Theoretical Studies on the Heats of Formation and the Interactions among the Difluoroamino Groups in Polydifluoroaminocubanes

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The heats of formation (HOFs) were calculated for a series of polydifluoroaminocubanes by using density functional theory (DFT), Hartree−Fock, and MP2 method with 6-31G* basis set as well as semiempirical methods. The cubane skeleton was not broken in the process of designing isodesmic reactions; i.e., the cubane skeleton was chosen for a reference compound. The contribution of difluoroamino group to the heat of formation deviates from group additivity. The semiempirical MO (MNDO, AM1, and PM3) methods did not produce accurate and reliable results for the HOFs of the title compounds. The relationship between HOFs and molecular structures was discussed. It was found that the HOFs decreased dramatically initially and then gradually with each difluoroamino group attached to the cubane skeleton. The distance between difluoroamino groups influences the values of HOFs. The interacting energies of polydifluoroaminocubanes are in the range 14−20 kJ/mol. The interaction of neighbor difluoroamino groups discords with the group additivity. The average interaction energy between the nearest-neighbor NF_2 group in the most stable conformer of octadifluoroaminocubane is 13.94 kJ/mol at the B3LYP/6-31G* level. The NF_2 group can rotate freely around the C−N bond. The relative stability of the title compounds was accessed on the basis of the calculated HOFs, the energy gaps between the frontier orbitals, and the bond order of C−NF_2. These results provide basic information for the molecular design of novel high energetic density materials.

Cubane and its derivatives contain a cage skeleton. To obtain novel high-density and high-energy materials, scientists have managed to attach more nitro groups to the cubane cage skeleton to form polynitrocubane. Research related to polynitrocubanes is motivated by their use as promising explosives with unusual high performance due to their high positive heat of formation, high density, and better thermal stability.[1−9] When the oxygen atom in polynitrocubanes is replaced by fluorine atom that is more electronegative, polydifluoroaminocubanes are formed. The difluoroamino is one of the essential functional groups for the combustion.[10−13] The internal rotation around the C−N bond would become easier when the smaller difluoroamino group replaces the nitro group. Consequently, the rupture of the C−N bond becomes difficult, and sensitivity is lowered since the rotation process could abate some stimulating energies. As the polydifluoroaminocubanes are potential novel explosive, propellant, and fuel, it is of technological importance to probe their valuable parameters related to detonation performance and to pioneer the design of new energetic materials.

It is well-known that the evaluation of explosive performances of energetic materials requires the knowledge of the heats of formation (HOFs). 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 to measure HOFs of energetic materials and unstable compounds experimentally. On the other hand, computational approaches have shown their great advantages and been employed to obtain HOFs of those demanding materials.[14−20] The group additivity method is an empirical model with some limits in its application.[14] MO methods are much more widely used. The parametrized semiempirical MO methods, such as MNDO, AM1, and PM3, are able to figure out HOFs directly and rapidly.[21−23] Although these semiempirical MO methods often bring significant HOFs errors for various groups and skeletons, the errors are sometimes systematic and can be corrected. Ab initio MO methods are employed to calculate HOF, too. For this purpose, certain reactions need to be designed and accurate energies are required. For obtaining accurate total energies, one often need to perform high-level calculations such as QCISD(T) and MP2 methods with electron correlation correction, which are computationally expensive and even impossible for large molecules. Nowadays, the density functional theory (DFT)[24,25] methods, especially the B3LYP[26,27] hybrid DFT method that not only produces 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.

In this paper, the HOFs have been calculated for 10 polydifluoroaminocubanes (the number of difluoroamino groups: $m = 1-8$) using the density functional theory B3LYP method, HF, and MP2 methods with 6-31G* basis set via designed isodesmic reactions. The approximate HOFs were also obtained from the semiepirical MO methods. Results from different methods were compared. The interactions between the difluoroamino groups in polydifluoroaminocubanes were investigated. The relationship between structure and stability was analyzed. These results provide useful information for the molecular design of novel high energetic density materials.

