

Consideration of π - π and CH- π Interactions as Dipole-Dipole Interactions in Biphenyl Stationary Phases

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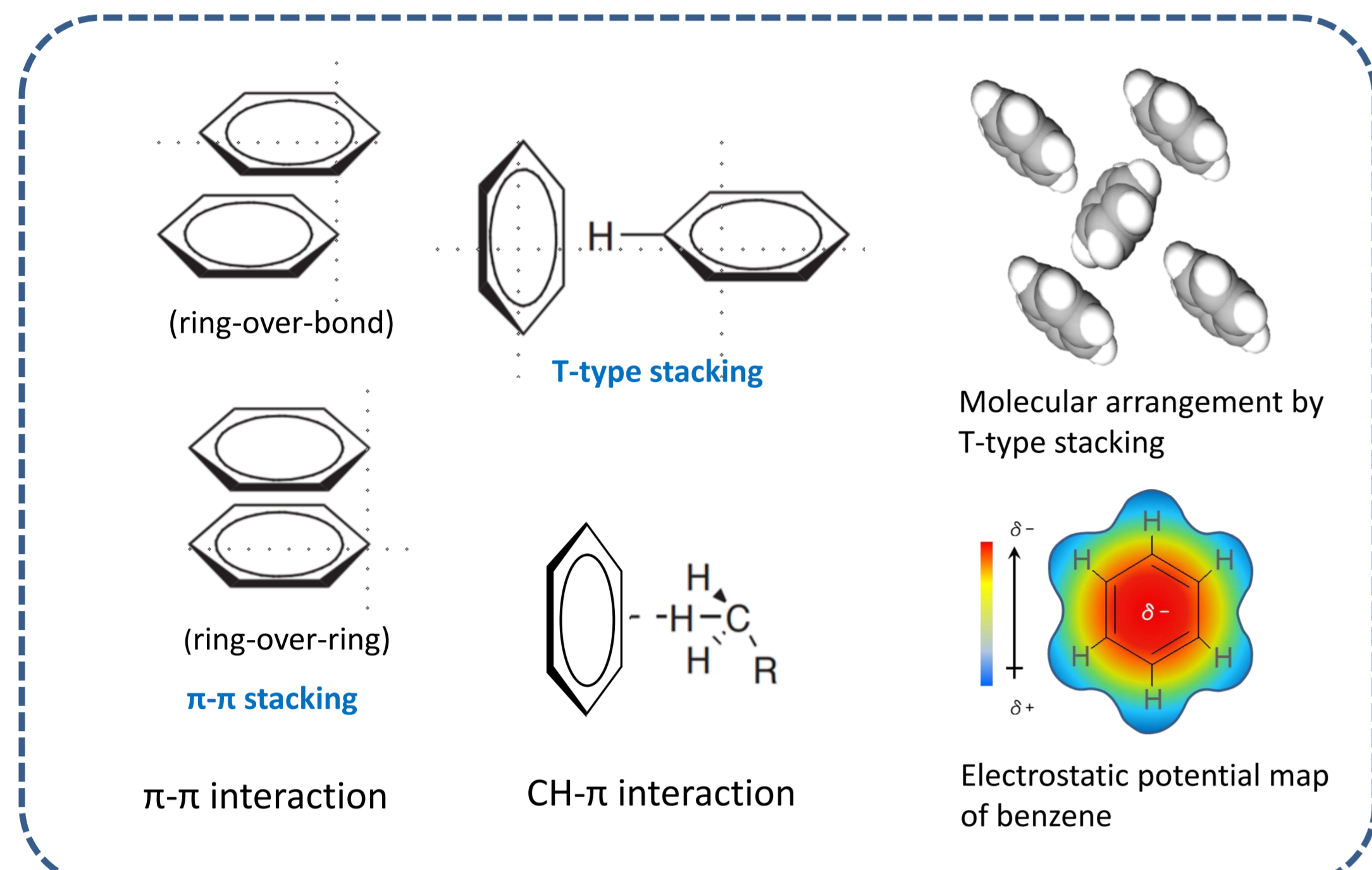
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Biphenyl stationary phase is classified in L11 category as LC columns as well as phenyl stationary phase by the United States Pharmacopeial Convention. Both Biphenyl and phenyl stationary phases have a phenyl group and are said to have dipole-dipole interaction that is absent in alkyl chain stationary phases such as C18 and C8. Furthermore, it is said that there are π - π interactions, CH- π interactions, OH- π interactions, NH- π interactions, halogen- π interactions, and lone pair electron- π interactions as dipole-dipole interactions.

