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Quantification of the *push–pull effect* in substituted alkenes

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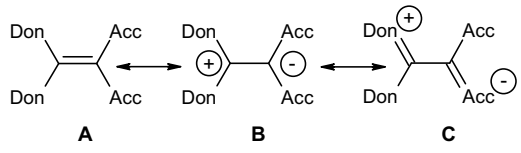
Abstract—The quotient of the occupation numbers of π bonding and π* antibonding orbitals of the central C=C partial double bond, $\pi^*_{C=C}/\pi_{C=C}$, proved to be a useful parameter to quantify the *push–pull effect* completely for the first time in substituted alkenes by examination of a comprehensive set of compounds.

Push–pull alkenes are substituted olefins with one or two electron-donating substituents (Don) on one end of a C=C double bond and with one or two electron-withdrawing substituents (Acc) on the other end (figure **A** in Scheme 1). With increased π-electron delocalization, the central C=C double bond becomes ever more polarized (**B**) and its π-bond order is reduced accordingly as the corresponding π-bond orders of the C-Don and C-Acc bonds increase (**C**) with rising push–pull character of the compound. This *push–pull effect* is of decisive influence on both the dynamic behaviour and the chemical reactivity of this class of compounds. Thus, it is of great interest to not only ascertain, but to also quantify the inherent *push–pull effect*.

Previously, the barrier to rotation of central partial C=C double bond ($\Delta G^{\neq}$, as determined by dynamic NMR spectroscopy) and the ^{13}C chemical shift difference of the two carbons of the double bond ($\Delta\delta_{C=C}$) were employed for this purpose.[1,2] However, these two push–pull parameters each bear a serious limitation. In



Scheme 1.

the case of the barrier to rotation, $\Delta G^{\neq}_{C=C}$ can simply be immeasurable on the NMR time scale (from either being too high or too low, the presence of strongly biased conformers, etc.). For $\Delta\delta_{C=C}$, the bond polarization depends on the individual combination of the four substituents and behaves in a non-additive manner.[3] Thus, a general parameter to quantify the *push–pull effect* is not yet available.

Ab initio MO calculations together with the NBO method have provided valuable information on the structure, bond energies, electron occupancies and bonding/antibonding interactions in a set of push–pull alkenes.[4] Besides $\Delta G^{\neq}_{C=C}$ (both experimentally determined and theoretically calculated) and $\Delta\delta_{C=C}$, additionally, the bond length of the C=C partial double bond (available from X-ray studies) was considered and it proved to be a more reliable parameter to quantify the push–pull effect in those compounds.[4] Equivalent to the bond length, the quotient of the occupation number of the π* anti-bonding orbitals of the central C=C partial double bond (quantitatively describing the electron-donor power of the Don substituents) and the corresponding occupation number of the π bonding orbital of this bond (quantitatively describing the electron-withdrawing power of the Acc substituents), $\pi^*_{C=C}/\pi_{C=C}$, can also be employed.[4] The application of the latter parameter for quantifying the *push–pull effect* in various classes of push–pull alkenes is now the topic of this letter.

In addition to the push–pull alkenes **2**–**4**, already studied both theoretically and experimentally[4,5] (see Scheme 2), a number of model compounds **1**, **5** and **6**, were also theoretically calculated with respect to both the bond length of the central C,C (C,N) partial double bond

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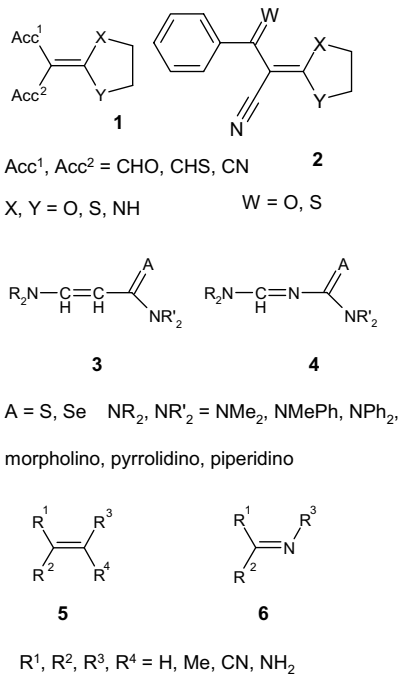

Scheme 2. The generalized structures of the compounds under study. Explicit structural motifs for all compounds can be found in Supporting data.

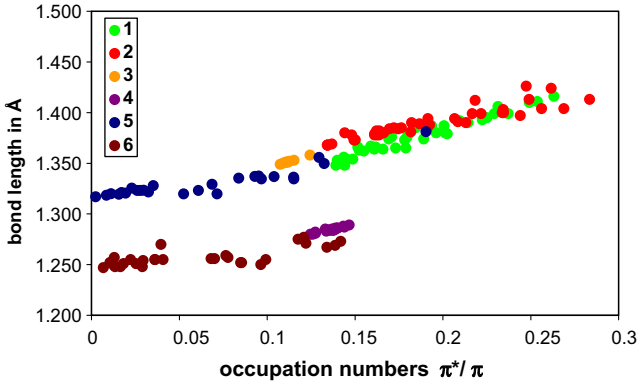

Figure 1. Correlation of bond length of the central C=C(C=N) partial double bond in **1**–**6** with the quotient of the occupation numbers of the anti-bonding π* orbital and of the bonding π orbital of the same bonds, $\pi^*_{C=C}/\pi_{C=C}$.

