

## Ab Initio Studies of Molecular Structures and Energetics. 3. Pentacoordinated $\text{NF}_n\text{H}_{5-n}$ Compounds

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**Abstract:** An ab initio quantum-chemical study has been made of the possible existence in terms of structural and thermodynamic stabilities of the pentacoordinated nitrogen hydrides and fluorides,  $\text{NF}_n\text{H}_{5-n}$  for  $n = 0$  to 5. Three structurally stable species have been identified corresponding to  $n = 3$  to 5:  $\text{NF}_3\text{H}_2$ ,  $\text{NF}_4\text{H}$ , and  $\text{NF}_5$ . Each exhibits a trigonal-bipyramidal structure. Hydrogen atoms are invariably equatorial. No stable structure was found for the other species such as  $\text{NH}_5$ . For the stable pentacoordinated compounds we report computed energies, vibrational frequencies, structural parameters, and multicenter analysis of total energies. For all except the last of these properties we employed the second-order many-body perturbation approximation to the electron-correlation energy.  $\text{NF}_5$  was studied in especial detail, including the enthalpies and free energies of two likely formation and decomposition reactions. Our analysis shows that each of these compounds contains a truly pentacoordinated first-row element, with five independent linkages to the central nitrogen atom.

The rapid development of the tools and resources of nonempirical quantum chemistry, both in terms of accuracy and scope of the systems amenable to study, has increasingly made possible reliable studies of chemical problems that are beyond the pale of common laboratory experience. In particular, the ability to compute reasonably accurate molecular energies (and enthalpies and free energies) and derivatives of the energy with respect to molecular deformations permits a reliable assessment of whether "existence" is possible for a posited species in terms of both its thermodynamic and structural stabilities. Existence in a thermodynamic sense implies that the free energy of the species in question is sufficiently smaller than those of its various sets of decomposition products to permit detectable amounts of the former to exist. Structural stability implies that there are no imaginary vibrational frequencies, so that spontaneous decomposition or rearrangement will not occur.

For many years synthetic chemists have had well-developed concepts, based mainly on experience, concerning the types of compounds in which the atoms or groups ought to hold together so that preparation of such compounds seems feasible. Recently, as theoretical techniques have expanded in scope and become more reliable and accurate, these concepts are being increasingly called into question as compounds are discovered for which "existence" is possible according to theoretical criteria, although appearing to violate the empirical rules governing molecular structure.

One of the more interesting such classes of compounds now accessible to theoretical study are those which at least superficially violate traditional concepts of valence and hence have been termed "hypervalent" or "hypercoordinated" due to the presence of an unanticipatedly high degree of coordination about a particular central atom. Practical considerations initially limited theoretical investigations to hydrides of first-row elements, for which no highly coordinated species were found. However, we have recently shown<sup>1</sup> that several highly coordinated hydrides of second-row elements, such as  $\text{ClH}_5$ , are structurally stable.

It must be emphasized, however, that the commonly employed concepts of hypervalence and hypercoordination are in general not well defined. For example, in analyzing the structure of a species either theoretically or empirically, account must be taken of possible stabilizing interactions between substituent atoms or groups (as in  $\text{CLi}_5^2$ ) as opposed to binding to the central atom, and of relatively weak types of interactions such as formation of complexes (e.g.,  $\text{BH}_5^3$  or  $\text{CH}_5^{+4}$ ) and electrostatic attractions

between oppositely charged atoms or groups (as in salts). Therefore, in the following we will place considerable emphasis on determining whether these other types of linkages are involved, as opposed to distinctively "covalent" interactions with the central atom. In other words, it is necessary to determine the energies of all the possible bonding interactions.

It has been often assumed that hypervalent compounds of first-row elements such as nitrogen cannot exist, this assumption founded largely on the mythos of the requirement for low-lying unoccupied atomic d orbitals. According to this view, as originally advocated by Pauling,<sup>5</sup> atoms exhibiting penta- rather than tetra-coordination would have to be surrounded by a decet rather than an octet of electrons, requiring excitation of the central atom to a high-energy electronic state with hybridization of  $\text{sp}^d$ . Of course, this point of view does not mean that the species exhibiting 5-fold coordination of a first-row element are structurally unstable, but only that they would be of relatively high energy.

Pauling's formulation has led to considerable confusion<sup>6</sup> between the concepts of d-polarization functions in a basis-set expansion of a molecular wave function as opposed to true excited eigenstates of the central atom. However, it has now been pointed out by several authors that in highly coordinated compounds, such as those of  $D_{3h}$  symmetry, orbitals are occupied whose symmetries preclude their formation by atomic orbitals of s and p symmetry centered *only on the central atom*.<sup>7</sup> Such orbitals can, however, readily be formed by contributions from substituent orbitals and/or from d-symmetry basis functions on the central atom.<sup>8,9</sup> From this it follows that in highly coordinated species basis functions of d symmetry should be particularly efficient for describing the electron distribution. However, this basis-set dependence does not in itself favor the structural stability of compounds from one region of the periodic table over others. Thus, not surprisingly, for all the molecules described herein we have determined that the presence or absence of d basis functions on the central atom made no qualitative differences in the molecular structures,

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structural symmetries and stabilities, or the nature of the occupied orbitals.

One previous nitrogen compound,  $F_3NO$ , has been well characterized both experimentally<sup>10</sup> and theoretically<sup>11,12</sup> and, although tetracoordinate, has been dubbed "hypervalent". Because of its  $C_{3v}$  symmetry and the observed F-N and N-O bond lengths, this compound clearly exhibits strong and distinct linkages to the nitrogen atom, and it has been pointed out that "rightly or wrongly, few chemists would invoke the 3d orbitals of nitrogen to explain the bonding in  $F_3NO$ ."<sup>13</sup>

The species we describe in this paper are of the form  $NF_nH_{5-n}$  for  $n = 0$  to 5. There have been a few prior studies of  $NH_5$ . Its possible existence as a transition state has been investigated experimentally by Olah et al.<sup>14</sup> who concluded that its existence as a stable intermediate is unlikely. Limited theoretical studies,<sup>15,16</sup> which did not include vibrational frequencies to ascertain structural stabilities, have focused on the relative energies of various symmetries of postulated structures. A recent presentation<sup>17</sup> has reported that only real vibrational frequencies were obtained by an ab initio theoretical study of  $NF_5$ . We have not been able to find a form exhibiting no imaginary vibrational frequencies for  $NH_5$  ( $n = 0$ ) nor for  $n = 1$  or 2, although we find that each of the three species  $NF_3H_2$ ,  $NF_4H$ , and  $NF_5$  exhibits structurally stable atomic arrangements.

