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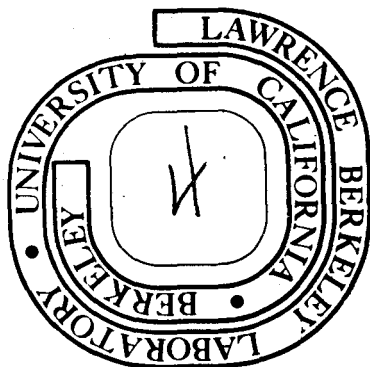
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Excited Electronic States of HNC, Hydrogen Isocyanide\*

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ABSTRACT

Walsh's rules suggest that the excited states of HNC should have bond angles similar to the analogous states of HCN. To test this hypothesis, ab initio calculations have been carried out and compared to earlier calculations on HCN. The most surprising result is the prediction that several of the excited electronic states of HNC lie below the corresponding states of HCN. Also unanticipated are the unusually long CN bond lengths found for several of the lower excited states of HNC. The excited singlet states have bond angles qualitatively similar, although somewhat smaller, than those of HCN. For the triplet states, Walsh's concept appears less successful, primarily due to strong mixing between several different electronic configurations. Mulliken populations are used in the discussion of these results.

## INTRODUCTION

The simplest isocyanide molecule, HNC, has never been prepared in the gas phase under laboratory conditions. However, hydrogen isocyanide has been identified by Milligan and Jacox<sup>1</sup> in matrix isolation experiments, i.e., in frozen inert gas matrices. Despite the lack of a microwave spectrum, Snyder and Buhl<sup>2</sup> tentatively identified HNC as the source of the interstellar emission signal they observed at 90.665 GHz. This rather daring hypothesis has been greatly strengthened by the extensive (6343 configurations) ab initio theoretical study of Pearson et. al.<sup>3</sup>, who predicted the HNC microwave line to lie at 90.48 GHz. The same calculations<sup>3</sup> predict HNC to lie only 14.5 kcal/mole above HCN, and additional work<sup>4</sup> suggests a large barrier, 34.9 kcal/mole. Thus it seems possible that HNC might have a substantial lifetime if it could be prepared in the gas phase.

It is difficult to overestimate the importance of the idea of Walsh<sup>5</sup> that the geometries of molecules can be predicted from simple orbital binding energy diagrams.<sup>6</sup> And one of the earliest qualitative confirmations of the Walsh model came from the HCN experiments of Herzberg and Innes,<sup>7</sup> who found three bent excited states of HCN. For triatomic HAB molecules, Walsh's original diagram<sup>5</sup> is reproduced in the Figure. Based on this diagram, one readily makes the predictions summarized in Table I. In a previous paper,<sup>8</sup> we have calculated the geometries of the

excited states of HCN using a new type of configuration interaction. The results<sup>8</sup> provided additional support for the qualitative validity of Walsh's rules, and one modification was suggested, that the  $5a'$  binding energy should decrease very slightly with bending.

The HNC molecule should provide a crucial test of Walsh's rules, since the basic assumption there is that molecular geometry depends only on the class (e.g. HAB) of molecule and the number of electrons. Thus it is seen that, according to the Walsh concept, the excited states of HNC should have the same bond angles as the corresponding states of HCN. For this reason we undertook the present ab initio theoretical study of the excited electronic states of HNC. The method used was identical to that employed in our earlier HCN calculations.<sup>8</sup> Briefly, a basis set of essentially double zeta<sup>9</sup> quality was chosen and self-consistent-field calculations performed on the ground state configuration

$$1a'^2 \ 2a'^2 \ 3a'^2 \ 4a'^2 \ 5a'^2 \ 6a'^2 \ 1a''^2 \quad (1)$$

After determination of the unoccupied orbitals (of which the  $7a'$  and  $2a''$  are particularly important), configuration interaction was carried out including all single excitations with respect to (1) and the other configurations seen in Table I. A fairly complete description of this method is given in the earlier paper.<sup>8</sup>

Geometry Search Procedure

The predicted geometry of each electronic state was obtained by minimizing the total energy with respect to the two bond distances  $r(\text{HN})$  and  $R(\text{NC})$  and the bond angle  $\theta(\text{HNC})$ . In contrast to our earlier work,<sup>8</sup> a fixed grid of  $r$ ,  $R$ ,  $\theta$  values was adopted.

