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A Computational Study of the Interactions among the Nitro Groups in Octanitrocubane

David A. Hrovat,[†] Weston Thatcher Borden,*[,†] Philip E. Eaton,[§] and Bart Kahr*[,†]

*Contribution from the Department of Chemistry, Box 351700, University of Washington,
Seattle, Washington 98195-1700, and Department of Chemistry, 5735 South Ellis Avenue,
University of Chicago, Chicago, Illinois 60637*

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Abstract: *Ab initio* molecular orbital and density functional calculations on isodesmic disproportionation reactions of nitrated cubanes indicate that the repulsion between nitro groups on adjacent carbons in octanitrocubane (ONC) is surprisingly small and that the energy required for successive substitutions of nitro groups on the cubane frame diminishes progressively with increasing substitution. Mulliken population analyses show that, as a consequence of the inductive effects of the nitro groups on one another, the negative charges on the oxygens also decrease with increasing substitution reducing the magnitudes of the Coulomb repulsion between nearest-neighbor nitro groups. The computed D_4 symmetric equilibrium conformation of ONC, which is essentially the same as the conformation found in the crystalline state, effectively interdigitates the nitro substituents, thereby avoiding close O···O contacts. The O···O interactions remain very small throughout 180° rotations about the $C-NO_2$ bonds, a process that is computed to be nearly barrierless. The mechanism involves dynamic gearing of the eight nitro groups in ONC by correlated disrotation of two tetrahedral subsets of four nitro groups. Enantiomerization of the chiral, D_4 equilibrium conformation of ONC by this threshold mechanism passes through a D_{2d} transition structure. Dynamic gearing in ONC effects pseudorotation of the unique 4-fold axes to an orthogonal position with every 15° rotation of the nitro groups, thereby generating in ONC the time-averaged O_h symmetry of the parent hydrocarbon.

Introduction

Octanitrocubane (ONC), sought by some as a potentially potent explosive,[1] has recently succumbed to synthesis.[2] The widespread attention[3] this molecule has received has to do not only with its applications, but also its intriguing symmetry. Like tetra-*tert*-butyltetrahedrane (TTT),[4] ONC is a Platonic hydrocarbon in which all the hydrogens have been replaced with other substituents. However, unlike the substituents in TTT, the substituents in ONC destroy the 3-fold symmetry at the carbon atom vertices.

Part of the difficulty faced by Zhang et al. in preparing ONC from tetrahedrally substituted 1,3,5,7-tetranitrocubane (TNC) is presumably the energetic cost of introducing a total of 12 repulsive interactions between nearest-neighbor nitro groups, plus 4 smaller interactions between nitro groups along the body diagonals of the cube. What is the total energy of the nearest-neighbor interactions between the nitro groups in ONC? What is the conformation that minimizes these repulsive interactions? Are the nitro groups constrained in their rotations with respect to one another and by what mechanism do they rotate?

We have attempted to answer these questions by carrying out *ab initio* and density functional calculations on ONC.[5] The results of these calculations, which are described herein, have revealed unexpected features of the static and dynamic interactions between the nitro groups.

Computational Methodology

RHF *ab initio* and B3LYP[6] density functional calculations were performed. The 6-31G* basis set[7] was used for both types of calculations. Geometry optimizations and vibrational analyses were carried out with the Gaussian 98 suite of programs.[8] The geometries of all the stationary points found are available as Supporting Information.

To determine which method was likely to give the more accurate results we calculated the disproportionation enthalpy for $2CH_3NO_2 \rightarrow CH_2(NO_2)_2 + CH_4$ at both the RHF and B3LYP levels of theory, since a gas-phase value of $\Delta H^{298} = 6.6$ kcal/mol can be obtained from the

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[†] University of Washington.

[§] University of Chicago.

(1) Eaton, P. E.; Gilardi, R.; Zhang, M.-X. *Adv. Mat.* **2000**, *12*, 1143−1148.

(2) Zhang, M.-X.; Eaton, P. E.; Gilardi, R. *Angew. Chem., Int. Ed.* **2000**, *39*, 391−393.

(3) See for example: *The New York Times*, Jan. 25, **2000**, CXLIX, p D3; *Science News*, Jan. 22, **2000**, 154, p 54.

