Nonbonded Interactions. A Thiophene S · · · N Intramolecular Attraction. Crystal Structure of 2-Formylthiophene Semicarbazone

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Thiophene derivatives can exhibit a novel intramolecular nonbonded S · · · N attraction which is observed in 2-formylthiophene semicarbazone, as well as other derivatives.

The interactions involved in the formation of a chemical bond are well understood. However, neither attractive nor repulsive interactions between nonbonded atoms have been studied extensively. We report an example of a nonbonded intramolecular attraction between a thiophene ring sulphur atom and an adjacent nitrogen atom.

We observed recently that a short S · · · N contact was a common feature in appropriately 2-substituted thiophenes.[1] We prepared and determined the crystal structure of 2-formylthiophene semicarbazone† to confirm and provide a simple example of this interaction.

Figure 1 illustrates the remarkably short S(1) · · · N(1) distance of 3.037(6) Å. This distance, much shorter than the expected van der Waals contact of 3.45 Å, represents a nonbonded intramolecular attraction. Support for this view is provided by the much smaller S(1)–C(1)–C(5) angle of 121.9(3)° compared to the C(2)–C(1)–C(5) angle of 125.9(4)°. Furthermore, the H(2) · · · H(5) distance is 2.56 Å, considerably larger than the expected van der Waals contact of 2.4 Å. Finally, the small torsion angle for S(1)–C(1)–C(5)–N(1) of −3.0(7)° would maximize the interaction.

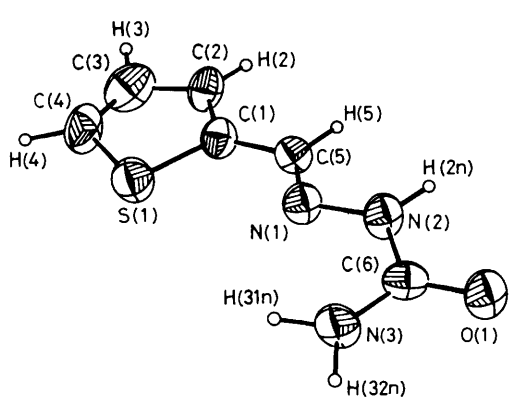

Figure 1. The crystal structure of 2-formylthiophene semicarbazone. Selected bond lengths: S(1)–C(1), 1.716(5); S(1)–C(4), 1.713(6); C(1)–C(2), 1.413(6); C(3)–C(4), 1.329(9); C(2)–C(3), 1.428(8); C(1)–C(5), 1.447(6); C(5)–N(1), 1.279(5); N(1)–N(2), 1.373(5); N(2)–C(6), 1.370(5); C(6)–O(1), 1.238(6); C(6)–N(3), 1.331(6) Å. Selected bond angles: C(1)–S(1)–C(4), 91.6(3); S(1)–C(1)–C(2), 112.1(3); S(1)–C(1)–C(5), 121.9(3); C(2)–C(1)–C(5), 125.9(4); C(1)–C(2)–C(3), 108.9(4); C(2)–C(3)–C(4), 115.3(5); S(1)–C(4)–C(3), 112.1(5); C(1)–C(5)–N(1), 121.1(4); C(5)–N(1)–N(2), 115.1(4); N(1)–N(2)–C(6), 119.2(4); N(2)–C(6)–N(3), 116.7(4); N(2)–C(6)–O(1), 118.5(4); N(3)–C(6)–O(1), 124.7(4)°.

† *Crystal data:* $C_6H_7N_3OS$, M = 169.21, monoclinic, space group $P2_1/c$, a = 11.717(4), b = 5.465(2), c = 12.468(5) Å, β = 100.61(3)°, U = 784.9(4) Å^3, D_c = 1.43 g cm^{-3}, $F(000)$ = 352, μ(Cu-K_α) = 31.2 cm^{-1}, Syntex P1 diffractometer, 1252 reflections ($1.5 \leq 2\theta \leq 112.5°$), 987 observed with $F_o > 2.0\sigma(F_o)$. The structure was solved by direct methods (SOLV included in SHELXTL system) and refined using the 'blocked cascade' least-squares method. 100 Parameters refined: co-ordinates and anisotropic thermal parameters of non-H atoms, and a scale factor. The final R and R_w ($w = 1/\sigma^2$) values are 0.068 and 0.078, respectively. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

The S· · · N nonbonded interaction appears to be a common feature of unrestricted 2-substituted thiophene derivatives with a nitrogen atom in the appropriate position.[2] Excluding compounds containing a thiophene ring as part of a ligand which is co-ordinated to a transition metal, there are 14 other known examples of S · · · N non-bonding interactions.[3–10] The torsion angles range from 0.3 to 10.8° with only two exceptions.[4,10] The S · · · N distances range from 2.927 to 3.094 Å. Considering the variety of examples, these are relatively small variations.

The C(5)–N(1) distance of 1.279(5) Å is identical to that found in acetone semicarbazone [1.278(3) Å][11] and similar to that in 5-nitro-2-furaldehyde oxime [1.268(4) Å][12] where no delocalization is possible. Therefore, the shortening of the C(1)–C(5) bond to 1.447(6) Å must be a consequence of the small internal S(1)–C(1)–C(2) angle [112.1(3)°] and subsequent increase in s character in the bond. A similar C–C bond length [1.443(4) Å] was also observed in the furan derivative[12] where there was no delocalization. Arguments also were presented recently that the shortening of C–C bonds in cubane-1,4-dicarboxylic acid was related to an angular compression.[13] In summary the planarity of the compound is a consequence of the S · · · N interaction and not of delocalization with the side chain.

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