

What are the possible axial point groups for a molecule of a certain size or formula?

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We list all possible point groups for 1, 2, 3, 4 and n atoms as well as for n -atom molecules with specified formulas. For each point group, we give examples of molecules of each size and formula if they are known, and hence we determine the yet-to-be discovered molecules with under 5 atoms for each point group. We establish a small set of principles that can be used for proofs about the possibility or impossibility for a molecule of a certain size and/or formula to have a point group symmetry.

INTRODUCTION

One might wonder why, despite group theory being applied to molecules for about 100 years [19], the questions that are being addressed in this paper do not appear to have been answered yet. Indeed we have asked all living authors of [1–18, 36] if they have ever come across a list of all possible point groups for a 4-atom (tetraatomic) system, and in all cases we were explicitly told that they were unaware of such a list, or we received no response at all. We have determined all possible point groups for systems with *any* number of atoms, and we have gone a step even further by determining all possible point groups for structures with a given chemical formula.

After searching through all of [1–18, 36] thoroughly, the closest work that we found to the results in this paper, is the table of “Shapes” found in the 2008 version of the famous “Tables for Group Theory” document by P. Atkins, M. Child and C. Phillips [1]. Nothing similar was found in any of [1–18, 36], and the table of “Shapes” in [1] has several shortcomings which we will address and fix in the next section, before we begin presenting the main results of our work in the following sections.

For investigating the novelty of our work, we believe that our thorough examination through all of [1–18, 36] was a fair survey of the known literature on the topic. The 2007 paper [39] reported a thorough survey of known published works that provided character tables for the S_8 and D_{8h} point groups, and our list [1–18, 36] includes all of those works, in addition to [39] itself, the papers that cited [39], and also thoroughly selected work on the topic that did not provide S_8 and D_{8h} character tables.

Motivation for this work

Our need for answers to the question in the present paper’s title, arose during other work. GW100 is a

dataset of 100 systems (95 molecules and 5 atoms) which was introduced in a 2015 paper [37] and by the end of 2020, already more than 100 electronic structure methods/codes were used to calculate energies for all systems in the GW100 dataset. It has therefore become a monumental dataset for benchmarking, and efforts were made in 2021 [20] and 2023 [21] to improve the most accurate calculations that had been done on the system until then [22], and therefore to create one of the best known sets of benchmark data in existence for electronic structure calculations.

However, for many of the molecules in the GW100 dataset, calculations are done at geometries that were optimized using density functional theory, which means that the results are dependent on the basis set and density functional used; and it also had an effect on the comparisons that have been made between calculations that were done for the GW100 dataset and experimental data on the same dataset. For many of those molecules, very accurate bond lengths and angles that were determined from high-resolution spectroscopic experiments, are available in places such as the Landolt–Börnstein volumes and related books [23–35] and also in the original papers in which the geometric data was determined.

The books [23–35] provide only the *point group*, a 3D diagram, and usually the minimum number of bond lengths, bond angles and dihedrals necessary to generate all XYZ coordinates or a z-matrix. An example is the entry for H_2Si_2 in [26] (this molecule is not in GW100 but it is useful for illustrating this point) which provides the point group (C_{2v}), a 3D shape that is redrawn in Fig. of this paper, and *only* two bond lengths and a dihedral angle: $r_{\text{Si-Si}} = (2.2154 \pm 0.0020)\text{\AA}$, $r_{\text{Si-H}} = (1.6680 + 0.0030)\text{\AA}$, $\varphi = (104.22 + 0.30)^\circ$ (the original experimental paper from which this data came [41] and the previous paper on the same molecule [40], also provided no additional bond lengths or angles). But to do electronic structure calculations we need either the XYZ coordinates of all atoms, or a z-matrix for the molecule, and there is no software for obtaining either

of these from just the limited information given (point group, 3D diagram, two bond lengths and a dihedral angle). A software for generating a z-matrix from this data would be significantly simpler to write than a software for generating XYZ coordinates of all atoms, but the z-matrix for this system would need at least one bond angle, and the reader might find it surprising that the simplest formula for the H-Si-H angle in H_2Si_2 is (in terms of the provided dihedral angle φ , the provided Si-Si bond length r_1 and the provided Si-H bond length r_2):

$$\theta = \arcsin \left(\frac{\sin \left(\frac{\varphi}{2} \right) \sqrt{4r_2^2 - r_1^2}}{r_2} \right). \quad (1)$$