In this paper we present several computed properties, including structural parameters, vibrational frequencies, and the multicenter resolutions of the total molecular energies for the  $n = 3$  to 5 species. We have also studied the enthalpies and free energies of two of the most likely types of reactions that might be used to prepare  $NF_5$  which, by analogy with  $PF_5$ , should be more easily prepared than the other two compounds and which our results indicate should be the most stable. For this purpose we have also computed molecular structures, energies, and vibrational frequencies of the possible precursor species  $NF_3$ ,  $NF_4^+$ , and  $NF_3^{2+}$  as well as  $F^-$  and  $F_2$  employing the same levels of approximation throughout. In the next section we summarize the computational methods employed, and then list the computed total energies and optimized molecular structures. The energies may be interpreted in terms of  $\Delta H^\circ_{298}$  and  $\Delta G^\circ_{298}$  for reactions bearing on the synthesis or decomposition of  $NF_5$ . To assess structural stabilities we give the computed vibrational frequencies of the three stable pentacoordinated species. Finally we show the energies of each of the possible bonding interactions. For comparison we also list these energies for  $NH_5$  (which is structurally unstable). This analysis shows that  $NF_5$  and, to a lesser extent, the two stable hydrogen-containing species represent truly pentacoordinated nitrogen compounds.

### Computational Details

All computations employed ab initio quantum-theoretical methods. Since our experience has been that the energy surfaces, particularly the curvatures in terms of the presence of real vibrational frequencies at extrema, may be sensitive to the presence of electron-correlation energy, all molecular structures, vibrational frequencies, and energies were found using the second-order many-body-perturbation ("MP2") approximation. The computer program was CADPAC Issue 4.0.<sup>18</sup> It has the useful feature of giving both the energy gradients and the force constant matrices analytically in the MP2 approximation.<sup>19</sup> However, structural stability for each species was found to be the same when electron correlation was omitted.

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Table I. Computed Total Energies<sup>a</sup>

species	RHF	MP2
$F^-$	-99.418 586 (-99.350 482)	-99.626 071 (-99.528 509)
$F_2$	-198.678 434 (-198.672 827)	-199.057 788 (-199.038 824)
$NF_3^{2+}$	-351.312 524 (-351.307 209)	-352.040 056 (-352.028 403)
$NF_3$	-352.545 669 (-352.531 887)	-353.271 130 (-353.236 611)
$NF_4^+$	-451.520 406 (-451.512 489)	-452.413 098 (-452.390 626)
$NF_3H_2$	-353.643 920 (-353.613 473)	-354.433 288 (-354.371 728)
$NF_4H$	-452.382 388 (-452.355 338)	-453.357 837 (-453.298 211)
$NF_5$	-551.109 478 (-551.088 192)	-552.283 155 (-552.228 780)

<sup>a</sup>Total energies computed in the MP2/basis II approximation at the commensurate optimized molecular structures, in hartrees. Values in parentheses are in basis I at the MP2/basis I optimized structures.

Table II. Optimized Molecular Structures<sup>a</sup>

species	symmetry	parameter	value
$F_2$	$D_{\infty h}$	F-F	1.4332 (1.4206)
$NF_3^{2+}$	$D_{3h}$	N-F	1.2336 (1.2329)
$NF_3$	$C_{3v}$	N-F	1.3897 (1.3834)
		$\angle FNF$	101.54 (101.65)
$NF_4^+$	$T_d$	N-F	1.3222 (1.3188)
$NF_3H_2$	$C_{2v}$	N-F <sub>ax</sub>	1.7070 (1.6745)
		N-F <sub>eq</sub>	1.3475 (1.3541)
		N-H	1.0121 (1.0079)
		$\angle HNH$	127.88 (126.60)
		$\angle HNF_{ax}$	87.43 (87.84)
		$\angle HNF_{eq}$	116.06 (116.70)
		$\angle F_{ax}NF_{ax}$	168.29 (170.39)
		$\angle F_{ax}NF_{eq}$	95.85 (94.81)
$NF_4H$	$C_{2v}$	N-F <sub>ax</sub>	1.6785 (1.6349)
		N-F <sub>eq</sub>	1.3441 (1.3558)
		N-H	1.0228 (1.0186)
		$\angle HNF_{ax}$	84.10 (85.29)
		$\angle HNF_{eq}$	122.86 (122.28)
		$\angle F_{ax}NF_{ax}$	168.20 (170.58)
		$\angle F_{ax}NF_{eq}$	93.20 (92.51)
		$\angle F_{eq}NF_{eq}$	114.27 (115.44)
$NF_5$	$D_{3h}$	N-F <sub>ax</sub>	1.5718 (1.5472)
		N-F <sub>eq</sub>	1.4073 (1.4098)

<sup>a</sup>Bond lengths in ångströms and angles in degrees, computed in the MP2/basis II approximation. Values in parentheses employed MP2/basis I.

A split-valence basis set was employed, augmented by d polarization functions on the nitrogen and each fluorine as well as p polarization functions on hydrogen. This has been designated as the 6-31G\*\* set.<sup>20</sup> For simplicity we will refer to it as basis I. However, in order to compute realistic reaction energies involving anions, it is necessary to add diffuse functions<sup>21,22</sup> to account for the anions' greater radial electron distribution. By the same token it is desirable to employ such additional basis functions (which if unneeded will be unoccupied) in order to describe concentrations of negative charge in species that are overall electrically neutral. With a diffuse s function on hydrogen and diffuse sp set on each of the other atoms, this is termed the 6-31++G\*\* basis. We will refer to it simply as basis II.

In searching for stable molecular structures we began in each case with a number of low-symmetry geometries and verified that in each case the optimization converged to the same equilibrium structure. In other words, we searched for but were unable to find more than one minimum in the energy hypersurface for each species.

