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ESTIMATION OF THERMODYNAMIC STABILITY AND CHARGE DISTRIBUTION FOR UNKNOWN MOLECULES: NITRO DERIVATIVES OF CUBANE

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Three useful procedures for estimating the thermodynamic stability and charge distribution of moderately complex unknown species are illustrated by the successive nitration of cubane. (1) Five different, but interrelated, energy criteria are employed, which leads to mutually supportive conclusions that overcome deficiencies in any one of the single measures. (2) Mulliken charge and overlap populations can lead to correct bond strength trends if appropriate averaging over bond types is carried out. (3) Lewis–Langmuir atomic charges, an interpolation between the formal charges of Lewis dot structures and oxidation numbers which does not require use of computers, provides atomic charges similar to those from *ab initio* wavefunctions. The simplicity of this scheme aids in identifying the chemical and topological origin of molecular charge distributions. *Ab initio* calculations for the strain energies and heats of reaction for four different reaction sequences are reported, together with Mulliken atomic charges and overlap populations for the nitrocubanes. Trends in these measures suggest that hexa- and octa-nitrocubane are thermodynamically stable species.

INTRODUCTION

A principal rationalization for carrying out electronic structure calculations has always been that they can provide molecular properties outside the range available to current physical measurements and synthetic techniques. Two of the most important such properties are clearly thermodynamic stability and molecular charge distribution. In many cases, particularly for molecules made up of only a few atoms, the methods for determining thermodynamic stability and molecular charge distribution are straightforward and the main problem is that of computing sufficiently accurate wavefunctions. For larger molecules, and especially those with unusual bonding patterns, interpretation of the computed wavefunctions becomes a central issue. Many man-years of intensive synthetic effort have so far failed to achieve higher nitrocubanes and, in addition, their highly strained bonds and size put a premium on interpretation methods for assaying their potential stability and atomic charges.

The first synthesis of cubane was accomplished in the early 1960s,[1a,b] and recently cubane derivatives with up to four nitro groups have also been synthesized.[1c–e] Synthetic efforts are currently being directed toward the larger hexa- and octa-nitrocubanes, but are complicated by the close proximity of the nitro groups and the opportunity for C—C bond cleavage in intermediates having an amine on one carbon and a vicinal nitro group. We studied cubane and its nitro derivatives shown in Figure 1 (the molecules are labelled according to the number of nitro groups present, e.g. disubsti-

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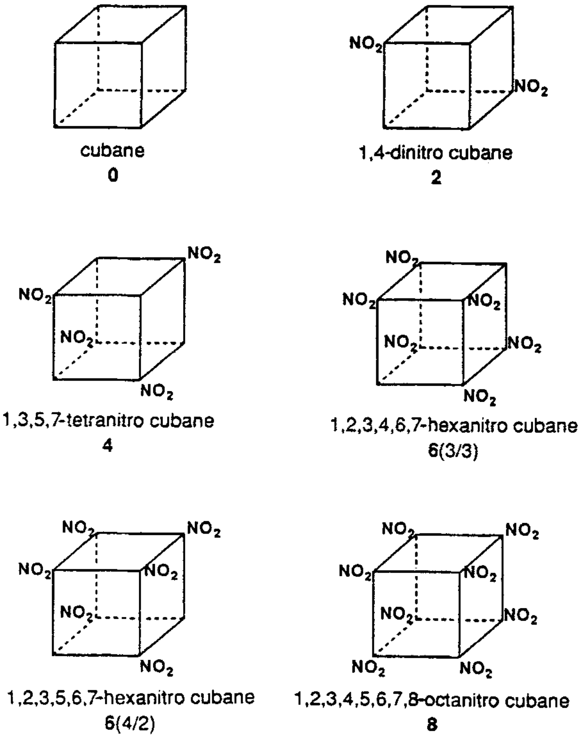

Figure 1. Cubane and its nitro derivatives (labelled according to the number of nitro groups present). Test of the thermodynamic stabilities of **6** and **8** was a principal aim of this investigation

tuted cubane will be referred to as **2**). The di- and tetranitrocubanes shown have already been synthesized, so only those isomers were examined, and in the hexanitro case the two most reasonable isomers were considered (and distinguished according to the number of nitro groups on the top/bottom faces). Our investigation examined total energies, strain energies, decomposition energies, atomization energies, heats of formation, oxidation energies, overlap populations and atomic charges.

