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Separation of the Energetic and Geometric Contributions to Aromaticity. Part VII. Changes of the Aromatic Character of the Rings in Naphthalene Induced by the Charged Substituent CH_2^+. The Dependence on the Position of the Substitution, Torsion Angle and the Exocyclic Bond Length Variation

Tadeusz M. Krygowski,[†] Michał K. Cyrański,[†*] Kazuhide Nakata,[‡] Mizue Fujio,[‡] Yuho Tsuno.[‡]
[†] Department of Chemistry, University of Warsaw, ul. L. Pasteura 1,
02-093 Warsaw, Poland
[‡] Institute for Fundamental Research of Organic Chemistry, Kyushu University, Hakozaki, Higashi-ku,
Fukuoka 812, Japan.

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Abstract: The 1- and 2- CH_2^+ derivatives are studied in terms of variation of the C-C exocyclic bond and the torsion around it in order to show the structural consequences in naphthalene moiety. It results that rotation around and elongation of this bond lead to the fluctuation of the electronic charge at atoms and variation of CC bond length in the whole moiety. The latter changes allow to evaluate variation in aromatic character of both rings in the system leading to the conclusion that rotation is a more substantial factor causing decrease of aromaticity than the mere elongation. Changes in the aromatic character are greater in the case of 2-substituted species than those observed in position 1.

Introduction

The CH_2^+-group is a strongly electron-accepting substituent whose activity depends evidently on the torsion angle.[1,2] Analysis of the derivatives of benzylic cation leads to the conclusion that the more non-coplanar is the conformation of this group with the plane of the aromatic ring (i.e. the greater torsion angle) - the smaller is the delocalization of the positive charge at the ring and hence its higher aromatic character.[3] A recent study on the CH_2^+ substituted arenes[4] has shown that the changes of the molecular geometry of particular rings and therefore also of their aromatic character depend strongly on the position of the substituent. In some positions the CH_2^+ substituent may induce long-range structural changes being in fact the quinoidal structure leading to the localization of the double bonds. Analysis of the aromatic character in this type of systems by use of the HOMA index[5] with the separation into the EN and GEO terms[6] has shown that the decrease of aromaticity is mostly due to the geometric term, i.e. to an increase of the bond length alternation. The exocyclic CC bond linking the CH_2^+ group with the arene moieties varied in length depending on the type of arene and the position, following the Hammett-Streitwieser position constants.[7,8] These findings prompted us to undertake the study in which the C-

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CH_2^+ bond is the subject of changing its length and independently of the torsion angle in the 1 and 2 substituted naphthalene derivatives. In this way two differently interacting π-systems can be investigated in respect of the structural consequences in the naphthalene moiety and its aromatic character.

Model calculations

Two kinds of geometry optimized calculation were carried out for 1- and 2- CH_2^+ derivatives of naphthalene, using Gaussian 94[9] program at the level HF/ 6-31G*:

i) the torsion angle $HC_{1'}C_1C_2$ (τ_1 in 1-substituted species) and $HC_{2'}C_2C_3$ (τ_2 in the 2-substituted one) is varied from 0° to 90° by 10° and

ii) the $C_1C_{1'}$(or $C_2C_{2'}$) bond is varied from 1.35 Å to 1.53 Å by 0.02 Å.

In both series the other molecular parameters were optimised and Mulliken population analysis[10] was carried out.

