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The Anti-Hydrogen Bond in Aromatic *N*-Sulfinylamines with Ortho H Atoms[†]

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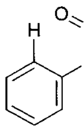
Calculated geometries are presented for five aromatic *N*-sulfinylamines, R−N═S═O. All carry at least one hydrogen atom on the aromatic ring ortho to the NSO substituent, and all show a preference for a planar isomer in which the substituent's oxygen atom is oriented toward an ortho hydrogen. All these isomers exhibit a shortening of the corresponding C−H bond. Using the quantum theory of atoms in molecules (AIM), it can be shown that a C−H···O bonding interaction exists that meets all the characteristics of an anti-hydrogen bond.

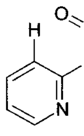
Introduction

N-sulfinylamines, R−N═S═O, have been known over a century now, as the first syntheses can be traced back to Michaelis in the early 1890's.[1] These compounds have drawn particular interest because of their geometry: the heterocumulene unit is not linear, and so syn and anti configurations are possible.[2] In 1975 it was shown that the small sulfinylamine CH_3−NSO is syn-configured.[3] And even though in 1989 the aromatic *N*-sulfinyl-*p*-bromoaniline was also shown to be syn-configured,[4] there was a controversy about *N*-sulfinylaniline (**1**). The finally accepted opinion that **1** also should be syn[5,6] was confirmed only last year in an X-ray diffraction experiment by Romano, Védova, and Boese.[7] A paper followed that contained a comparison between observed experimental and computed geometrical parameters of **1**.[8] At the levels of theory employed (reported were HF, MP2, Becke3LYP, and Becke3PW91 methods with the 6-31+G(d) basis set), there was a satisfactory agreement for bond lengths and angles with the exception of S═O (1.4584(10) Å) and N═S (1.5160(11) Å) bonds. HF underestimated these distances (1.4446 and 1.4917 Å, respectively), whereas the electron correlated methods showed a serious overestimation (1.49−1.50 and 1.54−1.56 Å, respectively). It was suggested that larger basis sets should show an improved performance.[8]

While many distances were included in the comparison, the O−H distance that results from a syn configuration of the NSO group in the planar molecule was not mentioned, which is understandable in light of the missing experimental data.[9] Yet an inclusion of the calculated distance would have been useful as even a simple model of the planar syn-configured **1** illustrates the proximity of O and ortho H atoms and therefore warrants the investigation of a possible interaction. Such a C−H···O interaction can be identified and characterized with the help of the quantum theory of "atoms in molecules" (AIM).[10,11] Performing AIM analyses at different levels of theory also helps in identifying the "adequate" theoretical level for the description of the system studied. It was our interest in weak bonding interactions that prompted the following study. Unsubstituted **1** and its 2-pyridyl (**2**) and 2-halo substituted (**3**) analogues are presented in terms of their preferred geometries and—for the first time—their underlying molecular structures (probed with AIM at different levels of theory). **2** and **3a**−**c** were chosen in order to modify **1** but leave one ortho hydrogen atom on the aromatic ring for a possible C−H···O interaction.



1



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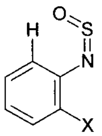

3

a X = F
b X = Cl
c X = Br

Computational Details

Geometry optimizations were carried out with Gaussian 94[12] or Gaussian 98[13] on CRAY T90 and Origin 2000, and SGI R10000 Impact computers. The molecules were optimized without constraints, and frequency calculations (performed on the Becke3LYP/6-31+G(d) geometries at the same level) showed all planar syn species reported here to be minima. That these species are minima at the higher levels also was evident from a torsional analysis (rotation of the C═C−N═S dihedral angle) performed at those levels. Wavefunctions were obtained at all levels of theory for the topological analyses.

The studies of the electronic charge density ρ and the integrations were carried out with the AIMPAC[14] series of programs.[15] In the plots of ρ, a solid cross indicates the position of a nucleus in the plane, a dot the position of a bond critical point (cp_b), and a triangle the position of a ring critical point (cp_r). Plotted are 20 contour lines between 0.001 and 40.0 au.

Various levels of theory were used for the geometry optimization of **1** in an attempt to reproduce its observed (X-ray)[7] geometry. While it is necessary to employ a large basis set, Dunning's cc-PVTZ,[16] with Becke3LYP or Becke3PW91 in order to achieve this, for the analysis of the charge density of **1** wavefunctions from as low a level as Becke3LYP/6-31+G(d) can be used (see below).