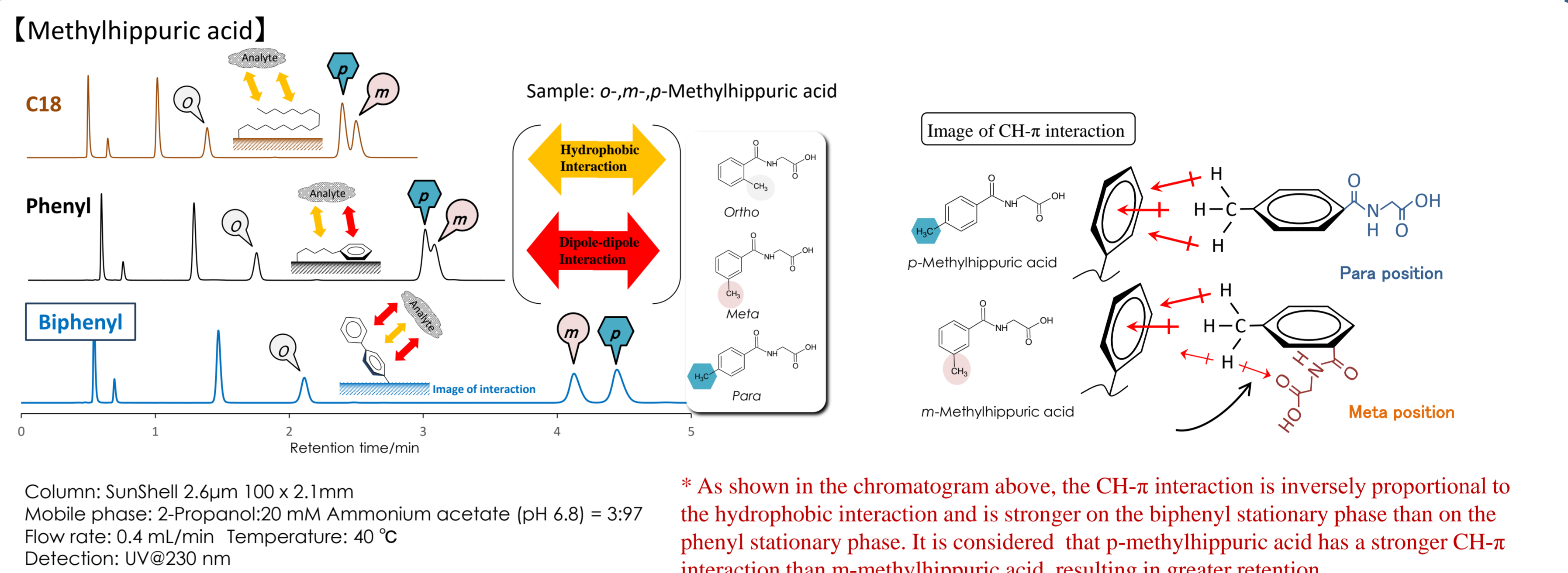
In this study, the π - π interaction and the CH- π interaction were discussed in the separation of various samples. Dinitrobenzene, trinitrobenzene and sulfonamides which have a lot of double bonds are used for evaluation of π - π interactions. The isomers of methylhippuric acid, organic acids, vanillin and isovanillin, leucine and isoleucine, n-butylaldehyde-DNPH and iso-butylaldehyde-DNPH have little difference of π electrons respectively, so that they are used for evaluation of CH- π interactions. Separation comparison of above compounds using biphenyl, phenyl and C18 stationary phases revealed each interaction. Comparing between biphenyl and phenyl stationary phases, biphenyl stationary phase showed both stronger π - π interaction and stronger CH- π interaction as dipole-dipole interaction than phenyl stationary phase.

