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The Conformational Energy Surface of *trans,trans,trans*-1,5,9-Cyclododecatriene

Frank A. L. Anet* and T. N. Rawdah

Contribution No. 3959 from the Department of Chemistry, University of California, Los Angeles, California 90024. Received February 10, 1978

Abstract: ^1H and ^{13}C NMR spectra of *trans,trans,trans*-1,5,9-cyclododecatriene (**1**) have been measured from -5 to -180 °C. A dynamic NMR effect is observed in the ^1H spectra only, and this effect is associated with a conformational process which has a free energy of activation of 8.6 kcal/mol. These results are consistent with a single D_3 conformation for the triene. The conformational energy surface for ring inversion of the D_3 conformation to its mirror-image conformation has been investigated by iterative force-field calculations. The (strain energy) barrier of the best path for the ring inversion of the D_3 conformation is calculated to be 9.5 kcal/mol, in good agreement with the experimental (free energy) barrier. A systematic nomenclature is introduced in order to describe the conformations and transition states associated with the complex energy surface of **1**.

The trimerization of 1,3-butadiene by Ziegler-type catalysts provides an important source of 12-membered rings.^{1,2} Under suitable conditions, *trans,trans,trans*-1,5,9-cyclododecatriene (**1**) is the predominant product, and it can be easily isolated in a pure state because of its relatively high melting point (34 °C). An x-ray diffraction structure of this isomer reveals a conformation with approximately D_3 symmetry;³ a very similar structure has also been found in the $\text{Ni}(0)$ complex⁴ of this triene. The infrared and Raman spectra of **1** have been analyzed⁵ in terms of a D_3 structure and valence force constants have been deduced for this molecule. Ermer and Lifson⁶ have made use of the known conformation and vibrational frequencies of this triene to optimize force-field parameters which can be applied to unsaturated hydrocarbons in general. Dale and Greig⁷ have observed a dynamic NMR effect in the methylene protons of **1** and have calculated a ΔG^\ddagger value of about 9 kcal/mol for site exchange of these protons. Dale has also briefly discussed conformational interconversions in **1**, and has pointed out that exchange of the methylene proton sites in the D_3 conformation requires a ring inversion to the mirror-image conformation.

In this paper, we investigate conformational interconversions in *trans,trans,trans*-1,5,9-cyclododecatriene by dynamic NMR and force field calculations.

Experimental Section

NMR spectra were obtained on a superconducting solenoid operating at 59 kG.^{9,10} The proton spectra were obtained with standard 5-mm sample tubes in a frequency-sweep mode. The ^{13}C spectra are Fourier transforms of accumulated free induction decays and were obtained with 10-mm tubes under the following conditions: 45° pulse angle, 8K data points, 11-kHz spectrum width, and an exponential broadening function corresponding to 4 Hz broadening. A mixture of $\text{CHCl}_2\text{F}-\text{CHClF}_2$ (4:1) was used as a solvent, and a ^{19}F line of the solvent was employed for lock purposes. All temperatures were

measured with a copper-constantan thermocouple situated in the probe a few centimeters below the sample.

Force-field calculations were carried out on an IBM-360/91 computer at the Campus Computer Network of UCLA, with a slightly modified version of Boyd's Molecular Builder IIA.¹¹

Results and Discussion

NMR Data. ^{13}C NMR spectra of *trans,trans,trans*-1,5,9-cyclododecatriene were obtained from -5 to -180 °C. The allylic and vinylic carbon resonances occur at 32.9 and 132.7 ppm, respectively, at -12 °C, and these resonances show little chemical shift changes at lower temperatures. No dynamic NMR effect of any kind was observed. These results are in agreement with a single conformation of D_3 symmetry for the triene.

The ^1H NMR spectra of the all-*trans* triene showed a clear dynamic NMR effect at about -90 °C (Figure 1). The methylene proton resonance changes from a single line (δ 2.06) at -60 °C to two somewhat broad resonances (δ 1.90 and 2.26) at -138 °C. The coalescence temperature is -92 °C. Some fine structure is visible in the spectrum at -138 °C. Splittings due to spin-spin couplings should be very complex and are not expected to be well resolved. Since the chemical shift between the nonequivalent methylene protons is much larger (90 Hz) than any anticipated coupling constant, the rate constant at the coalescence temperature should be well approximated by the equation¹² $k = \pi\Delta\nu/\sqrt{2}$. Application of the absolute rate theory¹³ with a transmission coefficient of 1 gives a free energy of activation (ΔG^\ddagger) of 8.6 ± 0.2 kcal/mol at -92 °C.

