less than 0.7%, which was worse than that for ^{14}C (<0.3%).

Kinetic isotope effects were then calculated by nonlinear regression analysis with use of eq 2 in the text. Error limits shown in Table I are the standard deviations of the isotope effect values calculated for each x with use of eq 4, in which A_∞ was the value determined by regression analysis with use of eq 2.

$$ {}^{H}k/{}^{T}k = \frac{\log(1-x)}{\log[1-(xA_x/A_\infty)]} \qquad (4) $$

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Registry No. 1 (Z = *m*-Br; X = *p*-Cl), 88801-92-7; **1** (Z = *m*-Br; X = H), 88801-93-8; **1** (Z = *m*-Br; X = *p*-CH_3), 88801-94-9; **1** (Z = *m*-Br; X = *m*-NO_2), 88801-95-0; **1** (Z = *m*-Br; X = *p*-CH_3O), 88801-96-1; **1** (Z = H; X = *p*-CH_3O), 53226-51-0; **1** (Z = H; X = CH_3), 1024-41-5; **1** (Z = H; X = H), 38632-84-7; **1** (Z = H; X = *p*-Cl), 13086-79-8; **1** (Z = H; X = *m*-NO_2), 55735-65-4; **2** (Y = *p*-CH_3O), 701-56-4; **2** (Y = *p*-CH_3), 99-97-8; **2** (Y = H), 121-69-7; **2** (Y = *m*-CH_3O), 15799-79-8; **3** (x = *p*-Cl; Y = *p*-CH_3O; Z = H), 88801-97-2; **3** (X = H; Y = *p*-CH_3O; Z = H), 88801-98-3; **3** (X = *p*-CH_3; Y = *p*-CH_3O; Z = H), 88825-18-7; **3** (X = *m*-NO_2; Y = *p*-CH_3; Z = H), 88825-19-8; **3** (X = *p*-Cl; Y = *p*-CH_3; Z = H), 88801-99-4; **3** (X = H; Y = *p*-CH_3; Z = H), 88802-00-0; **3** (X = *p*-CH_3; Y = *p*-CH_3; Z = H), 88802-01-1; **3** (X = *p*-CH_3O; Y = *p*-CH_3; Z = H), 88802-02-2; **3** (X = *m*-NO_2; Y = H; Z = H), 88802-03-3; **3** (X = *p*-Cl; Y = H; Z = H), 88802-04-4; **3** (X = Y = Z = H), 88802-05-5; **3** (X = *p*-Cl; Y = *p*-Br; Z = H), 88802-07-7; **3** (X = *m*-NO_2; Y = *p*-Br; Z = H), 88802-08-8; **3** (X = *m*-NO_2; Y = *m*-NO_2; Z = H), 88825-21-2; **3** (X = *p*-Cl; Y = *p*-CH_3O; Z = *m*-Br), 88802-10-2; **3** (X = *m*-NO_2; Y = *p*-CH_3; Z = *m*-Br), 88802-12-4; **3** (X = *p*-Cl; Y = *p*-CH_3; Z = *m*-Br), 88802-13-5; **3** (X = H; Y = *p*-CH_3; Z = *m*-Br), 88802-14-6; **3** (X = *p*-CH_3; Y = *p*-CH_3; Z = *m*-Br), 88802-15-7; **3** (X = *p*-CH_3O; Y = *p*-CH_3; Z = *m*-Br), 88825-22-3; **3** (X = *p*-Cl; Y = *m*-CH_3O; Z = *m*-Br), 88802-17-9; **3** (X = *p*-Cl; Y = *p*-Br; Z = *m*-Br, 88802-19-1; tritium, 10028-17-8; carbon-14, 14762-75-5; **2** (Y = *p*-Br), 586-77-6; **2** (Y = *m*-NO_2), 619-31-8.

Conformation of a Saturated 13-Membered Ring

B. H. Rubin,*[†] M. Williamson,[†] M. Takeshita,[†] F. M. Menger,[†] F. A. L. Anet,[‡] B. Bacon,[‡] and N. L. Allinger[§]

Contribution from the Department of Chemistry, Emory University, Atlanta, Georgia 30322, Department of Chemistry, University of Georgia, Athens, Georgia 30602, and Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024.

