TABLE II

PHYSICAL PROPERTIES OF NITROALKANES

Nitroalkane[a]	Method	Bp, °C (mm)	$n^{20}D$	Lit. bp, °C (mm)	Lit. $n^{20}D$	Ref
4-Nitrononane[b]	B	55–57 (0.2)	1.4266			
4-Ethyl-2-nitrooctane[b]	B	62–64 (0.1)	1.4336			
2-Methyl-1-nitropropane	B	63–65 (52)	1.4050	140 (760)	1.4050	*c*
Cyclohexylnitromethane	B	48 (1.5)	1.4632	63–64 (3)	1.4635	*d*
2-Phenyl-1-nitroethane	B	74–75 (0.1)	1.5261	126 (14)	1.5270	*e*
1-Phenyl-2-nitropropane	B	67–69 (0.2)	1.5167	96 (2)	1.5159	*f*
1-Nitrohexane	A	80–81 (14)	1.4212	81 (15)	1.4225	*g*
2-Nitroheptane	A	67–70 (1.5)	1.4236	194 (760)		*h*
3-Nitrooctane	A	64–65 (0.2)	1.4240	101 (20)	1.4253	*i*
3-Ethyl-1-nitroheptane[b]	A	66–67 (0.1)	1.4359			

[a] The ir spectra of all compounds contained strong absorption in the 6.45–6.50 and 7.4–7.5 regions; nmr spectra of all compounds were consistent with their structures. [b] A new nitroalkane. [c] H. B. Hass, E. B. Hodge, and B. M. Vanderbilt, *Ind. Eng. Chem.*, **28**, 341 (1936). [d] R. W. Rimmer, Ph.D. Thesis, Purdue University, 1953. [e] S. Kaneo, *J. Pharm. Soc. Jap.*, **58**, 256 (1938). [f] N. Kornblum, J. E. Ungnade, A. M. White, B. Taub, and S. A. Herbert, *J. Amer. Chem. Soc.*, **77**, 5528 (1951). [g] A. I. Vogel, *J. Chem. Soc.*, 1847 (1948). [h] F. Beilstein, *Ber.*, **13**, 2028 (1880). [i] F. Asinger, G. Geiseler, and M. Hoppe, *ibid.*, **90**, 115 (1954).

TABLE III

ANALYSES OF NEW NITROALKANES

	Calcd, %			Found, %		
Nitroalkane	C	H	N	C	H	N
4-Nitrononane	62.34	11.08	8.09	62.55	11.10	7.95
3-Ethyl-1-nitroheptane	62.34	11.08	8.09	62.29	11.00	8.21
4-Ethyl-2-nitrooctane	64.13	11.30	7.48	64.33	11.34	7.55

heptane led to an 18% conversion to 2-nitro-2-heptene: ir (neat) 6.01 (C=C), 6.59, 7.47 μ (-NO_2); nmr ($CDCl_3$) δ 7.19 (t, 1, -CH=CNO_2), 2.5–2.0 (s and m, 5, CH_3CNO_2= and -CH_2-CH=), 1.40 [m, 4, -$(CH_2)_2$-], and 0.90 (m, 3, CH_3CH_2-).

Isolation of an Aldehyde Diacetate.—In the preparation of 3-nitrooctane, pentanal diacetate was isolated as an impurity from the distilled product: ir (neat) 5.69 (C=O), 8.04 μ (CO); nmr ($CDCl_3$) δ 6.78 [t, 1, -CH$(OAc)_2$], 2.08 (s, 6, CH_3-CO-), and 1.8–0.9 (m, 9, aliphatic protons).

Preparation of Nitroalkanes from Isolated Nitro Alcohols.—The following general procedure (B) was used. Exactly 20.4 g (0.2 mol) of acetic anhydride was added to a solution of 0.2 mol of the nitro alcohol and 5 drops of concentrated sulfuric acid contained in a 300-ml Morton flask equipped with an overhead stirrer. The temperature was regulated at 30–40° by means of an ice bath. The solution was allowed to stand for 0.5 hr at room temperature and 100 ml of a DMSO solution containing the appropriate amount of sodium borohydride (95–67% purity) was added over a 0.5-hr period at 20–25° with vigorous stirring. After 1 hr an aliquot containing theoretically 0.01 mol of product was taken and worked up for vpc analysis as in A.

The rest of the solution was worked up and distilled as reported in A. The new nitroalkanes prepared by this procedure are 4-nitrononane and 4-ethyl-2-nitrooctane, and the analytical data for these compounds are to be found in Table III. Physical properties of these compounds are presented in Table II.

