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Fluorine Azide and Fluorine Nitrate: Structure and Bonding

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We report here predictions for the geometries of fluorine azide and fluorine nitrate and an analysis of their electronic structure based on ab initio calculations. Although the compounds were synthesized many years ago and some data exist on their reactivity,[1-3] both are explosive and there has been much uncertainity about their structure. This is not surprising in view of the high electron density and electronegativity of N, O, and F and the multiple-bond-forming capability of N and O: molecules made from these three atoms frequently exhibit unusual structures because of the delicate balance between short bonds induced by multiple bonding and long bonds induced by electron-electron repulsion. FN_3 and FNO_3 may also be identified as molecules where highly electronegative fluorine is bound to another highly electronegative group, N_3 or NO_3 (N_3 and NO_3 have high electron affinities).

The quantum-mechanical wave functions that we have computed contain all of the information required to fully describe the properties of the isolated molecules, but even the simple molecular orbital plots derived from our wave functions contain too much detail to be readily assimilated or employed as a guide to how FN_3 or $FONO_2$ compare with other N, O, F molecules. We have therefore given special attention to evaluating the use of Lewis dot resonance structures, the simplest of all electronic structure representations.

Computational Methods

All calculations were performed with the GAUSSIAN 82 programs[4] on a DEC VAX 11/780 computer. Fully optimized geometries were obtained for fluorine azide with single-configuration SCF wave functions and with correlated wave functions determined by second-order perturbation theory. Split-valence and d-orbital-polarized basis sets were employed (HF/4-31G,[5] HF/6-31G*,[6] and MP2/6-31G*[7]). For fluorine nitrate, fully optimized geometries were computed at the HF/4-31G and HF/6-31G* levels. MP2/6-31G* solutions were determined at the HF/4-31G and HF/6-31G* geometries and at a third, slightly different, geometry obtained from tabulated bond lengths.

Fluorine Azide

Table I lists the predicted bond lengths and bond angle for FN_3 at the three computational levels we have employed. The azide fragment, $N_aN_bN_c$, was assumed to be linear because of the space and time factors involved in the computation.[8] It has been demonstrated[9] that this computational level yields accurate geometries for single bonds between first-row atoms along with a systematic elongation of 0.02–0.03 Å for multiple bonds between NN, OO, and NO.

A survey of over a dozen neutral molecules containing FN bonds shows that their lengths vary continuously over a range from approximately 1.31 to 1.512 Å. (Compilations usually take FN in NF_3 as the reference length.) Table II lists experimentally measured bond lengths and angles for species selected as most relevant for comparison with FN_3, including those with FN lengths greater than 1.40 Å. Since we expect that the N_3 fragments in ClN_3 and FN_3 will be very similar, the fact that N_aN_b and N_bN_c observed in ClN_3 (Table II) differ little from the MP2/6-31G* results for FN_3 (Table I) tends to give confidence in the calculations.[10]

Table I. Optimized Geometries for FN_3[a]

	HF/4-31G	HF/6-31G*	MP2/6-31G*
$r(FN_a)$	1.462	1.383	1.434
$r(N_aN_b)$	1.286	1.253	1.280
$r(N_bN_c)$	1.105	1.010	1.152
$\angle FN_aN_b$	101.0	103.8	102.5

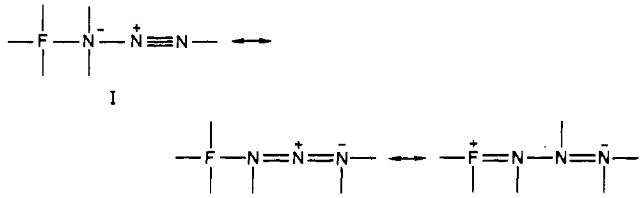
[a] Distances are in angstroms and angles in degrees.

