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Theoretical studies on heats of formation for polynitrocubanes using the density functional theory B3LYP method and semiempirical MO methods

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ABSTRACT: The heats of formation (HOFs) have been calculated for 21 polynitrocubane compounds using semiempirical MO methods (MINDO/3, MNDO, AM1 and PM3) and for eight of 21 polynitrocubanes containing one to four nitro groups using the density functional theory method at the B3LYP/6-31G* level by means of designed isodesmic reactions. The cubane cage skeletons in the polynitrocubane molecules have been kept in setting up the isodesmic reactions to produce more accurate and reliable results. It is found that there is a good linear relationship between the HOFs of eight polynitrocubanes calculated using the B3LYP/6-31G* and PM3 methods, but not for the other methods, and the linear correlation coefficient equals 0.9971. Subsequently, accurate HOFs at the B3LYP/6-31G* level of the other 13 polynitrocubanes containing four to eight nitro groups were obtained by systematically correcting their PM3-calculated HOFs. All 21 polynitrocubane compounds have high HOFs, implying that they can be very powerful energetic materials. The relationship between the HOFs and molecular structures for polynitrocubanes is discussed. Copyright © 2001 John Wiley & Sons, Ltd.

KEYWORDS: polynitrocubanes; heat of formation; density functional theory; semiempirical MO methods

INTRODUCTION

Cubane chemistry has undergone an intense development since the first synthesis of the cubane C_8H_8 with polycarbocyclic "cage" system three decades ago.[1] In addition to the theoretical and synthetic challenges inherent in this cage system, much current interest stems from the unusual stability, high density, and compact framework exhibited by cubane and its functionalized derivatives. Polynitrocubanes $C_8H_{8-m}(NO_2)_m$ $(1 \leq m \leq 8)$,[2–14] the nitro derivatives of cubane, have especially attracted much attention of chemists because they are very powerful energetic materials. To date, all of the eight nitro groups have been attached to cubane.[13]

It is well known that the evaluation of the explosive performance of energetic materials requires a knowledge of the heat of formation (HOF). Moreover, HOFs are of great importance for researchers involved in thermochemistry. For stable compounds, of course, there are many tables that contain experimental data of HOFs. However, it is impractical or dangerous for energetic materials and unstable compounds to measure their HOFs experimentally. In these cases, many computational methods are employed to obtain HOFs.[15–24] The group additivity method is an empirical model having some restrictions in application.[25] MO methods are much more widely used. The parameterized semiempirical MO methods, such as MINDO/3,[26] MNDO,[27] AM1[28] and PM3,[29] are able to figure out HOFs directly and rapidly. Although these semiempirical MO methods often cause large HOFs errors from various groups and skeletons, they are sometimes systematic and can be corrected. *Ab initio* MO methods are also employed to calculate HOFs. For this purpose, certain reactions need to be designed and accurate energies are required. To obtain accurate total energies, one often needs to perform high-level calculations such as QCISD(T) and MP2 concerning electron correlation correction, which are computationally expensive and even impossible for large molecules. Nowadays, density functional theory (DFT)[30–32] methods, especially the B3LYP[33,34] hybrid DFT method, which not only can produce reliable geometries and energies but also requires less time and computer resources, have been widely employed and have become an important and economical tool to deal with complex electron correlation problems.

To our knowledge, although many polynitrocubanes containing various numbers of nitro groups have been synthesized,[2,5,8–14] no experimental HOFs for polynitrocubanes are available. There are some theoretical HOFs

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of polynitrocubanes calculated using an empirical model[4] and other methods.[13,14] Owing to the presence of lone pairs of electrons on nitrogen and oxygen atoms in nitro groups, the electron correlation effects in nitrocubanes are great. Therefore, it is necessary to include the electron correlation correction to obtain accurate energies.

There are 21 polynitrocubanes in all. In this paper, accurate HOFs have been calculated for eight polynitrocubanes (number of nitro groups: $m = 1$–4) of relatively small size using the DFT B3LYP method and the 6-31G* basis set[35] *via* designed isodesmic reactions. It is shown that there is a good linear relationship between the HOFs calculated using the B3LYP/6-31G* and PM3 methods for these eight polynitrocubanes. The HOFs of the other 13 polynitrocubanes ($m = 4$–8) at the B3LYP/6-31G* level are obtained by systematically correcting their corresponding PM3-calculated HOFs. The relation between the HOFs and the molecular structures for polynitrocubanes is discussed.