$\theta$ : (100, 180) in 10 degree intervals

$r$ : (.95, 1.15) in .05 Å intervals

$R$ : (1.15, 1.45) in .05 Å intervals

For each state the lowest energy was found and six other calculations were selected which form an

( $r + .05 \text{ Å}$ ,  $R$ ,  $\theta$ )

( $r - .05 \text{ Å}$ ,  $R$ ,  $\theta$ )

( $r$ ,  $R + .05 \text{ Å}$ ,  $\theta$ )

( $r$ ,  $R - 0.05 \text{ Å}$ ,  $\theta$ )

( $r$ ,  $R$ ,  $\theta + 10^\circ$ )

( $r$ ,  $R$ ,  $\theta - 10^\circ$ )

octahedral structure about this minimum geometry. The seven energies are fit to the simple analytic form

$$E = a + b (r - r_e)^2 + c (R - R_e)^2 + d (\theta - \theta_e)^2$$

which determines the equilibrium geometry ( $r_e$ ,  $R_e$ ,  $\theta_e$ ). A final calculation was run at the predicted equilibrium



### Results and Discussion

The HNC results are summarized in Tables II and III. It should be noted that the ab initio excitation energies have all been reduced by 2.18 eV. As discussed in the earlier paper,<sup>8</sup> this semi-empirical adjustment is necessary because the calculations are predisposed in favor of the ground electronic state. That is, while our excited state wave functions yield total energies comparable to SCF wave functions, the ground state results include a significant amount of electron correlation. The ground state of HNC is predicted to lie 0.76 eV = 17.6 kcal/mole above that on HCN, a result in good agreement with the 14.5 kcal/mole difference obtained by Pearson<sup>3</sup> using much more reliable wave functions. This result strengthens our confidence in the energies of the HNC states relative to HCN.

The ordering by symmetry of the excited states is identical to that predicted for HCN. However, among several unanticipated results, the most surprising is that some of the excited states of HNC lie below the corresponding states of HCN. For example, the lowest  $^1A''$  state of HNC lies fully 0.77 eV below that of HCN. In fact the only singlet state of HCN lying below that of HNC is the  $3^1A'$  state. Among the triplets there are two

HCN states ( $1^3A'$  and  $2^3A'$ ) lying lower than the corresponding states of HNC. However, for the lowest triplet state, the HCN-HNC separation is substantial, 0.80 eV.

A second somewhat unanticipated result concerns the length of the NC bonds predicted for some of the lowest excited states of HNC. For HCN the CN bond length is known<sup>7</sup> to increase from 1.156 to 1.297 Å in going from the  $X^1\Sigma^+$  state to the  $\tilde{A}^1A''$  state (lowest excited singlet). Our earlier calculations predicted<sup>8</sup> this bond distance change to be 0.138 Å, in good agreement with experiment, 0.141 Å. However, for HNC this increase in bond distance with electronic excitation is much greater, 0.257 Å. Nearly as large a bond distance (1.444 Å) is predicted for the lowest  $^3A''$  state of HNC. Although these results have no direct bearing on the validity of Walsh's rules, they certainly serve to emphasize the significant differences between HNC and HCN. It should be pointed out that the two ( $1^1A''$  and  $1^3A''$ ) exceptionally long bond distances occur for electronic states dominated by the same configuration,  $5a'^2 6a'^2 1a'' 7a'$ . Note in this regard that the other states with long bond distance involve either the loss (relative to the ground state) of a  $1a''$  electron or gain of a  $7a'$  electron.

The excited singlet state bond angles are qualitatively very similar to those of HCN, and hence consistent with Walsh's rules. The HNC bond angles do tend to be somewhat less than those of HCN. This difference is greatest ( $14.4^\circ$ ) for the lowest  $1^1A''$  state. Although many simple arguments may be given to

explain this observation, the simplest rests on the notion that in HCN, the H-N repulsion discourages small bond angles, while in HNC, the H-C repulsion has the same effect. Since N is larger than C, one can hence argue that the H-C repulsion is the lesser, and the states of HNC are allowed to become slightly more bent.

For the triplet states, a more complicated situation exists, as there is not a direct correspondence between the HCN and HNC bond angles. This is first evidenced in the  $2^3A'$  bond angle of HNC, which is  $125.5^\circ$ , as opposed to that of HCN,  $160.0^\circ$ . Thus we appear to have a qualitative breakdown of Walsh's rules. Furthermore, this difference cannot be ascribed to a change in the ordering of the different electron configurations between HCN and HNC. For both isomers, the  $2^3A'$  state is dominated by the  $5a'^2 6a'^2 1a'' 2a''$  configurations, with the second most important configuration being  $5a'^2 6a' 7a' 1a''^2$ . As Table I shows clearly in this regard, a nearly linear  $2^3A'$  state would be associated with this wave function using Walsh's rules.

