Nuclear Magnetic Resonance Spectroscopy. Thermodynamics and Spectral Analysis of 7-Phenyl-7-carbomethoxynorcaradiene Valence Tautomerisms[1]

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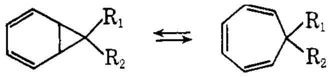
Abstract: The equilibria of 7-phenyl-, 7-(*p*-nitrophenyl)-, and 7-(*p*-methoxyphenyl)-7-carbomethoxynorcaradiene with their valence tautomers, the corresponding 1,3,5-cycloheptatrienes, have been studied by means of the 220-MHz pmr spectra at a series of temperatures. Although only time-averaged spectra of the rapidly equilibrating mixtures have been accessible, the enthalpy and entropy of the conversion of these three norcaradienes to the corresponding cycloheptatriene have been determined and found to be 5.4 ± 0.5 kcal mol^{-1} and 16.8 ± 2.0 cal mol^{-1} deg^{-1}, 3.5 ± 0.2 kcal mol^{-1} and 11.0 ± 0.8 cal mol^{-1} deg^{-1}, and 2.3 ± 0.3 kcal mol^{-1} and 7.4 ± 1.0 cal mol^{-1} deg^{-1}, respectively. LAOCN3 analyses at two temperatures of the norcaradiene–cycloheptatriene portion of the pmr spectra of the three equilibrium mixtures have made possible the determination of approximate parameters for the pmr absorptions of each of the six individual compounds.

The valence tautomerism of the norcaradiene–1,3,5-cycloheptatriene system has been deciphered only since the advent of nuclear magnetic resonance.[3] Examples of 7-substituted systems have been found where the norcaradiene predominates, where the cycloheptatriene predominates, and where there is a mixture with rapid equilibrium between the two.[4,5] Studies of the kinetics of such equilibria have recently been reported.[4,5] We now report a determination of the electrical effects of substituents on the thermodynamics of three such equilibria, together with proton magnetic resonance (pmr) spectral parameters of the equilibrating isomers.

In the simple norcaradiene–cycloheptatriene derivatives, substituents at the 7 position have a major effect on the relative stability of the valence tautomers:[4,5] the unsubstituted compound is cycloheptatriene (**2a**), the 7-cyano derivative is a cycloheptatriene (**2b**),[6] the 7,7-dicyano derivative is a norcaradiene (**1c**), the 7,7-bistrifluoromethyl derivative is a cycloheptatriene (**2d**), while the 7,7-dicarbomethoxy and 7-trifluoro-7-cyano derivatives are rapidly equilibrating mixtures of the two (**1e** ⇄ **2e**). We find that the 7-phenyl-, 7-(*p*-nitrophenyl)-, and 7-(*p*-methoxyphenyl)-7-carbomethoxy derivatives also form rapidly equilibrating mixtures (**1f** ⇄ **2f**, **1g** ⇄ **2g**, **1h** ⇄ **2h**).[7]

The 60-MHz spectrum (carbon tetrachloride, ambient temperature) of the *p*-nitrophenyl product is in agreement with the assigned structure: singlet at δ 3.58 (3 H, $-CH_3$), quartet at 4.23 (2 H, H-1 and -6), quartet at 5.90 (2 H, H-3 and -4), complex multiplet at 6.22 (2 H, H-2 and -5), and two doublets with further splitting at δ 7.19 and 7.91, 2 H each (aromatic). The 220-MHz spectra for all three of the products were also in agreement (see below). The assignments of the norcaradiene–cycloheptatriene absorptions were confirmed by double resonance: decoupling of the δ 4.23 band simplified the δ 6.22 complex multiplet to the mirror image of the quartet at δ 5.90, while decoupling of the δ 6.22 band reduced the δ 4.23 quartet to a weakly split singlet. The occurrence of a single band for the absorption of the 1,6 protons at a position intermediate between those reported for norcaradienes and cycloheptatrienes indicates a rapid equilibrium between the two.



