

Natural bond orbital approach to the transmission of substituent effect through the fulvene and benzene ring systems

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Abstract Electronic structure of 22 monosubstituted derivatives of benzene and exocyclically substituted fulvene with substituents: B(OH)₂, BH₂, CCH, CF₃, CH₃, CHCH₂, CHO, Cl, CMe₃, CN, COCH₃, CONH₂, COOH, F, NH₂, NMe₂, NO, NO₂, OCH₃, OH, SiH₃, SiMe₃ were studied theoretically by means of Natural Bond Orbital analysis. It is shown, that sum of π -electron population of carbon atoms of the fulvene and benzene rings, $pEDA(F)$ and $pEDA(B)$, respectively correlate well with Hammett substituent constants σ_p^+ and aromaticity index NICS. The substituent effect acting on pi-electron occupation at carbon atoms of the fulvene ring is significantly stronger than in the case of benzene. Electron occupations of ring carbon atoms (except C1) in fulvene plotted against each other give linear regressions with high correlation coefficients. The same is true for *ortho*- and *para*-carbon atoms in benzene. Positive slopes of the regressions indicate similar for fulvene and benzene kind of substituent effect – mostly resonance in nature. Only the regressions of occupation at the carbon atom in *meta*-

position of benzene against *ortho*- and *para*-positions gives negative slopes and low correlation coefficients.

Keywords DFT · Fulvene · NBO · $pEDA$ · Substituent effect

Introduction

Fulvene, a non-alternant isomer of benzene differs from it by almost all possible characteristics. It is unstable, its ASE (aromatic stabilization energy) equals to -3.1 whereas for benzene it is $32.4 \text{ kcal mol}^{-1}$ [1]. Fulvene is also chemically reactive [2], whereas benzene is rather inert [3]. Substituent effects influence the fulvene ring much stronger [4] than benzene [5]. In the case of benzene, typical approaches concern the di-substituted species, in which one group is fixed (so called “reaction site”, Y) and another one, X, varies [6–10]. Thus, the charge transfer in benzene derivatives takes place between X and Y and is transmitted by the aromatic ring [11]. In these cases a classical measure of transmission is just reaction constant ρ which compared for two systems indicates in which of them the transmission is easier, or in other words which of them is more sensitive for substituent effect [12, 13]. Transmission depends on nature of the reaction, medium in which it is carried out and obviously on the distance between the substituent and the reaction site [14, 15]. In cases where there is no experimental study in which the Hammett-like approach is applied to physicochemical properties but instead some quantum-chemically derived quantities, a similar understanding of the transmission can be in use *e.g.*, linear regression between $2p_z$ occupations for two atoms in a ring may indicate which of them is stronger influenced by a substituent. In the case of fulvene, most studies and interpretations of the substituent effects on structural and

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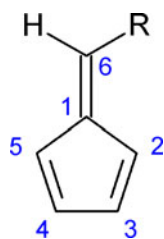


Fig. 1 The numbering scheme for the substituted fulvene molecule

other properties are related to the exocyclic substitution [4, 16–20]. Most aromatic indices exhibit strong variability and intercorrelate for 6-substituted derivatives of fulvene [20] which is not the case for monosubstituted benzene derivatives [11, 21]. Moreover, in the case of strongly electron donating substituents, fulvene exhibits clearly aromatic properties [20]. Due to these differences in response to substituent effects, a comparison of substituent effects influence on electron structure of fulvene and benzene seems to be interesting and therefore is the subject of this paper.

Some questions arise: how the pi-electron structure looks for the ring of fulvene and for the linking bond between the ring and the substituent (C1C6 bond, see Fig. 1). Then, how in detail the substituents affect pi-electron population for individual carbon atoms in 6-substituted fulvene derivatives. Finally, we intend to show a difference between the substituent effect in alternant hydrocarbon exemplified by benzene and non-alternant one – fulvene.

Methods

All calculations were performed at the B3LYP/6-311+G(d,p) level of theory using Gaussian 03 suite of programs [22]. Geometry optimizations were followed by frequency calculations to prove that the obtained stationary points are true minima on the potential energy surface. Natural Bond Orbital [23] analysis was performed by NBO 5.G program interfaced to Gaussian03. NICS [24] aromaticity index was calculated as a shielding constant of a ghost atom located at the geometric center of the ring taken with minus sign.

The *pEDA* [acronym from: **pi** Electron **D**onor-**A**ceptor] index was calculated by summation of the occupations of

$2p_z$ Natural Atomic Orbitals (NAOs) of benzene ring carbon atoms and subtracting number 6 – as for the ideal sextet (Eq. 1). This definition is slightly modified comparing to the original one [25].

$$pEDA(B) = \sum_{j=1}^6 \pi_{benzene}^j - 6 \quad (1)$$

where j index runs over all six benzene carbon atoms and $\pi_{benzene}$ is the occupation of the j th $2p_z$ NAO.

For the fulvene ring the definition is similar (Eq. 2) with the exception that the summation runs over only five atoms of the ring and to obtain *pEDA(F)* as relative value to the unsubstituted fulvene molecule we subtract the number 5. In this way the *pEDA(F)* parameter is comparable with that for benzene derivatives.

$$pEDA(F) = \sum_{j=1}^5 \pi_{fulvene}^j - 5 \quad (2)$$

The j index runs over all five fulvene ring carbon atoms and $\pi_{fulvene}$ is the occupation of the j th $2p_z$ NAO.