Dipole-Dipole Interaction (π - π and CH- π interactions)

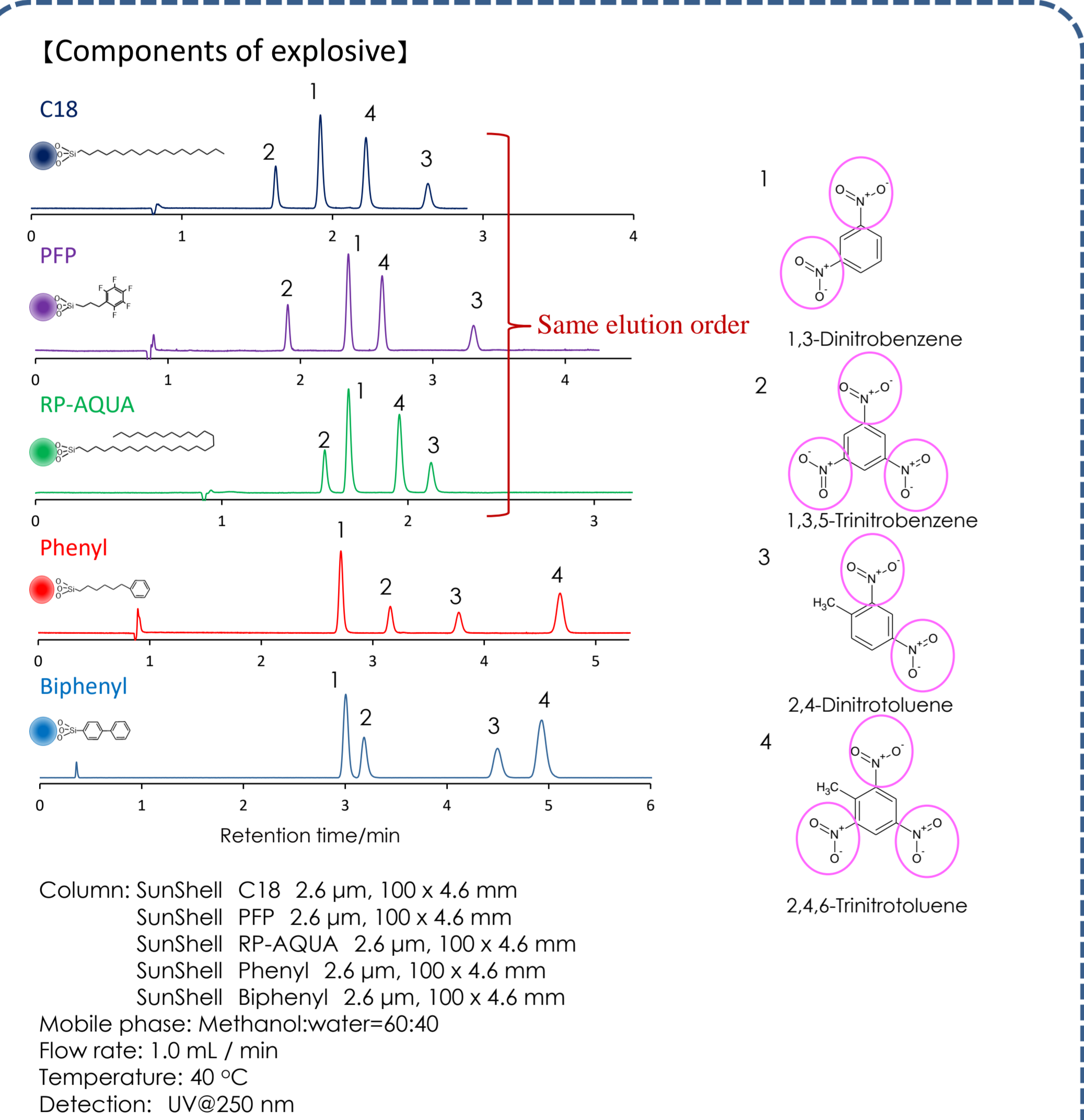


★ π - π stacking and T-type stacking are known as benzene arrangement states as π - π interaction. It is presumed that T-type stacking is close to the CH- π interaction, which is the interaction between the central part of benzene and hydrogen of CH.

