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ACENAPHTHO[5,6-cd]1,2,6-THIADIAZINE

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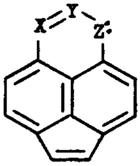
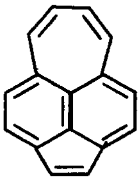
There has been a recent revival of interest in compounds with heterocyclic rings fused to the "peri" positions of naphthalene.

One aspect of work in this area in our laboratories has been concerned with an investigation of acenaphthylene analogues (I) in which the π-electron system is related to that of the non-benzenoid aromatic hydrocarbon (II).[1]



(I)



(II)

The recently reported trapping of the unstable thiapyran (I : $X{-}Y{-}\ddot{Z} = CH{-}\overset{+}{S}{-}\overset{-}{C}H$) as its N-phenylmaleimide adduct,[2] prompts us to record the isolation of the corresponding acenaphtho[5,6-cd]1,2,6-thiadiazine (III) as a stable crystalline solid.

The thiadiazine(III) is obtained in essentially quantitative yield when its dihydro-derivative (IV)[3] is oxidised with dichlorodicyanoquinone in warm benzene. It crystallises in black needles* m.p. 190-191° which dissolve to give violet solutions in a variety of organic solvents. Features of its electronic spectrum are compared with those of the triazine (V)[1] in the table. There is evident correspondence between the spectra,

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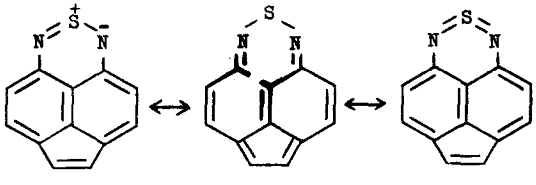
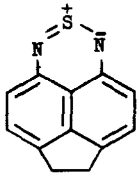
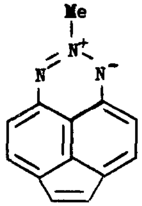
*Found C, 68.5; H, 3.2; N, 13,15%


(a) (b) (c)

(III)


(IV)


(V)

Electronic Spectra of Heterocycles (III) and (V) (in EtOH)

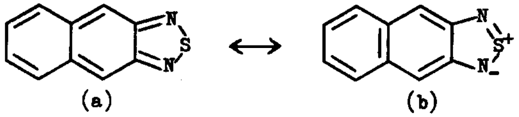
(III)		(V)	
254.5 mμ	(ε 2.73 x 10^4)	248	(ε 1.88 x 10^4)
335	(3.01 x 10^4)	322.5	(2.44 x 10^4)
343 (shoulder)	(3.30 x 10^4)	330	(2.54 x 10^4)
349	(5.67 x 10^4)	337	(3.53 x 10^4)
578	(1.58 x 10^3)	464	(1.47 x 10^3)

though that of the sulphur compound is shifted to longer wavelength.[*]

The n.m.r. spectrum of (III) is also instructive. The protons on the naphthalene rings, which appear as a 4-proton AB quartet, are deshielded by ca. 2 p.p.m. with respect to those in (IV). This may be associated with a ring current in the peripheral 14π electron system of (III). Furthermore, the AB coupling constant is 0.6 c.p.s. greater than in (IV), consistent[5] with the increased double-bond character implied in structure (IIIb). This extreme quinonoid structure is not possible in the dihydro-compound (IV), or the related naphthothiadiazine.[3,6] It is reminiscent of the structure written for

[*] It is not clear from preliminary solvent shift measurements whether the long wavelength band in these spectra arises from an $n\pi^*$ transition, or whether it may be related to the long wavelength band in the spectrum of(II).[4]

the naphthothiadiazole (VIa)[7]. Recent molecular orbital calculations on (VI),[8,9]



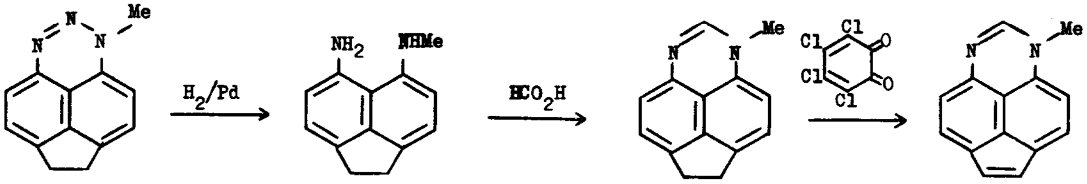
(a) (b)

(VI)

satisfactorily reflect its chemical properties without resorting to the incorporation of hybrids of sulphur d-orbitals in the π-system. They also reveal appreciable charge separation as shown in (VIb). We consider that the spectral similarity between (III) and the triazine (V) suggests that significant d-orbital involvement (structure IIIc) may likewise be unimportant in the thiadiazine.

It seems that the instability of isobenzothiophene[10] and the thiapyran (I ; $X{=}Y{-}Z = \text{CH}{=}\overset{+}{\text{S}}{-}\overset{-}{\text{C}}\text{H}$) compared with the thiadiazoles and thiadiazine (III) may qualitatively be related to the electronegativities of carbon and nitrogen, and the greater facility of nitrogen to accept a negative charge.[*]

We have also prepared the aromatic perimidine (VIII) from the triazine (VII)[1] by the route annexed; however, this compound has resisted all efforts at purification, and has only been characterised spectroscopically. The N.M.R. spectrum again shows a general downfield shift with respect to that of the hydroaromatic precursor (IX) (m.p. 208-209°)[**]



(VII) (IX) (VIII)

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[*] The electronic structures of cyclic sulphur compounds is the subject of a recent review.[12]

[**] Found: C, 80.5; H, 5.8; N, 13.2%

ACKNOWLEDGEMENT

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   Behringer and Leiritz report m.p. 188-189° for (IV). In our hands this product had m.p. 130-131° but showed identical spectral properties to those reported by Behringer (very different from those of (III), m.p. 190-191°).
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