Available online at www.sciencedirect.com

ScienceDirect

Mendeleev Commun., 2016, **26**, 338–340

Mendeleev Communications

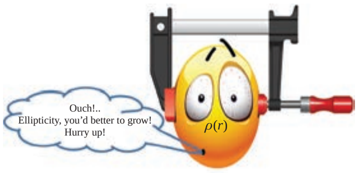
A chemist's point of view: the noncylindrical symmetry of electron density means nothing but still means something

Ivan V. Ananyev* and Konstantin A. Lyssenko

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation. E-mail: i.ananyev@gmail.com

DOI: 10.1016/j.mencom.2016.07.024

Some uncertainties of the ellipticity of electron density are discussed in terms of double-bonding and valence-shell electron pair repulsion.



Electron density [$\rho(r)$] studies are probably the most popular and indisputably powerful tool for elucidating molecular structure peculiarities commonly recognized by chemists as electronic effects.[1,2] Here, the means of $\rho(r)$ topological analysis[1(*a*),3] is especially worthy of note as a standard protocol for such a description of nuclei–electron systems. The magnitude of relations between the $\rho(r)$ topology and various chemical and physical properties has been established, thus giving rise to a broad bridging with the conventional orbital-based language of theoretical chemistry.[1(*d*),4] The core of many $\rho(r)$ studies is a search for $\rho(r)$ critical points and a further analysis of $\rho(r)$ topological features and local $\rho(r)$-based properties at these points. Owing to R. Bader and his quantum theory of 'Atoms in Molecules' (QTAIM),[1(*a*)] special attention is paid to the (3,–1) critical points of $\rho(r)$, which are now known, according to QTAIM, as a unique descriptor of attractive interaction between two atomic basins closed by zero-flux surfaces (so-called bond critical points, bcp). In addition to the value of the $\rho(r)$ function itself [$\rho(r)_{\text{bcp}}$], a variety of quantities commonly analyzed in bcp includes its Laplacian $\nabla^2\rho(r)$, eigenvalues of Hessian matrix of $\rho(r)$ (λ_i, i = 1–3), kinetic, potential and full electronic energy densities. Among these parameters, the λ_i values are rarely analyzed at a go since the curvature of $\rho(r)$ along a specific direction [three orthogonal directions, λ_3 corresponds to the trajectory of maximum $\rho(r)$] does not carry much information for chemists. Since the trajectory of maximum $\rho(r)$ going through bcp can be associated with an interatomic interaction and, in some cases, with a chemical bond (bond path), the ellipticity (ε) term is defined as $\varepsilon = \lambda_1/\lambda_2 - 1$ (λ_1 and λ_2 are negative eigenvalues, $\lambda_1 < \lambda_2$) in order to estimate the anisotropy of $\rho(r)$ curvature in directions normal to the bond.[5] Basically, the value of ε in bcp (hereafter, ε_{B}) indicates an extent of deviation of the $\rho(r)$ function from cylindrical symmetry along a chemical bond. The term ε is often and successfully used as a measure of double-bonded character of an interaction and corresponding electron delocalization,[5(*b*)] which not only helps one to estimate the contribution of a particular resonance form into molecule structures[6,7] but also allows one to distinguish the degree of charge transfer through weak interactions,[8] to analyze agostic interactions in metal complexes,[9] and even to explain organic reactivity in specific cases.[5(*b*)]

Nevertheless, in this study, we try to emphasize some uncertainties coming from an unreasonable but frequently assumed direct interrelation between ε_{B} and covalent bond multiplicity. For this purpose, several simple model systems were chosen to *ab initio* calculate $\rho(r)$ distribution in corresponding ground states and to analyze its curvature. The set considered below was designed to unveil cases when any considerable deviation of ε_{B} from zero can hardly be interpreted in terms of a double-bonded character; Table 1 summarizes all of the calculated species. The quantum chemistry calculations were performed on the MP2/6-311++G(d,p) level of theory[†] using the Gaussian 09 program.[10] The QTAIM analysis was performed using the AIMAll program package.[11]