(4) Maier, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 309−332.

(5) Previous molecular orbital computations of octanitrocubane were focused on C−N bond strengths and dissociation pathways. See: Owens, F. J. *Theochem.-J. Mol. Struct*. **1999**, *460,* 137−140. Chapman, D. A.; Kaufman, J. J.; Buenker, R. J. *Int. J. Quantum Chem*. **1991**, *40*, 389−403.

(6) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *B37*, 785.

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(8) All calculations were performed using Gaussian 98. See: Frisch, M.; Trucks, J. G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Chessemen, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochteriski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Ketih, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.6; Gaussian, Inc.: Pittsburgh, PA, 1998.

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Table 1. RHF and B3LYP/6-31G* Energies (kcal/mol) for the Disproportionation of *x*-Molecules of Mononitrocubane to Cubane$(NO_2)_x$ Plus $(x - 1)$-Molecules of Cubane[a]

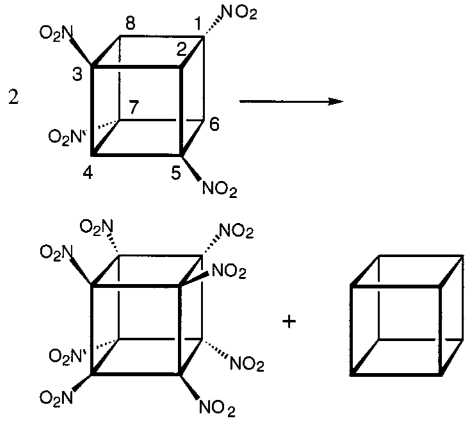
cubane$(NO_2)_x$ formed	disproportionation energy		avg charge on NO_2	
	RHF	B3LYP	RHF	B3LYP
1,2-dinitro	7.1	5.6	-0.395^b	-0.381^c
1,3-dinitro	4.3	3.5	-0.403	-0.384
1,4-dinitro	3.6	3.0	-0.407	-0.390
1,3,5,7-tetranitro	25.1 (25.8)	20.7 (21.0)	-0.362	-0.341
1,2,3,5-tetranitro	33.4 (34.2)	26.1 (27.3)	-0.346	-0.334
heptanitro	100.0 (113.4)	75.9 (90.9)	-0.285	-0.284
octanitro	129.6 (151.2)	97.3 (121.2)	-0.266	-0.272

[a] Values in parentheses are the disproportionation energies that would be obtained if the interaction energies in the dinitrocubanes were additive. Average Mulliken charges on the nitro groups of cubane$(NO_2)_x$ are also given. [b] -0.426 in mononitrocubane. [c] -0.410 in mononitrocubane.

experimental heats of formation of methane, nitromethane, and dinitromethane.[9] The RHF and B3LYP values are respectively $\Delta H^{298} = 11.7$ and 7.2 kcal/mol. Clearly, B3LYP provides a value for the enthalpy of this reaction that is in much better agreement with experiment than the RHF value, which is >75% too high.[10] This comparison suggests that the energies associated with the interactions between nitro groups in ONC are much more likely to be computed accurately at the B3LYP level of theory.

Static Interactions

To calculate the size of the nearest-neighbor interactions in ONC, we computed the disproportionation energy of two molecules of TNC to ONC plus cubane (eq 1). The energy of this isodesmic reaction was calculated to be 79.4 and 55.8 kcal/mol at the RHF and B3LYP levels of theory, respectively.



(1)

The total energy of the four interactions along the body diagonals, which are introduced by the disproportionation reaction in eq 1, can be approximated as four times the energy of disproportionation in Table 1 of two molecules of nitrocubane to 1,4-dinitrocubane plus cubane. Using the disproportionation energies in Table 1, the total energy associated with these four 1,4-interactions in ONC is thus estimated to be 14.4 and 12.0 kcal/mol at the RHF and B3LYP levels of theory, respectively.