Table II. Experimental Geometries[a]

NF_3	$r(NF)$	1.365		
F_2N_2	$r(NF)$	1.410	$\angle FNN$	114.4
F_3NO	$r(NF)$	1.432	$\angle FNO$	117.1
FNO_2	$r(NF)$	1.467	$\angle FNO$	112.
FNO	$r(NF)$	1.512	$\angle FNO$	110.1
NCl	$r(NCl)$	1.754		
$ClNO_2$	$r(NCl)$	1.840	$\angle ClNO$	114.7
$ClNO$	$r(NCl)$	1.975	$\angle ClNO$	113.3
NH_3	$r(NH)$	1.014		
H_2N_2	$r(NH)$	1.028	$\angle HNN$	106.9
HNO	$r(NH)$	1.063	$\angle HNO$	108.6
ClN_3	$r(NCl)$	1.745	$\angle ClN_aN_b$	108.7
	$r(N_aN_b)$	1.252	$\angle N_aN_bN_c$	170.9
	$r(N_bN_c)$	1.133		
HN_3	$r(NH)$	0.975	$\angle HNN$	114.1
	$r(N_aN_b)$	1.237	$\angle N_aN_bN_c$	180[b]
	$r(N_bN_c)$	1.133		

[a] Distances are in angstroms and angles in degrees. Harmony, M. D.; Laurie, V. M.; Kuczowski, R. L.; Swendeman, R. H.; Ramsay, D. A.; Lovas, F. J.; Lafferty, W. J.; Maki, A. G. *J. Phys. Chem. Ref. Data Ser.* **1979**, *8*, 619. [b] $\angle N_aN_bN_c$ assumed to be linear.

The three Lewis structures for FN_3 with the maximum number of bonds and with each atom surrounded by four pairs of electrons are


I

II III

Structure III contributes to a small degree compared to the contribution of I or II because of its unfavorable formal charge on F but supports a nonlinear N_3 fragment. I and II can account for the bond lengths in the N_3 fragment.

The possibility of writing a cyclic N_3 structure is eliminated immediately by an examination of the FN_3 molecular orbitals in

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(1) Lawless, E. W.; Smith, I. C. *Inorganic High Energy Oxidizers*; Marcel Dekker: New York, 1968.

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(3) Holzmann, R. T., Ed. *Advanced Propellant Chemistry*; Advances in *Chemistry* 54; American Chemical Society: Washington, DC, 1966.

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(8) ClN_3 is known to be slightly bent, $\angle N_aN_bN_c$ = 172°. Since the N_3 fragment in ClN_3 proves to have bond lengths very similar to those we find for FN_3, it is likely that FN_3 will be bent by almost the same amount.

(9) DeFrees, D. J.; Levi, B. A.; Pollock, S. K.; Hehre, W. J.; Binkley, J. S.; Pople, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 4085.

(10) Isoelectronic FNCO has been synthesized: Bielefeldt, D.; Gholivand, K.; Haas, A.; Willner, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1984**, *39B*, 1211. Michels has carried out MP2/6-31G* calculations and finds a long FN bond essentially identical with ours for FN_3: Michels, H. H., private communication.

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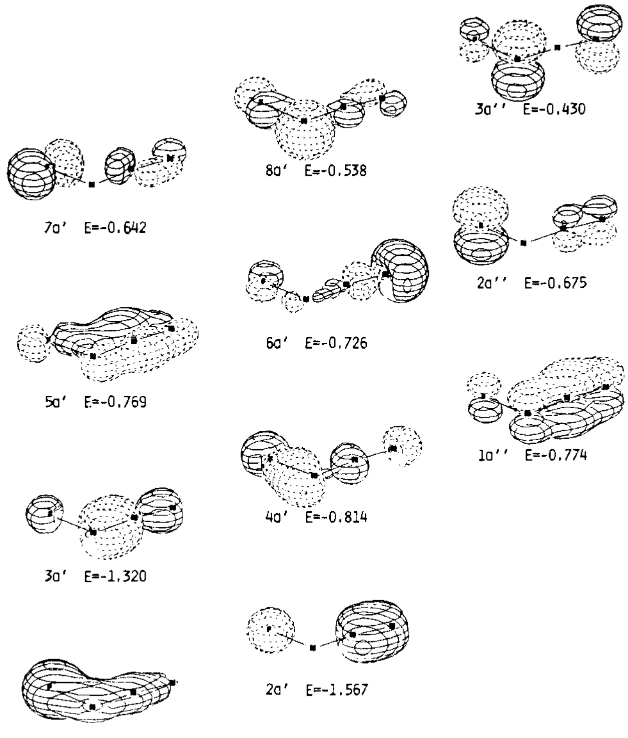
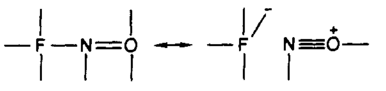