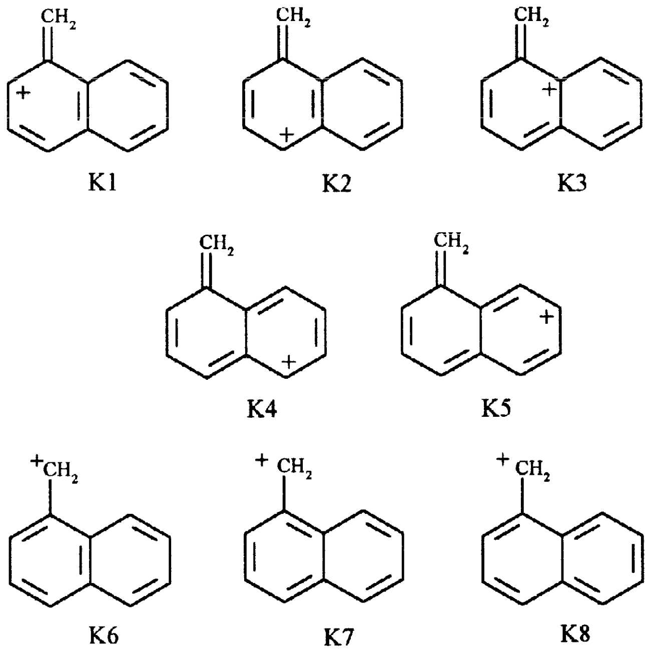
The 1-CH_2^+naphthalene derivative

Any change of the torsion angle τ_1 leads to substantial changes in the $C_1C_{1'}$ bond lengths from 1.348 Å for 0° to 1.454 Å for 90°, accompanied with marked changes in aromaticity of the substituted ring - HOMA value varies from 0.514 to 0.794, respectively. Contrary to that, the changes in the other ring are smaller: the HOMA values are 0.899 and 0.793, respectively, approaching in both rings the value for an unperturbed naphthalene (0.780).[4] Thus in the case where the CH_2^+ group is perpendicular to the naphthalene moiety both rings are equally aromatic with the dearomatization due to the geometric term (GEO term is 0.177, and 0.189, respectively), whereas, EN being very low (0.029 and 0.018). For comparison the Bird's I_6 index[11] calculated for these rings changes from 71.5 to 77.7 and from 84.4 to 76.9, for substituted and unsubstituted ring, respectively.

The picture is quite different for the case with the varied $C_1C_{1'}$ bond length. Here the change of the CC bond length from 1.35 Å to 1.53 Å is accompanied by the changes in HOMA values from 0.514 to 0.728 for the first ring but practically without changes in the other ring: 0.899 and 0.885, respectively. If we take into account bond length as for 90° twisted CH_2^+ group (i.e. 1.45 Å) then the HOMA is 0.646 and 0.892 for the first and second ring, respectively.

The above-mentioned changes in geometry reflected in the aromatic character of the ring in question may also be interpreted in terms of changes of the canonical structures weights for 1-CH_2^+-naphthalene. Fig. 1 presents the canonical structures for 1-CH_2^+ derivative. Elongation of the exocyclic CC bond takes place in both cases, but in the case of torsion it is smaller (from 1.348 Å for τ_1=0° to 1.454 Å for τ_1=90°). Thus the longer is the CC bond, the smaller is the weight of the canonical structures calculated *via* the HOSE model[12-13] with the charge transfer from the CH_2^+ group to the aromatic moiety (i.e. K1+...+K5 in Fig. 1). This sum is equal to 76.6% for the initial state (i.e. for the fully optimised molecular geometry) and goes down to 57.4%, for the $C_1C_{1'}$ bond length = 1.53 Å. Surprisingly, this sum is only 48.4% for the case with τ_1 = 90° for which $C_1C_{1'}$ bond length = 1.45 Å. If only the extension of this bond is applied in calculations, all other parameters being optimized, then for $C_1C_{1'}$ bond of the length 1.45 Å the sum is 63.3%. The following conclusion may be drawn from these data: the torsion of $HC_{1'}C_1C_2$ decreases the overlap of $2p_z$ orbital at $C_{1'}$ with the π electron system of the aromatic moiety to zero for the perpendicular conformation leading to a very small (if any) intramolecular charge transfer, whereas in the case of elongation of this bond the overlap is gradually decreased but still exists, leading to much stronger contributions of the quinoidal structures, i.e. the greater values of the above-mentioned above sum. This conclusion is supported by the high correlation between the electronic charge at $C_{1'}$, $q_{1'}$ values, and the sum of the weights (K1+...+K5) being -0.998 for the case with the torsion, and -0.996 for the case with $C_1C_{1'}$ bond length variation. It should also be mentioned that the changes at $q_{1'}$ are very strongly correlated with the $C_1C_{1'}$ bond lengths in both cases with the correlation coefficient more than 0.997. Thus the final correlation between the weight of the sum of quinoidal structures (K1+...+K5) and the $C_1C_{1'}$ bond length is expected and supported by the correlation coefficient R= -0.989 for both cases.