Subtracting these energies from the energies computed for the isodesmic reaction in eq 1 at the same levels of theory gives values of 65.0 and 43.8 kcal/mol for the RHF and B3LYP energies associated with the total of 12 nearest-neighbor nitro interactions in ONC.[11] The average energy of one such interaction is therefore 5.4 (RHF) and 3.7 (B3LYP) kcal/mol. These values are respectively 1.7 and 1.9 kcal/mol smaller than the corresponding values for the nearest-neighbor nitro interaction energy in 1,2-dinitrocubane, computed from the disproportionation energies for two molecules of nitrocubane in Table 1.

To understand why the repulsion energy associated with each pair of interactions between nearest-neighbor nitro groups is calculated to be 1.7−1.9 kcal/mol smaller in ONC than in 1,2-dinitrocubane, we computed the energies of some additional disproportionation reactions. The energies of these reactions, calculated at both the RHF and B3LYP levels of theory, are given in Table 1. The energies predicted for these reactions, based on the disproportionation reactions that form the dinitrocubanes, are shown in parentheses.

For example, formation of 1,3,5,7-tetranitrocubane by disproportionation of four molecules of nitrocubane introduces no 1,2 or 1,4 interactions. From the results in Table 1 for formation of 1,3-dinitrocubane, the six 1,3-interactions between nitro groups in TNC would be expected to give a disproportionation energy of $6 \times 4.3 = 25.8$ kcal/mol at the RHF level and $6 \times 3.5 = 21.0$ kcal/mol at B3LYP. As shown in Table 1, the actual disproportionation energies, computed for formation of 1,3,5,7-tetranitrocubane, are smaller than these estimated values, but by only 0.7 and 0.3 kcal/mol, respectively.

Formation of 1,2,3,5-tetranitrocubane from four molecules of nitrocubane introduces three 1,2- plus three 1,3-interactions between nitro groups. The energies of these 1,2- and 1,3-repulsive interactions in 1,2,3,5-tetranitrocubane are also similar to those in the dinitrocubanes, since, as shown in Table 1, the disproportionation energies, actually computed, are again close to the estimates that are based on the disproportionation energies in forming 1,2- and 1,3-dinitrocubane.

However, substantial deviations from additivity of the disproportionation energies for forming the dinitrocubanes become apparent in cubanes with larger numbers of nitro groups. For example, disproportionation of seven nitrocubanes to heptanitrocubane plus six cubanes introduces nine 1,2-interactions, nine 1,3-interactions, and three 1,4-interactions. The disproportionation energy for forming heptanitrocubane is thus expected to be 113. 4 (RHF) and 90.9 (B3LYP) kcal/mol, based on the disproportionation energies for forming the three dinitrocubanes. However, as shown in Table 1, the disproportionation energies actually computed are much smaller, amounting to 100.0 (RHF) and 75.4 (B3LYP) kcal/mol. The deviations from additivity of the dinitrocubane disproportionation energies are 13.4 and 15.5 kcal/mol, respectively, at these two levels of theory.

Similarly, disproportionation of eight nitrocubanes to ONC and seven cubanes is expected to be unfavorable by 151.2 and 121.2 kcal/mol, based on the dinitrocubane results. However, the RHF and B3LYP calculations actually give values of respectively 129.6 and 97.3 kcal/mol. The differences between the expected disproportionation energies and those actually computed are 21.6 and 23.9 kcal/mol.

The differences between the disproportionation energies that are expected on the basis of the dinitrocubane results and those actually computed are 50−60% larger in ONC than in heptani-

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[9] Mallard, W. G.; Linstrom, P. J., Eds. *NIST Chemistry WebBook, NIST Standard Reference Database*, Number 69, February 2000; National Institute of Standards and Technology: Gaithersburg MD, 20899 (http://webbook.nist.gov).

[10] The RHF enthalpy (ΔH^{298}) of 6.4 kcal/mol of reaction 2 $CH_3CH_2NO_2 \rightarrow NO_2CH_2CH_2NO_2 + CH_3CH_3$ is also higher than the B3LYP value of 5.4 kcal/mol; but, unfortunately, the gas-phase heats of formation necessary to obtain an experimental value are unavailable.

[11] This estimate assumes that the 1,3 interactions in TNC can be equated with the 1,3 interactions in ONC. This cannot be rigorously so. However, such approximations are necessary in trying to rationalize the chemical or physical properties of molecules by partitioning into sums of discrete effects.

trocubane. Thus, as cubane becomes more substituted with NO_2 groups, the average size of the destabilizing interactions between each pair of nitro groups apparently diminishes, and in a very nonlinear fashion.