Although we cannot reverse the discrepancy with Walsh's rules for the  $2^3A'$  state, it does seem possible to understand this result. To do this one notes that the  $3^3A'$  state is also predicted to be inconsistent with Walsh's rules and the earlier HCN theoretical study.<sup>8</sup> That is, as seen in Table I, a bent state is usually associated with the  $5a'^2 6a' 7a' 1a''^2$  configuration. With these facts in mind it seems clear the inapplicability of Walsh's rules is due to the strong mixing of

the  $5a'^2 6a'^2 1a'' 2a''$  and  $5a'^2 6a' 7a' 1a''^2$  configurations in the  $2^3A'$  and  $3^3A'$  states. The separation of these two states is seen in Table III to be only 0.74 eV, and this type of strong configuration mixing is not considered in the simple Walsh model. Our general conclusion is that one should be somewhat skeptical of Walsh's rules when states of the same symmetry lies close together.

There is a sizeable ( $18.5^\circ$ ) difference between the bond angles of the  $2^3A''$  states of HCN and HNC. This difference must also be viewed as a deviation from Walsh's rules. For HCN, the  $2^3A''$  state is dominated by the  $5a'^2 6a' 1a''^2 2a''$  (coefficient 0.8285) and  $5a'^2 6a'^2 1a'' 7a'$  (coefficient 0.4951) configurations. Since the latter configuration is associated with a bent structure, one might expect the  $2^3A''$  state of HCN to be more bent than that of HNC, since this configuration makes a stronger contribution to the HCN  $2^3A''$  wave function. The fact that this is not so is another reminder that HNC is not just a "carbon copy" of HCN.

Finally, in Table IV, Mulliken populations are presented for the ground states of HCN and HNC. Although population analyses were also obtained from single configuration SCF wave functions for several of the excited states, these tend to confuse rather than clarify the situation. This is because the character of each orbital depends not only (as expected) on the molecular geometry, but also the electronic state for which it is optimum. However, the difference in ground state populations

does appear to reflect on the nature of the electronic structures of HCN and HNC. Specifically, the nitrogen population in HCN is 7.09 electrons, while that in HNC is much greater, 7.40 electrons. Further, the carbon atom is negatively "charged" in HCN, but positively in HNC. Thus it seems clear that in going from HCN to HNC, a significant amount of electron density shifts into the vicinity of the nitrogen atom.

The orbital energies (also in Table IV) show that the  $1\pi$  ( $6a'$  +  $1a''$ ) orbital of HNC lies lower than the  $1\pi$  orbital of HCN. Thus if we had no additional information, one might expect the excited states (the lowest of which arise from  $1\pi \rightarrow 2\pi$  excitations) of HCN to lie relatively lower than those of HNC. However, as discussed earlier, it appears that the opposite is more often the case. The problem is that this analysis does not consider the  $2\pi$  ( $7a'$  +  $2a''$ ) orbital energy. And consideration of Table IV suggests that the  $2\pi$  orbital of HNC should be significantly lower than that of HCN. From Table IV it is clear that the  $2\pi$  orbital of HNC will be  $\sim 75\%$  carbon 2p and  $\sim 25\%$  nitrogen 2p. On the contrary the HCN  $2\pi$  orbital should be a nearly equal admixture of carbon and nitrogen 2p. In the isolated atom the 2p orbital energies of C and N are -0.4333 hartrees and -0.5675 hartrees. Thus one expects the HNC  $2\pi$  orbital, having much more carbon p character, to lie significantly lower than the  $2\pi$  orbital of HCN. This is perhaps the simplest

rationalization of the predicted relative energies of the excited states of the two isomers.

ACKNOWLEDGMENTS

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TABLE I. Predictions of the bond angles of HCN excited states based on Walsh's diagram, Fig. 1.

Symmetry	Electron configuration	Bond angle
$1^1 A'$ and $3^1 A'$	$5a'^2 6a' 1a''^2 7a'$	more bent
	$5a'^2 6a'^2 1a'' 2a''$	$180^\circ$
	$5a' 6a'^2 1a''^2 7a'$	most bent
$1^1 A''$ and $3^1 A''$	$5a'^2 6a'^2 1a'' 7a'$	bent
	$5a'^2 6a' 1a''^2 2a''$	slightly bent
	$5a' 6a'^2 1a''^2 2a''$	$180^\circ$



TABLE II. Summary of theoretical predictions for the singlet states of HNC. Excitation energies and bond angles given in parentheses are those predicted by analogous calculations on HCN. Bond distances are in Å.

