

Figure 1. The structure of monoclinic sulfur. Each twofold molecule may have either the orientation shown at  $x = 0$  or the orientation shown at  $x = 1$ .

special positions require centrosymmetric molecules, but the crown configuration is not centrosymmetric. A reasonable explanation is that the molecules which occupy special positions are disordered.

The structure of monoclinic sulfur has been determined from single crystal data. Crystals prepared from purified sulfur and annealed at  $100^\circ$  may be maintained at room temperature for up to a month. Complete data were collected by visually estimating the intensities on Weissenberg and precession photographs of these crystals. Enough signs to produce a recognizable Fourier were obtained by solving the Sayre-Cochran-Zachariasen relationship with the aid of Beurskens' IBM 1620 program.<sup>3</sup> The details of the determination and of the refinements will be published later. The discrepancy index  $R = \Sigma |F_o - F_c| / \Sigma |F_o|$  is presently 0.131 for 1270 observed reflections.

Table I. Atomic Parameters in Monoclinic Sulfur

Atom	$x$	$y$	$z$	Atom	$x$	$y$	$z$
1	0.234	0.525	0.031	9	0.182	-0.108	0.081
2	0.152	0.356	0.006	10	0.052	-0.069	0.206
3	0.256	0.252	-0.101	11	0.004	0.113	0.188
4	0.374	0.144	0.014	12	-0.152	0.126	0.079
5	0.537	0.228	0.037	13	-0.119	0.171	-0.093
6	0.553	0.315	0.208	14	-0.129	0.009	-0.193
7	0.512	0.498	0.176	15	0.053	-0.048	-0.201
8	0.332	0.525	0.202	16	0.094	-0.185	-0.073

The unit cell (Figure 1) contains four  $S_8$  crowns in general positions 4(e) of space group  $P2_1/c$ :  $\pm(x, y, z; x, 1/2 - y, 1/2 + z)$  with  $x = 0.367$ ,  $y = 0.356$ , and  $z = 0.072$ . The remaining two molecules occupy the special positions 2(a):  $0, 0, 0; 0, 1/2, 1/2$ . Each molecule in 2(a) can assume one of two possible orientations, related by a center of inversion; these are indicated in Figure 1 by different orientations at  $x = 0$  and at  $x = 1$ . The atomic coordinates are listed in Table I.

(3) P. T. Beurskens, *Acta Cryst.*, **17**, 462 (1964); P. T. Beurskens, "Technical Report on Sign Correlation by the Sayre Equation," Crystallography Laboratory, University of Pittsburgh, 1963.

The random orientations of the molecules in 2(a) are taken into account in the calculations by giving atoms 9 through 16 weights of one-half.

At the present stage of refinement the average bond length for each crystallographic type of molecule is  $2.06 \text{ \AA}$ . The average isotropic temperature factors are  $3.6 \text{ \AA}^2$  for the molecules in 4(e) and  $5.1 \text{ \AA}^2$  for the molecules in 2(a). The intermolecular contacts (minimum  $3.38 \text{ \AA}$ ) are comparable to those in orthorhombic sulfur and in rhombohedral sulfur.<sup>4</sup>

This disordered arrangement leads to a residual entropy of  $R/3 \ln 2$  per mole of  $S_8$  molecules, or  $0.057 \text{ e.u./g.-atom}$  of sulfur. The experimental entropy, based on the available heat capacity and enthalpy data for orthorhombic and monoclinic sulfur,<sup>5</sup> is  $0.045 \pm 0.050 \text{ e.u./g.-atom}$ .

(4) J. Donohue, A. Caron, and E. Goldish, *J. Am. Chem. Soc.*, **83**, 3748 (1961).

(5) E. D. Eastman and W. C. McGavock, *ibid.*, **59**, 145 (1937); E. D. West, *ibid.*, **81**, 29 (1959).

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#### The Influence of Ionic Strength on Polarographic Half-Wave Potentials. IV. Theoretical Considerations Involving Systems of Mixed Uni-Univalent Inert Electrolytes

Sir:

In an earlier communication,<sup>1</sup> we have shown that the shift in the half-wave potential of cadmium, in systems of mixed uni-univalent nitrate inert (supporting) electrolytes, followed the empirical relationship.

$$(E_{1/2})_{\text{obsd}} = (E_{1/2})_{\mu=0} + (\Delta E_{1/2})_{\text{obsd}} = (E_{1/2})_{\mu=0} + N_a(\Delta E_{1/2})_a + N_b(\Delta E_{1/2})_b \quad (1)$$

where  $(E_{1/2})_{\mu=0}$  is the half-wave potential of cadmium at zero inert electrolyte concentration, and  $N_a$  and  $N_b$  are the mole fractions of inert electrolytes a and b, respectively. The half-wave potential shifts,  $(\Delta E_{1/2})_a$  and  $(\Delta E_{1/2})_b$ , are the predicted shifts in systems of electrolyte a or b alone and have been theoretically shown to be<sup>2</sup> (in mv.)

$$(\Delta E_{1/2})_{a \text{ or } b} \cong \{29.5 \log \gamma_{\pm} + 4.62m\phi\}_{a \text{ or } b} \quad (2)$$

where  $\gamma_{\pm}$  is the mean activity coefficient and  $\phi$  is the osmotic coefficient of electrolyte a or b, respectively. It is the purpose of this investigation to show that eq. 1 possesses some theoretical significance.