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1. Computational Methods

The hybrid DFT-B3LYP, HF, and MP2 methods with 6-31G* basis set via designed isodesmic reactions were adopted for the prediction of HOFs.[17−19,28,29] The method of isodesmic reactions has been employed very successfully to calculate HOF from total energies obtained from ab initio calculations. The so-called isodesmic reaction processes, in which the number of each kind of formal bond is conserved, are used with application of the bond separation reaction (BSR) rules. The molecule is broken down into a set of two heavy-atom molecules containing the same component bonds.[29] However, usual bond separation reaction rules cannot be applied to the molecules with delocalized bonds and cage skeletons because of large calculation errors of HOFs. To solve this problem, we do not break down the cubane cage skeletons in polydifluoroaminocubanes. To be specific, we take cubane as a reference compound (the experimental HOF of cubane is 622.1 kJ/mol in the gas phase). This approach has been proved to be reliable.[18,19]

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

$$C_8H_{8-m}(NF_2)_m + mCH_4 \rightarrow C_8H_8 + mCH_3NF_2 \qquad (1)$$

where m is the number of the difluoroamino groups in polydifluoroaminocubane molecules $C_8H_{8-m}(NF_2)_m$ and C_8H_8 is cubane. For the isodesmic reaction 1, heat of reaction ΔH_{298} at 298 K can be calculated from the following equation:

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

where $\Delta H_{f,R}$ and $\Delta H_{f,P}$ are the HOFs of reactants and products at 298 K, respectively. As experimental HOFs of CH_3NF_2 are unavailable, additional calculations were carried out for the replacement reaction $CH_3NH_2 + F_2 \rightarrow CH_3NF_2 + H_2$ using the G2 theory to get an accurate value of ΔH_f for CH_3NF_2. Both the experimental HOFs of reference compounds C_8H_8 and CH_4 are available. The HOFs of polynitrocubanes ($C_8H_{8-m}(NF_2)_m$) can be figured out when the heat of reaction ΔH_{298} is known. Therefore, the most important thing is to compute the ΔH_{298}. ΔH_{298} can be calculated using the following expression:

$$\Delta H_{298} = \Delta E_{298} + \Delta(PV) = \Delta E_0 + \Delta ZPE + \Delta H_T + \Delta nRT \qquad (3)$$

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 (ZPE) of the products and the reactants at 0 K, and ΔH_T is thermal correction from 0 to 298 K. The $\Delta(PV)$ value in eq 3 is the PV work term. It equals ΔnRT for the reactions of an ideal gas. For the isodesmic reaction 1, $\Delta n = 0$, so $\Delta(PV) = 0$.

To determine the strength of the interactions among the difluoroamino groups, we computed the disproportionation energy[7] of n molar of monodifluoroaminocubanes to $C_8H_{8-n}(NF_2)_n$ and cubane (eq 4) according to the energy change of the isodesmic reaction:

$$nC_8H_7NF_2 \rightarrow (n-1)C_8H_8 + C_8H_{8-n}(NF_2)_n \qquad (4)$$

Computations were also performed with the Gaussian 98 package[30] at the MNDO, AM1, and PM3 levels as well as at the B3LYP, HF, and MP2 levels. 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 local energy minima on the potential energy surfaces without imaginary frequencies.

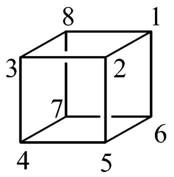


Figure 1. Molecular framework and atomic numbering of cubane.

