ELSEVIER
Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2005, 15(4), 135–138

Mendeleev
Communications

Energy of a short N–H···S intramolecular bond in the crystal of (2*Z*)-2-cyano-2-quinolin-2(1*H*)-ylideneethanethioamide from X-ray diffraction data

Konstantin A. Lyssenko,[*a] **Olesya R. Prokopenko,**[a,b] **Vladimir N. Nesterov,**[c] **Tatiana V. Timofeeva**[c] **and Mikhail Yu. Antipin**[a,c]

[a] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 095 135 5085; e-mail: kostya@xrlab.ineos.ac.ru*
[b] *Higher Chemical College, Russian Academy of Sciences, 125047 Moscow, Russian Federation*
[c] *Department of Natural Sciences, New Mexico Highlands University, Las Vegas, New Mexico 87701, USA*

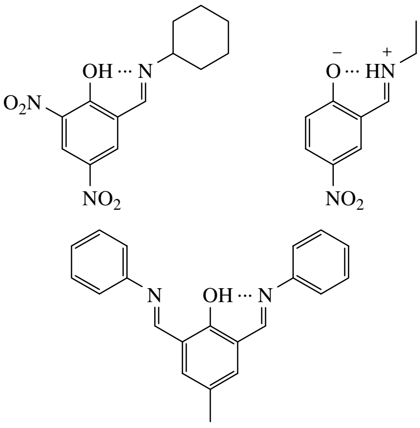
DOI: 10.1070/MC2005v015n04ABEH002149

The energy of a strong intramolecular N–H···S bond [N···S 2.9617(5) Å] in the crystal of titled compound has been estimated and compared with energies of intramolecular N–H···O and O–H···N H-bonds.

In the last decade, the usage of high-resolution X-ray diffraction (XRD) analysis of electron density distribution function $\rho(r)$ made it possible to analyse and estimate the energy of various strong intramolecular hydrogen bonds of O–H···O,[1] O–H···N,[2] N–H···O[2] and N–H···N[3] types. In all cases, it was demonstrated that these strong low-barrier H-bonds (SLBHB) are characterised by high energy[1–3] and correspond to intermediate type of interatomic interactions within R. F. Bader's 'Atoms in Molecule' theory (AIM).[4]

Assuming that H-bonds with sulfur are much weaker due to diffuse character of the electron lone pairs,[5] it is reasonable to suggest that main characteristics of intramolecular H-bonds with sulfur differ significantly from such characteristics of O–H···O or N–H···O H-bonds. In order to analyse the nature and to estimate the energy of intramolecular H-bonds in which the sulfur atom serves as an acceptor of proton, we have performed the topological analysis of $\rho(r)$ within AIM[4] theory for the molecule in a crystal and the isolated molecule of (2*Z*)-2-cyano-2-quinolin-2′(1*H*)-ylideneethanethioamide **1** (Figure 1) using high-resolution XRD[†] at 100 K and DFT calculation (B3LYP/6-311G**).[‡] We believe that data on energy of H-bond with sulfur will be very useful for improvement of force fields for crystal structures modelling where interactions with the S atom play a significant role.[6]

The XRD data have revealed that, in the solid state, **1** exists in the zwitterionic form with formal positive charge at nitrogen of quinolinium ring and negative charge delocalised on the cyanothioamide fragment. The zwitterionic form is stabilised by the presence of a six-memebred H-bond cycle which additionally promote charge delocalization between the fragments. The N(1)···S(1) [2.9617(5) Å] distance is close to the shortest H-bond distances for six-membered intramolecular N–H···S hydrogen bonds[7] and definitely can be considered as the strong one since the N(1)···S(1) distance is shorter than sum of van der Waals radii of N and S (3.16 Å).[7] Note that, taking into account differences in covalent radii of oxygen and sulfur, the N–H···S bond in **1** is compatible with strong intramolecular O–H···N [2.5626(5) Å] and N–H···O [2.6379(5)–2.6668(5) Å] H-bonds in Shiff bases,[2] for which $\rho(r)$ analysis in crystal has been carried out so far (Scheme 1).



