

Theoretical Aspects of a Novel Mode of Hydrogen–Hydrogen Bonding

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Received May 19, 1995[Ⓞ]

Abstract: The nature of the newly discovered intramolecular hydrogen–hydrogen interaction in iridium complexes (Ir–H···H–N) was studied using the extended Hückel method. Consistent with experimental results, the interaction is found to be weakly attractive. Electrostatic interactions probably contribute significantly to this bonding mode. This hydrogen–hydrogen interaction might also be realized intermolecularly; restricted Hartree–Fock (RHF)/6-31G* computation yields an H···H interaction energy of 9.29 kcal/mol in FH···HLi.

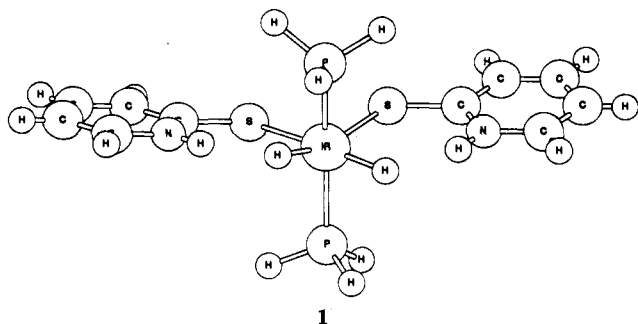
Hydrogen, the most abundant element in the universe, always seems to find new roles to play in the chemical theater. Recently, a novel intramolecular hydrogen–hydrogen interaction, exemplified by (Ir)H···H(N)^{1,2} and (Ir)H···H(O),³ was reported by the Morris and Crabtree groups. A related (N)H···H(Ir)···H(N) interaction was also found.⁴

The evidence for this new H···H interaction comes primarily from ¹H NMR experiments. The relaxation time *T*₁ for the hydrogens on N becomes relatively short as a result of the H···H interaction; furthermore, the H(N) peak increases about 10% on NOE decoupling of the hydride.¹ There is also structural evidence for a relatively close H···H contact.

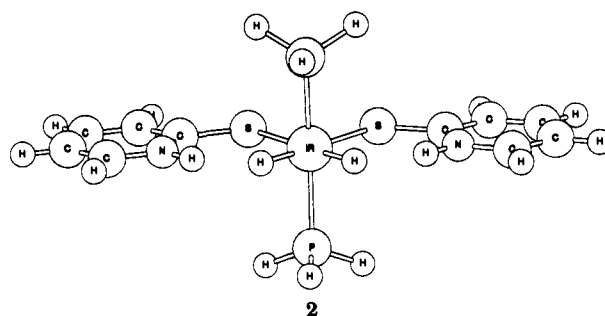
Consider the ion [Ir{H(η¹-SC₅H₄NH)(PCy₃)₂}]⁺, where Cy = cyclohexyl, synthesized by the Morris group.¹ Let us neglect the counterion, BF₄[−], for it does not appear to approach the region in which new bonding is exhibited. We count electrons first. The pyridinium thiolate [−]SC₅H₄N⁺H ligand, neutral as a whole, presumably acts as a two-electron donor to the metal. If the hydrides are assigned a formal negative charge, we have six ligands donating twelve electrons to Ir. As a result, iridium reaches a formal oxidation state of 3+ and a d⁶, 18-electron configuration. Given the unexceptional saturated Ir center, the H···H interaction is surprising, which is why we explore it here.

The Model

To simplify our calculations, we replace the PCy₃ group with the idealized PH₃ group, assuming that the basic electronic structure at the metal would not be significantly affected. We thus obtain model 1, [Ir{H(η¹-SC₅H₄NH)(PH₃)₂}]⁺. The structural details for 1, except for hydrogen atoms of course, are taken from the X-ray crystallographic data (see Appendix 1.1 for the parent compound). The two hydrides are placed 1.75 Å from the H(N) and 1.61 Å from iridium.¹ 1 is asymmetrical,



but reasonably close to a C_{2v} symmetry. In order to make the computational analysis more transparent, we go a step further, symmetrizing 1 to obtain model 2, a C_{2v} complex (see Appendix 1.2 for details).



The calculations reported here are done using the extended Hückel (EH) method⁵ and the Hartree–Fock SCF method. Please refer to Appendix 1 for details and EH parameters.