Results and Discussion

Geometries. While for **1** the two possible syn conformers are degenerate, **2** and **3a**−**c** only have one conformer each as a candidate for a C−H···O interaction. Only these isomers are considered here, their total energies are given in Table 1. An analysis of the full set of isomers will follow as part of a more extensive study.[17]

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TABLE 1: Total Energies (au) of *N*-Sulfinylamines 1 to 3a−c[a]

	B3LYP/6-31+G(d)
1[b]	−759.782232 (0.099875)
2	−775.817867 (0.088023)
3a	−859.019662 (0.091677)
3b	−1219.373389 (0.090229)
3c	−3330.906987 (0.091044)

[a] Zero-point vibrational energies are given in parentheses. [b] Total energy at other levels of theory: Becke3PW91/6-31+G(d) −759.588121, MP2(full)/6-31+G(d) −758.198934, Becke3LYP/6-311+G(d,p) −759.890310, Becke3LYP/cc-PVTZ −759.944071, Becke3PW91/cc-PVTZ −759.746005.

N-Sulfinylaniline (1). The experimental geometry from X-ray diffraction,[7] a planar, syn configured species, has been reported and compared to data from Becke3LYP/6-31+G(d), Becke3PW91/6-31+G(d), and MP2/6-31+G(d) calculations.[8] C−C and C−N distances as well as all available angles showed a reasonable correlation between experiment and calculation; for N═S and S═O distances this was not the case. For the benefit of the reader, selected distances and bond angles from experiment and above-mentioned 6-31+G(d) level calculations are given in Table 2. Instead of the MP2/6-31+G(d) data listed in ref 8 (the correlation calculation was not specified further) MP2(full)/6-31+G(d) data are given in the table. We have employed higher levels of theory to reproduce N═S and S═O distances. While Becke3LYP/6-311+G(d,p) shows no improvement in terms of these distances, both Becke3LYP/cc-PVTZ and Becke3PW91/cc-PVTZ do. The data are also listed in Table 2. As we were comparing a solid-state geometry to one in the gas phase, we concluded the search for a better agreement at that point.

The distances that are more important to the question of a possible C−H···O interaction—the O···H distance to the closest H, the O···C distance to the closest C (i.e., C2), and the C−H distances of the two ortho hydrogen atoms—are reported in Table 3 for those levels of theory that are used in the later analysis of the charge density. While the O···H distance is often missing from X-ray diffraction data of a C−H···O system,[9] O···C is always available, and as Desiraju has shown, it can be indicative of a weak interaction: O···C distances in a large variety of carbon acids with a C−H···O interaction lie between 3.00 and 4.00 Å.[18] Table 3 shows that the calculated value for O···C in *syn*-**1** is within that range at all levels of theory and compares well to the experimental distance of 305.8 pm (this quantity is taken from the reported parameters and was not part of ref 7). The O···C distances are accompanied by reasonable O···H distances that are consistent across the basis sets given in Table 3.

The ortho hydrogen atom involved in a possible interaction is referred to here as H_O. As can be seen from Table 3, the C−H_O distance is consistently shorter than the C−H distance. To determine which represents the normal, uninfluenced distance, the NSO substituent was rotated out of plane into the 90° position, where the two ortho hydrogens are equivalent. The transition state for this rotation, which resembles the 90° geometry, was located; it is labeled TS *syn*-**1** in Table 3 where its total energy is given.[19] C−H_O lengthens upon rotation of the NSO group until the C−H value is reached in the transition state. So C−H in the planar *syn*-**1** can be taken as uninfluenced by the oxygen. We will return to this in the analysis of the charge density. The difference between the two ortho C−H bonds is also apparent in the vibrational analysis. As expected from the distances, the calculated frequency of the stretching vibration is 3219.6 cm^{-1} for C−H (the normal mode is mostly due to the stretch of this bond with small contributions from meta and para C−H bonds) and 3245.6 cm^{-1} for C−H_O (there are no contributions from other bonds in the normal mode), and so the shorter C−H_O bond shows a blue shift of 26 cm^{-1} (Becke3LYP/6-31+G(d)).[20]