For good of the traditional ε_{B} usage and for ill of the current communication, a pronounced violation of $\rho(r)$ cylindrical symmetry is quite difficult to observe for formally single C–C bonds: the strained cyclopropane ring [ε_{B}(C–C) = 0.52] is an expected but almost exclusive example. Note that, for a standard dyad of ethylene/ethane molecules, the ε_{B} values are 0.36/0.00 and 0.02/0.00 for C–C and C–H bonds, respectively. In the further discussion, for simplicity, a value of 0.02 was chosen as a minorant border indicating considerable violation of the cylindrical symmetry of $\rho(r)$ in other calculated systems. This choice is arbitrary to some extent, but it seems quite reasonable since it has to fully account for possible numerical errors of calculation of $\rho(r)$ Hessian eigenvalues.

The unreasonably large values of ε_{B} are observed for formally single C–B and B–H bonds in two boradamantane isomers (B1 and B2). These polyhedral molecules are also slightly strained in the area of endocyclic boron atoms: in the first isomer, the boron atom is pyramidalized (the sum of the C–B–C angles is 349.8°), while the C–B–C angle in the second isomer is significantly smaller than the C–B–H one (112.7° *vs.* 123.7°). However, note that the ε_{B}(C–B) value is large (and even slightly larger than that in B2) in the C_3-symmetric and plane BMe_3 molecule, which cannot be considered as strained one at least at first glance. The $\rho(r)$ function can be even less 'cylindrical' for C–F bonds. The ε_{B}(C–F) value is only 0.05 in the planar CF_3^+ cation; however, it increases dramatically (up to 0.85) if one adds two more electrons and considers the pyramidal CF_3^- system. This result seems

---

[†] Test calculations were performed for the BH_3 molecule using the AUG-cc-pVTZ basis set within the Møller–Plesset 4th order perturbation theory (SDTQ). The ε_{B}(B–H) values were also pronouncedly large (0.29).

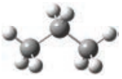
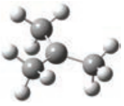
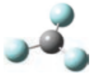
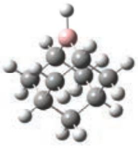
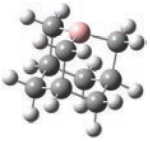
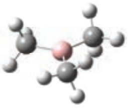
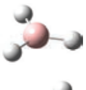
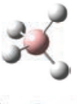
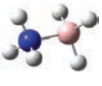
surprising due to the absence of formal factors responsible for the π bonding of carbon and fluorine atoms (both with lone electron pairs). Note that the cylindrical symmetry of $\rho(r)$ can be violated for X–H bonds in systems with electropositive central atoms; this follows from the calculations of a set of simple boranes and substituted boranes. The calculated BH_4^- anion is an exception clearly rationalized by symmetry restrictions of computed $\rho(r)$ that is in line with pronouncedly large ε_B(B–H) values in B_2H_6 (for not only bridged hydrogen atoms but also terminal ones) and BH_3NH_3 molecules with tetrasubstituted boron atoms.

Comparing X–H bonds in the calculated systems and accounting for the true sense of the term ε_B as a measure of orthotropy of $\rho(r)$ curvature near the bcp, one can find another obvious and chemist-friendly explanation of non-zero ε_B values rather than double bonding. According to QTAIM, the difference between two central (boron and nitrogen) atoms in BH_3NH_3, being formally the only difference between B–H and N–H bonds, is a difference between their integral properties such as atomic basin volumes. The expectedly smaller volume of a more electropositive atom always corresponds to a shorter distance between bcps located at its interatomic surface and corresponding increase of electron-electron repulsion between, at least, point charges [$\rho(r)_{bcp}$]. Based on the $\nabla^2\rho(r)$-based definition of electron pairs as charge concentrations,[12] it can be concluded that the $\rho(r)$ distribution near bcp is always 'biased' by the bonding electron pair, which together with the simple VSEPR theory implies that the $\rho(r)$ function in the vicinity of bcp can be 'pressed' by valence-shell electron pair repulsion (vsepr). The corresponding directions of vsepr-induced charge reconcentration and redepletion have to be observed when analyzing the second-order derivatives of $\rho(r)$ near the bcp and corresponding parameters (such as ε_B values) and have to be not collinear to the bond path as such subtle effects cannot significantly influence a charge distribution created by a pair of bonded atoms.

