Mendeleev Commun., 2004, 14(3), 98–100

How applicable are geometrical criteria for analysis of the intramolecular N···C=O interaction in the *peri*-substituted naphthalene system?

Konstantin A. Lyssenko,*[a] Sergei M. Aldoshin[b] and Mikhail Yu. Antipin[a]

[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] *Institute of Problems of Chemical Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax: +7 096 524 9676*

DOI: 10.1070/MC2004v014n03ABEH001881

Topological analysis of the electron density and potential energy density distribution functions in the crystal of 8-dimethylamino-*N′*,*N′*-dimethylnaphthalene-1-carboxamide in conjunction with geometrical criteria proposed by J. D. Wallis *et al.* (*J. Chem. Soc., Perkin Trans. 2*, 2001, 133), revealed unambiguously that the intramolecular $Me_2N\cdots C{=}O$ contact (2.71 Å) corresponds to attractive interaction.

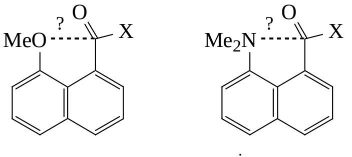
Through space interactions between the tertiary amino and carbonyl groups in cyclic azaketones were first described in the 1950s.[1] Since then, the transannular N···CO interaction has been found in a number of other bifunctional molecules including *peri*-substituted naphthalene systems.[2]

Taking into account that with decreasing the N···C distance the carbon atom becomes increasingly pyramidal, Bürgi, Dunitz and Schefter[3] proposed that such structures may be used for mapping nucleophilic addition reactions of the amine nitrogen to the carbonyl carbon atom of ketones. To our knowledge, the orientation of the dimethylamino group in *peri*-substituted naphthalenes is such that the lone electron pair of the nitrogen atom of the dimethylamino group is directed towards the adjacent carbonyl group. All these facts lead us to a conclusion that N···C contact corresponds to attractive donor–acceptor interaction, namely, an overlap of the lone pair of nitrogen with the LUMO of the carbonyl group.

The same type of interaction was found for a methoxy group, but despite the nucleophilicities of the oxygen and nitrogen atoms being different, there is no distinct systematic differences in the lengths of MeO···C(sp^2) and $Me_2N\cdots C$ contacts.[4,5] On the basis of detailed analysis of molecular geometry in the series of *peri*-substituted naphthalenes with methoxy and dimethylamino groups, recently,[4] it was proposed that a $Me_2N\cdots C$ interaction has an attractive component if the $Me_2N\cdots C$ separation is less than ~(MeO···C + 0.15) Å.

Using these geometrical criteria it was claimed that interactions of the dimethylamino group with the amide carbonyl in 8-dimethylamino-*N′*,*N′*-dimethylnaphthalene-1-carboxamide **1** and 8-dimethylamino-*N′*,*N′*-diisopropylnaphthalene-1-carboxamide **2** are dominated by steric effects [d(MeO···C) + 0.15 – d($Me_2N\cdots C$) = 0.049 and 0.009 Å].[4] Note that these data are in contradiction with recent data on the rate of racemization of 8-substituted tertiary 1-naphthamides.[6] In addition, even if any geometrical criteria are obtained using a significant number of structural data, some additional justification is always needed.

During the last decade, an estimation of the atom···atom interaction nature using experimental and/or theoretical analysis of the electron density distribution function $\rho(r)$ within Bader's 'Atom in Molecule' theory (AIM) has been commonly used.[7] There is a number of examples[8] of analysis of the nature of so-called 'forced' intramolecular interactions. As an example, the experimental analysis of the $\rho(r)$ in terms of AIM in the crystal of 2,2′-ethylenedibenzoic acid may be cited.[9] It was shown that the intramolecular O···C≡C interaction, similar to that in the above naphthalene system, corresponds to charge transfer from the oxygen lone electron pair to an antibonding orbital of the triple bond.



