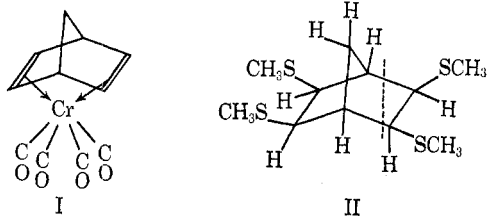
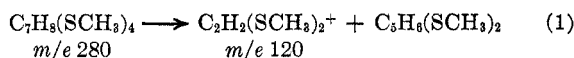


ternative all-*endo* isomer is expected to be about 4 cps on the basis of comparison with previously reported nmr data on other norbornane derivatives.⁵



The mass spectrum of II exhibited an intense parent molecular ion at m/e 280. This underwent fragmentation by several parallel pathways, including not only losses of neutral CH_3 and CH_3SH fragments and the formation of $\text{C}_5\text{H}_5(\text{SCH}_3)_2^+$ like other norbornane derivatives⁶ but also the following more unusual process (eq 1). This process appears to involve cleavage of



metastable ion: m/e 51.3 ($120^2/280 = 51.4$)

similar bonds (dotted lines in structure II) to the retro Diels-Alder fragmentations previously reported⁶ in the mass spectra of various derivatives of norbornadiene, norbornene, and benzonorbornene, but not generally in derivatives of norbornane, which cannot be formed by Diels-Alder reactions. This anomalous "pseudo retro Diels-Alder" fragmentation in the mass spectrum of II may occur because of the stabilization of the unsaturated product ion $\text{C}_2\text{H}_2(\text{SCH}_3)_2^+$ by overlap of the filled π orbitals of the C_2H_2 carbon atoms with the empty d orbitals of the sulfur atoms.

The preparation of II from the nonbornadiene complex I described in this note suggests that degradation of norbornadiene-metal carbonyl derivatives in various ways may provide routes to novel norbornane derivatives not readily accessible by more conventional synthetic techniques. Several attempts to prepare II by boiling various mixtures of norbornadiene and dimethyl disulfide failed even when catalytic amounts of iron pentacarbonyl were added.

Experimental Section

Preparation of 2,3,5,6-Tetrakis(methylthio)norbornane (II).—A mixture of 1.0 g (3.9 mmol) of norbornadienetetracarboxylchromium (I),⁷ 2.0 ml (2.1 g, 22.4 mmol) of dimethyl disulfide, and 40 ml of methylcyclohexane was boiled under reflux for 24 hr in a nitrogen atmosphere. The reaction mixture was filtered hot and the filtrate was cooled to room temperature and finally in a -78° bath. The pale yellow crystals which separated were filtered and dried to give 0.438 g (40%) of 2,3,5,6-tetrakis(methylthio)norbornane (II). The pure white, analytical sample, mp $140-144^\circ$, was obtained by sublimation of some of this crude product at 110° (0.1 mm).

Anal. Calcd for $\text{C}_{11}\text{H}_{20}\text{S}_4$: C, 47.2; H, 7.1; S, 45.7; mol wt, 280. Found: C, 46.6; S, 46.8; mol wt, 280 (mass spectrum).

The infrared spectrum (KBr) showed absorption at 2950 (w) and 2885 (w) (both CH), 1450 (w), 1435 (m), 1415 (m), 1315 (m), 1300 (w), 1277 (w), 1270 (w), 1248 (w), 1175 (w), 1140 (vw), 1028 (vw), 1008 (vw), 976 (w), 961 (w), 950 (w), 921 (w), and 900 cm^{-1} (w).

(5) F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961).

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(7) M. A. Bennett, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 2037 (1961); R. B. King, *Organometal. Syn.*, **1**, 122 (1965).

The proton nmr spectrum was taken on a Varian A-60 spectrometer in CS_2 solution and showed absorption at τ 7.06 (s, $W_{1/2} \cong 3$ cps), 7.62 (apparent t, $J = 1.5$ cps), 7.82 (s), and 8.15 (br, $W_{1/2} \cong 5$ cps). The approximate relative intensities were 4:2:12:2, respectively.

