proposed for the cationic polymerization of benzene[11] (using metal ions as catalyst–oxidant).

The utility of electrochemically producing phenyl radicals for synthetic purposes and the similarities in the electrooxidation mechanisms of some larger fused aromatic hydrocarbons such as anthracene, naphthalene, and phenanthrene are under active investigation.

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detect some biphenyl. This absence of low molecular weight intermediates is indicative of an addition polymerization as proposed above (see F. W. Billmeyer, Jr., "Textbook of Polymer Chemistry," Interscience Publishers, Inc., New York, N. Y., 1957).

(11) P. Kovacic and A. Kyriakis, *J. Am. Chem. Soc.*, **85**, 454 (1963).

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Azulene-Like Crystal Disorder in a Simple Thiepin. The Structures of Thieno[3,4-*d*]thiepin and Thieno[3,4-*d*]thiepin 6,6-Dioxide

Sir:

Recently, we reported the preparation of a remarkably stable simple thiepin system, thieno[3,4-*d*]thiepin (**1**).[1] The chemical and spectroscopic behavior of **1** has been compared to the thiepin sulfoxide **2** and the thiepin sulfone **3**.[2] These studies have shown that thiepin **1** possesses considerable aromatic-like character relative to heterocycles **2** and **3**.[2] It has been suggested that the unique properties of **1** may be due to ground-state contribution from azulene-like charge-separated species such as **4**.[1] In order to ascertain the nature of the π-electron delocalization in **1**, an X-ray determination of the molecular geometry of the thiepin along with the thiepin sulfone **3** was undertaken. We now wish to report that thiepin **1** is a planar system which has a crystal structure remarkably similar to the hydrocarbon azulene, while thiepin **3** shows nonplanar geometry which resembles that found for other thiepin sulfones.[3]

Thiepin **1** forms bright yellow plate-like crystals which are monoclinic, with $a = 8.273$, $b = 6.105$, and $c = 7.754$ Å, and $\beta = 103°\ 57'$. Systematic absences of the type ($h0l$) l odd, and ($0k0$) k odd, suggested the space group to be $P2_1/c$. However, the observed density (1.44 g/cc) indicated only two molecules per unit cell. Since the molecule lacks a center of symmetry, this implies that the structure is disordered with two molecules sharing four equivalent positions. Another possibility is that the true space group is Pc, the ($0k0$) absences being accidental; this would mean that there are two molecules per unit cell with no disorder.

Intensity data were taken at room temperature on a Picker 4-Circle automatic diffractometer with Cu Kα radiation, using the 2θ scan technique. Reflections (680) were recorded to a maximum 2θ angle of 130°, representing about 75% of the data theoretically accessible in the copper sphere. A sharpened three-dimensional Patterson function was calculated and heavy peaks corresponding to sulfur–sulfur vector interactions were observed. These could be explained equally well assuming an ordered structure (Pc) or a disordered structure ($P2_1/c$).

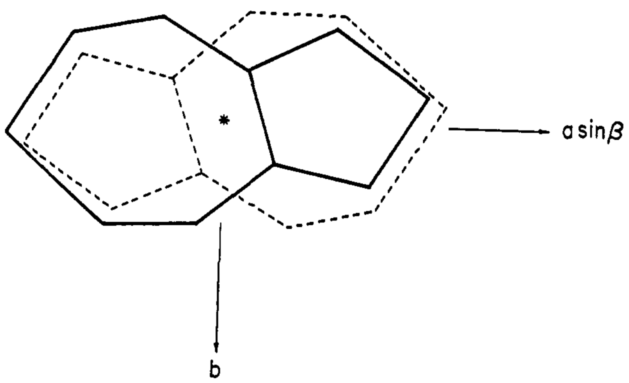

Figure 1. A projection of a portion of the disordered thieno[3,4-*d*]thiepin crystal structure viewed down the *c* axis. One molecule occupies either site randomly in the crystal lattice and this results in the center of symmetry shown by the asterisk. Disorder very similar to this occurs in the crystal structure of azulene.