Fig. 1. Canonical structures of 1-CH_2^+ naphthalene derivatives



The 2-CH_2^+ naphthalene derivative

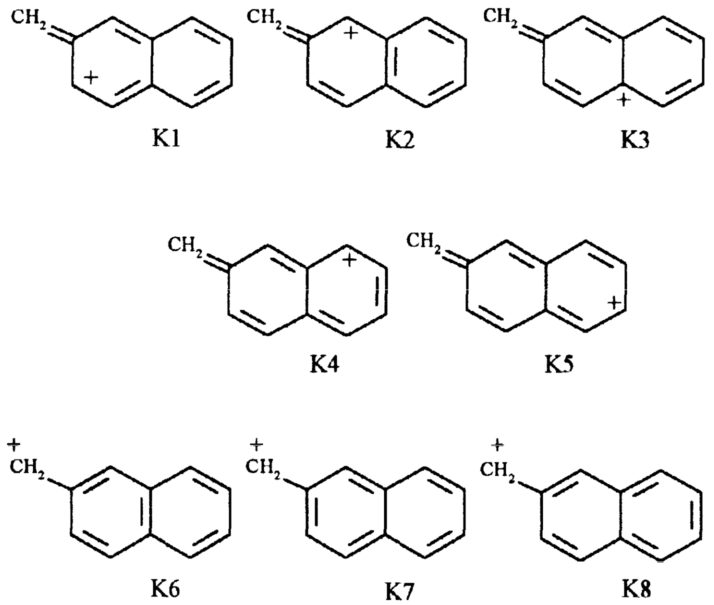
A Similar analysis carried out for the 2-substituted derivative leads to a slightly different picture. Variation of the torsion angle τ_2 changes the $C_2C_{2'}$ bond length from 1.351 Å for τ_2=0° to 1.452 Å for τ_2=90°, i.e. in a similar but slightly less extensive way than for the 1-derivative. These changes lead to the decrease of the aromatic character of both rings: from 0.409 to 0.760 for the substituted ring and from 0.742 to 0.794 for the other ring. This may result from induction of the long-range quinoidal structure overpassing onto the unsubstituted ring. The difference is also in the character of dearomatization of the substituted ring: almost 1/4 is due to the energetic term, EN= 0.153 for the substituted ring and 1/5 for the other ring (EN = 0.042) the remainder being caused by the geometric term. The Bird's I_6[11] changes from 63.79 to 75.74 and 75.42 to 76.96, for substituted and unsubstituted ring, respectively. Again it may be interpreted as a result of quinoidal structure expansion which always leads to the lengthening of the averaged bond length and hence to an increase of EN term. In the perpendicular conformation aromaticity of both rings becomes very similar to the dearomatization, mostly (about 90%) due to the geometric term.

The extension of the $C_2C_{2'}$ bond lengths also leads to a different picture. The aromatic character of the substituted ring increases from HOMA = 0.409 for the optimized geometry to 0.610 for the case with $C_2C_{2'}$ bond length = 1.53 Å. For both states the HOMA value is lower by about 0.1 than in the analogous situation for the 1-derivative. For the unsubstituted ring the changes for both derivatives are similar.

Canonical structures for 2-substituted naphthalene are presented in Fig. 2. The changes in τ_2 from 0° to 90° lead to a substantial decrease of the quinoidal structure weight expressed by the sum (K1+...+K5) from 81.0% to 51.4%, respectively. For both limits of the torsion angle, the weight of the quinoidal structures is larger than in the 1-substituted derivative. The same finding is observed for expansion of the $C_2C_{2'}$ bond length. For the values of bond lengths: 1.35 Å, 1.45 Å (approximately equal to the case of the torsion with τ_2 = 90°) and 1.53 Å the associated sum of the weights of the quinoidal structures is 81.1%, 66.3% and 59.1%, respectively.