Registry No.—3-Ethyl-1-nitroheptane, 34566-10-4; 4-nitrononane, 34566-11-5; 4-ethyl-2-nitrooctane, 34566-12-6; 4-nitro-5-nonanol, 34566-13-7; 2-nitro-1-butyl *N*-phenylcarbamate, 6526-60-9.

The Conformational Effect of the Spiro Linkage between Three- and Six-Membered Rings

JOSEPH B. LAMBERT,*[1a] JACK L. GOSNELL, JR.,[1b] AND DAVID S. BAILEY

Department of Chemistry, Northwestern University, Evanston, Illinois 60201

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The conformational properties of a six-membered ring linked in a spiro fashion to a three-membered ring are examined in spiro[2.5]octane (**1**), dispiro[2.2.2.2]decane (**2**), and 6-methylenespiro[2.5]octane (**3**). In contrast to the *exo*-methylene group, the spirocyclopropyl substituent has little effect on the barrier to ring reversal, and brings about only a slight flattening of the ring. It is concluded that the spiro linkage alters the hybridization of the orbitals of the quaternary carbon in comparison to those in unsubstituted cyclopropane. The free energies of activation to ring reversal were found to be 10.5 kcal/mol for **1**, 10.9 for **2**, and 8.7 for **3**. A complete line-shape analysis for the spectral changes of **2** gave E_a = 12.1 kcal/mol and log A = 13.8. The R values for **2** and **3** were measured to be 2.01 and 1.73, respectively.

Both the static and the dynamic conformational properties of a six-membered ring are considerably altered by the introduction of an *exo*-methylene or oxo grouping. The substituted carbon atom becomes nearly sp^2 hybridized, so that the valence angle within the ring is expanded over that in cyclohexane. A structural alteration of this type gives rise to a flattening distortion in the ring[2] and a diminished barrier to ring reversal.[3] The magnitude of the directly bonded ^{13}C-H coupling constant indicates that the hybridization of orbitals emanating from a cyclopropyl ring is similar to that from an ethylenic source. We therefore wished to investigate the effect of a spiro linkage between a six- and a three-membered ring on the shape

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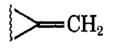
(1) (a) This work was supported by the National Science Foundation (Grant GP-22942) and by the Petroleum Research Fund, administered by the American Chemical Society (Grant 2970-AC4,5). (b) NDEA Fellow, 1966–1969; National Science Foundation Trainee, 1969–1970.

(2) J. B. Lambert, *J. Amer. Chem. Soc.*, **89**, 1836 (1967); J. B. Lambert, *Accounts Chem. Res.*, **4**, 87 (1971).

(3) J. T. Gerig and R. A. Rimerman, *J. Amer. Chem. Soc.*, **92**, 1219 (1970); F. R. Jensen and B. H. Beck, *ibid.*, **90**, 1066 (1968).

and the barrier to reversal of the larger ring. Three possible results could be imagined. (1) The spirocyclopropyl linkage (A) could give rise to a flattened


A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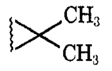
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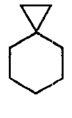
ring and a lower barrier, by analogy with the *exo*-methylene group (B). (2) The spirocyclopropyl linkage could more closely resemble a simple dialkyl substituent (C) and cause almost no observable effect on either. (3) An intermediate situation could transpire.

We selected the series **1**–**3** in order to examine these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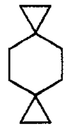
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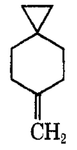
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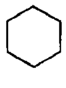
effects. For comparison with unsubstituted,[4] *gem*-dimethyl-substituted,[2,5] and *exo*-methylene-substituted[2,3,6] systems, we include for discussion literature data on **4**–**7**. We conclude that the spirocyclopropyl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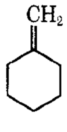
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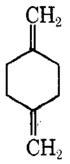
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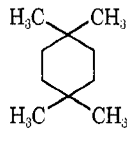
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group is conformationally more closely related to the *gem*-dimethyl group than to the *exo*-methylene group (case 2 above) and that the hybridization of the quaternary carbon in **1**–**3** is quite different from that in cyclopropane. The spiro linkage between three- and six-membered rings has previously been considered in a conformational context for certain 1,3-dioxanes,[7] for spiro[2.5]octan-6-ol,[8] and by us for dispiro[2.2.2.2]decane.[9]