The Ir–H···H–N Interaction in [Ir{H(η¹-SC₅H₄NH)(PH₃)₂}]⁺

As a first step, we study the geometry in the (N)H···H(Ir) region. In general the EH method is not suitable for optimizing bond lengths, such as H–Ir, so we keep these constant. By changing the H–Ir–H angles in 2 symmetrically (keeping C_{2v} symmetry, H–Ir at 1.61 Å), we find that the total energy is minimized when the (N)H···H(Ir) distance is 1.75 Å and the H–Ir–H angle 85.7°.

Interestingly, one can also envisage a dihydrogen complex isomer of this molecule (which also satisfies the 18-electron rule⁶). We have computed the Walsh diagram⁷ for opening the H–Ir–H angle in 2. A dihydrogen complex (H–H 0.80 Å, H–Ir–H angle 28.8°) lies about 2.5 eV higher than 2. The main source of the destabilization is the third MO below the highest occupied molecular orbital (at the bottom of 3) of the dihydride complex, which is hydrogen–hydrogen antibonding in character. This orbital is destabilized along the reaction

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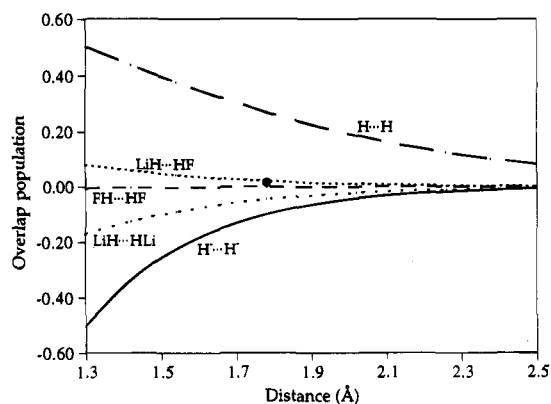
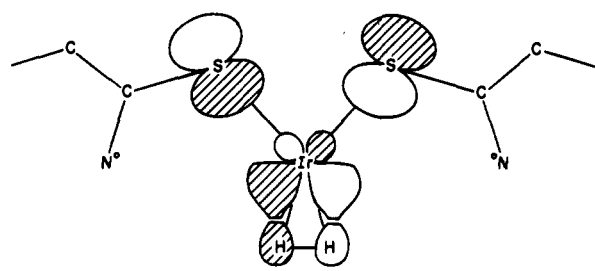


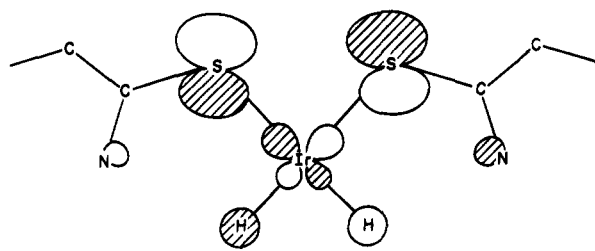
Figure 1. Mulliken overlap population vs distance for five reference systems. The calculated (N)H \cdots H(Ir) overlap population in model **2** is indicated by the filled circle.

coordinate to become the highest occupied molecular orbital (HOMO, **3**, top) in the hypothetical dihydrogen complex geometry. Interestingly, the Ir $d_{x^2-y^2}$ orbital undergoes a phase



HOMO of "dihydrogen" variant of **2**

3 (top)



HOMO-3 of dihydride model **2**

3 (bottom)

change with respect to the H 1s and S 3p orbitals (see **3**), which might be a result of an avoided crossing. The S lone pair contributions to this orbital also change their tilt.

Returning to the dihydride, molecular model **2** has a HOMO–LUMO (lowest unoccupied molecular orbital) gap of about 2 eV, indicating moderate stability. The Mulliken net atomic charges⁸ are +0.22 and –0.27 for H(N) and H(Ir), respectively. These charges are chemically intuitive, given the electronegativity of the atoms bonded to hydrogen. It appears that there should be an attractive electrostatic interaction between the two H atoms, as was suggested in the original paper.⁴ However, it is difficult to factor out explicitly such an electrostatic contribution from an MO calculation.

One indication of a stabilizing or bonding interaction is a positive Mulliken overlap population (OP).⁸ The calculated OP for (N)H \cdots H(Ir) is 0.016. This index as computed is positive, but too small to classify immediately as being of significance. Let us look at some reference calculations to put this OP into context. Two H atoms attract each other, and two H $^-$ ions repel.