2. Results and Discussion

2.1. Heat of Formation. Figure 1 shows the molecular framework and atomic numbering of cubane. Table 1 lists the total energies, zero-point energies, and the values of thermal correction at the B3LYP/6-31G* and HF/6-31G* levels for three reference compounds being enlisted in the isodesmic reaction 1. The experimental HOFs of reference compounds C_8H_8 and CH_4 are taken from refs 31 and 32. An accurate value of ΔH_f for CH_3NF_2 was obtained from the replacement reaction $CH_3NH_2 + F_2 \rightarrow CH_3NF_2 + H_2$ using the G2 theory.[33] Table 2 summarizes the total energies, zero-point energies, and the values of thermal correction for title compounds and the values of HOFs obtained through using eq 2. Previous studies showed that the theoretically predicted values of HOF were in good agreement with experiments by choosing appropriate reference compounds in the isodesmic reaction. An efficient strategy of reducing errors of HOF is to keep the conjugated bonds or cage skeletons being unbroken. This approach has been proved to be reliable.[18,19,34,35] On that basis, data in Table 2 are supposed to be credible, although the experimental values of HOFs are unavailable for comparison.

As for the HOFs obtained from B3LYP method, it can be seen from Table 2 that the value of HOF relates to the number of difluoroamino groups. Also noteworthy is that the HOFs of polydifluoroaminocubane isomers with the same number of $-NF_2$ groups are affected by the position of difluoroamino groups. As for three di-difluoroaminocubane isomers, the HOFs of the 1,3- and 1,4-isomers are close to each other, while the HOF value of the 1,2-isomer is larger than those of the former two isomers by over 11 kJ/mol, indicating that the polydifluoroaminocubanes are more stable when the difluoroamino groups are kept away from each other. It is on this basis that we only compute the most stable isomers with the lowest HOF. Variations of HOFs with the number of difluoroamino group show that the HOF decreases with each additional difluoroamino group being introduced to the cubane skeleton. However, the degree of the decrement depends on the number of the difluoroamino group already on the skeleton. The general trend is that the HOF decreases dramatically at the beginning and then gradually as the number of groups increases. The contribution of the difluoroamino group to the heat of formation deviates from group additivity. The difference between the HOFs of cubane and monodifluoroaminocubane is as large as 78.6 kJ mol^{-1}, which is the largest decrement for one difluoroamino group added. It is mainly due to the electronic effect when the strong withdrawing NF_2 group is attached to the cubane skeleton.

We also calculated the HOFs at both the HF and the MP2//HF level to evaluate the method dependence. The HOFs from the MP2//HF level, as well as their variations with the number of difluoroamino group, are close to those obtained from the B3LYP method. There is a very good linear relationship between the HOFs from these two methods. $HOF_{MP2} = 1.1652HOF_{DFT} - 92.562$, with $R^2 = 0.9986$. However, there is big difference

TABLE 1: Calculated Total Energy (E_0), Zero-Point Energy (ZPE), Values of Thermal Correction (H_T), and Heats of Formation (HOF*)* of the Reference Compounds[a]

	DFT/6-31G*			HF/6-31G*			
compd	E_0	ZPE	H_T	E_0	ZPE	H_T	HOF
C_8H_8	−309.46034	338.06	14.94	−307.393906	338.30	14.74	622.1[31]
CH_4	−40.51838	113.98	10.02	−40.19517	111.63	10.02	−74.4[32]
CH_3NF_2	−294.20586	119.32	13.79	−292.78521	120.75	13.55	−115.23[b]

[a] E_0 is in au; ZPE, HOF, and H_T are in kJ/mol. The scaling factors for the ZPE are 0.96 and 0.89 at the DFT and HF levels, respectively. [b] Calculated value at the G2 level from the permutation reaction: $CH_3NH_2 + F_2 \rightarrow CH_3NF_2 + H_2$.

TABLE 2: Total Energy (E_0), Zero-Point Energy (ZPE*)*, Values of Thermal Correction (H_T), and Heats of Formation (HOF) of the Title Compounds[a]