COMPUTATIONAL METHODS

Ab initio molecular orbital calculations were carried out with the GAUSSIAN 86[2] program using the STO-3G basis set[3] on an ETA 10. Experimental geometries[1e,f,4] are known for **0**, **2** and **4** and geometries for **6** and **8** were obtained using AM1, a semi-empirical electronic structure calculational approach.[5] It was found that energy-optimized geometries from this scheme gave good agreement with experiment for the known geometries noted (Table 1). We have previously found it to yield correspondingly good agreement with the substituted propellanes,[6] the other set of highly strained substituted hydrocarbons for which geometries are known. Strain energies were calculated via isodesmic reactions[7] and a Mulliken population analysis[8] was performed to obtain charges and overlaps. The heats of various reactions involving the nitrocubanes were obtained using the calculated total energies of the nitrocubanes and archive values[9] for other species. Hariharan *et al.*[10] have previously studied all of the nitrocubanes using their *ab initio* MODPOT/VRDDO/MERGE method. They determined molecular electrostatic potentials and skeletal overlap populations, the latter of which can be compared with our results. A recently developed scheme, Lewis–Langmuir atomic charges,[11] employs an electronegativity ratio of bonded atoms to give polarity to Lewis dot structures, and it has been applied here to give chemical insight into the pattern of Mulliken atomic charges obtained from the *ab initio* calculations.

RESULTS

Total energy and strain energy

Table 1 gives the calculated total energies and strain energies for the selected compounds **0**–**8**, together with the calculated geometries. Total energy versus number of nitro groups (Figure 2) yields the expected linear relationship (the total energies of the two **6** isomers are too close to determine unequivocally which isomer is the more stable).

Strain energies were calculated using the isodesmic reactions given in Scheme 1. An isodesmic reaction is one in which there are the same number of bonds of a given type on both sides of the reaction but with a change in the structural relationships between them. Strain energy defined in this way is a comparison of the energy of the system as a ring with that as an open chain. The cubane strain energy calculated here compares favorably with the experimental value (154·7 kcal mol^{-1})[12] and other calculated values (164·3 kcal mol^{-1}; STO-3G).[13] More importantly, we wish to examine the trend in strain energies here. The graph of strain energy vs number of nitro groups (Figure 3) is smooth and similar in form to other strain-energy curves.[6] The 4/2 isomer of **6** fits the curve better than the 3/3 isomer. Comparison of strain energies per C—C bond shows the strain of the largest synthesized nitrocubane **4** to be comparable to the strained hydrocarbon [1.1.1]propellane (17·6 kcal mol^{-1}; 6–31G*, from an isodesmic reaction in the reference cited),[6] also a known compound. The strain of the larger nitrocubanes is in the range of that of tetra-*tert*-butyltetrahedrane (experimental strain energy of 21·5 kcal mol^{-1} per skeletal C—C bond), the only tetrahedrane definitely synthesized and the most highly

Table 1. *Ab initio* STO-3G total energies and strain energies of nitrocubanes[a]

Cubane	Total energy (au)	Strain energy (kcal mol^{-1})[b]	Strain energy per C—C (kcal mol^{-1})[b]	C—C (Å)	C—H (Å)	C—N (Å)
0	−303·7785	166·87	13·91	1·5680	1·1069	—
				1·551	1·06	
2	−705·1525	180·45	15·04	C_1—C_2 1·5927	1·1056	1·4366
				1·551		1·466
				C_2—C_3 1·5607		
				1·564		
				Av. 1·5767		
4	−1106.5022	209.25	17.44	1.5844	1.1071	1.4474
				1.558		1.472
6 (3/3)	−1507.7923	275.46	22.96	C_1—C_2 1.5890	1.0944	1.4832
				C_1—C_8 1.5855		
				Av. 1·5873		
6 (4/2)	−1507·8420	244·32	20·36	C_1—C_2 1·5789	1·0963	C_1—N 1·5344
				C_3—C_4 1·5734		C_2—N 1·5377
				C_2—C_3 1·5789		C_3—N 1·5204
				C_1—C_8 1·5738		Av. 1·5308
				Av. 1·5762		
8	−1909·1536	297·04	24·75	1·5781	—	1·5496

[a] Geometries obtained from energy-optimized AM1 semi-empirical calculations. Experimental values for **0**, **2** and **4** are listed immediately below AM1 values. For references, see text.