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a, $R_1 = H$; $R_2 = H$
b, $R_1 = H$; $R_2 = CN$
c, $R_1 = CN$; $R_2 = CN$
d, $R_1 = CF_3$; $R_2 = CF_3$
e, $R_1 = CF_3(COOCH_3)$; $R_2 = CN(COOCH_3)$
f, $R_1 = C_6H_5$; $R_2 = COOCH_3$
g, $R_1 = p\text{-}C_6H_4NO_2$; $R_2 = COOCH_3$
h, $R_1 = p\text{-}C_6H_4OCH_3$; $R_2 = COOCH_3$

Proton nmr spectra of each of the three equilibrium mixtures in deuteriochloroform solution were recorded at five or six temperatures in the range −57 to +133° (Table I). The chemical shift of the 1,6 protons is strongly temperature dependent, best accounted for by a change in the relative proportion of protons in the cyclopropane positions of the norcaradiene to those in the vinylic positions of the cyclotriene. The shift of the 3,4 protons is less markedly temperature dependent, while the 2,5 proton shift is nearly insensitive to temperature. The clear absorption patterns obtained at −9° and above show that equilibrium between the norcaradiene and cycloheptatriene valence tautomers must be rapidly established on the nmr time scale at those temperatures. At −57° each system gave a smooth band without fine structure for the 1,6 protons; the 2,5 proton band lost some of its fine structure, while the 3,4 proton band was only slightly affected. These changes indicate a slowing of the interchange of the isomers at that temperature.

The observed, time-averaged chemical shift of the 1,6 protons of the equilibrium mixtures was used to

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[1] Supported by the National Science Foundation.

[2] On leave from Mount Holyoke College.

[3] G. Maier, *Angew. Chem., Int. Ed. Engl.*, **6**, 402 (1967).

[4] M. Görlitz and H. Günther, *Tetrahedron*, **25**, 4467 (1969).

[5] H. J. Reich, E. Ciganek, and J. D. Roberts, *J. Amer. Chem. Soc.*, **92**, 5166 (1970), and references cited therein.

[6] C. H. Bushweller, M. Sharpe, and S. J. Weininger, *Tetrahedron Lett.*, 453 (1970).

[7] E. Ciganek, *J. Amer. Chem. Soc.*, **93**, 2207 (1971). We are indebted to Dr. Ciganek for samples of these compounds.

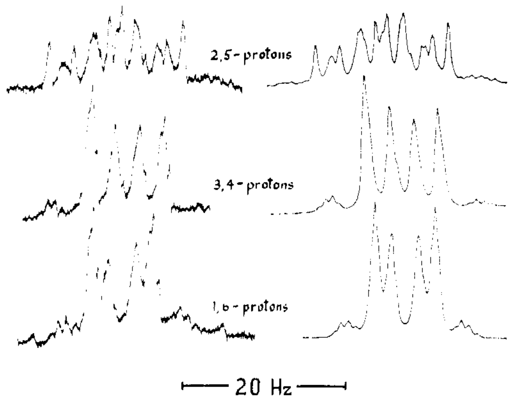

Figure 1. Experimental and calculated spectra, 7-(*p*-methoxyphenyl)-7-carbomethoxynorcaradiene-1,3,5-cycloheptatriene equilibrium mixture, $CDCl_3$ solution, 33°, 220 MHz, 100-Hz sweep width.

calculate the chemical shifts of these protons of the individual isomers and the thermodynamic parameters for each system, essentially by the method used previously in the study of the conformational properties of cyclobutanes.[8] The pertinent equations are

$$\delta = \delta_a + p(\delta_b - \delta_a) \qquad (1)$$

and

$$p = \frac{1}{1 + e^{\Delta G/RT}} \qquad (2)$$

where δ is the measured chemical shift, δ_a and δ_b are the chemical shifts of the two valence tautomers, and p is the population of tautomer b.[9] In the previous work,[8] a Fortran program was used to select from an incremental series the ΔG value which resulted in the best least-squares fit of eq 1 in a plot of δ *vs.* p. The intercept and slope of this line then yield values of δ_a and δ_b. In the study of the cyclobutanes there could be essentially no difference in entropy between the conformers and ΔG was taken to be invariant with temperature. In contrast, the norcaradiene to cycloheptatriene isomerization might be expected to have a considerable entropy change. Accordingly, the previous Fortran program was modified to include incremental series of both ΔH (steps of 0.020 kcal mol^{-1}) and ΔS (steps of 0.2 kcal mol^{-1} deg^{-1}).[10] The data converged in both directions for both parameters to a "best" least-squares fit. Table II gives for each system the thermodynamic parameters found in this way.