Such a formula is not expected to be found in any compilation of formulas. Determining this formula can be accomplished with some high school level trigonometry (applications of the ordinary cosine law), and applications of the *dihedral cosine law* which is unlikely to be taught in high school or university-level curricula, but can be learned and applied to such small molecules within a day by most researchers; however with the pace of research today, the derivation of such a formula *would ideally be done by software rather than by hand*. Unfortunately, not even the most advanced symbolic computation or computer algebra software can provide a user with Eq. 1 based on the information given.

Furthermore, the interest today in machine learning and big data analysis has lead to the introduction of much larger datasets than GW100, such as GW5000 and OE62 (both from Stuke *et al.* [38]) which involve more than 5000 and 61000 molecules respectively, but the geometries for the molecules in these datasets have issues similar to the ones for the GW100 dataset. This reinforces our motivation for constructing a software that could, for example, convert the thousands of geometries from the Landolt–Börnstein series and related compilations of spectroscopically determined geometry data, into z-matrices or XYZ coordinates.

We believe that as machine learning and big data analysis become more popular over the next century, there will be a rise in interest in being able to categorize molecules (e.g. for training neural networks) and the question of which point groups are possible for molecules of a certain size of formula, will be asked more and more. Anyone seeking the answers to these questions will be able to find them in this paper.

A software to generate z-matrices (or even XYZ coordinates) for molecules with the data presented in experimental papers, such as for H_2Si_2 , would require specific code blocks for each molecular shape. It is possible for two molecules with the same point group and formula to have very different shapes (for example see Fig. X, in which two isomers of H_2Si_2 are shown, both with the C_{2v} point group, but one of them being pyramidal and the other one being planar),

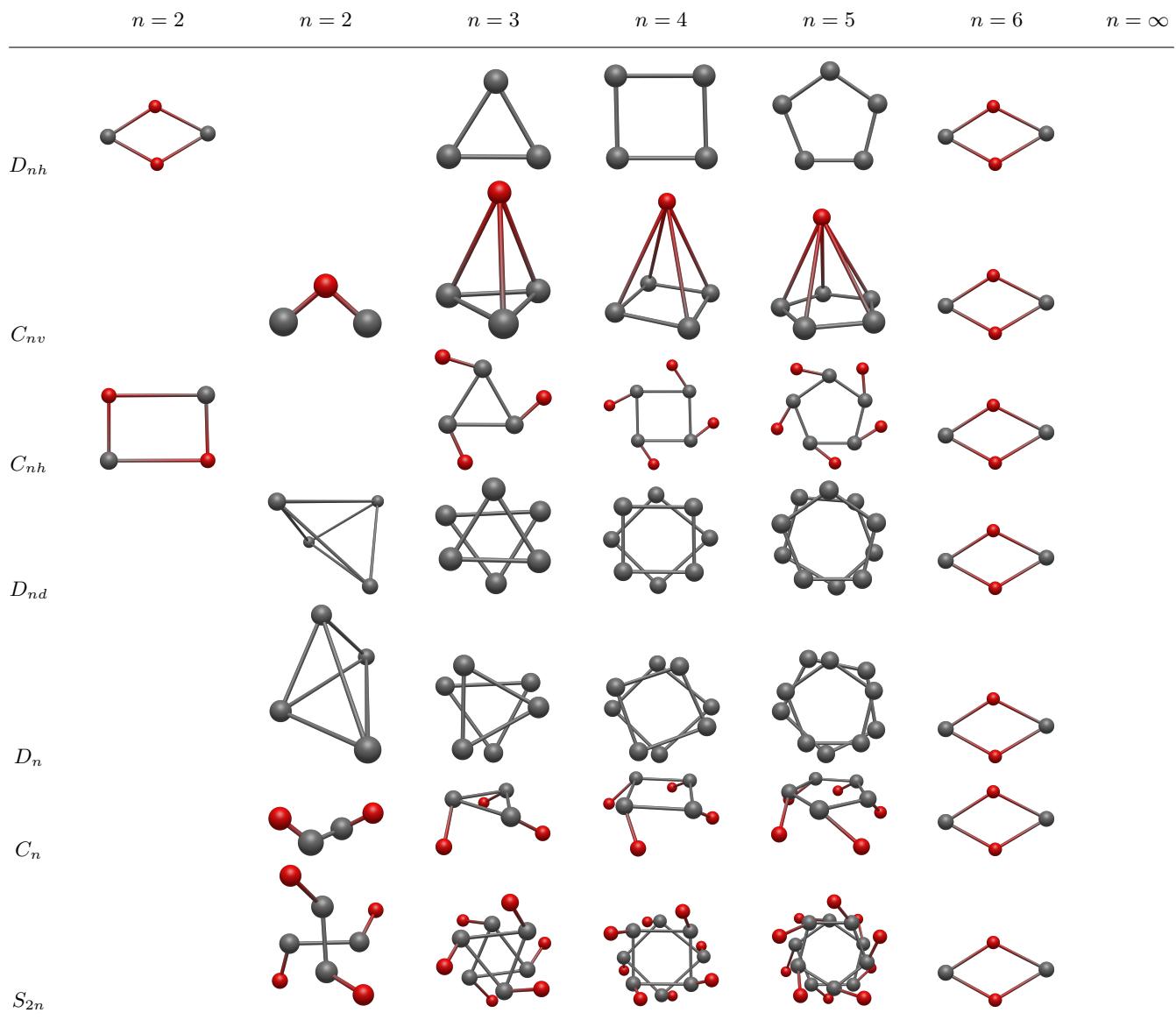
so a general-purpose “z-matrix constructor” or “XYZ-coordinates constructor” that uses only bond lengths, bond angles and dihedral angles, would need specific code blocks based on their point groups and formulas, in addition to other characteristics. However, a natural first step towards constructing such a software would be to categorize n -atom molecules based on their molecular formulas and point groups (the Landolt–Börnstein volumes and related books [23–35], the CCCBDB [42], and the CRC Handbook of Chemistry and Physics are some examples in which point groups are already used to help describe molecules), and then to write the relevant z-matrix-construction or XYZ-construction code for each case, adding sub-cases when necessary (e.g. to distinguish between the two types of C_{2v} shapes for A_2B_2 molecules as depicted in Fig. X).