*N-Sulfinyl-2-pyridine (**2**) and 2-Halo-Substituted N-Sulfinylanilines (**3a−c**).* As for the parent compound **1**, the most stable isomer of **2** and **3a−c** prefers the syn over the anti configuration, is planar, and has the substituent's oxygen atom pointing toward the one ortho hydrogen atom. Experimental geometries of **2** and **3a−c** are not available, yet all computed geometries for these species are remarkably similar to that of **1**. The relevant distances and angles for **2** and **3a−c** are given in Table 4. As in **1**, O···C and O···H distances suggest a possible C−H···O interaction. C−H_O is the same for all species **1** to **3a−c**. To determine whether the C−H_O distance in **2** and **3a−c** exhibits a similar shortening as was observed for **1**, the NSO substituent was rotated again. Just as C−H in **1** was shown to be "uninfluenced", when the oxygen is pointing at the pyridine N in **2** and the halogen in **3a−c** (the other stable rotamer of **2** and **3a−c**) C−H is uninfluenced by the oxygen. These C−H distances are also given in Table 4 and, as for **1**, they are longer than those of C−H_O.

Molecular Structures. The theory of "atoms in molecules" (AIM) allows one to identify and characterize bonding interactions between atoms through an analysis of the charge density ρ.[10] In AIM, an interaction between two atoms is evident through a line of maximum density linking the two nuclei, called an atomic interaction line. For an equilibrium geometry where there are no forces acting on the nuclei, this line is termed a bond path and indicates a bonding interaction.[23] The curvature along the bond path is positive and at its minimum lies the bond critical point cp_b. If the weak bonding interaction involves a hydrogen atom, we usually term it a hydrogen bond. On the basis of numerous AIM studies of conventional hydrogen bonds (a hydrogen is shared by two electronegative atoms) and their characteristics in the charge density,[24−29] Koch and Popelier have established a set of criteria (composed of local properties of ρ at the cp_b of the interaction and integrated properties for the H atom) through which hydrogen bonding can be confirmed in C−H···O systems (yet not restricted to these).[11] In such a system, one finds (a) a bond critical point cp_b and the associated bond path between H and O atoms, (b) a value of ρ at the cp_b within a certain low range, (c) a positive value for the Laplacian of the charge density $\nabla^2\rho$ at the cp_b, (d) a mutual penetration of H and O atoms, (e) a loss of electronic charge on H_O as compared to the uninfluenced H, (f) an energetic destabilization of H_O, (g) a decrease in the dipolar polarization of H_O, and (h) a decrease in the volume of H_O (although there seems to be one exception to this).[11] Subsequently, Popelier has shown that these criteria are also applicable to the dihydrogen bond (a hydrogen is donated to another H atom).[30]

Finally, when in a C−H···O system all of the criteria for a hydrogen bond apply but the C−H bond is shortened (with a corresponding blue shift of the C−H stretching frequency),[31] the interaction has been termed an "anti-hydrogen bond" by Hobza et al.[32,33] Hobza and co-workers recently also provided experimental evidence for such an anti-hydrogen bond.[34] As predicted by calculations, they were able to show a blue shift of the aliphatic C−H stretching frequency in the chloroform-fluorobenzene complex by double-resonance infrared ion-depletion (IR−R2PI) spectroscopy. The remainder of this chapter is dedicated to the discussion of the above criteria for **1** to **3a−c**.

TABLE 2: Selected Geometrical Parameters (Distances in pm, Bond Angles in degrees) of *syn-N*-Sulfinylaniline (1)

		6-31+G(d)			6-311+G(d,p)	cc-PVTZ	
	exp[7,a]	B3LYP[8,a]	B3PW91[8,a]	MP2(full)	B3LYP	B3LYP	B3PW91
S=O	145.8	149.8	149.1	149.8	149.1	147.9	147.5
N=S	151.6	154.8	154.2	155.9	154.3	153.5	153.0
C1−N	140.1	139.4	139.0	140.6	139.3	139.1	138.8
C1−C2	140.6	141.5	141.1	140.9	141.1	140.6	140.4
C1−C6	140.2	141.1	140.9	140.6	140.8	140.4	140.1
NSO	120.6	119.8	120.0	121.1	119.7	120.0	120.2
C1NS	131.2	131.8	131.8	129.8	131.8	132.1	132.1
C2C1N	124.2	124.8	124.8	124.9	124.8	124.7	124.7
C6C1N	116.0	115.6	115.6	115.0	115.7	115.9	115.9
C6C1C2	119.8	119.5	119.6	120.1	119.5	119.4	119.5

[a] Distances in the original paper were reported in Å. Both distances and angles in this table were reduced in precision for ease of comparison.