The explanation of this counterintuitive finding is contained in the average Mulliken charges on each nitro group, which are given in Table 1. As increasing numbers of electron-withdrawing nitro groups are attached to the cube, the negative charge on each nitro group decreases by about a third in going from nitrocubane to ONC. The results in Table 1 show that, not surprisingly, nitro groups have the largest effect on reducing each other's negative charges when they are nearest neighbors.

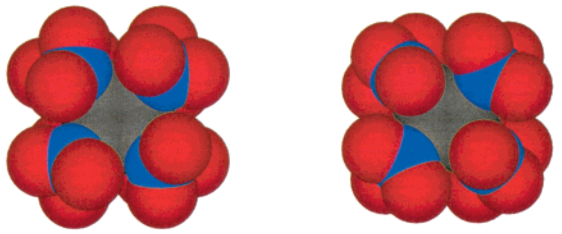
More detailed Mulliken analyses of the RHF and B3LYP charge distributions reveal that electrons are lost about equally from the nitrogen and each of the two oxygens with increasing nitro substitution. Although electron loss decreases the negative charge on each oxygen atom, it increases the positive charge on each nitrogen atom. Consequently, as the number of nitro groups attached to the cube increases, loss of negative charge from each nitro group substantially reduces the electrostatic repulsions between the oxygens, without greatly affecting the electrostatic attractions between the oppositely charged nitrogen and oxygens.

Table 1 shows that the decrease in the average negative charge on each nitro group is roughly proportional to the number of nitro groups. However, the Coulombic repulsions between oxygens involve the product of the negative charge on each oxygen; so the repulsion energies vary as the square of the average negative charge on each nitro group. Consequently, although the average negative charge on each nitro group decreases approximately linearly with the number of nitro groups, the electrostatic repulsion energy between each pair of nitro groups decreases approximately quadratically with the number of nitro groups that are attached to the carbon cube. Presumably, this is the origin of the nonlinear dependence of the repulsion energies between pairs of nitro groups on the number of nitro groups in each nitrocubane.

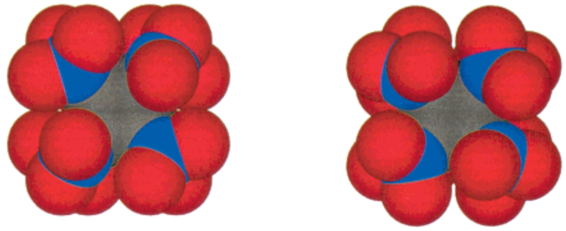
To verify that charge redistribution really does reduce the electrostatic repulsion between the nitro groups in ONC, we calculated this repulsion energy for ONC using the Mulliken charges on nitrogen and oxygen in both ONC and in 1,3,5,7-tetranitrocubane (TNC). The TNC Mulliken charges gave a nitro−nitro electrostatic repulsion energy for ONC that was considerably higher than that computed from the actual ONC Mulliken charges. The difference between the repulsion energies amounted to 55 kcal/mol, using the B3LYP Mulliken charges for TNC and ONC, and to 104 kcal/mol using the RHF Mulliken charges.

Since the nitro−nitro electrostatic repulsion energies do not include any of the other electrostatic interactions in ONC (e.g. nitro−carbon and carbon−carbon), their absolute magnitudes have no significance. However, the difference between the nitro−nitro repulsion energies in ONC, computed with the charges on nitrogen and oxygen in the nitro group of TNC and with the actual charges on these atoms in the nitro group of ONC, confirms that charge redistribution within the nitro groups in ONC does, indeed, lower the electrostatic repulsion between these groups.

Although inductive loss of charge from oxygen helps to reduce the O···O electrostatic repulsions in highly nitrated cubanes, conformations that minimize O···O repulsions and maximize O−N attractions between each nitro group and those on adjacent carbons are, of course, favored. The nearest-neighbor interactions between nitro groups play a major role in determining not only the preferred conformation of ONC but also its dynamical behavior.