For n atoms, how many cases do we need to consider in order to cover each point group at least once in the software? That is the essence of the question in the present paper’s title, and everyone tell us that it hasn’t been done yet. We take this even one step further, by looking at the possible formulas, for example for a 7-atom molecule to have the point group Ci you need its formula to be $\text{A}_2\text{B}_2\text{C}_2\text{D}$ (with any of B,C,D being allowed to be a duplicate of one of the previous letters) but a molecule with any other formula cannot have the point group Ci (for example $\text{A}_2\text{B}_2\text{C}_2$ would no work unless B and C are A, which would bring us back to the previously mentioned formula in the case in which A=B=C=D).

In the initial stages of the development of our z-matrix constructor, we found that the Landolt–Börnstein series had all these molecules, but we realized that we missed the tadpole structure because we know that there’s 6 connected 4-vertex graphs. Likewise we tried to see if we had representation from all possible point groups, and this required us to first determine the possible point groups for 4-atom molecules (which surprisingly we couldn’t find, and we found that experts who wrote books on the topics were also unaware). In doing this, we discovered that D_2 and D_{2d} are possible but not yet found, so this may be an avenue for further experimental research.

Another motivation was geometry optimization. Roland Lindh and others have discovered that you can get fewer cycles, but if point group symmetry is included, then we can have a smaller Wilson-B matrix.

In this paper we provide general principles, 3-atom and 4-atom possible groups, formulas and examples, n -atom groups and formulas for minimal structures, all of which seems to be novel. We skip the polyhedral groups $T, T_d, T_h, O, O_h, I, I_h$ since we discovered something with fewer vertices than the snub cube that has O symmetry.



GENERAL PRINCIPLES FOR POSSIBLE MOLECULES

The following general principles will be used. They might seem obvious, but we don't see them in textbooks (maybe the first one is in textbooks) [1–18, 36].

Ability to orient a molecule according to the valid point group operations on the molecule:

Any molecule with a rotation axis, called a C_n -axis, can be oriented in an xyz (Cartesian) coordinate system such that for the largest possible n value in C_n , the z -axis is aligned with a C_n axis, and a σ_h plane is a mirror plane coinciding with the xy -plane in the coordinate system.