Following the same interpretation as in the case of 1-substituted derivative we have analysed the inter-correlations between the charge at the exocyclic carbon, $q_{2'}$, the $C_2C_{2'}$ bond length and the sum of weights of the quinoidal structures (K1+...+K5). All correlation coefficients were better than 0.99 in modulo. The following conclusion may be drawn: **The shorter is the $C_1C_{1'}$ (or $C_2C_{2'}$) bond the greater are the weights of the quinoidal structure K1...K5 and the less positive is the charge at $C_{1'}$ ($C_{2'}$). The short bonds linked to the aromatic moiety decrease its aromatic character along the path of the developped quinoidal structure.**

Fig. 2. Canonical structures of 2-CH_2^+ naphthalene derivatives

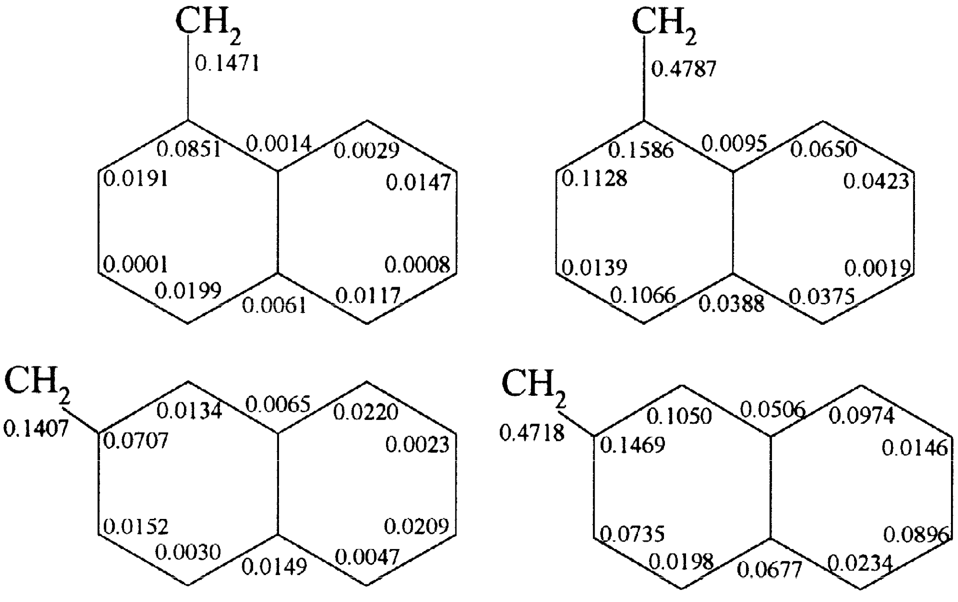


Variation of the electronic charge at carbon atoms

Undoubtedly the greatest changes in the values of the electronic charge q_i are at the position of the exocyclic carbon atoms. The changes of $q_{1'}$ ($q_{2'}$) are reflected in the charge density changes at all other carbon atoms q_i which exhibit great variability in their values. Usually q_i correlate strongly with $q_{1'}$ ($q_{2'}$). Fig. 3 presents the ranges of the changes of q_i for both isomers and for both cases, i.e. for the changes of the torsion angles τ_1 and τ_2 and $C_1C_{1'}$ ($C_2C_{2'}$) bond lengths. These values inform about the sensitivity of various positions *i* to the changes of the electronic charge at $C_{1'}$ ($C_{2'}$), which is the source of the variability of all other changes. In other words, these values illustrate pulsation of the electron charges due to the CH_2^+ rotation or $C_1C_{1'}$ ($C_2C_{2'}$) bond elongation.

In the case of 1-substituted derivatives the changes in electron charges are mostly limited to the substituted ring: the sum of ranges in the substituted ring amounts to 69% for the twist around $C_1C_{1'}$ bond and 58% for the twist around $C_2C_{2'}$ in 2-substituted derivative. This is clearly the effect of a longer pathway for the intramolecular charge transfer in 2-substituted derivative, as illustrated in an earlier paragraph. For the changes of the torsion angle τ_1 (τ_2) an interesting rule can be observed: apart from the ipso carbon C_1 (or C_2) an increase of the range of q_i changes occurs at positions indicated in canonical structures (Figs 1 and 2) by a positive charge (an unexplained big range is only observed at C_8 in 1- CH_2^+naphthalene derivative). Qualitatively similar effects are observed for $C_1C_{1'}$ ($C_2C_{2'}$) elongation. The changes at ipso atoms C1 and C2 may be easily explained by a simple electrostatic picturing of the changes at CH_2^+; the other ones need to use the mesomeric effect.

Fig 3. Ranges of changes of q_i for changes of (a) $C_1C_{1'}$ ($C_2C_{2'}$) bond length and (b) torsion angle τ_1 (τ_2).