(a) D_4 (viewed // to C_4 axis) (c) D_{2d} (viewed // to S_4 axis)



(b) D_4 (viewed ⊥ to C_4 axis) (d) D_{2d} (viewed ⊥ to S_4 axis)

Figure 1. Views of the RHF D_4 minimum energy structure and D_{2d} transition structure for ONC.

Dynamic Interactions

In approaching the conformational analysis of ONC it is reasonable first to identify and evaluate the energies of the structures with the highest possible symmetry. The substitution of cubane hydrogen atoms for nitro groups destroys the 3-fold axes that run along the body diagonals of the O_h frame. One 4-fold axis in either of two D_{4h} structures may be preserved by arranging the nitro groups parallel (C−C−N−O = 0° or 180°) or perpendicular (C−C−N−O = ±90°) to the C−C bonds that are parallel to the unique 4-fold axis. However, it is easy to discount these structures as possible energy minima, as they have nearest-neighbor nitro groups in which, respectively, four and eight pairs of N−O bonds are directed toward each other, thus engendering substantial O···O repulsive interactions. At both levels of theory, these structures are stationary points of very high order.

To avoid O···O repulsions, ONC might adopt a conformation belonging to one of the subgroups of D_{4h} of order 12, either D_4 or D_{2d}. Both RHF and B3LYP calculations find a D_4 geometry to be an energy minimum (Figure 1a,b) in which nitro groups minimize O···O repulsions by adopting a propeller conformation with respect to the 4-fold axis (Figure 1a). Viewed perpendicular to the 4-fold axis, in this conformation the N−O bonds of pairs of 1,3-nitro groups do point toward one another, but only obliquely across the face diagonals of the cube (Figure 1b). At the D_4 energy minimum, the computed torsion angles of 43.8° (RHF) and 44.0° (B3LYP) between the N−O bonds and the C−C bonds parallel to the unique axis are very similar to those found in the approximate D_4 geometry of crystalline ONC (av C−C−N−O = 45.8°).[2] A detailed comparison of the X-ray, RHF, and B3LYP geometries is given in Table 2. The B3LYP geometry is in excellent agreement with the geometry obtained by X-ray diffraction, whereas the RHF bond lengths are shorter than those both computed by B3LYP and determined experimentally.

Table 2. X-ray, RHF, and B3LYP/6-31G* Structural Parameters for Octanitrocubane

	X-ray	RHF	B3LYP
$C-C_{exo}$ (Å)[a]	1.563(3)	1.553	1.567
$C-C_{endo}$ (Å)[b]	1.559(3)	1.550	1.563
$C-N$ (Å)	1.478(3)	1.461	1.482
$N-O_{exo}$ (Å)[c]	1.207(3)	1.184	1.221
$N-O_{endo}$ (Å)[d]	1.201(3)	1.183	1.220
$O-N-O$ (deg)	128.0(2)	129.1	128.9
$O_{exo}-N-C-C$ (deg)[c,e]	−45.1(2)	−43.8	−44.0
$O_{endo}-N-C-C$ (deg)[d,e]	136.2(2)	137.8	137.4

[a] Exo refers to the C−C bond perpendicular to the 4-fold or pseudo-4-fold axis. [b] Endo refers to the C−C bond parallel to the 4-fold or pseudo-4-fold axis. [c] With respect to the 4-fold axis exo oxygens point toward one another. [d] With respect to the 4-fold axis endo oxygens point away from one another. [e] C−C bond as in footnote *b*.

The D_{2d} structure (Figure 1c,d), in which four N−O bonds eclipse four C−C bonds of the cube, was identified as the lowest energy transition structure. The D_4 minimum and D_{2d} transition structure are separated by only a very small amount of energy—0.017 kcal/mol (RHF) and 0.006 kcal/mol (B3LYP)—and connected through a continuum of D_2 geometries. The total energies and geometries of all the stationary points are available as Supporting Information.

Unlike the D_{2d} transition structure, the D_4 minimum is chiral. The conceptually simplest enantiomerization mechanism might be accomplished by conrotating all the nitro groups by ~90°. However, this motion passes through the D_{4h} structure which is ca. 60 kcal/mol higher in energy than the D_4 minimum at the RHF/6-31G* level of theory. A much lower energy pathway for enantiomerization of a D_4 minimum-energy structure involves the nearly barrierless, coupled *disrotation* of the nitro groups in two tetrahedral subsets through the D_{2d} transition structure.