The splitting of the methylene resonance into two equal intensity peaks at -138 °C and the lack of any splitting in the ethylenic proton resonance (δ 5.08) are in agreement with a D_3 conformation. Our ^1H NMR results are in reasonable agreement with the 60-MHz data of Dale and Greig,^{7,8} who report a ΔG^\ddagger of about 9 kcal/mol.

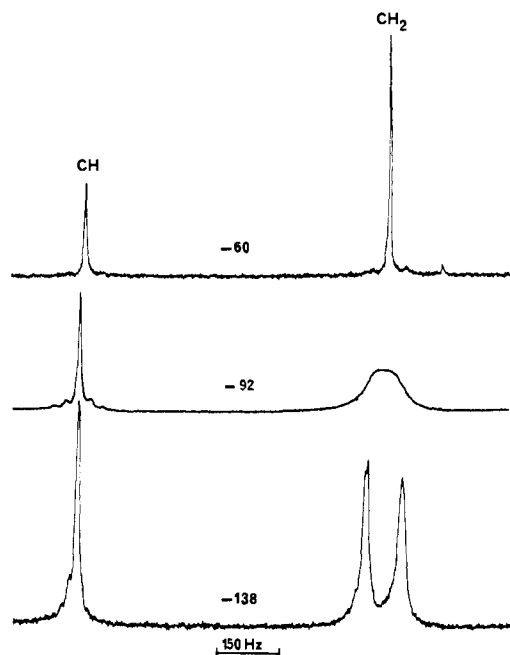


Figure 1. 251-MHz ^1H NMR spectra of *trans,trans,trans*-1,5,9-cyclododecatriene in $\text{CHCl}_2\text{F}/\text{CHClF}_2$ (4:1).

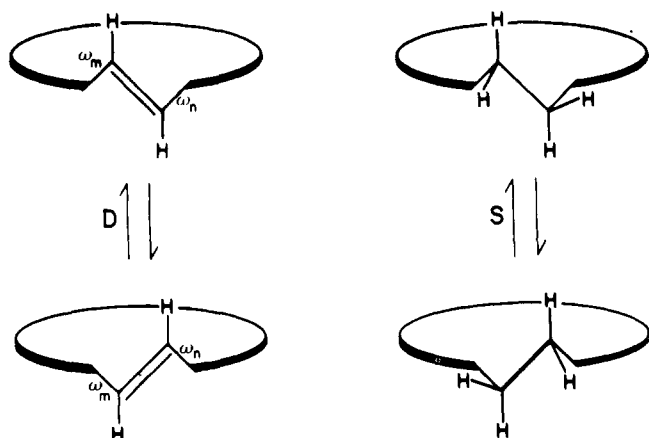


Figure 2. Orientations of $\text{CH}_2\text{-CH}_2$ and *trans* $\text{CH}=\text{CH}$ groups with respect to the general plane of the ring, and diagrammatic representations of *D* and *S* processes.

Conformational Nomenclature. As pointed out by Dale,⁸ ring inversion of the D_3 conformation of **1** requires a rotation of each of the three *trans* double bonds by 180° and changes in the signs of the torsional angles of the three $\text{CH}_2\text{-CH}_2$ bonds. The planes of the double bonds are approximately at right angles to the general plane of the ring, as shown in Figure 2. It is convenient to refer to a process which changes the sign of the torsional angle of a $\text{CH}_2\text{-CH}_2$ single bond as an *S* process;¹⁴ also, rotation of a *trans* double bond by $120\text{-}180^\circ$ will be called a *D* process (Figure 2). Force-field calculations to be described below show that a *D* process always changes the sign of the *average* value of the torsional angles of the two $\text{sp}^3\text{-sp}^2$ single bonds (ω_n and ω_m) that are adjacent to the double bond (Figure 2). *D* and *S* processes can be carried out on molecular models of **1** in any arbitrary order and this generates new conformations, which may be intermediates in the ring inversion of the D_3 conformation. The lowest energy path for ring inversion is not readily apparent from molecular models, but it can be investigated by iterative force-field calculations. Before presenting the results of such calculations, it is desirable to set up a nomenclature to describe all the