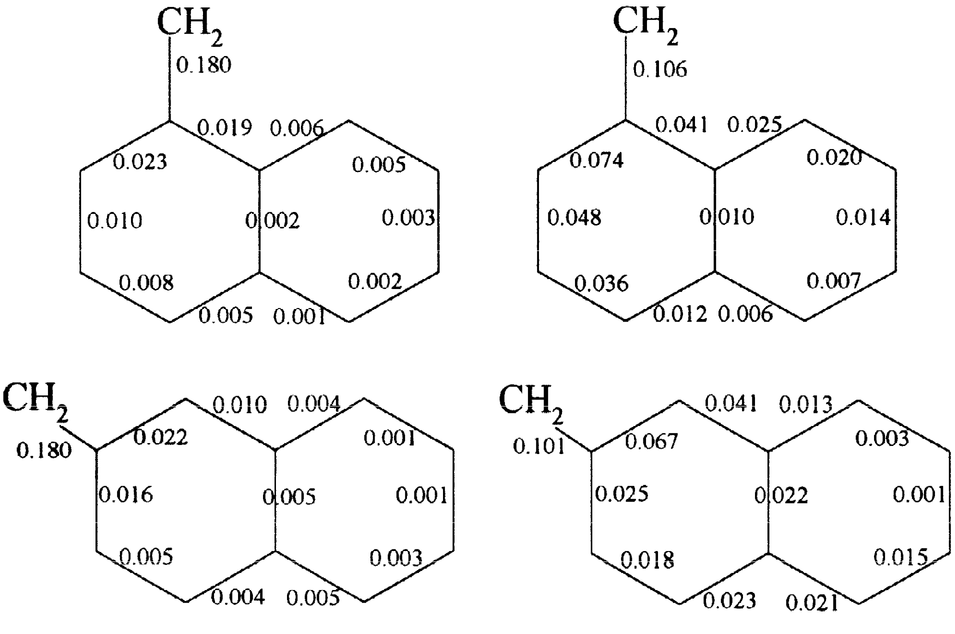
The barrier to rotation of CH_2^+ group is in both cases rather high, ca 220 kJ/mole, as compared with the energetic cost of the $C_1C_{1'}$ ($C_2C_{2'}$) elongation equal to ca 24 kJ/mole if the elongation is from 1.35 Å to 1.45 Å.

Variation of the CC bond length due to the changes in $C_1C_{1'}$($C_2C_{2'}$) bond lengths

Another molecular parameter varying considerably with the changes in $C_1C_{1'}$ ($C_2C_{2'}$) bond lengths is the individual CC bond length in the naphthalene moiety. Its range of variation is the highest for $C_1C_{1'}$ ($C_2C_{2'}$) bond lengths, which may be taken as an independent variable with which are compared the changes in bond lengths in naphthalene moiety. Fig. 4 presents the observed changes.

Comparison of the changes in bond lengths changes due to $C_1C_{1'}$($C_2C_{2'}$) elongation (by 0.18 Å) and those due to the changes in torsion angle τ_1 (τ_2) which produce the range of about 0.10 Å leads to an important observation that in the latter case smaller changes produce much greater changes of bond lengths in the naphthalene moiety than it is in the former case. It seems justified to conclude that twisting the C-CH_2^+ bond produces a much stronger structural effect than its elongation.

Fig 4. Ranges of the changes of bond lengths for changes of (a) $C_1C_{1'}$($C_2C_{2'}$) bond length and (b) torsion angle τ_1 (τ_2).



Conclusions

The Changes in the electron charge at atoms as well as in the aromatic character of the rings in 1- and 2-CH_2^+ -substituted naphthalenes differ due to the fact that in the second case the path of the intramolecular charge transfer (*via* a quinoidal structure) is transmitted over the whole molecule, whereas in the first case they are partly limited to the substituted ring only.

Rotation of the CH_2^+ group as well as the elongation of the C_{ipso} C_{exo} bond length causes the fluctuation (pulsation) of the electronic charges at carbon atoms which should be subject to a more refined study.

Rotation of the CH_2^+ group produces much bigger structural effects (bond lengths) and charge density changes at C-atoms than elongation of the C-CH_2^+ bond. Effects of rotation of the CH2+ group and of the elongation of C-CH_2^+ bond may be taken as a model for rotation and oscillation of substituent which should also lead to a similar "pulsation" of the charge density and molecular geometry.

Acknowledgements

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