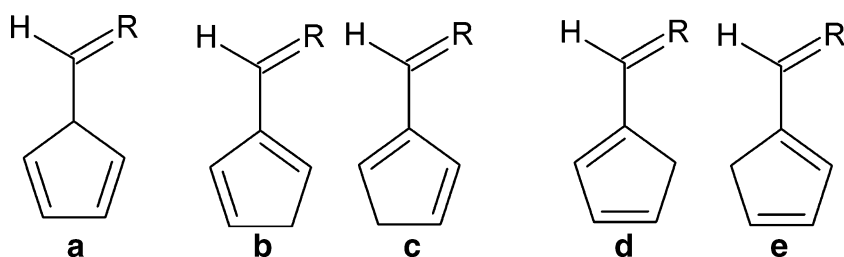
22 substituted species span a wide range of substituents with varying donor-acceptor properties: B(OH)₂, BH₂, CCH, CF₃, CH₃, CHCH₂, CHO, Cl, CMe₃, CN, COCH₃, CONH₂, COOH, F, NH₂, NMe₂, NO, NO₂, OCH₃, OH, SiH₃, SiMe₃ and all of them plus an unsubstituted compound are taken into account in Figs. 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17 and 18.

Results and discussion

Let us begin with a glimpse at the substituent effect in *exo*-cyclically monosubstituted fulvene and benzene presented by means of resonance structures. Figures 2 and 3 present the resonance structures in which R may be either electron donating (D) or electron accepting (A). The ring carbon atoms with only two single bonds to other carbon atoms are charged, either negatively when R = D, or positively if R = A.

There are three aspects to be considered: (i) how differences in substituent effect transmission through benzene and fulvene affect the overall electron structure of benzene and fulvene rings, (ii) how they operate for

Fig. 2 Resonance structures of the fulvene molecule



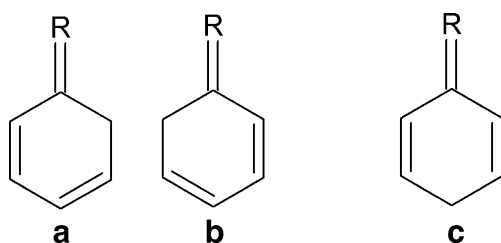


Fig. 3 Resonance structures of the benzene molecule

individual carbon atoms in the rings and (iii) how the changes in the ring correlate with those in the transmitter of the substituent effect: C1=C6 moiety.

First, let us consider the overall effects observed in fulvene and benzene derivatives. In both cases $pEDA$ [25] correlate well with Hammett σ_p^+ [4, 26] and aromaticity index NICS [24] as shown in Fig. 4, 5, 6 and 7. The first observation is that π -electron populations at carbon atoms of the ring in fulvene and benzene, $pEDA(F)$ and $pEDA(B)$ plotted against σ_p^+ differ dramatically in values of the slopes of the regressions. Sensitivity of fulvene and benzene rings on substituent effect estimated by ratio of the slopes for fulvene and benzene derivatives is $0.245/0.155=1.58$. It means that in fulvene it is 1.58 times greater than in benzene derivatives. Alike is the situation for scatter plots of $pEDA$ against NICS. When $pEDA$ values for fulvene and benzene derivatives are plotted against each other, (Fig. 8) the regression shows qualitatively the same picture, the substituent effect on the π -electron population at carbon atoms in fulvene is 1.44 times greater than in benzene ring (Eq. 3). This difference in sensitivity on the substituent effect is caused by a strong π -electron accepting