Figure 1. Valence molecular orbitals for fluorine azide (0.1 e/Å contour level; one-electron energies in atomic units, 1 au = 27.21 eV).

Figure 1 because there is no evidence for a bond between N_a and N_c that does not include N_b.

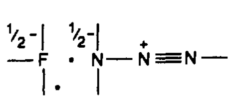
Table II lists the four other N, O, F molecules that have FN lengths in the same range as in FN_3 (two longer, two shorter). The FN bond length in all four are often explained by no-bond resonance, e.g.



IV

However, no-bond resonance is not possible for FN_3 because there is no lone pair on N_b in either I or II.

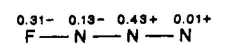
We show that the energetics of electron transfer from the FN bond to F in structure I provides an explanation of the bond polarity, $F^{\delta-}$–$N^{\delta+}$, in FN_3. The strength of a normal FN bond is 68 kcal/mol,[11] and it would thereby cost 34 kcal/mol to remove one electron. This energy is more than made up, however, by the electron affinity of F, which is 77 kcal/mol.



V

This transfer is possible because N_a in structure I carries a formal negative charge.

Strong support for FN to F electron transfer comes from two properties of the FN_3 wave functions we have calculated. First, the Mulliken atomic charges[12] are



$$\overset{0.31-}{F}—\overset{0.13-}{N}—\overset{0.43+}{N}—\overset{0.01+}{N}$$

VI

Table III. Optimized Geometries for $FONO_2$[a,b]

	HF/4-31G	HF/6-31G*
$r(FO_a)$	1.418	1.359
$r(NO_a)$	1.459	1.386
$r(NO_b)$	1.194	1.171
$r(NO_c)$	1.187	1.165
$\angle O_bNO_c$	132.5	132.5
$\angle O_bNO_a$	109.5	109.5
$\angle FO_aN$	107.4	108.4

[a] Distances are in angstroms and angles in degrees. MP2/6-31G* total energies for HF/4-31G, HF/6-31G*, and a third geometry are as follows: −379.056 976 74, −379.043 366 87, and −379.051 654 10 hartree, respectively. Third geometry: $r(FO_a)$ = 1.42 Å, $r(O_aN)$ = 1.40 Å, $r(NO_b)$ = 1.20 Å, $r(NO_c)$ = 1.20 Å, $\angle O_bNO_c$ = 1.33°, $\angle O_bNO_a$ = 113.5°, FO_aN = 105°. [b] All atoms in one plane for all levels of calculation.

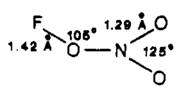
Second, contours around F and N_a in the 1a′ molecular orbital (Figure 1)[13] closely approximate the shape of the FN σ bond and it is apparent that bond polarization produces an almost spherical charge distribution around the F nuclear center suggestive of a partially charged F ion.

The small FN_aN_b angle has its origin in the strong bonding and linear (or nearly linear) conformation of the N_3 fragment. Thus, an in-plane π-like orbital of this fragment overlaps with an in-plane π orbital of F to form a bridge of charge between F and N_a (Figure 1, MO 5a′). The energy required to bend this long bond is small.