Fourier syntheses phased on sulfur-scattering contributions were calculated for both space groups, and these were interpreted to give two trial model structures. Each model was then refined isotropically using least-squares refinement. The ordered structure refined isotropically to a residual of 16.2%; however, several large residual peaks were observed after difference Fourier synthesis. The disordered structure, on the other hand, rapidly refined to a residual of 12.8%, and no large peaks were observed after difference Fourier synthesis. Bond lengths and angles calculated at this time clearly favored the disordered structure to the ordered structure. This was confirmed by subsequent anisotropic least-squares refinement, which reduced the residual to 10.0% and gave acceptable bond lengths and angles.[4]

Figure 1 shows a portion of the structure as viewed down the *c* axis. The structure consists of thiepin molecules occupying the sites shown 50% of the time. Very similar disorder exists in the azulene crystal structure[5] whose unit cell constants and fractional atomic coordinates closely resemble this thiepin structure. Azulene, in addition, forms molecular complexes with trinitrobenzene[6] and Mo_2Co_6[7] which have similar disorder. Least-squares planes have been calculated for the thiepin ring and these show the molecule to be almost planar. The two sulfur atoms, however, deviate significantly from the molecular least-squares plane (0.06 Å) and this gives the molecule a slight boat shape. Similar but smaller deviations from planarity have been found in azulene.[8] Although the crystal disorder limits the accuracy of this analysis, the transannular carbon–car-

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(1) R. H. Schlessinger and G. S. Ponticello, *J. Am. Chem. Soc.*, **89**, 7138 (1967).

(2) R. H. Schlessinger and G. S. Ponticello, *Tetrahedron Letters*, 3017 (1968).

(3) H. L. Ammon, P. H. Watts, J. M. Stewart, and W. L. Mock, *J. Am. Chem. Soc.*, 90, 4501 (1968).

(4) Refinement of this structure is continuing by full-matrix least-squares analysis. The complete details of the structure analysis of **1** will be published elsewhere.

(5) J. M. Robertson, H. M. M. Shearer, G. A. Sim, and D. G. Watson, *Acta Cryst.*, **15**, 1 (1962).

(6) A. W. Hanson, *ibid.*, **19**, 19 (1966).

(7) A. W. Schluster, *Dissertation Abstr.*, **27B**, 3071 (1967).

(8) Deviations of carbon atoms in analogous positions in azulene are 0.0088 Å. See ref 6.

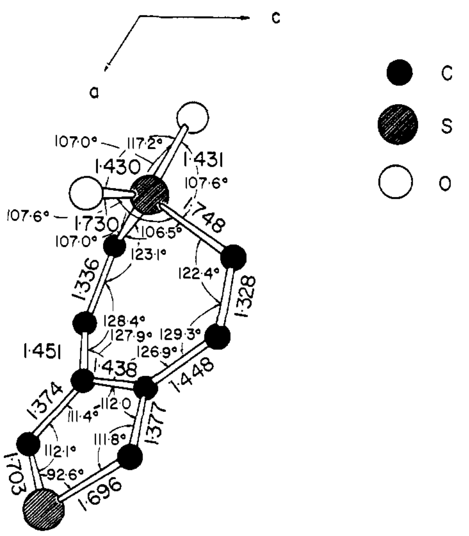
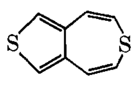


Figure 2. A projection of the thieno[3,4-*d*]thiepin 6,6-dioxide molecule down the *b* axis showing bond distances and angles. Estimated standard deviations are C–C = 0.006, C–S = 0.005, and S–O = 0.003 Å and 0.4° for angles. These have been obtained from coordinate standard deviations estimated from inverse elements of the inverse matrix after block diagonal anisotropic least-squares refinement.

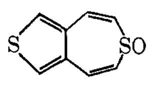
bon bond distance has been determined with reasonable accuracy and appears to be predominantly single bonded in character (1.46 ± 0.02 Å).[9] The other bond lengths appear to be quite reasonable at this stage of refinement and will be reported in a subsequent communication.

