The Molecular Structure of Triasterane: An Experimental and Theoretical Study☆

Bjørn Ahlquist[a], Arne Almenningen[a], Birgit Benterud[a], Marit Trætteberg*[b], Pirkko Bakken[b], and Wolfgang Lüttke[c]

Department of Chemistry, University of Oslo[a],
P.O. Box 1033 Blindern, N-0315 Oslo 3, Norway

Department of Chemistry, University of Trondheim, AVH[b],
N-7055 Dragvoll, Norway

Organisch-Chemisches Institut der Universität Göttingen[c],
Tammannstraße 2, W-3400 Göttingen, F.R.G.

Received November 22, 1991

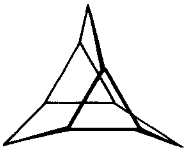
Key Words: Triasterane / Electron diffraction / Calculations, ab initio, force-field

The molecular structure of triasterane (tetracyclo[3.3.1.$0^{2,3}$.$0^{2,6}$]nonane) has been investigated by using the gas-phase electron-diffraction method and by theoretical calculations. The experimental data are in accordance with the molecule having D_{3h} symmetry. The C–C bonds in the three-membered rings are observed to be slightly shorter than those in the methylene bridges [r_a 1.508(5) versus 1.520(4) Å; 2σ in parentheses]. The C–C–C angle at the methylene bridges is observed to be 118.9(3)°, while the M–C–CH_2 angle is determined to be 123.9(2)° (C–M is bisecting the cyclopropyl ring). Theoretical force-field, semiempirical, and ab initio calculations of the triasterane molecule have also been carried out. The semiempirical results deviate substantially from the experimentally determined parameters, while the ab initio results, using a 6-31G* basis set, are in excellent agreement with the latter. The steric strain in triasterane has its origin mainly in nonbonded repulsion between the cyclopropyl groups and in torsion at the C–C bonds involving the methylene groups.

Introduction

In his first independent scientific publication[1] Hans Musso presented an unambiguous proof of the molecular structures of litmus and other orcein dyes. Many scientists had for a long time been trying to solve these problems, but with little success. In subsequent papers Musso was able to elucidate the reaction mechanisms involved in the syntheses of the litmus and orcein dyes[2].

When Musso, in 1964, accepted an offer of a guest professorship at the Department of Chemistry, at the University of Wisconsin, Madison, U.S.A. he decided to take up a completely new field of research, remote from that of natural compounds which he had been studying up to then. In his new research project he aimed at synthesizing a new class of highly symmetric cyclic hydrocarbons. Because of their star-like structures he named these compounds "asteranes". The synthesis of the smallest member of the new class of compounds, triasterane (**1**), was completed relatively soon after he entered his new field of research[3–5], while the successful preparation of tetraasterane (**2**) required many years of hard and dedicated work[6].



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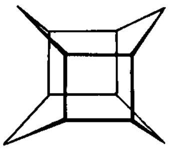

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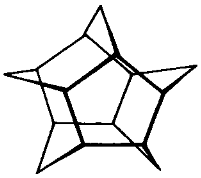

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The asteranes are polycyclic molecules with two equal carbocycles interconnected by methylene bridges between corresponding carbon atoms. The trivial names of the asteranes reflect their star-like shape, as viewed in the direction of the 3-, 4- or 5-fold axis, as well as the size of the two interconnected carbon rings. Triasterane (tetracyclo[3.3.1.$0^{2,8}$.$0^{4,6}$]nonane; **1**) contains, for example, two interconnected cyclopropane rings, while tetraasterane (**2**) and pentaasterane (**3**) have methylene bridges between corresponding carbon atoms in two cyclobutane and two cyclopentane rings, respectively.

The molecular structures of the [n]asteranes are also characterized by n cyclohexane rings in the boat conformation. The methylene hydrogen atoms of the bridges occupy the "bowsprit" and "flagpole" positions of the boat forms. The deviation from planarity of the [n]asterane cyclohexane boat-form subunits depends on n, the number of carbon atoms of the interconnected rings. The asteranes with the smallest interconnected rings have the flattest cyclohexane boat forms, and accordingly the largest distance between neighboring methylene hydrogen atoms (cf. Table 7).

Triasterane (**1**) appears to be a sterically highly strained molecule. So far no experimental structure study of **1** has been published, while structural data for tetraasteranes are known[7, 8]. The photoelectron spectrum of **1** was, however, measured in 1972[9], and recently crystal and molecular structures of some derivatives of triasterane[10] were published. These derivatives were, however, systematically different from the parent compound, as their cyclopropyl rings were interconnected by unsaturated carbon atoms. The

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study[10] pointed out that a high-precision structure determination of the parent substance would be of importance to the interpretation of the results obtained for the derivatives.

Some theoretical calculations related to the molecular structure of **1** have been published. Randić, Maksić, and coworkers applied the method of maximum overlap in order to study the hybridization of some highly strained systems, including **1**[11,12]. They calculated the degree of hybridization of all orbitals involved in bonding, and concluded that the methylene C–C bonds in **1** are bent towards the center of the molecule, the bending being small, but significant.

As part of their study of the role of p_σ-p_σ interactions in the stabilization of framework structures, Minyaev and Minkin calculated the molecular geometry of **1** by the MINDO/3 method[13]. The cyclopropyl C–C bond was found to be 0.01 Å longer than those in the methylene bridges (1.535 versus 1.525 Å).