Molecular orbital plots at a specified contour level (0.1 e/Å^3), ordered according to their ionization energies, are displayed in Figure 1 for the 11 pairs of electrons in FN_3. Because of the planarity of FN_3, symmetry allows separation into two classifications: a′ σ orbitals and a″ π orbitals (with a node in the plane of the molecule). In spite of this symmetry simplification, the intricacy and complexity of these plots compared to the Lewis structures is striking. Their precision is required to understand many of the FN_3 molecular properties in detail, but for general purposes it is essential to select only their central features. These may be identified as follows: The first three a′ orbitals, 1a′, 2a′, and 3a′, are the three σ bonds. There are two π bonds, one in the molecular plane, 5a′, and one perpendicular to the plane, 1a″, which largely contribute to the N_2-like fragment, N_bN_c, but also partly extend over N_a. The rest of the orbitals are lone pairs: N_a (3a″ and 8a′), N_c (6a′), F (a″, 7a′, and 4a′).

Fluorine Nitrate

Many years ago Pauling and Brockway[14] performed a low-resolution electron diffraction study of $FONO_2$, yielding the geometry



VII

with a 90° dihedral angle (FO perpendicular to the ONO_2 plane). With the exception of the dihedral angle, no other geometry determination has been reported. Much controversy has accompanied the dihedral angle assignment,[15-20] the most recent and

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(11) Huheey, J. E. *Inorganic Chemistry*, 2nd ed.; Harper & Row: New York, 1978; p 848. The average dissociation energy for NF_3 is 68 kcal/mol. The 58 kcal/mol dissociation energy of $NF_3 \rightarrow NF_2 + F$ may be more relevant. Wagman, D. D.; Evans, W. H.; Parker, V. B.; Halow, I.; Bailey, S. M.; Schuman, R. H. *NBS Tech. Note (U.S.)* 1969, *No. 270–273.*

(12) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833, 1841, 2238, 2343 **1962**, *36*, 3428. Mulliken changes are known to be very basis set dependent, and 6-31G* values have generally proved more chemically significant than 4-31G values, and thus we use 6-31G* values. Unfortunately, Mulliken overlap populations are not useful indications of bond strengths or bond length in N, O, F molecules; e.g., the σ overlap populations for F–N in NF_3 (1.365 Å), F_2N_2 (1.410 Å), and FNO_2 (1.467 Å) are 0.06, 0.07, and 0.09, respectively. The high density of N, O, and F evidently does not permit a clear separation between lone pairs and bond pairs in the LCAO-based overlaps.

(13) Jorgensen, W. L. *QCPE* **1977**, *340*. 6-31G* and 4-31G plots do not show qualitative difference in these three-dimensional orbital plots, and we report those generated at 4-31G.

(14) Pauling, L.; Brockway, L. O. *J. Am. Chem. Soc.* **1937**, *59*, 13.

(15) Brandle, K.; Schmeisser, M.; Luttke, W. *Chem. Ber.* **1960**, *93*, 2300.

Table IV. Experimental Geometries Relevant to NO_2 and FO in FNO_3[a]

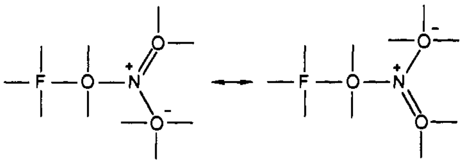
	r(NO)	r(FO)	∠ONO
FNO_2	1.180		136.0
$HO'NO_2$	1.206		130.3
N_2O_3	1.211[b]		129.8
N_2O_4[c]	1.211[b]		134.0
F_2O		1.405	
FOH		1.442	

[a] Distances are in angstroms and angles in degrees. Harmony, M. D.; Laurie, V. W.; Luczowski, R. L.; Swendeman, R. H.; Ramsay, D. A.; Lovas, F. J.; Lafferty, W. J.; Maki, A. G. *J. Phys. Chem. Ref. Data Ser.* **1979**, *8*, 619. [b] NO length in the NO_2 group. [c] Bibart, C. H.; Ewing, G. E. *J. Chem. Phys.* **1974**, *61*, 1248. Snyder, R. G.; Hisatsune, I. C. *J. Mol. Spectrosc.* **1979**, *1*, 139.

definitive experimental study of which[20] was carried out at the same time as our calculations, unknown to us. We both agree on a planar (zero dihedral angle) molecule. It may be noted that high-resolution microwave spectroscopy showed long ago that both $HONO_2$[21] and CH_3ONO_2[22] were also planar, but these well-known facts have had no impact on the $FONO_2$ controversy.

