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.

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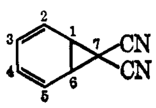
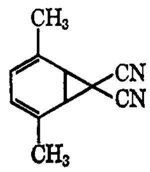
Abstract: Complete analysis of the six-spin proton high-resolution n.m.r. spectrum of 7,7-dicyanonorcaradiene (I) at room temperature has been achieved at 60 and 100 Mc.p.s. Only one set of parameters with all of the couplings having a positive sign gave good agreement between observed and calculated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

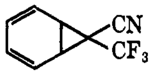
The existence of simple norcaradiene derivatives has recently been demonstrated by Ciganek.[2] The adducts of dicyanocarbene to benzene and *p*-xylene exist in the norcaradiene form. Earlier efforts to obtain stable bicyclo[4.1.0]heptadiene derivatives were successful only when C-1 and C-6 were bridged 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] 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]



I



II



III

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.

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[1] Supported in part by the National Science Foundation.

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[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.

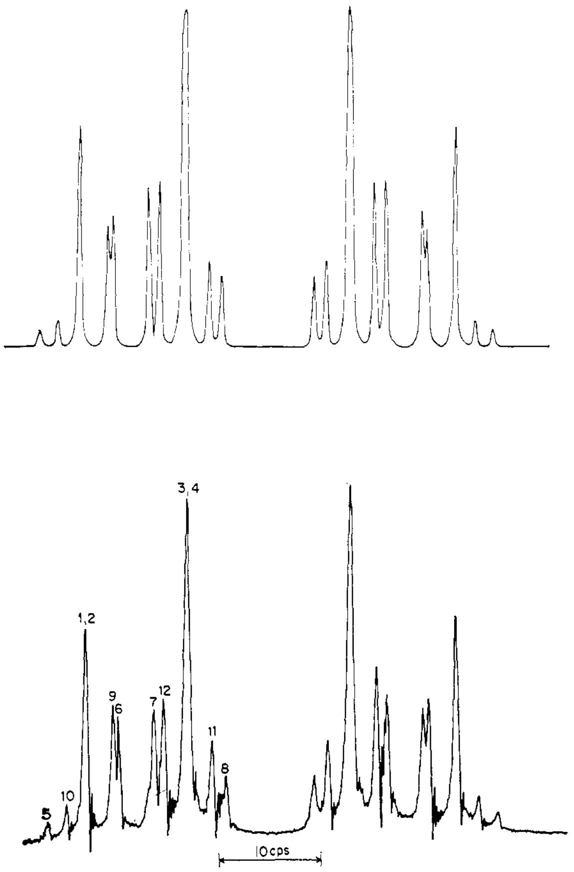

Figure 1. The observed (below) and calculated (above) 100-Mc.p.s. decoupled AA'BB' spectra of the vinyl protons of 7,7-dicyanonorcaradiene.

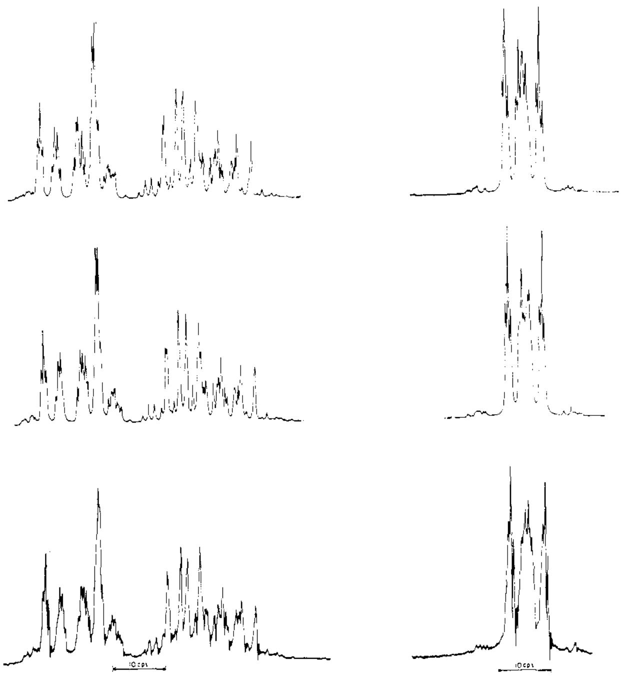

Figure 2. The observed (bottom), calculated set 1 (middle), and calculated set 2 (top) 100-Mc.p.s. spectra of 7,7-dicyanonorcaradiene.