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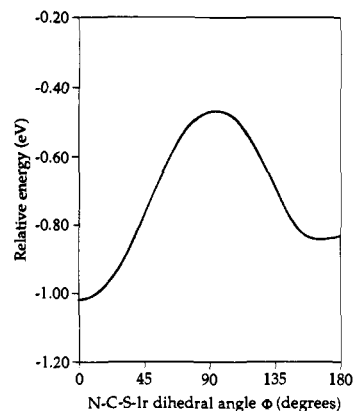


Figure 2. The potential energy surface for changing the N–C–S–Ir dihedral angle Φ . Model **2** corresponds to $\Phi = 0^\circ$.

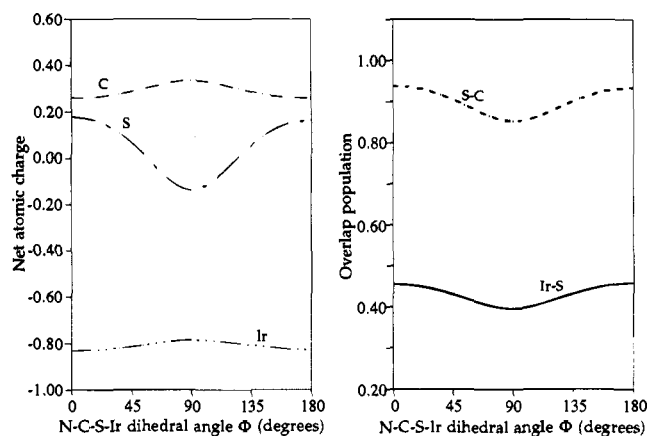


Figure 3. The variations of net atomic charges (left) and overlap populations (right) when the N–C–S–Ir dihedral angle Φ is changed.

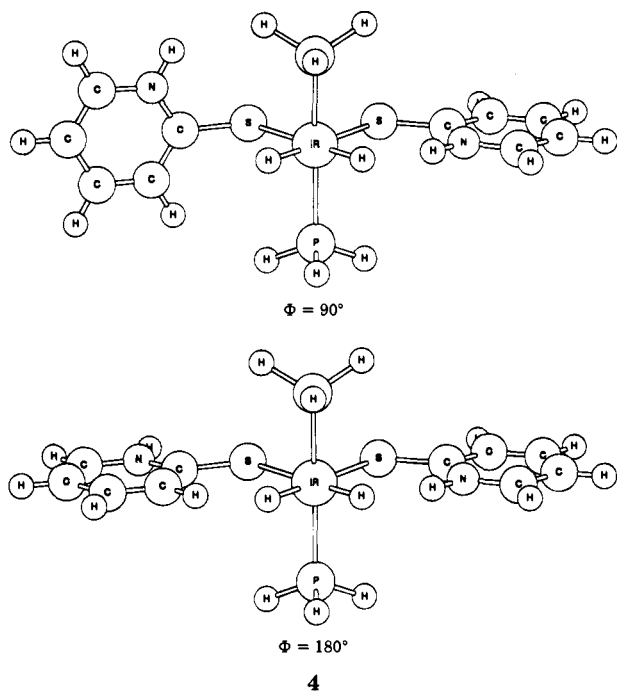
In Figure 1 we show the distance dependence of OP's for H \cdots H and H \cdots H $^-$. The OP is always positive for the former, but negative for the latter. Also shown are OP's for (Li)H \cdots H(Li), (F)H \cdots H(F), and (Li)H \cdots H(F). These are models for various extremes of polarity of interacting hydrogens. Only that of (Li)H \cdots H(F) is slightly positive, consistent with a simplistic attribution of Coulombic contribution to H \cdots H interactions. Surprisingly the (F)H \cdots H(F) OP is very small and almost independent of the distance. Comparing these, we can only say that the H \cdots H interaction in the organometallic system is very weak. It is certainly not repulsive, and matches most closely that in the model polar (Li)H \cdots H(F) system.

Another Way To Probe the New (Ir)H \cdots H(N) Bonding

One way to turn off the (N)H \cdots H(Ir) interaction, and thus study its nature, is to rotate the protonated 2-pyridinyl ring (C₅H₄NH) around the C–S or S–Ir bond. Rotation around the S–Ir bond turns out to be limited to small angles—steric repulsions between the ring and one of the hydrogen atoms in the PH₃ group are quickly turned on, even though there are no bulky cyclohexyl groups on the phosphines in **2**.