COMPUTATIONAL METHODS AND DETAILS

The hybrid DFT method based on Becke's 3-functional[36] with nonlocal correlation provided by the Lee, Yang, and Parr functional (LYP),[33] designated as B3LYP, is used throughout. The basis sets used in the calculation of total energies have large effects on both the calculated HOFs and on the CPU time. In this study, the 6-31G* basis set is used. Many studies[24,37–39] have shown that the B3LYP method in combination with the 6-31G* basis set is able to obtain total energies that are very close to the results of high-level *ab initio* calculations.

Although DFT methods need less time and computer resources compared with post Hartree–Fock *ab initio* calculations, with increasing numbers of nitro groups the geometry optimizations and frequency computations become quite difficult, owing to the limitation of computer resources or because too much CPU time is required. Another problem is that calculations often produce more than one imaginary frequency when the number of nitro groups is greater than four. In order to obtain a stable molecular geometry without imaginary frequencies, much time has to be spent to eliminate these imaginary frequencies. For example, in optimizing the structure of 1,3,5,7-tetranitrocubane, we found a total of seven imaginary frequencies that were fully eliminated after three rounds of calculations. Therefore, it is very difficult or impractical to calculate the HOFs of all 21 polynitrocubanes at the B3LYP/6-31G* level. In this paper, only eight polynitrocubanes of relatively small size are calculated using the B3LYP/6-31G* method.

We have tried to look for other more suitable approaches to computing accurate HOFs for the other 13 polynitrocubane compounds containing more than four nitro groups. As is well known, HOFs of many kinds of compound can be obtained easily from semiempirical MO methods such as MINDO/3, MNDO, AM1 and PM3. However, various parameterized MO methods may lead to quite different results. Thus, it is important to choose an appropriate semiempirical MO method, and certain correction is often necessary.

In this paper, four semiempirical MO methods, i.e. MINDO/3, MNDO, AM1 and PM3, are employed besides the B3LYP/6-31G* method. The initial structures of the 21 polynitrocubane molecules were built with the Hyperchem program package.[40] The B3LYP/6-31G* and semiempirical MO calculations were performed with the GAUSSIAN 94 program package[41] and the MOPAC 6.0 program package[42] respectively. The optimizations were performed without any symmetry restrictions using the default convergence criteria in the programs. All of the optimized structures were characterized to be true relative energy minima of the potential surfaces by frequency calculations (no imaginary frequencies were found).

The method of isodesmic reactions has been employed very successfully to calculate HOFs from total energies obtained from *ab initio* calculations.[43] Isodesmic reaction processes, in which the number of each kind of formal bond is conserved, are used with application of the bond separation reaction rules. The molecule is broken down into a set of two heavy-atom molecules containing the same component bonds.[44] However, the usual bond separation reaction rules cannot be applied to molecules with delocalized bonds and cage skeletons because of the large calculation errors of HOFs. To solve this problem, we do not break down the cubane cage skeletons in the polynitrocubane molecules. To be specific, we take cubane as a reference compound (the experimental HOF of cubane is 622.1 kJ mol^{-1} in the gas phase[45]). This approach has been proved to be reliable.[23,24]

First, eight polynitrocubanes of a relatively small size were chosen, and their accurate HOFs calculated at the B3LYP/6–31G* level from a series of isodesmic reactions. These eight polynitrocubanes include nitrocubane, three dinitrocubane isomers, three trinitrocubane isomers and one tetranitrocubane (1,3,5,7-tetranitrocubane), which is the most stable among the six tetranitrocubane isomers.

The isodesmic reactions used to derive the HOFs of the eight polynitrocubanes at 298 K are designed as follows:

$$C_8H_{8-m}(NO_2)_m + mCH_4 \rightarrow C_8H_8 + mCH_3NO_2 \qquad (1)$$

where m is the number of nitro groups in the polynitrocubane molecules $C_8H_{8-m}(NO_2)_m$, and C_8H_8 is cubane.