[b] 1 kcal = 4·184 kJ.

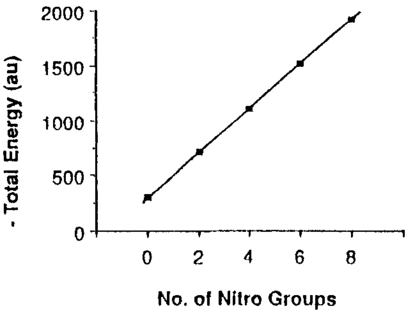

Figure 2. Negative of total energy versus number of nitro groups. *Ab initio* calculations using an STO-3G basis set

$$\text{NITROCUBANE} + x\,CH_4 \longrightarrow a\,CH_3-CH_3 + b\,CH_3-NO_2$$

Scheme 1

strained saturated hydrocarbon.[14] Since calculated strain energies tend to be slightly higher than experimental values, the calculated range of 20–25 kcal mol^{-1} for **6**–**8** compares favorably with the tetrahedrane experimental measurement. Although there is no thermodynamic law governing allowed strain energies, prior synthetic experience suggests no impediment to the realization of the higher nitrocubanes as far as strain energy is concerned.

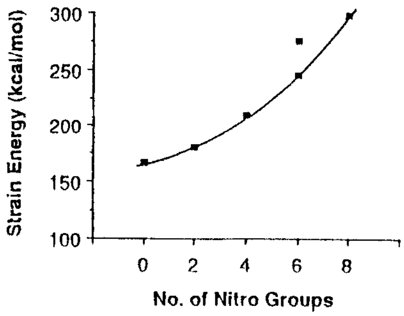

Figure 3. Strain energy versus number of nitro groups. See Scheme 1 for definition of strain energies. This curve shows approximately the same shape and magnitudes as those for other highly strained molecules and therefore suggests no impediment to the synthesis of the higher nitrocubanes

Thermodynamic analysis

The heats of reaction of four reactions involving the nitrocubanes (Scheme 2, I–IV) were calculated by $E_{\text{products}} - E_{\text{reactants}}$. The results are given in Table 2. Note that no correction was made for zero-point energies, heat capacities or PV work.

The first reaction examined was the decomposition to H_2O, CO_2, CO, C and N_2, the products usually seen in the laboratory (Scheme 2, I; Figure 4). For **2** the reaction is endothermic, for **4** almost thermoneutral and for **6** and **8** exothermic. Although this is intuitively

Table 2. Thermodynamic analysis of nitrocubanes (STO-3G) (all values in kcal mol^{-1})

Cubane	ΔH Decomp.	ΔH O_2	ΔH Form.	ΔH Atom.	ΔH Atom. per bond broken
0	—	−698·93	−1626·33	+2089·06	+104·45
2	+1193·24	−723·83	−1555·87	+2434·68	+93·64
4	+23·37	−763·95	−1470·19	+2765·10	+86·41
6 (3/3)	−263·80	−841·48	−1347·10	+3058·09	+80·48
6 (4/2)	−232·66	−810·34	−1378·24	+3089·24	+81·30
8	−874·38	−874·38	−1268·64	+3395·73	+77·18

I. ΔH Decomp.

$$\text{NITROCUBANE} \longrightarrow a\,H_2O + b\,CO_2 + c\,CO + d\,C + e\,N_2$$

II. ΔH O_2

$$\text{NITROCUBANE} + x\,O_2 \longrightarrow a\,CO_2 + b\,H_2O + c\,N_2$$

III. ΔH Form.

$$a\,C + b\,H_2 + c\,N_2 + d\,O_2 \longrightarrow \text{NITROCUBANE}$$

IV. ΔH Atom.

$$\text{NITROCUBANE} \longrightarrow a\,C + b\,N + c\,O + d\,H$$

Scheme 2

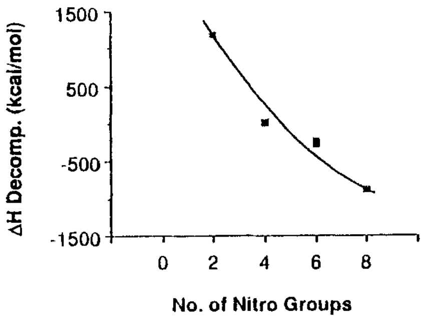

Figure 4. ΔH of decomposition to H_2O, CO_2, CO, C and N_2 versus number of nitro groups. See Scheme 2 for reactions defining ΔH for this curve and those in Figures 5, 6 and 7