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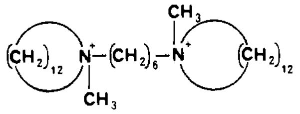
Abstract: The synthesis and X-ray structure elucidation of α,ω-bis(methyldodeca-1,12-diylammonio)hexane dibromide permitted an examination of the conformation of a 13-atom macrocycle. Such rings are of interest because they lie on the borderline between "medium" and "large" ring systems and are generally considered very complex with a variety of conformational possibilities. It is shown that the ring assumes a [33331] geometry in agreement with force-field calculations carried out on cyclotridecane and 1,1-dimethylcyclotridecane. Disorder in one portion of the molecule was resolved by a combination of molecular mechanics and crystallographic least-squares refinement.

In the course of synthesizing space-encompassing molecules,[1] we secured a crystalline bolaform electrolyte[2] bearing two saturated 13-membered rings.



This substance afforded us an opportunity to determine the conformation of a 13-atom heteromacrocycle for which the "the conformational situation is very complex, with a variety of conformational candidates".[3] A diamond-lattice model has been used for defining idealized geometries for macrocyclic rings; however, only rings containing an even number of atoms can be made to superimpose on a diamond lattice, since all bonds must occur in pairs.[4] It has been suggested, on these grounds, therefore, that these odd-membered macrocyclic rings must be distorted with respect to their bond lengths, bond angles, dihedral angles, or combinations thereof.[4] In these odd-membered macrocycles bonding distortion is expected to be minimized when the rings exist as three- or five-cornered conformations.[5] Anet and Rawdah[6] and Dale[7] have calculated the energy for a number of cyclotridecane conformations and find the three- and five-cornered conformations depicted in Figure 1 to be among those of lowest energy. A crystal structure of a hydroxylcyclotridecylphosphonate containing two independent molecules in the asymmetric unit has been reported in which each of the molecules has a strikingly different conformation.[8]

Much more is known about rings with 12 and 14 atoms. Cyclododecane assumes a "square" [3333] conformation in preference to the diamond lattice configuration since the latter possesses three unfavorable H/H repulsions. Both X-ray data and low-temperature ^{13}C NMR confirm this picture.[9,10] Cyclotetradecane, on the other hand, is a totally strain-free diamond-lattice system (the smallest saturated ring above six atoms so endowed).[11] The 14-membered ring has a "rectangular" [3434] geometry with two parallel chains held at roughly van der Waals distances.[11] Unfortunately, cyclotridecane (on the borderline between the

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[†] Emory University.

[‡] University of California.

[§] University of Georgia.

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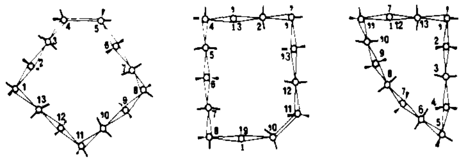
Table I. Crystallographic Data and Data Collection Summary for $C_{32}H_{66}N_2Br_2$

space group	$P\bar{1}$	crystal dimensions, mm	0.4 × 0.2 × 0.1
M_r	638	radiatn	Mo Kα(λ = 0.7107 Å)
Z	1	μ, mm^{-1}	1.93
unit cell dimensions			
a, Å	7.581 (4)	scan type	$\theta/2\theta$
b, Å	7.315 (4)	$2\theta_{max}$, deg	45
c, Å	18.470 (12)	scan rate (min), deg min^{-1}	2.02
α, deg	109.96 (4)	scan rate (max), deg min^{-1}	29.3
β, deg	99.23 (4)	scan width (min), deg	±1
γ, deg	107.67 (4)	peak/bkgd scan time	1
V, Å^3	876.5 (8)	unique reflcns measured	2297
d(calcd), mg m^{-3}	1.21	unique reflcns $\|F\| > 3\sigma(F)$	1769
d(exptl), mg mm^{-3}	1.19 (2)	F(000)	342



[33331] [43312] [643]

Figure 1. Numbering scheme for the cyclotridecane conformation considered.

"medium" and "large" rings) has defied ^{13}C NMR analysis[9] because fast pseudorotation processes lead to a single peak, even at −135 °C. We thus thought it valuable to examine the conformation of our macrocyclic bolaform by X-ray crystallography, to compare its structure to those previously reported for saturated 13-membered rings, and to estimate the relative conformational energies of these and related structures. A novel approach combining energy minimization and least-squares crystallographic refinement, used to resolve the disorder in the ring structure, is also reported.