A gas-electron diffraction (GED) study of **1** was carried out as part of a cand. real. thesis by one of us (B. A.) in 1972. At that time it proved difficult to distinguish with certainty between the two kinds of C–C bonds, and the results have therefore never been published. As the structure of **1** is of fundamental interest, as a prototype polycyclic system, it was decided to carry out a reinvestigation, based on the 18-year old experimental data. Even though the most widely used experimental GED technique has not undergone dramatic changes during the time span between the two investigations – except for special purposes – the development of the methods of extracting structural information from the experimental data has been substantially improved during this period. It is therefore possible to obtain more accurate structural information on **1** at present, compared to the first GED study of this molecule. Control studies, based on simultaneous studies of similarly old data and new GED recordings carried out for vinylcyclopropane[14], confirmed that identical structural results were obtained from both sets of data.

Structure Analysis

Figure 2 includes a molecular model of **1**, showing the numbering of the atoms referred to in this paper. If D_{3h} symmetry is assumed, the geometry of the molecule is determined by 7 parameters. In the triasterane reinvestigation these parameters were chosen as follows: the four bond lengths $r(C^1-C^2)$, $r(C^3-C^4)$, $r(C^1-H)$, $r(C^4-H)$ and the three valence angles $C^1-C^8-C^7$, H–C–H, $M-C^1-H$.

At the time when the original study of the triasterane structure was carried out, normal coordinate calculations of vibrational parameters were not a standard procedure. The reinvestigation included the use of calculated vibrational amplitudes (u) and perpendicular correction coefficients (K). The normal coordinate calculations were based on a valence force field transferred from cyclopropane and other strained hydrocarbons[15]. The triasterane molecular model was defined in terms of the geometrically consistent r_α distance parameters, and the calculated vibrational quantities permitted the transformation between the geometrically consistent (r_α) and the operationally GED (r_a) internuclear distances. The calculated vibrational amplitudes of the most important internuclear distances of **1** are listed in Table 2.

The experimental GED study of the molecular structure of **1** was based on least-squares analyses by fitting a com-

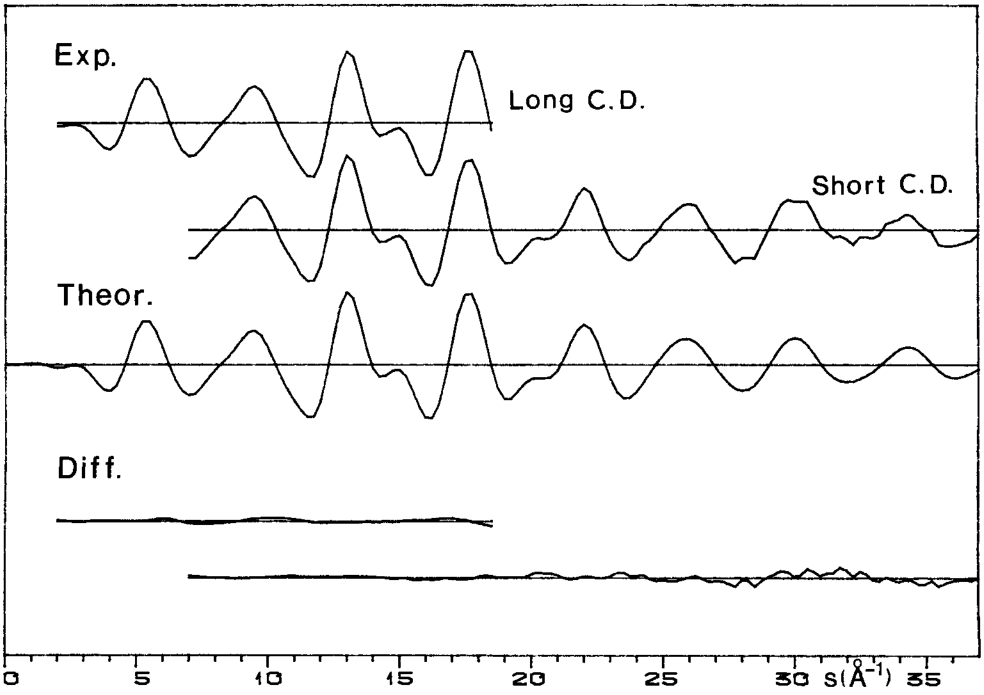


Figure 1. Experimental and theoretical molecular intensities for triasterane (**1**) and the difference curves; the theoretical curves are calculated from the parameters in Table 2