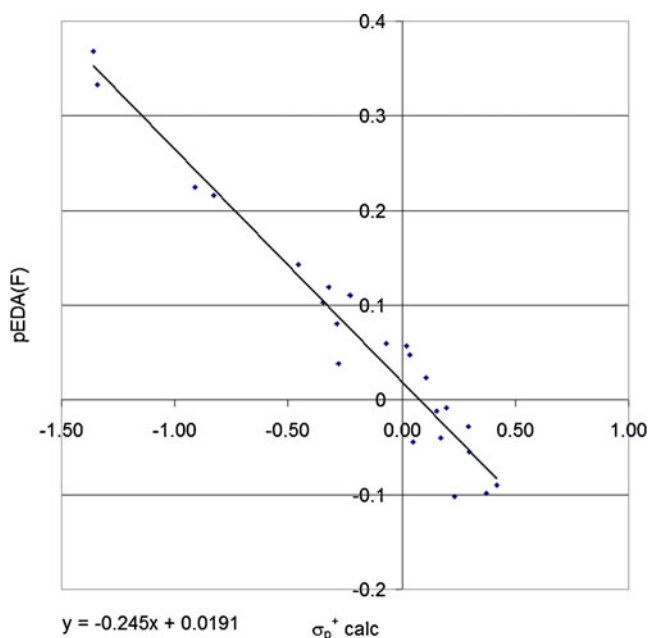


Fig. 4 Dependence of $pEDA(F)$ for fulvene on σ_p^+ with $cc=0.974$

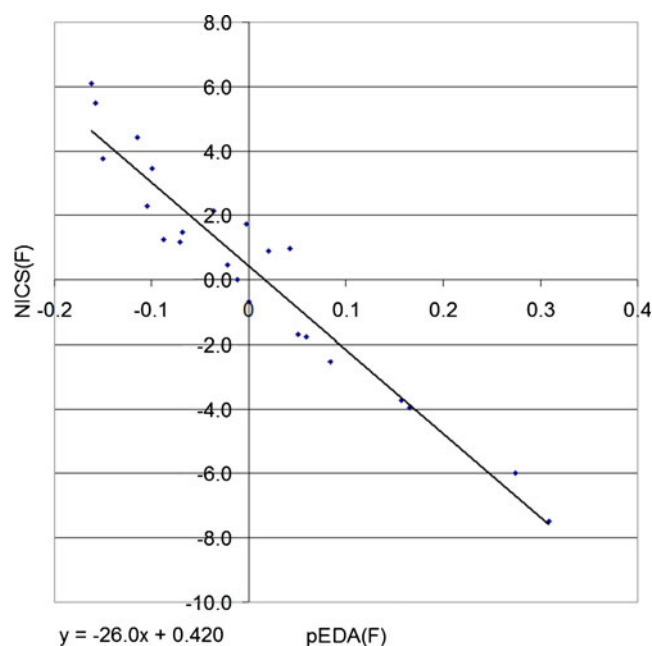


Fig. 5 Dependence of NICS(F) on $pEDA(F)$ with $cc=-0.963$

characteristics of fulvene ring, which contains 5 π -electrons and tends to achieve the Hückel value $4N+2$ electrons; whereas in the case of benzene containing 6 electrons no such effect takes place.

$$pEDA(F) = 1.44 pEDA(B) \quad (3)$$

In the following figures cc means correlation coefficient.

Next, let us consider how the population of π -electrons on the individual carbon atoms in fulvene ring depends on

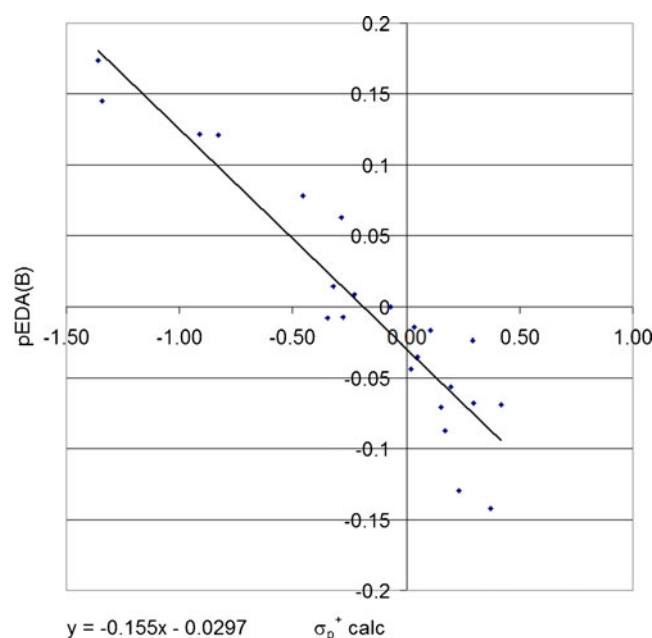


Fig. 6 Dependence of $pEDA(B)$ for benzene on σ_p^+ with $cc=-0.933$

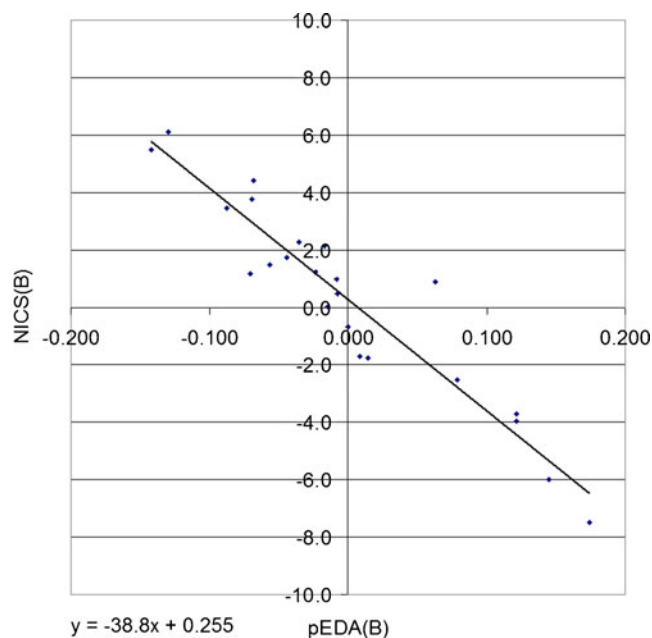


Fig. 7 Dependence of NICS(B) on $pEDA(B)$ for benzene with $cc=-0.945$

substituent constants. Figures 9, 10 and 11 present appropriate dependences.