Rotation around the C–S bond also would break the H \cdots H interaction in question. The calculated potential energy surface for this torsion is shown in Figure 2. Here only one of the two C₅H₄NH rings is rotated. The N–C–S–Ir dihedral or torsion angle, Φ , is defined to be 0° for model **2**. Structure **4** shows the geometries with $\Phi = 90$ and 180°. The computations indicate that **2** ($\Phi = 0^\circ$) corresponds to the energy minimum. A barrier of 0.56 eV is computed, its high point coming at $\Phi = 90^\circ$.

Why would there be such a barrier? At $\Phi = 90^\circ$, the HOMO is most destabilized, the net atomic charge is maximal for C



and minimal for S, and the C–S and S–Ir OP's are minimized. We show these results in Figure 3. All of these findings can be rationalized by invoking a partial C–S double bond for $\Phi = 0^\circ$. The presence of such partial double bonding and the source of the barrier are explored further in Appendix 2. Here we note just that the mean experimental C–S bond length, 1.71 Å, is in between a single (1.82 Å) and a double C–S bond (1.55 Å)⁹. The C–S overlap population in model 2 is 0.937 at the experimental bond length. At the same C–S bond length the OP in a single bond model, CH₃–SH, is 0.711, while in a double bond model, [CH₂=SH]⁺, it is 1.040.

Given the high energy of the $\Phi = 90^\circ$ conformation of model 2, a preference we have assigned above as being due to C–S partial double bonding, we are forced to compare the 0° and 180° conformers to gain insight into the nature of the (N)H···H(Ir) interaction. That complicates matters a little bit, since for the 180° conformer still another interaction, now (C)H···H(Ir) (at a separation of 1.73 Å), is turned on. What we get is the relative energy of these two different interactions. An energy difference of 0.19 eV is computed, the $\Phi = 0^\circ$ conformer being more stable. The (C)H···H(Ir) interaction is weaker. Note that the torsional minimum appears a little bit shifted away from $\Phi = 180^\circ$. This is consistent with a steric repulsion also entering at this geometry, in addition to the attractive H···H interaction. The calculated (C)H···H(Ir) OP is 0.009. This is consistent with the higher polarity developed in an NH (vs CH) bond.

A recent *ab initio* Hartree–Fock SCF calculation on a related model compound, IrH₃L(PH₃)₂ (L = formamidine), gave similar computational results (such as charges on H's, small positive H···H OP's, and the interaction energy) to those reported here.¹⁰ Our analysis is slightly different and we believe complements quite well the *ab initio* results.

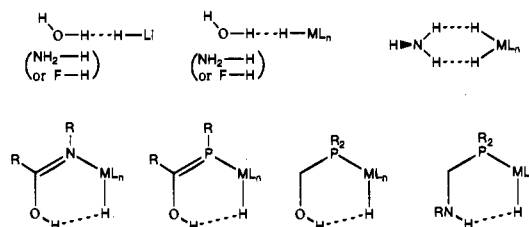
Similar calculations done on the parent asymmetrical structure 1 yielded almost the same results as for 2. Were the bulky cyclohexyl groups included in the computation, we are sure that their primary effect would be to increase the barrier of rotation around the C–S bond.

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Possible Extensions and Two Models

We conclude that the (N)H···H(Ir) interaction studied here is indeed weakly attractive. As for the classical H bond, this interaction probably has a significant electrostatic contribution.^{11–13} This ionic component is clearly enhanced by the polarity of the bonds under consideration. We also find that in the [HSC₅H₄NH]⁺ ion the H(S) atom prefers a coplanar conformation with respect to the six-membered ring, determined mainly by partial C–S double bonding. This should be true even if the H(S) is replaced by other bulky groups.

Further examples of this novel metal-assisted hydrogen–hydrogen bonding might be realized intramolecularly in other transition metal compounds and intermolecularly in the gas phase between metal hydrides and organic molecules containing H(N), H(O), or even H(P) components. We depict a few possible candidates in 5.



M = group VIA, VIIA, VIIIA transition metals with an unspecified ligand set.

5

To test these ideas, we studied two models, FH···HLi and FH···HMn(CO)₅. We carried out computations on the FH···HLi complex using the restricted Hartree–Fock (RHF)¹⁴ method with 6-31G*¹⁵ basis set (see Appendix 1.4). The optimized structure has an H···H distance of 1.658 Å, with C_s symmetry. The optimized bond angles are nearly linear, 162.8° for Li–H···H and 179.6° for F–H···H. Without basis set superposition error (BSSE) correction,¹⁶ the energy by which the complex is stabilized relative to separated molecules is 9.29 kcal/mol. If we calculate an approximation to the electrostatic contribution using Mulliken atomic charges, it comes to 6.65 kcal/mol. For comparison, the stabilization of the complex HF···HF is computed to be 5.64 kcal/mol using the same method. (We found that the Møller–Plesset theory to second order (MP2)¹⁷ fails to give a reasonable geometry for HF···HF, so we did not apply it to the FH···HLi system.)