Table I. Chemical Shifts and Equilibrium Constants, 7-R-Carbomethoxynorcaradiene–Cycloheptatriene Mixtures

T, °C	R = C_6H_5, shift[a]	R = *p*-$C_6H_4NO_2$, shift[a]	R = *p*-$C_6H_4OCH_3$, shift[a]
	1,6 Protons		
−57	(787.4)[b]	774.8	779.6
−9	908.2	837.3	869.7
32.5	962.9	909.6	943.7[c]
67	1013.6		
75	1021.2	970.4	1006.6
113	1055.6	1010.5	1046.0
	2,5 Protons		
−57	1378.9	1383.0	1373.7
−9	1375.6	1380.1	1370.8
32.5	1374.9	1379.7	1370.5[c]
75	1373.8	1379.8	1369.3
113	1372.2	1379.8	1368.2
	3,4 Protons		
−57	1294.3	1290.4	1298.3
−9	1311.5	1303.0	1312.1
32.5	1320.6	1308.9	1321.2[c]
75	1328.8	1318.8	1329.9
113	1333.7	1325.8	1335.0
	K_{eq}[d]		
−57		0.0732	0.174
−9	0.151	0.323	0.471
32.5	0.616	0.795	0.869[c]
67	1.52		
75	1.83	1.61	1.39
113	3.98	2.65	1.94

[a] Downfield shift from internal TMS, in hertz at 220 MHz. [b] Overlaps with $-COOCH_3$ absorption, value uncertain. Not used in calculation of ΔH and ΔS. [c] 33°. [d] Equilibrium constant, population cycloheptatriene:population norcaradiene. Populations from least-squares fit of eq 1.

Table II. Thermodynamic Values for Conversion of Norcaradienes to Cycloheptatrienes

Reaction	ΔH, kcal mol^{-1}	ΔS, cal mol^{-1} deg^{-1}	$\Delta H/\Delta S$,[a] °K
1f → **2f**	5.4 ± 0.6	16.8 ± 2.0	3.2×10^2
1g → **2g**	3.5 ± 0.2	11.0 ± 0.8	3.2×10^2
1h → **2h**	2.3 ± 0.3	7.4 ± 1.0	3.1×10^2

[a] Best values.

For each of the three equilibrium systems the absorptions due to the protons of the norcaradiene–cycloheptatriene group were analyzed at 33 and 113°. The LAOCN3 program,[11] with the addition of a plotting routine,[12] was used. A succession of trials and fits was carried out until a fit gave no significant change in order by frequency of the approximately 120 lines that could be assigned and the plot of the calculated spectrum gave good visual agreement with the experimental. The first calculated fit usually gave good agreement with the 1,6 proton and 3,4 proton bands; a second trial and fit were necessary in most cases before there was good agreement with the complex 2,5 proton band. Table III gives the results of these analyses. Figure 1 shows a typical experimental spectrum and its calculated fit. The ΔH and ΔS values for the valence tautomerism were used in turn to find the populations of norcaradiene and cycloheptatriene in each of the equilibrium mixtures; the spectral parameters for the equilibrium mixtures could then be extrapolated to the values for the individual isomers. A computer program was written for this calculation[10] using eq 3–6, where p_i is the

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(8) J. B. Lambert and J. D. Roberts, *J. Amer. Chem. Soc.*, **87**, 3884 (1965).

(9) We have assumed δ_a and δ_b to be invariant with temperature. Such invariance has been found for cycloheptatriene (F. R. Jensen and L. A. Smith, *ibid.*, **86**, 956 (1964)) and 7,7-dicyanonorcaradiene (E. Ciganek, *ibid.*, **89**, 1454 (1967)).

(10) We wish to thank Mr. Raymond E. Carhart for consultation in the computer programming.