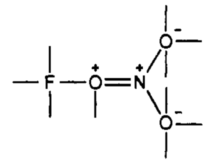
Table III records the optimized geometries we have obtained at the 4-31G and 6-31G* SCF levels and the MP2/6-31G* calculations at selected geometries. On the basis of these results and previous experience[23] our best estimates are the HF/4-31G values. There appears to be an approximate cancellation between the effect of correlation and that of d-polarization functions on geometry such that an optimization at 4-31G yields geometries only slightly inferior to an MP2/6-31G* optimization.[24] Table IV gives known geometries of other molecules containing the NO_2 and FO groups, and it is apparent that our results fit in with the rather rigidly preserved NO_2 entity and with a normal bond length for FO (1.42 Å is the value most often tabulated as a reference length[25]). In many respects, the most interesting bond length is that for the NO_a single bond. NO single bonds are known to vary from 1.39 Å in *cis*-nitrous acid[26] to 1.50 Å in N_2O_5.[27] Although longer than that in $HONO_2$,[21] our value for $FONO_2$ (1.46 Å) is within the range to be expected for N, O, F molecules.

The only important Lewis structures are



VIII IX

The planarity of $FONO_2$ is a result of very weak π bonding across the NO_a bond (the bond energy involved is comparable to a rotational barrier). Again the π bond in question is hinted at by the Lewis dot structure



X

The actual bonding involved represents minor components of two molecular orbitals. First, the antibonding NO_a π component of the 2a″ orbital does not completely cancel the NO_a π bond in the 1a″ orbital. Second, there is a small in-plane NO_a π-bond component in the 7a′ orbital (see Figure 2).[13]

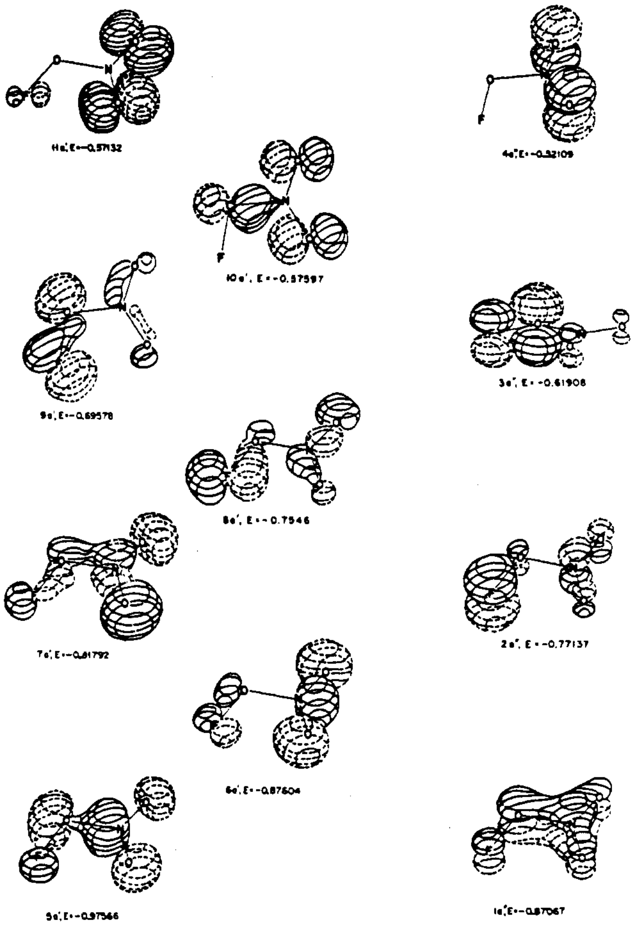


Figure 2. Highest 11 valence molecular orbitals for fluorine nitrate (0.1 e/Å contour level; one-electron energies in atomic units).