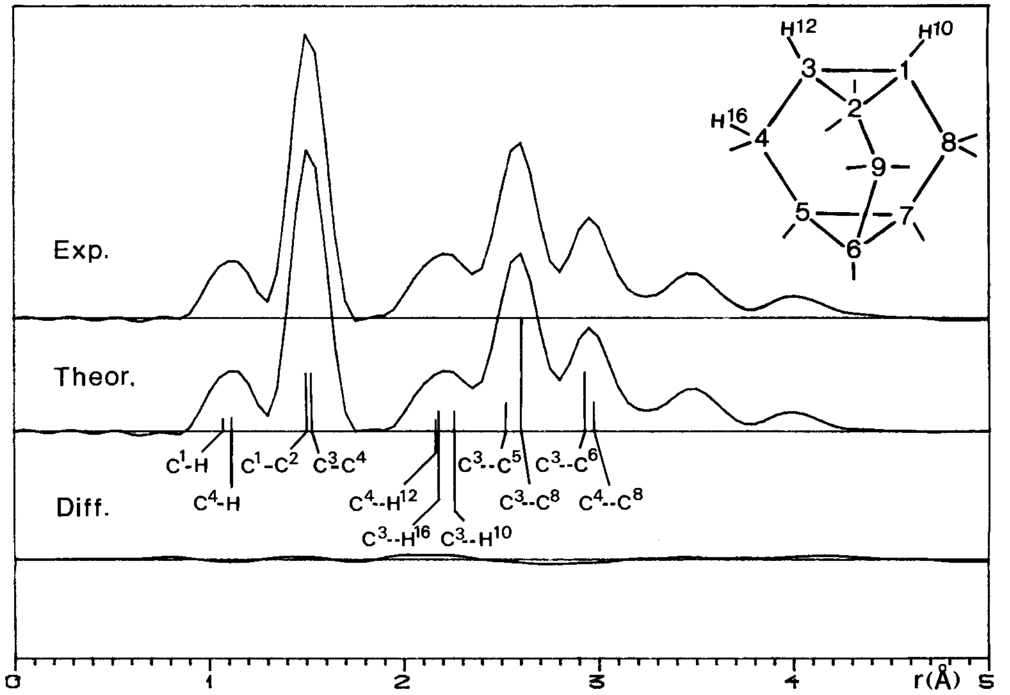


Figure 2. Experimental and theoretical radial distribution curves for triasterane (1); the theoretical curve is calculated from the parameters in Table 2

Table 1. Refinement results obtained for 1 under varying refinement conditions, illustrating the problems encountered when the outer part of the S. C. data were included (distances and vibrational amplitudes in Å, angles in degrees, σ in parentheses)

	S.C. data(Å^{-1}):[a]		
	Not included	**7.0 - 20.0**	**7.0 - 40.0**
r_a(C^1-C^2)	1.509(3)	1.506(4)	1.518(5)
r_a(C^3-C^4)	1.522(2)	1.523(3)	1.513(4)
r_a(C^1-H)	1.056(6)	1.066(9)	1.093(26)
r_a(C^4-H)	1.178(10)	1.157(13)	1.103(29)
∠C^1-C^8-C^7	113.3(3)	112.2(4)	112.7(4)
∠H-C-H	105.2(21)	106.3(28)	105.1(52)
∠M-C^1-H	119.0(18)	121.4(32)	120.6(59)
u(C^1-C^2)	0.050(1)	0.054(1)	0.051(1)
u(C-H)	0.074(8)	0.061(10)	0.070(4)
u(C^3···C^5)	0.070(2)	0.065(3)	(0.059)
u(C^3···C^6)	0.067(2)	0.067(2)	0.068(3)
u(C···C)	0.108(3)	0.114(3)	0.102(11)
R$_1$ (%)	2.26	4.37	6.46
R$_2$ (%)	-	4.63	14.23

posite theoretical intensity curve to the two average experimental curves. Because of the poor quality of the scattering data in the outer s region (see Figure 1), a large number of least-squares refinements were carried out under varying conditions, differing primarily in the s_{max} value. The most noticeable effects of the large-angle scattering data were on the relative size of the C–C bond distances and on the M–C^1–H angle. The R values (fitness factors) increased sharply with increasing s_{max} value outside the region 25–30 Å^{-1}. This is illustrated in Table 1 which shows the structural and vibrational parameters obtained by using three different refinement conditions. A closer evaluation of the various refinement results and the intensity curves indicated that the S. C. data were reliable only to ca. 27 Å^{-1}, and data outside this s value were therefore omitted in the further study. The relatively small outer cut-off value of the experimental intensities (s_{max}) does, however, not seriously complicate a high-quality structure determination of **1**, as the quality of the L.C. data are excellent.

If the vibrational amplitudes of the C–H bonds are included in the refinements (see Table 1) unrealistic u(C–H) and r(C–H) values are obtained. The final results (Table 2) are therefore based on refinements where the C–H vibrational amplitudes are fixed at the values calculated in the normal coordinate analysis.

The final structural results obtained for **1** are presented in Table 2, while the theoretical molecular intensity curve and corresponding radial distribution curve calculated for this model are shown in Figures 1 and 2, together with their experimental counterparts. The molecular intensities are shown for the entire range of the observed data (s_{max} = 40.00 Å^{-1}), but the contributions beyond s = 27.25 Å^{-1} were omitted in the least-squares intensity refinements of the molecular parameters as well as in the calculation of the radial distribution curve.

Because of the high symmetry of **1** there are relatively few different interatomic distances in the molecule. The positions of all interatomic C–C distances are indicated in Figure 2. Additionally, the position of the bonded C–H distances and the nonbonded 1,3-C$\cdots$H distances are shown. The major contributions to the radial distribution peak at $r \approx 3.5$ Å are due to C–H distances of type $C^5 \cdots H^{12}$, $C^2 \cdots H^{16}$ and $C^4 \cdots H^{10}$, while the peak at $r \approx 4.0$ Å shows contributions from distances of type $C^5 \cdots H^{10}$ and $C^9 \cdots H^{16}$ (see Figure 2 for the numbering of the atoms).