The mass spectrum was taken on a Perkin-Elmer Hitachi RMU-6 mass spectrometer at 70 eV and a chamber temperature of 210° . It showed peaks at m/e (rel intensity, ion) 280 [100, $\text{C}_7\text{H}_8\text{S}_4(\text{CH}_3)_4^+$], 265 [17, $\text{C}_7\text{H}_8\text{S}_4(\text{CH}_3)_3^+$], 233 [10, $\text{C}_7\text{H}_8\text{S}_3(\text{CH}_3)_3^+$], 232 [13, $\text{C}_7\text{H}_7\text{S}_3(\text{CH}_3)_3^+$], 217 [12, $\text{C}_7\text{H}_7\text{S}_3(\text{CH}_3)_2^+$], 185 [52, $\text{C}_7\text{H}_7\text{S}_2(\text{CH}_3)_2^+$], 169 [11, $\text{C}_7\text{H}_6\text{S}_2\text{CH}_3^+$], 159 [12, $\text{C}_7\text{H}_5\text{S}_2(\text{CH}_3)_2^+$], 146 [13, $\text{C}_4\text{H}_4\text{S}_2(\text{CH}_3)_2^+$], 145 [12, $\text{C}_4\text{H}_3\text{S}_2(\text{CH}_3)_2^+$], 139 [21, $\text{C}_7\text{H}_8\text{SCH}_3^+$], 138 [27, $\text{C}_7\text{H}_7\text{SCH}_3^+$], 137 [94, $\text{C}_7\text{H}_6\text{SCH}_3^+$], 133 [21, $\text{C}_3\text{H}_3\text{S}_2(\text{CH}_3)_2^+$], 125 [23, $\text{C}_7\text{H}_7\text{S}^+$], 123 [48, $\text{C}_7\text{H}_6\text{S}^+$], 122 [99, $\text{C}_7\text{H}_6\text{S}^+$], 121 (ca. 100, $\text{CH}_3\text{SC}_2\text{H}_3\text{SCH}_3^+$), 120 [very intense (off scale), $\text{CH}_3\text{SC}_2\text{H}_2\text{SCH}_3^+$], 113 [52, $\text{C}_6\text{H}_6\text{SCH}_3^+$], 107 (ca. 140, $\text{CH}_3\text{SC}_2\text{H}_3\text{S}^+$), 105 [48, $\text{CH}_3\text{SC}_2\text{H}_2\text{S}^+$], 99 [25, $\text{C}_6\text{H}_7\text{S}^+$], 97 [64, $\text{C}_6\text{H}_6\text{S}^+$], 91 [95, C_7H_7^+], 87 [86, $\text{C}_4\text{H}_7\text{S}^+$], 85 [26, $\text{C}_6\text{H}_5\text{S}^+$], 79 [36, C_6H_7^+], 77 [37, C_6H_5^+], 73 [26, $\text{C}_3\text{H}_5\text{S}^+$], 67 [87, C_5H_7^+], 65 [67, C_5H_5^+], 61 [150, $\text{C}_2\text{H}_5\text{S}^+$], 47 [31, CH_3S^+], 45 [92, CH_3S^+], 41 [33, C_3H_5^+], and 39 [42, C_3H_3^+]. Metastable ions were observed at m/e 250.7 (280 \rightarrow 265), 192.9 (280 \rightarrow 232), 101.8 (185 \rightarrow 137), 51.3 (280 \rightarrow 120), and 39.8 (280 \rightarrow 105).

Registry No.—II, 22003-57-2.

Acknowledgment.—The author is indebted to the U. S. Air Force Office of Scientific Research for partial support of this work under Grants AF-AFOSR-580-64 and AF-AFOSR-68-1435, and acknowledges helpful discussions with Professor P. R. Story of the University of Georgia.

