Table IV. Intensity Ratios of Vibrational Components in the ^{1}W Band

Compd	Cyclohexane ϵ_B/ϵ_C	Ethanol ϵ_B/ϵ_C
4	1.33	1.07
6	1.34	1.04
7	1.35	1.00
8	1.33	0.99
9	1.31	0.96
10	1.30	0.88
1	1.27	0.74

It has been suggested previously[6] that the oxygen atom is the most basic site on the NNO chromophore. In the planar **1**, structure E′ is stabilized by resonance of the extracyclic double bond with the benzene ring leading to a buildup of negative charge on the oxygen atom, and an enhanced basicity; this argument establishes the order **1** > **10**. In all the highly twisted compounds, the benzene ring exerts a significant −I effect, explaining the observation that **10** is more basic than these twisted compounds. Since all these compounds are so strongly twisted that resonance stabilization of E′ is negligible, the sequence within this group depends on inductive effects alone. The −I effect of the 2,6-xylyl groups is less than that of *o*-tolyl, which in turn is less than that of phenyl; finally, the order of **9** > **8**, and **7** > **6**, depends on the order +I of isopropyl greater than that of methyl.

D. Summary of Band Assignments. Band assignments in the nitrosoanilines have been collected in a diagram of states (Figure 5) for the series studied, along with dimethylnitrosamine (**10**) for comparison. Excited states arising from the twisted nitrosoanilines appear in order of decreasing energy in the left column, while those arising from planar and near-planar geometries are listed at the right. The positions of these horizontal bars represent the energies (λ_{max}) of these excited states while the lengths of the bars are proportional to the intensities of the absorption bands resulting from each excited state; dotted lines connect the bars common to each excited state throughout the series. Because the excited states in the planar and twisted nitrosoanilines are not readily comparable (except for the ^{1}W state), a double line separates the states in these two types of geometry (**3** was not included because of its close similarity to **2**).

The observations made earlier about these states may be clearly seen in this visual representation. Note that the states most sensitive to twist are those associated with the NNO chromophore, the $^1B_{NNO}$ and the ^{1}W; in both states, the increased interactions of the benzene ring cause bathochromic shifts; the inductive effect of the N-alkyl substituent may also be seen to affect the energy of the ^{1}W state in the expected fashion. The ^1L_a state in the twisted geometries undergoes a small but definite hypsochromic shift with a decrease of substitution on the ring, while the ^1L_b band becomes hidden beneath the more intense $^1B_{NNO}$ band as the latter shifts bathochromically. Finally, the hypochromic effects and constant positions of both charge-transfer bands are clearly apparent.

Acknowledgments. J. T. D. would like to thank Dr. Janet Del Bene and Professor Donald Duffey for many helpful discussions during the early portions of this research.

Nuclear Magnetic Resonance Spectroscopy. Kinetics of a 7,7-Dicyanonorcaradiene Valence Tautomerism[1]

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Abstract: The rate of inversion of 7,7-dicyano-2,5-bis(difluoromethyl)norcaradiene (**10**), presumably by way of its valence tautomer, 7,7-dicyano-2,5-bis(difluoromethyl)cycloheptatriene (**11**), was studied through the temperature dependence of the magnetic nonequivalence of the *gem*-fluoro groups. The activation energy E_a was found to be 14.6 ± 0.4 kcal/mol and log A is 13.4 ± 0.3.

Valence tautomerism in the norcaradiene–cycloheptatriene system (**1** $\rightleftarrows$ **2**) and various heterocyclic analogs has been the subject of much research in recent years.[5] Cycloheptatriene (**2a**) and most derivatives do not contain detectable amounts of their norcaradiene valence tautomers at equilibrium, but nmr[6,7] and X-ray crystallographic[8] studies have shown that the 7,7-dicyano derivative (**1b**) is a norcaradiene. The bistri-

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(2) National Research Council of Canada Postdoctoral Fellow.

(3) California Institute of Technology.

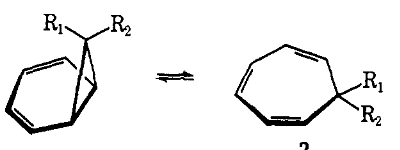
(4) Central Research Department of E. I. du Pont de Nemours and Co.

(5) G. Maier, *Angew. Chem. Intern. Ed. Engl.*, **6**, 402 (1967).