$p_{C=C(C=N)}$ and the quotient $\pi^*_{C=C}/\pi_{C=C}$ (results given in Tables S4–S8 in *Supporting data*). In Figure 1, the correlations between these two parameters are portrayed. As a starting reference, ethylene was used ($p_{C=C} = 1.32$ Å, $\pi^*_{C=C}/\pi_{C=C} = 0.002$) from which the various structures were generated by progressive substitution. Several interesting observations on the two parameters $p_{C=C}$ and $\pi^*_{C=C}/\pi_{C=C}$ can be noted:

(i) Methyl as a substituent, obviously due to hyperconjugation, gradually increases the value of the quotient $\pi^*_{C=C}/\pi_{C=C}$ (in **5** up to 0.035 in case of tetrasubstitution, cf. Table S7 in *Supporting data*), but the bond length remains constant at 1.32 Å. Similarly for cyano substitution. However, amino substitution, due to strong π-donation, has a larger influence on $\pi^*_{C=C}/\pi_{C=C}$ (0.052, in case of geminal disubstitution), though the bond length still does not alter significantly. The exception is, if the two opposing substituents are CN and NH_2 whereby the heightening *push–pull effect* is also indicated by the increased bond length of the central C=C(C=N) double bond {(NC)CH=CH(NH_2): 0.084/1.335 Å; (NC)CH=CH(NH_2)$_2$: 0.132/1.35 Å; (NC)$_2$CH=CH(NH_2): 0.093/1.34 Å; (NC)$_2$CH=CH(NH_2)$_2$: 0.130/1.36 Å}. The same effects are also observed in the imino analogues **6** whereby the shorter bond length of the corresponding C=N bond changes from 1.25 Å in CH_2=NH to 1.27 Å in (CN)$_2$C=N(NH_2) while $\pi^*_{C=C}/\pi_{C=C}$ varies from 0.0105 to 0.122, thus indicating the latter parameter to be much more sensitive to the *push–pull effect*.

(ii) In case of the presence of only two push–pull substituents, viz. compounds **3** and **4**, fine linear dependences $p_{C=C}$ versus $\pi^*_{C=C}/\pi_{C=C}$ were obtained. The ranges in **3** ($p_{C=C} = 1.35$–1.36 Å and $\pi^*_{C=C}/\pi_{C=C} = 0.107$–$0.124$) and **4** ($p_{C=N} = 1.28$–$1.29$Å and $\pi^*_{C=C}/\pi_{C=C} = 0.126$–$0.147$), though, are obviously characteristic for the one Don / one Acc combination [cf. (i)].

(iii) These linear dependencies are perpetuated by compounds **1** and **2** with four push–pull substituents in the compounds. Due to the ever increasing *push–pull effect* in **1** and **2**, the bond length of the central C=C partial double bond is substantially elongated (up to a value of 1.42 Å) and the quotient $\pi^*_{C=C}/\pi_{C=C} = 0.126$–$0.147$ rises appropriately (up to a value of 0.284).

(iv) The extent of the *push–pull effect*, however, is dependent on the particular combination of the push–pull substituents present though the donor activity is still enhanced even if strong donor substituent is combined with a weak acceptor substituent (and conversely), as noted previously.[4]

(v) The only barriers to rotation obtained experimentally are those of compounds **2**, which are presented in Table S5 in Supporting data. These barriers to rotation about the central partial C=C double bond are only sufficiently low enough to be studied on the NMR time scale due to the remarkable *push–pull effect* of two donor and two acceptor substituents. The smallest barrier obtained in this set was 41.5 kJ/mol (for W = S; X, Y = NH) with the highest being 95.3 kJ/mol (for W = S, X, Y = S). If these extreme barriers are taken as the nominal limits of measurement, then they define the NMR window for the quantitative study of the *push–pull effect* by this dynamic NMR spectroscopy. But within this range the *push–pull effect* can also be expressed by both parameters $p_{C=C}$ and $\pi^*_{C=C}/\pi_{C=C}$. Though the variation of the bond length was only minor ($\Delta p_{C=C} = 0.03$ Å), the change in the occupation number quotient seems to be sufficiently large enough ($\Delta\pi^*_{C=C}/\pi_{C=C} = 0.085$) to adjudge both the dynamic behaviour and the extension of the *push–pull effect* already present.

In conclusion, the quotient of the occupation numbers of the π* antibonding orbital and of the π bonding orbital of the central C=C partial double bond, $\pi^*_{C=C}/\pi_{C=C}$, is a very sensitive measure of the *push–pull effect* present in any substituted alkene and can thus be employed as a very effective replacement for either the barrier to rotation ($\Delta G^{\neq}_{C=C}$) or to ^{13}C chemical shift differences ($\Delta\delta_{C=C}$). The variation of the bond length $p_{C=C}$ is also a useful parameter for this purpose but is hampered by the need for strong bond polarization to effect discernible variation.

Experimental: Ab initio quantum mechanical calculations were performed on SGI Octane and SGI Origin 2000 work stations using the Gaussian 98 and 03 program.[6] Geometry optimization was performed at the HF/6-31G* level of theory without constraints;[7] the size of the basis set (6-31G**, 6-31+G**, 6-311G**) as well as inclusion of diffuse functions was found to be of only negligible influence on the quality of $p_{C=C}$ versus $\pi^*_{C=C}/\pi_{C=C}$ correlations. NBO 5.0 population analysis[8] was produced by linking to the Gaussian 98 and 03 program packages with the keywords nlmo for NLMO analysis and print for graphical evaluation.

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Supplementary data

Tables of the ab initio calculations of the occupation numbers of the π* antibonding and of the π bonding orbitals and the bond lengths of the central C=C partial double bonds for compounds **1**–**6**. Explicit structural motifs for all compounds **1**–**6** are also presented. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2005.07.030.

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