A short C–H···N hydrogen bond with a very strong IR spectroscopic effect

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The crystal structure of 3-methylthio-4-propargylselenoquinoline contains a very short C≡C–H···N hydrogen bond with H···N and C···N distances of 2.17 and 3.225(4) Å, respectively. The bathochromic shift of the infrared acetylenic C–H stretching vibration ν_{CH} is 176 cm^{-1}. The geometry as well as the spectral effects come close to the shortest well-studied C–H···N hydrogen bond, which occurs in solid HCN (C···N = 3.18 Å, bathochromic shift 180 cm^{-1}). The hydrogen bond energy is calculated as −3.4 kcal mol^{-1}. A correlation of ν_{CH} bathochromic shift against C···N distance is established for C≡C–H···N hydrogen bonds.

Terminal alkynes R–C≡C–H are very interesting model donors for research on non-conventional hydrogen bonds.[1] The reason is that they are very acidic for a C–H group, hence they are strong donors, readily available, and well suited for structural, IR-spectroscopic and theoretical studies. By far the largest part of the experimental material on C≡C–H···X hydrogen bonds is for O-acceptors (*e.g.*, ref. 2–5), but there are also case studies with X = N,[6–8] F–C,[9] π-acceptors[10] and halide ions.[11] For all the latter examples, though, the experimental material is quite unsystematic, and in particular, the support of structural results by complementary methods is poor. In this general context, we have become interested in acetylenic derivatives of thioquinolines,[12–14] which show potential as bactericides[15] and anticancer agents.[16] In a new crystalline compound of this family, 3-methylthio-4-propargylselenoquinoline, **1**, we have found an exceptionally short C≡C–H···N hydrogen bond that deserves closer investigation.

In the crystalline state, **1** adopts the molecular conformation shown in Fig. 1. Neighboring molecules are linked by hydrogen bonds (Fig. 2) with a geometry of H···N = 2.17, C···N = 3.225(4) Å, C–H···N = 164° (for C–H normalized to 1.08 Å). In terms of C···N distance, this is only 0.04 Å longer than the shortest of all well-studied C–H···N hydrogen bonds, that is the N≡C–H···N≡C–H interaction in solid HCN (3.18 Å).[17] To examine the hydrogen bond in **1** further, we have measured the IR absorption spectra of crystals and of a dilute $CDCl_3$ solution, shown in Fig. 3. The relevant absorption band $\nu_{\equiv C-H}$ (acetylenic C–H stretching vibration) in solution is found at 3307 cm^{-1}, which is a typical value for 'free' C≡C–H groups.[2] In crystals, $\nu_{\equiv C-H}$ is reduced to 3131 cm^{-1}, giving a bathochromic shift $\Delta\nu_{\equiv C-H}$ of 176 cm^{-1}. This is almost as large as in solid HCN ($\Delta\nu_{\equiv C-H} = -180$ cm^{-1}). For

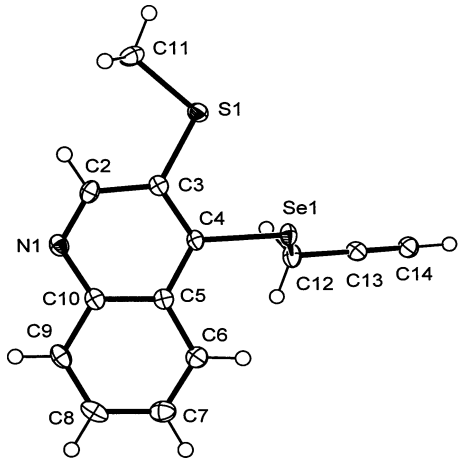


Fig. 1 Molecular structure of **1**; displacement ellipsoids are drawn at the 50% probability level.

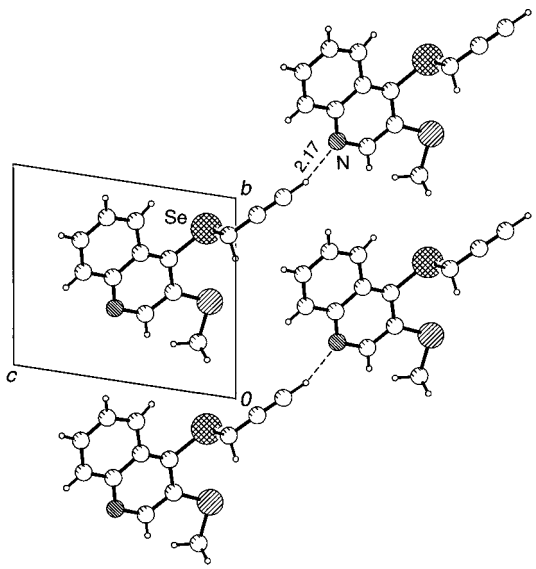


Fig. 2 A layer of the crystal structure of **1** in a projection highlighting the short C≡C–H···N hydrogen bonds.