(6) E. Ciganek, *J. Amer. Chem. Soc.*, **89**, 1454 (1967).

(7) C. Ganter and J. D. Roberts, *ibid.*, **88**, 741 (1966).

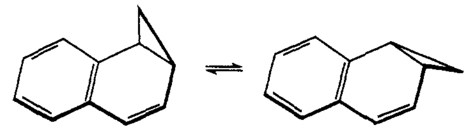
(8) C. J. Fritchie, Jr., *Acta Cryst.*, **20**, 27 (1966).



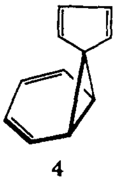
1 2

a, $R_1 = H; R_2 = H$
b, $R_1 = CN; R_2 = CN$
c, $R_1 = CF_3; R_2 = CF_3$
d, $R_1 = CF_3; R_2 = CN$

fluoromethyl compound (**2c**) is a cycloheptatriene[9,10] but the 7-trifluoromethyl-7-cyano derivative (**1d** ⇄ **2d**) is a rapidly equilibrating mixture of the two isomers at room temperature.[11] Although **1b** is the only simple stable norcaradiene so far reported, other systems, including the 2,3-benzo (**3**),[12] 7,7-spiro (**4**,**5**),[13] 1,6-trimethylene (**6**),[14] 7-oxa (**7** ⇄ **8**),[15] and 3,4-diaza (**9**)[16] compounds exist partially or wholly as norcaradienes.



3a 3b



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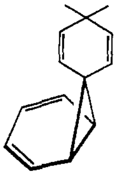

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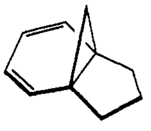

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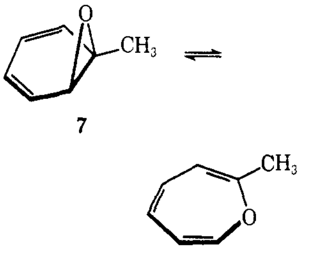
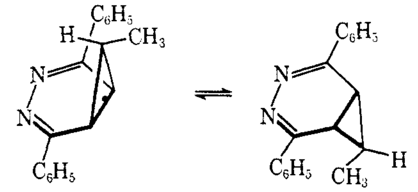
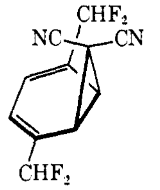


7 8



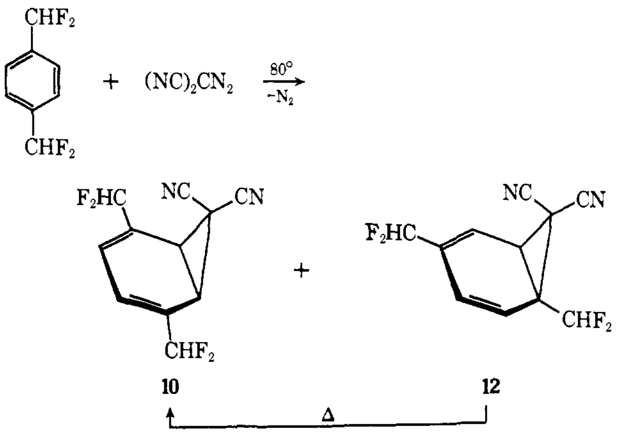
9a 9b



10

Establishment of norcaradiene–cycloheptatriene equilibria has been demonstrated for some of the systems studied and indirect evidence implicates such equilibria in many others. Thus, the cycloheptatriene **2b** has been proposed as an intermediate in thermal rearrangements of **1b**.[17] Because of the remarkable (not wholly clarified[6]) ability of the 7,7-dicyano grouping to stabilize the norcaradiene structure, it was of interest to study the proposed equilibration **1b** ⇄ **2b**. To this end, we have investigated the nmr spectrum of 7,7-dicyano-2,5-bis(difluoromethyl)norcaradiene (**10**).

This compound was obtained, in addition to the 1,4-isomer **12**, by thermolysis of dicyanodiazomethane in tetrafluoro-*p*-xylene at 80°. At slightly more elevated temperatures, isomer **12** rearranged cleanly to isomer **10**; this reaction is another example of the skeletal rearrangement discovered by Berson and Willcott.[18,19]



The proton nmr spectrum of **10** is fully consistent with the assigned structure: triplet at δ 3.90 (bridgehead H, $^4J_{HF}$ = 0.5 Hz); closely spaced multiplet, 6.71 (vinyl H); triplet with further small splittings at 6.77 (CF_2H, $^2J_{HF}$ = 54 Hz). The ^1H nmr spectrum is essentially temperature independent.