Table 2. Final structural results for triasterane (**1**) as determined by GED least-squares intensity refinements [distances and vibrational amplitudes (u) in Å, angles in degrees, 2σ in parentheses]

Bond lengths	r_a	$u_{obsd.}$	$u_{calcd.}$
C^1-C^2	1.508(5)	0.056 (1)	0.050
C^3-C^4	1.520(4)	0.055	0.049
C^1-H	1.087(10)	(0.077)	0.077
C^4-H	1.127(12)	(0.077)	0.077
Dependent distances			
$C^3 \cdots C^5$	2.520(6)	0.065 (2)	0.059
$C^3 \cdots C^8$	2.605(2)	0.072	0.066
$C^3 \cdots C^6$	2.936(4)	0.069 (2)	0.066
$C^4 \cdots C^8$	2.973(6)	0.089	0.086
$C^4 \cdots H^{12}$	2.161(54)	0.106	0.103
$C^3 \cdots H^{16}$	2.166(14)	0.112 (13)	0.109
$C^3 \cdots H^{10}$	2.248(40)	0.105	0.102
Independent angles		**Dependent angles**	
C^1-C^8-C^7	112.2(3)	M-C^1-C^8	123.9(2)
M-C^1-H	124.8(44)	C^1-C^2-C^8	118.9(3)
H-C-H	107.4(32)	C^8-C^1-H	111.3(44)
R_1 (%)	4.42		
R_2 (%)	3.89		

Theoretical Structure Calculations

In the original GED study of **1** carried out by one of us (B. A.) it was difficult to distinguish with certainty between the two types of C–C bond distances, but the study indicated that the bonds in the cyclopropyl units might be longer than those in the methylene bridges. The same conclusion could be drawn from MINDO/3 calculations reported by Minyaev and Minkin[13]. As these results are in conflict with those obtained in the present GED reinvestigation, it was decided to carry out some theoretical calculations of the triasterane structure in the hope of obtaining more insight into the problem.

A minimum-energy structure of **1** was first calculated by the molecular mechanics method, using Allinger's MM3 program[16]. The resulting triasterane structure has bond distances that are in fairly good agreement with those from the experimental GED study (see Table 3). The calculated MM3 valence angles differ, however, considerably from those observed experimentally. This is especially true for the $C^1-C^8-C^7$ angle, which is of major importance for the overall structure of the molecule.

Table 3. Structural parameters for triasterane (**1**), as calculated by molecular mechanics, by various semiempirical, and by ab initio methods (bond lengths in Å, angles in degrees); the experimental GED results are given for comparison

	MM3	HF/3-21G	HF/6-31G*	MP2/6-31G*	GED
Bond lengths					
C^1-C^2	1.513	1.514	1.5019	1.5075	1.508
C^3-C^4	1.520	1.517	1.5169	1.5114	1.520
C^1-H	1.090	1.074	1.0776	1.0885	1.087
C^4-H	1.115	1.087	1.0884	1.0992	1.127
Valence angles					
C^1-C^8-C^7	117.6	112.2	111.71	111.80	112.2
H-C^8-H	106.2	107.6	106.58	106.46	107.4
H-C^1-C^8	115.6	113.0	114.69	115.00	111.3
M-C^1-C^8	121.2	123.9	124.14	124.10	123.9
M-C^1-H	123.2	123.1	121.17	120.90	124.8

Semiempirical calculations were then carried out (AM1, MINDO3 and MNDO). All the semiempirical calculations resulted in optimized geometries where the cyclopropyl C–C bond is longer than the other type of C–C bond in the molecule (AM1: $\Delta = 0.013$ Å; MINDO3: $\Delta = 0.012$ Å; MNDO: $\Delta = 0.015$ Å), in disagreement with the experimental results. Even though the semiempirical methods are often stated to give generally satisfactory predictions of bond lengths and valence angles[17], this seems to be highly questionable for seriously strained molecules like triasterane.

As the MM3 and the semiempirical calculations did not unambiguously support the experimentally obtained structure of **1**, it was decided to extend the study by carrying out ab initio calculations. The results from two HF calculations, with the basis sets 3-21G and 6-31G* are shown in Table 3. In the 3-21G ab initio calculation the two types of C–C bonds were found to be nearly equal, while the results based on a larger basis set, including polarization functions (6-31G*), reveal almost the same relative C–C bond distribution as observed in the experimental reinvestigation of **1**, with the cyclopropyl C–C bond being the shortest of the two structurally different C–C bonds.

In order to study to what extent the inclusion of electron correlation will influence the ab initio results, an additional Møller-Plesset calculation was carried out (MP2/6-31G*). The calculated difference between the two C–C bond lengths is reduced to 0.004 Å (see Table 3), but the cyclopropyl C–C bond is also in this case the longest one. The calculated ab initio structures of **1**, based on large basis sets, do therefore support the results obtained in the experimental study.

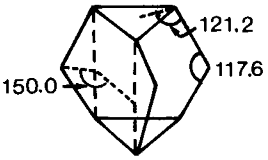
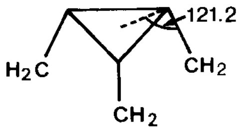
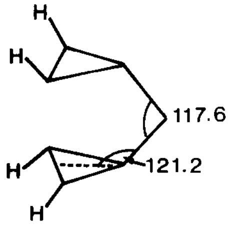
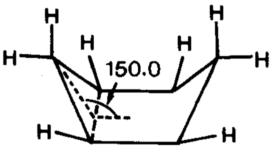
The semiempirical and the ab initio calculations were performed with a CRAY X-MP supercomputer at SINTEF, Trondheim, using the program GAUSSIAN 90[18]. The results from the various calculations are presented in Table 3.