Figure 2 shows the 11 molecular orbitals (doubly occupied) of highest energy (least stable), and again there is a separation into a′ σ orbitals and a″ π orbitals. The lowest four orbitals, 1a′, 2a′, 3a′, and 4a′ (not shown), are the four σ bonds. These are quite ordinary except for the notable lack of a complete NO_a σ bond. The missing charge is restored by NO_a σ bonding in the 5a′ and 10a′ MOs. However, these latter charge density increments occur in orbitals of much higher energy than the 1a′, 2a′, 3a′, and 4a′ orbitals and this accounts for the relatively long NO_a bond. The one π bond in $FONO_2$ is immediately recognizable as the 1a″ MO, but it seems to encompass O_a as well as the NO_2 unit. The inclusion of NO_a in the 1a″ π bond is nearly canceled by the component in 2a″, which is antibonding NO_a but bonding NO_b and NO_c. Besides the 1a″ π-bond MO, the other orbitals represent the 10 lone pairs and these are identified as F (8a′, 9a′, and 2a″), O_a (5a′ and 3a″), and O_b and O_c (6a′, 7a′, 10a′, 11a′, and 4a″). This MO analysis, based on ab initio wave functions at an accuracy level that has been demonstrated to yield chemically useful geometries and other properties, helps validate the Lewis structure.

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The structure of FN_3 has recently been determined experimentally by Christen et al. (private communication). The N_3 moiety is slightly bent (170.9°), the FN bond is 1.444 Å, and the FN_aN_b angle is 103.8° in agreement with our conclusions. They have also fully optimized the structure (including the $N_aN_bN_c$ angle) using ab inito molecular orbital calculations, which concur with our results.

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Registry No. FN_3, 14986-60-8; FNO_3, 7789-26-6.

Contribution from the Department of Industrial
and Engineering Chemistry, Swiss Federal Institute
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Stereochemistry of PtO_2-Catalyzed Hydrogenation of [Ethylenebis(indenyl)]zirconium Dichloride

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[Ethylenebis(4,5,6,7-tetrahydro-1-indenyl)]MX_2 (M = Ti, Zr; X = Me, Cl) complexes,[1] in the presence of methylaluminoxanes, are highly active homogeneous catalyst precursors for the stereospecific polymerization[2,3] and hydrooligomerization[4] of α-olefins. The tetrahydroindenyl complexes are prepared by catalytic hydrogenation of the corresponding indenyl derivatives under 100 bar of H_2 in the presence of a PtO_2 catalyst.[1] We are interested in preparing stereochemically defined substituted analogues of these catalysts, and thus it was necessary to establish unambiguously the stereochemistry of the hydrogenation reaction.[5] The stereochemistry of catalytic hydrogenations of coordinated ligands is highly dependent on the metal center; participation of the metal center has been demonstrated for Zr,[6] Fe,[7] and Ni[8] systems. For nickelocene,[8] it was shown that catalytic hydrogenation in the presence of Raney nickel, Pd/C, or $(PPh_3)_3RhCl$ occurs stereospecifically from the sterically hindered endo face of the cyclopentadienyl ring. In this paper, we report deuterium-labeling studies that establish that the PtO_2-catalyzed hydrogenation of [ethylenebis(indenyl)]zirconium dichloride occurs with cis stereochemistry at the exo face of the indenyl ligand.

Catalytic deuteriation of [ethylenebis(indenyl)]zirconium dichloride (**1**) with PtO_2 under 100 bar of D_2 in CH_2Cl_2 was carried out according to the published procedure[1] to give [ethylenebis-(4,5,6,7-tetradeuterio-1-indenyl)]zirconium dichloride (**3**). The ^1H and ^2H NMR spectra of the nondeuteriated and deuteriated dichloride derivatives (**2** and **3**, respectively) are presented in Figure 1. The ^1H NMR spectrum of **3** consists of four doublets (J_{HH} = 5.5–5.8 Hz) corresponding to eight protons of the tetradeuterioindenyl ligand (Figure 1b). Resonances corresponding to the other eight protons are barely discernible in the ^1H NMR spectrum but can be clearly observed in the ^2H NMR spectrum (Figure 1c). Integration of the resonances of 1.57 and 2.57 ppm in the ^1H NMR spectrum of **3** reveals a small amount (<8%) of residual hydrogenation.[9] A molecular ion peak at m/z 432 in the mass spectrum confirmed that eight deuterium atoms were incorporated into the indenyl ligands. A DEPT[10] experiment provided evidence against scrambling processes and confirmed that each carbon of the tetradeuterioindenyl ligand is bonded to only one protium atom.