While this work was under review, a vibrational analysis of ONC, using density functional theory, was published by Kortus, Pederson, and Richardson.[12] They called the reader's attention to an unusual, near zero-frequency, vibrational mode that was predicted to be present in ONC, in addition to the expected zero-frequencies for translation and rotation. This vibrational mode was associated with a torsional motion of the nitro groups. More specifically, the authors' illustration of this mode revealed that the oscillatory motions of adjacent nitro groups are disrotatory. Our near-barrierless, correlated enantiomerization mechanism for ONC is wholly consistent with this finding by Kortus et al.

Coupled disrotations of the eight nitro groups by 15° converts a D_4 minimum into an achiral D_{2d} transition structure, but one in which the unique, improper 4-fold axis (S_4) is now orthogonal to the proper 4-fold axis (C_4) in the initial D_4 structure. Continued disrotation by 15° generates the enantiomer of the initial D_4 structure, but with the unique axis now parallel to the third Cartesian direction.

The interconversion of stationary points is shown in Figure 2[13] and symbolized by the following sequence: $D_4^z \rightarrow D_{2d}^x \rightarrow D_4^{y'} \rightarrow D_{2d}^z \rightarrow D_4^x \rightarrow D_{2d}^y \rightarrow D_4^{z'} \rightarrow D_{2d}^x \rightarrow D_4^y \rightarrow D_{2d}^z \rightarrow D_4^{x'} \rightarrow D_{2d}^y \rightarrow D_4^z$. In this symbolic representation, the symmetries of the stationary points are indicated; primes designate the enantiomer of the first D_4 structure; the superscripts indicate the direction of the unique axis in Cartesian space; and each arrow corresponds to a 15° rotation along the coupled disrotation path. Thus, rotation by a full 180° is required to simultaneously return to the initial enantiomer and unique axis orientation. If when viewing the cube along the N−C vector of a nitro group the motion begins by a clockwise rotation of that group, the unique axis appears to pseudorotate in a counterclockwise direction.

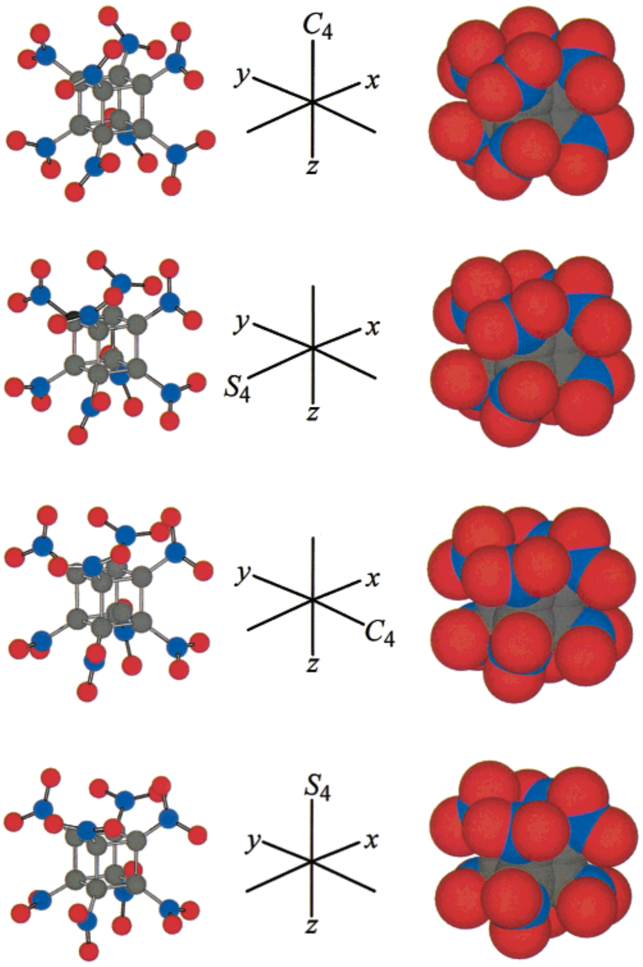


Figure 2. Series of structures along the dynamic correlated disrotation pathway represented by ball-and-stick (left column) and space-filling models (right column). The unique axis is indicated in each case.