For the isodesmic reaction (1), the heat of reaction ΔH_{298} at 298 K can be calculated from the following equation:

$$\Delta H_{298} = \sum \Delta H_{f,P} - \sum \Delta H_{f,R} \qquad (2)$$

Table 1. Total energies E_0, ZPE, thermal correction values H_T and experimental HOFs for the reference compounds[a]

Compound	E_0 (Hartree)	ZPE (kJ mol^{-1})	H_T (kJ mol^{-1})	HOF (kJ mol^{-1})
C_8H_8	−309.460 37	352.19	14.33	622.1
CH_4	−40.518 38	118.69	10.00	−74.4
CH_3NO_2	−245.009 33	131.74	13.93	−74.3

[a] Experimental HOFs ($T = 298$ K) are from the literature,[45,46] and the others are calculated at the B3LYP/6–31G* level.

where $\Delta H_{f,R}$ and $\Delta H_{f,P}$ are the HOFs of the reactants and products respectively at 298 K, and the experimental HOFs of reference compounds (CH_4,C_8H_8 and CH_3NO_2) are all available. The HOFs of polynitrocubanes ($C_8H_{8-m}(NO_2)_m$) can be obtained when the heat of reaction ΔH_{298} is known. Therefore, the most important thing is to compute ΔH_{298}, which can be calculated using the following expression:

$$\begin{aligned}\Delta H_{298} &= \Delta E_{298} + \Delta(PV)\\ &= \Delta E_0 + \Delta \text{ZPE} + \Delta H_T + \Delta nRT \qquad (3)\end{aligned}$$

where ΔE_0 is the change in total energy between the products and the reactants at 0 K, ΔZPE is the difference between the zero-point energies (ZPEs) of the products and the reactants at 0 K, and ΔH_T is thermal correction from 0 to 298 K. $\Delta(PV)$ in Eqn. (3) is the PV work term. It equals ΔnRT for reactions in the gas phase. For the isodesmic reaction (1), $\Delta n = 0$, so $\Delta(PV) = 0$.

Table 1 contains the total energies, ZPE, thermal correction values and experimental HOFs for the three reference compounds in the isodesmic reaction (1).

Table 2 lists the calculated HOFs for the eight polynitrocubane compounds using the B3LYP/6–31G* method (by designed isodesmic reactions) and the PM3 method; their total energies, ZPEs and thermal correction values at the B3LYP/6–31G* level are also listed. Both thermal correction (from 0 to 298 K) and ZPE correction are included in all calculations. It should be pointed out that the frequencies used for both thermal correction and ZPE correction in this paper are unscaled. The reason is that the calculated HOFs can be very satisfactory using the unscaled frequencies at the B3LYP/6–31G* level.[24] Moreover, for the 1,4-dinitrocubane investigated here, its unscaled computational frequencies are in good agreement with corresponding experimental data.[5] All calculations in this paper were performed on a Pentium personal computer in our laboratory.

RESULTS AND DISCUSSION

Figure 1 shows the correlation between the HOFs calculated using the B3LYP/6–31G* (see Table 2) and semiempirical MO methods (MINDO/3, MNDO, AM1 and PM3) for the eight polynitrocubane compounds. From Fig. 1(a) we can see that there is a good linear relationship between the HOFs calculated at the B3LYP/6–31G* and PM3 levels, and the linear correlation coefficient is 0.9971. However, Fig. 1(b) reveals that the correlation for the AM1, MNDO and MINDO/3 methods is much poorer than that for PM3, which shows that different semiempirical MO methods can cause large differences in the HOF. Obviously, the HOFs obtained from the PM3 method are very satisfactory. In fact, the PM3 method derives from a mathematical reparameterization of the MNDO method. Adjacent lone pair/lone pair repulsions are better described at the PM3 level.[47] The PM3 method gives results for HOFs that are clearly superior to the other semiempirical MO methods for the systems containing —NO_2 in which there are strong interactions between adjacent nitro groups.[39,47,48] As is well known, the DFT methods are able to deal with complex electron correlation problems, which seems to be a bit similar to the adjacent lone pair/lone pair repulsions from the PM3 method. In polynitrocubane molecules, the interactions between adjacent nitro groups confined on the cubane skeleton are strong. These may be quite important reasons why there is a good linear

Table 2. Total energies E_0, ZPEs, thermal correction values H_T and HOFs obtained from the B3LYP/6–31G* and PM3 methods for the eight polynitrocubane compounds[a,b]

