The Crystal and Molecular Structure of Dehydrodithizone

By YOSHIHIKO KUSHI and QUINTUS FERNANDO*

(*Department of Chemistry, University of Arizona, Tucson, Arizona* 85721)

Summary The structure of the orange oxidation product of dithizone has been determined by X-ray analysis and shown to be dehydrodithizone, a tetrazole ring system with two phenyl groups substituted in the 2- and 3-positions and an exocyclic sulphur atom in the 5-position.

IN an attempt to prepare the adduct of 1,10-phenanthroline and the nickel(II) chelate of 3-mercapto-1,5-diphenylformazan (dithizone), an orange crystalline product was isolated after several days from an ethanol solution of the reactants. Elemental analysis and the molecular weight determined from the X-ray data suggested that the compound was probably the known[1] dehydrodithizone, $C_{13}H_{10}N_4S$. Its formulation as a sydnone[2] prompted us to carry out a single crystal X-ray structure determination of the compound.

The crystals are monoclinic with $a = 15{\cdot}490 \pm 0{\cdot}02$, $b = 12{\cdot}12 \pm 0{\cdot}02$, $c = 6{\cdot}98 \pm 0{\cdot}01$ Å, $\beta = 109{\cdot}0 \pm 0{\cdot}3°$, $U = 1239{\cdot}0$ Å^3, $Z = 4$, $D_c = 1{\cdot}36$, $D_m = 1{\cdot}37 \pm 0{\cdot}1$ g./cm.^{3} (by flotation), space group: Ic or $I2/c$ (alternatively, Cc or $C2/c$).† The cell dimensions were obtained from oscillation and Weissenberg photographs using Cu-K_α radiation ($\lambda = 1{\cdot}5418$ Å) and precession photographs with Mo-K_α radiation, ($\lambda = 0{\cdot}7107$ Å); μ (Cu-K_α) = 22·3 cm.$^{-1}$

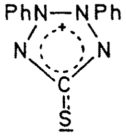
The intensity data were collected by visual estimation of equi-inclination Weissenberg photographs $hk0$—$hk4$ and $0kl$—$9kl$, obtained with Cu-K_α radiation. The structure was determined by Patterson and Fourier methods with 1121 independent reflections (1051 observed). Refinement of the structure by full-matrix least-squares techniques with anisotropic temperature factors for all atoms, led to a conventional R factor of 7·9%. The space group $I2/c$, confirmed by the structure analysis, requires that the molecule has a 2-fold axis. The bond distances and bond

---

† These results are in agreement with those obtained by H. Irving and his co-workers at the University of Leeds. (H. Irving, private communication.)

angles with their estimated standard deviations are shown in the Figure which is a perspective view of the molecule when projected down the *c*-axis.

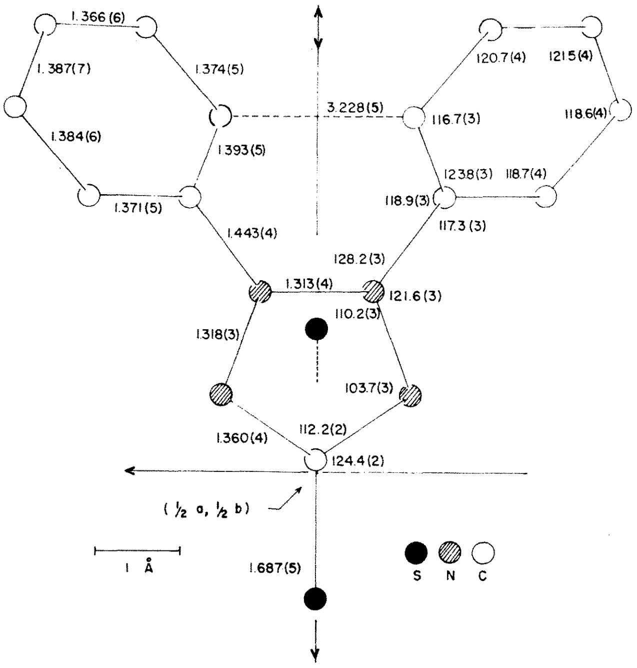
The crystal structure consists of discrete molecules of dehydrodithizone, ($C_{13}H_{10}N_4S$). The five-membered tetrazole ring and the sulphur atom form one plane. The N–N distances in the ring are all equal (average 1·316 Å), and are intermediate between 1·44 Å (single bond) and 1·24 Å (double bond).[3] The C–N distance in the ring of 1·360 Å shows that it has partial double bond character.[3] The C–S distance is 1·687 Å and is also intermediate between the C=S (double bond) distance of 1·56 Å and the C–S (single bond) distance of 1·81 Å.[3] These bond distances clearly show that electrons are delocalized throughout the ring system and the exocyclic sulphur atom; the structure of the compound is best represented by (I).



(I)

The phenyl groups are planar and the shortest intramolecular nonbonded C–C distance is 3·228 Å. The dihedral angle between the plane of the phenyl ring and the plane of the tetrazole ring is 45·0°. The C–N distance between the two rings is 1·443 Å which is the normal C–N single bond distance. Hence the phenyl groups are not conjugated with the tetrazole ring system.

The Figure also shows the position of another sulphur atom in the unit cell. The distance between the plane of the tetrazole ring and the sulphur atom is 3·48 Å. The crystal structure therefore consists of infinite chains of the type, · · · S · · tetrazole ring · · · · S · · · in the direction of the *c*-axis. This interaction between the sulphur atom and the π-system of the tetrazole ring indicates the presence of a residual negative charge on the sulphur atom as shown in structure (I).



FIGURE

We thank the National Science Foundation for financial assistance.

(*Received, August 18th, 1969; Com. 1270.*)

---

[1] E. Fischer and E. Besthorn, *Annalen*, 1882, **212**, 316; H. Fischer, *Angew. Chem.*, **1937**, **50**, 919; W. S. McDonald, H. M. N. H. Irving, G. Raper, and D. C. Rupainwar, *Chem. Comm.*, 1969, 392.

[2] P. Grammaticakis, *Compt. rend.*, 1952, **234**, 528; J. W. Ogilvie and A. H. Corwin, *J. Amer. Chem. Soc.*, 1961, **83**, 5023.

[3] "International Tables for X-Ray Crystallography," vol. III, pp. 257—276, Kynoch Press, Birmingham, 1962.