(11) A. A. Bothner-By and S. Castellano, "LAOCN3," Mellon Institute, Pittsburgh, Pa., 1966.

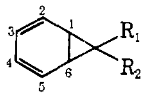
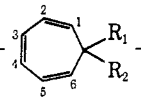
(12) K. Matsumoto, unpublished.

Table III. Analyses of Spectra, 7-R-7-Carbomethoxynorcaradiene–Cycloheptatriene Equilibrium Mixtures[a,b]

	R = C_6H_5		R = p-$C_6H_4NO_2$		R = p-$C_6H_4OCH_3$	
T, °C	32.5	113	32.5	113	33	113
$\delta_{1,6}$	962.7 ± 0.04	1055.5 ± 0.05	909.4 ± 0.02	1010.2 ± 0.05	943.6 ± 0.04	1046.0 ± 0.05
$\delta_{2,5}$	1374.7 ± 0.05	1372.0 ± 0.05	1379.6 ± 0.02	1379.4 ± 0.04	1370.2 ± 0.04	1368.0 ± 0.05
$\delta_{3,4}$	1320.8 ± 0.05	1334.1 ± 0.05	1309.0 ± 0.03	1326.1 ± 0.05	1321.5 ± 0.04	1335.5 ± 0.05
J_{12}, J_{56}	7.33 ± 0.08	7.98 ± 0.08	6.94 ± 0.04	7.63 ± 0.08	7.32 ± 0.07	7.94 ± 0.08
J_{13}, J_{46}	0.39 ± 0.10	0.69 ± 0.11	0.56 ± 0.05	0.49 ± 0.11	0.40 ± 0.08	0.50 ± 0.11
J_{14}, J_{36}	0.47 ± 0.10	0.44 ± 0.11	0.50 ± 0.05	0.58 ± 0.11	0.49 ± 0.08	0.50 ± 0.11
J_{15}, J_{26}	0.14 ± 0.08	−0.16 ± 0.08	0.18 ± 0.04	−0.27 ± 0.08	0.11 ± 0.07	−0.08 ± 0.08
J_{16}	5.65 ± 0.09	4.20 ± 0.10	6.25 ± 0.05	5.30 ± 0.18	5.72 ± 0.07	4.51 ± 0.09
J_{23}, J_{45}	8.13 ± 0.08	7.69 ± 0.10	8.36 ± 0.04	7.77 ± 0.09	8.13 ± 0.07	7.81 ± 0.09
J_{24}, J_{35}	0.67 ± 0.03	0.79 ± 0.10	0.74 ± 0.04	0.59 ± 0.08	0.75 ± 0.07	0.71 ± 0.09
J_{25}	1.01 ± 0.07	0.71 ± 0.08	1.05 ± 0.04	0.81 ± 0.10	0.99 ± 0.06	0.61 ± 0.08
J_{34}	8.22 ± 0.10	8.58 ± 0.10	7.66 ± 0.05	8.09 ± 0.11	7.95 ± 0.08	8.63 ± 0.11
RMS error[c]	0.207	0.249	0.116	0.202	0.172	0.219
Population, cyclotriene	0.381	0.799	0.443	0.726	0.465	0.660

[a] Values in hertz. [b] Error limits are twice "probable error of parameter set" from LAOCN3 calculation. [c] Root-mean-square difference between experimental and calculated line frequencies.

Table IV. Proton Magnetic Resonance Values for Simple 7-Substituted Norcaradienes and Cycloheptatrienes[a,h]