Discussion

Comparison between Experimental and Calculated Structure Results for Triasterane

The experimental structural study of **1** shows that its cyclopropyl C–C bonds are ca. 0.01 Å shorter than the other type of C–C bonds in the molecule. The observed bond difference is almost the same as that calculated by the ab initio method, using a 6-31G* basis set. Generally, the agreement between the experimentally determined structure of **1** and the calculated ab initio 6-31G* structure is excellent (see Table 3), at least for the parameters defining the skeleton of carbon atoms. The positions of the hydrogen atoms are generally less accurately determined by the GED

Table 4. Angle parameters and energies for triasterane (**1**) and its subunits, *cis,cis*-1,2,3-trimethylcyclopropane (**4**), *syn,syn*-dicyclopropylmethane (**5**), and cyclohexane, *boat* conformation (**6**), as calculated by the MM3 method[16] (angles in degrees, energies in kcal/mol)

	 (20.21)	
 4a* (8.72)	 5a* (12.28)	 6a* (15.71)
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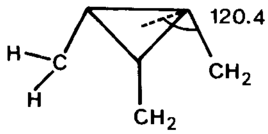
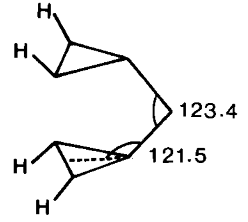
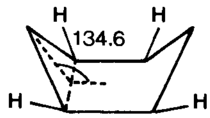
 4b (8.26)	 5b (10.58)	 6b (9.38)
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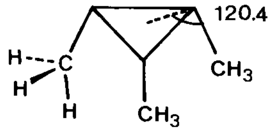
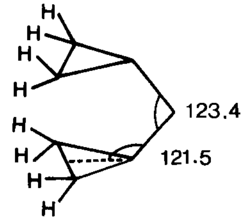
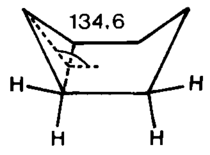
 4c* (20.86)	 5c* (50.86)	 6c* (15.80)
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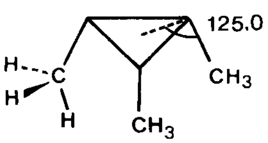
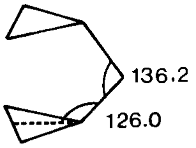
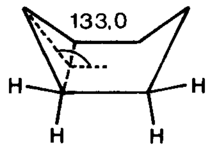
 4d (16.18)	 5d (23.44)	 6d (14.57)

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[a] S. C.: Short-camera distance; the long-camera (L. C.) data are fully included in all three refinements.

method, and this is certainly true in the present case, as indicated by the large standard errors of the parameters involving hydrogen atoms (see Table 2).

The semiempirical calculations resulted in the cyclopropyl C–C bonds being the longest ones. This is probably due to the parametrization inherent in these methods, which might be less appropriate for sterically severely strained molecules. The MM3 calculation gave bond distances that are essentially equal to those observed, while the C–C–C angles at the methylene bridges were calculated to be ca. 5° larger than the observed ones and those calculated by the other methods. This might be due to an overestimation of the MM3 repulsive potentials involving the two cyclopropane rings.

The *triasterane* cyclopropyl C–C bond lengths were observed to be equal to those in cyclopropane (r_g: 1.512 Å; r_e: 1.501 Å)[19], within the accuracy of the method.

Steric Strain in Triasterane Analyzed in Terms of the Strain in Its Constituent Subunits

Triasterane (**1**) may be described as a molecule constructed from the following three subunits: *cis,cis*-1,2,3-trimethylcyclopropane (**4**), *syn,syn*-dicyclopropylmethane (**5**), and cyclohexane in *boat* conformation (**6**). In order to investigate the nature of the sterical strain in **1** it may be of interest to analyze the strain in terms of that present in the three molecular subunits **4**, **5**, and **6** by use of MM3 calculations.

Table 4 shows the MM3 results obtained for **1** and its constituting subunits **4**, **5**, and **6**. In the calculations the subunits were subjected to systematically varying conditions, and the calculated energies (in kcal/mol) and most relevant valence angles, for four sets of conditions, are presented. The other geometrical parameters changed only insignificantly throughout the series and are therefore not included in Table 4.

The first entries (**4a**, **5a**, **6a**) show the computed energies for the frozen geometries of the three substructures in the absence of any sterical influence exerted by the other parts of the triasterane **1** molecule. In the **b** series the geometries of the substructures are allowed to relax (except for the conformations). In the third series (**4c**, **5c**, **6c**) hydrogen atoms are added to the "radical" ends of the fragment units, while the geometries, with exception of the added hydrogen atoms are kept equal to those in the **b** series. Finally, the geometries of the hydrogenated fragments are allowed to relax, except for the conformations of **5d** and **6d**.

