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Note

A Calculation of the ESR Parameters of the Hydrogen Bonded Complex Radical ($H_2NO \dots HF$)

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The isotropic constant (a) and the dipolar tensor (B) have been calculated for the radical H_2NO bonded to HF . The semi-empirical SCF (INDO) method has been used to describe the electronic configuration of the complex radical $H_2NO \dots HF$. It is suggested that a and B of the proton from HF are amenable to experimental verification.

INTRODUCTION

The study reported in this paper attempts to predict the values of some parameters that could be observed in ESR. It is well known that solvents have a pronounced effect on the g -factor and a of radicals¹. This study describes the calculation of B and a for the H_2NO radical hydrogen-bonded with HF . The primary aim is to calculate a and B for HF in the complex $H_2NO \dots HF$ and to show that these quantities could be experimentally observed.

CALCULATION AND DISCUSSION

The geometry of the H_2NO radical was taken from ref. 2 and the complex radical $H_2NO \dots HF$ was supposed to be linear (Fig. 1). The wave functions that have been used were obtained by the all-valence electrons SCF method

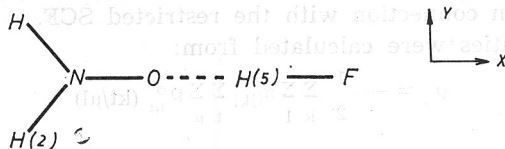


Fig. 1. The geometry of the $H_2NO \dots HF$.

in the INDO approximation³ with the parametrization from ref. 4. The values of the isotropic contact constant (a) and dipolar tensor (B) have been evaluated for atoms H (2), N, H (5) and F at various distances R .

i) Calculation of Dipolar Tensor B

Dipolar tensor B has the following form:

$$B = \gamma_e \gamma_D \hbar^2 \sum_{\mu} \sum_{i,j} \sum_{\text{unpaired MO's}} c_{\mu i} c_{\mu j} \left\langle \varphi_i \left| \frac{1}{r^3} \begin{pmatrix} \frac{3x^2 - r^2}{r^2} & \frac{3yx}{r^2} & \frac{3zx}{r^2} \\ \frac{3xy}{r^2} & \frac{3y^2 - x^2}{r^2} & \frac{3yz}{r^2} \\ \frac{3xz}{r^2} & \frac{3yz}{r^2} & \frac{3z^2 - r^2}{r^2} \end{pmatrix} \right| \varphi_j \right\rangle$$

where φ_i , φ_j are atomic orbitals.

For the atoms N and F only the one-center local terms were retained:

$$B = \gamma_e \gamma_D \hbar^2 \left\langle \frac{1}{r^3} \right\rangle_{2p} \sum_{\mu}^{\text{unpaired MO's}}$$

$$\left\{ \begin{array}{ccc} \frac{2}{5}(2c_{\mu x}^2 - c_{\mu y}^2 - c_{\mu z}^2) & \frac{6}{5} c_{\mu x} c_{\mu y} & \frac{6}{5} c_{\mu x} c_{\mu z} \\ \frac{6}{5} c_{\mu y} c_{\mu x} & \frac{2}{5}(2c_{\mu y}^2 - c_{\mu z}^2 - c_{\mu x}^2) & \frac{6}{5} c_{\mu y} c_{\mu z} \\ \frac{6}{5} c_{\mu x} c_{\mu z} & \frac{6}{5} c_{\mu z} c_{\mu y} & \frac{2}{5}(2c_{\mu z}^2 - c_{\mu x}^2 - c_{\mu y}^2) \end{array} \right\}$$

The inclusion of the non-local terms changes the values only slightly⁵ (about 0.2) and the approximation is thus justified. The expectation values

$\left\langle \frac{1}{r^3} \right\rangle_{2p}$ for N and F were calculated using Slater 2p orbitals.