										
	R_1 = $-COOCH_3$,[b] R_2 = $-C_6H_5$	R_1 = $-COOCH_3$,[b] R_2 = $-C_6H_4NO_2$	R_1 = $-COOCH_3$,[b] R_2 = $-C_6H_4OCH_3$	R_1 = $-CN$,[c] R_2 = $-CN$	R_1 = $-COOCH_3$,[b] R_2 = $-C_6H_5$	R_1 = $-COOCH_3$,[b] R_2 = $-C_6H_4NO_2$	R_1 = $-COOCH_3$,[b] R_2 = $-C_6H_4OCH_3$	R_1 = $-H$,[d] R_2 = $-H$	R_1 = $-H$,[e] R_2 = $-C_6H_5$	R_1 = $-CF_3$,[d] R_2 = $-CF_3$
$\delta_{1,6}$	3.99 ± 0.04	3.41 ± 0.02	3.17 ± 0.07	3.47	5.00 ± 0.04	5.04 ± 0.05	5.57 ± 0.11		5.315	
$\delta_{2,5}$	6.26 ± 0.01	6.27 ± 0.01	6.25 ± 0.01	6.1–6.8[f]	6.23 ± 0.01	6.27 ± 0.01	6.20 ± 0.01		6.137	
$\delta_{3,4}$	5.95 ± 0.01	5.83 ± 0.01	5.85 ± 0.01		6.09 ± 0.01	6.10 ± 0.01	6.18 ± 0.03		6.629	
J_{12}, J_{56}	6.7 ± 0.3	5.8 ± 0.3	5.8 ± 0.5	5.87	8.3 ± 0.2	8.3 ± 0.3	9.1 ± 0.6	8.58	8.82	
J_{13}, J_{46}	0.1 ± 0.3	0.7 ± 0.3	0.2 ± 0.6	0.48	0.8 ± 0.3	0.4 ± 0.3	0.7 ± 0.5	1.56[g]	1.64[g]	
J_{14}, J_{36}	0.5 ± 0.3	0.4 ± 0.3	0.5 ± 0.6	0.25	0.4 ± 0.2	0.7 ± 0.3	0.5 ± 0.5			
J_{15}, J_{26}	0.4 ± 0.3	0.9 ± 0.3	0.6 ± 0.4	0.74	−0.3 ± 0.2	−0.7 ± 0.3	−0.5 ± 0.4	0.0		
J_{16}	7.0 ± 0.4	7.8 ± 0.4	8.6 ± 0.7	8.38	3.5 ± 0.3	4.4 ± 0.5	2.4 ± 1.0			
J_{23}, J_{45}	8.5 ± 0.3	9.3 ± 0.3	8.9 ± 0.5	9.42	7.5 ± 0.2	7.2 ± 0.3	7.2 ± 0.5	5.26	5.65	6.86
J_{24}, J_{35}	0.6 ± 0.3	1.0 ± 0.3	0.8 ± 0.5	0.77	0.8 ± 0.2	0.4 ± 0.3	0.6 ± 0.5	0.80	0.64	0.80
J_{25}	1.3 ± 0.3	1.4 ± 0.3	1.9 ± 0.5	1.15	0.6 ± 0.2	0.6 ± 0.3	−0.1 ± 0.5	0.0	0.66	0.10
J_{34}	7.9 ± 0.3	7.0 ± 0.3	6.3 ± 0.6	6.28	8.8 ± 0.3	8.5 ± 0.4	9.9 ± 0.7	10.67	10.95	10.37
$\Delta(\delta_1, \delta_2)$	2.27 ± 0.05	2.86 ± 0.03	3.08 ± 0.08	2.81	1.23 ± 0.05	1.23 ± 0.06	0.63 ± 0.12		0.822	
$\Delta(\delta_1, \delta_3)$	1.96 ± 0.05	2.42 ± 0.03	2.68 ± 0.08	3.06	1.09 ± 0.05	1.06 ± 0.06	0.61 ± 0.14		1.314	
$\Delta(\delta_2, \delta_3)$	0.31 ± 0.02	0.44 ± 0.02	0.40 ± 0.02	0.247	0.14 ± 0.02	0.17 ± 0.01	0.02 ± 0.04	0.384	0.492	0.074

[a] Chemical shifts in parts per million, coupling constants in hertz. [b] This work. [c] C. Ganter and J. D. Roberts, *J. Amer. Chem. Soc.*, **88**, 741 (1966). [d] J. B. Lambert, L. J. Durham, P. Lepoutere, and J. D. Roberts, *ibid.*, **87**, 3896 (1965). [e] H. Günther, M. Görlitz, and H.-H. Hinrichs, *Tetrahedron*, **24**, 5665 (1968). [f] $\delta_{2,5}$ and $\delta_{3,4}$. [g] $J_{13} + J_{14}$. [h] The values found in this work and, for comparison, those of selected, closely related compounds are included. Other spectra have been analyzed (*e.g.*, footnote *e*).