Separations mainly by CH- π interaction

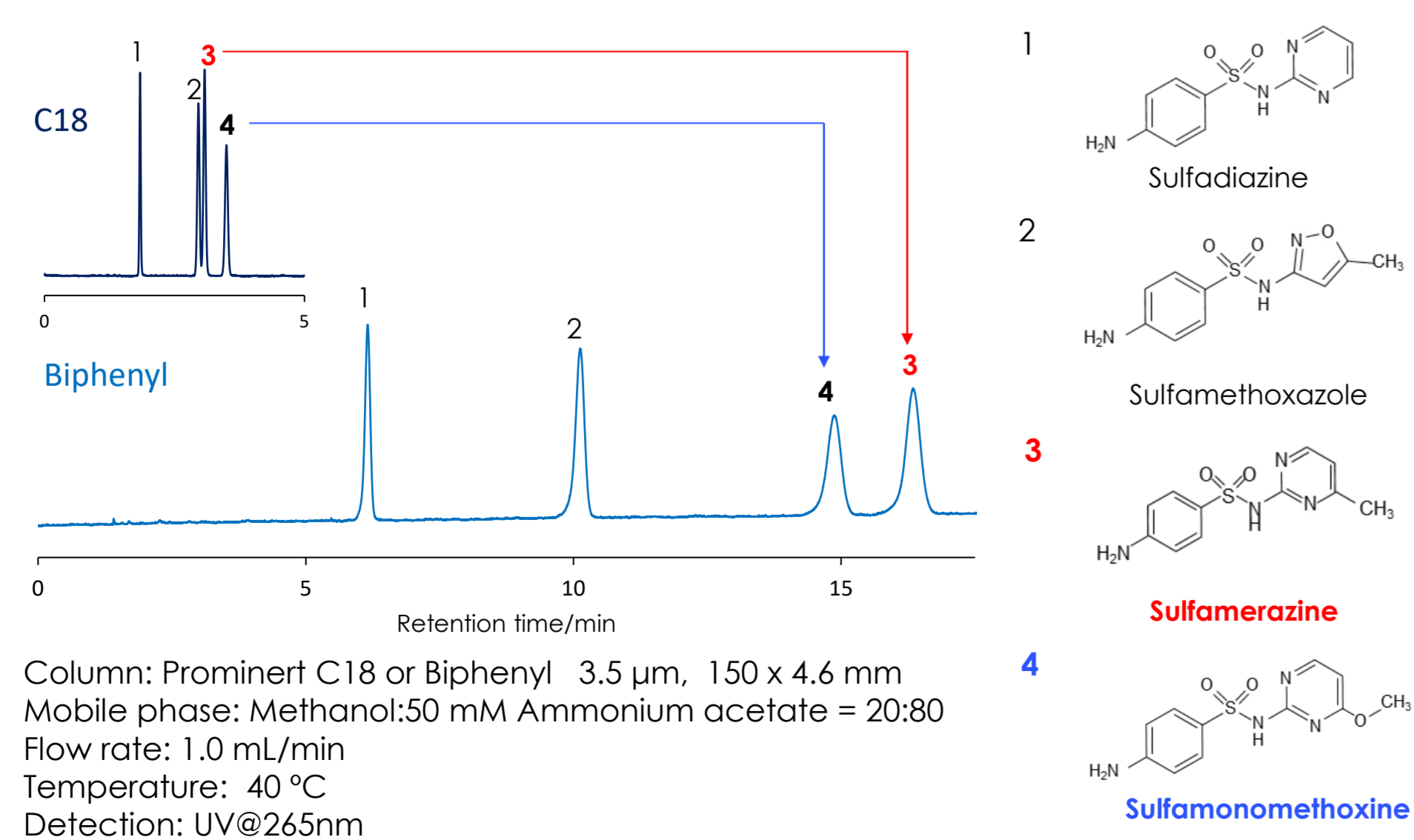


Separations mainly by π - π interaction



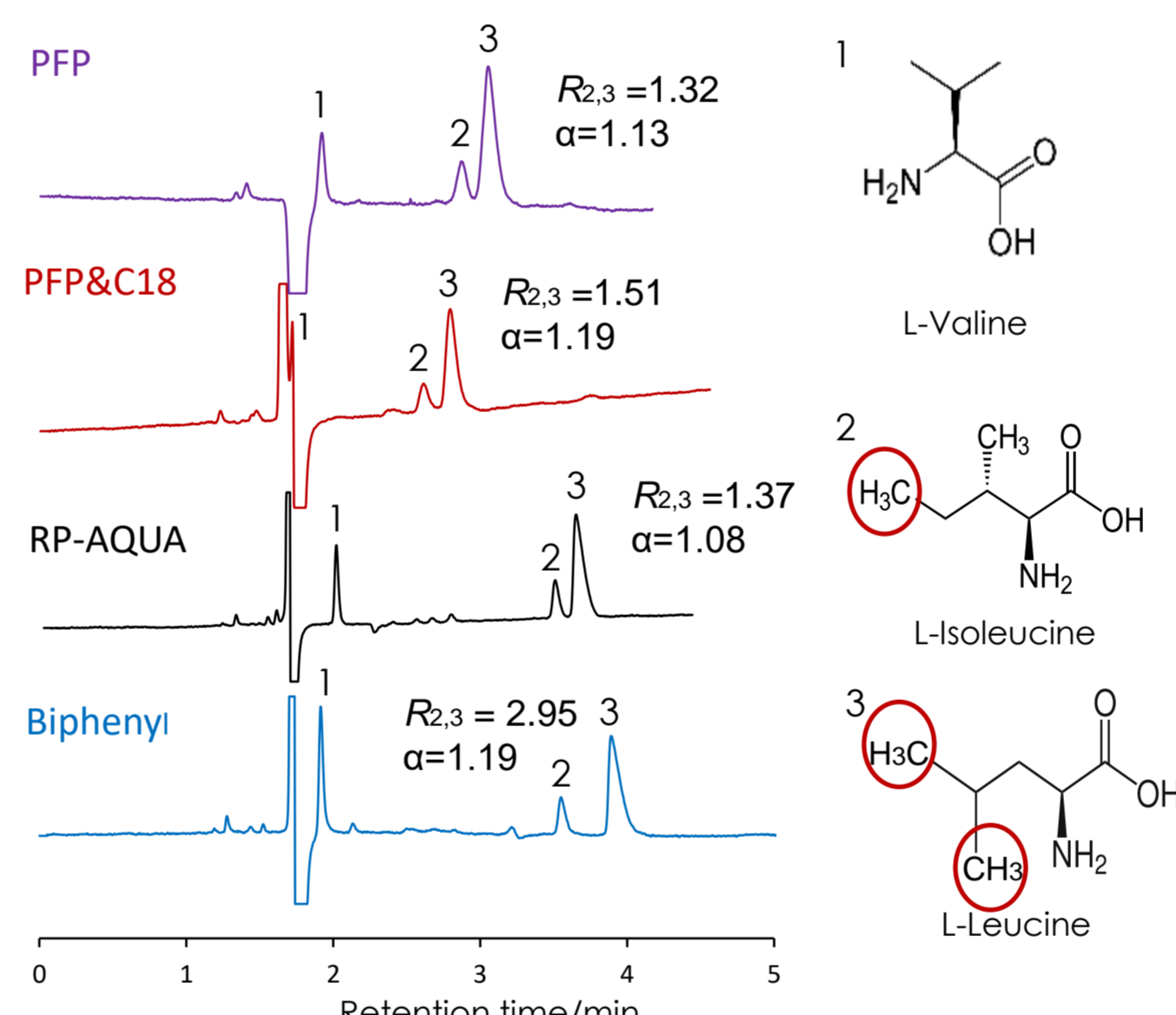
*Phenyl stationary phases exert strong π - π interactions between nitro groups and phenyl or biphenyl groups, altering the elution order of analytes. The PFP stationary phase showed the same elution order as C18. This result implies that PFP does not have π - π interactions like phenyl groups.

[Sulfonamides]