Existence of a C_n axis:

The existence of a C_n axis is only possible if the molecule contains a subset of atoms that are vertices

of an n -sided polygon with equal side-lengths (a regular n -gon). A C_n axis would be in the center of this polygon, and since we can call this axis the z -axis, all atoms that form vertices of the polygon, would have to have the same z -coordinates. Therefore, a minimum of n atoms is needed in order to have a C_n axis.

If a C_n axis is the z -axis, then after a C_n rotation, an atom that originally had coordinates (x, y, z) , will have coordinates (x', y', z) in which the z -coordinate does not change, because of the definition of a C_n rotation, and the new coordinates (x', y') can be different from the old ones (x, y) but will coincide with the original (x, y) coordinates of another identical atom in the molecule if the axis is indeed a C_n axis.

Necessary and sufficient conditions for the D_{nh} point group:

A regular n -gon with uniform vertices (in a molecule, this would mean the presence of identical

atoms at the vertices) has a point group of D_{nh} , and any object with the D_{nh} point group must contain a subset of identical vertices that form a regular n -gon if with $n \geq 3$.

Action of the S_n operation:

An S_n operation is by definition a C_n operation followed by a σ_h reflection operation. If we define the associated C_n -axis to be the z -axis, and the σ_h plane to be the xy -plane, then if an atom originally had coordinates (x, y, z) , it will have coordinates (x', y', z) after the C_n rotation, and coordinates $(x', y', -z)$ after the σ_h reflection. So S_n operation moves atoms from (x, y, z) to $(x', y', -z)$. As described in the section about the existence of a C_n axis, the new coordinates (x', y') can be different from the old ones (x, y) but will coincide with the original xy -coordinates of another identical atom in the molecule if the molecule indeed has a C_n axis.

Action of the inversion operation, i :

We can always choose center of inversion to be at the origin $(0, 0, 0)$, so if an atom is located at (x, y, z) , the inversion operator will move it to $(-x, -y, -z)$.

MINIMUM NUMBER OF ATOMS AND POSSIBLE MOLECULAR FORMULAS FOR EACH POINT GROUP

As usual, we only consider the maximum point group. All in order of number of atoms (except C_i is before others).

C_s

Any two atoms form a line, and if all atoms of a molecule are on the same line, then the point group will be promoted to either $C_{\infty v}$ or $D_{\infty h}$. Likewise, a single atom has the point group K_h , so it is not possible for a molecule with fewer than three atoms to have the point group C_s . Three atoms is enough for the point group of a molecule to be C_s though, as in the example ABC. **The minimum number of atoms required is three, and any formula is allowed.**

C_1

Any three atoms form a plane or a line, and if all atoms of a molecule are on the same plane, then that plane is a reflection/mirror plane. Therefore if a molecule has three or fewer atoms, it will at least have one reflection plane, and would be promoted from C_1 to at least C_s . Four atoms is enough for the point group of a molecule to be C_1 though, as in the example ABCD. **The minimum number of atoms required is four, and any formula is allowed.**

C_i

Any five atoms with an inversion center will lie on the same plane (or same line) and will therefore have a reflection/mirror plane. Since the C_i point group does not have any reflection elements, for any five atom molecule with an inversion center the maximal point group must be larger than C_i .

If we have three or fewer atoms, then there does not even need to be an inversion center for the atoms to be confined to a plane (or line).

If we have four atoms, and we make the inversion center the origin, the atoms must come in pairs according to the inversion operation i that was described earlier: $A = (x_1, y_1, z_1)$ will be paired with $-A = (-x_1, -y_1, -z_1)$ and $B = (x_2, y_2, z_2)$ will be paired with $-B = (-x_2, -y_2, -z_2)$. Assuming that no two atoms will have the same xyz -coordinates, none of these four atoms can be on the origin. A and $-A$ form a line, and B and $-B$ form another line, and that these two lines both intersect at the origin, and two lines that cross are always co-planar.