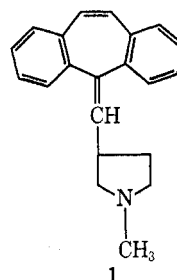
Nuclear Magnetic Resonance Spectra of 5-(1-Methyl-3-pyrrolidinylmethylene)-5H-dibenzo[*a,d*]cycloheptene

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Recently, Ebnöther, Jucker, and Stoll² showed the presence of atropisomerism in certain 5H-dibenzo[*a,d*]cycloheptene derivatives. We wish to report a similar observation of nmr spectroscopy studies on 5-(1-methyl-3-pyrrolidinylmethylene)-5H-dibenzo[*a,d*]cycloheptene.



The nmr spectrum of 1 in chloroform-*d* at room temperature had two N-methyl singlet bands at 2.15 and 2.28 ppm and two olefinic proton doublet absorptions centered at 5.58 and 5.63 ppm ($J = 9.1$ and 10.0 cps, respectively). As the temperature (nitrobenzene and *p*-anisaldehyde solutions) was increased, the nmr spectrum remained fairly constant up to about

(1) To whom inquiries should be directed.

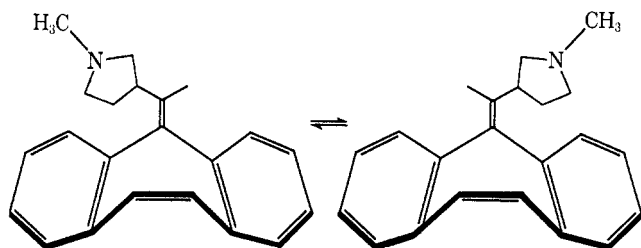
(2) A. Ebnöther, E. Jucker, and A. Stoll, *Helv. Chim. Acta*, **48**, 1237 (1965).

150°. The N-methyl peaks and the olefinic doublets started to coalesce between 150 and 160°. At the observed coalescence temperature, 200°, the two N-methyl peaks coalesced into a single, fairly sharp peak. The coalescence of the two olefinic doublets into one doublet was difficult to observe due to the small initial separation of the two doublets. The process was reversible, for as the temperature in the probe was lowered to the ambient probe temperature, the peaks reverted to the previously observed separations. The results were the same in both *p*-anisaldehyde and nitrobenzene solutions.

Cycloheptatriene has been shown,^{3,4} on the nmr time scale, to consist of an equilibrium pair of nonplanar conformers at -140°.



The more rigid 5H-dibenzo[*a,d*]cycloheptene structure consists of two conformers at even higher temperature⁵ (30°). The attachment of the bulky 1-methyl-3-pyrrolidinyl-methylene group to the 5 position of the dibenzocycloheptene system strongly affects the rate of inversion of the cycloheptatriene ring. Below the observed coalescence temperature (200°), the two nonplanar conformers are optical isomers. The 1-methyl-3-pyrrolidinylmethylene group contains an asymmetric carbon atom. These factors made **1** act below the coalescence temperature as though it were a mixture of the *dl* pairs.



Calculation⁶ of the free energy of activation (ΔG^\ddagger) and the rate constant (K_1) at the coalescence temperature (T_c) were made with the assumption that the conformers existed in an equimolar ratio and were of equal lifetimes. These assumptions are nearly correct, as the mixture ratio was *ca.* 60:40, and both isomers have small line width signals.

The calculation results are: $T_c = 200^\circ$; $K_1 = 22.2 \text{ sec}^{-1}$; $\Delta G^\ddagger = 25.0 \text{ kcal/mol}$.

Repeated attempts to separate the two *dl* pairs or to change the isomer ratio were unsuccessful.

Experimental Section

5-Hydroxy-5-(1-methyl-3-pyrrolidinylmethyl)-5H-dibenzo[*a,d*]cycloheptene.—The usual Grignard reagent technique was used for the preparation of 1-methyl-3-pyrrolidinylmethylmagnesium chloride from 10.0 g (0.075 mol) of 1-methyl-3-pyrrolidinylmethyl chloride,⁷ 1.82 g of magnesium, and 50 ml of THF.