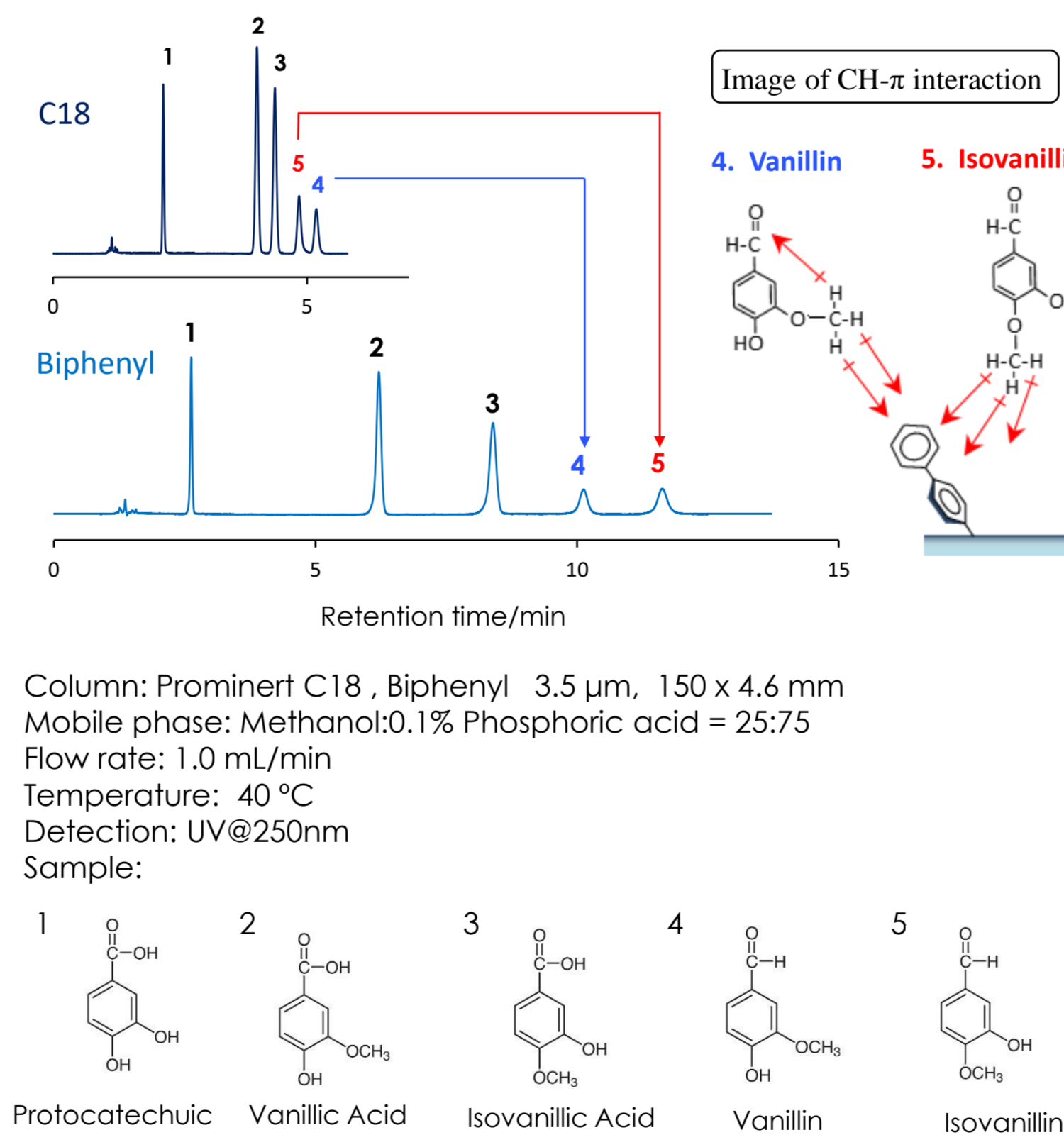


*Retention by the biphenyl stationary phase was significantly higher than that by the C18 stationary phase due to π - π interactions. In addition, when the organic solvent concentration in the mobile phase was low, the π - π interaction became significant. The change in the elution order of peak numbers 3 and 4 is thought to be due to CH- π interactions.

[Amino acids]