Experimental Section

Synthesis of α,ω-Bis(methyldodeca-1,12-diylammonio)hexane Dibromide. An ethanol solution (25 mL) containing 3.2 g (0.016 mol) of *N*-methylazacyclododecane[12] and 1.86 g (0.0076 mol) of 1,6-dibromohexane was heated to reflux for 72 h. After allowing for the reaction mixture to cool, the solvent was removed by evaporation and the product recrystallized from diethyl ether/ethanol solution as colorless, poorly formed crystals: yield 50%; mp 256–257 °C; ^{1}H NMR ($CDCl_3$) δ 3.98–3.33 (12 H, m, NCH_2), 3.43 (6 H, br, s, NCH_3), 2.40–1.25 (48 H, m, CH_2). Anal. Calcd for $C_{32}H_{66}N_2Br_2$: C, 60.18; H, 10.42; N, 4.39. Found: C, 59.99; H, 10.43; N, 4.32.

X-ray Crystallographic Studies. A crystal with a waxy appearance approximately 0.4 × 0.2 × 0.1 mm was affixed on a quartz fiber, using epoxy cement, mounted on a goniometer head, and used for measuring cell dimensions and intensities. The measurements were made at 292 K by using a Syntex $P2_1$ four-circle diffractometer equipped with molybdenum X-ray tube and graphite monochromator. The cell constants and orientation matrix were determined by unconstrained least-squares refinement of 15 reflections with Bragg angles between 9.48 and 17.32°. The cell constants and other crystallographic data are given in Table I.

A total of 2297 unique reflections were collected with $\theta_{max} = 22.5°$. Of these, 1769 reflections had intensities greater than $3\sigma(F)$ and were used in the structure solution and refinement. The 004, 020, and 200 reflections were measured every 100 reflections and fluctuated by less than 5% over the course of the data collection. The data were corrected for background, and by a Lorentz and polarization factor, but were not corrected for absorption. The linear absorption coefficient for the molecule under Mo Kα radiation is 1.93 mm^{-1}. Crystallographic computations were carried out on a Digital Equipment PDP-10 computer using SHELX-76,[13] on an Eclipse 140/S using SHELXTL (Nicolet XRD, Fremont, CA), on a Univac 90/80 using ORTEP,[14] and on a Tektronix 4054 using MODIS.[15] The analytical approximation for the atomic scattering factors from the "International Tables for Crystallography"[16] were used in the structure factor calculations.

Structure Refinement. The bromine atom was located from a Patterson synthesis, and the rest of the non-hydrogen atoms were placed after successive difference Fourier syntheses. The atom C_6 was particularly difficult to locate and appeared to have distorted bond lengths and bond angles with the adjacent atoms. Anisotropic refinement showed this atom and those adjacent to it to have pronounced ellipticity approximately parallel to the plane of the ring. A Fourier synthesis at this stage of the refinement showed a peak of 1.9 e/Å^3 near C_6. Repositioning C_6 at this site simply produced difference density near the original C_6 position. In addition the bond distances and angles about C_6 deviated by as much as 0.13 Å and 6° from accepted values.

Cycles of blocked cascade least-squares refinement were repeated until convergence starting from the ordered, anisotropic model which minimized the size of the residual electron density. The positions of the hydrogens on atom C_{3-10} were fixed at their calculated values while the remaining hydrogen atoms were located from electron density difference syntheses and their positions were allowed to refine independently. An isotropic temperature factor was refined for each hydrogen atom. The R value for the ordered anisotropic model was 0.075; R_w was 0.075 ($w = 1.0/(\sigma(F)^2 + 0.00205F^2)$).

A number of disordered models were tested, none of which profoundly improved the fit to the observed diffraction data. The most successful of these was a disordered model constructed by taking the positions of the atoms from the anisotropic model and allowing the occupancy factors for atoms C_5, C_6, and C_7 to vary along with alternate positions for these atoms. Likely alternate positions were chosen by examining models and carrying out energy minimization using the MM2 program.[17] Three conformations, A, B, and C, were found, which had energies in the order: A more stable than B, B more stable than C. Using these three structures, preliminary refinement showed that C had a very low average occupancy factor. Accordingly, C was eliminated and the two remaining sets of positions, conformations A and B, were used in the subsequent refinement. The A coordinates were those from the ordered anisotropic refinement. The alternate C_{6B} position was fixed at a site corresponding to the residual electron density. The C_{5B} and C_{7B} were then determined by minimizing the strain energy in the ring keeping all other atoms fixed. The positional and thermal parameters for all atoms and the occupancy factors for the disordered atoms were then allowed to vary by using the crystallographic data as the basis for least-squares refinement. Temperature factors for the disordered atoms were isotropic and hydrogens on these atoms were not included in the model. The hydrogens on the remaining atoms in the structure were treated as they were in the refinement of the ordered structure. The occupancy of atom C_{5B} refined to a near zero value, and it was eliminated from the model. The refinement converged with $R = 0.077$ and $R_w = 0.078$ ($w = 1.0/((F)^2 + 0.00243F^2)$. While the fit to the data is slightly poorer than when the ordered structure was used, the bond lengths and angles now become more reasonable.