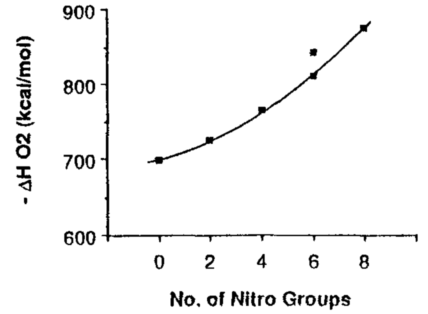

Figure 5. $-\Delta H$ of oxidation versus number of nitro groups

suggestive of decreasing stability as one progresses to higher nitro substitution, the smooth, slightly concave curve does not imply that octanitrocubane is unrealizable.

The next reaction examined was oxidation of the nitrocubanes to form CO_2, H_2O and N_2 (Scheme 2, II; Figure 5). The negative of the reaction energy (i.e. the energy released) was plotted, and can be seen to be rising continuously with no breaks in the curve. The 4/2 isomer of **6** fits the rising trend better than the 3/3 isomer.

The heat of formation from the elements in their most stable form was the third reaction considered (Scheme 2, III; Figure 6). The graph of $-\Delta H$ Form versus number of NO_2 groups shows that the heat evolved becomes smaller as the nitrocubane becomes larger, indicating that the larger nitrocubanes are less

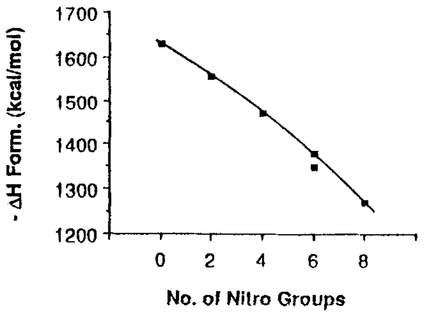

Figure 6. $-\Delta H$ of formation from the elements versus number of nitro groups

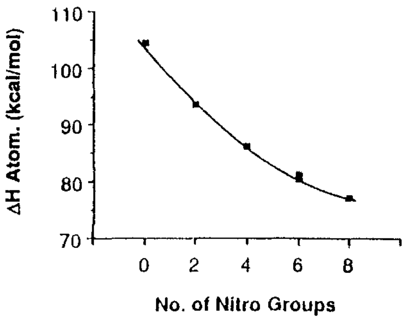

Figure 7. ΔH of atomization (for all bonds broken) versus number of nitro groups. This and Figures 4, 5 and 6 show that although the stability of the nitrocubanes systematically decreases for successively higher nitration levels, the trends give no reason to believe that **6** and **8** are unrealizable

stable. However, the diminishing trend is fairly constant and not precipitous. Again, the 4/2 isomer of **6** gives a slightly better fit to the trend.

The fourth reaction examined was the complete atomization of the nitrocubanes (where all bonds are being broken) (Scheme 2, IV; Figure 7). The quantity plotted is the heat of atomization per number of bonds broken, and produces a smooth curve. From this we see that the energy needed to accomplish the atomization becomes less as the nitrocubane becomes larger, since the skeleton becomes weaker as more nitro groups are withdrawing electrons.

The straightforward conclusion from all four of these possible reaction sequences is that the stability of the nitrocubanes systematically decreases with successively higher nitration levels, but the trends give no reason to suggest that octanitrocubane is unrealizable. Determination of the kinetic barriers is required to ascertain whether or not the higher nitrocubanes can, in principle, be synthesized.

Mulliken charges

Table 3 gives the results of Mulliken population analysis. Averaging over all carbons, the carbon charge is seen to decrease from negative to positive (Figure 8). This is reasonable, since more charge is being pulled off the cubane skeleton as more nitro groups are added. Averaging over the two types of carbons present, C attached to H and C attached to NO_2, gives a more meaningful result than treating them separately because of the well-known problem in Mulliken population