There is quite strong interaction between F and Li in HF···LiF, LiF···LiLi, and LiF···LiF.¹⁸ Calculations on HF···LiH complex with C_s symmetry at the HF-STO level have been reported.¹⁹ However, our RHF/6-31G* optimization on HF···LiH does not yield such a C_s complex, but a weakly bound H₂···FLi complex instead. This indicates kinetic instability for the HF/LiH system. Thermodynamically, this system is also unstable. The calculated and experimental energy of hydrogenation of

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Table 1. Parameters Used in Extended Hückel Calculations

atom	orbital	H_{ii} (eV)	ζ_{i1}	c_1	ζ_{i2}	c_2
H	1s	-13.6	1.30			
C	2s	-21.4	1.625			
	2p	-11.4	1.625			
F	2s	-40.0	2.425			
	2p	-18.1	2.425			
Li	2s	-5.4	0.65			
	2p	-3.5	0.65			
N	2s	-26.0	1.95			
	2p	-13.4	1.95			
P	3s	-18.6	1.75			
	3p	-14.0	1.30			
S	3s	-20.0	2.122			
	3p	-11.0	1.827			
Ir	6s	-11.36	2.50			
	6p	-4.50	2.20			
	5d	-12.17	5.796	0.6698	2.557	0.5860

LiF, i.e., $\text{LiF} + \text{H}_2 \rightarrow \text{LiH} + \text{HF}$, is about 50 kcal/mol.²⁰ Thus, it might be difficult to observe this predicted strong H...H interaction in HF/LiH.

Calculations have been done on $\text{H}_3\text{N}\cdots\text{LiH}$ and $\text{H}_2\text{O}\cdots\text{LiH}$,^{19,21} but again the focus in these studies was on N...Li and O...Li interactions. Based on our calculation on $\text{FH}\cdots\text{HLi}$, we believe strong H...H interaction would also exist in these two systems. It might be possible to see this interaction in gas phase NH_3/LiH and $\text{H}_2\text{O}/\text{LiH}$ systems.

We also carried out calculations on another model, $\text{FH}\cdots\text{HMn}(\text{CO})_5$. Using RHF/3-21G(*)^{22,23} calculations (with a C_s symmetry constraint), we found a minimum at an H...H distance of 1.683 Å, stabilized by 6.55 kcal/mol relative to separated molecules. Both the F-H and the H-Mn bonds are elongated a little upon complexation (F-H goes from 0.938 (optimized in HF) to 0.943 Å, H-Mn from 1.738 (optimized in $\text{HMn}(\text{CO})_5$) to 1.754 Å). Here the H...H interaction is not as strong as in $\text{FH}\cdots\text{HLi}$, but it is still within the range of classical H-bonding strengths.²⁴ With higher level computations and geometry optimizations, a larger stabilization might result.

To summarize, two hydrogen atoms may interact weakly, but significantly, if one is bonded to an electropositive element (donor), and the other to a very electronegative element (acceptor). This is not the only contribution to attractive H...H interactions, but it seems to be an important component.

Acknowledgment. Hugh Genin made critical comments on our manuscript. Norman Goldberg also gave us helpful remarks. We are grateful to the National Science Foundation for supporting this work through Research Grant CHE-9408455, and through the NSF-MRL program under Award No. DMR-9121654 to the Materials Science Center at Cornell.

Appendix 1

1. The crystallographic coordinates of the molecule studied were obtained via ACS's Gopher service. The two hydrides are placed 1.75 Å from the H(N) and 1.61 Å from iridium.¹