TABLE 3: O···H and O···C Distances of *syn*-1, and Both Ortho C−H Distances (pm) of *syn*-1 and of the Transition State for C=C−N=S Rotation of *syn*-1, TS *syn*-1

		B3LYP		
		6-31+G(d)	6-311+G(d,p)	cc-PVTZ
syn-**1**	O···H	233.7	233.0	233.9
	O···C	310.0	309.1	309.8
	C−H$_O$[a]	108.3	108.1	107.8
	C−H	108.6	108.3	108.1
TS *syn*-**1**	C−H	108.6[b]	*c*	108.1[d]

[a] Hydrogen atom closer to oxygen. [b] Total energy −759.771810 au. [c] Transition state was not determined. [d] Total energy −759.935329 au.

TABLE 4: Selected Geometrical Parameters (Distances in pm, Bond Angles in degrees) of 2 and 3a−c at Becke3LYP/6-31+G(d)

	2	3a	3b	3c
O···H	230.3	233.1	231.2	230.3
O···C	307.2	309.9	309.5	308.9
C−H$_O$[a]	108.3	108.3	108.3	108.3
C−H[b]	108.5	108.6	108.6	108.5
S=O	149.6	149.7	149.7	149.7
N=S	154.3	154.7	154.7	154.6
C1−N	139.9	138.5	138.5	138.5
NSO	120.1	119.6	119.8	119.8
C1NS	131.4	131.4	132.2	132.2

[a] Hydrogen atom involved in a possible interaction. [b] Oxygen atom rotated away from H in another conformer.

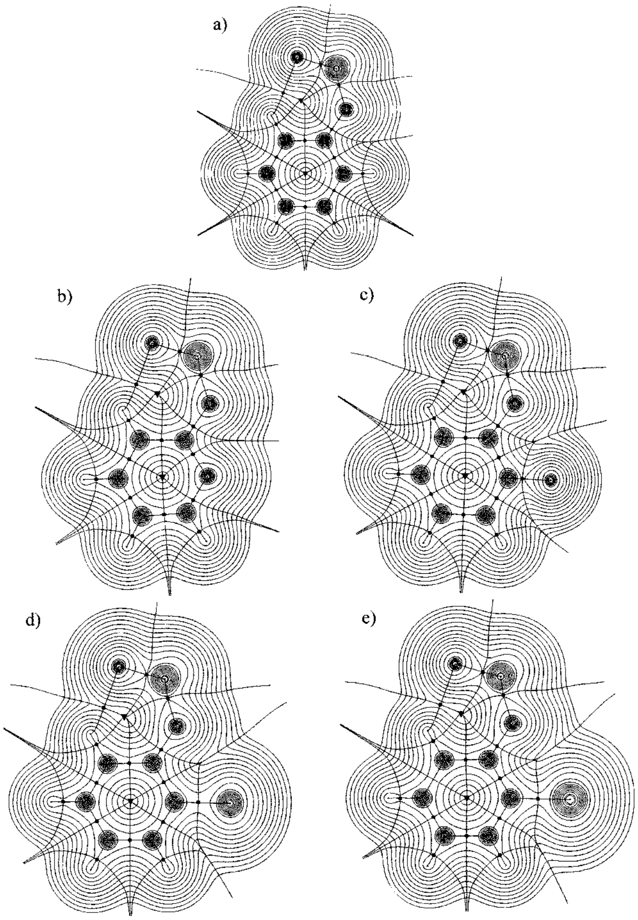

Figure 1. Contour plots of the charge density of (a) **1**, (b) **2**, (c) **3a**, (d) **3b**, and (e) **3c** at Becke3LYP/6-31+G(d). Molecular graphs and interatomic surfaces are superposed. Bond critical points are given as black dots, ring critical points as triangles.