	DFT/6-31G*				HF/6-31G*				
compd[b]	E_0	ZPE	H_T	HOF	E_0	ZPE	H_T	HOF	HOF[c]
1-	−563.160985	335.91	23.04	543.53	−559.993033	339.53	22.40	553.66	537.01
1,2-	−816.853905	333.57	31.15	485.06	−812.584452	340.52	30.22	505.37	471.18
1,3-	−816.858084	333.32	31.30	473.98	−812.588641	340.34	30.30	494.27	460.36
1,4-	−816.858942	333.20	31.34	471.66	−812.589614	340.32	30.32	491.72	458.30
1,3,5-	−1070.55226	330.40	39.78	430.69	−1065.18121	340.78	38.38	462.55	411.12
1,3,5,7-	−1324.24376	327.39	48.32	357.02	−1317.77074	340.95	46.60	398.93	328.96
1,2,3,5,7-	−1577.92388	324.61	56.47	331.76	−1570.34687	341.50	54.60	390.52	298.64
1,2,3,4,5,7-	−1831.60188	321.28	64.96	311.84	−1822.92064	341.95	62.55	388.17	272.68
hepta-	−2085.27824	318.24	73.20	296.28	−2075.49218	342.23	70.53	391.50	250.18
octa-	−2338.95277	315.52	81.04	285.44	−2328.06135	342.49	78.42	400.98	231.93

[a] E_0 is in au; ZPE, HOF, and H_T are in kJ/mol. The scaling factors for the ZPE are 0.96 and 0.89 at the DFT and HF levels, respectively. [b] 1- and 1,2- denote 1-difluoroaminocubane and 1,2-di-difluoroaminocubane, respectively; the others are similar. [c] HOF at the MP2/6-31G*//HF/6-31G* level.

TABLE 3: Heats of Formation (kJ/mol) Obtained from Three Semiempirical MO Methods for Polydifluoroaminocubanes[a]

compd	MNDO	AM1	PM3
1-	391.45	607.99	456.81
1,2-	382.89	594.32	444.79
1,3-	377.78	590.93	444.47
1,4-	375.55	589.28	443.18
1,3,5-	371.84	581.00	438.13
1,3,5,7-	373.18	576.97	436.72
1,2,3,5,7-	394.03	577.51	446.60
1,2,3,4,5,7-	420.58	582.20	450.06
hepta-	451.71	590.31	460.55
octa-	487.40	601.45	486.62

[a] 1- and 1,2- denote 1-difluoroaminocubane and 1,2-di-difluoroaminocubane, respectively; the others are similar.

TABLE 4: Disproportionation Energies (kJ/mol) of Polydifluoroaminocubanes and Average Mulliken Charges on NF_2 Groups at the B3LYP/6-31G* Level[a]

compd	$E_{disproportion}$	avg charge on NF_2
1-	0.00	−0.3482
1,2-	20.28	−0.3353
1,3-	9.31	−0.3317
1,4-	7.06	−0.3343
1,3,5-	26.30	−0.3167
1,3,5,7-	50.30	−0.3029
1,2,3,5,7-	104.20	−0.2939
1,2,3,4,5,7-	163.64	−0.2867
hepta-	227.40	−0.2789
octa-	295.97	−0.2729

[a] 1- and 1,2- denote 1-difluoroaminocubane and 1,2-di-difluoroaminocubane, respectively; the others are similar.

between the HOFs from the HF method and those from the B3LYP or MP2 method when the number of difluoroamino group is over 4. The more the number of difluoroamino group is, the more the difference of HOF. This discrepancy indicates that it is necessary to include the electron correlation in the computation of HOF.

2.2. Comparison of DFT and Semiempirical Results. Semiempirical MO methods could give the HOFs directly and rapidly for a series of compounds. However, its validity is limited. Table 3 shows that the HOFs obtained from the AM1 method are relatively large, the HOFs from MNDO method are smaller, and those from PM3 method are somewhere between. There are large discrepancies between the semiempirical MO results and the DFT results for the HOF values and for the changes of the values with the numbers of substituent groups. The HOFs from semiempirical MO initially decrease but then increase with more substituent groups attached to the cubane skeleton, while the DFT HOFs always decrease with the increase of difluoroamino groups. For three di-difluoroaminocubanes, the HOFs from MNDO and AM1 become smaller with the substituent groups being apart from each other, while those from PM3 are hardly affected by the distance between the groups. On the other hand, when the number of difluoroamino group varies from 7 to 8, the HOFs obtained from MNDO and PM3 increase, while the HOFs from AM1 hardly change. Therefore, there are large discrepancies among these three methods for the repulsion of difluoroamino groups. If the HOFs from DFT are referred to as criteria, semiempirical MO are unsuitable for computing the HOFs of title compounds.