Compound	E_0 (Hartree)	ZPE (kJ mol^{-1})	H_T (kJ mol^{-1})	HOF (kJ mol^{-1}) B3LYP/6–31G*	PM3
Nitrocubane	−513.964 28	357.98	21.18	583.83	437.26
1,4-Dinitrocubane	−718.463 27	364.64	29.26	560.58	410.36
1,2-Dinitrocubane	−718.459 17	365.17	28.85	571.47	423.19
1,3-Dinitrocubane	−718.462 42	364.83	29.15	562.90	412.37
1,2,3-Trinitrocubane	−922.949 38	370.87	36.34	569.72	419.78
1,2,4-Trinitrocubane	−922.953 46	370.61	36.54	558.95	407.72
1,3,5-Trinitrocubane	−922.955 70	370.28	36.77	552.97	402.59
1,3,5,7-Tetranitrocubane	−1127.443 95	374.97	44.66	555.76	402.93

[a] E_0, ZPE and H_T are B3LYP/6–31G* results, and the HOFs at the B3LYP/6–31G* level are derived from reaction (1).
[b] Experimental HOF of cubane is 622.1 kJ mol^{-1} in the gas phase.[45]

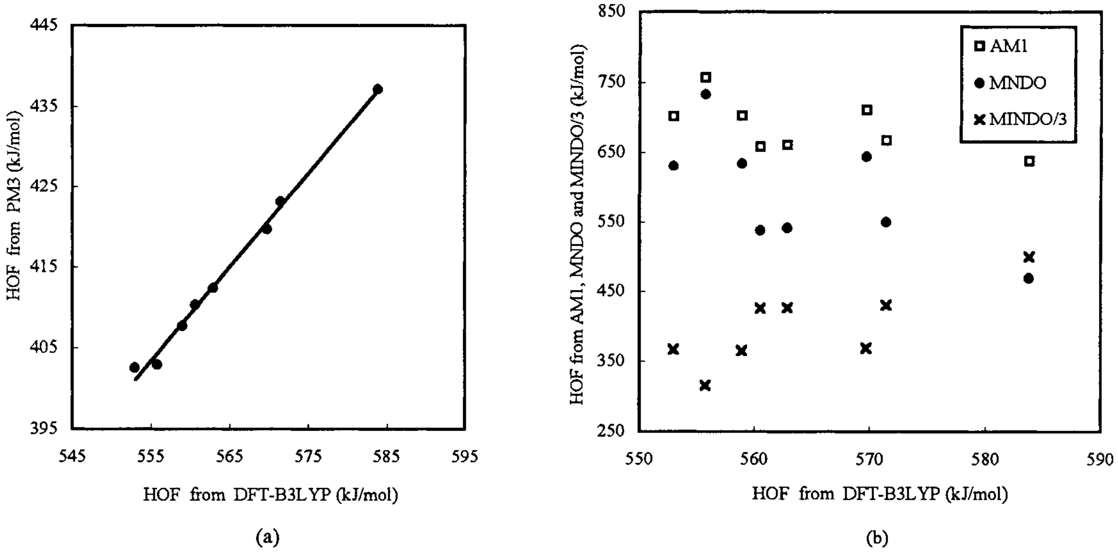


Figure 1. Correlation between the HOFs obtained from semiempirical MO (MINDO/3, MNDO, AM1 and PM3) and DFT-B3LYP/6–31G* calculations

relationship between the HOFs calculated with the B3LYP/6–31G* and PM3 methods.

Studies[23,24] have demonstrated that, when suitable reference compounds are chosen in isodesmic reactions, satisfactory HOFs that are very close to their corresponding experimental values in the gas phase can be obtained using the B3LYP/6–31G* method. Hopefully, the HOFs in Table 2 obtained using the B3LYP/6–31G* method are quite accurate, though there are no experimental HOFs available for comparison.