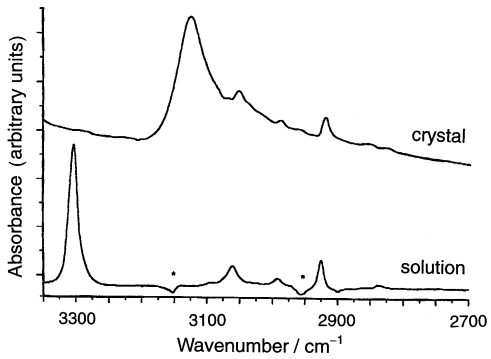


Fig. 3 Infrared absorption spectra of microcrystalline **1** between KBr plates with the most prominent peak at 3131 cm^{-1} (top), and a dilute solution of **1** in $CDCl_3$, showing a peak at 3307 cm^{-1} (bottom); * symbols denote noncompensation of solvent bands. Only the relevant sections with the acetylenic ν_{C-H} are shown.

comparison, the bathochromic shifts of $\nu_{\equiv C-H}$ in the two shortest C≡C–H···O hydrogen bonds known are 202 cm^{-1} for C···O = 3.02 Å[5] and 149 cm^{-1} for C···O = 3.06 Å (both with highly activated acceptors).[3] More typical values are found in the range 30–80 cm^{-1}.[2] This means that the spectral effect of the hydrogen bond in **1** is dramatic, one of the largest ever observed for C–H···X bonds in crystals. Since the donor is not particularly more activated than in other terminal acetylenes (C≡C–H is separated from Se by a methylene group that is only a poor conductor for charges), one must assume that the heavy substituents on the acceptor are responsible for the large spectral effect.

In C≡C–H···O interactions, hydrogen bond distances (C···O) and $\nu_{\equiv C-H}$ peak positions (or bathochromic shifts) are correlated.[1,2,18] It is important to see if such a correlation holds for C≡C–H···N interactions too. Unfortunately, IR data are available only for a very few of the published crystal structures with C≡C–H···N hydrogen bonds, so that we have to use primarily spectra measured on our own crystals. Despite the small number of data, the plot of $\nu_{\equiv C-H}$ against C···N (Fig. 4) clearly shows a systematic reduction of $\nu_{\equiv C-H}$ with decreasing C···N distance, with the data point from **1** forming the low extremity (details in the Figure legend).

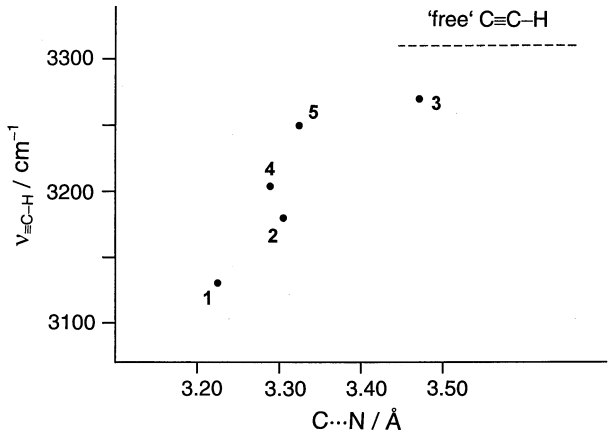
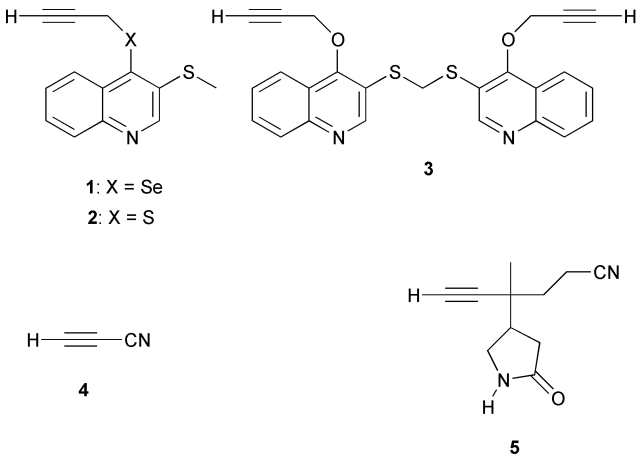