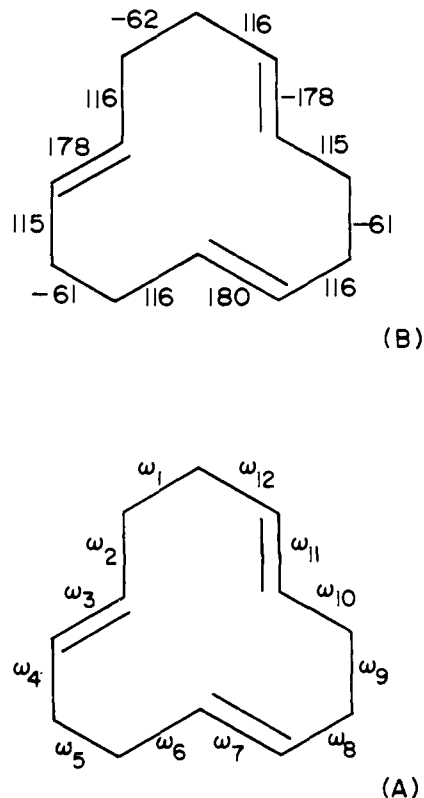


Figure 3. (A) Labeling of torsional angles in **1**. (B) Calculated torsional angles in the lowest energy conformation of **1** (defined as [00]).

Table I

binary number	octal form	binary number	octal form
000	0	100	4
001	1	101	5
010	2	110	6
011	3	111	7

conformations generated by sequences of *D* and *S* processes.

Since both the *S* and *D* processes are twofold in nature, i.e., two successive *S* or *D* processes applied to the same residue restore the original conformation, the "isomers" generated by these processes can be labeled by the binary digits, 0 and 1. With six centers of twofold isomerism six binary digits are required to describe the 64 (2^6) conformational combinations. There are 12 ring torsional angles, which are labeled $\omega_1\text{-}\omega_{12}$, as shown in Figure 3A. We arbitrarily assign to the D_3 conformation shown in Figure 3B the designation [000 000] in binary notation. The first three digits (from left to right) define the isomerism which is associated with the signs of ω_1 , ω_5 , and ω_9 , respectively (Figure 3A) and can be altered by *S* processes. The second three digits define the isomerism which is associated with the signs of $\omega_{2,4}^{\text{av}}$ (average of ω_2 and ω_4), $\omega_{6,8}^{\text{av}}$ (average of ω_6 and ω_8), and $\omega_{10,12}^{\text{av}}$ (average of ω_{10} and ω_{12}), respectively (Figure 3A) and can be altered by *D* processes. As an example, the set [100 000] defines a conformation obtained from the [000 000] conformation by an *S* process carried out on ω_1 . The set [110 011], on the other hand, defines a conformation formed from the [000 000] conformation by two *S* and two *D* processes carried out on ω_1 , ω_5 , $\omega_{6,8}^{\text{av}}$, and $\omega_{10,12}^{\text{av}}$. The sequence in which these *S* and *D* operations are carried out, e.g., *SSDD*, *SDSD*, etc., gives rise to distinct paths having different energy barriers.

For simplicity, the binary representation of a conformation

Table II. Conformational Combinations, Equivalences, and Names in *trans,trans,trans*-1,5,9-Cyclododecatriene

conformational combinations ^a and equivalences ^b	name ^a
[00]	[00]
[77]	[77]
[01], [02], [04]	[01]
[76], [75], [73]	[73]
[10], [20], [40]	[10]
[67], [57], [37]	[37]
[11], [12], [22], [24], [41], [44]	[11]
[66], [65], [55], [53], [36], [33]	[33]
[13], [26], [45]	[13]
[64], [51], [32]	[32]
[03], [05], [06]	[03]
[74], [72], [71]	[71]
[14], [21], [42]	[14]
[63], [56], [35]	[35]
[17], [27], [47]	[17]
[60], [50], [30]	[30]
[15], [16], [23], [25], [43], [46]	[15]
[62], [61], [54], [52], [34], [31]	[31]
[07]	[07]
[70]	[70]