Because there is a good linear relationship between the HOFs calculated using the B3LYP/6–31G* and the PM3 methods for the eight polynitrocubanes, accurate HOFs for the other 13 polynitrocubanes can be obtained by systematically correcting their corresponding PM3-calculated HOFs. Based on the data in Table 2, the linear equation for the HOFs can be expressed as follows:

$$\mathrm{HOF}_{\mathrm{B3LYP}} = 0.8589\mathrm{HOF}_{\mathrm{PM3}} + 208.50 \qquad (4)$$

where $\mathrm{HOF}_{\mathrm{B3LYP}}$ and $\mathrm{HOF}_{\mathrm{PM3}}$ denote the HOFs obtained using the B3LYP/6-31G* and the PM3 calculations respectively. From Eqn. (4), we can easily evaluate accurate HOFs for the other 13 polynitrocubane compounds at the B3LYP/6-31G* level, since the PM3 HOFs of these compounds can be obtained easily. All of the calculated HOFs for these polynitrocubanes are listed in Table 3.

Examining the HOF data from the B3LYP/6-31G* method shown in Tables 2 and 3, we find that the number of nitro groups in the polynitrocubane has a significant influence on the HOFs. To clarify the problem, Fig. 2 shows the B3LYP/6-31G* HOFs with respect to the number of nitro groups in the nitro-substituted cubanes that have the lowest HOFs among the isomers. In Fig. 2, the HOF of cubane is an experimental value.[45] All the molecular structures of these stable compounds are shown in Fig. 3. It is clearly shown in Fig. 2 that when the number of —NO_2 groups m changes from zero to three, the HOFs decrease; then, the HOFs increase a little as m increases from three to four. However, when m changes from four to eight, it is very interesting that the HOFs increase rapidly and linearly (the linear correlation coefficient is equal to 0.9969). This is because the strongly electron-withdrawing nitro groups can stabilize the cubane skeleton when the number of nitro groups in the polynitrocubane molecule is not too great,[2,3] hence, as the number of nitro groups increases, the HOF decreases. However, when there are more than four nitro groups in a polynitrocubane molecule, stronger repul-

Table 3. PM3-calculated HOFs and B3LYP/6-31G* HOFs obtained by correcting the corresponding PM3-calculated HOFs for 13 polynitrocubane compounds

Compound	$\mathrm{HOF}_{\mathrm{PM3}}$ (kJ mol^{-1})	$\mathrm{HOF}_{\mathrm{B3LYP}}$ (kJ mol^{-1}) (correction)
1,2,3,4-Tetranitrocubane	435.67	582.70
1,2,3,6-Tetranitrocubane	423.78	572.48
1,2,3,5-Tetranitrocubane	415.41	565.30
1,2,5,6-Tetranitrocubane	411.93	562.31
1,2,3,7-Tetranitrocubane	427.84	575.97
1,2,3,4,5-Pentanitrocubane	446.98	592.41
1,2,3,5,6-Pentanitrocubane	438.47	585.10
1,2,3,5,7-Pentanitrocubane	433.12	580.51
1,2,3,4,5,6-Hexanitrocubane	476.32	617.61
1,2,3,4,5,7-Hexanitrocubane	470.31	612.45
1,2,3,5,6,8-Hexanitrocubane	470.74	612.82
Heptanitrocubane	510.38	646.87
Octanitrocubane	555.26	685.41

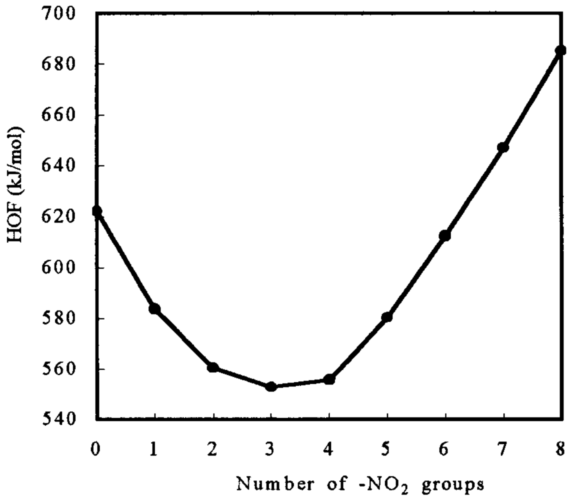


Figure 2. Changes of HOF with increasing number of nitro groups in nitro-substituted cubanes. The HOF of cubane is an experimental value,[45] and the HOFs of the eight polynitrocubanes are obtained using the B3LYP/6-31G* method