Strain Energy Calculations. Strain energy calculations were carried out with Boyd's iterative program MOL-BUILD.[18-23] This program was

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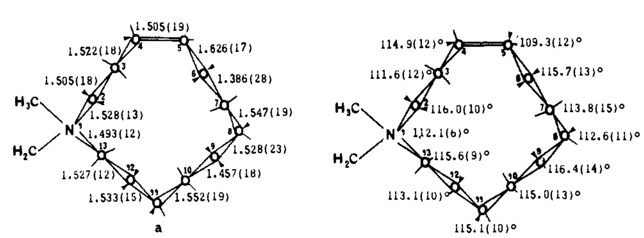

Figure 2. Bond distances and angles for the ordered, anisotropic refined model of the 13-atom macrocycle. The distances are in angstrom units and the numbers in parentheses indicate the estimated standard deviation in the least significant digits.

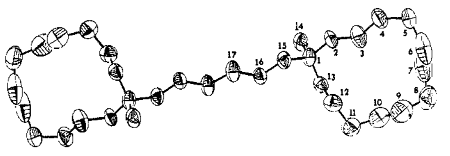

Figure 3. ORTEP drawings showing the ordered, anisotropic structure. The designations indicated for the asymmetric unit correspond to those used in the tables.

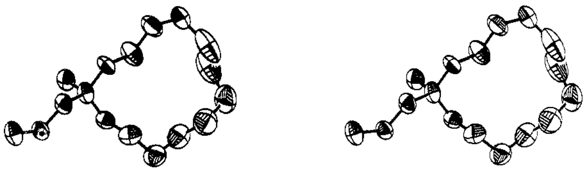

Figure 4. Stereoview of the ring portion of the refined, ordered, anisotropic structure.

modified to allow conformational changes to occur by varying the appropriate torsional angles as described by Wiberg and Boyd.[24] Approximate coordinates for trial geometries were obtained by using the torsional and internal angles derived from previous strain energy calculations for the parent cyclotridecane. Although the strain energies reported correspond to molecules in a hypothetical motionless state at 0 K, the zero-point energy and vibrational enthalpy effects are expected to be similar for the different conformations of a given cycloalkane. All conformations reported are true energy minima as is evidenced by the fact that these are all calculated to have $3N - 6$ real vibrational frequencies.

A nomenclature based on Dales "wedge" system has been adopted to represent the three lowest three-dimensional molecular conformations of *gem*-dimethyl-substituted cyclotridecanes and the parent compound (Figure 1).

Results and Discussion

X-ray Crystal Structure. Positional and equivalent isothermal thermal parameters for the ordered, anisotropic structure are presented in Table II. The bond distances and angles for the ordered anisotropic structure are summarized in Figure 2. Figure 3 shows the entire molecule with the atom designations for the asymmetric unit, and Figure 4 shows a stereoview of the ring portion of this molecule resulting from the ordered, anisotropic treatment of the structure. In viewing the thermal ellipsoids and scanning the list of equivalent isotropic thermal parameters in Table II, one notes the highest values for atom C_9 and the atoms flanking it. There is a trend of decreasing thermal motion in the ring carbons on either side of these atoms. In itself this is suggestive of the conformational disorder in the macrocycle. The appearance of the residual electron density in the electron density maps based on the ordered, anisotropic refinement result gives additional evidence of disorder. The distances and angles resulting from the refinement of the disordered structure are summarized in Figure 5, and a stereoimage of the superimposed A and B conformations is presented in Figure 6. The "interwoven" structure, shown shaded in Figure 6 represents result of the disordered structure refinement. These shaded atoms account for less than 20% of the scattering from the two disordered atoms, and the R value for the disordered structure is significantly larger than that for the ordered, anisotropic model. The bond angles and distances in the disordered structure show no better agreement with expected values as well.[25]