The four-spin system was also analyzed using the computer program of Swalen and Reilly.[17] The parameters for the only assignment which was found to give good agreement between the observed and the calculated spectrum (line positions and intensities) are also listed in Table I as "calculated" parameters and the corresponding calculated spectrum is shown in Figure 1. The average deviations between the observed and calculated line positions are about 0.1 c.p.s. The errors in the coupling constants are also about ±0.1 c.p.s. Analysis of the decoupled AA'BB' spectrum alone for the vinyl protons does not reveal whether the A or B protons are upfield in I. The assignment of the upfield protons as those which are adjacent to the ones on the cyclopropane ring (X and X') is based on the undecoupled spectrum. The high-field protons are much more strongly coupled to the protons on the cyclopropane ring and are therefore the 2,5 protons.

Table I. Spectral Parameters (in c.p.s.) for 7,7-Dicyanonorcaradiene at 100 Mc.p.s.

	AA'BB'[a]		AA'BB'XX' calcd.	
	Obsd.	Calcd.	Set 1	Set 2
δ_{12}	...	...	281.16	281.25
δ_{13}	...	...	305.81	305.96
δ_{23}	24.68	24.64	24.65	24.71
J_{12}, J_{56}	...	...	+5.87	+5.80
J_{13}, J_{46}	...	...	+0.48	−0.53
J_{14}, J_{36}	...	...	+0.25	−0.75
J_{15}, J_{26}	...	...	+0.74	+0.86
J_{16}	...	...	+8.38	+8.45
J_{23}, J_{45}	9.19	+9.38	+9.42	+9.34
J_{24}, J_{35}	0.82	+0.84	+0.77	+0.78
J_{25}[b]	$J_{34} - 5.12$	+1.12	+1.15	+1.16
J_{34}[b]	$J_{25} + 5.12$	+6.22	+6.28	+6.18

[a] Decoupled spectrum. [b] $M = J_{AA'} - J_{BB'} = J_{34} - J_{25} = 5.12$ c.p.s.

B. AA'BB'XX' Spectrum. The six-spin proton spectrum of 7,7-dicyanonorcaradiene (I) in deuteriochloroform at 35° was obtained at 100 Mc.p.s. (Figure 2) using a Varian Model HA-100 spectrometer[14] and at 60 Mc.p.s. (Figure 3) using a Varian Model A-60 spectrometer. If we disregard the small couplings J_{13} and J_{14}, the couplings between the 1,6 and 2,5 protons can be considered to be first order. The separation between the two outside triplets in the XX' part, centered on the frequency ν_x, is then 6.5 c.p.s. which corresponds to the sum of $J_{12} + J_{15}$.[16]

The Wiberg[18] and magnetic equivalence factoring[19] programs were used to find approximate parameters for the 100-Mc.p.s. spectrum and the six-spin system was subsequently analyzed according to the method of Swalen and Reilly.[17]

Two sets of parameters, differing only in J_{13} and J_{14}, were found for the 100-Mc.p.s. spectrum and are shown in Table I. The corresponding observed and calculated spectra are shown in Figure 2. The average deviations between the observed and calculated line positions are about 0.1 c.p.s. The errors in the coupling constants are also about ±0.1 c.p.s. These two sets of parameters calculated for the 100-Mc.p.s. spec-

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(17) J. D. Swalen and C. A. Reilly, *J. Chem. Phys.*, 37, 21 (1962).

(18) K. B. Wiberg and B. J. Nist, "The Interpretation of NMR Spectra," W. A. Benjamin, Inc., New York, N. Y., 1962.

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Table II. Chemical Shifts (in c.p.s.) for 60-Mc.p.s. Spectrum[a]

	Set 1	Set 2
δ_{12}	168.70	168.75
δ_{13}	183.49	183.58
δ_{23}	14.79	14.83

[a] Calculated from the calculated 100-Mc.p.s. spectra.

trum when applied to the 60-Mc.p.s. spectrum correspond to the chemical shifts listed in Table II.

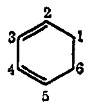
Only the first set with all of the couplings having a positive sign gave good agreement between observed and calculated resonance lines at both frequencies. The corresponding observed and calculated spectra at 60 Mc.p.s. are shown in Figure 3. Further support for the coupling J_{13} having a positive sign will be presented in the Discussion.

Discussion

The couplings between the vinyl protons of I show great similarity to those of naphthalene,[15] phenanthrene,[20] and *ortho*-disubstituted benzene derivatives.[21] They are all positive in sign and their magnitudes are very similar. Similar geometries and coupling mechanisms are probably responsible.