$$p_i = \frac{1}{1 + e^{(\Delta H - T_i\Delta S)/RT_i}} \tag{3}$$

$$D = \frac{j_1 - j_2}{p_1 - p_2} \tag{4}$$

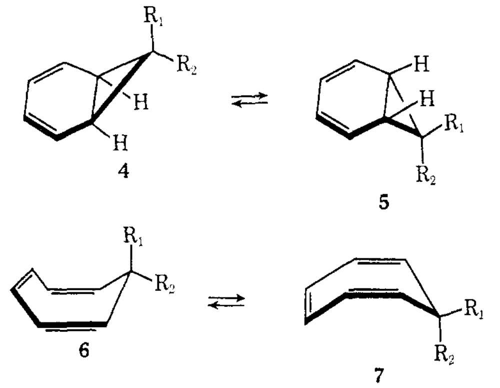
$$J_a = j_1 - p_1 D \tag{5}$$

$$J_b = J_a + D \tag{6}$$

population of the cycloheptatriene and j_i is the value of the spectral parameter at temperature T_i, J_a and J_b are the values of the parameter for the cycloheptatriene and the norcaradiene, and $D = J_a - J_b$. The results are given in Table IV.

The use of 220-MHz spectra in this work not only gave well-separated bands but also permitted accurate determination of the chemical shifts. The 1,6 proton band was sufficiently displaced from the 2,5 and 3,4 bands to be essentially first order. Chemical shifts measured directly from the spectrum agreed to ±0.3 Hz with the value from the LAOCN3 analysis. For the other two bands, the agreement was ±0.5 Hz. The limiting quantity in the determination of the thermodynamic parameters was the temperature at which the spectra were recorded, which has a ±1° uncertainty. To determine the magnitude of the resulting uncertainty in the values of ΔH and ΔS the Fortran calculations were carried out with the temperatures varied to the limits of the ±1° range; the maximum changes in ΔH and ΔS were produced by skewing the temperatures by raising the higher temperatures and lowering the lower, and *vice versa*. The error limits in the values in Table II include these extremes. In the evaluation of the spectral parameters for each of the valence tautomers two uncertainties are involved, the equilibrium constants, *i.e.*, ΔH and ΔS, and the values of the parameter at two temperatures as found by spectral analysis. The LAOCN3 program gives a "probable error" for each parameter, but the validity of that quantity is uncertain. In their presentation of the original LAOCOON program, Castellano and Bothner-By themselves suggested that in strongly coupled spectra the probable errors should be viewed with skepticism.[13] Castellano has without further comment increased these probable errors by a factor of five in estimating the reliability of certain of his results.[14] Cooper and Manatt made a comparison of the results of the analysis of different sets of spectra and found differences of about twice the LAOCN3 probable error.[15] Diehl and Kellerhals modified the error computation so that its validity was no longer limited to weak coupling, but found in all practical cases that they examined that the magnitude of the error never changed by more than 5%.[16] In the present work, a factor of two has been used. To produce the maximum change in the slope of the extrapolation line, the values from the two spectra were used at the opposite extremes of their uncertainty ranges. For each of these two combinations, two computations were performed using the two limiting sets of ΔH and ΔS values found above. The error limits given in Table IV include all values found by this procedure. The small value of the enthalpy change in the 7-*p*-methoxyphenyl system and the resulting low sensitivity of the composition of the equilibrium mixture to temperature is reflected in the large error limits for the parameters for these isomers.

We wish to make clear that, in the treatment of the data, we have assumed that there is no change in the relative populations of endo–exo configurational isomers of the norcaradienes (**4** $\rightleftarrows$ **5**) or the cycloheptatrienes (**6** $\rightleftarrows$ **7**) with temperature that significantly affects their spectral parameters, *i.e.*, that either one configuration (as **4** and **6**) predominates at all temperatures, or that the equilibrium constant between the two is insensitive to temperature, or that the spectral parameters of the two are essentially the same. No evidence to contradict this assumption has been found in this study; otherwise the assumption is unsupported.