At the equilibrium structures we verified for each species the stability of its restricted Hartree-Fock (RHF) wave function with respect to determinants of lower energy (including those of lower symmetry) employing the GAUSSIAN 86 computer program.<sup>23</sup> The electronic stability is essential not only in obtaining a qualitatively correct description of the electronic structure, but also is a mathematical requirement for the correct computation of the electron correlation and the force constant

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Table III. Nuclear-Motion Corrections<sup>a</sup>

species	$H^{\circ}_{298}$	$G^{\circ}_{298}$
F <sup>-</sup>	1.48	-8.88
F <sub>2</sub>	3.54	-10.89
NF <sub>3</sub> <sup>2+</sup>	11.81	-6.04
NF <sub>3</sub>	9.43	-9.13
NF <sub>4</sub> <sup>+</sup>	13.41	-5.28
NF <sub>3</sub> H <sub>2</sub>	25.31	5.14
NF <sub>4</sub> H	19.88	-0.88
NF <sub>5</sub>	14.32	-6.99

<sup>a</sup>In kcal/mol, including rotational, translational and vibrational terms at 298.15 K and 1 atm pressure. Computed employing MP2/basis I approximation.

matrices employing the coupled Hartree-Fock algorithms.<sup>19</sup> In addition we computed the stability of each species with respect to unpaired-spin (unrestricted Hartree-Fock or UHF) wave functions. This is especially important for NF<sub>3</sub>H<sub>2</sub>, NF<sub>4</sub>H, and NF<sub>5</sub> since in these cases both the highest occupied and lowest unoccupied orbitals computed in basis II are of the same symmetries (completely symmetric), suggesting a possible instability with respect to diradicals. However, in each case no UHF wave function was found to be of appreciably lower energy (more than ca. 1 kcal/mol) than the RHF functions we employed.

All other computed properties, such as the multicenter analysis to compute interaction energies between atoms, were obtained using specialized programs written in our laboratories.

The computed total electronic energies of the eight species included in this study are given in Table I. The optimized structural parameters of the seven molecules are listed in Table II. Table III shows the nuclear-motion contributions to the enthalpy and free energy due to rotation, translation, and vibration. The following sections discuss the individual classes of species.

### Stable Species

**F<sub>2</sub>, NF<sub>3</sub>, NF<sub>3</sub><sup>2+</sup>, and NF<sub>4</sub><sup>+</sup>.** For F<sub>2</sub>, NF<sub>3</sub>, and NF<sub>4</sub><sup>+</sup> experimental structural parameters are known. The experimental F-F bond length<sup>24</sup> in F<sub>2</sub> is 1.412 Å. In NF<sub>3</sub> the equilibrium N-F length is 1.365 Å and the bond angle is 102.4°. <sup>25</sup> Thus the computed values in Table II are in agreement with experiment to only the second significant figure, with the smaller of the two basis sets giving somewhat better results. This level of disagreement between theory and experiment is most likely due to incomplete correction for electron correlation. For example, in basis I the F-F distance in F<sub>2</sub> is only 1.345 in the Hartree-Fock approximation, increasing to 1.415 in the third order of perturbation, but is only 1.399 with configuration interaction (including double excitations).<sup>26</sup>

There have apparently been no prior experimental or theoretical studies of NF<sub>3</sub><sup>2+</sup>. We compute it to be structurally quite stable with a planar triangular geometry. Note that it exhibits a remarkably short N-F distance.

Although several stable salts of NF<sub>4</sub><sup>+</sup> are now known experimentally,<sup>27</sup> there are little data concerning the cation's physical properties. <sup>19</sup>F NMR as well as vibrational spectra indicate that it is tetrahedral.<sup>28</sup> The bond length has long resisted experimental measurement because of the considerable difficulty in crystallizing NF<sub>4</sub><sup>+</sup> salts in order to obtain X-ray diffraction spectra. Although it was initially estimated<sup>29</sup> to be 1.24 Å, an analysis based on vibrational spectra<sup>30</sup> has proposed a value of 1.31. Very recently an X-ray analysis<sup>31</sup> of crystalline NF<sub>4</sub>BF<sub>4</sub> has yielded NF bond lengths ranging from 1.265 to 1.321 Å. These agree with our value

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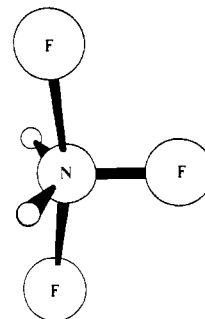


Figure 1. Structure of NF<sub>3</sub>H<sub>2</sub> as computed in the MP2/basis II approximation and reproduced to scale.

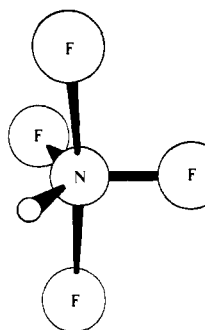


Figure 2. Structure of NF<sub>4</sub>H as computed in the MP2/basis II approximation and reproduced to scale.

and with one (and apparently the only) previous computed value<sup>32</sup> of 1.32.

**NF<sub>3</sub>H<sub>2</sub> and NF<sub>4</sub>H.** As part of this investigation we initially examined a number of symmetric and asymmetric geometrical structures for each of the NF<sub>n</sub>H<sub>5-n</sub> species for  $n = 0$  to 5. In each case we employed the following procedure. First the structure was optimized in the RHF approximation in a relatively small split-valence basis. If a minimal-energy structure was found (corresponding to vanishing energy gradients), we computed its force constant matrix and vibrational frequencies to determine its structural stability at that level of approximation. If the species were found to be stable, the entire process was repeated for the MP2/basis I description and, if this also indicated structural stability, its structure was recomputed in MP2/basis II. The result was the identification of three pentacoordinated nitrogen compounds with both vanishing gradients (with MP2/basis I and MP2/basis II) and all real frequencies (with MP2/basis I). It is important to note that the equilibrium symmetry of each of the three molecules was consistently found to be structurally stable in *all* of these levels of approximation, while other geometries of these compounds as well as all geometries tested for the remaining molecules in the NF<sub>n</sub>H<sub>5-n</sub> series were found to be consistently unstable.