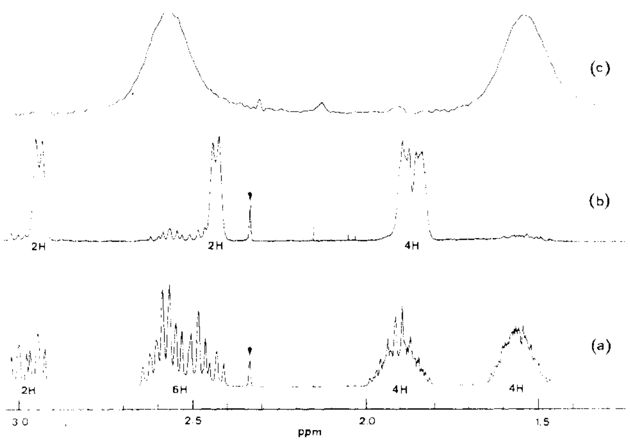

Figure 1. ^1H and ^2H NMR spectra. (a) ^1H NMR spectrum of **2** ($CDCl_3$); (b) ^1H NMR spectrum of **3** ($CDCl_3$); (c) ^2H NMR spectrum of **3** ($CDCl_3$). Arrows indicate peaks due to an impurity.

The loss of multiple couplings upon deuteriation and the good peak separation of the remaining four resonances of **3** allowed us to assign the chemical shifts of all eight protons of the tetradeuterioindenyl ligand by homo decoupling and difference NOE experiments (Figure 2). These experiments, carried out in C_6D_6 due to larger peak separations in that solvent, took advantage of the small allylic coupling (J = 0.7 Hz) between the cyclopentadienyl proton at 6.35 ppm (assigned as H3) and the proton appearing at 3.14 ppm (assigned as H4). Once H4 was assigned, assignments of the remaining protons followed straightforwardly. Peak assignments are given in Table I.

To confirm the cis stereochemistry of the hydrogenation reaction and establish that hydrogenation occurs at the exo face of the indenyl ligand, difference NOE experiments were carried out on the deuteriated dichloride and dimethyl derivatives (**3** and **5**) and the nondeuteriated dimethyl derivative **4**. The dimethyl derivatives were prepared as previously described;[11] the ^1H NMR spectra of these compounds are given in Table I.

Irradiation of the cyclopentadienyl resonance of **3** at 5.26 ppm (corresponding to H2) led to enhancement of one resonance at 2.16 ppm (10.3%) corresponding to H7 of the opposite ring. A similar result was obtained for **5**; irradiation of the resonance at 5.13 ppm (H2) led to enhancement of the resonance at 1.98 ppm (11.7%). These results confirm that H7 is in the endo position. The endo disposition of the remaining protons was established by irradiation of the methyl resonance of **5**; irradiation at −0.1 ppm led to enhancement of 3 resonances at 2.82 (17.8%), 1.69 (10.2%), and 1.61 ppm (8.6%) corresponding to H4, H6, and H5, respectively. Similar experiments on the fully hydrogenated dimethyl derivative **4** led to similar results; no enhancements were observed for those resonances that disappear upon deuteriation (centered at 2.67, 2.25, and 1.42 ppm), providing further support for a cis hydrogenation mechanism.

These labeling studies clearly establish the stereochemistry of catalytic hydrogenation of [ethylene-bridged bis(indenyl)]zirconium dichloride with PtO_2. Exo-face hydrogenation implies that

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[9] Residual hydrogenation is most likely due to H_2 impurities in the deuterium but could also be due to a small amount of H/D exchange.[5] Given the limitations of the NMR integration method, we hesitate to ascribe any mechanistic significance to the amount of residual hydrogenation.

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