Unfortunately, this assumption is not easy to confirm by directly analyzing equilibrium data when vsepr is minimized. For instance, even considering only point charges at bcps or nuclei coordinates, a comparison between $\rho(r)_{bcp}$ values and corresponding bcp···bcp or interatomic separations in different ground states is meaningless to measure vsepr since there are a lot of more other forces compensating each other at the energy minima. Nevertheless, in order to be substantive and to test the hypothesis, we have analyzed the presented set including the interatomic pressure concept, which equalizes pressure between two contacting atomic basins to one third of the virial field integrated over a corresponding interatomic surface.[13] Since the basins of peripheral non-bonded atoms in isolated systems are divided by $\rho(r)$ zero-flux surfaces and the basins of central atoms, it has been reductionistically proposed that an increase of repulsion between the bonding electron pairs of non-bonded atoms enlarges a pressure between these atoms, which, in turn, reduces a pressure between bonded ones. The proposition limits the analysis of the calculated set and works fine if one only compares simple non-cyclic AB_n systems by pairs (A is the central atom, and B are peripheral groups, Table 2). Indeed, the interatomic pressure has to account for other forces, as is clear from the analysis of more complex and strained systems: (*a*) the ε_B(C–B) value is only slightly larger in BMe_3 than that in strained boradamantane B2 while the total pressure on the central boron atom (P_{cent}) is significantly smaller in BMe_3 (167.4 *vs.* 248.0 GPa); (*b*) the carbon atoms in the cyclopropane molecule are pressed even larger than the central carbon atom in the propane molecule (251.6 *vs.* 193.7 GPa) though the ε_B(C–C) is very close to zero in the latter.

In line with the proposed vsepr-induced changes of $\rho(r)$ curvature, the analysis of each AB_n system reveals the following

Table 1 The ellipticity of $\rho(r)$ at bond critical points (ε_B) corresponding to specific chemical bonds in various systems calculated at the MP2/6-311++G(d,p) level of theory.

System		Bonds						
		C–C	C–H	C–F	B–C	B–H	N–H	B–N
Ethane		0.00^a	<0.01					
Ethylene		0.36	0.02					
Propane		<0.01	<0.01					
Cyclopropane		0.52	0.03					
CMe_3^+		0.06	0.02					
CF_3^+				0.05				
CF_3^-				0.85				
Borada- mantane B1		<0.01	<0.02		0.32	0.33		
Borada- mantane B2		<0.01	<0.02		0.28			
BMe_3			0.02		0.29			
BH_3						0.37		
BH_4^-						0.00^a		
B_2H_6						0.11^b		
BH_3NH_3						0.18	0.02	0.00^a
CH_3F			0.05	0.00^a				
CH_3^+			0.05					
CH_4			0.00^a					

[a] The value of ε_B is lower than 10^{-6}; corresponding bonds lie on the C_3 symmetry axis. [b] The value is given for the terminal B–H bond.

Table 2 A pairwise comparison of simple AB_n systems in terms of $\rho(r)$ ellipticity at the bond critical point corresponding to the specific chemical bond (ε_B), volumes[a] of the peripheral atom/group (V_per), volumes of the central atom (V_cent) and total pressure[b] on the basin of central atom (P_cent).

Pairs	Bonds	ε_B	V_per/Å^3	V_cent/Å^3	P_cent/GPa
CF_3^-	C–F	0.85	138.8	127.6	298.3
CF_3^+	C–F	0.05	119.5	16.1	670.3
CF_3^+	C–F	0.05	119.5	16.1	670.3
BF_3	B–F	0.06	147.5	12.9	342.2
CF_3^+	C–F	0.05	119.5	16.1	670.3
CMe_3^+	C–C	0.06	264.1	66.7	201.9
BF_3	B–F	0.06	147.5	12.9	342.2
BMe_3	B–C	0.29	519.2	213.6	167.4
CMe_3^+	C–C	0.06	264.1	66.7	201.9
BMe_3	B–C	0.29	519.2	213.6	167.4
BF_3	B–F	0.06	147.5	12.9	342.2
BH_3	B–H	0.37	122.9	33.1	204.7