If we have five atoms, the fifth one must be at the origin, because atoms need to either be paired or at the origin in order for the inversion operation to be valid on the system of atoms. However, the other four atoms form a plane that contains the origin (because the plane is formed by two lines that intersect at the origin). Therefore the fifth atom will also be on the same plane as the other four atoms, and the point group will be promoted beyond C_i .

Six atoms is enough for a molecule's maximal point group to be C_i , for example $C_2H_2Br_2Cl_2$ with the two carbons removed. **The minimum number of atoms required is six, and the formula must be of the form $A_2B_2C_2D_2\dots$ or $AB_2C_2D_2\dots$ depending on if the number of atoms is even or odd.**

C_{nv}

$$\underline{n = 2}$$

If we have any fewer than three atoms, the point group of the system will be promoted to K_h , $D_{\infty h}$ or $C_{\infty v}$, however three atoms is indeed enough for the point group of a molecule to be C_{2v} , as in the case of H_2O . **The minimum number of atoms required is three, and the most general formula is $A_2BCD\dots$ since the extra atoms C,D,... can be placed on the C_2 axis without any loss of valid symmetry operations, and without allowing any new valid symmetry operations.**

$$\underline{n \geq 3}$$

Since the point group of a regular n -gon with identical atoms at each vertex is required in order to have the C_n axis that forms part of the point group C_{nv} and we have already mentioned in the previous section that the point group of such a structure would be D_{nh} , we would need at least one additional atom to break any

symmetries in D_{nh} that are not present in C_{nv} . It turns out that one additional atom is not only necessary, but also sufficient, since if this atom is placed on a C_n axis that goes through the center of the n -gon, but the atom is not placed on the plane of the n -gon, it will break the horizontal mirror plane and any S_n axes, while maintaining the n vertical mirror planes that are in C_{nv} . The only point group with a C_n axis and n vertical mirror planes, without having any horizontal mirror planes or S_n axes, is C_{nv} , so the pyramid that we have formed must have the point group C_{nv} . **The minimum number of atoms required is $n+1$, and the most general formula is $A_nBCD\cdots$**

D_{nh}

$n = 2$

If we have any fewer than three atoms, the point group of the system will be promoted to K_h , $D_{\infty h}$ or $C_{\infty v}$, however all D_{nh} point groups with even values of n (including D_{2h}) have an inversion element i , and the only way for a three atom system to have an inversion element is for it to be linear, which would promote it either to $D_{\infty h}$ or $C_{\infty v}$. If we choose the origin $(0, 0, 0)$ to be the center of inversion, and one atom is at the position (x, y, z) , then an identical atom would need to be at the position $(-x, -y, -z)$ and the third atom would need to be at the origin. We therefore would have two identical atoms on a *line* going through the origin, and a third atom in the center of that line. We therefore would need a minimum of four atoms for the D_{2h} point group, and indeed four atoms is enough as in the case of Br_2Na_2 . **The minimum number of atoms required is four, and the most general formula for the minimal structure is $A2B2$.**

$n \geq 3$

Since a regular n -gon with identical atoms at each vertex is both necessary and sufficient for the point group of a system of atoms to be D_{nh} for $n \geq 3$, we can conclude the **the minimum number of atoms required is n , and the formula for this minimal structure would be A_n** . An even number of additional atoms can be added along the C_n axis in such a way that no new valid symmetry operations are made possible, and

such that none of the existing valid symmetry operations are invalidated, provided that these atoms are added in pairs on each side of the plane formed by the n -gon. One additional atom can also be added at the center of the n -gon. Therefore **the most general formula for a structure with n atoms plus an even number of additional atoms would be $A_nB_2C_2D_2\cdots$, and for an odd number of additional atoms the most general formula would be $A_nBC_2D_2\cdots$**