Several mechanisms have been proposed for long-range couplings. Manatt and Elleman[22] recently have analyzed the spectra of the vinyl protons of cyclopentadiene (IV) and 1,3-cyclohexadiene (V). Comparison of our results with theirs (see Table III) shows substantial agreement for I and V. In all cases the couplings are found to be positive. Manatt and Elleman[22] discuss the relative importance of the contributions to long-range proton-proton couplings through the σ-bond framework, through the π electrons and through space in IV and V. The usual σ contribution for a four-bond coupling is known to be smaller than 0.3 c.p.s.[22] and couplings transmitted through π electrons, according to Karplus,[23] should have a negative sign if the two protons are separated by an even number of bonds and a positive sign if separated by an odd number of bonds. Manatt and Elleman conclude that there is a large positive contribution to the coupling J_{24} from a mechanism which is significant when the angular disposition of the C–H bonds is such that lines through these bonds will nearly cross somewhere behind the carbon atoms to give an angle in the range of 90–180°. This mechanism is similar to that responsible for the large four-bond couplings observed in some bridged-ring systems.[24]

IV



V

A similar cross-ring, through-space mechanism may be operative in the five-bond coupling J_{25}, the magnitude being dependent on the angular disposition between the C–H bonds and the intracarbon distance. All these arguments appear to apply also to I.[25]

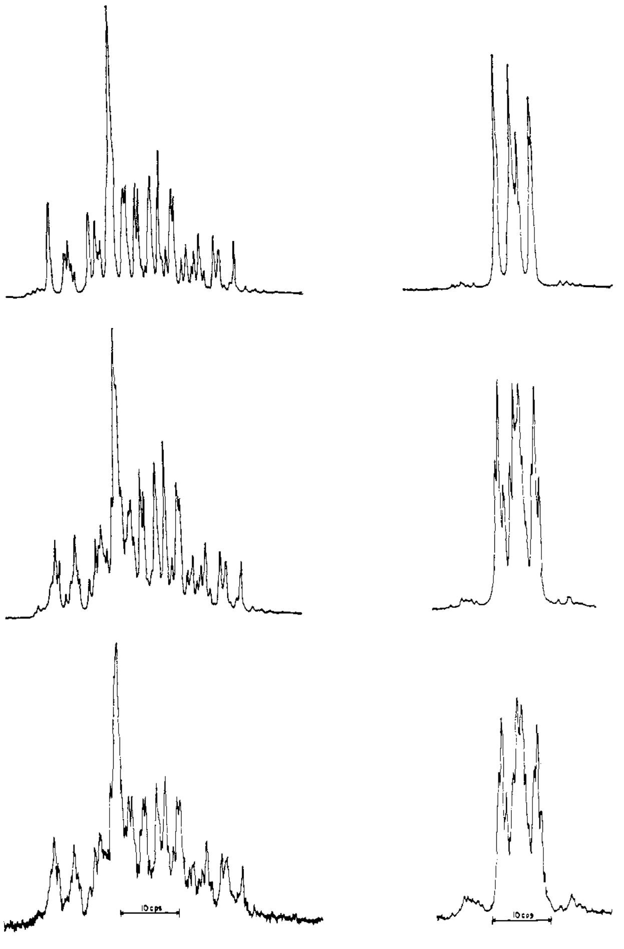
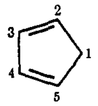
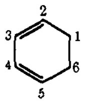
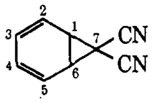


Figure 3. The observed (bottom), calculated set 1 (middle), and calculated set 2 (top) 60-Mc.p.s. spectra of 7,7-dicyanonorcaradiene.

Table III. Comparison of Parameters in Cyclopentadiene, 1,3-Cyclohexadiene, and 7,7-Dicyanonorcaradiene[a]

	δ_{23}[b]	J_{23}[b]	J_{24}[b]	J_{25}[b]	J_{34}[b]
	8.08[c]	+5.06	+1.09	+1.94	+1.94
	6.39[c]	+9.42	+1.06	+0.91	+5.14
	24.64[d]	+9.38	+0.84	+1.12	+6.22

[a] Parameters of decoupled spectra. [b] All quantities are expressed in units of c.p.s. [c] 60 Mc.p.s. [d] 100 Mc.p.s.

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(20) P. M. G. Bavin, K. D. Bartle, and J. A. S. Smith, *Tetrahedron*, 21, 1087 (1965).

(21) D. M. Grant, R. C. Hirst, and H. S. Gutowsky, *J. Chem. Phys.*, 38, 470 (1963).

(22) L. S. Manatt and D. D. Elleman, to be published. We thank Drs. Manatt and Elleman for the permission to use part of their results prior to publication.

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(24) For discussion see D. D. Elleman, S. L. Manatt, and C. D. Pearce, *ibid.*, 42, 650 (1965).