[a] Volumes are estimated as space integrals over atomic basins bounded by interatomic surfaces [$\nabla\rho(r)n(r) = 0$] and $\rho(r)$ isosurfaces (0.0004 eÅ^{-3}).
[b] $P_\mathrm{cent} = -{}^1/_3\iint_{S_\mathrm{IAS}} \upsilon(r)\,\mathrm{d}rS_\mathrm{IAS}^{-1} \cdot 2.941\times10^4$, $\iint_{S_\mathrm{IAS}} \upsilon(r)\,\mathrm{d}r$ – virial field (a.u.) integrated over all interatomic surface of the central atom (S_IAS).

main factors influencing ε_B: the number of electron-rich fragments repulsing each other and their size and location. An increase in the number of peripheral atoms (the number of bonding electron pairs) always leads to a decrease in ε_B values, as is clear from a comparison of CH_3^+ and CH_3F, BH_3 and BH_3NH_3, BH_3 and B_2H_6 (see Table 1). We note that small ε_B values were also observed for the terminal B–H bonds in carboranes and boranes, where any boron atom has an even larger number of substituents.[14] On the contrary, the addition of a lone electron pair and the corresponding pyramidalization of a central atom lead to an increase in pressure between non-bonded fluorine atoms in CF_3 and a corresponding increase in the ε_B(C–F) value. Here, we note the significant role of the $\rho(r)$ symmetry once again; the ε_B values for bonds lying on the C_n ($n > 2$) symmetry axis are always equal to zero: the examples are the C–F bond in CH_3F, the C–H bond in CH_4, the B–H bond in BH_4^-, the B–N bond in BH_3NH_3, and the C–C bond in C_2H_6. It can also confuse the investigations of double-bonding using the term ε: the $\rho(r)$ symmetry for the P–O bond in the PH_3O system is cylindrical.

A comparison of CF_3^+, BF_3, CMe_3^+ and BMe_3 systems is consistent with the simple mechanistic concepts of the VSEPR theory and the above proposition: larger ε_B values and larger pressure between non-bonded atoms (smaller P_cent value) correspond to a larger volume of peripheral atomic basins. The absence of correlation with the central basin volume (see, for instance, a comparison of CMe_3^+ with BMe_3 in Table 2), meanwhile, makes more reasonable the usage of P_cent values as a scaled measure of vsepr. At this point, another interesting bridging with the conventional chemical language occurs: larger ε_B values are observed for more electropositive central atoms whose orbitals can be considered as hybridized with a more pronounced *p* character. The volumes of atomic basins are even more meaningless when comparing atoms from different rows of the periodic table: the pressure between hydrogen atoms in BH_3 is larger (in terms of P_cent) than the pressure between fluorines in BF_3.

The case-based reasoning given above is still quite ambiguous and cannot be ultimate. However, the following several points should be remembered. The estimations of double-bonding or aromaticity, when basing on the $\rho(r)$ ellipticity analysis, can be overestimated in systems with polar bonds and/or bonds between atoms from different rows of the periodic table. Any nonzero ellipticity values and even quite large ones can be, in principle, caused simply by the repulsion of valence-shell electron pairs. When analyzing an atomic environment with a constant number of substituents, this repulsion can be estimated, at least qualitatively, by interatomic pressure calculations.

This study was supported by the Russian Science Foundation (project no. 14-13-00884).

Online Supplementary Materials

Supplementary data associated with this article (results of electron density analysis, as well as integration and geometry data for all calculated systems) can be found in the online version at doi:10.1016/j.mencom.2016.07.024.