N-Sulfinylaniline (1). A contour plot of the charge density of **1**, overlaid with the molecular graph (the network of bond paths) and the interatomic surfaces, is shown in Figure 1a (Becke3LYP/6-31+G(d)). The plot from this "cheap" level of theory compares very well with those from Becke3LYP/6-311+G(d,p), which includes polarization functions on hydrogen atoms (usually deemed important for weak interactions involving hydrogen atoms), and Becke3LYP/cc-PVTZ, which describes best the observed experimental geometry (plots not given); in fact, the three are almost identical. MP2 and Becke3PW91 results are not part of the following discussion: all the data are very close to those presented here and lead to the same conclusions. From the appearance of the charge density plots, Becke3LYP/6-31+G(d) delivers a wavefunction that is adequate for the description of **1**; this is supported by comparisons of the numerical data given in the following paragraphs. With the network of bond paths, Figure 1a illustrates nicely, and for the first time, the molecular structure of **1**. Besides all of the "expected" bonding interactions (where the usual bonds are drawn), the charge density reveals the additional bonding interaction, C−H···O. This interaction leads to the bicyclic structure with its two ring critical points (cp_r).

With about 230 pm, the O···H distance is fairly large, and so the absolute value of ρ (about 0.09 e·Å^{-3}) at the cp_b is found to be relatively small. Yet compared to other values of ρ in C−H···O systems, which lie between 0.026 and 0.138 e·Å^{-3},[11] ρ in **1** is found among the stronger weak interactions. Also in accord with a large distance is the positive value of $\nabla^2\rho$, indicating the closed-shell interaction, and the nonzero ellipticity ϵ.[35] The data are given in Table 5 for the three levels of theory and the comparison shows that Becke3LYP/6-31+G(d) values are very close to those obtained with the larger basis sets. The short distance between cp_b and cp_r of the weak interaction that is apparent from Figure 1a (it is given in Table 5) leads to a charge density at cp_r that is only slightly smaller than that at cp_b and to very similar values for $\nabla^2\rho$, well-known features for this kind of ring formation.[10,11,33,36] Also illustrated in Figure 1a is the mutual penetration of O and H atoms involved in the C−H···O interaction. The outer contour line represents 0.001

TABLE 5: Critical Point Data (Becke3LYP/6-31+G(d), ρ in e·Å^{-3}, $\nabla^2\rho$ in e·Å^{-5}) for Bond and Ring Critical Points Formed upon C−H···O Interaction in 1 to 3a−c[a]

	cp_b			cp_r		
	ρ	$\nabla^2\rho$	ϵ	ρ	$\nabla^2\rho$	$cp_b \cdots cp_r$
1	0.091	1.16	0.08	0.063	1.16	69.7
b	0.092	1.14	0.09	0.067	1.14	66.5
c	0.087	1.25	0.23	0.069	1.21	60.4
2	0.098	1.23	0.07	0.066	1.21	70.8
3a	0.092	1.17	0.08	0.063	1.16	69.3
3b	0.096	1.20	0.07	0.065	1.20	69.8
3c	0.097	1.22	0.07	0.066	1.21	70.1

[a] The distance (pm) between cp_b and cp_r is also included. [b] At B3LYP/6-311+G(d,p). [c] At B3LYP/cc-PVTZ.

TABLE 6: Integrated Atomic Properties[a] **(au) of H and H_O in 1 to 3a−c and Their Change upon Interaction (Becke3LYP/6-31+G(d))**

		N	*E*	*M*	*V*[b]
1	H	0.925	−0.585945	0.152	45.38
	H_O[c]	0.888	−0.577324	0.129	39.21
	Δ	−0.037	+0.008621	−0.023	−6.17
d	H	0.948	−0.602159	0.138	47.53
	H_O[c]	0.912	−0.593842	0.115	40.91
	Δ	−0.036	+0.008317	−0.023	−6.62
e	H	0.956	−0.609876	0.139	47.27
	H_O[c]	0.921	−0.602162	0.119	41.26
	Δ	−0.035	+0.007714	−0.020	−6.01
2	H[f]	0.916	−0.582061	0.150	44.97
	H_O[c]	0.879	−0.573187	0.128	39.53
	Δ	−0.037	+0.008874	−0.022	−5.44
3a	H[f]	0.922	−0.585012	0.151	45.22
	H_O[c]	0.882	−0.574705	0.128	38.85
	Δ	−0.040	+0.010307	−0.023	−6.37
3b	H[f]	0.924	−0.585535	0.151	45.29
	H_O[c]	0.882	−0.574559	0.127	38.53
	Δ	−0.042	+0.010976	−0.024	−6.76
3c	H[f]	0.924	−0.586293	0.150	45.23
	H_O[c]	0.881	−0.574893	0.127	38.45
	Δ	−0.043	+0.011397	−0.023	−6.78

[a] Symbols are explained in the text. [b] For the 0.001 au contour. [c] Hydrogen atom involved in a possible interaction. [d] At B3LYP/6-311+G(d,p). [e] At B3LYP/cc-PVTZ. [f] Oxygen atom rotated away from H in another conformer.