If the effect of the electrolytes a and b on the change in the half-wave potential for cadmium is a purely extensive one, then eq. 2 for systems of mixed electrolytes would become

$$(\Delta E_{1/2})_{\text{obsd}} = \{29.5 \log (\gamma_{\pm})_t + 4.62m\phi_t\} \quad (3)$$

where  $m$  is the total molality and  $(\gamma_{\pm})_t$  and  $\phi_t$  are the total activity and osmotic coefficients of the system, respectively.

When the two inert electrolytes have an ion in com-

(1) Part II: N. E. Vanderborgh and D. E. Sellers, *J. Am. Chem. Soc.*, **86**, 2790 (1964).

(2) D. E. Sellers and N. E. Vanderborgh, *ibid.*, **86**, 1934 (1964).

mon, it has been shown<sup>3</sup> that  $\phi_t$  can be represented as a linear function of the solution composition, or

$$\phi_t = \phi_b + (\phi_a - \phi_b)N_a = \phi_a + (\phi_b - \phi_a)N_b \quad (4)$$

If  $\phi_t$  is a linear function of a or b, then  $\log(\gamma_{\pm})_t$  would also be expected to be, such that

$$\log(\gamma_{\pm})_t = \log(\gamma_{\pm})_a + [\log(\gamma_{\pm})_b - \log(\gamma_{\pm})_a]N_b \quad (5)$$

Substitution of eq. 4 and 5 into eq. 3 yields, after rearrangement

$$(\Delta E_{i/2})_{\text{obsd}} = \{29.5[(1 - N_b) \log(\gamma_{\pm})_a + N_b \log(\gamma_{\pm})_b] + 4.62m[(1 - N_b)\phi_a + N_b\phi_b]\} \quad (6)$$

Now,  $1 - N_b$  is equal to  $N_a$ , and eq. 6 becomes

$$(\Delta E_{i/2})_{\text{obsd}} = \{N_a[29.5 \log(\gamma_{\pm})_a + 4.62m\phi_a] + N_b[29.5 \log(\gamma_{\pm})_b + 4.62m\phi_b]\} \quad (7)$$

and since

$$[(\Delta E_{i/2})_{\text{obsd}}]_b = \{29.5 \log(\gamma_{\pm})_b + 4.62 m\phi_b\} \quad (8)$$

then eq. 7 becomes identical with eq. 1 when one considers that  $(\Delta E_{i/2})_{\text{obsd}} = (E_{i/2})_{\text{obsd}} - (E_{i/2})_{\mu=0}$ .

(3) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd Ed., Butterworths, London, 1959, p. 437.

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## The Synthesis of Apo- $\beta$ -erythroidine

Sir:

In their work directed toward the elucidation of the structure of  $\beta$ -erythroidine, a physiologically active alkaloid isolated from several species of *Erythrina*, Boekelheide and co-workers obtained a rearranged demethoxy derivative which they called apo- $\beta$ -erythroidine.<sup>1</sup> The latter compound, to which structure XV was assigned,<sup>1a</sup> was of interest for its unusual tetracyclic structure, its relationship to the parent alkaloid, and its own physiological activity. Several attempts at synthesizing apo- $\beta$ -erythroidine or its analogs were unsuccessful<sup>2-4</sup>; most noteworthy with respect to the results reported in this communication was the observed<sup>4</sup> inactivity of the carbonyl of 1-methyl-2,3,4,5-tetrahydro-5-oxo-1-benzazepine toward normal addition reactions (presumably due to nitrogen-carbonyl resonance interaction) and the well-known<sup>3</sup> difficulty in preparing 7-substituted indolines.