A number of proposals have been made for an explanation of the effect of 7 substituents on the relative stability of norcaradiene–1,3,5-cycloheptatriene valence tautomers. Ciganek[9] has suggested repulsion between such substituents, this repulsion increasing the angle between the substituents, with the accompanying decrease in the angle within the ring at C-7 favoring the norcaradiene. An X-ray structure analysis[17] and the stability of the cycloheptatriene isomer in the spiro system where C-7 is part of a three-membered ring[18] as opposed to the stability of the norcaradiene in spiro systems where C-7 is part of a five- or six-membered carbocyclic ring[19] support this proposal. Such repulsion between groups cannot result only from simple bulk; the cyano group is linear and two such groups can have little steric interaction. A mutual dipole–dipole repulsion could account for the effect of two cyano groups, of two carbomethoxy groups, or of a cyano and a trifluoromethyl in favoring the norcaradiene, but is difficult to accommodate to the decrease in ΔH caused by *both* the *p*-nitro and *p*-methoxy substituents on the phenyl group. Increase in the steric bulk of the substituents by solvation is not a tenable explanation; comparison of spectra of carbon tetrachloride solutions of the *p*-nitro compound shows no difference in the position of the 1,6 proton absorption from that of the deuteriochloroform solution.

One possibly valid means of accounting for the effect of the nitro and methoxy groups in lowering the enthalpy of the cycloheptatriene relative to the norcaradiene is that both of these groups increase the polarity of the phenyl substituent, this polarity in turn inducing a polarity in the carbomethoxy group. Any resulting attraction between the two substituents would decrease the bond angle between them.

Ingold has suggested that the existence of the dicyano compound as the norcaradiene **1c** results "...from quasi-conjugation of the *cyclo*propane ring with the cyano-group...."[21] The phenyl group might also participate in such conjugation, but the parallel effects of the nitro and methoxy groups are in contradiction to the opposite signs of their Hammett σ constants. Still another approach is the application of homoaromaticity to the cycloheptatriene as a homolog of benzene.[22,23] Electron withdrawal from the σ-electron system by electronegative substituents at the 7 position will increase by induction the electron density in the π system at positions 1 and 6, thereby increasing the p–π homoaromatic bonding between these two positions. To the extent that such a bond exists in the cycloheptatriene, both the enthalpy and entropy differences between the valence tautomers should decrease; such a parallelism between enthalpy and entropy are observed here (Table II). But again there are serious difficulties. For the systems studied here, the enthalpy and entropy differences are least for **2**, requiring the strongest homoaromatic bonding in **2h**; but of the three cycloheptatrienes, J_{16} is least for **2h**. More generally, electron-withdrawing 7 substituents should favor the cycloheptatriene, yet it is in systems containing such substituents that norcaradienes have

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(13) S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, **41**, 3869 (1964).

(14) S. Castellano, C. Sun, and R. Kostelnik, *Tetrahedron Lett.*, 5205 (1967); S. Castellano and R. Kostelnik, *ibid.*, 5211 (1967).

(15) M. A. Cooper and S. L. Manatt, *J. Amer. Chem. Soc.*, **91**, 6325 (1969).

(16) P. Diehl and H. P. Kellerhals, personal communication.

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been found. But whatever the mechanism of the substituent interaction, the proportionality found here between ΔH and ΔS (Table III, an isoequilibrium relationship[24]) suggests that only a single mechanism operates in the systems under study.

The smaller shifts to lower fields (δ values) of the 1,6 protons in the norcaradienes rather than in the cycloheptatrienes are evident here as in previous reports (*cf.* Table IV), consistent with the position of these protons on the cyclopropane ring of the norcaradiene. In the vicinal coupling constants an increase with carbon to carbon double bonding over single bonding is evident; J_{12} and J_{34} are greater for the cycloheptatrienes, J_{23} and J_{25} are greater for the norcaradienes.