TABLE 7: Bond Critical Point Data (Becke3LYP/6-31+G(d), ρ and $\Delta\rho$ in e·Å^{-3}, $\nabla^2\rho$ in e·Å^{-5}) for the Ortho C−H Bond(s) and Distances (pm) from the cp_b to the C and H Nuclei in 1 to 3a−c

		ρ	$\nabla^2\rho$	ϵ	$cp_b \cdots C$	$cp_b \cdots H$
1	C−H	1.884	−24.00	0.01	70.3	38.3
	C−H_O[a]	1.906	−24.92	0.01	70.9	37.4[b]
	Δ	0.022			+0.6	−0.9
c	C−H	1.914	−23.70	0.02	69.8	38.4
	C−H_O[a]	1.937	−24.32	0.02	70.3	37.7[b]
	Δ	0.023			+0.5	−0.7
d	C−H	1.996	−28.68	0.01	69.5	38.6
	C−H_O[a]	2.022	−29.38	0.01	70.0	37.8[b]
	Δ	0.026			+0.5	−0.8
2	C−H[e]	1.886	−24.12	0.01	70.3	38.1
	C−H_O[a]	1.905	−24.99	0.01	71.0	37.2[b]
	Δ	0.019			+0.7	−0.9
3a	C−H[e]	1.883	−23.98	0.01	70.3	38.3
	C−H_O[a]	1.908	−25.06	0.01	71.0	37.3[b]
	Δ	0.025			+0.7	−1.0
3b	C−H[e]	1.883	−23.93	0.02	70.2	38.3
	C−H_O[a]	1.908	−25.06	0.01	71.0	37.3[b]
	Δ	0.025			+0.8	−1.0
3c	C−H[e]	1.883	−23.92	0.02	70.2	38.3
	C−H_O[a]	1.908	−25.06	0.01	71.0	37.3[b]
	Δ	0.025			+0.8	−1.0

[a] Hydrogen atom involved in a possible interaction. [b] Distance to H_O. [c] At B3LYP/6-311+G(d,p). [d] At B3LYP/cc-PVTZ. [e] Oxygen atom rotated away from H in another conformer.

au and an atom's nonbonded radius is based on it, whereas the bonded radius is taken to the cp_b.[11] The penetration is determined as the difference between the two radii. In Figure 1a, the penetration of H is estimated to be about 40 pm (radii: 134 pm nonbonded, 94 pm bonded), and that of O 39 pm (radii: 179 pm nonbonded, 140 pm bonded), values not unlike those observed in intermolecular C−H···O interactions.[11] Because of the intramolecular interaction in **1** it is difficult to get accurate nonbonded radii (the quantities stated above were taken from the transition state, TS *syn*-**1**), and therefore the mutual penetration remains an estimate. The bonded radii are very similar at all levels of theory (around 94 pm for H and 140 pm for O), and so the values given should be valid for the higher levels of theory as well.

The values for the integrated properties of the undisturbed H atom (H) and the interacting H atom (H_O) are given in Table 6 along with their differences (Δ). First we notice that indeed all remaining criteria are fulfilled. We find that the electronic population (*N*) of H is reduced upon interaction; the hydrogen atom is destabilized as demonstrated through its higher total energy (*E*) when interacting; the interacting hydrogen suffers a reduction in dipolar polarization (*M*); and H_O is smaller in volume (*V*) than H. While it is understood that the absolute values of *N*, *E*, *M*, and *V* differ at the various levels of theory, there is a good agreement in all relative values Δ, which again qualifies Becke3LYP/6-31+G(d) for the description of **1**. All Δ figures in Table 6 compare rather favorably with C−H···O data of the benzene−formaldehyde complex (Δ*N* −0.035, Δ*E* 0.0136, Δ*M* −0.013, Δ*V* −13.03 au),[11] maybe with the exception of Δ*V*, which is smaller in **1**. This smaller Δ*V* results primarily from an already smaller uninfluenced volume of H in **1** due to the nitrogen substituent in the ortho position.