The MM3 calculations involving subunit **4** indicate that the contribution to the sterical strain related to the M–C–CH_2 (C–M is bisecting the cyclopropyl ring) angles of **1** is modest. Relaxation of these angles in **4b** resulted in slightly decreased angles compared to those in **1**. In the hydrogenated fragment the M–C–CH_2 angles were increased by 4–5°. This is, however, mainly a result of nonbonded repulsion between the *endo* hydrogen atoms. A similar effect is not operative to the same degree in **1** as the three corresponding *endo* bonds, extending from the methylene groups in this molecule, form a (bound) cyclopropyl group.

In fragment **5** the calculated energies and valence angles change dramatically from one series to the next. In **1** the calculated C–CH_2–C angle is already larger (117.6°) than in linear aliphatic hydrocarbons (e.g. propane: 112.0°[20]). On going down through the series this angle increases drastically, to 136° in **5d**. The obvious reason behind this effect is the repulsion between the two cyclopropyl subunits. The conformation of subunit **5** is fixed in the *syn,syn* position in the calculations reported in Table 4. It is of interest to note that the central C–C–C angle of the *syn,anti* and the *anti,anti* conformations of **5d** were calculated to be 120.3° and 114.6°, respectively.

The M–C–CH_2 angles in subunit **5** are much less effected by the variations in the calculation conditions than is the C–CH_2–C angle. One reason is that it appears to require more energy to bend the former angle, another is that the cyclopropyl units are more effectively separated from one another by a given increase in the C–CH_2–C angle compared to a similar increase in one of the M–C–CH_2 angles.

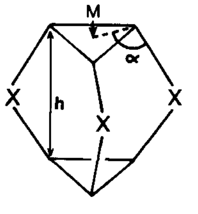
In addition to the nonbonded repulsion between the two cyclopropyl groups in subunit **5** there is a rather large contribution of torsional energy, due to the forced *syn,syn* conformation of the CH_2 groups. Similar torsional energy contributions are of course also inherent in the triasterane structure.

The calculated flip angles in the subunits **6a**–**6d** show that the cyclohexane boat substructure in **1** is considerably flatter than the minimum energy boat conformation of cyclohexane[21], resulting in relatively minor increases in bending and torsional energy contributions. The high strain energy of subunit **6a**, relative to that of **1**, is due to the replacement of the cyclopropyl carbon atoms in **1** (type 22) by C_{sp^3} carbons (type 1). Calculations similar to **6a** and **6b**, but retaining the types of cyclopropyl carbon atoms, give strain energies of 8.33 and 5.68 kcal/mol, with a flip angle of 137.8° in the relaxed structure (**6b**).

The Molecular Structure of Triasterane Compared to the Structures of Triasterane Derivatives

In Table 5 the most important GED structure parameters determined for **1** are compared with X-ray structural data recently reported for three triasterane derivatives[10]. The distance between the planes of the cyclopropane rings is 2.52 Å in **1**, i.e. ca. 0.9 Å shorter than the sum of the van der Waals radii. Similarly short interring distances are observed also for the three triasterane derivatives, and all four molecules are therefore subject to considerable nonbonded interatomic repulsion. The interplane distance is primarily determined by the magnitude of the C–X bond and of the C–X–C and M–C_{cpr}–X angles. In the triasterane derivatives the bridging carbon atoms (in X) are sp^2-hybridized, while they are sp^3-hybridized in **1**. As a consequence of this the C–X bonds in the derivatives are expected to be shorter than in **1**, in agreement with the observations. Another consequence of the hybridization difference is that the ideal C–X–C angle should be close to 120° in the derivatives and to 109° in **1**. The observed C–X–C angle in **1**, 112.2°, is approximately equal to the C–C–C angles observed in nonstrained aliphatic hydrocarbons[22]. In the derivatives these angles are also close to what is observed in similar fragment molecules. A C–X–C valence angle of 115.6° is for example observed in 2-methyl-1-propene[23], compared to 114.9° in the triasterane derivative with X = C=CH_2. Similarly, the C–X–C angle in acetone is measured to be 116°[24], compared to 115.4° in the derivative with X = C=O. Due to the differences in hybridization of the bridging carbon atoms, the triasterane derivatives have therefore generally shorter C–X bonds and larger C–X–C angles than in the parent compound. These two structural characteristics have opposite effects on the distance between the two cyclopropyl rings, and it is accordingly reasonable that the interplane distances in **1** and in the derivatives are observed to be practically the same. It should be noted that the structure parameters of the triasterane derivatives may be affected by π-electron delocalization since the cyclopropyl groups are conjugated with the unsaturated X groups. Such effects are indeed observed for the compounds with X = C=CH_2 or C=O [see $(C-C)_{cpr}$ and C_{cpr}–X in Table 5], but not when X is a cyclopropyl group[10].

Table 5. Experimentally determined parameters (GED) for triasterane (**1**) compared to those for triasterane derivatives (X-ray data)[10] (distances in Å, angles in degrees)

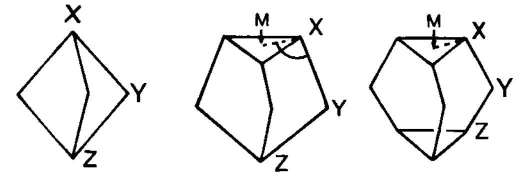


X:	CH_2 (1)	C=CH_2	C=O	
$r(C\text{-}C)_{cpr}$	1.508	1.517	1.517	1.506
$r(C_{cpr}\text{-}X)$	1.520	1.470	1.481	1.487
h	2.520	2.476	2.504	2.489
∠C-X-C	112.2	114.9	115.4	113.6
$\angle C_{cpr}\text{-}C_{cpr}\text{-}X$	118.7	117.8	117.5	118.3
$\angle M\text{-}C_{cpr}\text{-}X$	123.7	122.6	122.2	123.2