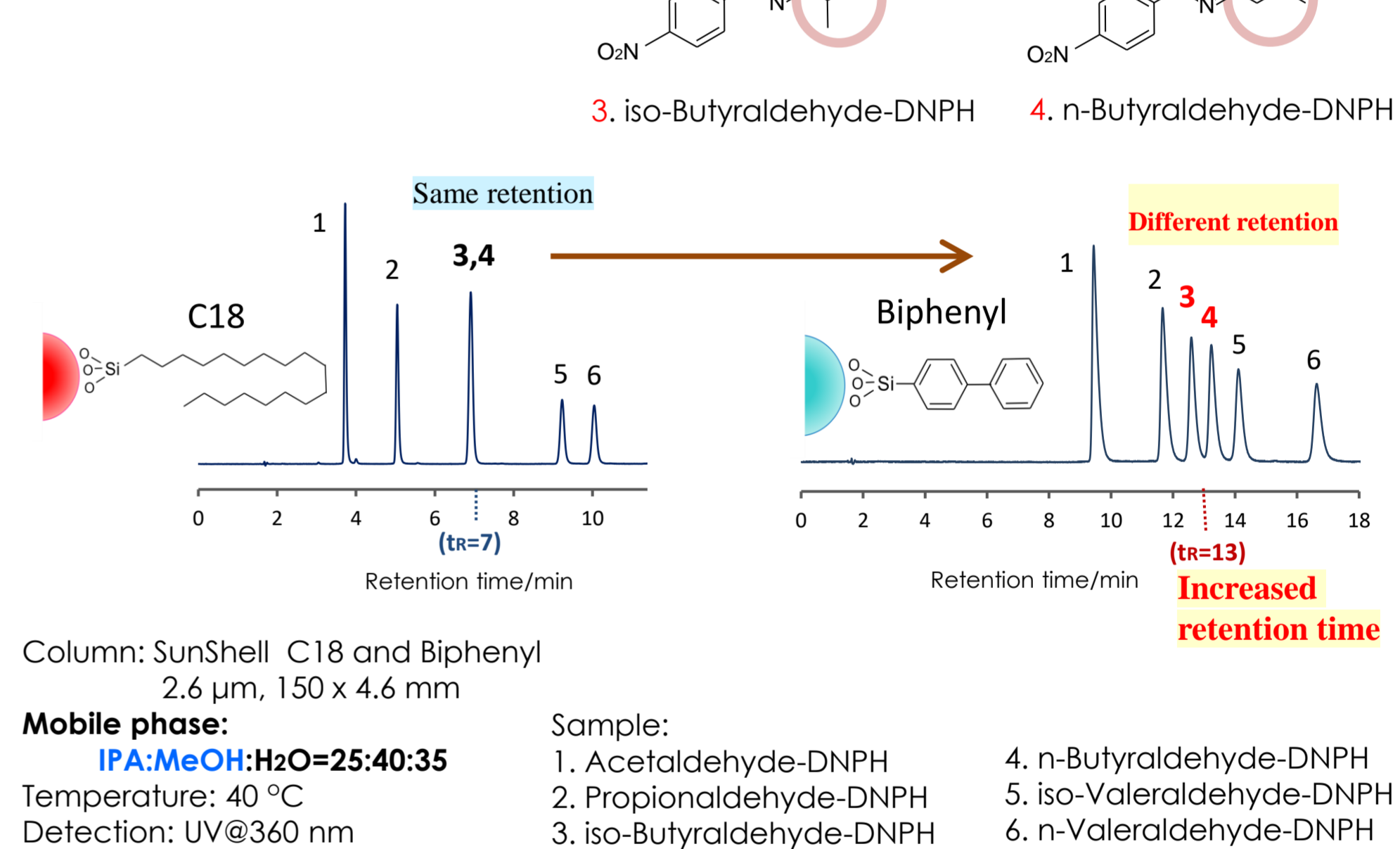


[Vanillin and Isovanillin]