Nonetheless, we should point out the well-known logical difficulty in attempting to prove a negative assertion, i.e., that other stable species do *not* exist. We can only report those that, according to our computations, *do* exist. With that caveat, it is interesting to note two prominent classes of compounds for which we were unable to find any stable geometry. The first class comprises the structural isomers of NF<sub>2</sub>H<sub>3</sub>, NFH<sub>4</sub>, and NH<sub>5</sub>. These were generally found to be structurally unstable with respect to formation of salts, e.g., NFH<sub>4</sub> → NH<sub>4</sub><sup>+</sup>F<sup>-</sup>. It is perhaps not surprising that adding electronegative atoms such as fluorine to the nitrogen to form the more highly fluorinated compounds would make this kind of charge separation less likely. Secondly, the hydrogens in the pentacoordinated compounds are invariably in equatorial positions. Although this effect has not been seen previously in nitrogen compounds, the strong preference of

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Table IV. Computed Vibrational Frequencies<sup>a</sup>

	$NF_3H_2$	$NF_4H$	$NF_5$
$\nu_1$	251, 281 ( $B_1$ )	230 ( $A_1$ )	173 ( $E'$ )
$\nu_2$	323, 298 ( $A_1$ )	394 ( $B_1$ )	173 ( $E'$ )
$\nu_3$	383, 381 ( $B_2$ )	458 ( $A_1$ )	426 ( $A_1'$ )
$\nu_4$	477, 453 ( $A_1$ )	491 ( $B_2$ )	551 ( $E'$ )
$\nu_5$	513, 495 ( $B_1$ )	493 ( $A_2$ )	551 ( $E'$ )
$\nu_6$	1031, 1061 ( $A_2$ )	573 ( $A_1$ )	578 ( $E''$ )
$\nu_7$	1044, 1064 ( $A_1$ )	711 ( $B_2$ )	578 ( $E''$ )
$\nu_8$	1123, 1111 ( $B_1$ )	958 ( $B_1$ )	614 ( $A_2''$ )
$\nu_9$	1158, 1177 ( $B_2$ )	990 ( $A_1$ )	690 ( $A_1'$ )
$\nu_{10}$	1542, 1542 ( $A_1$ )	1186 ( $B_2$ )	936 ( $A_2''$ )
$\nu_{11}$	3612, 3574 ( $A_1$ )	1348 ( $B_1$ )	969 ( $E'$ )
$\nu_{12}$	3816, 3780 ( $B_2$ )	3563 ( $A_1$ )	969 ( $E'$ )

<sup>a</sup> Computed in the MP2/basis I approximation at the commensurate optimized molecular structures, in  $cm^{-1}$ . For  $NF_3H_2$  the second of the two values was computed in basis II.

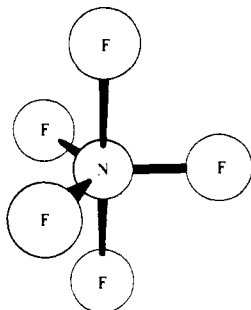


Figure 3. Structure of  $NF_5$  as computed in the MP2/basis II approximation and reproduced to scale.

electron-withdrawing atoms or groups for the axial positions in trigonal-bipyramidal phosphorus compounds has been thoroughly studied.<sup>33</sup> Nitrogen species with hydrogens in axial positions are unstable with respect to a pseudorotation to a structure with hydrogens equatorial. This is seen to be in precise agreement with the behavior predicted by Rauk et al.<sup>34</sup> for the pentacoordinated phosphorus compounds  $PX_3H_2$  and  $PX_4H$ , where X is an electronegative substituent, except that they predict a slight barrier to pseudorotation in the case of  $PXH_4$ , leading to a stable higher energy structure with the hydrogens in the axial positions. We find no such barrier in the nitrogen compounds,  $NF_3H_2$  and  $NF_4H$ .

The structural parameters of  $NF_3H_2$  and  $NF_4H$  with hydrogens equatorial as computed with the MP2/basis I and MP2/basis II approximations are listed in Table II. Their structures, drawn to scale, are shown in Figures 1 and 2. Both are trigonal bipyramids with relatively long axial N-F bonds. The addition of diffuse basis functions is seen to give a somewhat longer N-F<sub>ax</sub> distance, shown in the first column of numerical values, all other structural parameters being only modestly affected.

The vibrational frequencies and symmetries of the associated normal modes for  $NF_3H_2$  and  $NF_4H$  computed with the MP2/basis I method are given in the first three columns of data in Table IV. As a check we also computed the frequencies of the former at the MP2/basis II level, given as the second of the two sets of values. The additional basis functions made little difference in the computed frequencies. All the frequencies are appreciable, the lowest ones corresponding to deformation of bond angles. The vibration corresponding to symmetric stretching of the N-F<sub>ax</sub> bonds is  $\nu_4$  in  $NF_3H_2$  and  $\nu_3$  in  $NF_4H$ .

$NF_5$ . The optimized molecular structures of  $NF_5$  in basis sets I and II are given in Table II. The vibrational frequencies are listed in Table IV. For comparison with  $NF_3H_2$  and  $NF_4H$  its structure is also shown drawn to the same scale in Figure 3. Perhaps its most remarkable structural feature is the N-F<sub>ax</sub> distance, which is quite short compared to the other two pentacoordinated species and more nearly equal to the N-F<sub>eq</sub> distance.

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Table V. Computed Reaction Enthalpies and Free Energies<sup>a</sup>

reaction	RHF		MP2	
	$\Delta H^\circ_{298}$	$\Delta G^\circ_{298}$	$\Delta H^\circ_{298}$	$\Delta G^\circ_{298}$
$NF_4^+ + F^- \rightarrow NF_5$	-107.55	-99.81	-153.67	-145.93
$NF_3 + F_2 \rightarrow NF_5$	73.28	84.96	30.06	41.75
$NF_4^+ + F^- \rightarrow NF_3 + F_2$	-180.83	-184.77	-183.74	-187.68
$NF_3^{2+} + 2F^- \rightarrow NF_5$	-602.72	-585.46	-622.28	-605.02

<sup>a</sup> Computed in basis II at the MP2/basis II optimized molecular structures, in kcal/mol.

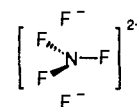
However these are still not so nearly equal as in  $PF_5$ , for which the experimental lengths in the gas phase are  $P-F_{ax} = 1.577$  and  $P-F_{eq} = 1.534$ .<sup>35</sup>

As shown in Table IV all the frequencies are appreciable. The lowest one,  $\nu_1 = 173 \text{ cm}^{-1}$ , is virtually the same as the lowest frequency in  $PF_5$ , 174.<sup>36</sup> The lowest stretching frequency is  $\nu_3$ , the symmetric N-F<sub>ax</sub> stretch.