Table II. Fractional Coordinates and Equivalent Isotropic Thermal Parameters. The Numbers in Parentheses Represent the Estimated Standard Deviation in the Least Significant Digits

atom	x/a	y/b	z/b	$U_{eq}{}^a$
Br	0.9113 (1)	0.7786 (2)	0.6290 (1)	0.069 (1)
N1	0.770 (10)	0.6160 (10)	0.3467 (4)	0.058 (4)
C2	0.8277 (13)	0.6217 (14)	0.2717 (5)	0.060 (5)
C3	0.9193 (17)	0.4702 (19)	0.2356 (6)	0.086 (7)
C4	0.9674 (18)	0.4861 (18)	0.1605 (6)	0.092 (7)
C5	1.0252 (18)	0.3140 (18)	0.1120 (7)	0.094 (7)
C6	0.8352 (25)	0.0948 (27)	0.0660 (8)	0.138 (12)
C7	0.8162 (24)	−0.0473 (24)	0.1011 (9)	0.138 (11)
C8	0.6078 (19)	−0.2141 (20)	0.0741 (8)	0.116 (8)
C9	0.4725 (22)	−0.1239 (22)	0.1133 (7)	0.123 (8)
C10	0.4991 (17)	−0.0819 (18)	0.1981 (7)	0.098 (7)
C11	0.3826 (16)	0.0417 (16)	0.2395 (7)	0.090 (6)
C12	0.4681 (13)	0.2797 (15)	0.2627 (6)	0.074 (5)
C13	0.6514 (13)	0.3974 (14)	0.3344 (5)	0.060 (5)
C14	0.9513 (13)	0.7050 (15)	0.4151 (6)	0.070 (5)
C15	0.6600 (13)	0.7626 (13)	0.3664 (5)	0.061 (5)
C16	0.5915 (12)	0.7884 (13)	0.4388 (5)	0.060 (4)
C17	0.5297 (14)	0.9779 (15)	0.4616 (5)	0.068 (5)

[a] Equivalent isotropic U defined as one-third the trace of the orthogonalized U tensor.

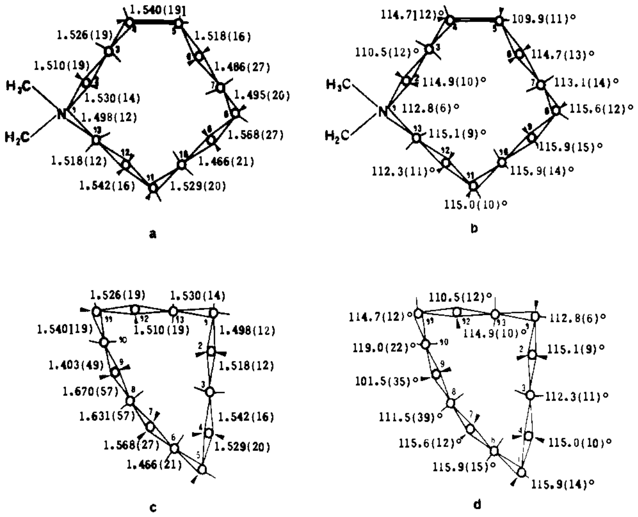

Figure 5. Bond distances and angles for A and B conformations of the 13-atom macrocycle. (a) and (b) are the distances and angles for conformation A; (c) and (d) are the distances and angles for conformation B. Distances are in angstrom units and the numbers in parentheses represent the estimated standard deviation in the least significant digits.

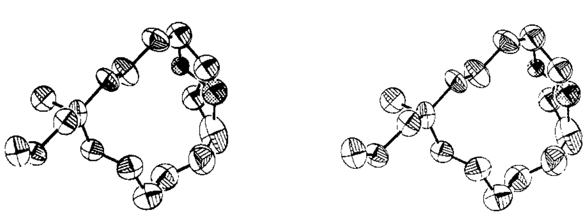

Figure 6. ORTEP stereoimage of the superimposed A and B conformations of the 13-membered macrocyclic ring. The shaded atoms represent less than 20% of the scattering from atoms C_5 and C_6.

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Table III. Calculated Strain Energies[a] (kcal/mol) of Various Energy Minimum Conformations of Cyclotridecane[b] and 1,1-Dimethylcyclotridecane