$X = NMe_2, NPr^i_2$

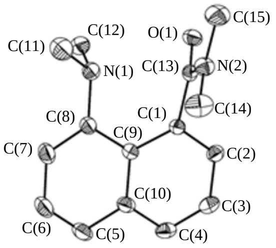


Figure 1 The general view of a molecule of **1** at 147 K with non-hydrogen atoms represented by thermal ellipsoids at the 50% probability level, and hydrogen atoms excluded. Selected geometrical parameters: C(13)···N(1) 2.700(1) Å, C(7)–C(8)–N(1) 123.0(1)°, C(7)–C(8)–C(9) 117.17(09)°, C(1)–C(9)–C(8) 123.37(9)°, C(2)–C(1)–C(13) 115.35(9)°, C(9)–C(1)–C(13) 124.54(9)°, C(7)–C(8)–N(1)–C(11) 29.34(1)°, C(7)–C(8)–N(1)–C(12) –97.9(1)°, deviation of the C(13) atom from O(1)N(2)C(1) plane is 0.056(1) Å.

Although the validity of analysis of the $\rho(r)$ within the AIM for weak interactions has been debated,[10] the recent comparison of the $\rho(r)$ topology and potential energy density distribution function $\nu(r)$ have resolved this controversy.[11] Bader demonstrated that each bond path in the electron density is mirrored by the virial path, a line of maximum potential energy density, which in turn indicates that the presence of the bond path or critical point (3, –1) between the pair of atoms in question is the 'universal indicator of bonding between atoms'.[11]

The potential energy density is usually calculated with quantum chemistry methods, but it was shown recently[12] that it can also be evaluated through the semiqualitative approximation for the kinetic energy density function $g(r)$ proposed by Kirzhnits.[13] According to Kirzhnits,[13] the $g(r)$ function is described as $(3/10)(3\pi^2)^{2/3}[\rho(r)]^{5/3} + (1/72)|\nabla\rho(r)|^2/\rho(r) + 1/6\nabla^2\rho(r)$, which in conjunction with the virial theorem $[2g(r) + \nu(r) = 1/4\nabla^2\rho(r)]$ leads to the expression for $\nu(r)$.

It should be noted that the application of this approximation to $g(r)$ not only gives an opportunity to define correctly the type of interatomic interactions but it is also a unique way to obtain the electron localization function (ELF)[14] and the localised-orbital locator (LOL)[15] directly from experimental X-ray diffraction data. Both of these functions describe the bonding in terms of local kinetic energy density[16] and in the case of experimentally derived functions they are preferable for analysis of weak closed-shell interactions.[14,15]

Thus, to estimate the reliability of the above geometrical criteria for the analysis of N···CO contacts,[4] we studied the electron density and potential energy density distribution functions in the crystal of 8-dimethylamino-*N′*,*N′*-dimethylnaphthalene-1-carboxamide. The crystal and molecular structures of the compound were previously analysed in detail at both 298[6,17] and 147 K[17] (Figure 1). A low-temperature high-resolution X-ray diffraction study of the dynamic deformation electron density

Table 1 Topological parameters of the $\rho(r)$ and $-\nu(r)$ functions for N(1)···C(13) contact in **1**.[a]

CP	CP in	$\rho(r)$/eÅ^{-3} or $-\nu(r)$ (a.e.)	$\nabla^2\rho(r)$/eÅ^{-5} or $-\nabla^2\nu(r)$ (au)	CP: *x*	CP: *y*	CP: *z*	λ_1/eÅ^{-5} (or au)	λ_2/eÅ^{-5} (or au)	λ_3/eÅ^{-5} (or au)
(3, –1)	$\rho(r)$	0.110	1.45	0.6813	0.1247	0.7835	–0.34	–0.11	1.90
	$-\nu$(r)	0.011	0.26	0.6788	0.1258	0.7910	–0.04	–0.02	0.32
(3, +1)	$\rho(r)$	0.108	1.47	0.6412	0.1304	0.7784	–0.32	0.14	1.64
	$-\nu$(r)	0.011	0.26	0.6464	0.1295	0.7775	–0.04	0.02	0.28

[a] $\lambda_{1,2,3}$ are principle curvatures of electron density and potential energy functions at the bond critical point (3, –1) or ring critical point (3, +1). CPs positions are fractional crystallographic coordinates.