Scheme 1

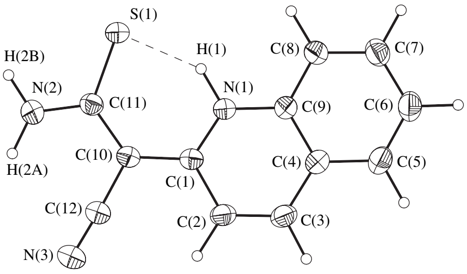


Figure 1 The general view of **1** with presentation of atoms by thermal ellipsoids at the 80% probability level. Selected bond lengths (Å): S(1)–C(11) 1.7066(6), N(1)–C(1) 1.3466(7), N(1)–C(9) 1.3759(8), N(2)–C(11) 1.3420(8), N(3)–C(12) 1.1580(8), C(1)–C(10) 1.4233(8), C(10)–C(11) 1.4377(8), C(10)–C(12) 1.4234(8); selected bond angles (°): C(1)–N(1)–C(9) 124.73(5), C(1)–N(1)–H(1) 116.0(8), C(9)–N(1)–H(1) 119.2(8), C(11)–N(2)–H(2B) 115.7(9), C(11)–N(2)–H(2A) 123.4(9), H(2B)–N(2)–H(2A) 120.4(12), N(1)–C(1)–C(10) 121.28(5), C(1)–C(10)–C(12) 116.34(5), C(1)–C(10)–C(11) 127.33(5), C(12)–C(10)–C(11) 116.31(5), N(2)–C(11)–C(10) 117.74(5), N(2)–C(11)–S(1) 117.16(4), C(10)–C(11)–S(1) 125.09(5), N(3)–C(12)–C(10) 177.41(7).

The molecule of **1** in a crystal is almost planar. The geometry of the NC–C(=S)–NH_2 group in **1** is characterised by pronounced delocalization in comparison to corresponding geometry in similar non-zwitterionic structures.[9,10] Actually in the two available according to the CSD[7] molecules[9,10] NH_2C=S and C–CN fragments are noncoplanar with the torsion angle S=C–C(CN) equal to 8.6–13.4°, what in turn leads to shortening of C–NH_2 [1.319 *vs.* 1.3420(8) Å] and elongation of (S=)C–C(CN) [av. 1.488 *vs.* 1.4234(8) Å] bonds in comparison with **1**. In addition, the significant elongation of the C(11)–S(1) bond [1.7066(6) Å *vs.* 1.653–1.665 Å in refs. 9 and 10] should be noted. Thus, we can conclude that formation of short intramolecular N–H···S bonds leads to pronounced equalization of C–C bonds in six-membered H-cycle, which is a well-known characteristic of keto–enol and keto–enamine systems.[5(a)]

Note that the B3LYP/6-311G** calculation rather well reproduced experimental geometry – difference in the bond lengths does not exceed 0.01 Å (av. 0.004 Å). In turn, the intramolecular N–H···S bond in the isolated molecule is slightly elongated up to 2.991 Å. For some extent, the observed differences in geometry of **1** in solid and isolated molecules can be attributed to crystal packing. Actually, in the crystal of **1**, molecules are assembled by N–H···N [N(2)···N(3A) 3.0136(8) Å] and N–H···π [N(2)···C(7A) 3.396(1) Å] intermolecular H-bonds, as well as by stacking interaction (interplane distance is 3.394 Å) into a three-dimensional network.

To obtain direct information on charge density distribution in **1**, to analyse the character and to estimate the energy of the N(1)–H(1)···S(1) bond, we have carried out the multipole refinement and obtained the electron density function in the analytical form.[§]

The static deformation electron density distribution (DED) is characterised by the expected features. The DED section passing through the molecular mean plane (Figure 2) shows that the local charge accumulation is observed in the interatomic area of all chemical bonds and electron lone pairs of S(1) and N(3) atoms. In contrast in the S(1)···H(1) area DED is locally depleted.