compound	methyls[c]	E_r	E_θ	E_ϕ	E_{nb}	E_T	E_{Δ_1}	E_{Δ_2}	E_{Δ_3}
1, [33331] cyclotridecane		0.73	2.00	4.49	5.01	12.23			
1a, [33313] 1,1-dimethylcyclotridecane	C1	1.04	2.58	4.43	5.25	13.30	0	0	0
1b, [33133] 1,1-dimethylcyclotridecane	C11	1.11	2.81	4.53	5.69	14.14	0.84	0	0.84
1c, [33313] 1,1-dimethylcyclotridecane	C8	1.10	2.63	4.82	5.82	14.36	1.06	0	1.06
1d, [33331] 1,1-dimethylcyclotridecane	C5	1.15	3.41	4.02	6.02	14.60	1.30	0	1.30
1e, [33331] 1,1-dimethylcyclotridecane	C4	1.14	3.12	4.61	5.99	14.85	1.55	0	1.55
2, [43312] cyclotridecane		0.77	2.26	5.15	5.38	13.56			
2a, [34213] 1,1-dimethylcyclotridecane	C1	1.10	2.83	5.11	5.65	14.68	1.38	1.33	0.05
2b, [42133] 1,1-dimethylcyclotridecane	C4	1.11	2.88	5.09	5.68	14.76	1.46	1.33	0.13
2c, [43312] 1,1-dimethylcyclotridecane	C8	1.12	2.91	5.19	5.94	15.17	1.87	1.33	0.54
3, [643] cyclotridecane		0.76	2.06	5.67	5.32	13.81			
3a, [634] 1,1-dimethylcyclotridecane	C5	1.07	2.47	5.83	5.57	14.94	1.64	1.58	0.06
3b, [463] 1,1-dimethylcyclotridecane	C1	1.08	2.61	5.67	5.67	15.02	1.72	1.58	0.14
3c, [643] 1,1-dimethylcyclotridecane	C11	1.19	2.97	5.66	6.70	16.53	3.23	1.58	1.65

[a] The following symbols are used: E_r, bond length strain; E_θ, angle strain; E_ϕ, torsional strain; E_{nb}, nonbonded interaction strain. Total strain energy, $E_T = E + E_\theta + E_\phi + E_{nb}$. Additional strain energy of 1,1-dimethylcyclotridecane relative to 1,1-dimethylcyclotridecane having lowest total strain energy, $E_{\Delta_1} = E_T - E_T(1a)$. Difference in strain energy ascribed only to conformation of ring skeleton, neglecting effects of methyl groups, $E_{\Delta_2} = E_T(\text{parent cyclotridecane}) - E_T(1)$. Strain energy of adding a gem-dimethyl group relative to the strain energy of placing the dimethyl group at C-1 of [33331] conformation, $E_{\Delta_3} = E_{\Delta_1} - E_{\Delta_2}$. [b] Data reproduced from: Anet, F. A. L.; Rawdah, T. N. *J. Am. Chem. Soc.* 1978, *100*, 7810. [c] For numbering, refer to Figure 1.

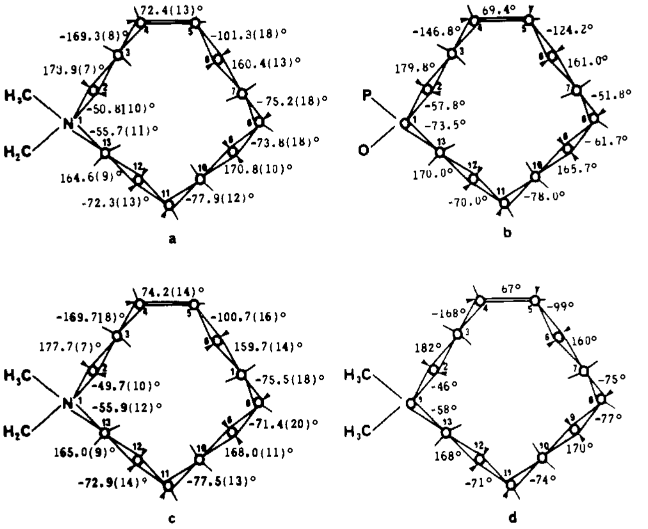

Figure 7. Torsion angles for minimum energy conformation and the X-ray crystal structures of 13-membered rings. The dihedral angles for the following structures are indicated: (a) the ordered anisotropic refinement of dodeca-1,12-diylammonium bromide, (b) molecule **1** of the cyclotridecane hydroxyl phosphonate structure from Samuel and Weiss[8] with the torsion angles inverted to simplify comparison, (c) the refined conformation A of the disordered model, (d) calculated lowest energy *gem*-dimethyl-substituted cyclotridecane corresponding to **1c** in Table V.