At 60°, the ^{19}F nmr spectrum of **10** is the A doublet of an A_2X system centered 118 ppm upfield from internal $CFCl_3$ ($^2J_{FH}$ = 54.1 Hz). Each peak of the doublet has shoulders, a result of long-range H–F couplings. If the temperature is lowered, each peak of the doublet broadens (T_c = 31.5°) and then sharpens to form the superimposed AB quartets of an ABX system. At $-20°$, δ_{FF} = 113 Hz, $^2J_{FF}$ = 306 Hz, $^2J_{FH}$ = 54.1 Hz. Further lowering the temperature to $-95°$ results only in gradual changes in the spectra, indicative of small temperature dependences of δ_{FF} and $^2J_{FF}$. These spectral changes show that the geminal fluorines, which are nonequivalent at $-20°$, become equivalent at 60° by some symmetrizing process rapid on the nmr time scale.

No significant temperature dependence in $^2J_{FH}$ could be detected, but between -95 and $-20°$ J_{FF} changed from 313 to 306 Hz.[20] A reasonably linear change of J_{FF} with temperature was obtained,[21] and this correlation was used to calculate δ_{FF} at various temperatures. The fluorine chemical-shift differences were substantially linear with $1/T$ (°K) between -95 (192.0 Hz) and 10° (94.5 Hz).[22] At higher tempera-

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(9) D. M. Gale, W. J. Middleton, and C. G. Krespan, *J. Amer. Chem. Soc.*, 87, 657 (1965).

(10) J. B. Lambert, L. J. Durham, P. Lepoutere, and J. D. Roberts, *ibid.*, 87, 3896 (1965).

(11) E. Ciganek, *ibid.*, 87, 1149 (1965).

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

(13) D. Schönleber, *ibid.*, 81, 83 (1969); M. Jones, Jr., *ibid.*, 81, 83 (1969). See, however, M. Jones, Jr., *J. Org. Chem.*, 33, 2538 (1968).

(14) E. Vogel, W. Wiedemann, H. Kiefer, and W. F. Harrison, *Tetrahedron Lett.*, 673 (1963).

(15) H. Günther, R. Schubart, and E. Vogel, *Z. Naturforsch.*, 22B, 25 (1967).

(16) G. Maier and U. Heep, *Chem. Ber.*, 101, 1371 (1968).

(17) E. Ciganek, *J. Amer. Chem. Soc.*, 89, 1458 (1967).

(18) J. A. Berson and R. W. Willcott, *Rec. Chem. Progr.*, 27, 139 (1966).

(19) The thermal behavior of 12 is in marked contrast to that of the fluorine-free analog, 7,7-dicyano-1,4-dimethylnorcaradiene, which on heating aromatizes to 2,5-xylylmalononitrile.[17] The rearrangement of 12 to 10 in perdeuterioacetone at 93, 108, and 121° was found to follow first-order kinetics with half-lives of 6.4, 1.72, and 0.58 hr, respectively. The activation energy is 26 kcal/mol, the activation entropy is -11 eu.

(20) Because of changes in δ_{FF} and exchange broadening, the outer peaks of the AB quartet could not be observed above $-20°$.

(21) The best least-squares line corresponded to $J_{FF} = (-0.108 \pm 0.007)T + 303.3 \pm 0.5$.

(22) The best least-squares line corresponded to $\delta_{FF} = (46.0 \pm 0.3)\cdot(1000/T + 273) - 69.1 \pm 1.4$.

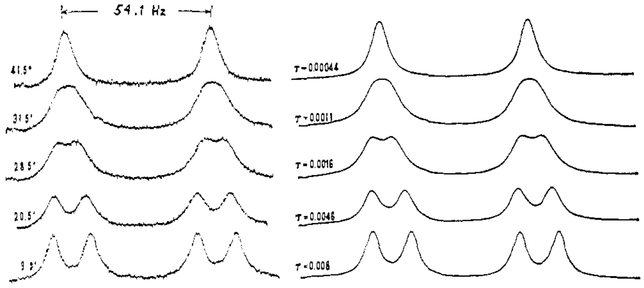


Figure 1. Experimental and calculated line shapes for the change of ^{19}F spectra of 7,7-dicyano-2,5-bis(trifluoromethyl)norcaradiene (**10**) as the result of changes in the rate of conversion of **10a** to **10b**. Experimental curves as a function of temperature on the left and calculated curves as a function of τ on the right.