(DED) was also reported.[17] The main conclusion drawn from the DED analysis was that the lone electron pair of the nitrogen atom is directed towards the carbonyl group and is significantly polarised. To obtain the $\rho(r)$ and $\nu(r)$ functions for **1**, we carried out a multipole refinement[†] of the high-resolution X-ray diffraction data measured at 147 K.[17]

Topological analysis of the $\rho(r)$ and $-\nu(r)$ functions revealed that they are characterised by the same set of critical points (CPs). The characteristic set of these points includes not only all expected CPs (3, –1) for C–C, C–N, C–H and C–O bonds and two ring CPs (3, +1) in the centres of the six-membered rings, but also a CP (3, –1) in the N(1)···C(13) interatomic area and, as a result, an additional CP (3, +1) due to formation of the five-membered N(1)C(8)C(9)C(1)C(13) ring (Figure 2). Topological characteristics of the CP (3, –1) and CP (3, +1) associated with N(1)···C(13) contact are listed in Table 1. Comparison of the gradient field of these two functions in the N(1)C(13)O(1) plane has revealed that homeomorphism between the gradient of the electron density and virial field is also satisfied, as was previously observed for the O···O contact in the dinitramide anion[20] and the B···Cl contact in the 3-chloro-7α-phenyl-3-borabicyclo[3.3.1]nonane[21] for functions derived from experimental data.

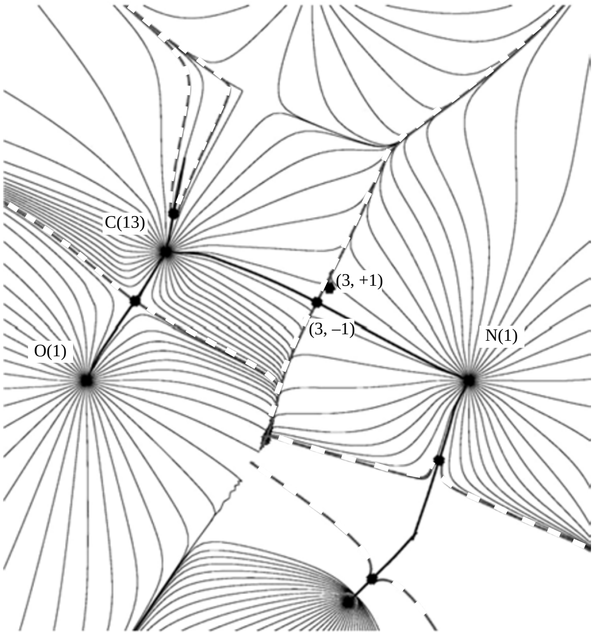


Figure 2 Gradient lines of electron density, bond paths and interatomic surface paths in **1** in the N(1)C(13)O(1) plane. The gradient lines are thin, bond paths are thick and surface interatomic lines are dashed. The deviation of C(12) atom from N(1)C(13)O(1) plane is 0.56 Å.

Topological parameters of the $\rho(r)$ at the (3, –1) critical points for the C–C bonds of the naphthalene system, as well as for C=O and N–C bonds, are usual and close to those observed in this class of compounds. Thus, for example, the $\rho(r)$ and $\nabla^2\rho(r)$ values for C–C bonds in the naphthalene fragment vary in the ranges from 2.05(4) to 2.25(5) eÅ^{-3} and from –16.2(1) to –20.01(1) eÅ^{-5}, respectively. All these bonds, as well as the C=O and N–C bonds, correspond to the shared type of interatomic interactions. The values of ellipticity for C–C bonds vary in the range 0.13–0.36, which are in line with bond length alternation and distortion of a naphthalene core. The ellipticity for the N(1)–C(8) bond is low (0.04) indicating that delocalization from the nitrogen lone pair into the aromatic ring is negligible.