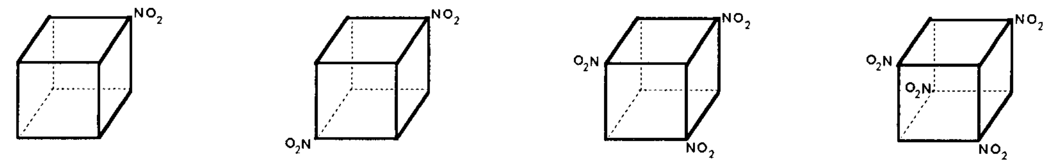
sions will be caused because of the close crowding of the nitro groups. Thus, the total energies of the polynitrocubane molecules increase, and, correspondingly, the HOF increases. The calculated results suggest that substituted cubanes with more nitro groups have higher HOFs, especially for molecules with six to eight nitro groups. So they may be very powerful explosives, and it will be worthy of further experimental study to synthesize highly nitrated cubanes, although the work may be quite difficult.

Analyzing the data listed in Tables 2 and 3, one can also see that the HOFs of polynitrocubane isomers with the same number of —NO_2 groups are affected by the positions of the nitro groups and molecular symmetry. However, the positions of the nitro groups on the cubane skeleton have greater effects on their HOFs. In general, the closer the nitro groups in a molecule, the higher the HOF it has. For example, the HOF of 1,3,5,7-tetranitrocubane using the B3LYP/6-31G* method is the lowest (555.76 kJ mol^{-1}) among the six tetranitrocubane isomers because the four nitro groups attached to the cubane skeleton are the most scattered. On the contrary, the HOF of 1,2,3,4-tetranitrocubane is the highest (582.70 kJ mol^{-1}) among the six tetranitrocubane isomers owing to the crowding of the four nitro groups in its molecule. Similar results for the other four tetranitrocubanes can also be found. According to the above conclusions, if the relative positions of the nitro groups in each isomeric molecule are known, one is able to estimate the relative order of the HOF values for the polynitrocubane isomers with the same number of nitro groups. Accordingly, the relative stability of these polynitrocubane isomers can also be predicted.

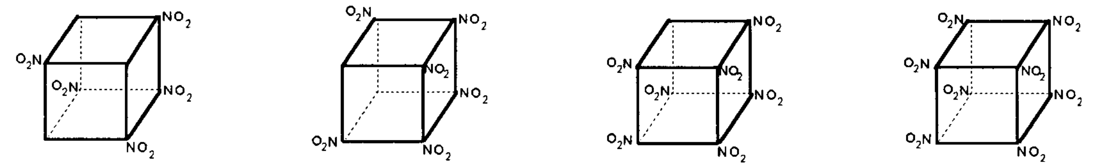
CONCLUSIONS

From the calculated HOF results for 21 polynitrocubanes using the DFT-B3LYP and semiempirical MO methods, the following conclusions can be drawn.

1 Accurate HOFs of polynitrocubanes can be obtained when the DFT-B3LYP/6-31G* method is used and the cubane cage skeletons in the polynitrocubane molecules have been kept in setting up the isodesmic reactions.
2 There is a good linear relationship between the HOFs calculated using the B3LYP/6-31G* and the PM3 methods for polynitrocubanes. Therefore, it is possible to obtain accurate HOFs for the polynitrocubanes by systematically correcting their PM3 results, for which high-level calculations may not be performed.
3 All 21 polynitrocubane compounds have high HOFs, which means that they might be very powerful energetic materials.
4 For the most stable polynitrocubane isomers with



Nitrocubane 1,4 -dinitrocubane 1,3,5-trinitrocubane 1,3,5,7-tetranitrocubane



1,2,3,5,7-pentanitrocubane 1,2,3,4,5,7-hexanitrocubane Heptanitrocubane Octanitrocubane

Figure 3. The molecular structures of the most stable isomers of polynitrocubanes

different numbers of —NO_2 groups m, the substitutions of nitro groups on cubane decrease the HOF when $m < 3$, but increase the HOF when $m > 4$. Furthermore, the HOFs of polynitrocubanes increase linearly when m is changed from four to eight.

5 Generally, for polynitrocubane isomers with the same number of —NO_2 groups, the closer the nitro groups in a molecule, the higher the HOF it has.

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