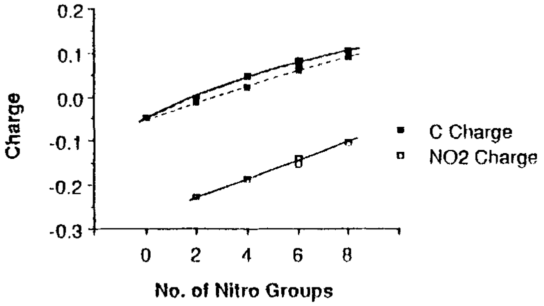

Figure 8. (■) Carbon and (□) nitro group charges from Mulliken population analysis versus number of nitro groups. Dashed line: Lewis–Langmuir atomic charges

Table 3. Mulliken population analysis and Lewis–Langmuir (LL) atomic charges

Cubane	Carbon charge (Mulliken)	Carbon charge (LL)	NO_2 charge (Mulliken)	C—C overlap	C—N overlap
0	−0·0493	−0·0504	—	0·6562	—
2	C_1 +0·0827		−0·2263	C_1—C_2 0·6329	0·5865
	C_2 −0·0318			C_2—C_3 0·6654	
	Av. −0·0032	−0·0146		Av. 0·6492	
4	C_1 +0·0929		−0·1882	0·6438	0·5865
	C_2 −0·0115				
	Av. +0·0450	+0·0213			
6(3/3)	C_1 +0·1105		−0·1519	C_1—C_2 0·6311	0·5561
	C_5 −0·0127			C_1—C_8 0·6470	
	Av. +0·0797	+0·0572		Av. 0·6391	
6 (4/2)	C_1 +0·1036		—C_1 −0·1349	C_1—C_2 0·6340	C_1—N 0·5336
	C_2 +0·1042		—C_2 −0·1302	C_3—C_4 0·6494	C_2—N 0·5309
	C_3 +0·1023		—C_3 −0·1567	C_2—C_3 0·6337	C_3—N 0·5430
	C_4 −0·0201		Av. −0·1406	C_1—C_8 0·6505	Av. 0·5357
	Av. +0·0725	+0·0572		Av. 0·6418	
8	+0·1036	+0·0930	−0·1039	0·6368	0·5229

analysis that atomic orbital radial maxima frequently occur at the nuclear center of adjacent atoms.

Nitro group charges were also examined and are negative, as expected. A decrease as more nitro groups are added occurs since it becomes increasingly more difficult to remove electrons. Figure 8 plots NO_2 charge vs number of NO_2 groups on the same graph as that of the average C charge. Both plots are smooth, with the lines remaining about the same distance apart throughout the series, suggesting an almost constant bond dipole.

Lewis–Langmuir (LL) atomic charges require a Lewis dot structure and an electronegativity table as input, but are otherwise trivial to obtain. Moreover, since the formula employs an electronegativity ratio, the particular scale is not critical; we have used one recently proposed.[15] For example,

$$\begin{aligned} LL_C \text{ for cubane} &= 4 - [3 + 2\chi_C/(\chi_C + \chi_H)] \\ &= 4 - [3 + 2(2{\cdot}544)/(2{\cdot}544 + 2{\cdot}300)] \\ &= -0{\cdot}0504. \end{aligned}$$

Table 3 gives carbon atom average values and they are plotted in Figure 8; they clearly parallel the *ab initio* results. The extreme simplicity of the LL formula yields only two different carbon atom charges (C_3C—H = $-0{\cdot}0504$ and C_3C—N = $+0{\cdot}0930$), hence it is immediately apparent that differences in the carbon charge distribution for successively higher levels of nitration is solely a function of molecular topology. Because the LL formula, like Lewis dot structures themselves, depends only on nearest neighbor interactions, the NO_2 group charge appears to remain constant for all nitration levels. This is readily corrected, however, by utilizing the common chemical knowledge that it is successively harder for a given nitro group to pull charge from its carbon where more nitro groups are attached to the other carbons (as observed above for the *ab initio* nitro group charges). Therefore, increasing the electronegativity of the carbon by a small 3% increment for each pair of NO_2 groups added reproduces the NO_2 group charge trend seen in Figure 8 (the initial LL nitro group charge is $-0{\cdot}093$, in the same range as that found from the *ab initio* calculations).