In the remainder of this section we will focus on  $NF_5$  since it is likely, by analogy with the phosphorus pentahalides,<sup>37</sup> to be the most readily prepared. The few (apparently unsuccessful) attempts<sup>38,39</sup> to synthesize  $NF_5$  to date have primarily relied on the addition of  $F^-$  to  $NF_4^+$ . However the synthesis<sup>27</sup> of  $NF_4^+$  and of the phosphorus pentahalides<sup>37</sup> is generally based on the addition of the neutral species: in the latter case halogen with phosphorus trihalide, for which  $\Delta H$  is negative, as contrasted to the positive  $\Delta H$  in Table V for the similar reaction of  $F_2$  with  $NF_3$ . In Table V we list the values of  $\Delta H^\circ_{298}$  and  $\Delta G^\circ_{298}$  computed in basis II with both the Hartree-Fock (RHF) and second-order-perturbation (MP2) procedures for both synthetic approaches, i.e.,  $NF_4^+ + F^- \rightarrow NF_5$  and  $NF_3 + F_2 \rightarrow NF_5$ . (For later comparison we also give the results for the reaction of the dication,  $NF_3^{2+} + 2F^- \rightarrow NF_5$ .) Note that energies for the addition of  $F_2$  to  $NF_3$  are quite sensitive to electron correlation, as would be expected from the well-known difficulties in accurately computing properties of  $F_2$  with procedures not including correlation energy, such as RHF alone.  $\Delta H^\circ_{298}$  for the reaction  $NF_3 + F_2 \rightarrow NF_5$  was estimated by Goetschel et al.<sup>38</sup> based on an interpretation of related experimental data to be  $+26 \pm 10 \text{ kcal/mol}$ , in remarkable agreement with our value.

Since  $\Delta G^\circ_{298}$  is computed to be  $+42 \text{ kcal/mol}$ , this reaction is moderately endothermic (although, since there are no inordinately small vibrational frequencies, there should be an appreciable barrier to the concomitant decomposition of  $NF_5$ ). Hence it might appear less favored thermodynamically than the addition of  $F^-$  to  $NF_4^+$ , for which  $\Delta G^\circ_{298} = -146$ . However, an important competing reaction is the third one listed in Table V,  $NF_4^+ + F^- \rightarrow NF_3 + F_2$ , which is significantly more exothermic ( $\Delta G^\circ_{298} = -188$ ). It seems quite apparent from these considerations that the choice of reactants for making  $NF_5$  is much less important than the choice of the reaction conditions, which should be arranged so as to avoid thermodynamic equilibration between the gas-phase molecules  $NF_5$  and  $NF_3$ .

As noted above, in dealing with highly coordinated species for which decomposition to ions is quite possible, it is necessary to establish whether the coordination is due to strong "covalent" interactions or simply the formation of complexes that are weakly bound by electrostatic forces. Thus it might be argued that since  $NF_3^{2+}$  exhibits  $D_{3h}$  symmetry,  $NF_5$ , which is also of  $D_{3h}$  symmetry, might be partially or completely a complex of the form



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**Table VI.** Multicenter Resolution of the RHF Energy<sup>a</sup> of (Unstable) NH<sub>5</sub>

centers	individual energy	total energy
One-Center		
N	-53.326 73	-53.326 73
H <sub>ax</sub>	-0.413 61	-0.827 22
H <sub>eq</sub>	-0.11000	-0.330 00
total one-center		-54.483 95
Two-Center		
N-H <sub>ax</sub>	-0.178 86	-0.357 72
N-H <sub>eq</sub>	-1.058 69	-3.176 07
H <sub>ax</sub> -H <sub>ax</sub>	-0.160 34	-0.160 34
H <sub>ax</sub> -H <sub>eq</sub>	0.022 64	0.135 84
H <sub>eq</sub> -H <sub>eq</sub>	0.145 97	0.437 91
total two-center		-3.120 40
Three-Center		
H <sub>ax</sub> -N-H <sub>ax</sub>	-0.077 59	-0.077 59
H <sub>ax</sub> -N-H <sub>eq</sub>	0.150 63	0.903 78
H <sub>eq</sub> -N-H <sub>eq</sub>	-0.089 60	-0.268 80
H <sub>ax</sub> -H <sub>eq</sub> -H <sub>eq</sub>	0.081 88	0.491 28
H <sub>ax</sub> -H <sub>ax</sub> -H <sub>eq</sub>	-0.084 41	-0.253 23
H <sub>eq</sub> -H <sub>eq</sub> -H <sub>eq</sub>	0.003 52	0.003 52
total three-center		0.798 95
total four-center		-0.314 22

<sup>a</sup>Computed in basis II at the MP2/basis II optimized molecular structure, in hartrees.

If this were the case, substituting negative charges for fluorines in the axial positions would have to increase the N-F<sub>eq</sub> distances in the NF<sub>3</sub><sup>2+</sup> cation to the much larger values shown in Table II for NF<sub>5</sub>. As a test of this possibility, we recomputed the energy and molecular structure of NF<sub>3</sub><sup>2+</sup> employing the MP2/basis II approximation with negative point charges in each of the two axial positions and at the same distances from the nitrogen atom as N-F<sub>ax</sub> in NF<sub>5</sub>. The resulting system is lower in energy than NF<sub>3</sub><sup>2+</sup> by -684 kcal/mol, which is nearly the same as for the last reaction in Table V. This shows that most of the energy decrease for this and presumably for the other two ionic reactions in Table V are due primarily to cancellation of the respective positive and negative charges. However, the N-F distance in NF<sub>3</sub><sup>2+</sup> is now 1.2054 Å, and hence even *shorter* than for NF<sub>3</sub><sup>2+</sup> in vacuo. The optimized molecular structures therefore give strong, although indirect, evidence that NF<sub>5</sub> is primarily covalently rather than ionically bound. More direct evidence requires a rigorous analysis of the energies of interaction between all the atoms, as presented in the next section.