Results

Spiro[2.5]octane (**1**) is a conformationally unbiased system in which ring reversal occurs rapidly on the nmr time scale at room temperature. The 60-MHz spectrum (Figure 1) consists of a broad singlet (δ 1.6) from the cyclohexyl protons not adjacent to the cyclopropyl group, a broad singlet (δ 1.4) from the protons on the adjacent carbons, and a sharp singlet (δ 0.38, not shown) from the cyclopropyl protons. As the temperature is lowered, the δ 1.4 peak broadens, passes through coalescence at $-49°$, and emerges as a well-resolved multiplet at $-107°$. This multiplet consists of a doublet at high field due to the equatorial protons and further resonances at low field due to the axial protons but obscured by other peaks. The assignment of the high-field resonance is determined from its doublet structure. The equatorial protons next to the spiro linkage, with only one major (geminal) coupling, are expected to give a doublet, whereas the axial protons, with two major couplings (geminal and axial–axial vicinal), should be a triplet. The peak at δ 1.6 also changes with temperature, although less drastically. The cyclopropyl peak broadens only slightly. The spectral changes for the δ 1.4 protons can be treated as a coupled A_2-to-AB system, and the free energy of activation for ring reversal is calculated from eq 1 and 2. The chemical-shift difference, determined by doubling the distance between the room-temperature δ 1.4 peak and the mean of the $-107°$ upfield doublet, was found to be 0.97 ppm, and the coupling constant 11 Hz. Insertion of these figures into eq 1 and 2 gives $\Delta G^{\ddagger} = 10.6$ kcal/mol at $-49°$.

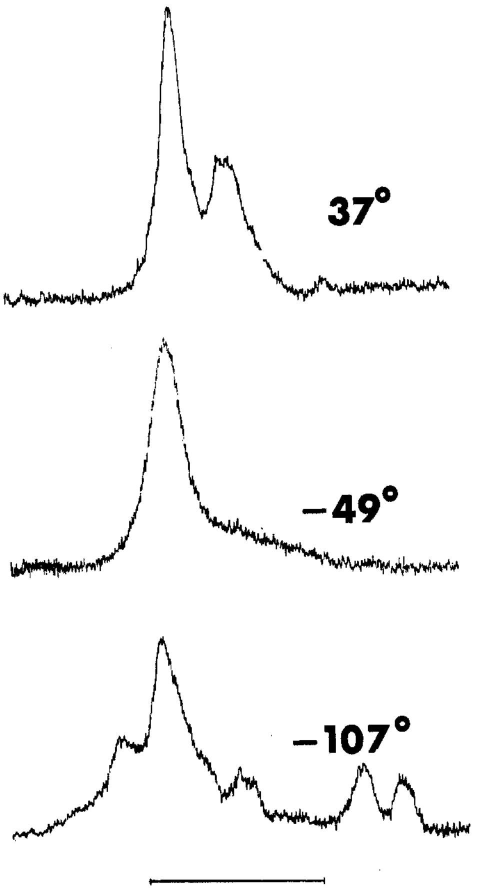

Figure 1.—The 60-MHz proton spectrum of spiro[2.5]octane (1) in 1:1 toluene-d_8/CH_2Cl_2 as a function of temperature. Only the cyclohexyl resonances are shown. The index bar represents 40 Hz.

$$k_c = \frac{\pi}{\sqrt{2}}(\Delta\nu_{AB}^2 + 6J_{AB}^2)^{1/2} \qquad (1)$$

$$\Delta G_c^{\ddagger} = 2.3RT_c(10.32 + \log T_c/k_c) \qquad (2)$$

The spectrum of dispiro[2.2.2.2]decane (**2**) is composed of two equal-area singlets (δ 0.1 and 1.2). The cyclohexyl resonance (Figure 2) passes through coalescence at about $-45°$ to give an AA′BB′ spectrum

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[4] F. A. L. Anet, M. Ahmad, and L. D. Hall, *Proc. Chem. Soc.*, 145 (1964); F. A. Bovey, F. P. Hood, III, E. W. Anderson, and R. L. Kornegay, *J. Chem. Phys.*, **41**, 2041 (1964); E. W. Garbisch, Jr., and M. G. Griffith, *J. Amer. Chem. Soc.*, **90**, 6543 (1968).

[5] H. Friebolin, W. Faisst, H. G. Schmid, and S. Kabuss, *Tetrahedron Lett.*, 1317 (1966).

[6] M. St.-Jacques and M. Bernard, *Can. J. Chem.*, **47**, 2911 (1969).