All regressions presented in Figs. 9, 10 and 11 have acceptable correlation coefficients and hence their regression slopes may be the subject of further analysis. As we see, the slope for dependence of $2p_z$ occupation at C1 is 2.8 times greater than for mean value for $2p_z$ occupations at C3 and C4 and 5.7 times greater than mean value for $2p_z$ occupations at

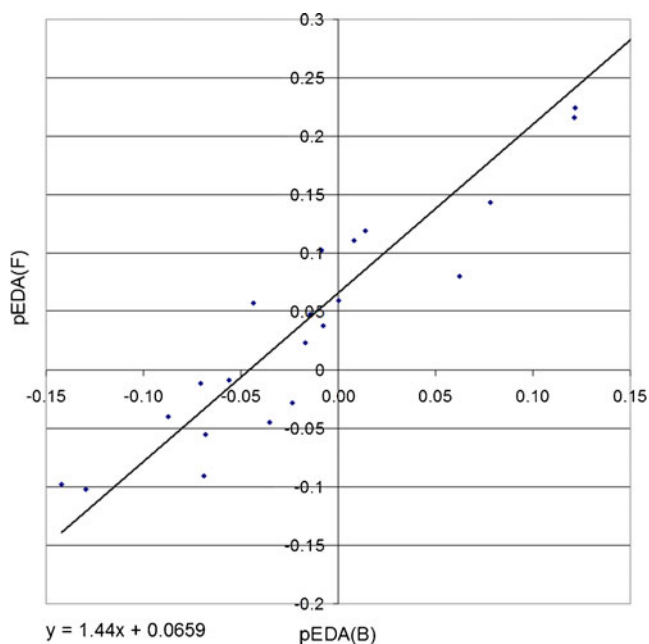


Fig. 8 Dependence of $pEDA(F)$ on $pEDA(B)$ with $cc=0.949$

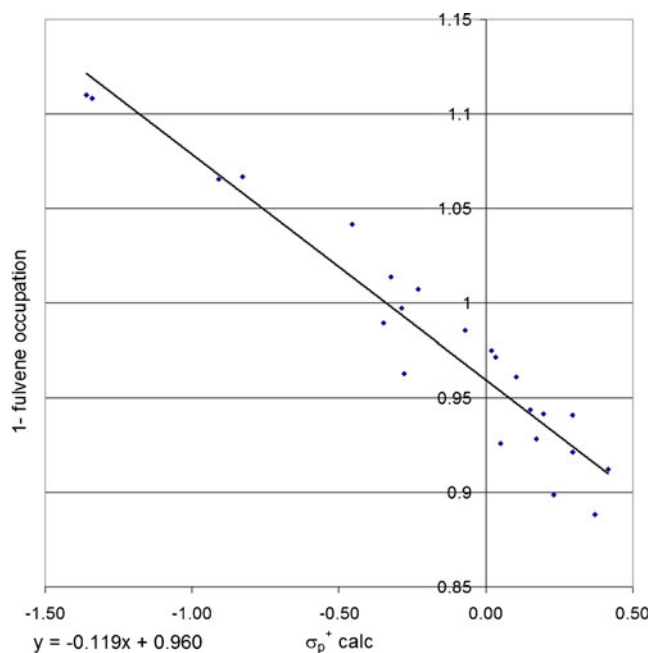


Fig. 9 Dependence of π -occupation of C1 atom in fulvene on substituent constants σ_p^+ with $cc=-0.960$

C2 and C5 despite the longer distance from substituent to C3 and C4 atoms.

Now, let us look at the direct comparison of substituent effect on π -electron population at individual carbon atoms in benzene and fulvene. Figures 12, 13, and 14 show the occupations at carbon atoms which are distant from the substituent by one, two, and three CC bonds. Figure 12

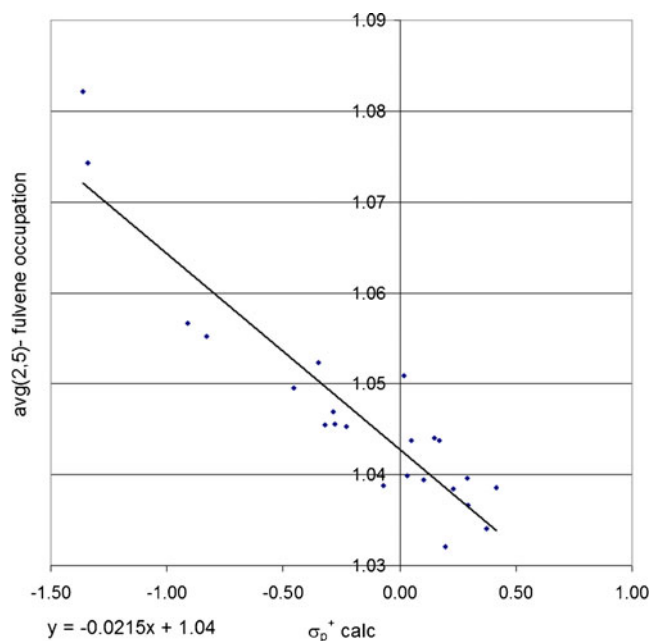


Fig. 10 Dependence of the averaged π -occupation of C2 and C5 carbon atoms in fulvene on substituent constants σ_p^+ with $cc=-0.924$