The Molecular Structure of Triasterane Compared to the Structures of Homologous Hydrocarbons

In Table 6 results from MM3 and AM1 calculations carried out for triasterane (**1**) and two structurally related compounds, bicyclo[1.1.1]pentane (BCP; **7**) and tricyclo[2.2.1.0^{2,6}]heptane (TCH; nortricyclene; **8**), are shown in order to illustrate the effects on the structure parameters and on the steric energy by replacing one or two of the bridgehead carbon atoms in BCP (**7**) by cyclopropyl rings. The molecular structure of BCP has been studied experimentally[25,26] and theoretically[27,28], and for TCH (**8**) an experimental GED study[29] is known. For both molecules the published structures are in acceptable agreement with those presented in Table 6.

Table 6. Comparison of results from MM3 and AM1 (in parentheses) calculations carried out for compounds structurally related to triasterane (**1**) (distances in Å, angles in degrees, energies in kcal/mol)



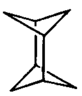
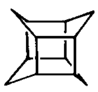
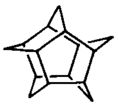
	7	8	1
$r(C^X\text{-}C^Y)$	1.558 (1.571)	1.521 (1.530)	1.520 (1.498)
$r(C^Y\text{-}C^Z)$	1.558 (1.571)	1.553 (1.557)	1.520 (1.498)
$r(C\text{-}C)_{cpr}$	-	1.517 (1.527)	1.513 (1.511)
$r(C^X\text{-}H)$	1.104 (1.085)	1.085 (1.092)	1.090 (1.107)
$r(C^Y\text{-}H)$	1.111 (1.104)	1.112 (1.113)	1.115 (1.123)
$\angle C^X\text{-}C^Y\text{-}C^Z$	71.7 (73.3)	96.7 (97.9)	117.6 (112.2)
$\angle C^Y\text{-}C^Z\text{-}C^{Y'}$	89.1 (88.1)	101.7 (100.9)	-
∠H-C-H	114.9 (111.4)	110.1 (109.6)	106.2 (107.6)
$\angle C^Y\text{-}C^X\text{-}H$	125.9 (126.6)	122.2 (120.2)	115.6 (113.0)
$\angle M\text{-}C^X\text{-}C^Y$	-	109.8	121.2 (123.9)
$\angle M\text{-}C^X\text{-}H$	-	128.0	123.2 (123.1)
E_{Strain}	81.93 (82.87)	42.34 (33.70)	20.21 (32.62)
E_{Bend}	64.98	28.38	1.68
$E_{Tors.}$	5.75	10.59	13.00
$E_{vdW}(1,4)$	5.75	2.45	6.16

The replacement of the bridgehead atoms in BCP (**7**) by cyclopropyl groups reduces the calculated strain energy substantially, namely from 81.9 kcal/mol [BCP (**7**)] to 42.3 kcal/mol [TCH (**8**)] and further to 20.2 kcal/mol [triasterane (**1**)]. The main reason for this is the accompanying reduction in bending energies. The torsion energy increases when the bridgehead carbon atoms of BCP (**7**) are replaced by cyclopropyl groups, and is thereby counteracting the effect from the bending energy. The effect on the torsion energy is, however, only a fraction of that associated with bending. In **1** the bending energy is almost negligible, while the contribution from the torsional energy is dominating, as each of the 12 $C_{cpr}-C_{cpr}-CH_2-C_{cpr}$ dihedral angles, calculated to be ca. ±34°, contributes by ca. 1.0 kcal/mol to the torsion energy. The van der Waals repulsion, due to the proximity of the two cyclopropyl groups, is the second largest contributor to the total steric energy.

The Molecular Structure of Triasterane Compared to the Structures of Di-, Tetra-, and Pentaasteranes

Table 7 shows calculated MM3 structural parameters and sterical strain energies for di-, tri-, tetra-, and pentaasteranes (**9**, **1**, **2**, **3**). The overall sterical strain energies reflect the feasibility of the syntheses of the compounds, as triaster-

Table 7. Structure parameters and strain energies calculated for [*n*]asteranes (n = 2, 3, 4, and 5) by using the MM3 method (distances in Å, angles in degrees, energies in kcal/mol)

				
	9	**1**	**2**	**3**
r(C-C)$_{ring}$	1.547	1.513	1.567	1.559
r(C-CH$_2$)	1.562	1.520	1.536	1.542
r(C^{br}...C^{br})[a]	2.69	2.88	2.82	2.62
r(H^{br}...H^{br})[b]	1.85	3.14	2.49	2.00
∠C^r-C^r-CH$_2$	111.4	116.7	114.1	110.1
∠M-C^r-CH$_2$	-	121.2	125.3	125.7
∠C-CH$_2$-C	81.8	117.6	109.5	108.6
∠H-C-H	108.8	106.2	106.8	104.0
∠θ_{flip}[c]	118.9	150.0	135.0	126.0
E_{Strain}(total)	97.05	20.21	86.04	85.20
$E_{Compr.}$	2.86	0.32	2.45	4.28
E_{Bend}	53.22	1.68	22.01	2.60
$E_{Tors.}$	17.30	13.01	50.22	53.32
E_{vdW}(1,4)	12.86	6.16	13.21	21.05
ΔE_{vdW}(1,4)[d]	6.43	2.05	3.30	4.21

[a] Distance between carbon atoms in adjacent CH$_2$ bridges. — [b] Shortest distance between hydrogen atoms in adjacent CH$_2$ bridges. — [c] For definition see Table 4. — [d] Per cyclohexane subunit.

ane — synthesized years before the others — has a drastically lower steric energy than the other compounds, while the successful preparation of the most highly strained compound, diasterane (**9**), was reported for the first time in 1987[30].