Topological parameters of the $\rho(r)$ function for the molecule of **1** in a crystal and for the isolated molecule are very similar. The characteristic set for **1** in addition to critical points (3,–1) [CP(3,–1)] for C–C, C–S, C–H, N–C and N–H bonds includes the CP(3,–1) for H(1)···S(1) bond and three CP(3,+1) for the

---

[†] *Crystallographic data*: crystals of **1** ($C_{12}H_9N_3S$, $M = 227.28$) are monoclinic, space group $P2_1/c$; at 110 K, $a = 4.3545(1)$, $b = 16.6924(3)$ and $c = 14.3822(2)$ Å, $\beta = 93.259(1)°$, $V = 1043.71(3)$ Å^3, $Z = 4$ ($Z' = 1$), $d_{calc} = 1.446$ g cm^{-3}, (MoKα) = 2.81 cm^{-1}, $F(000) = 472$. Intensities of 30028 reflections were measured with a Smart 1000 CCD diffractometer [λ(MoKα) = 0.71072 Å, ω-scans with a 0.3° step in ω, $2\theta < 100°$] and 10164 independent reflections ($R_{int} = 0.0249$) were used in further refinement. The absorption correction was applied semiempirically from equivalents using the SADABS programme. The structure was solved by a direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic–isotropic approximation. Hydrogen atoms were located from the Fourier synthesis of the electron density and refined in the isotropic approximation. For **1**, the refinement converged to $wR_2 = 0.091$ and GOF = 0.923 for all independent reflections [$R_1 = 0.0407$ was calculated against F for 7007 observed reflections with $I > 2\sigma(I)$]. All calculations were performed using SHELXTL PLUS 5.0.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference number 274699. For details, see ‘Notice to Authors’, *Mendeleev Commun.*, Issue 1, 2005.

[‡] The *ab initio* calculations of **1** were performed with the Gaussian 98 program package[13] at the B3LYP/6-311G** level of theory. As convergence criteria, the normal threshold limits of 2×10^{-6} and 6×10^{-6} were applied for the maximum force and displacement, respectively. To enhance the B3LYP calculation accuracy, the pruned (99590) grid was used. Topological analysis of the $\rho(r)$ function was performed using the MORPHY 98 program,[14] basing on the wave functions obtained from the B3LYP calculations.

[§] The multipole refinement was carried out within the Hansen-Coppens formalism[15(a)] using the XD program package[15(b)] with the core and valence electron density derived from wave functions fitted to a relativistic Dirac–Fock solution.[15(c)] Before the refinement, N–H and C–H bond distances were normalised to the values obtained in the B3LYP/6-311G(*d*,*p*) calculation. The level of multipole expansion was octopole for carbon, nitrogen and sulfur atoms and dipole for hydrogens. For atoms H(1), H(2A) and H(2B) for more accurate description of H-bonding pattern the hexadecapoles were added. The refinement was carried out against F and converged to $R = 0.0288$, $wR = 0.0241$ and GOF = 1.23 for 6830 merged reflections with $I > 3\sigma(I)$. All bonded pairs of atoms satisfy the Hirshfeld rigid-bond criteria[15(d)] (difference of the mean square displacement amplitudes along the bond were not larger than 8×10^{-4} Å^2). The residual electron density was no more than 0.14 eÅ^{-3}. Analysis of topology of the $\rho(r)$ function was carried out using the WINXPRO program package.[16]

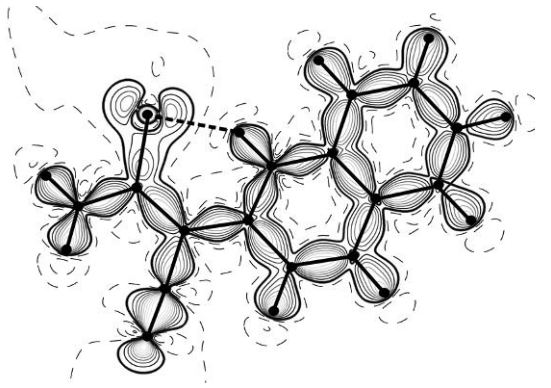


Figure 2 The section of deformation electron density in the molecular plane of **1**. The contours are drawn with a 0.1 e$Å^{-3}$ step. The negative values of DED are dashed.

six-membered rings: two for quinolinium and one for H-cycle. The CP(3,+1) for H-cycle is situated approximately in its centre thus indicating the stability of this molecular graph and pronounced strengths of the N–H···S bond.

To obtain the atomic charges in the molecule of **1**, we have determined the atomic basins (Ω) surrounded by zero-flux surface and have integrated $\rho(r)$ over each Ω. Although the integrated Langrangian [$L(r) = -1/4\nabla^2\rho(r)$] for every Ω has to be exactly equal to zero, a reasonably small numbers with averaged value equal to 9×10^{-5} a.u. with maximum $L(r)$ observed for H(2A) atom (3×10^{-4} a.u.) were obtained. The sum of atomic volumes (260.23 $Å^3$) reproduces well the unit cell volume per molecule [260.93(3) $Å^3$] with a very small (0.26%) difference.