2. Experimental S-Ir-S and P-Ir-P angles are used. The distances are chosen as 1.09 Å for C-H, 1.01 Å for N-H, and

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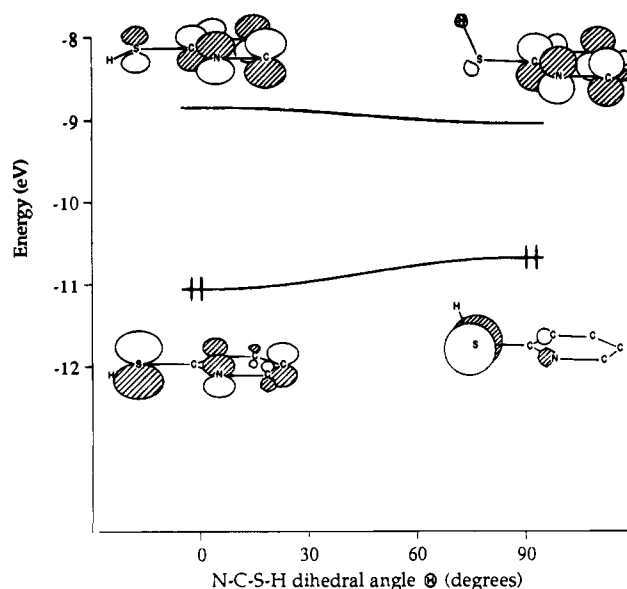


Figure 4. Walsh diagram for the HOMO and LUMO of the $[\text{HSC}_5\text{H}_4\text{NH}]^+$ ion. Hydrogen atoms on the C_5N ring are omitted for clarity.

1.44 Å for P-H.⁹ The Ir-P-H angle used is 110°. Mean experimental values (see 1) are used for all the other bond lengths and angles.

3. Table 1 shows the extended Hückel parameters used in our calculations. For H, C, F, Li, N, P, S, and Ir, values are taken from earlier work.^{5,25-28} The CACAO program²⁹ was used to draw some of the orbitals.

4. Ab initio calculations were carried out on an IBM RISC System/6000 (donated by IBM) using the Spartan code (versions 3.0 and 3.1) provided generously by WaveFunction, Inc. In all cases singlet ground states were assumed.

Appendix 2: C-S Partial Multiple Bonding in $[\text{HSC}_5\text{H}_4\text{NH}]^+$

To understand the origin of the computed barrier better, we go back to a simpler model, the protonated 2-pyridinethiol ion, $[\text{HSC}_5\text{H}_4\text{NH}]^+$. The H-S distance is set at 1.34 Å,³⁰ while the rest of the geometry of this ion is taken from model 2. A rotation around the C-S bond encounters, again, a substantial barrier of 0.70 eV at the N-C-S-H dihedral angle $\Phi = 90^\circ$. We observe exactly parallel trends for the C-S OP and net atomic charges on C and S for this simpler model as for 2. The 0° and 180° conformations have almost the same energy. In an X-ray structural study of methoxyphenyls not substituted at the *ortho* positions, the analogous methoxy group was found to prefer a coplanar conformation with respect to the phenyl ring.³¹ Microwave spectra of anisole (methoxybenzene) also indicated a similar coplanar conformation.³² Both calculation and experiment yield a planar conformation for thiophenol, $\text{C}_6\text{H}_5\text{SH}$.³³

In Figure 4, we depict the HOMO's and LUMO's for the $\Phi = 0^\circ$ and 90° conformations of the $[\text{HSC}_5\text{H}_4\text{NH}]^+$ ion and the way their energies vary with rotation, a Walsh diagram.⁷ The energy destabilization due to the two electrons in the HOMO alone is 0.75 eV. 6 are schematic drawings indicating relative phases and contributions of the atomic p orbitals for the $\Phi =$

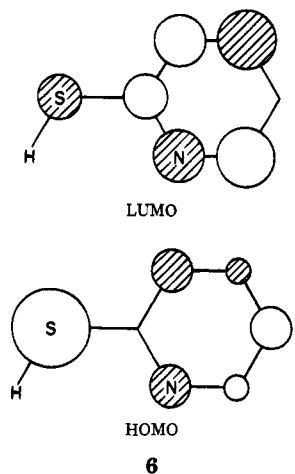
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0° conformation. The HOMO is mainly the S 3p π -type lone pair. The LUMO is an out-phase combination of the S 3p and

a benzene-like LUMO, perturbed asymmetrically by SH and N substitution. Note the resemblance of the HOMO to that of the isoelectronic benzyl anion.

There is some partial double bonding character between C and S in the planar geometry, stabilizing this conformation, as the OP's indicate. Accompanying it, some electrons are transferred away from the S lone pairs. This effect is almost totally lost for the $\Theta = 90^\circ$ conformer. The trends for the C-S OP and charges on C and S are consistent with this picture. Thus in $[\text{HSC}_5\text{H}_4\text{NH}]^+$, the hydrogen bonded to S prefers to be in the plane defined by the six-membered C_5N ring.

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