^a Conformations are arranged vertically in pairs. The members within a pair are mirror images of each other. ^b Horizontally arranged conformations are equivalent (i.e., they are superposable in the absence of labeling).

can be written in octal form by grouping the binary digits into two groups of three, with each group translated as shown in Table I. Thus, the octal representations of [000 000] and [110 001] are [00] and [61], respectively. The 64 conformational combinations are listed in Table II, and may be divided into two sets of 32 enantiomeric conformations. Enantiomeric pairs have representations which are complementary, i.e., their sum is [77]; e.g., [13] and [64] are enantiomeric conformations, even if the atoms of a given torsional angle are labeled. Owing to the presence of symmetry in **1** only 10 enantiomeric pairs (a total of 20 conformations) are nonsuperposable. Equivalent conformations are represented by the conformation with the smallest octal representation (Table II). As an example, the equivalent conformations [11], [12], [22], [24], [41], and [44] are represented by [11].

Force-Field Calculations. Approximate coordinates of the D_3 conformation, [00], of *trans,trans,trans*-1,5,9-cyclododecatriene (Figure 3B) were obtained from the program COORD¹⁵ using torsional angles estimated from a Dreiding-Fieser molecular model. Refined torsional angles (Table IV), coordinates, and strain energy contributions (Table III) were then obtained by applying Boyd's iterative computer program, MOLBUILD IIA.^{11,16} In order to determine the lowest path for ring inversion of the [00] conformation, we have

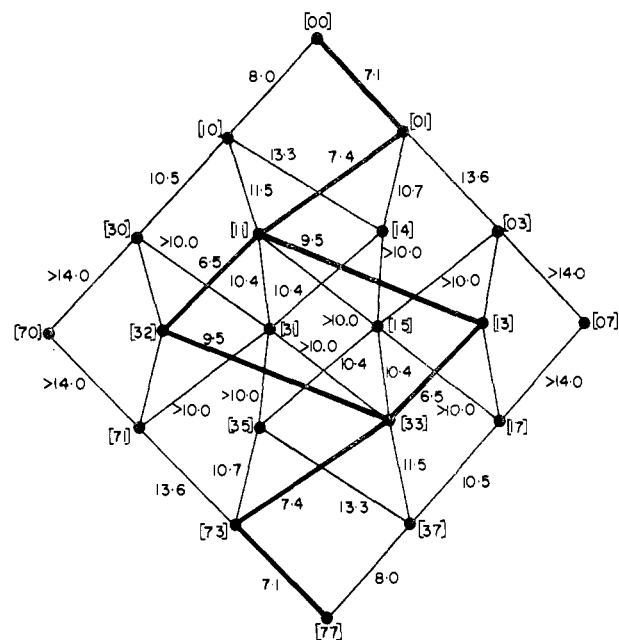


Figure 4. Graph of intermediate conformations (shown by circles) obtained by all possible sequences of *S* and *D* processes carried out on the [00] (D_3) conformation of *trans,trans,trans*-1,5,9-cyclododecatriene. The numbers shown alongside the lines are the calculated strain energies (kcal/mol) of the transition states relative to the strain energy of the [00] or [77] conformations.

systematically investigated all possible paths (based on sequences of *S* and *D* processes)¹⁷ from the [00] to the [77] conformation. The graph of these paths¹⁸ is shown in Figure 4. The circles represent conformational intermediates, whose strain energies and torsional angles are given in Tables III and IV, respectively. A number next to a line in the graph represents the strain energy, relative to that of the [00] conformation, of the transition state associated with that line. Strain energy contributions and torsional angles for these transition states are given in Tables V and VI, respectively. Strain energies were not calculated for all the possible transition states, since this is unnecessary for the purpose of determining the best ring inversion path, as will be discussed below. Each possible path from [00] to [77] is associated with several intermediates and transition states and it is the transition state with the highest absolute energy (the path barrier) which determines the kinetics of the ring inversion process via that path. Thus, the best path for ring inversion in **1** is that with the lowest path barrier. As can be seen from the graph, there are two equivalent but distinct paths, and these are indicated by thick lines in the graph. These paths are shown as energy profiles in Figure 5.