### Multicenter Analysis

The method and rationale for the multicenter resolution of the total molecular energies in applications to highly coordinated species was presented previously.<sup>1</sup> The central principle is that the total energy of any molecule in the RHF approximation, assuming the resulting wave function is expanded in terms of basis functions, may be written as a sum of terms, each of which is identified only by basis-function indices. So any criterion that is used to segregate basis functions into unique sets, such as the nuclei on which they are centered, will lead to an exact decomposition of the energy. In general,

$$E^{\text{total}} = \sum_n E_n^{(1)} + \sum_{mn} E_{mn}^{(2)} + \sum_{lmn} E_{lmn}^{(3)} + \sum_{klmn} E_{klmn}^{(4)}$$

where the sum in each case is over all sets to which each of the basis functions belongs, such as all the nuclei on which the basis functions are centered in the system under study. It is important to note that this resolution is independent of the nature of the individual orbitals, e.g., whether a delocalized wave function or any localized equivalent is employed. However, since this procedure directly yields energies of all of the specific interactions among atoms, it unambiguously reflects generally employed concepts of "bond energies" including multicenter interactions such as the linear three-center "hypervalent bonds" proposed by Musher.<sup>9</sup>

**Table VII.** Multicenter Resolution of the RHF Energy<sup>a</sup> of NF<sub>3</sub>H<sub>2</sub>

centers	individual energy	total energy
One-Center		
N	-53.108 01	-53.108 01
F <sub>ax</sub>	-99.349 36	-198.698 72
F <sub>eq</sub>	-99.225 05	-99.225 05
H	-0.085 54	-0.171 08
total one-center		-351.202 86
Two-Center		
N-F <sub>ax</sub>	-0.346 44	-0.692 88
N-F <sub>eq</sub>	-0.676 72	-0.676 72
N-H	-1.092 68	-2.185 36
F <sub>ax</sub> -F <sub>ax</sub>	0.006 66	0.006 66
F <sub>ax</sub> -F <sub>eq</sub>	0.049 95	0.099 90
F <sub>ax</sub> -H	-0.059 95	-0.239 80
F <sub>eq</sub> -H	0.034 60	0.069 20
H-H	0.176 77	0.176 77
total two-center		-3.442 20
Three-Center		
F <sub>ax</sub> -N-F <sub>ax</sub>	-0.035 10	-0.035 10
F <sub>ax</sub> -N-F <sub>eq</sub>	0.124 05	0.248 10
F <sub>ax</sub> -N-H	0.217 84	0.871 36
F <sub>eq</sub> -N-H	0.050 17	0.100 34
H-N-H	-0.081 85	-0.081 85
F <sub>ax</sub> -F <sub>eq</sub> -F <sub>ax</sub>	-0.021 01	-0.021 01
F <sub>ax</sub> -F <sub>eq</sub> -H	0.018 89	0.075 56
F <sub>ax</sub> -F <sub>ax</sub> -H	-0.024 37	-0.048 74
F <sub>ax</sub> -H-H	0.035 98	0.071 96
F <sub>eq</sub> -H-H	0.014 17	0.014 17
total three-center		1.194 84
total four-center		-0.193 69

<sup>a</sup>Computed in basis II at the MP2/basis II optimized molecular structure, in hartrees.

**Table VIII.** Multicenter Resolution of the RHF Energy<sup>a</sup> of NF<sub>4</sub>H

centers	individual energy	total energy
One-Center		
N	-52.659 36	-52.659 36
F <sub>ax</sub>	-99.326 92	-198.653 84
F <sub>eq</sub>	-99.216 02	-198.432 04
H	-0.082 93	-0.082 93
total one-center		-449.828 17
Two-Center		
N-F <sub>ax</sub>	-0.650 95	-1.301 90
N-F <sub>eq</sub>	-0.833 02	-1.666 04
N-H	-1.048 57	-1.048 57
F <sub>ax</sub> -F <sub>ax</sub>	0.001 39	0.001 39
F <sub>ax</sub> -F <sub>eq</sub>	0.075 36	0.301 44
F <sub>ax</sub> -H	-0.032 66	-0.065 32
F <sub>eq</sub> -H	0.022 95	0.045 90
F <sub>eq</sub> -F <sub>eq</sub>	-0.020 38	-0.020 38
total two-center		-3.753 50
Three-Center		
F <sub>ax</sub> -N-F <sub>ax</sub>	0.002 77	0.002 77
F <sub>ax</sub> -N-F <sub>eq</sub>	0.190 95	0.763 80
F <sub>ax</sub> -N-H	0.242 81	0.485 62
F <sub>eq</sub> -N-H	0.044 63	0.089 26
F <sub>eq</sub> -N-F <sub>eq</sub>	0.008 20	0.008 20
F <sub>ax</sub> -F <sub>eq</sub> -F <sub>ax</sub>	-0.020 69	-0.041 38
F <sub>ax</sub> -F <sub>eq</sub> -F <sub>eq</sub>	0.009 88	0.019 76
F <sub>ax</sub> -F <sub>ax</sub> -H	-0.019 77	-0.019 77
F <sub>ax</sub> -F <sub>eq</sub> -H	0.030 52	0.122 08
F <sub>eq</sub> -F <sub>eq</sub> -H	-0.005 05	-0.005 05
total three-center		1.425 30
total four-center		-0.226 02

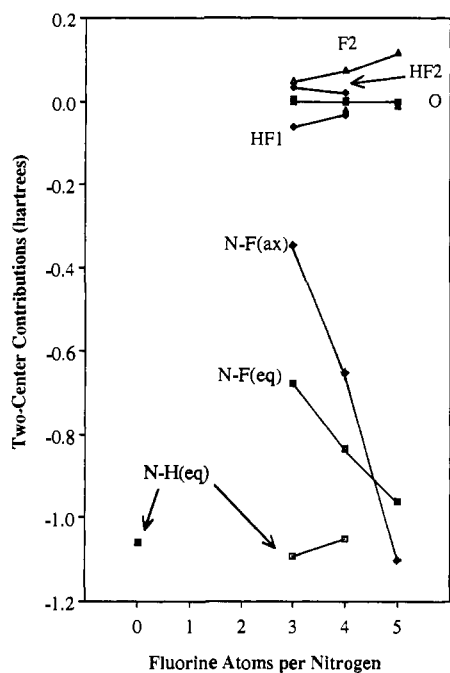
<sup>a</sup>Computed in basis II at the MP2/basis II optimized molecular structure, in hartrees.