2.3. Interactions among the Difluoroamino Groups in Polydifluoroaminocubanes. The disproportionation energies $E_{disproportion}$ of three di-difluoroaminocubanes shown in Table 4 indicated that the distance between the substituent groups influences the interactions and the interaction of adjacent groups is much stronger than that of para groups. The interactions between the difluoroamino groups increase rapidly as the number of groups increases. For polysubstituted cubane, the group interactions include those of ortho, meta, and para groups.

The disproportionation energy of two molecules of tetradifluoroaminocubane to octadifluoroaminocubane plus cubane (Scheme 1) was computed to evaluate the size of the nearest-neighbor interactions in octadifluoroaminocubane. The energy of this isodesmic reaction was calculated to be 195.36 kJ/mol at the B3LYP/6-31G* level. The energy change in Scheme 1

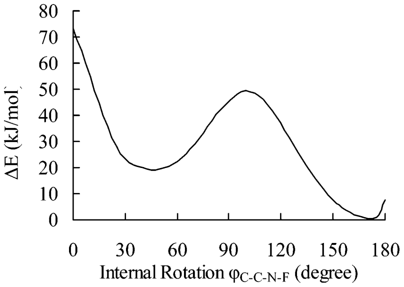
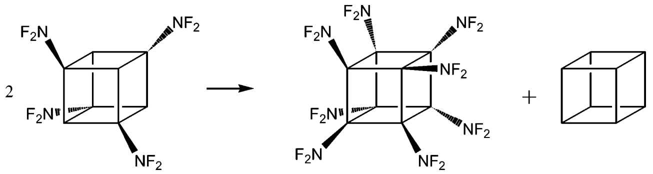


Figure 2. Energy profile for C−N internal rotation of NF_2 group of octadifluoroaminocubane.

SCHEME 1



contains 4 interactions along the body diagonals and 12 interactions of nearest-neighbor. The former can be estimated as 4 times the disproportionation energy of the isodesmic reaction [$2C_8H_7NF_2 \rightarrow 1,4\text{-}C_8H_6(NF_2)_2 + C_8H_8$]. From Table 4, the total energy associated with these 4 times of the 1,4-interactions in octadifluoroaminocubane is thus estimated to be 28.24 kJ/mol. Subtracting this energy from the energy computed for the isodesmic reaction in Scheme 1 gives values of 167.12 kJ/mol, which is associated with the total of 12 nearest-neighbor difluoroamino interactions in octadifluoroaminocubane. The average energy of each such interaction is therefore 13.94 kJ/mol at the B3LYP level of theory. This value is 6.34 kJ/mol smaller than the corresponding values 20.28 kJ/mol for the nearest-neighbor difluoroamino interaction in 1,2-di-difluoroamimocubane. This demonstrates that the nearest-neighbor difluoroamino interaction deviates from group additivity and that the nearest-neighbor group interaction decreases as the number of groups increases. The nearest-neighbor interactions in other polydifluoroaminocubanes are between those of di-difluoroamino and octa-difluoroaminocubane, ca. 14−20 kJ/mol. The contribution of the difluoroamino group to the heat of formation deviates from group additivity, just due to that the nearest-neighbor interactions relate to the substituent numbers. Obviously, the nearest-neighbor group interactions of octadifluoroaminocubane are referred to its most stable conformer. Table 4 also shows that the average charge on the NF_2 group decreases as the number of groups increases. There is the same variability of average charge on the NF_2 group and HOFs with the changes of the number of difluoroamino groups. It is therefore deduced that the nearest-neighbor interaction is partly electrostatic. Figure 2 shows the energy profile for the C−N internal rotation of NF_2 group of octadifluoroaminocubane, with the largest rotation barrier of 54.3 kJ/mol. This demonstrates that the C−N internal rotation of NF_2 group could take place freely at room temperature since the neighbor group interactions are small. In addition, the C−NF_2 internal rotation barrier in the monodifluoroaminocubane is 27.8 kJ/mol at most, which is about one-half of that in the octadifluoroaminocubane, so there are significant steric interactions between neighboring NF_2 group in fully substituted derivatives; that is, steric effects account for a portion of the nonadditivity of HOFs.