[7] (a) J. E. Anderson, *Chem. Commun.*, 669 (1969); 417 (1970); (b) J. E. Anderson, *Org. Magn. Resonance*, **3**, 475 (1971).

[8] A. S. Orahovats, V. S. Dimitrov, and S. L. Spassov, *J. Mol. Struct.*, **6**, 405 (1970); R. D. Stolow, T. Groom, and P. D. McMaster, *Tetrahedron Lett.*, 5781 (1968).

[9] J. B. Lambert, J. L. Gosnell, Jr., D. S. Bailey, and L. G. Greifenstein, *Chem. Commun.*, 1004 (1970).

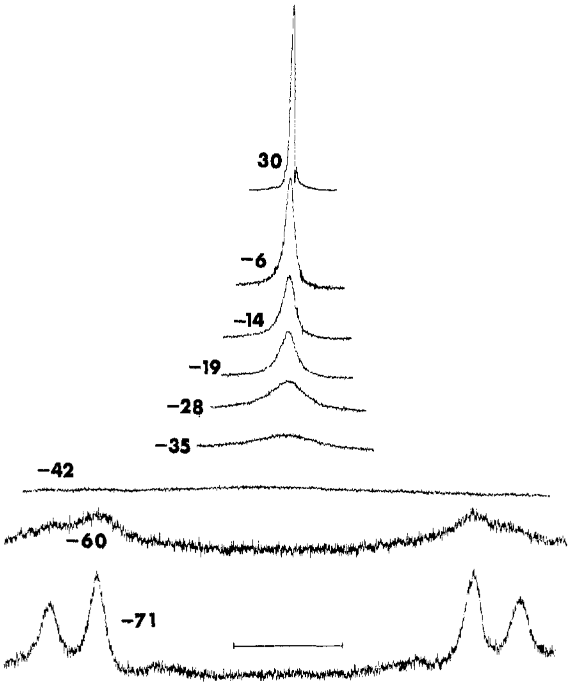


Figure 2.—The 60-MHz proton spectrum of dispiro[2.2.2.2]-decane (2) in toluene-d_8 as a function of temperature. Only the cyclohexyl resonances are shown. The index bar represents 20 Hz.

below −70°. The form of the spectral pattern closely resembles an AB quartet ($\Delta\nu$ = 1.21 ppm) because of the particular magnitudes of the coupling constants. Below −100° the cyclopropyl resonance broadens to a poorly resolved multiplet. We have performed a complete line-shape analysis on the spectral changes of the cyclohexyl resonance for each of 25 temperatures (Experimental Section). The following activation parameters were obtained from the Arrhenius plot (correlation coefficient = 0.998): E_a = 12.1 kcal/mol; log A = 13.8; $\Delta H^{\ddagger}$ = 11.5 kcal/mol; $\Delta S^{\ddagger}$ = 2.5 eu; $\Delta G^{\ddagger}$ (−45°) = 10.9 kcal/mol. An identical free energy of activation was calculated at the coalescence temperature by eq 1 and 2. The downfield carbon-13 side band of the cyclohexyl resonances was examined at room temperature for both 60- and 90-MHz spectra. Analysis of the side-band spectrum by usual techniques[2] gave J_{trans} = 7.75 Hz and J_{cis} = 3.85 Hz, for a ratio R of 2.01.

The spectrum of 6-methylenespiro[2.5]octane (**3**) contains a broad singlet at δ 4.7 from the alkenic protons, and AA′BB′ spectrum at δ 2.25 and 1.45 from the cyclohexyl protons, and a sharp singlet at δ 0.4 from the cyclopropyl protons. The lower field half of the AA′BB′ spectrum is attributed to the protons next to the *exo*-methylenic substituent, because of the presence of a long-range coupling. Irradiation of the alkenic protons produces an AA′BB′ spectrum with the required mirror symmetry. Analysis of this pattern gave J_{trans} = 8.04 and J_{cis} = 4.61 Hz for a ratio R of 1.74. As the temperature is lowered, the spectrum of **3** undergoes several changes. The upfield portion of the AA′BB′ spectrum (the methylene protons next to the spiro linkage) coalesces at −93° (60 MHz) and gives a slow-exchange spectrum at −111° that is very similar to the pattern produced by the δ 1.4 peak of **1**: a high-field doublet and a low-field multiplet, separated by 0.98 ppm. Application of eq 1 and 2 to these specific changes gives a free energy of activation at T_c (−93°) of 8.7 kcal/mol.