The dynamic stereochemistry of ONC is analogous to the apparent rotation of the S_4 axis of D_{2d} tetraphenylmethane (TPM),[14] which has been likened to a "conjuring trick".[15] By virtue of the pseudorotation of the unique axes, the time-averaged symmetries of TPM and ONC are thus T_d and O_h, respectively.

Gear slippage in ONC is an energetically demanding process, especially if it is compared to the almost barrierless, coupled disrotation of the nitro groups. For example, the energy required to rotate a single nitro group by 90° from the D_4 minimum, while holding the others fixed, is computed to be 26.9 and 21.2

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(12) Kortus, J.; Pederson, M. R.; Richardson, S. L. *Chem. Phys. Lett.* **2000**, *322*, 224−230. This paper also contains an excellent discussion of the appropriateness of DFT calculations for problems of this sort.

(13) A movie showing the dynamic stereochemistry of ONC can be found on the internet at the following address: http://depts.washington.edu/chemfac/kahr_movie.html. The animation was developed from AM1 (Dewar, M. J. S.; Zoebisch, E. G.; Healy; E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902−3909. Stewart, J. J. P. Quantum Chemistry Program Exchange, Bloomington, Indiana, No. 455.) structures to minimize the computational cost. The AM1 computations were in essential agreement with RHF results except that the constrained D_4 AM1 structure had one imaginary frequency. The less constrained D_2 structure was a genuine minimum but its energy was unchanged and its geometry was nearly indistinguishable from D_4.

(14) Hutchings, M. G.; Nourse, J. G.; Mislow, K. *Tetrahedron* **1974**, *30*, 1535−1549.

(15) Dunitz, J. D. *X-ray Analysis and the Structure of Organic Molecules*; Cornell University Press: Ithaca, NY 1979; p 484.

kcal/mol at the RHF and B3LYP levels of theory, respectively. Almost certainly, the lowest energy mechanism for gear slippage is less. Identification of the lowest energy pathway among the many that scramble the positions of the oxygens with respect to one another is the subject of ongoing investigation.[16]

The analysis presented herein raises general questions about per-substituted platonic hydrocarbons, the first and most celebrated of which is tetra-*tert*-butyltetrahedrane (TTT).[4] The fact that in TTT all four substituents are nearest neighbors precludes correlated disrotatory motions of the type that we have found in ONC.[17] It has previously been computed that TTT, with T symmetry, undergoes rapid enantiomerization through a D_{2d} transition state that lies 2−5 kcal/mol above the conformation of minimum energy.[18] Although small, this barrier is considerably larger than the barrier to enantiomerization of D_4 ONC. How much of this difference in barrier heights is due to the respective size, shape, and electronic structure of the *tert*-butyl and nitro substituents and how much to parity restrictions[17] on dynamic gearing in per-substituted tetrahedranes will be the subject of a future study.

Acknowledgment. This work was supported by the National Science Foundation. We are grateful to F.-G. Klärner for the results of preliminary AM1 calculations and to Richard Gilardi for providing the X-ray coordinates.

Supporting Information Available: Cartesian coordinates and energies for all stationary points (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[16] If gear slippage is energetically costly, technologists may find a use for ONC, as a three-dimensional gear system, in a futuristic nanoscale machine.

[17] The motion of adjacent gears in a cyclic, odd-membered train is necessarily disallowed by virtue of the fact that any one gear will experience opposing forces from its neighbors as they begin to turn. See: Mislow, K. *Chemtracts-Org. Chem*. **1989**, *2*, 151. Chance, J. M.; Geiger, J. H.; Mislow, K. *J. Am. Chem. Soc*. **1989**, *111*, 2326−2327. Chance, J. M.; Geiger, J. H.; Okamoto, Y.; Aburatani, R.; Mislow, K. *J. Am. Chem. Soc*. **1990**, *112*, 3540−3547.

[18] Hounshell, W. D.; Mislow, K. *Tetrahedron Lett.* **1979**, 1205−1208. Schweig, A.; Thiel, W. *J. Am. Chem. Soc*. **1979**, *101*, 4742−4743.