tures, the apparent chemical shift of the AB quartets decreases rapidly as the result of exchange. Spectra calculated as a function of τ (the mean lifetime) using extrapolated values of J_{FF} and δ_{FF} for this exchanging ABX $\rightleftarrows$ BAX system could be accurately fitted to the experimental curves at 17 temperatures between -10 and 60° (Table I). Some sample experimental and calculated spectra are shown in Figure 1. The Arrhenius parameters, together with values from the literature for related systems, are presented in Table II.

Table I. Mean Lifetimes as a Function of Temperature for the Inversion of 7,7-Dicyano-2,5-bis(difluoromethyl)norcaradiene (**10**)

Temp, °C	τ, sec
59.5	0.00014
55.0	0.00019
51.0	0.00028
47.5	0.00030
41.5	0.00044
33.0	0.00095
31.5	0.00105
30.5	0.00120
30.0	0.00125
29.5	0.0014
28.5	0.0016
25.0	0.0024
20.5	0.0046
15.0	0.0046
9.5	0.008
−6.5	0.03
−9.5	0.04

Table II. Thermodynamic and Activation Parameters for Norcaradiene–Cycloheptatriene Interconversions

Reaction	E_a, kcal/mol	Log A	$\Delta G^{\ddagger}$, kcal/mol	Ref
10a $\rightleftarrows$ **10b**	14.6 ± 0.4	13.4 ± 1.0	13.8	This work
3a $\rightleftarrows$ **3b**	19.4	11.8	20.8	12
9a $\rightleftarrows$ **9b**	22.4 ± 2.5		23.1	16
7 → **8**	9.2 ± 0.7	14.2 ± 0.9	7.3	15
8 → **7**	8.7 ± 0.7	13.1 ± 0.9	8.3	15

It seems certain that the process observed is the valence tautomerism to give the corresponding 7,7-dicyanocycloheptatriene (**11a**) which is expected to be in rapid equilibrium with its ring-flip conformer (**11b**). Ring closure of **11b** gives **10b**. Such a process would result in the interchange of the environments of the two fluorines.[23]

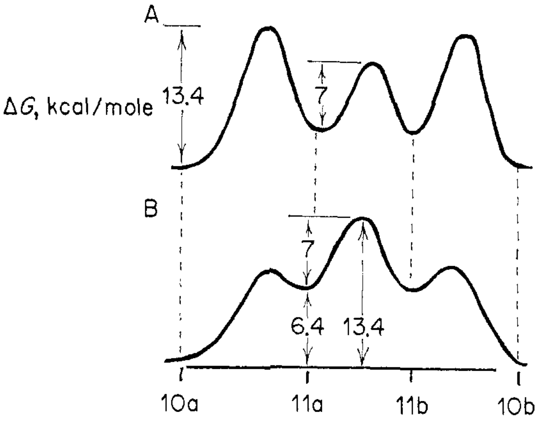
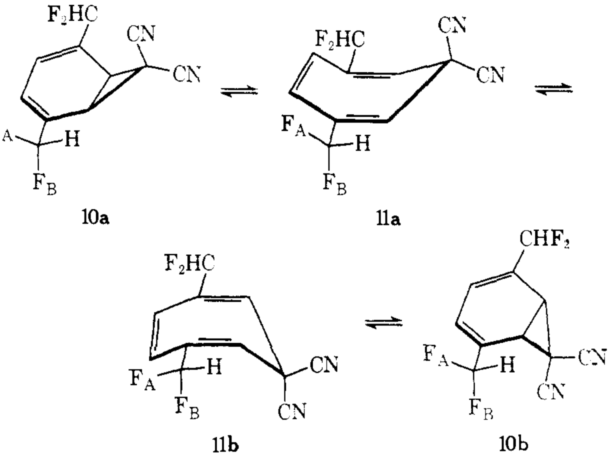


Figure 2. Possible free-energy profiles for the interconversion **10a** $\rightleftarrows$ **11a** $\rightleftarrows$ **11b** $\rightleftarrows$ **10b**.



The possibility that the changes in spectra are the result of slow rotation around the C–CHF_2 bond appears highly unlikely. The observed barrier is too high[24] and the interconversion **10a** $\rightleftarrows$ **10b** would have to be rapid down to -95° (or the two fluorines would have to have an accidental chemical-shift equivalence).