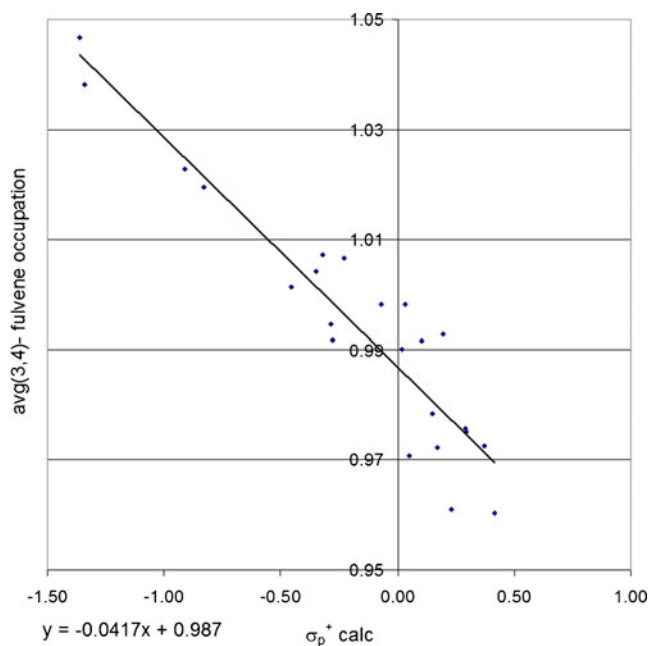


Fig. 11 Dependence of the averaged π -occupation of C3 and C4 carbon atoms in fulvene on substituent constants σ_p^+ with $cc=-0.936$

presents the dependence of π -orbital occupation of C1 in fulvene on π -orbital occupation of *ortho*-carbon atom in benzene. The slope of the regression is 1.45 and shows that π -occupation of carbon atom C1 in fulvene is 1.45 times more sensitive to the substituent effect than the *ortho*-carbon atom in benzene.

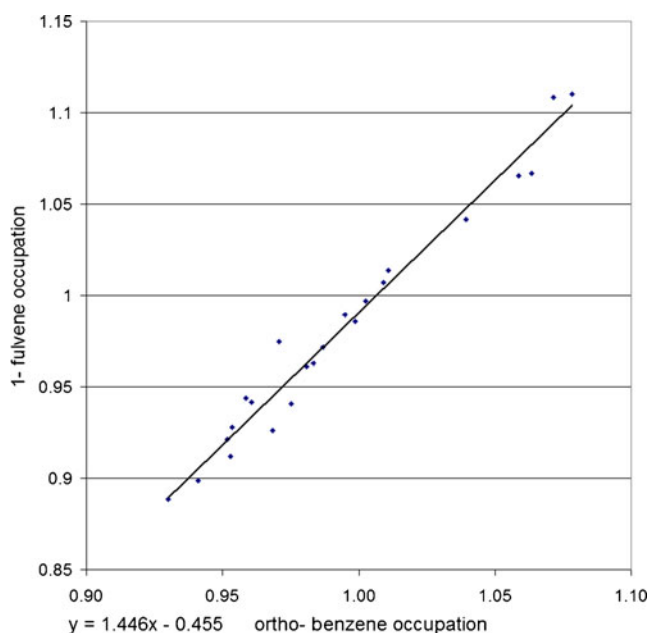


Fig. 12 Dependence of π -occupation of C1 atom of fulvene on occupation of *ortho*-carbon atom in benzene with $cc=0.986$

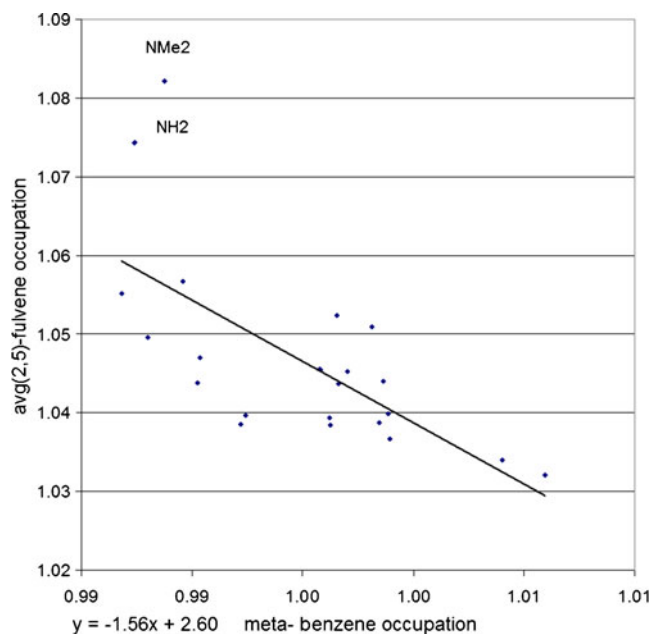


Fig. 13 Dependence of averaged π -occupations of C2, C5 atoms of fulvene on occupation of *meta*- carbon atoms of benzene with $cc=0.675$

A direct comparison reveals a very important difference between changes in $2p_z$ occupation at carbon atoms in benzene and fulvene rings. The slopes of the regression of π -occupation of C1 atom of fulvene *vs.* π -occupation of carbon atoms in *ortho*-position of benzene and of averaged π -occupations of C3, C4 atoms of fulvene *vs.* π -occupations