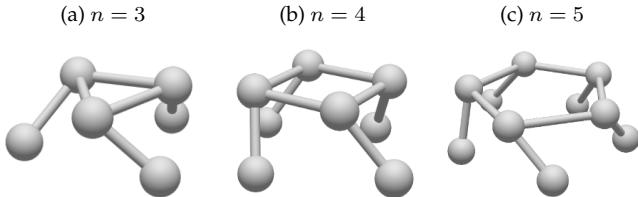
C_n
 $n = 2$

If we have any fewer than three atoms, the point group of the system will be promoted to K_h , $D_{\infty h}$ or $C_{\infty v}$; and if we have only three atoms, they form a plane which will be a mirror plane, meaning that the point group of the system which contains a C_2 axis will be promoted to C_{2v} or D_{3h} . Four atoms would be enough for the point group of the system to be C_2 though, as in the case of H_2O_2 . **The minimum number of atoms required is four.** In terms of the possible formulas, if we have two atoms at positions A and B , then after rotation around the C_2 axis (which we will make the z -axis, as we described in the previous section), these atoms will be at positions $A' = (-x_1 - y_1, z_1)$ and $B' = (-x_2 - y_2, z_2)$ respectively, and for the C_2 operation to be valid, the atoms that were originally at positions A and A' need to be identical, and likewise for the atoms that were originally at B and B' . **The most general formula is therefore $A_2B_2CD\cdots$ since the extra atoms C,D,\dots can be placed on the C_2 axis without any loss of valid symmetry operations, and if their positions are chosen carefully, no new valid symmetry operations would be introduced.**

$n \geq 3$

Since the point group of a regular n -gon with identical atoms at each vertex is required in order to have a C_n axis, and we have already mentioned in the previous section that the point group of such a structure would be D_{nh} , we would need at least one additional atom to break any symmetries in D_{nh} that are not present in C_n . In order for the C_n operation to remain valid, we can either add any number of atoms (including just one) on the C_n axis, or a full set of n more atoms that form a regular n -gon with the C_n axis going through its center and perpendicular to the plane formed by the n -gon. However, adding any number of

Figure 1: Structures with the point group C_n and with the minimum number of atoms, $2n$.



atoms to the C_n axis will not break the σ_v planes, so by adding one or more atoms to the C_n axis that goes through the center of a regular n -gon, would form a structure with a C_{nv} point group, so instead of adding any number of atoms to the C_n axis, we must add at least one set of n more atoms forming a regular n -gon (and we know that this one set is enough for us to form a structure in which C_n is the point group, as in Fig. 1). The two parallel n -gons, A_n and B_n , must lie on different planes so that the molecular is not planar, and therefore would not get promoted to C_{nh} . **The minimum number of atoms required is $2n$, and the most general formula would be $A_nB_nCD\cdots$ since in addition to the A_nB_n structure, extra atoms C,D,\dots can be placed on the C_n axis without any loss of valid symmetry operations, and if their positions are chosen carefully, no new valid symmetry operations would be introduced.**

D_n
 $n = 2$

Not explained well.

$n \geq 3$

Not explained well.

D_{nd}
 $n = 2$

Not explained well.

$n \geq 3$

We can repeat everything that was written in the section about C_n , except with the second regular n -gon (the one that is added) being rotated by π/n radians (and the two regular n -gons still being on two different planes). Such a structure with $2n$ atoms is possible, as in the case of...

C_{nh}
 $n = 2$

d

$n \geq 3$

We can repeat everything that was written in the section about C_n , except that the structure is now allowed for the two regular n -gons to be on the same plane (and therefore concentric since they share the same C_n axis) since having all atoms on the same plane means that the structure lies on a σ_h plane, which is allowed (and needed) for the point group to be C_{nh} . All other elements of the C_{nh} point group can be generated from the C_n and σ_h operations, so the point group of the described structure is indeed C_{nh} . Such a structure with $2n$ atoms is possible, as in the case of...

S_{2n}
 $n = 2$

If we have any fewer than three atoms,

$n \geq 3$

Since S_{2n} is a generator of the S_{2n} point group, C_n is in the point group because $S_{2n}^2 = C_n$. This means we need a regular n -gon with the C_n axis cutting perpendicularly through its center, but a regular n -gon will not satisfy the S_{2n} operation unless all atoms are at the origin. You need $2n$ to have an S_{2n} axis, but then you'd get D_{nh} , so you need another $2n$ to break the D_{nh} . **The minimum number of atoms required is $4n$.**