The best path has a barrier of 9.5 kcal/mol, and the highest

Table III. Calculated Strain Energies^a (kcal/mol) in Energy-Minima Conformations of *trans,trans,trans*-1,5,9-Cyclododecatriene

conformation	E_r	E_θ	E_ϕ	E_δ	E_{nb}	E_T	E_Δ
[00]	0.174	0.727	0.184	0.030	0.580	1.7	0.0
[01]	0.288	1.539	0.939	0.240	1.936	4.9	3.2
[10]	0.319	1.982	1.046	0.291	2.287	5.9	4.2
[11]	0.275	1.466	2.848	0.375	1.908	6.9	5.2
[13]	0.254	1.001	4.095	0.432	1.842	7.6	5.9
[03]	0.413	2.427	2.428	0.538	3.202	9.0	7.3
[14]	0.416	2.409	3.693	0.407	3.412	10.3	8.6
[17]	0.425	2.313	3.990	0.491	3.618	10.8	9.1
[15]	0.358	1.950	6.068	0.270	2.664	11.3	9.6
[07]	0.522	2.841	7.618	0.516	4.100	15.6	13.9

^a The following symbols are used: E_r , bond length strain; E_θ , angle strain; E_ϕ , torsional strain; E_δ , out-of-plane strain; E_{nb} , nonbonded interaction strain. Total strain energy, $E_T = E_r + E_\theta + E_\phi + E_\delta + E_{nb} + E_\Delta$, strain energy relative to the [00] conformation.

Table IV. Calculated Torsional Angles in Energy-Minima Conformations of *trans,trans,trans*-1,5,9-Cyclododecatriene

conformation ^b	sp ³ -sp ³ torsional angles ^a			sp ³ -sp ² torsional angles ^a						sp ² -sp ² torsional angles ^a		
	ω_1	ω_5	ω_9	ω_2	ω_4	ω_6	ω_8	ω_{10}	ω_{12}	ω_3	ω_7	ω_{11}
[00] ^c	-62	-62	-62	116	116	116	116	116	116	-178	-178	-178
[01]	-50	-63	-57	-107	-10	128	116	117	113	177	-177	-170
[03] ^d	-42	-66	-42	-101	-2	-2	-101	116	116	177	177	-163
[07]	-47	-32	-61	-27	-56	-85	-3	-8	-71	165	174	172
[10] ^d	63	-53	-53	16	120	116	116	120	16	-175	-170	-175
[17] ^d	55	55	-49	26	26	27	123	123	27	-171	-170	-170
[11]	63	-40	-50	-116	-96	116	123	121	31	178	-166	-177
[14]	-41	-55	57	-92	-12	131	20	30	117	171	-172	-169
[13] ^d	36	-69	36	95	108	108	95	-124	-124	179	179	164
[15]	36	-50	-57	89	103	-69	-6	-42	-123	-177	173	170

^a See Figure 3A for the disposition of torsional angles ω_1 - ω_{12} . ^b All conformations have C_1 symmetry, except where otherwise stated. ^c D_3 symmetry. ^d C_2 symmetry.

Table V. Calculated Strain Energies^a (kcal/mol) in Various Energy-Maxima Geometries of *trans,trans,trans*-1,5,9-Cyclododecatriene