The activation energy for ring inversion in cycloheptatriene is known to be of the order of 6 kcal/mol,[25] while $\Delta G^{\ddagger}$ for the more hindered 2-*t*-butyl-3,7,7-trimethylcycloheptatriene[26] has been estimated to be 9 kcal/mol.[25a] Methyl substitution at C-7 in cycloheptatriene does not seem to have a very marked effect on the ring inversion, and so perhaps it can be assumed that **2b** (and **11**) invert at the same rate as normal cycloheptatrienes and with a $\Delta G^{\ddagger}$ of 7 kcal/mol.

The free-energy profile for the reaction **10a** $\rightleftarrows$ **10b** can have two limiting forms as shown in Figure 2.[27]

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[23] The ^{19}F nmr spectrum of isomer **12** also is temperature dependent, but in this case the signal of only one of the two CHF_2 groups changes from an A_2 to an AB pattern on cooling. The other CHF_2 group shows an A_2 pattern over the whole temperature range. The reason for this may be that the CHF_2 group in 4 position is too far away from, and in an unfavorable steric position relative to, the asymmetric center for the two fluorines to experience different environments.

[24] F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, **90**, 3577 (1968), report approximate values of E_a of 6–8 kcal/mol for rotation about the C–CF_3 bond in the relatively highly hindered 1,2-bistrifluoromethyltetrachloroethane.

[25] (a) F. A. L. Anet, *J. Amer. Chem. Soc.*, **86**, 458 (1964); (b) F. R. Jensen and L. A. Smith, *ibid.*, **86**, 956 (1964).

[26] K. Conrow, M. E. H. Howden, and D. David, *ibid.*, **85**, 1929 (1963).

The rate-determining transition state could be the one for the valence tautomerization (**10** → **11**, curve A), in which case we can only deduce that there must be 6 or less kcal/mol difference in energy between **10** and **11**. However, the activation energy for the norcaradiene–cycloheptatriene valence isomerization in the system **1d** ⇄ **2d** was found to be in the order of 7 kcal/mol.[28] It is therefore reasonable that curve B is correct, and we conclude that there is a free energy difference of ~6 kcal/mol between **10** and **11**. The entropy of activation for ring inversion of cycloheptatriene is close to zero,[25a] which indicates that the enthalpy difference between **10** and **11** is also 6 kcal/mol.[29] This means that, if the estimate of 11 kcal for the difference in energy between norcaradiene and cycloheptatriene is correct,[30] then the *gem*-cyano group must change the energy difference between the forms by some 17 kcal/mol! It is, of course, not known with certainty whether the cyano groups stabilize the norcaradiene and/or destabilize the cycloheptatriene.

As already mentioned, the reason for the unusual stability of the 7,7-dicyanonorcaradienes is not clear. Two explanations have been advanced.[6] First, widening of the NCCCN angle as a result of dipole–dipole repulsions, a hypothesis which is supported by the X-ray structure of 2,5-dimethyl-7,7-dicyanonorcaradiene.[8,31] Second, stabilization of the norcaradiene might occur through formation of an intramolecular charge transfer or π complex. However, there are no abnormalities in the ultraviolet spectrum, even though one would certainly expect detectable differences to accompany intramolecular π bonding of sufficient strength to account for the observed stabilization.