Ambiguities in the coupling constants may occur in the analysis of a single spectrum; a test of such an analysis is to use the values obtained from a spectrum at one frequency to calculate the spectrum at another frequency.[25] Both 60- and 100-MHz spectra for the 7-*p*-nitrophenyl system were calculated from the values found by analysis of a 220-MHz spectrum; both calculated spectra agreed with the experimental. In Table IV it will be noted that J_{15}, J_{26} for the cycloheptatrienes is negative; in view of the small magnitude of these couplings, the reality of the negative sign is not certain.

Experimental Section

Nuclear magnetic resonance spectral measurements were made of degassed 10% solutions in deuteriochloroform[26] containing TMS as an internal standard in sealed tubes. The 220-MHz spectra[27] were recorded with a Varian HR-220 spectrometer equipped with a variable temperature probe,[28] the 100-MHz spectra[27] with a Varian HA-100 spectrometer, and the 60-MHz spectra with either a Varian A-56/60 or Varian A-60A spectrometer. Decoupled spectra were obtained with a Varian T-60 spectrometer. Analyses were of spectra recorded at 100-Hz sweep widths; spectra were also recorded at greater sweep widths. Frequency calibration was by the side-band technique. The temperature calibration of the 220-MHz instrument was by methanol and ethylene glycol peak separations.

Calculations were done with IBM 360/75 and IBM 360/50 computers.

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(26) Some of the 60-MHz spectra were of carbon tetrachloride solutions.

(27) We are indebted to Mr. David H. Live for the 220- and 100-MHz spectra.

(28) This instrument was purchased with the aid of National Science Foundation Grant No. GP8450.

The Cycloheptatriene–Norcaradiene System. III. Dependence of the Ground-State Enthalpy Difference on Substituents in the 7 Position[1]

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Abstract: The adducts of phenylcyanocarbene, carbomethoxycyanocarbene, carbomethoxyphenylcarbene, carbomethoxy-*p*-methoxyphenylcarbene, carbomethoxy-*p*-nitrophenylcarbene, and cyano(trifluoromethyl)carbene to benzene have been prepared. Except for the latter, they are crystalline solids that have the norcaradiene structure. In solution, methyl 7-phenyl-7-norcaradienecarboxylate, its *p*-methoxyphenyl and *p*-nitrophenyl analogs, and 7-cyano-7-phenylnorcaradiene are in rapid equilibrium with the corresponding cycloheptatriene valence isomers. The liquid adduct of cyano(trifluoromethyl)carbene to benzene is at room temperature a rapidly equilibrating mixture of 7-cyano-7-(trifluoromethyl)norcaradiene (**2f**, 15%) and 7-cyano-7-(trifluoromethyl)cycloheptatriene (**3f**, 85%), having $\Delta H^\circ = 0$, $\Delta S^\circ = +5$ eu, and E_a for interconversion of about 7 kcal/mol. Raman spectroscopy is shown to be a useful diagnostic method supplementing nmr spectroscopy in the detection of valence isomerizations in the norcaradiene–cycloheptatriene system. Catalytic hydrogenation of **2f**/**3f** and of ethyl 7-cycloheptatrienecarboxylate gave norcaranes in excess of the amounts expected on the basis of the equilibrium concentrations of norcaradienes in the starting materials.

In previous papers, we reported the synthesis and structure proof,[2] and some reactions[3] of 7,7-dicyanonorcaradiene, the first simply substituted stable norcaradiene. To shed some light on the unexpected stabilization of a norcaradiene relative to the valence isomeric cycloheptatriene by two cyano groups, we varied the substituents in the 7 position and attempted to estimate the ground-state enthalpy difference for each pair of valence isomers obtained.[4]

Results

Synthesis. All compounds reported here were prepared by addition of the appropriate carbene to benzene; the carbenes were generated by photolysis or

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(1) Parts of this paper were reported in preliminary form: E. Ciganek, *J. Amer. Chem. Soc.*, **87**, 1149 (1965).

(2) E. Ciganek, *ibid.*, **89**, 1454 (1967).

(3) E. Ciganek, *ibid.*, **89**, 1458 (1967).

(4) For an estimate of the ground-state enthalpy difference between 7,7-dicyanonorcaradiene and 7,7-dicyanocycloheptatriene, see H. J. Reich, E. Ciganek, and J. D. Roberts, *ibid.*, **92**, 5166 (1970).