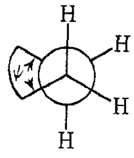
Discussion

The conformational effects of the spirocyclopropyl group may be discussed in terms of the static property of ring deformation and the dynamic property of barrier size to ring reversal. Table I collects the available data on these subjects for compounds **1–7**, *i.e.*, free energies of activation calculated at the coalescence temperature and torsional angles for the $-CH_2CH_2-$ fragment (**8**) calculated from the R values.[2]

TABLE I

FREE ENERGIES OF ACTIVATION AND DISTORTION PARAMETERS

Compd	$\Delta G_c^{\ddagger}$, kcal/mol	T_c, °C	R	Ψ, deg	Ref
1	10.5	−43			This work
2	10.9	−45	2.01	57	This work
3	8.7	−93	1.74	54	This work
4	10.2	−67	2.16	58	4
5	8.4	−100	1.83	55	3
6	7.5	−118	1.42	51	2, 6
7	11.5	−53	2.05	57	2, 5



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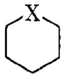
The spirocyclopropyl group, like the *gem*-dimethyl group, conveys almost no distortion to the cyclohexane ring, at most a flattening of about a degree. In contrast, the *exo*-methylene group gives rise to a considerable flattening. Comparison of **2** with **6**, in which the six-membered ring bears either two *exo*-methylene or two spirocyclopropyl groups, reveals a torsional difference of 6°. The compound that contains both the methylene and the spirocyclopropyl groups (**3**) exhibits a flattening (ψ ~54–55°) similar to that in molecules with only the methylene group (**5**). Analogy between the double bond and the cyclopropane ring therefore does not hold up in the conformational sense.

A similar conclusion is reached from consideration of barriers to ring reversal. The barriers for compounds with zero (**4**), one (**1**), and two (**2**) spirocyclopropyl substitutents are 10.2, 10.5, and 10.9 kcal/mol. The corresponding series for molecules possessing exocyclic double bonds (**4**, **5**, **6**) is 10.2, 8.4, and 7.5 kcal/mol. The contrast between the double-bond and the cyclopropyl systems is particularly evident in a comparison of the dimethylene compound with the dispiro compound (**6** and **2**), in which the barriers differ by about 3.4 kcal/mol.

The conclusion from both the ring-deformation and the ring-reversal data is that the spirocyclopropyl group has little conformational effect on the six-membered ring. The spiro linkage must actually change the hybridization of the cyclopropyl orbitals at the quaternary carbon in comparison with those in unsubstituted cyclopropane. The central carbon in spiro[2.2]pentane is sp^3 by symmetry, despite its location in three-membered rings.[10] Although lacking the precise symmetry constraints of spiropentane, the spiro carbon of **1**–**3** apparently has four orbitals that are all close to sp^3, in contrast to those in cyclopropane itself, which contains two sp^2 C–H orbitals and two sp^5 C–C orbitals.

It is interesting that the barrier to reversal is not an additive function of substitution or of ring deformation. Addition of the first double bond (**4** → **5**) reduces the barrier by about 1.8 kcal/mol, but the second double bond (**5** → **6**) provides an additional decrease of only 0.9 kcal/mol. For the same reason, the barrier for the functionally mixed compound **3** is not midway between those for **2** and **6**. The barrier to ring reversal is primarily a function of the ease of rotation about the bonds within the ring. Steric hindrance and ring deformations, unless extreme, have a less important role. The presence of one exocyclic double bond provides a fragment of the six-membered ring that has a lower torsional barrier than any in cyclohexane. Reversal therefore probably begins with deformation of this portion of the ring. Introduction of the second exocyclic double bond provides an additional site for the same process, rather than for any new torsional operation. The fact that exocyclic double bonds flatten the ring probably does not bear directly on the question of the magnitude of the reversal barrier. Thus, **5** is flattened by about 3° with respect to cyclohexane and has a barrier 1.8 kcal/mol lower, whereas **6** is flattened an additional 4° but has a barrier only another 0.9 kcal/mol lower. Analogously, ring puckering does not raise the barrier to reversal. In the series tetrahydropyran, thiane, selenane, tellurane (**9**, X = O, S, Se, Te) puckering increases significantly but the barrier decreases monotonically.[2,11]



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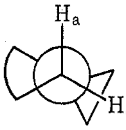
One further aspect of the nmr spectra of **1**–**3** deserves comment. The chemical-shift difference between the axial and equatorial protons on the carbons adjacent to the spirocyclopropyl group is 0.97, 1.21, and 0.98 ppm, respectively for **1**, **2**, and **3**, greatly enhanced from 0.48 ppm observed for cyclohexane.[4] The doublet pattern observed in each of the spiro cases for the upfield resonance is attributed to the equatorial proton, with only one major coupling, rather than to the axial proton, with two major couplings, as noted already. Because the reverse situation occurs in the spectrum of cyclohexane (axial resonance upfield), the net relative shift must be the sum of the chemical-shift differences observed in **1**–**3** and that in cyclohexane, or a total of 1.5–1.7 ppm.