Symmetry	$T_e$ (eV)	$r_e$ (HN)	$r_e$ (NC)	$\theta_e$ (HNC)	Most important configurations	Coefficients
1 $1A'$ ( $1\Sigma^+$ )	0.00 (0.00)	0.987	1.204	180° (180°)	$5a'^2 6a'^2 1a''^2$	0.968
1 $1A''$	4.95 (6.48)	1.022	1.461	112.8° (127.2°)	$5a'^2 6a'^2 1a'' 7a'$	0.939
2 $1A'$	5.51 (6.78)	1.015	1.417	119.7° (124.9°)	$5a'^2 6a' 7a' 1a''^2$	0.819
					$5a'^2 6a'^2 1a'' 2a''$	0.444
2 $1A''$	6.22 (7.52)	0.996	1.418	156.8° (164.4°)	$5a'^2 6a' 1a''^2 2a''$	0.910
3 $1A'$	7.34 (7.85)	1.021	1.266	142.0 (141.2°)	$5a' 6a'^2 1a''^2 7a'$	0.771
					$5a'^2 6a' 7a' 1a''^2$	0.365
					$5a'^2 6a'^2 1a'' 2a''$	0.358
3 $1A''$	8.17 (8.97)	0.979	1.220	180° (180°)	$5a' 6a' 1a''^2 2a''$	0.944
4 $1A'$	8.50 (9.54)	1.150	1.198	180° (180°)	$5a' 6a' 8a' 1a''^2$	0.813

TABLE III. Triplet excited states of HNC. The format is identical to that of Table II.

