successful only when C-1 and C-6 were bridged with a three-atom bridge[3-5] or when one or both double bonds were incorporated into an aromatic system.[6-11] In the present work, the proton n.m.r. spectrum of 7,7-dicyanonorcaradiene (I)[2] was analyzed to find out more about the structure of this unusual molecule. The possibility that I, in solution, is in equilibrium with a small amount of its valence tautomer, 7,7-dicyanocycloheptatriene, cannot be excluded.[2] However, X-ray diffraction of crystalline 2,5-dimethyl-7,7-dicyanonorcaradiene (II) indicates the norcaradiene structure.[12]



I



II



III

It is interesting to note that the adduct of cyanotrifluoromethylcarbene to benzene (III) is, at room temperature, a very rapidly equilibrating mixture of the cycloheptatriene and norcaradiene derivatives.[13]

Results

A. AA′BB′ Spectrum. The proton spectrum of 7,7-dicyanonorcaradiene (I) is of the AA′BB′XX′ type. The large chemical-shift difference between the vinyl protons (AA′BB′) and the protons on the cyclopropane ring (XX′) permitted simplification of the spectrum by double irradiation of the 1,6 protons. The decoupled AA′BB′ spectrum of the vinyl protons in deuteriochloroform was recorded at 35° on a Varian Model HA-100 spectrometer[14] and is shown in Figure 1. This spectrum shows a marked similarity to that of naphthalene,[15] and it turned out that many of the lines could be assigned on the same basis, as shown in Figure 1. The chemical-shift difference and the four different spin-coupling constants were calculated from the explicit expressions for the transition energies, using the relations $K = J_{AA} + J_{BB'}$, $L = J_{AB} - J_{AB'}$, $M = J_{AA'} - J_{BB'}$, and $N = J_{AB} + J_{AB'}$ in accordance to Pople, Schneider, and Bernstein.[16] From the positions of lines 1, 3, 9, and 11, the following were obtained: $N = E_1 - E_3 = 10.01$ c.p.s., $(M^2 + L^2)^{1/2} = E_9 - E_{11} = 9.81$ c.p.s., $[(\nu_0\delta)^2 + N^2]^{1/2} = E_1 + E_3 = 26.63$ c.p.s., and $[(\nu_0\delta + M)^2 + L^2]^{1/2} = E_9 + E_{11} = 21.27$ c.p.s. The resulting "observed" chemical-shift and spin-coupling constants are listed in Table I.

---

(1) Supported in part by the National Science Foundation.

(2) E. Ciganek, *J. Am. Chem. Soc.*, **87**, 652 (1965). We wish to thank Dr. E. Ciganek for the sample of 7,7-dicyanonorcaradiene used in this work.

(3) J. Schreiber, W. Leimgruber, M. Pesaro, P. Schudel, T. Threlfall, and A. Eschenmoser, *Helv. Chim. Acta*, **44**, 540 (1961).

(4) R. Darms, T. Threlfall, M. Pesaro, and A. Eschenmoser, *ibid.*, **46**, 2893 (1963).

(5) E. Vogel, W. Wiedemann, H. Kiefer, and W. F. Harrison, *Tetrahedron Letters*, No. **11**, 673 (1963).

(6) W. von E. Doering and M. J. Goldstein, *Tetrahedron*, **5**, 53 (1959).

(7) M. J. S. Dewar and C. R. Ganellin, *J. Chem. Soc.*, 3139 (1959).

(8) R. Huisgen and G. Juppe, *Chem. Ber.*, **94**, 2332 (1961).

(9) E. Vogel, D. Wendisch, and W. R. Roth, *Angew. Chem.*, **76**, 432 (1964).

(10) E. Müller, H. Kessler, and H. Suhr, *Tetrahedron Letters*, No. **8**, 423 (1965).

(11) G. E. Hall and J. P. Ward, *ibid.*, No. **8**, 437 (1965).

(12) C. J. Fritchie, private communication.

(13) E. Ciganek, *J. Am. Chem. Soc.*, **87**, 1149 (1965).

(14) We thank Drs. Norman S. Bhacca and Leroy Johnson, Varian Associates, Palo Alto, Calif., for recording these spectra.

(15) J. A. Pople, W. G. Schneider, and H. J. Bernstein, *Can. J. Chem.*, **35**, 1060 (1957).

(16) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp. 138–149.