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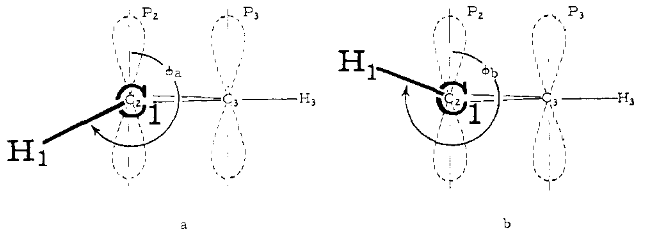
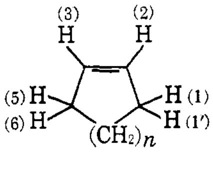


Figure 4. Possible conformations for 7,7-dicyanonorcaradiene looking down the C-1-C-2 bond.

The vicinal coupling between the two protons on the cyclopropane ring is J_{16}. Vicinal proton–proton couplings are known to be positive[26] and the magnitudes for *cis* couplings are 8–11 c.p.s.[27] The calculated value for J_{16} (+8.38 or +8.45 c.p.s.) is in good agreement with the expected sign and magnitude.

Data for cycloalkenes[28–30] indicate that J_{12} will most probably be positive. Smith and Kriloff[29] presented evidences for variation of J_{12} with ring size and for a possible correlation of J_{12} with dihedral angles for cycloalkenes. For cyclohexene (VI, n = 2), they calculated the angles ϕ_{12} = 43° and $\phi_{1'2}$ = 77° for the observed J_{12} = 3.1 c.p.s. which is an averaged coupling for ϕ_{12} and $\phi_{1'2}$. Laszlo and Schleyer[30] reported J_{12} = 3.6 c.p.s. A Dreiding model of I indicates the angle ϕ_{12} to be about 20–30°. The relationship based on the Karplus equations[31] used by Smith and Kriloff,[29] suggests a coupling J_{12} of about +9 c.p.s. as compared to the observed J_{12} of +5.87 or +5.80 c.p.s. The agreement is not very good, but then this is hardly a compound for which the Karplus equations would be expected to apply rigorously.



VI

As mentioned earlier the sum of the couplings J_{12} and J_{15} is about 6.5 c.p.s. Therefore J_{15} has to be about +0.7 c.p.s. which is found in the two calculated sets (+0.74 or +0.86 c.p.s.). Several other values for J_{15} were tried but none gave satisfactory agreement with the observed spectrum.

The only two couplings that differ substantially in the two calculated sets are J_{13} and J_{14}. In set 1 they have both a positive sign and in set 2 both a negative sign. J_{13} is an allylic coupling (H—C=C—C—H). Such couplings are very often negative in sign, and the effect is transmitted mainly through the π-electron system.[32] However, several recent studies of allylic couplings in substituted norbornenes[33,34] and norbornadienes[35] show significant positive coupling constants across four bonds. Barfield[36] has a theoretical treatment of long-range proton spin–spin coupling across four bonds in saturated and unsaturated hydrocarbons. The "indirect" ("through-the-bond") contributions to the allylic coupling constants were determined as a function of the dihedral angle, ϕ, of the C-1-H-1 bond for 30° intervals and plotted. The most significant features of these plots are the positive maxima at ϕ = 90 and 270°. The dihedral angle ϕ is measured from a plane perpendicular to the C-1-C-2 axis which intersects the axis of the $2p_x$ orbital, P_2. Figure 4 represents the situation in I.[37] The two conformations shown represent the situations at carbon atoms C-1 to C-3 with the cyclopropane ring either above or below the plane of the C-2 to C-5 bonds, and also the environment at C-1 to C-3 and C-4 to C-6 simultaneously for one conformation of I. The estimated dihedral angles from Dreiding models for I are ϕ_a = 240–250° and ϕ_b = 290–300°, which correspond to a calculated "indirect" contribution for J_{13} of about +0.2 to +0.7 c.p.s., in reasonable agreement with the positive coupling J_{13} = +0.48 c.p.s. of set 1. This, combined with the fact that only set 1, with all of the couplings having a positive sign, gives good agreement between observed and calculated resonance lines at two different frequencies, 100 and 60 Mc.p.s., indicates that the couplings in 7,7-dicyanonorcaradiene (I) are most probably all positive in sign.

The large chemical shift between the 2,3 protons, compared to the corresponding protons in cyclohexadiene (V), is probably mainly due to the contribution of magnetic anisotropy of the cyano group above the six-membered ring.

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(30) P. Laszlo and P. von R. Schleyer, *ibid.*, **85**, 2017 (1963).

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(37) For convenience the same symbols are used here as by Barfield.[36]