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(6) J. A. Pople, W. G. Scheider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 218 and 366.

(7) Y. H. Wu and R. F. Feldkamp, *J. Org. Chem.*, **26**, 1519 (1961).

The Grignard reagent was treated with 5H-dibenzo[*a,d*]cyclohepten-5-one (10.3 g, 0.05 mol) of 50 ml of THF over a period of 30 min. The reaction mixture, after being stirred and refluxed for 18 hr, was decomposed with 35 ml of a saturated NaCl solution. The mixture was filtered and the solid cake was extracted with THF. The combined filtrates and extracts were concentrated to a glass residue (11.6 g, 75.4%). The glass product failed to crystallize. The hydrochloride salt melted at 222–224° (EtOH-ether).

Anal. Calcd for $C_{21}H_{23}NO \cdot HCl$: C, 73.78; H, 7.07; Cl, 10.37. Found: C, 73.94; H, 7.41; Cl, 10.20.

5-(1-Methyl-3-pyrrolidinylmethylene)-5H-dibenzo[*a,d*]cycloheptene.—A mixture of 5-hydroxy-5-(1-methyl-3-pyrrolidinylmethyl)-5H-dibenzo[*a,d*]cycloheptene (13 g, 0.043 mol), glacial acetic acid (200 ml), and concentrated HCl (80 ml) was refluxed for 1 hr. The mixture was concentrated to a syrupy mass, which was treated with 40 ml of water, made basic with 40% NaOH, and extracted with ether. The dried ethereal extract ($MgSO_4$) was concentrated and the oily residue was distilled under reduced pressure, giving an oily product, bp 170–190° (0.2 mm), yield 9.9 g (81%). The fumarate salt melted at 203–205° (absolute EtOH).

Anal. Calcd for $C_{21}H_{21}N \cdot \frac{1}{2}C_4H_4O_4$: C, 79.97; H, 6.71; N, 4.06; O, 9.26. Found: C, 79.69; H, 7.01; N, 3.93; O, 9.41.

Nmr Spectra.—Proton magnetic resonance spectra were obtained on a Varian A-60 spectrometer using the variable temperature controller. Line positions were measured with respect to tetramethylsilane as an internal reference, with the spectrometer calibration was checked according to the method of Tiers and Hotchkiss.⁸

Registry No.—**1**, 22158-31-2; hydrochloride of 5-hydroxy-5-(1-methyl-3-pyrrolidinylmethyl)-5H-dibenzo[*a,d*]cycloheptene, 22158-32-3; **1** (fumarate salt), 22188-55-2.

Acknowledgment.—We wish to thank Mr. Ross G. Pitcher of Varian Associates for providing the high-temperature spectra in nitrobenzene solution.

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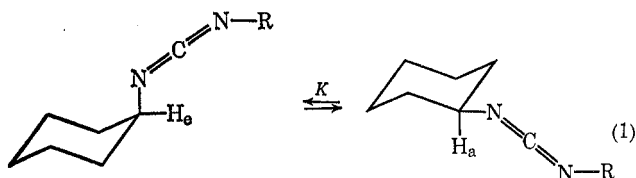
The *A* Value of the Carbodiimido Group. Conformational Requirements of "sp²-Hybridized" Lone Pairs

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In the course of an investigation of the conformational idiosyncrasies of heterocycles possessing atoms with lone pairs of electrons, we found it necessary to obtain an estimate of the relative steric requirement of sp²-hybridized nitrogen. This report concerns the measurement of the *A* value (eq 1 and 2)¹ of the carbodiimido group (N=C=NR).



R = cyclohexyl

$$A \text{ value} = -\Delta G^\circ = \frac{RT \ln K}{1000} \quad (2)$$

(1) S. Winstein and N. J. Holness, *J. Amer. Chem. Soc.*, **77**, 5562 (1955).