The higher shielding of the axial proton in cyclohexane has been attributed to its location in the shielding region of the anisotropic single bonds elsewhere in the molecule. The reversed and enhanced effect for these spirocyclopropyl systems can be understood by examination of the Newman projection **10**. The equatorial proton is located directly over the shielding region of the highly anisotropic cylopropane ring, and the axial proton is located in the neutral or deshielding zone. The net result is a strong shift of the equatorial protons to higher field. Effects along these lines have been observed previously in related systems.[7b,9,12]



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Experimental Section

Nmr spectra were recorded on Varian Associates T-60 and A-60 spectrometers and the Bruker HFX-90 spectrometer. Line-shape analyses were carried out on the Control Data Corp. 6400 computer equipped with a CalComp plotting accessory. Vapor phase chromatography was performed on the F & M Model 700.

Spiro[2.5]octane (1) was purchased from Chemical Samples Co., Columbus, Ohio, and used without further purification.

6-Methylenespiro[2.5]octane (3) and Dispiro[2.2.2.2]decane (2).—To 7.5 g (0.13 mol based on zinc) of Zn/Cu couple stirred in 300 ml of dry ether was added a mixture of 26 g (0.095 mol) of CH_2I_2 in 100 ml of dry ether. After the mixture had refluxed for 1 hr, 5.0 g (0.045 mol) of 1,4-bis-*exo*-methylenecyclohexane (**6**, Chemical Samples Co.) in 200 ml of dry ether was added, and the stirred mixture was refluxed overnight. The cooled mixture was filtered under vacuum and the filtrate was washed with 3 × 50 ml of saturated aqueous NH_4Cl, 3 × 50 ml of saturated aqueous $NaHCO_3$, and 3 × 50 ml of saturated aqueous NaCl. A flocculent white precipitate was observed in the combined aqueous washings. The ether solution was dried ($MgSO_4$), filtered, and reduced by distillation to a small volume. Separation of the two products was afforded by preparative vapor phase chromatography utilizing a 6 ft × 0.25 in. column (15% THEED, 3% KOH, Chromosorb W 60/80) at 120° or a 14 ft × 2 in. column (Dow-Corning 550 on Chromosorb P) at 150°. Retention times on the former column were 12, 15, and 18 min for **6**, **3**, and **2**. On the latter column the times were 35, 45, and 55 min, respectively. At the ice–water collection temperature **3** was a liquid and **2** a solid. The collected materials were chromatographically pure. The structures were confirmed by their nmr spectra.

Complete line-shape analysis of the temperature-dependent spectra of **2** (Figure 2) gave the following values for the mean lifetime ($\tau = k^{-1}$): 28.3° (0.000010), 14.3 (0.000032), 9.8 (0.000045), 5.8 (0.000063), −1.0 (0.000081), −4.2 (0.000095), −6.5 (0.000120), −9.3 (0.000140), −12.1 (0.000160), −14.4 (0.00020), −16.7 (0.00032), −19.6 (0.00040), −22.9 (0.00055), −25.7 (0.00073), −28.1 (0.00100), −31.5 (0.00160), −35.8 (0.0023), −43.6 (0.0060), −44.1 (0.0060), −46.5 (0.0065), −47.5 (0.0100), −50.5 (0.0120), −53.5 (0.020), −58.4 (0.026), −61.4 (0.056).

Registry No.—**1**, 185-65-9; **2**, 24518-94-3; **3**, 34959-75-6.

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[10] R. D. Bertrand, D. M. Grant, E. L. Allred, J. C. Hinshaw, and A. B. Strong, *J. Amer. Chem. Soc.*, **94**, 997 (1972).

[11] J. B. Lambert, R. G. Keske, and D. K. Weary, *ibid.*, **89**, 5921 (1967); unpublished results with D. H. Johnson and C. E. Mixan.

[12] J. Tadanier and W. Cole, *J. Org. Chem.*, **27**, 4610 (1962); J. B. Uebel and J. C. Martin, *J. Amer. Chem. Soc.*, **86**, 4618 (1964).