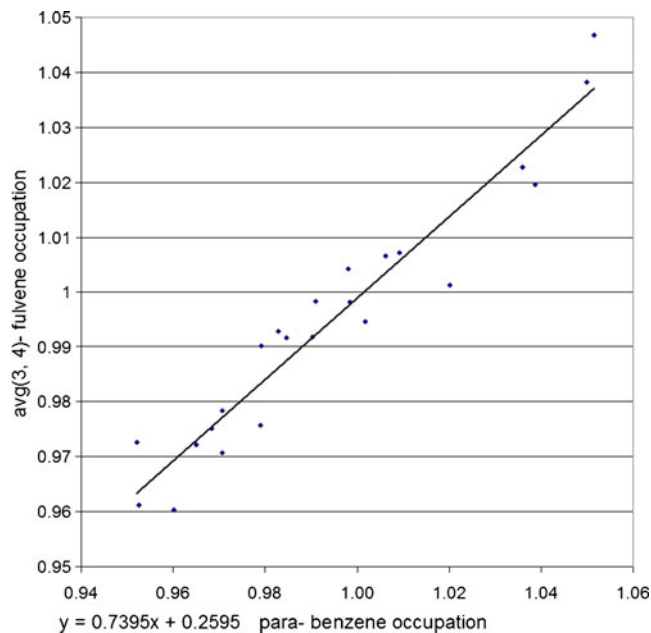


Fig. 14 Dependence of averaged π -occupations of C3, C4 atoms of fulvene on occupations at carbon atom in *para*-position of benzene with $cc=0.962$

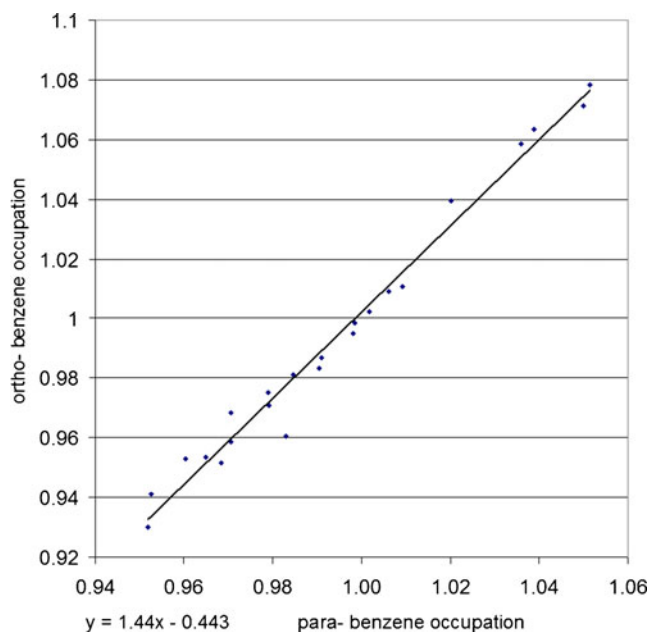


Fig. 15 Dependence of π -occupation of *ortho*- on the π -occupation at *para*-carbon atoms in benzene derivatives with $cc=0.991$

of carbon atoms in *para*-position of benzene are positive and with relatively high correlation coefficients. Completely different is the regression of π -occupations of averaged C2, C5 atoms of fulvene *vs.* *meta*-position of benzene. Its slope is negative and correlation coefficient is very low. How to interpret this strange result? As presented in Figs. 2 and 3, in the case of fulvene, all carbon atoms in the ring may

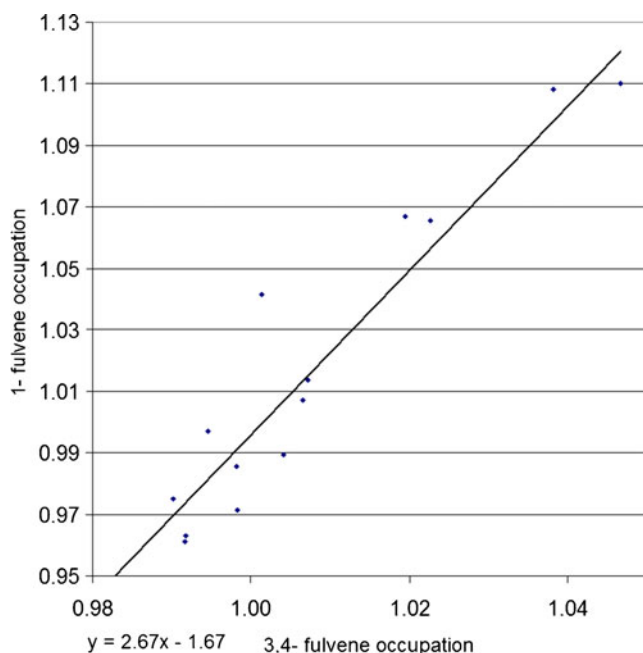


Fig. 16 Dependence of π -occupation in C1-carbon atom on the averaged π -occupations at C3, C4 atoms in fulvene derivatives with $cc=0.960$