Experimental Section

Addition of Dicyanocarbene to Tetrafluoro-*p*-xylene. To a sample of solid dicyanodiazomethane,[32] prepared from 2.64 g of carbonyl cyanide hydrazone and 15.35 g of lead tetraacetate in 150 ml of methylene chloride, was added 15 ml of $\alpha,\alpha,\alpha',\alpha'$-tetrafluoro-*p*-xylene,[33] and the stirred mixture was heated slowly to 80°. After the nitrogen evolution had ceased, the excess tetrafluoro-*p*-xylene was removed at 40° (0.5 μ), leaving 4.48 g of a dark viscous oil. Chromatography over 140 g of Florisil gave first additional tetrafluoro-*p*-xylene, eluted with benzene–hexane (1:1). Elution with methylene chloride then gave 2.76 g (40% yield) of a mixture of the two isomeric 7,7-dicyanobis(difluoromethyl)norcaradienes, the 2,5 isomer **10** being eluted first. Complete separation of the two isomers could not be achieved by chromatography. Crystallization of the later fractions from isopropyl alcohol gave 7,7-dicyano-1,4-bis(difluoromethyl)norcaradiene (**12**), mp 144–145°. The ^{1}H nmr [$(CD_3)_2CO$] had δ 3.8 (broadened doublet, 1, J = 6.5 Hz), 6.0 (t, 1, J = 54 Hz), 6.2 (t, 1, J = 55 Hz), and 6.0–6.7 (m, 3) and the ^{19}F nmr (at −60° in $[CD_3]_2CO$, with internal $CFCl_3$ as standard) +116 ppm (d, 2, J = 55 Hz) and AB portion of an ABX pattern centered at +120 ppm (2; the outer lines were too weak to be observed), at +34° the ABX pattern had changed to the A part of an A_2X pattern. The coalescence temperature was estimated at between 0 and 10°. There were two uv max (MeCN) at 265 mμ (ϵ 2400) and 227 (1900).

Anal. Calcd for $C_{11}H_6F_4N_2$: C, 54.55; H, 2.50; N, 11.57. Found: C, 54.10; H, 2.40; N, 11.28.

Pure 7,7-dicyano-2,5-bis(difluoromethyl)norcaradiene (**10**), mp 97–98°, was obtained by heating the earlier fractions of the chromatography in acetone to 130° for 3 hr, removal of the solvent and crystallization of the residue from isopropyl alcohol. The uv max (MeCN) was at 275 mμ (ϵ 4400).

Anal. Calcd for $C_{11}H_6F_4N_2$: C, 54.55; H, 2.50; N, 11.57. Found: C, 54.46; H, 2.54; N, 11.63.

Nuclear magnetic resonance spectral measurements were made on a 20% solution of 7,7-dicyano-2,5-bis(difluoromethyl)norcaradiene (**10**) in acetone-d_6. A small amount of $CFCl_3$ was added as an internal standard and for homogeneity adjustments. A Varian A56/60 spectrometer with a variable temperature accessory was used for recording the spectra. Sweep widths were calibrated using the audio side-band technique. Temperatures were measured by the methanol $OH-CH_3$ peak separations, using the equation for the temperature dependence of δ_{OH-CH_3} determined by van Geet.[33] Line shapes were calculated using a computer program (ROT)[34] based on the equations of Alexander.[35]

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(27) It is assumed that the reverse tautomerization (**11** → **10**) is fast' so that the rate of the reaction **10** → **11** (curve A) or **10** → transition state between **11a** and **11b** (curve B) is twice the rate of the reaction **10a** → **10b** (the measured rate). This corresponds to a difference in activation entropy of R ln 2 (1.4 eu).

(28) E. Ciganek, to be published.

(29) An entropy of activation of 0.8 eu was obtained for **10a** ⇄ **10b** which agrees well with the value for cycloheptatriene but the accuracy of the measurements for **10a** ⇄ **10b** is rather strongly dependent on the choice of line widths in the absence of exchange broadening. The fluorine resonances in both the high-temperature and low-temperature forms have some structure as a result of long-range H–F (and possibly F–F) couplings, making the choice of line widths more arbitrary than one would like.

(30) K. N. Klump and J. P. Chesick, *J. Amer. Chem. Soc.*, **85**, 130 (1963).

(31) The general argument that the angles between substituents at the 7 carbon may be crucial to the position of cycloheptatriene–norcaradiene equilibria receives substantial support from the recent finding that 7,7-spiro[2,6]derivatives exist in this form, not as norcaradienes; *cf.*, M. Jones, Jr. and E. W. Petrillo, Jr., *Tetrahedron Lett.*, **45**, 3953 (1969), and C. J. Rostek and W. M. Jones, *ibid.*, 3957 (1969).

(32) E. Ciganek, *J. Org. Chem.*, **30**, 4198 (1965).

(33) W. R. Hasek, W. C. Smith, and V. A. Engelhardt, *J. Amer. Chem. Soc.*, **82**, 543 (1960).

(33) A. L. van Geet, paper presented at 10th Experimental NMR Conference, Carnegie-Mellon University, Pittsburgh, Pa., March 29, 1969.

(34) J. T. Gerig and J. D. Roberts, *J. Amer. Chem. Soc.*, **88**, 2791 (1966).

(35) S. Alexander, *J. Chem. Phys.*, **37**, 974 (1962).