In Table VI we list, for comparison with the stable species, the individual one-, two-, and three-center energies of NH<sub>5</sub> in basis II for its minimal-energy structure constrained to be of D<sub>3h</sub> symmetry. Tables VII, VIII, and IX contain similar analyses for the stable species NF<sub>3</sub>H<sub>2</sub>, NF<sub>4</sub>H, and NF<sub>5</sub>. In each case the individual four-center energies are small, so only the sum of all

Table IX. Multicenter Resolution of the RHF Energy<sup>a</sup> of  $NF_5$ 

centers	individual energy	total energy,
One-Center		
N	-51.985 86	-51.985 86
F <sub>ax</sub>	-99.313 25	-198.626 50
F <sub>eq</sub>	-99.215 62	-297.646 86
total one-center		-548.259 22
Two-Center		
N-F <sub>ax</sub>	-1.101 10	-2.202 20
N-F <sub>eq</sub>	-0.960 97	-2.882 91
F <sub>ax</sub> -F <sub>ax</sub>	-0.001 78	-0.001 78
F <sub>ax</sub> -F <sub>eq</sub>	0.115 64	0.693 84
F <sub>eq</sub> -F <sub>eq</sub>	-0.011 97	-0.035 91
total two-center		-4.428 99
Three-Center		
F <sub>ax</sub> -N-F <sub>ax</sub>	0.035 50	0.035 50
F <sub>ax</sub> -N-F <sub>eq</sub>	0.300 26	1.801 56
F <sub>eq</sub> -N-F <sub>eq</sub>	0.013 35	0.040 05
F <sub>ax</sub> -F <sub>eq</sub> -F <sub>eq</sub>	0.010 97	0.065 82
F <sub>ax</sub> -F <sub>ax</sub> -F <sub>eq</sub>	-0.013 36	-0.040 08
F <sub>eq</sub> -F <sub>eq</sub> -F <sub>eq</sub>	-0.005 82	-0.005 82
total three-center		1.897 01
total four-center		-0.318 28

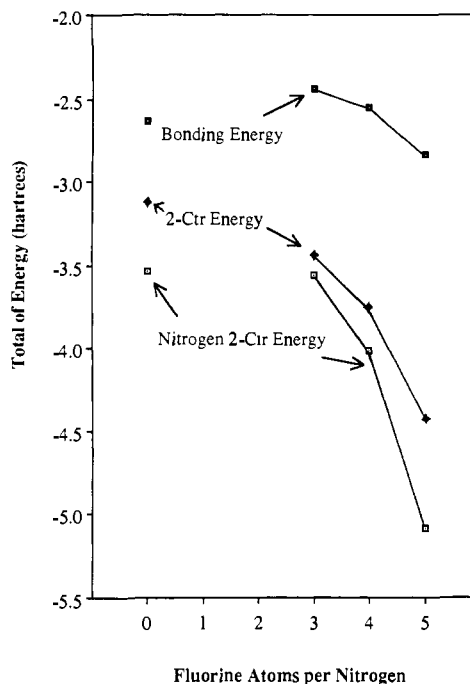
<sup>a</sup>Computed in basis II at the MP2/basis II optimized molecular structure, in hartrees.



**Figure 4.** The energies of classes of individual two-center contributions to the energy, with a pair-interaction between the nitrogen and either a hydrogen or fluorine being indicated, for example, as N-F(ax). The individual pair-interactions between fluorines and/or hydrogens are designated as follows: F<sub>ax</sub>-F<sub>eq</sub> as F2, H<sub>eq</sub>-F<sub>ax</sub> as HF1, and H<sub>eq</sub>-F<sub>eq</sub> as HF2, with O corresponding to the other individual interactions, all of which are quite small.

these terms is given. (The sum of the four types of interactions in each case equals the corresponding RHF energy in Table I.)

On intercomparing the molecules  $NH_5$ ,  $NF_3H_2$ ,  $NF_4H$ , and  $NF_5$ , several important trends become evident as shown in Figure 4, which depicts the variation in the individual two-center energy contributions. Note that each individual two-center energy involving the nitrogen and a fluorine becomes more negative as hydrogen atoms are substituted by fluorines. Thus, not only are there more N-F bonds, but each of these individually becomes stronger. Also the N-F<sub>ax</sub> bonds individually increase in strength more than do the N-F<sub>eq</sub> so that the latter, which is much the stronger of the two in  $NF_3H_2$ , is the weaker in  $NF_5$ . Individual N-H<sub>ax</sub> bonds are somewhat stronger in  $NF_3H_2$  than in  $NF_4H$  but much weaker in  $NH_5$ . Clearly the strengths of two-center bonds



**Figure 5.** Summations of energy contributions, where the caption of "Bonding Energy" corresponds to the total SCF energy minus all of the one-center contributions or alternatively the sum of all of the two-, three-, and four-center contributions. "Nitrogen 2-Ctr Energy" refers to the sum of only those two-center energy contributions in which one of the centers is the nitrogen atom, while "2-Ctr Energy" includes these plus all other two-center energies.

(as defined herein from fundamental theory) are not additive quantities but vary with the number and kind of the other bonds to the central atom. Not surprisingly, this effect applies not only to two-center interactions but also to three- and four-center contributions. For example, the three-center "hypervalent bond" F<sub>ax</sub>-N-F<sub>ax</sub> ranges from being stabilizing in  $NF_3H_2$  to destabilizing by about the same amount (0.035 hartree) in  $NF_5$ . Note in Figure 4 that the two-center interactions involving pairs of fluorine and/or hydrogen substituents are all small and often, as chemical lore dictates, destabilizing. The only exception is the H<sub>eq</sub>...F<sub>ax</sub> interaction (HF1 in the figure), which is slightly stabilizing.