For both the ordered anisotropically refined structure and the refined conformation A of the disordered model, the "corner geometry" of the ring remains the same. The macrocycle appears as a [33331] systems with "corners" at N_1, C_4, C_5, C_8 and C_{11}. The dihedral angles for the methyldodeca-1,12-diylammonium salt are summarized in Figures 7 and 8. If one considers the dihedral angles of the ordered structure, there is a pseudodiad axis passing from C_{10} to midway between the C_3–C_4 bond. These dihedral angles and their symmetry very closely resemble the structure observed in one of the two molecules in the hydroxylcyclotridecylphosphonate crystal structure. Samuel and Weiss[8] denote this molecule as molecule **1**. It too has [33331] geometry. In the second molecule of the hydroxylcyclotridecylphosphonate crystal structure, however, larger thermal parameters and a different geometry are observed. The second independent molecule in the hydroxylcyclotridecylphosphonate structure, molecule **2**, displays a pseudodiad along a line from atom C_6 to the midpoint of the C_{12}–C_{13} bond, which Samuel and Weiss note.[8] In addition molecule **2** has a second, less perfect diad axis passing from C_1 through the midpoint of the C_7–C_8 bond. Thus molecule **2** appears to have approximate [33133] geometry.

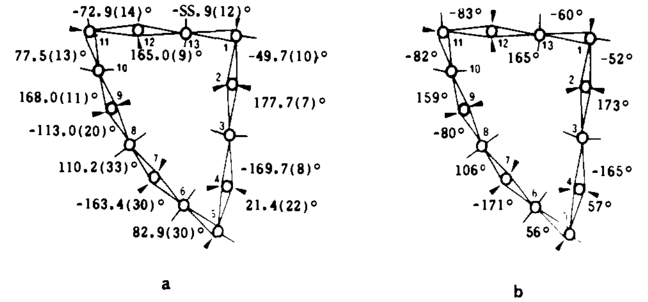

Figure 8. Torsion angles for refined disordered conformation B and for the calculated [643] conformation. (a) shows the crystallographically determined torsion angles for the disordered structure, and (b) shows the angles calculated for the [643] configuration.

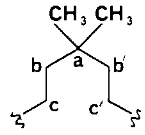

Figure 9. *gem*-Dimethyl angle designations.

Strain Energy Calculations. The results of the strain energy calculations performed on the cyclotridecane with *gem*-dimethyl groups placed at various "corner" positions, along with the parent compound, are shown in Table III. The dimethyl derivatives are all seen to have total strain energies from 1 to 2.7 kcal/mol higher than the parent cyclotridecane having the same conformation. Approximately 1 kcal/mol of this increase is ascribed to a uniform increase of 0.3–0.4 kcal/mol in bond length strain (E_r) and to an increase of approximately 0.6 kcal/mol in angle strain (E_θ). These increases arise generally from elongation of bonds C_a–C_b and C_a–$C_{b'}$ and from expansion of angles C_a–C_b–C_c and C_a–$C_{b'}$–$C_{c'}$ (Figure 9).

The only real discrepancies to these generalizations occur in the additional angle strain energy exhibited by compounds 1d and 1e. These additional increases appear to be due to the additional expansion of the "corner" angle opposite to the corner containing the *gem*-dimethyl groups. Since the torsional strain energy (E_ϕ) for each dimethyl compound is approximately the same as that for the parent cyclotridecane having the same conformation, the largest fluctuation in strain energy is therefore due to the nonbonded interaction strain (E_{nb}); additional E_{nb} strain involving

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(25) Fractional coordinates, anisotropic thermal parameters, and structure factor tables for the ordered and disordered structures are available as supplementary material.

Table IV. Deviation in Torsional Angles of 1,1-Dimethylcyclotridecanes Relative To Those Found in the Parent Cyclotridecane Having the Same Conformation

compd	conformation	methyls	Σ|dev in ϕ|	largest |dev in ϕ|
1a	[33331]	C1	5°	2°
1b	[33331]	C11	18°	4°
1c	[33331]	C8	36°	7°
1d	[33331]	C5	22°	7°
1e	[33331]	C4	28°	6°
2a	[43312]	C1	15°	4°
2b	[43311]	C4	14°	3°
2c	[43312]	C8	30°	7°
3a	[643]	C5	18°	4°
3b	[643]	C1	11°	2°
3c	[643]	C11	38°	6°

the methyl group carbon atoms is present. This additional strain varies according to the methyl group placement.

In Table III, E_{Δ_3} represents the additional strain energy in adding a *gem*-dimethyl group to cyclotridecane relative to the lowest energy case; the difference in strain energy due merely to the ring skeleton conformation has been corrected for by subtracting E_{Δ_2} from E_{Δ_1}. Table IV suggests that this additional strain energy is higher in cases where the methyl groups force larger changes in the torsional angles than those found in the respective parent cyclotridecane.