Thiepin **3** forms transparent needles which are monoclinic, $P2_1/c$, with $a = 8.897$, $b = 11.295$, and $c = 9.504$ Å, and $\beta = 121°\ 13'$. Intensity data were taken as described previously. Reflections (1384) were recorded to a maximum 2θ angle of 130°, representing about 75% of the data theoretically accessible in the Cu sphere. The structure was determined by the heavy-atom method. A sharpened three-dimensional Patterson function was calculated, and this revealed the positions of the sulfur atoms. Successive Fourier syntheses gave the complete structure. The structure was refined by block diagonal least-squares using individual isotropic temperature factors ($R = 11.5\%$), and finally with individual anisotropic temperature parameters ($R = 6.0\%$). Difference Fourier synthesis has revealed the positions of all of the hydrogen atoms.[10] Figure 2 shows the bond distances and angles of sulfone **3** as determined from this analysis. The seven-membered ring of this molecule exists in the boat conformation in much the same fashion as thiepin 1,1-dioxide.[3] The dihedral angles describing the ring puckering of sulfone **3** are 45.2 and 19.8°.[11]

The crystal structure of thiepin **1** bears a striking resemblance to that of azulene. This result lends weight to our previous suggestion that **1** is an extensively delocalized aromatic system in which species such as **4** contribute significantly to the ground state.[1] The degree of ring puckering present in **3** does not, in our opinion, indicate that any significant π-electron delocalization occurs in the seven-membered ring of this annulated thiepin sulfone.



1



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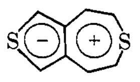

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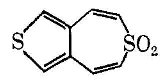

3

Work on other annulated thiepins related to **1** is in progress and will be reported shortly.

Acknowledgment. H. M. S. is a recipient of a Research Career Development Award from the U. S. Public Health Service, National Institutes of Health. This work has been supported in part by the National Institutes of Health, U. S. Public Health Service, the National Science Foundation, and the American Cancer Society. Facilities for this work were supplied in part by the U. S. Atomic Energy Commission at the University of Rochester Atomic Energy Project. This paper has been assigned Report No. UR-49-1090. Computations were done on an IBM 360-65 at the University of Rochester Computation Center.

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[9] In azulene, this bond length is 1.483 Å after full-matrix least-squares refinement.

[10] The complete details of the structure analysis of 3 will be published elsewhere.

[11] Similar dihedral angles of 44.6 and 22.8° have been found for thiepin 1,1-dioxide. See ref 3, Figure 1.

Lithium Cyanohydridoborate, a Versatile New Reagent

Sir:

In connection with our work on the hydride reduction of imino esters,[1] we had occasion to examine the reducing power of a variety of hydride reagents. We wish to report here our results with lithium cyanohydridoborate; in contrast to a previous report,[2] this versatile reagent will reduce a variety of functional groups with remarkable selectivity.

The utility of lithium cyanohydridoborate[3] is enhanced by its two important chemical properties: (1) the reagent is stable in acid up to pH ∼3, and at low pH the hydrogens can be readily exchanged;[4] (2) at pH <7, the reduction of an imminium group is much faster than the reduction of a carbonyl group. Thus, functional groups sensitive to the high pH required in sodium borohydride reductions (*cf.* thiamine, Table I) are easily reduced at pH 7, and by prior exchange of the hydrogens for deuterium or tritium an efficient and economical route is available for deuteride or triteride reduction of aldehydes and ketones. The faster rate of reduction of the imminium moiety provides an excellent method for reductive amination of aldehydes and ketones under exceedingly mild conditions.

The reductions of some representative functional groups are summarized in Table I. It should be noted that the rates of reduction are much slower than with

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(1) R. F. Borch, *Tetrahedron Lett.*, 61 (1968).

(2) G. Drefahl and E. Keil, *J. Prakt. Chem.*, **6**, 80 (1958).

(3) Available from Alfa Inorganics, Inc., Beverley, Mass.

(4) M. M. Kreevoy and J. E. C. Hutchins, submitted for publication.