

EXPLAINING DIFFERENCES IN TOXICITY OF AZAARENES (NPAHS) TO LARVAE OF THE MIDGE *CHIRONOMUS RIPARIUS*

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AZAARENES

- nitrogen substituted polycyclic hetero-aromatic hydrocarbons (NPAHs)



sources

- natural
- combustion of fossil fuels
- oil drilling, refining, storage
- coal tar distillation
- wood preservation

occurrence

- air
- water
- sediment

research

- most research on homocyclic PAH
- lack of toxicity data

a reliable hazard assessment for this family of compounds is hampered by the lack of toxicity data for the variety of NPAHs and test organisms

CHIRONOMUS RIPARIUS

- widely distributed
- frequently the most abundant group of insects in freshwater ecosystems
- major food source for fish and other predators
- important position in aquatic food webs
- larvae live in sediment
- species can easily be cultured

AIM

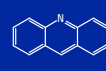
- to determine the acute toxicity of seven different azaarenes, (ranging from a two-ringed structure to a five-ringed structure), to larvae of the midge *Chironomus riparius*
- to seek a relation between the biological effects and chemical structures of the compounds, in order to give insight in the underlying mechanisms responsible for the toxic effects

MATERIALS AND METHODS

azaarenes used in this study



quinoline



acridine



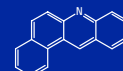
phenanthridine



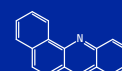
benzo[f]quinoline



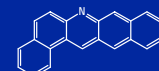
benzo[h]quinoline



benz[a]acridine



benz[c]acridine



dibenz[a,i]acridine

experimental setup

- 50 newly hatched first instar larvae
- 2 controls, 5 different concentrations
- glass vessel, 100 ml Dutch Standard Water
- 1 ml food (trouvit in DSW)
- after 96h determination of growth and survival

toxicant concentrations

- water samples taken after 1h and 96h, measured by HPLC
- average actual exposure concentration, recovery

LC50 values

molecular descriptors

- molecular volume
- molecular surface
- dipole moment
- LUMO, ionisation potential
- HOMO, electron affinity
- heat of formation
- connectivity indices

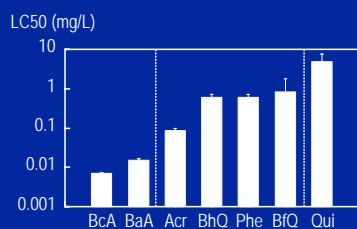
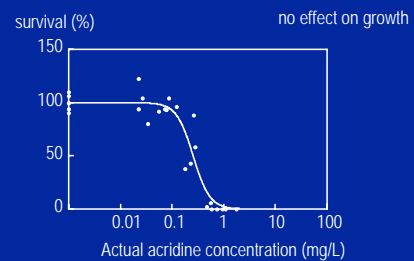
Correlation between molecular descriptors and LC50 values

RESULTS AND DISCUSSION

recovery	(%)
benz[c]acridine	22 ± 6
benz[a]acridine	25 ± 9
acridine	48 ± 8
benzo[h]quinoline	93 ± 3
phenanthridine	86 ± 9
benzo[f]quinoline	96 ± 10
quinoline	90 ± 4

- lipophylicity
- sorption to glass, food, midges
- effect on LC50 values

toxicity



- toxicity increased with increasing number of aromatic rings
- dibenz[a,f]acridine not acute toxic at max. water solubility

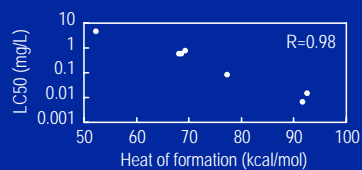
- toxicity increased with increasing number of aromatic rings
- increasing lipophylicity
 - facilitating celmembrane crossing
 - facilitating bioaccumulation
 - hindering excretion
- high correlations between toxicity and size related molecular descriptors

molecular surface 0.94

molecular volume 0.94

isomer toxicity

- acridine more toxic than other isomers
- most molecular descriptors are unable to discriminate between isomers
- Heat of formation is the only descriptor that discriminates between isomers and therefore gives the highest correlation with all toxicity data



why is acridine more toxic than the other isomers?

- heat of formation highly correlated with isomer toxicity
- low recovery

indications for degradation of acridine

- PAHs exhibiting photo-induced toxicity are consistently within HOMO-LUMO gap window of 7.2 ± 0.4 eV (Mekenyan, 1994)

acridine	7.5
other isomers tested	8.2 - 8.7

degradation under influence of UV light causes increased, photo-induced toxicity of acridine

IN CONCLUSION

- toxicity of NPAHs on *Chironomus riparius* larvae increases with increasing number of aromatic rings. Consequently,
- good correlations were observed between size- and shape related molecular descriptors and LC50 values
- most descriptors are unable to discriminate between isomers
- Heat of formation values discriminate most between isomers and are highly correlated with all toxicity data
- acridine, with a HOMO-LUMO gap in the highly phototoxic region, a high heat of formation and a low recovery is possibly degraded under influence of UV-light, causing increased photo-induced toxicity