transition state	E_r	E_θ	E_ϕ	E_δ	E_{nb}	E_T	E_Δ
{[00] \rightleftharpoons [01]} [#]	0.401	1.586	3.435	0.379	2.987	8.8	7.1
{[01] \rightleftharpoons [03]} [#]	0.613	3.012	5.967	0.859	4.820	15.3	13.6
{[00] \rightleftharpoons [10]} [#]	0.243	1.444	6.651	0.148	1.223	9.7	8.0
{[10] \rightleftharpoons [30]} [#]	0.406	2.442	6.025	0.139	3.177	12.2	10.5
{[01] \rightleftharpoons [11]} [#]	0.247	1.500	5.352	0.212	1.764	9.1	7.4
{[01] \rightleftharpoons [14]} [#]	0.372	2.283	7.078	0.063	2.630	12.4	10.7
{[10] \rightleftharpoons [14]} [#]	0.522	3.572	6.199	0.618	4.136	15.0	13.3
{[10] \rightleftharpoons [11]} [#]	0.438	1.822	6.263	0.989	3.710	13.2	11.5
{[11] \rightleftharpoons [32]} [#]	0.272	1.121	4.629	0.088	2.133	8.2	6.5
{[11] \rightleftharpoons [31]} [#]	0.345	1.572	7.582	0.271	2.284	12.1	10.4
{[11] \rightleftharpoons [13]} [#]	0.387	1.744	5.408	0.485	3.176	11.2	9.5
{[14] \rightleftharpoons [31]} [#]	0.449	2.576	4.828	0.185	4.043	12.1	10.4

^a See Table III for meaning of symbols.

Table VI. Calculated Torsional Angles in Various Energy-Maxima Geometries of *trans,trans,trans*-1,5,9-Cyclododecatriene

transition state ^b	sp ³ -sp ³ torsional angles ^a			sp ³ -sp ² torsional angles ^a						sp ² -sp ² torsional angles ^a		
	ω_1	ω_5	ω_9	ω_2	ω_4	ω_6	ω_8	ω_{10}	ω_{12}	ω_3	ω_7	ω_{11}
{[00] \rightleftharpoons [01]} [#]	-54	-75	-59	-152	40	124	121	117	106	178	-176	-167
{[01] \rightleftharpoons [03]} [#]	-40	-77	-50	-98	-16	60	-146	106	123	177	169	-161
{[00] \rightleftharpoons [10]} ^{#c}	20	-62	-63	75	94	123	123	93	77	176	-172	176
{[10] \rightleftharpoons [30]} [#]	62	15	-56	-3	83	79	104	130	23	-177	-177	-172
{[10] \rightleftharpoons [11]} [#]	76	-38	-61	-49	155	107	116	124	28	-160	-168	-175
{[01] \rightleftharpoons [11]} [#]	15	-43	-63	-111	-72	126	123	99	103	-177	-171	175
{[01] \rightleftharpoons [14]} [#]	-50	-63	15	-86	-11	120	66	89	95	174	-178	180
{[10] \rightleftharpoons [14]} [#]	-45	-53	61	176	51	125	25	18	110	-167	180	-165
{[11] \rightleftharpoons [32]} [#]	0	-44	67	113	121	-84	-102	-119	-110	-173	-178	178
{[11] \rightleftharpoons [13]} [#]	36	-51	65	86	105	177	-10	-135	-128	-173	-169	170
{[11] \rightleftharpoons [31]} [#]	49	-59	-35	67	116	-30	-47	-75	-111	-177	170	173
{[14] \rightleftharpoons [31]} [#]	56	0	-58	23	114	-105	-10	-30	-134	-173	175	173

^a See Figure 3A for the disposition of torsional angles ω_1 - ω_{12} . ^b All transition states have C_1 symmetry, except where otherwise stated. ^c Approximate C_2 symmetry.

energy transition state which occurs during this sequence of conformational changes is associated with a *D* process and lies either between the [11] and [13], or the [32] and [33] conformations. The sequence starts with a *D* process and is followed by an *S* process. The third step can be either an *S* or a *D* process, and the fourth step is of an opposite kind to that in the third step. The last two steps are the same as the first two steps, but in reverse order.

As can be seen from the graph, sequences of three *S* or three *D* processes are very unfavorable as they lead to the high-energy [70] or [07] conformation. Also, an initial *D* process is preferred over an initial *S* process. Thus, the [11] conformation can be obtained starting at [00] by passage over a barrier of 7.4 kcal/mol by the sequence *DS*, or alternatively,

and with more difficulty, by passage over a barrier of 11.5 kcal/mol by the sequence *SD*.