What about the topological parameters of the N(1)···C(13) contact? They have expected values corresponding to those typical of the interaction of the closed-shell type. This follows not only from the positive value of the $\nabla^2\rho(r)$ function but also from the positive value of the electron density distribution function [$h_e(r) = g(r) + \nu(r)$], which is equal to 0.002 au at the CP (3, –1). It should be noted that while the $\rho(r)$ value at CP (3, –1) of the N(1)···C(13) contact is rather small [0.11(1) eÅ^{-3}], it is greater than the corresponding value 0.06(1) eÅ^{-3} for the O···C contact in the crystal of 2,2′-ethylenedibenzoic acid[8] thus indicating more pronounced charge transfer in **1**.

To give more insight into the nature of the N···C interaction, we analysed sections of the LOL and ELF functions (Figure 3) in the plane of N(1)C(13)O(1) atoms. Both of these functions demonstrate clearly that the lone electron pair of the nitrogen atom is oriented towards the area of electron density depletion at the C(13) atom. Thus, this contact may be described in terms of peak and hole interactions, *i.e.*, the overlap of the lone pair of the nitrogen atom with the LUMO of the carbonyl group.

The results of the experimental topological analysis of the electron density distribution, as well as potential energy density distribution functions, revealed that in conjuction with geometrical criteria[4] the N···C=O contact in the 8-dimethylamino-*N′*,*N′*-diisopropylnaphthalene-1-carboxamide is an attractive interaction of the donor-acceptor type but with pronounced charge transfer. This result in conjunction with recent investigation of forced contacts in similar systems[8] shows clearly the limitations of geometrical criteria, which may not only overestimate the role of steric effects as in the current molecule but also underestimate the importance of shortened distances as, for example, in the case of [2.2]paracyclophane and its derivatives.[8(f)]

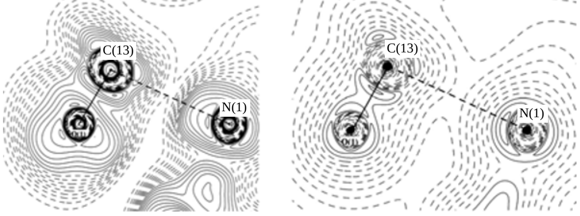


Figure 3 (*a*) Distribution of the electron localization function (ELF) and (*b*) localised orbital locator (LOL) from experimental data in the plane of N(1)C(13)O(1) in the crystal of **1**. The contours are drawn with a step of 0.05. The values of ELF and LOL less than 0.5 are dashed.

[†] The multipole refinement was carried out within the Hansen–Coppens formalism[18(a)] using the XD program package[18(b)] with the core and valence electron density derived from wave functions fitted to a relativistic Dirac–Fock solution.[18(c)] Before the refinement, all C–H bond distances were normalised to the ideal value 1.08 Å. The levels of multipole expansion were octopole for carbon, nitrogen and oxygen atoms and dipole for hydrogens. The refinement was carried out against *F*. The multipole refinement converged to *R* = 0.03275, *wR* = 0.03144 and GOF = 1.12 for 4919 merged reflections with sin θ/λ_{max} = 0.995 Å^{-1} and $F > 3\sigma(F)$. All bonded pairs of atoms satisfy the Hirshfeld rigid-bond criteria[18(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 not more that 0.08 eÅ^{-3}. Analyses of ELF, LOL and topology of the $\rho(r)$ and $\nu(r)$ functions were carried out using the WINXPRO program package.[19]

This work was supported by the Russian Foundation for Basic Research (grant no. 03-03-32214) and the Presidential Programme for Leading Russian Scientific Schools (grant nos. 1060.2003.3 and YS-1209.2003.03).

References

1 N. J. Leonard, D. F. Morrow and M. T. Rogers, *J. Am. Chem. Soc.*, 1957, **79**, 5476.

2 (*a*) H. B. Bürgi, *Faraday Discuss.*, 2002, **122**, 41; (*b*) A. S. Cieplak, *J. Am. Chem. Soc.*, 1985, **107**, 271; (*c*) A. S. Cieplak, in *Structure Correlation*, eds. H. B. Bürgi and J. D. Dunitz, Verlag Chemie, Weinheim, 1994, p. 205.