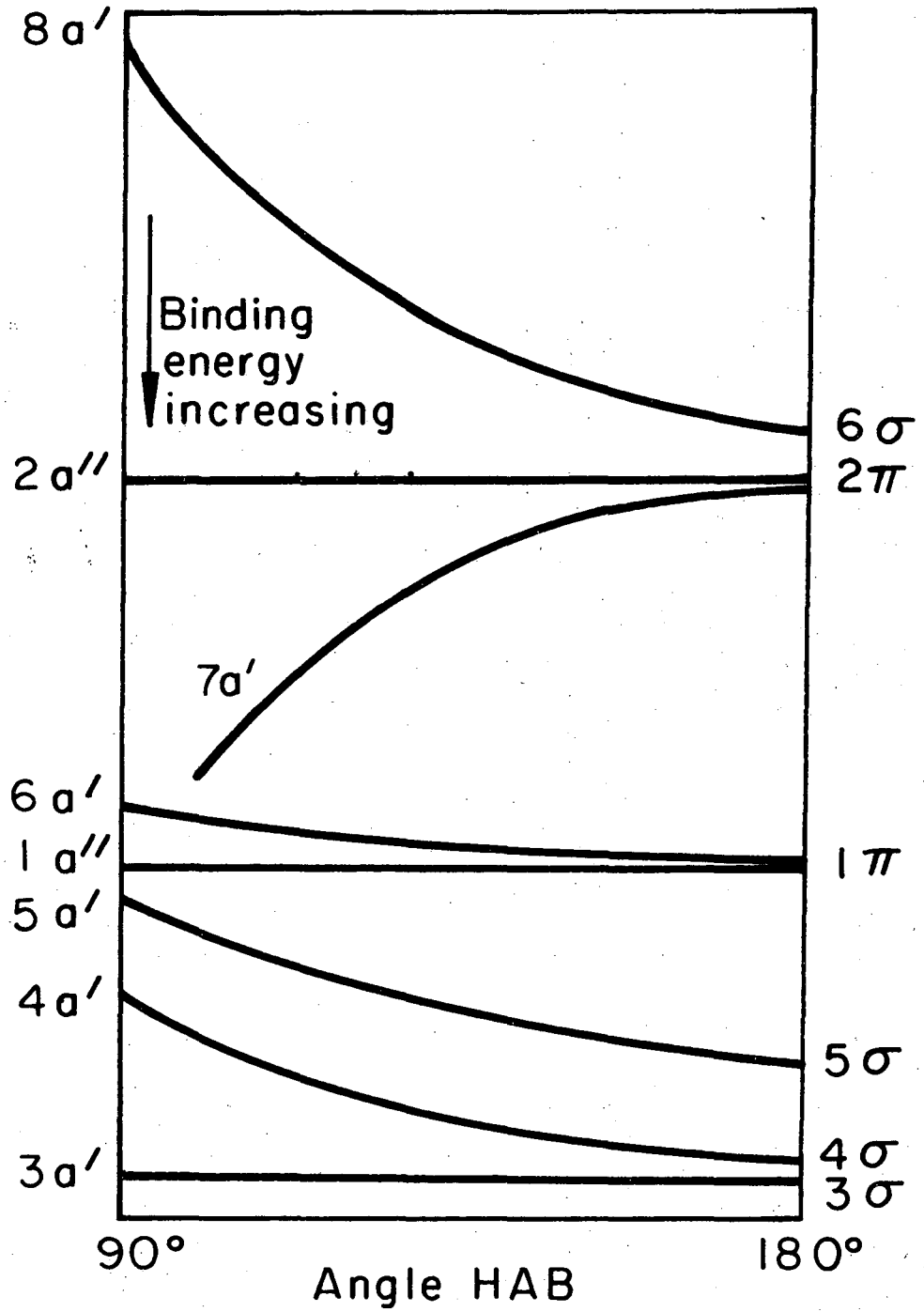
Symmetry	$T_e$ (eV)	$r_e$ (HN)	$r_e$ (NC)	$\theta_e$ (HNC)	Most important configurations	Coefficients
$1^3 A'$	4.46 (4.42)	1.012	1.314	117.7° (128.6°)	$5a'^2 6a' 7a' 1a''^2$	0.946
$1^3 A''$	4.60 (5.46)	1.021	1.444	114.2° (117.0°)	$5a'^2 6a'^2 1a'' 7a'$	0.942
$2^3 A'$	5.22 (5.91)	1.007	1.386	125.5° (160.0°)	$5a'^2 6a'^2 1a'' 2a''$	0.874
					$5a'^2 6a' 7a' 1a''^2$	0.353
$2^3 A''$	5.44 (6.85)	0.991	1.299	138.9° (157.4°)	$5a'^2 6a' 1a''^2 2a''$	0.850
					$5a'^2 6a'^2 1a'' 7a'$	0.303
$3^3 A'$	5.96 (6.98)	0.992	1.301	180° (132.6°)	$5a'^2 6a' 7a' 1a''^2$	0.838
					$5a'^2 6a'^2 1a'' 2a''$	0.502
$3^3 A''$	6.09 (7.41)	0.980	1.337	180° (180°)	$5a'^2 6a'^2 1a'' 7a'$	0.697
					$5a'^2 6a' 1a''^2 2a''$	0.655

TABLE IV. Mulliken atomic populations and orbital energies for the ground states of HCN and HNC near their equilibrium geometries. The HCN populations are given first, followed by the HNC results in parenthesis.

		3a'	4a'	5a'	6a'	1a''	Total
H	s	-0.01 (0.000)	0.65 (0.56)	0.07 (0.05)	0.00 (0.00)	0.00 (0.00)	0.71 (0.61)
C	s	0.63 (0.56)	0.56 (0.30)	0.04 (0.96)	0.00 (0.00)	0.00 (0.00)	3.23 (3.81)
	p	0.22 (0.24)	0.65 (0.03)	0.23 (0.84)	0.94 (0.54)	0.94 (0.54)	2.97 (2.18)
	total	0.85 (0.80)	1.21 (0.33)	0.27 (1.80)	0.94 (0.54)	0.94 (0.54)	6.20 (5.99)
N	s	0.99 (1.18)	0.10 (0.23)	0.60 (0.02)	0.00 (0.00)	0.00 (0.00)	3.70 (3.42)
	p	0.16 (0.03)	0.04 (0.88)	1.06 (0.13)	1.06 (1.46)	1.06 (1.46)	3.39 (3.98)
	total	1.15 (1.21)	0.14 (1.11)	1.66 (0.15)	1.06 (1.46)	1.06 (1.46)	7.09 (7.40)
Orbital energies (hartrees)		-1.259 (-1.266)	-0.818 (-0.878)	-0.580 (-0.495)	-4.98 (-0.513)	-0.498 (-0.513)	

FIGURE CAPTION

Figure 1 Original Walsh diagram<sup>5</sup> for HAB molecules. The labelling of the orbitals has been changed to reflect current notation.



XBL 734- 2652

Fig. 1

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