Finally for **1**, Table 7 gives the bond critical point data for the undisturbed C−H and the interacting C−H_O bond. Also listed are the distances from the cp_b's to their respective C and H nuclei. As expected, the shortening of the C−H distance upon interaction is accompanied by an increase in ρ at the cp_b and a more negative $\nabla^2\rho$. All three levels of theory agree on the change in ρ as well as on the change in distance from cp_b to C and H nuclei. Again, the calculated changes compare well to those found earlier in benzene: in the benzene−benzene C−H···π anti-hydrogen bond, $\Delta\rho$(C−H) is 0.031 e·Å^{-3}, $\Delta(cp_b \cdots C)$ +0.5 pm, and $\Delta(cp_b \cdots H)$ −0.9 pm.[33] Even though **1**, benzene−formaldehyde, and benzene−benzene represent only three cases to judge from, the data seem to suggest that the nature of the anti-hydrogen bond acceptor (oxygen atom or C=C double bond) is only of minor importance to the interacting H atom. This is in accord with a previous comment by Desiraju on the effect of O atom basicity on the C−H···O distance, which was, even though detectable, "far less noticeable than that of C−H group acidity".[18] As has been commented on before,[33] the bond critical point moves away from C toward H upon interaction, leading to an increased $cp_b \cdots C$ and a decreased $cp_b \cdots H$, but these trends do not cancel out. Table 7 shows that $\Delta(cp_b \cdots H)$ is more pronounced, which results in an overall shortening of the C−H bond as it becomes involved in the C−H···O interaction.

The preceding paragraphs have shown that there is indeed a C−H···O interaction in **1** and that it has the characteristics of an anti-hydrogen bond.

*N-Sulfinyl-2-pyridine (**2**) and 2-Halo-Substituted N-Sulfinylanilines (**3a**−**c**).* Due to the demonstrated good performance of

Becke3LYP/6-31+G(d), **2** and **3a**−**c** were only studied at this level. The above analysis of **1** was repeated for **2** and **3a**−**c** to check whether the replacement of one ortho C−H bond by a nitrogen atom or a C−halogen bond has an influence on the anti-H bond. All critical point and integrated data are reported in Tables 5−7. Figures 1b−e show contour plots of ρ for the four species with their molecular graphs and interatomic surfaces, and it is clear from a comparison with Figure 1a that **1** to **3a**−**c** show a similar C−H···O interaction. This finds support in the numerical data in that not only all trends (increases or decreases) are recovered correctly, but also all quantities for **1** are very close to those for **2** and **3a**−**c** (given in Tables 5−7). The differences that are observed (e.g., ρ at cp_b of the anti-H bond is largest in **2** (0.098 $e{\cdot}Å^{-3}$) and smallest in **3a** (0.092 $e{\cdot}Å^{-3}$)) seem to be too small to be discussed. And so, as for **1**, there is an intramolecular anti-hydrogen bond in each species **2** and **3a**−**c**, between oxygen and ortho hydrogen atoms. Changing the other ortho position on the aromatic ring does not influence the anti-H bond markedly.

The anti-hydrogen bond in the intermolecular complex between chloroform and fluorobenzene has been attributed to an increase in dispersive attraction,[34] whereas it seems to be due to electrostatic interaction in the complex between fluoroform and oxirane.[37] The above discussion has led to the identification of an intramolecular anti-hydrogen bond in the aromatic *N*-sulfinylamines **1** to **3a**−**c**. While we have given a characterization of this interaction, we still have to establish its origin.

Conclusion

The calculated charge densities of the preferred planar geometries of five aromatic *N*-sulfinylamines have been analyzed with the theory of "atoms in molecules". In each case, the analyses have revealed an ortho hydrogen atom involved in an intramolecular C−H···O interaction that exhibits all the characteristics of a hydrogen bond except for one. The C−H bond gets shorter upon interaction by about 0.3 pm with the consequence of a calculated blue shift of its stretching frequency of 26 cm^{-1}. Such an interaction has been termed an anti-hydrogen bond. Even though the number of compounds studied here is small, it seems that an available ortho H atom in an aromatic *N*-sulfinylamine will always lead to a preferred planar conformation and an anti-H bond.

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