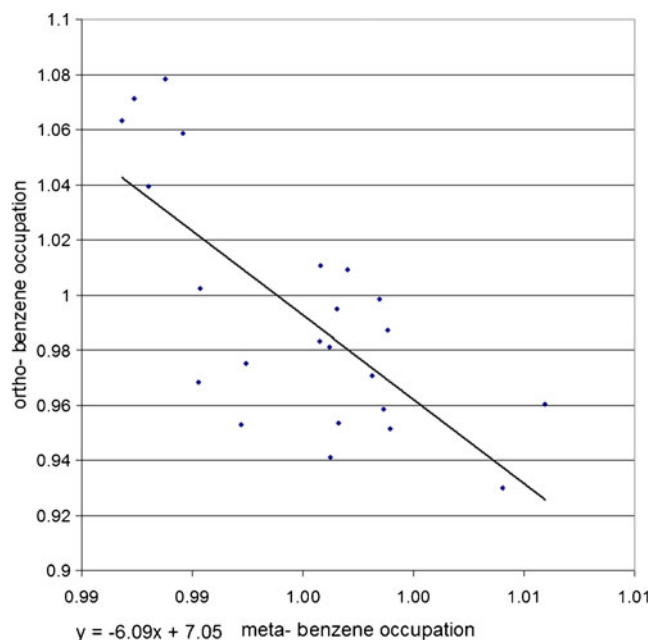


Fig. 17 π -occupations of *ortho*- *vs.* *meta*- position in benzene derivatives with $cc=-0.720$

communicate with the substituent by resonance effect, withdrawing or donating π -electrons from the substituent if it is donating/withdrawing in nature. That is not the case of benzene, where only two *ortho*-positions and one *para*- are able to communicate with the substituent by means of resonance effect. The *meta*- position is more strongly influenced by inductive/field effect than by resonance

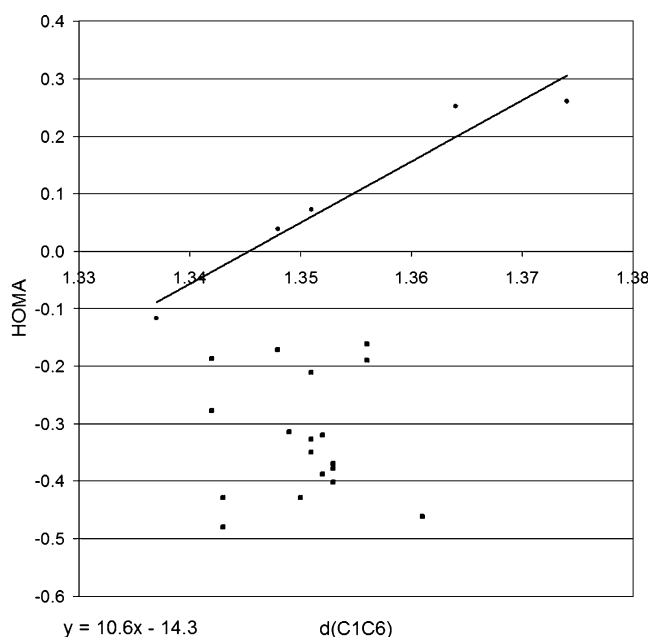


Fig. 18 The dependence of HOMA of the ring on C1C6 bond lengths with $cc=0.970$

[27, 28]. The inductive/field effect is mostly electrostatic in nature and acting through the space [29–31]. Thus, the π -occupation at carbon atoms in *meta*- position of benzene has weak contribution from resonance effect, react *via* different mechanism on substituent effect than is the case for fulvene in 2,5 positions.

This point is well supported by a direct comparison of slopes of the regressions of π -electron occupation for pairs of resonance accessible carbon atoms in benzene and fulvene derivatives, shown in Figs. 15 and 16.

Despite the fact that there are two *ortho*-carbon atoms in benzene ring and only one *para*-carbon atom, the substituent effect acts in *ortho*-position much stronger than in *para*- as documented by the slope of regression shown in Fig. 15 which is equal to 1.44 with correlation coefficient 0.991. In the case of the fulvene (Fig. 16) the slope for the regression of π -occupation at C1- vs. averaged values of π -occupation at C3 and C4 atoms is even larger – 2.67 and the correlation coefficient amounts to 0.959. It seems reasonable to relate this difference to much stronger withdrawing ability of 4N+1 ring of fulvene than that of benzene fulfilling the Hückel rule.

To support the conclusion dealing with a different mechanism presented in discussion of results shown in Figs. 12, 13 and 14, we plotted the π -electron occupation of carbon atoms in *ortho*- against *meta*- position in benzene shown in Fig. 17. There are two important differences when compared with the picture in Figs. 15 and 16. The slope in Fig. 17 is negative and the correlation coefficient much lower. Additionally, it is also shown that the range of π -occupation changes in the case of carbon atoms in *meta*- position is only 0.02e whereas for atoms in *para*-position it is 0.16e. This is in excellent agreement with the simple reasoning that results from Figs. 2 and 3: carbon atom in *meta*- position in benzene is not accessible for resonance interactions (as far as only single excited resonance structures are concerned) [32] and other effects may play an important role.

Another aspect of changes in π -electron structure of 6-substituted fulvene derivatives is a relation of parameters describing the C1C6 bond, the transmitter of the substituent to the ring, and the ring itself. Figure 18 presents the dependence of HOMA aromaticity index [33, 34] on the C1C6 bond lengths.