References

1 (*a*) R. F. W. Bader, *Atoms in Molecules. A Quantum Theory*, Clarendon Press, Oxford, 1990; (*b*) S. Fux and M. Reiher, in *Structure and Bonding*, ed. D. Stalke, Springer, New York, 2012, vol. 147, p. 99; (*c*) L. Bertini, F. Cargnoni and C. Gatti, *Theor. Chem. Acc.*, 2007, **117**, 847; (*d*) I. S. Bushmarinov, K. A. Lyssenko and M. Yu. Antipin, *Russ. Chem. Rev.*, 2009, **78**, 283 (*Usp. Khim.*, 2009, **78**, 307); (*e*) P. L. A. Popelier, *Atoms in Molecules: An Introduction*, Prentice Hall, London, 2000; (*f*) C. F. Matta and R. J. Boyd, *The Quantum Theory of Atoms in Molecules. From Solid State to DNA and Drug Design. Chapter 1. An Introduction to the Quantum Theory of Atoms in Molecules*, Wiley-VCH, Weinheim, 2007.

2 (*a*) U. Flierler and D. Stalke, in *Structure and Bonding*, ed. D. Stalke, Springer, New York, 2012, vol. 146, p. 1; (*b*) I. L. Kirby, M. B. Pitak, S. J. Coles and P. A. Gale, *Chem. Lett.*, 2015, **44**, 2; (*c*) P. Macchi, J. M. Gillet, F. Taulelle, J. Campo, N. Claiser and C. Lecomte, *IUCrJ*, 2015, **2**, 441; (*d*) K. A. Lyssenko, *Mendeleev Commun*., 2012, **22**, 1; (*e*) Yu. V. Nelyubina, A. A. Korlyukov and K. A. Lyssenko, *Mendeleev Commun*., 2014, **24**, 286; (*f*) K. A. Lyssenko, A. V. Vologzhanina, Yu. V. Torubaev and Yu. V. Nelyubina, *Mendeleev Commun*., 2014, **24**, 216.

3 J. Gomes, *J. Mol. Struct.: THEOCHEM*, 1983, **93**, 111.

4 F. Weinhold, *J. Comput. Chem*., 2012, **33**, 2440.

5 (*a*) G. Merino, A. Vela and T. Heine, *Chem. Rev*., 2005, **105**, 3812; (*b*) C. S. López and Á. R. de Lera, *Curr. Org. Chem.*, 2011, **15**, 3576.

6 R. F. W. Bader, T. S. Slee, D. Cremer and E. Kraka, *J. Am. Chem. Soc.*, 1983, **105**, 5061.

7 C. L. Firme, N. B. P. Barreiro, P. M. Esteves and R. J. Correa, *J. Phys. Chem. A*, 2008, **112**, 686.

8 J. Cioslowski, S. T. Mixon and W. D. Edwards, *J. Am. Chem. Soc.*, 1991, **113**, 1083.

9 (*a*) P. L. A. Popelier and G. Logothetis, *J. Organomet. Chem.*, 1998, **555**, 101; (*b*) S. Scheins, M. Messerschmidt, M. Gembicky, M. Pitak, A. Volkov, P. Coppens, B. G. Harvey, G. C. Turpin, A. M. Arif and R. D. Ernst, *J. Am. Chem. Soc*., 2009, **131**, 6154; (*c*) W. Scherer, P. Sirsch, D. Shorokhov, G. S. McGrady, S. A. Mason and M. G. Gardiner, *Chem. Eur. J*., 2002, **8**, 2324.

10 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09, Revision A.01*, Gaussian, Inc., Wallingford, CT, 2009.

11 T. A. Keith, *AIMAll (Version 16.01.09)*, 2016, aim.tkgristmill.com.

12 N. O. J. Malcolm and P. L. A. Popelier, *Faraday Discuss*., 2003, **124**, 353.

13 R. F. W. Bader and M. A. Austen, *J. Chem. Phys*., 1997, **107**, 4271.

14 (*a*) A. V. Vologzhanina, A. A. Korlyukov, V. V. Avdeeva, I. N. Polyakova, E. A. Malinina and N. T. Kuznetsov, *J. Phys. Chem. A*, 2013, **117**, 13138; (*b*) A. F. Smol’yakov, A. A. Korlyukov, F. M. Dolgushin, E. V. Balagurova, I. T. Chizhevsky and A. V. Vologzhanina, *Eur. J. Inorg. Chem*., 2015, 5847.

Received: 26th February 2016; Com. 16/4858