3 H. B. Bürgi, J. D. Dunitz and E. Schefter, *J. Am. Chem. Soc.*, 1973, **95**, 5065.

4 P. C. Bell, J. O’Leary, J. D. Wallis and W. B. Schweizer, *J. Chem. Soc., Perkin Trans. 2*, 2001, 133.

5 P. C. Bell, W. Skranc, X. Formosa, J. O’Leary and J. D. Wallis, *J. Chem. Soc., Perkin Trans 2*, 2002, 878.

6 J. Clayden, C. McCarthy and M. Helliwell, *Chem. Commun.*, 1999, 2059.

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

8 (*a*) R. Destro and F. Merati, *Acta Crystallogr.*, 1995, **B51**, 559; (*b*) V. Tsirelson, Yu. Abramov, V. Zavodnik, A. Stash, E. Belokoneva, J. Sthan, U. Peitch and D. Feil, *Struct. Chem.*, 1998, **9**, 249; (*c*) W. Scherer, M. Spiegler, M. Tafipolsky, W. Hieringer, B. Reinhard, A. J. Downs and G. S. McGrady, *Chem. Commun.*, 2000, 635; (*d*) A. Bach, D. Lentz and P. Luger, *J. Phys. Chem. A*, 2001, **105**, 7405; (*e*) A. A. Korlyukov, K. A. Lyssenko, M. Yu. Antipin, V. N. Kirin, E. A. Chernyshev and S. P. Knyazev, *Inorg. Chem.*, 2002, **41**, 5043; (*f*) K. A. Lyssenko, M. Yu. Antipin and D. Yu. Antonov, *Chem. Phys. Chem.*, 2003, **8**, 817.

9 G. T. Smith, J. A. K. Howard and J. D. Wallis, *Phys. Chem. Chem. Phys.*, 2001, **3**, 4501.

10 (*a*) J. Cioslowski, S. T. Mixon and W. D. Edwards, *J. Am. Chem. Soc.*, 1991, **113**, 1083; (*b*) J. Cioslowski, P. B. O’Connor and E. D. Fleischmann, *J. Am. Chem. Soc.*, 1991, **113**, 1086; (*c*) J. Cioslowski and S. T. Mixon, *J. Am. Chem. Soc.*, 1992, **114**, 4382; (*d*) J. Cioslowski, L. Ediginton and B. B. Stefanov, *J. Am. Chem. Soc.*, 1995, **117**, 10381.

11 R. F. W. Bader, *J. Chem. Phys. A*, 1998, **102**, 7314.

12 (*a*) 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.

13 D. A. Kirzhnits, *Sov. Phys. JETP 5*, 1957, 64.

14 V. Tsirelson and A. Stash, *Chem. Phys. Lett.*, 2002, **351**, 142.

15 V. Tsirelson and A. Stash, *Acta Crystallogr.*, 2002, **B58**, 780.

16 A. Savin, R. Nesper, S. Wengert and T. Fassler, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1809; (*b*) H. L. Schmider and A. D. Becke, *J. Mol. Struct. (Theochem)*, 2000, **527**, 51.

17 V. D. Kiryukhin, I. I. Chuev, M. Yu. Antipin and S. M. Aldoshin, *Mol. Cryst. Liq. Cryst.*, 1996, **275**, 241.

18 (*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.

19 (*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*, Moscow, 2001. Further information available at http://xray.nifhi.ru/wxp/.

20 E. A. Zhurova, V. G. Tsirelson, A. I. Stach and A. A. Pinkerton, *J. Am. Chem. Soc.*, 2002, **124**, 4574.

21 K. A. Lyssenko, M. Yu. Antipin, M. E. Gurskii, Yu. N. Bubnov, A. L. Karionova and R. Boese, *Chem. Phys. Lett.*, 2004, **384**, 40.

Received: 23rd December 2003; Com. 03/2207