The charges obtained by the integration of Ω clearly show that, although a distinctive zwitterionic structure is not observed, we can identify the areas of positive and negative charges. The positive charge is mainly localised on the carbon atoms of the nitrogen-containing cycle while negative ones are localised on S(1), C(3), C(8), C(10) and all nitrogen atoms (Figure 3).

The analysis of topological parameters of $\rho(r)$ has revealed that all bonds with the only exception of H(1)···S(1) are characterised by the negative value of $\nabla^2\rho(r)$ and thus correspond to the shared type of atomic interactions. On the contrary, the H(1)···S(1) bond is characterised by the positive value [2.05(2) e$Å^{-5}$] that is characteristic of both closed-shell and intermediate types of interactions. However, it is noteworthy that the value of ρ(r) in the CP(3,-1) of H(1)···S(1) bond [0.23(1) e$Å^{-3}$] is relatively high and electron energy density [$h_e(r)$] estimated using Kirzhnits approximation[11] is negative (–0.0036 a.u.). Although the latter value in crystal is close to zero, the same qualitative result is observed for the isolated molecule (–0.00668 a.u.) and thus we can undoubtedly conclude that N–H···S interactions also correspond to intermediate type of interactions[4] as all previously investigated low-barrier strong H-bonds.[1–3]

At the same time, according to Lecomte's correlation scheme[11(*b*)] the estimated from experimental $\rho(r)$ function energy of N–H···S bond is relatively low (8.9 kcal mol^{-1}) in comparison with intramolecular O–H···N [46.2 kcal mol^{-1} with O···N equal to 2.5626(5) Å][2] and N–H···O [16–21 kcal mol^{-1} with O···N equal to 2.6668(5)–2.6379(5) Å][2] bonds in Schiff bases. Furthermore, the energy obtained for N–H···S bond in **1** (8.9 kcal mol^{-1}) is nearly equal to energy (8.3 kcal mol^{-1}) of the intramolecular N–H···O bond (2.745 Å), which was recently estimated in the isolated molecule of methyl 2-{2-[(*E*)-(diethoxyphosphoryl)methylidene]-4-oxo-1,3-thiazolan-5-ylidene}acetate (**C**).[12] The energy of N–H···S bond that we obtained using Dreiding force field was significantly lower than the experimental one (1.29 kcal mol^{-1}), that shows again that some improvements to existing force fields that include the sulfur atom should be done.

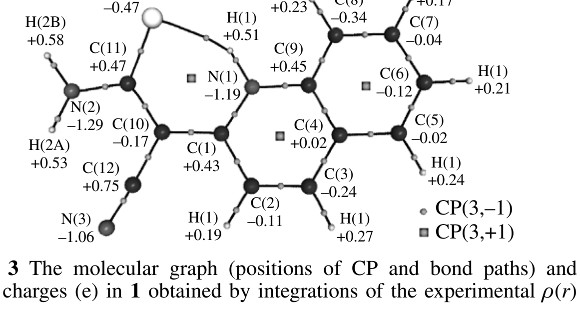
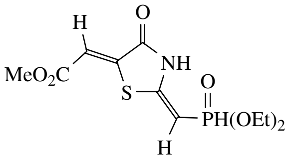


Figure 3 The molecular graph (positions of CP and bond paths) and atomic charges (e) in **1** obtained by integrations of the experimental $\rho(r)$ over Ω.



C

Thus, the results of topological analysis of electron density function in **1** have revealed that in spite of the fact that the N–H···S bond in this compound can be classified as a strong one from geometrical criteria and that the H···S bond corresponds to the intermediate type of interactions its energy is at least two times weaker than similar strong intramolecular N–H···O bonds.

This work was supported by the Russian Foundation for Basic Research (grant no. 03-03-32214), the Support of Leading Schools of the President of the Russian Federation (grant no. 1060.2003.3) and the NASA sponsored Alliance for Nonlinear Optics (grant no. NAG8-1709).