The calculation of B for atom H, e.g. H(5), is more complicated. The local term is zero and we calculated the contribution of non-local terms with the center of the operator B being on atom H and the wave functions φ_i and φ_j on atoms

O ($\varphi_i = \varphi_j$), N ($\varphi_i = \varphi_j$), F ($\varphi_i = \varphi_j$) and on N (φ_i) and O (φ_j). The integrals were calculated using Slater orbitals with the method from ref. 5.

ii) Calculation of the Isotropic Contact Constants (a)

H₂NO and the complex radical H₂NO...HF have a half-occupied π molecular orbital and thus the restricted SCF method predicts zero spin density (s orbitals) on all atoms. Finite values can be obtained with e.g. the unrestricted SCF method. The difference between Hartree-Fock operators for electrons with spin α and spin β is small and it is allowed to use the perturbation theory⁶ in connection with the restricted SCF.

The spin densities were calculated from:

$$\rho_{ij} = -\frac{1}{2} \sum_k \sum_l \pi_{ijkl} \sum_t \sum_{\mu} p_{t\mu}^{\circ} (kt/\mu l)$$

where

$$\pi_{ijkl} = 2 \sum_{\substack{w \\ \text{unpaired} \\ \text{vacant} \\ \text{MO's}}} (c_{vi} c_{wj} + c_{wi} c_{vj}) c_{wk} c_{vl} / (E_v - E_w)$$

$p_{t\mu}^{\circ}$ is the bond order and $(kt/\mu l)$ is the exchange integral. The exchange integrals only between atomic orbitals centered on the one center were included. $[\varphi_{2s}(\text{O})]^2$ for N and F and $[\varphi_{1s}(\text{O})]^2$ for H were taken from ref. 7. Calculated values of B and a at various distances R are in Tables I, II, III and IV.

The calculated values for the H₂NO radical are in good agreement with experiment. Experimentally⁸ a (N) and a (H) have both values 11.9. Recently the united molecule approach of the hydrogen bond complex based on the molecular orbital approach proved to be useful in describing its stability and its configuration. The same approach with only one Slater determinant does not

TABLE I
Dipolar Tensor B (Gauss) for N and F

R (Å)	$B_{xx}^N = B_{yy}^N$	B_{zz}^N	$B_{xx}^F = B_{yy}^F$	B_{zz}^F
∞	-10.0893	20.1786		
1.82	-10.0599	20.1198	0	0
1.62	-10.2404	20.4808	0	0
1.42	-10.2201	20.4402	0	0
1.32	-10.2162	20.4324	$-26 \cdot 57 \cdot 10^{-4}$	$53 \cdot 11 \cdot 10^{-4}$

TABLE II
Dipolar Tensor B (Gauss) for $H(2)$

R (Å)	B_{xx}	B_{yy}	B_{zz}	B_{xy}
∞	-4.939	10.412	-5.547	-15.72
1.82	-4.912	10.378	-5.541	-15.69
1.62	-5.083	10.584	-5.577	-15.90
1.42	-5.064	10.565	-5.574	-15.87
1.32	-5.062	10.565	-5.574	-15.87

TABLE III
Dipolar Tensor B (Gauss) for $H(5)$

R (Å)	B_{xx}	B_{yy}	B_{zz}
1.82	3.692	-1.968	-1.724
1.62	4.654	-2.526	-2.128
1.42	6.182	-3.454	-2.729
1.32	7.176	-4.093	-3.088

TABLE IV
Isotropic Constant a (Gauss)

R (Å)	a (N)	a [H (2)]	a [H (5)]	a (F)
∞	12.71	-10.84		
1.82	12.93	-10.97	-0.0623	0
1.62	12.92	-10.90	-0.1201	
1.42	12.91	-10.81	-0.2199	
1.32	12.89	-10.76	-0.2912	

necessarily describe various spectroscopically observable properties. However, recent results obtained with the molecular orbital approach suggest that the approach using one determinant is adequate for the calculation of ESR parameters⁹. This point and the good agreement between the calculated a and B for the H_2NO radical are the bases for the following conclusion: it would be possible not only to observe experimentally changes of a and B of the radical but also a and B of the hydrogen donor. The calculated a and B increase with the strenght of the complex resulting in quite large values if a strong hydrogen bond is formed.

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IZVLEČEK

Račun ESR parametrov kompleksa H_2NO-HF

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Izračunana sta izotropna konstanta in dipolarni tenzor kompleksa H_2NO radikala vezanega na HF. Račun potrjuje domnevo da je možno meriti obe količini protona donorja.

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