Mulliken overlap populations

The C—C and C—N bond overlap populations are given in Table 3. Averaging over all C—C bonds produces the top curve in Figure 9(a), where overlap is plotted versus number of nitro groups. From this plot, it is clear that the C—C overlap is slightly decreasing, consistent with the relatively constant C—C bond lengths throughout the series. Figure 9(a) also shows the plot of C—N overlap versus number of nitro groups. The C—N overlap parallels C—N length in that the overlap decreases as the C—N length increases, suggesting a decrease in the strength of the C—N bonds. That the C—C overlap is greater than that of C—N is not surprising in light of the conventional bond energies of 85 kcal mol^{-1} for C—C and 50–60 kcal mol^{-1} for C—N. In terms of C—C overlap the 4/2 isomer of **6** is favored, while for C—N overlap the 3/3 isomer is favored. Both the C—C and C—N overlap curves are entirely in line with and supportive of the stability conclusions we obtained from the analysis of the four reaction sequences given above, i.e. the stability of nitrocubanes decreases systematically as more nitro groups are added.

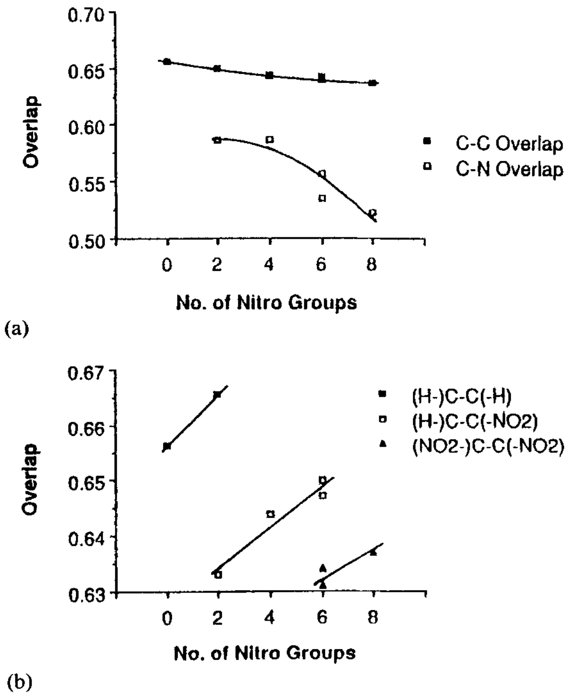

Figure 9. (a) Average (■) C—C and (□) C—N overlap versus number of nitro groups. (b) C—C overlap versus number of nitro groups, with each type of C—C bond treated separately: (■) (H)C—C(H); (□) (H)C—C(NO_2); (▲) (NO_2)C—C(NO_2). In this and Figure 8 full averaging is needed to obtain chemically meaningful charges and overlap populations

It is now instructive to plot the same data, but separating out each type of C—C bond: those in which the carbons are bonded to two hydrogens, to two nitro groups or to one hydrogen and one nitro group. The resulting plots are given in Figure 9(b). Each curve individually shows a nearly linear *increase* in overlap with increasing nitration, thereby suggesting a greater stability for **6** and **8** over that of **2** or **4**! Moreover, at least initially, one is inclined to favor Figure 9(b) over 9(a) because it treats each C—C bond type independently and, in addition, appears to yield more detailed information. The results obtained by Hariharan *et al.*[10] parallel those in Figure 9(b). The problem with Figure 9(b) has basically the same origin as that noted above with regard to Mulliken atomic charges: the coefficients of atomic orbitals on a specified nucleus often reflect the effective potential of an adjacent atom in addition to the parent atom. This is particularly severe in an interconnected cage structure such as the cubanes, and the only way to eliminate contamination of the C—C overlaps by their attached atoms (or groups) is to average over all the C—C bond types.

CONCLUSIONS

Ab initio wavefunctions were obtained for cubane and its derivatives with an even number of nitro group substituents to assay the thermodynamic stability of the larger nitrocubanes. Trends as a function of number of nitro groups in strain energies, decomposition energies, oxidation energies, formation energies, atomization energies, atomic charges and overlap populations suggest that hexa- and octa-nitrocubane are thermodynamically stable species. The 4/2 isomer of **6** may be slightly more stable than the 3/3 isomer. The use of five different, but interrelated, energy criteria leads to mutually supportive conclusions and helps overcome deficiencies in any single measure. Mulliken charge and overlap populations can lead to correct interpretations when full averaging is used, but may otherwise yield erroneous conclusions. Lewis–Langmuir (LL) atomic charges for the carbon atoms of the nitrocubanes closely parallel those from the *ab initio* wavefunctions. The simplicity of the LL formula shows that the carbon charges for successively higher nitration are governed solely by molecular topology.

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