References

1 (*a*) K. A. Lyssenko, D. V. Lyubetsky and M. Yu. Antipin, *Mendeleev Commun.*, 2003, 60; (*b*) K. A. Lyssenko and M. Yu. Antipin, *Izv. Akad. Nauk, Ser. Khim.*, 2001, 400 (*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 418); (*c*) G. K. H. Madsen, B. B. Iversen, F. K. Larsen, M. Kapon, G. M. Reiser and F. H. Herbstein, *J. Am. Chem. Soc.*, 1998, **120**, 10040; (*d*) D. Madsen, C. Flensburg and S. Larsen, *J. Phys. Chem.*, 1998, **A102**, 2177.

2 P. M. Dominiak, E. Grech, G. Barr, S. Teat, P. R. Mallinson and K. Wozniak, *Chem. Eur. J.*, 2003, **9**, 963.

3 P. R. Mallinson, K. Wozniak, G. T. Smith and K. L. Mccormack, *J. Am. Chem. Soc.*, 1997, **119**, 11502.

4 R. F. W. Bader, *Atoms in Molecules. A Quantum Theory*, Clarendron Press, Oxford, 1990.

5 (*a*) T. Steiner, *Angew. Chem., Int. Ed. Engl.*, 2002, **41**, 58; (*b*) F. H. Allen, C. M. Bird, R. S. Rowland and P. R. Raithby, *Acta Crystallogr.*, 1997, **B53**, 680.

6 T. V. Timofeeva, T. Kinnibrugh, O. Ya. Borbulevych, B. B. Averkiev, V. N. Nesterov, A. Sloan and M. Yu. Antipin, *Cryst. Growth Des.*, 2004, **4**, 1265.

7 *Cambridge Crystallographic Database*, release 2004.

8 R. S. Rowland and R. Taylor, *J. Phys. Chem.*, 1996, **100**, 7384.

9 V. N. Nesterov, N. G. Montoya, M. Yu. Antipin, M. Sanghadasa, R. D. Clark and T. V. Timofeeva, *Acta Crystallogr.*, 2002, **C58**, o72.

10 V. N. Nesterov, M. Yu. Antipin, T. V. Timofeeva and R. D. Clark, *Acta Crystallogr.*, 2000, **C56**, 88.

11 (*a*) D. A. Kirzhnits, *Zh. Eksp. Teor. Fiz.*, 1957, **32**, 115 (*Sov. Phys. JETP*, 1957, **5**, 64); (*b*) Yu. A. Abramov, *Acta Crystallogr.*, 1997, **A53**, 264; (*b*) E. Espinosa, E. Molins and C. Lecomte, *Chem. Phys. Lett.*, 1998, **285**, 170; (*c*) E. Espinosa, I. Alkorta, I. Rozas, J. Elguero and E. Molins, *Chem. Phys. Lett.*, 2001, **336**, 457; (*d*) V. G. Tsirelson, *Acta Crystallogr.*, 2002, **B58**, 632.

12 V. A. Kozlov, I. L. Odinets, K. A. Lyssenko, S. G. Churusova, S. V. Yarovenko, P. V. Petrovskii and T. A. Mastryukova, *Heteroatom. Chem.*, 2005, **16**, 159.

13 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon,

E. S. Replogle and J. A. Pople, *Gaussian 98, Revision A.9*, Gaussian, Inc., Pittsburgh PA, 1998.

14 P. Popelier, *Chem. Phys. Lett*., 1994, **228**, 160.

15 (*a*) N. K. Hansen and P. Coppens, *Acta Crystallogr.*, 1978, **A34**, 909; (*b*) T. S. Koritsansky, S. T. Howard, T. Richter, P. Macchi, A. Volkov, C. Gatti, P. R. Mallinson, L. J. Farrugia, Z. Su and N. K. Hansen, *XD – A Computer Program Package for Multipole Refinement and Topological Analysis of Charge Densities from Diffraction Data*, 2003; (*c*) Z. Su and N. K. Hansen, *Acta Crystallogr.*, 1998, **A54**, 646; (*d*) F. L. Hirshfeld, *Acta Crystallogr.*, 1976, **A32**, 239.

16 (*a*) A. Stash and V. Tsirelson, *J. Appl. Crystallogr.*, 2002, **35**, 371; (b) A. Stash and V. Tsirelson, *WinXPRO – a Program for Calculation of the Crystal and Molecular Properties Using The Model Electron Density*, 2001. Further information available at *http://xray.nifhi.ru/wxp/*

Received: 18th March 2005; Com. 05/2472