As reflected by E_{Δ_1} (in Table III) the dimethylcyclotridecane having the *gem*-dimethyl group at C_1 of the [33331] conformation (Figure 1) has the lowest strain energy (13.30 kcal/mol) with the strain energies of the other dimethyl compounds increasing largely according to the respective increase in nonbonded interaction strain (E_{nb}). This lowest energy conformation compares with that found crystallographically for the 13-membered ring compound reported here and one of the two molecules reported by Samuel and Weiss[8] (Figure 7). The second molecule in the cyclotridecane hydroxyl phosphonate appears to have a geometry corresponding to compound **1b** and thus to have a calculated strain energy approximately 0.84 kcal/mol greater than that of the other molecule in the asymmetric unit and the structure reported here.

Conformational Interconversions in 1,1-Dimethylcyclotridecanes. Since the X-ray data indicate disorder, which could involve a facile conformational interconversion, molecular mechanics calculations were carried out on the energy required to distort the [33331] conformation, particularly in the vicinity of C_5 to C_8. Major changes in the two torsional angles, C_6–C_7–C_8–C_9 and C_4–C_5–C_6–C_7 in fact result in and interchange of the [33331] and the [643] conformations, with a calculated barrier of 6.9 kcal/mol (from the more stable [33331] conformation). This barrier, which is quite high compared to thermal energies at room temperature, implies two distinct conformations. Interconversion between them, however, would be rapid on the laboratory or NMR time scales.

While the torsional angles for the ordered structure (Figure 7a) and for conformation A (Figure 7c) agree to approximately 10° with those calculated for the [33331] conformation, one torsional angle of conformation B, C_7–C_8–C_9–C_{10}, deviates by 36° from that calculated for the respective [643] conformation (Figure 8). To see what this deviation does to the strain energy, torsional angle C_7–C_8–C_9–C_{10} of the [643] conformation was driven from the initial −80° value to −112° by 8° increments. An energy maximum of 15.21 kcal/mol is found at a torsional angle of −97°, and this represents a conformational energy barrier of only 0.25 kcal/mol.

The further driving of the same torsional angle gives the previously calculated [33124] conformation, whose strain energy is very slightly lower that that of the the [643] conformation (Table III). Thus these two conformations are close in energy and are separated by a very small barrier. Such a situation should lead to a favorable entropy for this group of conformations when considered as a unit. In fact, this system should be considered as a single conformation that is undergoing a rapid librational motion.

A proper calculation of the entropy requires a knowledge of the potential energy surface, followed by vibrational analysis. However, an approximate treatment can be used in which the librating system is replaced by several distinct species. Thus, if, for simplicity, three equally energetic species are considered (e.g., the [643], [33124], and an intermediate "conformation") and if the energy difference with the [33331] conformation is 1.6 kcal/mol (approximately the mean difference), then the combined population of the three species is 17% at room temperature, in excellent agreement with the 20% minor conformation required by the X-ray data.

Acknowledgment. We are grateful to the National Science Foundation and the National Institutes of Health for support of this work.

Supplementary Material Available: Tables I–IX of atomic coordinates, temperature factors, hydrogen coordinates, and structure factors for disordered anisotropic and ordered model refinement and crystallographic data (30 pages). Ordering information is given on any current masthead page.

9-Mesityl-9,10-dihydro-9-boraanthrylidene: A Probe of Structure and Reactivity for Aromatic Carbenes

Stephen C. Lapin, Beth-Ellen Brauer, and Gary B. Schuster*

Contribution from the Department of Chemistry, Roger Adams Laboratory, University of Illinois, Urbana, Illinois 61801. *Received August 18, 1983*

Abstract: Photolysis of 10-diazo-9-mesityl-9,10-dihydro-9-boraanthracene (**1**) causes loss of nitrogen and formation of 9-mesityl-9,10-dihydro-9-boraanthrylidene (BA). Direct irradiation leads first to the singlet carbene, which intersystem crosses to the triplet. Photosensitization with triplet 2-acetonaphthone gives the triplet carbene directly. The singlet carbene reacts with isopropyl alcohol to give the appropriate ether. The triplet carbene forms cyclopropanes nonstereospecifically from terminal olefins and abstracts hydrogen atoms from hydrocarbons and alcohols. Kinetic and product analysis shows that, in contrast to fluorenylidene, the rate of equilibrium between ^{1}BA and ^{3}BA is slow compared with most of the bimolecular reactions of the triplet. This is believed to be a consequence of the larger energy gap between ground-state ^{3}BA and ^{1}BA compared with that of fluorenylidene. The effect of carbene structure on the magnitude of this energy gap is discussed.

The chemical and physical properties of carbenes have intrigued a generation of chemists.[1] Intensive experimental and computational research has focused on the difference in structure, in energy, and in reactivity between the two lowest electronic states

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