SUMMARY OF OUR RESULTS

Point groups		Number of atoms								
		Minimum	1	2	3	4	5	6	7	8
K_h	1		✓	X	X	X	X	X	X	X
$D_{\infty h}$	2		X	✓	✓	✓	✓	✓	✓	✓
$C_{\infty v}$	2		X	✓	✓	✓	✓	✓	✓	✓
D_{nh}	$n \geq 3$	n	X	X	✓	✓	✓	✓	✓	✓
	$n = 2$	4	X	X	X	✓	✓	✓	✓	✓
D_{nd}	$n \geq 2$	$2n$	X	X	X	✓	✓	✓	✓	✓
D_n	$n \geq 2$	$2n$	X	X	X	✓	✓	✓	✓	✓
S_{2n}	$n \geq 2$	$4n$	X	X	X	X	X	X	X	✓
C_{nv}	$n \geq 2$	$n + 1$	X	X	✓	✓	✓	✓	✓	✓
C_{nh}	$n \geq 2$	$2n$	X	X	X	✓	✓	✓	✓	✓
C_n	$n \geq 2$	$2n$	X	X	X	✓	✓	✓	✓	✓
C_s	3		X	X	✓	✓	✓	✓	✓	✓
C_i	6		X	X	X	X	✓	✓	✓	✓
C_1	4		X	X	X	✓	✓	✓	✓	✓

Possible point groups for 3-atom (triatomic) molecules

Point group	Chemical formula type		
	A ₃	A ₂ B	ABC
$D_{\infty h}$	C ₃	CO ₂	X
$C_{\infty v}$		N ₂ O	HOS
D_{3h}	H ₃ ⁺	X	X
C_{2v}	O ₃	H ₂ O	X
C_s	H...H ₂	HO ₂	HNO

Possible point groups for 4-atom (tetraatomic) molecules

OUTLOOK

Apart from finding molecules to fill in the tables, z-matrix generator in OpenMolcas.

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N Possible groups (not including subgroups)

								K_h
1								
2								
3	C_s		C_{2v}			D_{3h}		$D_{\infty h} C_{\infty v}$
4	C_s	C_1 C_2	C_{2h}	$C_{2v} C_{3v}$		D_2	D_{2d}	$D_{2h} D_{3h} D_{4h}$
5	C_s	C_1 C_2	C_{2h}	$C_{2v} C_{3v}$ C_{4v}		D_2	D_{2d}	$D_{2h} D_{3h} D_{4h} D_{5h}$
6	C_s C_i	C_1 C_2 C_3	C_{2h} C_{3h}	$C_{2v} C_{3v}$ C_{4v} C_{5v}		D_2 D_3	$D_{2d} D_{3d}$	$D_{2h} D_{3h} D_{4h} D_{5h} D_{6h}$
7	C_s C_i	C_1 C_2 C_3	C_{2h} C_{3h}	$C_{2v} C_{3v}$ C_{4v} C_{5v} C_{6v}		D_2 D_3	$D_{2d} D_{3d}$	$D_{2h} D_{3h} D_{4h} D_{5h} D_{6h} D_{7h}$
8	C_s C_i	C_1 C_2 C_3 C_4	C_{2h} $C_{3h} C_{4h}$	$C_{2v} C_{3v}$ C_{4v} C_{5v} C_{6v} C_{7v}		D_2 D_3	$D_{2d} D_{3d}$	$D_{2h} D_{3h} D_{4h} D_{5h} D_{6h} D_{7h} T_d$
								$O_h D_{\infty h} C_{\infty v}$
								$O_h D_{\infty h} C_{\infty v}$

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Group	Chemical formula type					
	A ₄	A ₃ B	A ₂ B ₂	A ₂ BC	ABCD	
T_d		X X X X				
P_4						
$D_{\infty h}$		X		X X		
C_4						
$C_{\infty v}$		Unlikely		ABAB?		
C_3H						
$ABAB?$						
C_2HF						
$HCNO$						
D_{4h}		X X X X				
S_4^{2+}						
D_{3h}			X X X			
S_4						
H_3B						
D_{2h}		X		X X		
Br_2Na_2						
D_{2d}		X X X X				
S_4						
D_2		X X X X				
D_2						
C_{3v}			X X X			
H_3N						
C_{2v}					X	
S_4						
IF_3						
H_2Si_2						
CH_2O						
C_{2h}		X		X X		
H_2N_2						
C_2		X		X X		
S_4^-						
H_2O_2						
C_s						
HO_3^+						
Cl_2S_2						
Cl_2OS						
$CHFO$						
C_1						
$HCl \cdots HCl$						
H_2OS						
$CHBrCl$						