It is clear that for π -electron donating substituents (NMe₂, NH₂, OMe, OH and F in Fig. 18), parameters of the ring (HOMA) and of the bond (bond length) vary in line with a very high correlation coefficient (cc=0.970) indicating strong cooperation of π -electron structure in the ring and in the bond. This agreement is dramatically broken for electron accepting substituents, which form a cluster of points below the line HOMA=0. For the latter case it may be interpreted as follows: both parts of molecules, the ring and the substituent

from the point of view of π -electron properties, are the electron withdrawing moieties. Thus, there does not exist one dominant effect, but rather a composition of many effects, which contribute to the changes in geometry of both kinds of fulvene derivatives and hence lead to irregular changes.

Conclusions

- (i) π -electron population at carbon atoms of the ring - *pEDA* in fulvene and benzene correlates well with substituent constant σ_p^+ and with aromaticity index NICS indicating that *pEDA* may serve in some cases as a useful indicator of aromaticity.
- (ii) π -electron occupations of carbon atoms in benzene and in fulvene rings are mutually well correlated for positions *ortho*- and *para*- in benzene and 1 and 3,4 positions in fulvene with positive regression slopes, whereas for position *meta*- vs. 2,5 in fulvene correlation is much worse and with a significant negative slope.
- (iii) Direct comparison by means of linear regression of π -electron occupation at *ortho*- vs. *meta*- carbon atoms in benzene gives negative regression slope and weak correlation coefficient. This is explained by a different mechanism of substituent effect on *ortho*- and *meta*- carbon atoms: the dominant resonance effect in the case of *ortho*-atoms and dominant inductive/field effect in the case of *meta*- positions.
- (iv) The difference between substituent effect in benzene and fulvene is not only quantitative (greater effects in fulvene) but also that in fulvene all carbon atoms in the ring communicate by resonance with the substituent whereas in benzene ring only *ortho*- and *para*-positions can do that.

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References

1. Cyrański MK (2005) Chem Rev 105:3773–3811; isodesmic reaction #11 in Table 13, p 3793
2. Lloyd D (1990) The chemistry of conjugated compounds: To be or not to be like benzene. Wiley, Chichester, pp 91–94
3. Smith MB, March J (2001) March's Advanced Organic Chemistry, Reactions, Mechanisms and Structure. Wiley, pp 693–694
4. Stepień BT, Cyrański MK, Krygowski TM (2001) Chem Phys Lett 350:537–542
5. Krygowski TM, Ejsmont K, Stepień MK, Poater J, Sola M (2004) J Org Chem 69:6634–6640
6. Jaffe HH (1953) Chem Rev 53:191–261
7. Charton M (1981) Progr Phys Org Chem 13:119–251

8. Exner O (1988) Correlation analysis of chemical data. Plenum, New York
9. Krygowski TM, Stepień BT (2005) Chem Rev 105:3482–3512
10. Exner O, Bohm S (2006) Curr Org Chem 10:763–778
11. Krygowski TM, Stepień BT (2004) Pol J Chem 68:2213–2217
12. Exner O (1972) In: Chapman NB, Shorter J (eds) Advances in linear free energy relationships, chpt 1. Plenum, London, pp 20–27
13. Godfrey M (1991) In: Zalewski RI, Krygowski TM, Shorter J (eds) Similarity models in organic chemistry, biochemistry and related fields. Elsevier, Amsterdam, pp 149–175
14. Hammett LP (1970) Physical organic chemistry, Chpt. IX. McGraw–Hill, New York, pp 251–290
15. Krygowski TM, Fawcett WR (1977) J Chem Soc Perkin II, 2033–2037
16. Ammon HL (1974) Acta Cryst B30:1731–1738
17. Wingert LM, Staley SV (1992) Acta Cryst B 48:782–789
18. Krygowski TM, Ciesielski A, Cyranski MK (1995) Chem Papers 49:128–132
19. Peterson ML, Stranad JT, Markotan TP, Morales CA, Staley SV (1999) J Org Chem 64:9067–9076
20. Stepień BT, Krygowski TM, Cyrański MK (2002) J Org Chem 67:5987–5992
21. Krygowski TM, Stepień BT, Cyranski MK, Ejsmont K (2005) J Phys Org Chem 18:886–891
22. Gaussian 03, Rev E.01 (2001) Gaussian Inc, Wallingford CT
23. Reed AE, Curtiss LA, Weinhold F (1988) Chem Rev 88:899–926
24. PvR S, Maerker C, Dransfeld A, Jiao H, NJRvE H (1996) J Am Chem Soc 118:6317–6318
25. Oziminski WP, Dobrowolski JC (2009) J Phys Org Chem 22:769–778
26. Hansch C, Leo A, Taft RW (1991) Chem Rev 91:165–195
27. Taft RW, Lewis IC (1958) J Am Chem Soc 60:2436–2443
28. Exner O (1972) Chapt 1. In: Chapman NB, Shorter J (eds) Adv. In Free Linear Energy relationships. Plenum, London, pp 35–41
29. Bowden K, Grubbs EJ (1996) Chem Soc Rev 25:171–177
30. Wiberg KB (2002) J Org Chem 67:161–168
31. Wiberg KB (2002) J Org Chem 67:4787–4794
32. Krygowski TM, Palusiak M, Płonka A, Zachara-Horeglad JE (2007) J Phys Org Chem 20:297–306
33. Kruszewski J, Krygowski TM (1972) Tetrahedron Lett 3839–3842
34. Krygowski TM (1993) J Inf Comput Sci 33:70–78