Diasterane (tricyclo[3.1.1.1^{2,4}]octane; **9**) does not fit the general description of the molecular structure of an asterane as given above (two equal carbocycles interconnected by methylene bridges between corresponding carbon atoms). In this molecule the two [*n*]carbocycles, that are integrated parts of other asterane molecules, are replaced by ethyl fragments. The only subunit type that diasterane (**9**) has in common with the other asteranes is the *boat* cyclohexane one.

The sterical strain in **9** is dominated by the bending energy term. The molecule contains two four-membered rings, whose C–C–C angles are responsible for ca. 40% of the bending energy contribution [cf. the bending energy calculated for tetraasterane (**2**)]. The other major contribution stems from the C–C–C angles at the bridgehead carbon atoms that are part of the cyclohexane rings. The van der Waals energy of **9** will be discussed below.

The added steric strain in the tetra- and pentaasteranes (**2** and **3**) compared to that of triasterane (**1**), is mainly due to the increased torsional energy contributions related to the bonds in the four-membered and five-membered rings, which are folded in the free molecules, cyclobutane[31] and cyclopentane[32], but are structurally forced to be planar in the asteranes.

The calculated strain energies of tetraasterane (**2**) and pentaasterane (**3**) are nearly equal. The energies of both molecules are dominated by very large contributions from torsion energy. The torsion energy that is associated with the C–C bridging bonds is similar to that present in **1**. In addition, there are, however, large contributions from torsions related to the bonds in the four-membered and five-membered rings.

Tetraasterane (**2**) has a relatively large contribution to the strain energy from angle bending associated with the 90° valence angles in the four-membered rings. In pentaasterane (**3**) the analogous bending energy is modest, and the nonbonded van der Waals repulsion is the second largest contributor to the total steric energy.

The differences in van der Waals energy between the asteranes **9**, **1**, **2**, and **3** presented in Table 7 reflect the size of the flip angles in their boat cyclohexane substructures and the inherent distances between their methylene groups in the bridges. The shortest distance between "flagpole" hydrogen atoms decreases on going from triasterane (**1**) (3.14 Å) to tetraasterane (**2**) (2.49 Å), pentaasterane (**3**) (2.00 Å), and diasterane (**9**) (1.85 Å). This parallels the increase in the calculated van der Waals energy per cyclohexane subunit for these molecules, i.e. 2.05, 3.30, 4.21, and 6.43 kcal/mol. The flip angle in tetraasterane (**2**) is nearly ideal for a "free" boat cyclohexane fragment (see Table 4), even though the CH$_2$ groups in adjacent bridges are close enough to cause a minor, but significant contribution to the repulsion energy of the molecule. Increased flip angles, as in triasterane (**1**), reduce the nonbonded repulsion energy, but this effect is more than outweighed by other types of strain deformation energies connected to valence and torsion angles. In pentaasterane (**3**) and diasterane (**9**) the CH$_2$ groups are forced together, as the flip angles are reduced to 126° and 119°, respectively, resulting in a substantially increase in the van der Waals energy contributions.

Experimental

The sample of triasterane (**1**) used in the present study was kindly provided by H. Musso[3–5]. The compound was purified by gas chromatography.

The electron diffraction scattering data were recorded with the Oslo apparatus[33] under the following conditions: nozzle-to-plate distances: 481.83 mm (6 plates) and 201.30 mm (3 plates). The temperature at the nozzle tip was 65°C during the experiments. The electron wavelength was 0.064542 Å, corresponding to an accelerating potential of ca. 36 kV. The ranges of the scattering data were 1.5–19.5 (Δs = 0.25 Å^{-1}) and 7.25–40.00 Å^{-1} (Δs = 0.25 Å^{-1}).

Reduction of the data was performed according to standard procedures[34,35], and in the reinvestigation a calculated background[36] was subtraced from the data for each plate to yield the experimental molecular intensity distribution in the form sI_m (s). Electron scattering amplitudes and phase shifts were calculated by the use of Hartree-Fock potentials for C[37], while molecularly bonded potentials were used for H[38].

The averages of the molecular intensities for the two camera lengths are shown in Figure. 1. The quality of the data recorded at the long-camera (L. C.) distance is excellent, while that of the data from the small-camera distance (S. C.) is rather poor, especially in the outer large-angle scattering range. As there was no more compound available at this stage, supplementary short camera length recordings could not be made. In the final structure determination the scattering data for $s \leq 27.25$ Å^{-1} were omitted (see above).

CAS Registry Numbers

1: 3105-29-1 / **2**: 259-77-8 / **3**: 86475-57-2 / **9**: 51273-49-5

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[*] In memoriam *Hans Musso*. – For an obituary see: H. Hopf, *Chem. Ber.* **1992**, *125*, I.

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