As stated previously, all possible transition states were not investigated in detail, and the justification for this will now be presented. As an example, the conformational step [01] to [03] involves a transition state of 13.6 kcal/mol relative to that of the [00] conformation. This transition state has a higher strain energy than does the path barrier for the previously discussed best path in the [00] to [77] interconversion. Hence all subsequent conformational steps emanating from the [03] conformation, i.e., [03] to [07], [03] to [15], and [03] to [13], become unimportant and need not be calculated. The same is true for the conformational steps in the graph which are preceded by the [10] to [30] conformational step. The confor-

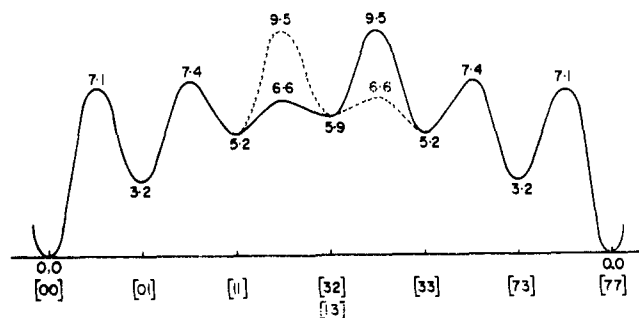


Figure 5. Preferred energy profile for ring inversion (i.e., for the [00] to the [77] interconversion) in *trans,trans,trans*-1,5,9-cyclododecatriene. In the central region of the profile there are two equivalent paths, which are distinguished by being shown as full and broken lines.

mational steps in the graph linking conformation [15] or its mirror image conformation [31] to any other conformation were also not calculated. Conformations [15] and [31] have relative strain energies of 9.6 kcal/mol, which are already so high that these two intermediates cannot be involved in the ring inversion of the [00] conformation. The transition states separating the [15] and [31] conformations from any other conformational in the graph are expected to have relative strain energies significantly larger than 9.6 kcal/mol and are labeled in the graph with the indication ">10 kcal/mol."

The vibrational frequencies of all the conformations in graph 4 were calculated.¹¹ In each case $3N - 6$ real vibrational frequencies were obtained, indicating that each conformation corresponds to a true (local) energy minimum with respect to any small distortion of the molecule. The [00] conformation is the only conformation in **1** with D_3 symmetry. Both the internal ($124.4, 111.7^\circ$) and torsional ($62.1, -115.6, 177.9^\circ$) angles of the [00] conformation are in agreement with the corresponding internal ($124.1, 111.1^\circ$) and torsional ($63.4, -116.5, 178.0^\circ$) angles of the D_3 conformation determined by Ermer and Lifson.⁶ The average internal ($124.3, 111.2^\circ$) and torsional ($63.1, -116.3, 177.1^\circ$) angles obtained from the x-ray diffraction³ of **1** are also in agreement with the calculated geometry of the [00] conformation.

Actually, the x-ray structure deviates slightly from strict D_3 symmetry. For example, the $\text{CH}_2\text{-CH}_2$ torsional angles have values of $61.3, 66.7, \text{ and } 61.3^\circ$. Inducing such a distortion into the [00] conformation results in a rise of 0.3 kcal/mol in the strain energy. The distortions observed in the x-ray structure are probably due to crystal lattice effects.

The [07] conformation, which might have had D_3 symmetry, distorts to a C_1 symmetry in order to relieve extensive torsional

and nonbonded strain. For the same reason, both the [01] and [14] conformations distort to C_1 symmetry¹⁹ from the ideal C_2 symmetry.

In conclusion, among all the possible paths for the ring inversion of the [00] conformation to its mirror image [77] conformation, there exist two distinct but equivalent best paths. The path barrier (9.5 kcal/mol) is in good agreement with the free energy of activation (8.6 kcal/mol) for the site exchange of the methylene protons in **1** as obtained from dynamic NMR spectra of this triene.

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- (18) The graph shown in Figure 4 omits path degeneracies. For example, the line [00] to [01] is threefold degenerate since the D process can be applied to any one of the three double bonds of the [00] conformation.
- (19) Since the [01] conformation distorts from the ideal C_2 conformation, there are two distinct paths for the interconversion of the [01] and [11] conformation. Both of these paths were calculated and the one associated with the transition state having the lower strain energy is reported (Tables V and VI).