Fig. 4 Correlation of the acetylenic ν_{C-H} with the C···N distance in crystals containing C≡C–H···N hydrogen bonds. Labeling of data points corresponds to compound labeling in Scheme 1. **1**: C···N = 3.225 Å, ν_{cryst} = 3131, ν_{solut} = 3307 cm^{-1}. **2**: C···N = 3.305 Å,[13] ν_{cryst} = 3180, ν_{solut} = 3306 cm^{-1}. **3**: two relevant interactions, C···N = 3.428 and 3.514 Å,[14] mean value plotted in the figure, ν_{cryst} = 3270, ν_{solut} = 3307 cm^{-1}. **4**: cyanoacetylene, C···N = 3.29 Å, ν_{cryst} = 3204, ν_{solut} = 3328 cm^{-1}.[6] **5**: C···N = 3.324 Å, ν_{cryst} = 3250 cm^{-1}; the acceptor of the C≡C–H···N interaction is the cyano N atom.[19] IR spectra for **1**–**3** were measured in this work; data for **4** and **5** are given in the respective publications of their structures.



Scheme 1 **1**: main compound under study, **2**–**5**: compounds for which IR data are shown in Fig. 4.

Recently, a general correlation between bathochromic shifts of ν_{X-H} and H···A distances has been set up for many different kinds of hydrogen bonds in crystals and the gas phase: $\Delta\nu_{X-H} = 0.011\ r(H\cdots A)^{-6.1}$ (ν in cm^{-1}, r in nm).[20] Published data on C≡C–H···O hydrogen bonds obey this relation well,[20] but for C≡C–H···N interactions, despite the same tendency, there are some deviations. For points **2**–**4** of Fig. 4, the calculated and experimental values concide reasonably well, but for **1**, the calculated shift (120 cm^{-1}) is significantly lower than the experimental one (176 cm^{-1}) while for **5**, it is 30 cm^{-1} too high (90 cm^{-1} calc. *vs.* 60 cm^{-1} expt.).

Finally, to get an idea of the hydrogen bond energy involved, we performed *ab initio* calculations on a gas phase complex of the relatively realistic fragments 3-methylseleno prop-1-yne···3-mercapto-4-methylselenoquinoline. The calculated energy after geometry optimization, −3.4 kcal mol^{-1}, must only be taken as a qualitative measure of the bond energy in the crystal, but clearly indicates that the interaction does not represent a 'weak' but rather a moderately strong hydrogen bond.

These complementary results show that C–H···N hydrogen bonds may be fairly strong, even if C–H groups with smaller acidity than strong carbon acids like HCN or $CH(NO_2)_3$ are involved. The classification 'weak hydrogen bond' is certainly justified for the majority of C–H···N interactions,[21] and possibly also for many formed by C≡C–H donors. On the other hand, some are placed in the intermediate energy region −3–5 kcal mol^{-1}, as has already been demonstrated for the more abundant C–H···O interactions.[1] This is the region where the energy ranges of 'normal' O/N–H···O/N and of C–H···O/N hydrogen bonds overlap. We expect that more C–H···N hydrogen bonds with similar or even shorter distances will be found in the future, making that overlap region even broader than it is now.

Experimental

3-Methylthio-4-propargylselenoquinoline, **1** ($C_{13}H_{11}NSSe$, M = 292.25, m.p. 97–98 °C), was prepared analogously to the procedure described for 3-methylthio-4-propargylthioquinoline[13] and recrystallized from MeOH.[16]

X-Ray diffraction data were collected at 125 K on a Nonius Kappa-CCD diffractometer with Mo-Kα radiation [yellow plate with dimensions 0.5 × 0.3 × 0.05 mm, $P\bar{1}$ (no. 2), a = 8.6112(3), b = 8.8243(3), c = 9.2589(3) Å, α = 75.170(2), β = 71.033(3), γ = 63.789(2)°, V = 591.65(3) Å^3, D_c = 1.64 g cm^{-3}, 2704 unique reflections, 2424 with $I > \sigma(I)$]. The structure was solved and refined with standard methods[22,23] (H atoms refined in the default riding model with displacement parameters allowed to vary, R = 0.047, wR = 0.109 for 157 refined parameters).

CCDC reference number 166477. See http://www.rsc.org/suppdata/nj/b1/b102727c/ for crystallographic data in CIF or other electronic format.

IR absorption spectra were recorded at room temperature on a Bruker 113v FTIR spectrometer and processed using the Bruker OPUS program. Microcrystalline samples of **1**, 3-methylthio-4-propargylthioquinoline,[13] **2**, and bis(4-propargyloxy-3-quinolinylthio)methane,[14] **3**, were measured between KBr plates and in dilute (less than 10^{-2} M) $CDCl_3$ solutions using 1 cm infrasil cells.

Ab initio calculations were performed with GAUSSIAN98[24] using the LANL2DZ RMP2 (FC) basis set. Electron correlation and BSSE were taken into account and geometries were optimized.

Acknowledgements

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