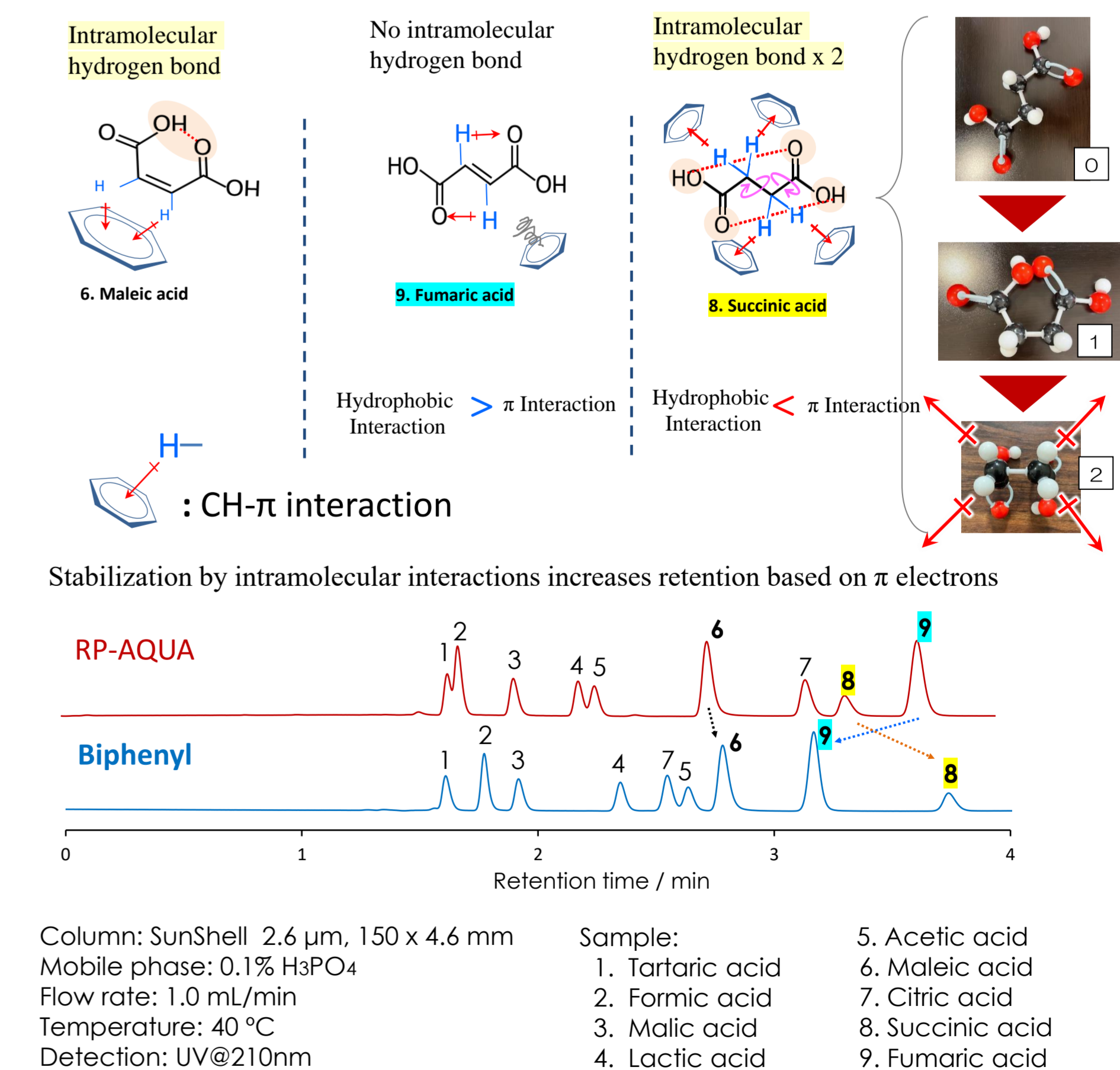
* Vanillin and isovanillin were more retained on the biphenyl stationary phase than on the C18 stationary phase. Furthermore, the elution order of vanillin and isovanillin was reversed. Isovanillin is thought to have a stronger CH- π interaction with the Biphenyl stationary phase than vanillin.

[Aldehyde-DNPH]



* In the separation of leucine, isoleucine and n-butylaldehyde-DNPH, iso-butylaldehyde-DNPH in the above separation, the CH- π interaction differs depending on the position of the branched methyl group, and the biphenyl stationary phase also showed the best separation. Leucine and n-butylaldehyde-DNPH, which have a methyl group at the farthest position from the functional group, were well-retained.

[Organic acids]



* In the case of the RP-AQUA stationary phase, the organic acids are eluted in the reverse order of hydrophobicity, but in the case of the biphenyl stationary phase, the elution order of the organic acids differs from the reverse order of hydrophobicity due to the CH- π interaction. Succinic acid with strong CH- π interaction showed relatively large retention.

Conclusion

- ✓ Phenyl groups such as phenyl and biphenyl are known to have dipole-dipole interaction.
- ✓ Dipole-dipole interaction include not only π - π interaction but also CH- π interaction.
- ✓ CH- π interaction is considered to cause larger selectivity changes than π - π interactions.
- ✓ In the case of organic acid separations, there may not be much difference in π - π interaction between different analytes, and CH- π interaction could explain the change in selectivity.