

Bound Brook Laboratories, American Cyanamid Company

The 1,2-Dithiolium Cation. V Higher No-bond Resonance Systems

Erwin Klingsberg

Sir:

The thiothiophene "no-bond resonance" system (1) embodies a structural principle that is capable of indefinite extension. Repetition of the vinylene group $-\text{CH}:\text{CH}-$ gives rise to the open-chain conjugated polyenes, and somewhat similarly, repetition of the vinylenethio group $-\text{CH}:\text{CH}-\text{S}-$ would give rise to a succession of higher meripolycyclic systems, each composed of dithiole rings characterized by sulfur no-bond resonance.

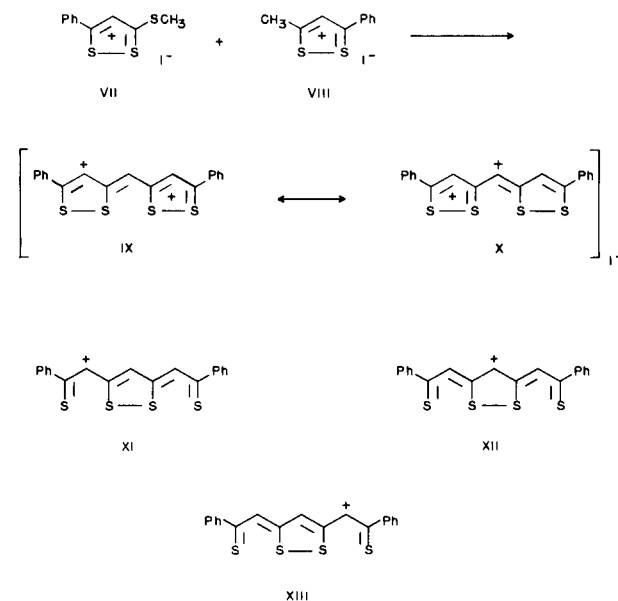
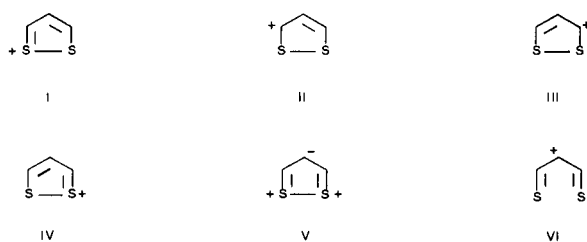
The prototype five-membered conjugated rings containing the vinylenethio group and a second sulfur atom are the 1,2- and 1,3-dithiolium cations. Since the latter (2) does not contain an S-S bond, the former (1) may be considered the parent of the thiothiophene and higher systems. No-bond resonance in the 1,2-dithiolium ring itself would require contributing form VI in addition to those forms I-V already recognized.

In the absence of experimental (3,4) or theoretical (5) support for VI, the parental relationship may be considered, for the present, to be purely formal. A simple test would be provided by the ultraviolet spectrum of a 4-phenyl-1,2-dithiolium salt substituted by a positive group such as *p*-dimethylamino. In any event, the 1,2-dithiolium and thiothiophene systems, as the first two members of the succession, exemplify the characteristic alternation of charge type to be expected throughout: systems with an even number of sulfur atoms are positively charged, while those with an odd number are neutral.

3-Methylthio-5-phenyl-1,2-dithiolium iodide [VII, prepared from 5-phenyl-1,2-dithiole-3-thione and methyl iodide (3)] and 3-methyl-5-phenyl-1,2-dithiolium iodide [VIII, prepared from the chloride (6) and sodium iodide] condensed smoothly in warm alcohol, liberating methyl mercaptan and giving a good yield of deep purple product crystallizing as fine needles, dec. 200-204°, from alcohol containing a little hydriodic acid. [Anal. Calcd. for $\text{C}_{19}\text{H}_{13}\text{IS}_4$: C, 46.0; H, 2.6; I, 25.6; S, 25.8. Found: C, 45.5; H, 3.1; I, 25.5; S, 25.4.] Considered simply as a cyanine dye of the 1,2-dithiolium series, this may be written as IX-X.

Hordvik, however, finds by X-ray analysis (7) that the four sulfur atoms are nearly collinear, with partial bonding of the internal pair; these are 3.00-3.10 Å apart, a distance considerably shorter than

twice the van der Waals radius of sulfur. Partial bonding suggests the contributing resonance forms XI-XIII and the character of the no-bond resonance system next above thiothiophene.



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Bound Brook, New Jersey 08805