2.4. Electronic Structure and Molecular Stability. Table 5 lists energies (au) of frontier molecular orbitals and their gaps (ΔE) and average Mulliken populations on C−NF_2 bonds for the optimized polydifluoroaminocubane at the B3LYP/6-31G* level. As for three di-difluoroaminocubane isomers, the ΔE value of the 1,2-isomer is slightly smaller, while that of the 1,4-isomer is slightly larger, indicating the latter is slightly more stable than the former. The stability here refers to the chemical or photochemical processes with electron transfer or electron leap. From the ΔE values in Table 5, it can be deduced that the stability generally decreases as the substituent number increases.

TABLE 5: Energies (au) of Frontier Molecular Orbitals and Their Gaps; Average Mulliken Populations on C−NF_2 Bonds at the B3LYP/6-31G* Level[a]

compd	E_{HOMO}	E_{LUMO}	$\Delta E_{\text{LUMO-HOMO}}$	P_{CN}
1-	−0.2641	0.0250	0.2891	0.1136
1,2-	−0.2731	0.0026	0.2757	0.0975
1,3-	−0.2767	0.0050	0.2817	0.1165
1,4-	−0.2773	0.0072	0.2845	0.1139
1,3,5-	−0.2903	−0.0124	0.2779	0.1175
1,3,5,7-	−0.3019	−0.0272	0.2747	0.1186
1,2,3,5,7-	−0.3067	−0.0395	0.2672	0.0956
1,2,3,4,5,7-	−0.3141	−0.0498	0.2643	0.0802
hepta-	−0.3188	−0.0602	0.2586	0.0661
octa-	−0.3241	−0.0685	0.2556	0.0572

[a] 1- and 1,2- denote 1-difluoroaminocubane and 1,2-di-difluoroaminocubane, respectively; the others are similar.

Table 5 also collects the average Mulliken populations on the C−NF_2 bonds. As a whole, the larger the populations are, the more the bonding overlaps are. Therefore, bonds with large populations are relatively strong and resistant to rupture. Our recent computational results show that the energy barrieres for the skeleton C−C ruptures of cage compounds are much larger than those of the C−NO_2 ruptures.[34,35] By judging from the similarity of NF_2 and NO_2 as an electron-withdrawing group, it can be predicted that the C−NF_2 bond is an initiator during the thermolysis process. This prediction is further supported by the fact that the C−N population is only 0.3−0.5 times of the C−C population. According to the principle of the smallest bond order (PSBO),[19] octadifluoroaminocubane has the smallest C−N population of 0.0572; its sensitivity is therefore large, and it is relatively unstable for thermolysis. While the 1,3,5,7-tetradifluoroaminocubane has the largest C−N population of 0.1186, its sensitivity is therefore small, and it is relatively stable for thermolysis.

3. Conclusion

On the basis of the HOFs calculated for a series of polydifluoroaminocubanes at DFT-B3LYP, HF, and MP2 levels of theory, the following conclusions can be drawn:

(1) The HOFs for the title compounds decreased dramatically initially and then gradually with each difluoroamino group attached to the cubane skeleton. The nearest-neighbor difluoroamino interaction deviates from group additivity, and the nearest-neighbor group interaction decreases as the number of the substituted groups increases.

(2) The average charge on the NF_2 group decreases as the number of groups increases. The nearest-neighbor interaction is partly electrostatic. The steric effects account for a portion of the nonadditivity of HOFs.

(3) The HOFs from the MP2//HF level and the B3LYP method are similar. The HF method gives different values of HOFs when the number of difluoroamino group is over 4. It is necessary to include the electron correlation in the computation of HOFs.

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