Figure 5 demonstrates that the sum of the two-center energies involving the nitrogen paired with its substituents is the dominant stabilizing factor for the nitrogen hydridofluorides while the total effect of the other energy contributions, especially the sum of the three-center ones, is destabilizing. Although the sum of the N-F and N-H energy contributions is much more stabilizing in  $NF_5$  than in  $NF_3H_2$ , the bonding energy which is the sum of all of the two-, three-, and four-center contributions does not show as great a gain in stability from  $NF_3H_2$  to  $NF_5$  since the destabilizing effect, primarily due to the sum of the three-center interactions, increases from molecule to molecule in this series in step with the increase in stabilization. When  $NF_5$  is contrasted to  $NH_5$ , the most noteworthy difference is the much greater stability of the fivefold set of N-F bonds as compared to the set of N-H bonds. This difference is accompanied by a smaller destabilization of the  $NH_5$  as compared to the  $NF_5$  molecule by the remaining two-center as well as the three- and four-center contributions as may be seen in Figure 5.

We conclude that the  $NF_nH_{5-n}$  compounds exhibit three key similarities with the highly coordinated second-row hydrides we have described previously.<sup>1</sup> First they are stabilized primarily by two-center interactions, with comparatively little three-center bonding. Also, adding substituents to the central atom or replacing hydrogen by fluorine tends to make all bonds to this atom stronger. Finally, the primary factor leading to instability is a three-center "through-bond" interaction between the central atom and adjacent pairs of substituents (particularly connecting axial and equatorial positions).

## Conclusions

We have shown that, at least at the levels of approximation employed herein, there are three pentacoordinated compounds of nitrogen, i.e.,  $\text{NF}_3\text{H}_2$ ,  $\text{NF}_4\text{H}$ , and  $\text{NF}_5$ , that are structurally stable. Examination of several sets of computed properties, particularly their molecular structures, vibrational frequencies, and multicenter energies, shows that in addition they are truly pentacoordinated species with appreciable and distinct bonding to the central atom. This study has not rigorously ruled out the existence of other  $\text{NF}_n\text{H}_{5-n}$  compounds, but their structural stabilities now appear unlikely. Also it should be emphasized that the role played by electron correlation in determining the shapes of the energy surfaces in such compounds is presently not well understood. Although the methods we employed in this study are quite adequate based on our experience to date, energies and structures of fluorine compounds are notoriously difficult to compute accurately, and the numerical values reported here may exhibit lower accuracy than would be expected from similar computations on other nitrogen-containing molecules. This is reflected to some extent by the computed structures in Table II.

Our computed properties of  $\text{NF}_3\text{H}_2$ ,  $\text{NF}_4\text{H}$ , and  $\text{NF}_5$  are to our knowledge the first evidence of stable pentacoordinated nitrogen compounds. There is little evidence for neutral highly coordinated compounds (with distinct and separate linkages to the central atom) of any of the other first-row elements except for a small number of experimental studies involving bi- and tridentate ligands.<sup>40</sup>

Further it now appears that the ability to form pentacoordinated compounds such as  $\text{NF}_5$  is unique to nitrogen among the first-row elements. For example, calculation of the structural stability of the isoelectronic species  $\text{OF}_5^+$  employing the same techniques as described above showed it to be stable at the RHF/basis I level, but unstable with MP2/basis I. (A similar situation was found for  $\text{OF}_4$ , which is stable with RHF/basis I but unstable with MP2/basis I.) Conversely we found the isoelectronic carbon compound,  $\text{CF}_5^-$ , to be *unstable* with RHF/basis I but *stable* with MP2/basis I. Hence, although the stabilities of these two species is still uncertain, it now appears unlikely that they will be found to be stable at higher levels of approximation. The isoelectronic boron and fluorine compounds,  $\text{BF}_5^{2-}$  and  $\text{F}_6^{2+}$ , were found to be structurally unstable at both of the levels of approximation discussed above.

Finally, our computed results suggest several other types of compounds that may be structurally stable. The considerable affinity of  $\text{PF}_5$  for fluoride ions to form  $\text{PF}_6^-$  suggests that there should be a similar tendency of  $\text{NF}_5$  to form  $\text{NF}_6^-$ , and we have found that, in fact,  $\text{NF}_6^-$  is structurally quite stable. Thus this line of investigation leads to the conclusion that the existence of pentacoordinated and hexacoordinated compounds of first-row elements is possible, and these should be amenable to synthesis providing that the thermodynamic instabilities which usually characterize them can be overcome.

**Acknowledgment.** The authors are indebted to Professor J. C. Martin for several helpful discussions. This work was supported by the Air Force Office of Scientific Research, AFSC, under Grant AFOSR-86-0146. The computations were performed on an SCS-40 computer acquired with the assistance of SCS Corp., Vanderbilt University, and NSF Grant CHE-8808018.

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## Azines. A Theoretical Study of $\pi$ -Electron Delocalization

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**Abstract:**  $\pi$ -Electron delocalization in benzene and the azines has been studied theoretically in several ways: via an analysis of the first  $\pi \rightarrow \pi^*$  transitions, via calculation of hydrogenation energies, and via an analysis of the wave functions. The electronic transitions suggest that the delocalization energies are essentially the same for all the compounds. The calculated energies for the addition of 1 equiv of hydrogen suggest that the "resonance energies" of benzene, pyridine, pyrazine, and pyrimidine are essentially the same. The values for the other azines appear to be smaller, but this may in part arise from changes in the  $\sigma$ -systems. The distribution of  $\pi$ -electron density around the rings does not appear to be strongly perturbed by the replacement of CH by N.

### 1. Introduction

The azines form the basic structures of some of the most important compounds in nature. As such, they deserve especially careful examination. One of the most important characteristics of these compounds is  $\pi$ -electron delocalization,<sup>1</sup> which leads to reduced reactivity,<sup>2</sup> marked changes in keto/enol equilibria,<sup>3</sup> and substitution rather than addition.<sup>4</sup> A study of the monocyclic azines should provide useful information on the origin of this interaction. This would appear particularly appropriate at this

time in view of the recent interest in the subject. Although benzene and the azines are generally considered to have significant resonance stabilization,<sup>5</sup> we may note the calculations of Berry in 1965,<sup>6</sup> which suggested that it is the  $\sigma$ -bonds that cause benzene to be a regular hexagon and that the  $\pi$ -electrons would prefer a "Kekule"-like structure. The suggestion has recently been further amplified by Shaik and Hiberty, et al.,<sup>7</sup> and Epitotis has called into question the entire notion of  $\pi$ -electron delocalization.<sup>8</sup>

(1) For an excellent general summary of the aromaticity problem, see: Garratt, P. J. *Aromaticity*; Wiley: New York, 1986.

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