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2,3-NAPHTHOQUINONOID HETEROCYCLES. II. A HIGHLY STABILIZED THIADIAZOLE ANALOG OF ANTHRACENE.[1]

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The electronic nature of 1,2,5-thiadiazole is a subject of considerable theoretical interest.[2,3] As in the case of thiophene,[2] two cannonical forms (Ia and Ib) lacking charge separation may be written;[3] the form containing divalent sulfur (Ia) appears to be the major contributor to the ground state of the molecule.[4] The stability of the well-known thiadiazole derivatives benzo[c]-1,2,5-thiadiazole (II)[5] and naphtho[1,2-c]-1,2,5-thiadiazole (III),[6] however, implies a significant degree of tetravalent character in the sulfur atom of these compounds; this assumption has received support from X-ray crystallographic analysis.[7] We wish now to report the synthesis of naphtho[2,3-c]-1,2,5-thiadiazole (IV), a highly stable anthracene analog which behaves predominantly as a tetravalent sulfur structure (IVb ↔ IVc).

The reaction of 2,3-diaminonaphthalene with thionylaniline (3 equivalents) in pyridine at 95° gave, in 95% yield, red-orange needles of thiadiazole IV, m.p. 85-86°, λ_{max} 221 mμ (ϵ = 17,800), 252 (34,200), 327 (sh, 3,160), 335 (sh, 5,060), 343 (7,450), 351 (7,000), 359 (10,170), 436 (2,050), and 460 (sh, 1,620).[8] The NMR spectrum of IV ($CDCl_3$ solution) showed the four aromatic protons of the outer ring as a multiplet centered at 2.45 τ in addition to a highly deshielded singlet at 1.55 τ representing the remaining two central aromatic protons.

Thiadiazole IV reacted slowly with N-phenylmaleimide and maleic anhydride in refluxing benzene solution to give the corresponding Diels-Alder adducts V (m.p. 234°) and VI (m.p. 328°) in yields of 75% and 48%, respectively. On the basis of spectral evidence these adducts have been assigned structures resulting from the addition of a dienophile to the central ring of the naphthothiadiazole system. Thus, the ultraviolet spectrum of adduct

V has its longest absorption band at 272 mμ (ϵ = 14,060); the absence of an absorption band at higher wave lengths precludes the presence in V of either a naphthalene or a benzo[*c*]-1,2,5-thiadiazole chromophore, thereby eliminating the possibility of addition of the dienophile to either of the outer rings of IV. The NMR spectrum of adduct V shows, in addition to aromatic protons in the range of 2.60 to 2.85 τ, peaks centered at 6.58 τ (protons α to the carbonyl) and 4.82 τ (benzhydryl-type bridge protons), analogous to the corresponding protons at 6.47 τ and 5.00 τ in the spectrum of the anthracene-*N*-phenylmaleimide adduct VII.[9] Since the protons α to the carbonyl appear at essentially identical positions in both adducts V and VII, they probably lie in identical environments; we favor, therefore, a configuration for V (and by analogy for VI) in which the carbonyl functions lie over the thiadiazole ring.

Thiadiazole IV was found to be a less reactive diene than anthracene in the Diels-Alder reaction, as evidenced by a competitive reaction using *N*-phenylmaleimide as the dienophile: thus, equimolar amounts of thiadiazole IV, anthracene, and *N*-phenylmaleimide in refluxing benzene afforded only the anthracene-*N*-phenylmaleimide adduct (VII) (70% yield after purification) and no detectable amount of the thiadiazole adduct V. This result was one of kinetic rather than thermodynamic control, as shown by the fact that anthracene did not react with thiadiazole adduct V on prolonged refluxing in benzene.

Brief oxidation of IV with sodium dichromate in acetic acid at room temperature gave the orange anthraquinone analog VIII, m.p. 246° (dec.) in 46% yield. Compound VIII was readily rearomatized reductively to the corresponding hydroquinone as evidenced by the formation of a green vat color with basic sodium hydrosulfite solution.

Ultraviolet irradiation of thiadiazole IV in benzene solution afforded, in 95% yield, a colorless photodimer (IX), m.p. 305° (dec.); mol. wt. (chloroform) equals 358. The ultraviolet spectrum of dimer IX in dioxane showed maxima only at 218 mμ (ϵ = 18,200) and 280 mμ (ϵ = 25,300), consistent only with the presence of simple benzene and thiadiazole chromophores in the molecule. Dimer IX is, therefore, analogous to the photodimer of anthracene; although IX consists of a single, pure compound, a choice between *syn* and *anti* structures cannot be made at this time.

In conclusion, the chemical and physical facts outlined above indicate that thiadiazole IV behaves as a highly delocalized aromatic system analogous to anthracene in its general chemical properties, but less prone to enter into Diels-Alder additions. It appears, therefore, that the sulfur atom in this molecule must possess an unusual degree of tetravalent character.

Further studies on the chemistry of IV and related compounds are in progress and will be reported at a later date.

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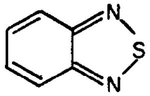
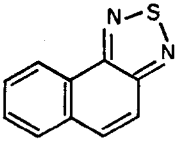
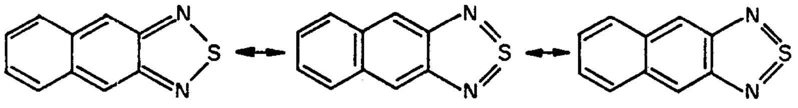
I a I b



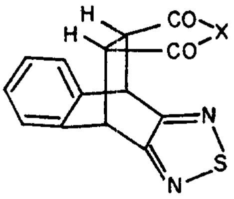
II



III

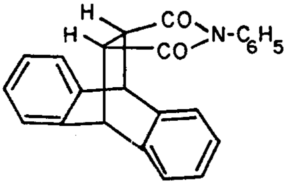


IV a IV b IV c

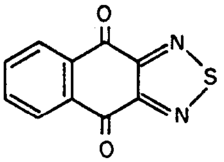


V: $X = N-C_6H_5$

VI: $X = O$



VII



VIII