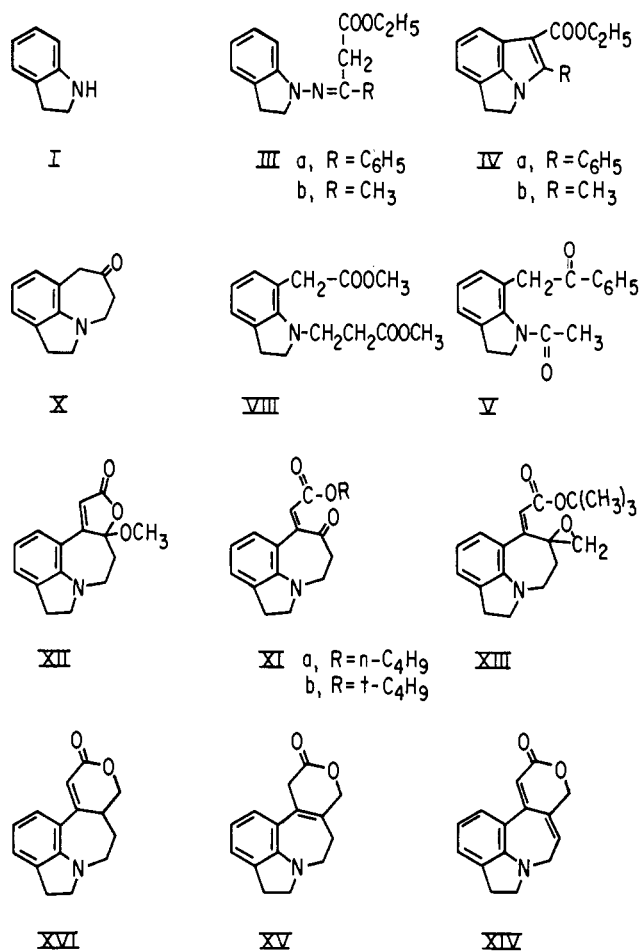
We now wish to report the synthesis of apo- $\beta$ -erythroidine (XV) and isoapo- $\beta$ -erythroidine (XVI).<sup>5</sup>

(1) (a) See V. Boekelheide, J. Weinstock, M. F. Grundon, G. L. Sauvage, and E. J. Agnello, *J. Am. Chem. Soc.*, **75**, 2550 (1953), for a summary of the structural work on  $\beta$ -erythroidine. (b) Also see V. Boekelheide in "The Alkaloids," Vol. VII, R. H. F. Manske, Ed., Academic Press Inc., New York, N. Y., 1960, pp. 201-227, for a recent summary of the structural work on the *Erythrina* alkaloids. (c) F. Koniuszy and K. Folkers, *J. Am. Chem. Soc.*, **73**, 333 (1951), isolated a derivative of  $\beta$ -erythroidine. The latter differed in melting point and particularly in optical rotation from the apo- $\beta$ -erythroidine isolated by Boekelheide, *et al.*,<sup>1a</sup> and thus was apparently impure or not the same compound.

(2) V. Boekelheide and W. G. Gall, *J. Org. Chem.*, **19**, 504 (1954).

(3) W. G. Gall, B. D. Astill, and V. Boekelheide, *ibid.*, **20**, 1538 (1955).

(4) B. D. Astill and V. Boekelheide, *J. Am. Chem. Soc.* **77**, 4079 (1955).



This synthesis was made possible by an interesting, partial reversal of the Fischer indole ring closure in the 1,2-dihydropyrrolo[3,2,1-*hi*]indole series and constitutes a practical synthesis of 7-substituted indolines.

Indoline<sup>6</sup> (I) was nitrosated and then reduced with lithium aluminum hydride to give 1-aminoindoline<sup>7</sup> (II) in 70% yield. Treatment of the substituted hydrazine II with either ethyl benzoylacetate or ethyl acetoacetate gave the hydrazones IIIa,b, which were unstable and could not be readily characterized but were converted, by sulfuric acid in absolute ethanol at reflux, to 4-phenyl-5-ethoxycarbonyl-1,2-dihydropyrrolo-[3,2,1-*hi*]indole (IVa) in 83% yield [m.p. 137-138°;  $\lambda_{\text{max}}^{\text{CH}_3\text{OH}}$  309 ( $\epsilon$  9500) and 251  $\mu$  (18,000)], and to the methyl analog IVb in 54% yield [m.p. 89-90°;  $\lambda_{\text{max}}^{\text{CH}_3\text{OH}}$  297 ( $\epsilon$  14,000), 240 (22,600), and 220  $\mu$  (38,000)]. This ring system was previously synthesized for the first time by a Fischer reaction on the hydrazone of 1-aminoindoline and ethyl pyruvate to give the 1,2-dihydro-4-ethoxycarbonyl derivative.<sup>8</sup>

When IVa was treated with sulfuric acid in aqueous ethanol at reflux, we obtained 7-phenacylindoline, which was acetylated to facilitate isolation and give 1-acetyl-7-phenacylindoline (V) in 90% yield (m.p. 136-137°). This hydrolytic opening is unknown in simpler systems and presumably is the result of considerable steric strain in the 6,5,5-fused ring system of IV.

(5) Isoapo- $\beta$ -erythroidine is an isomer of apo- $\beta$ -erythroidine obtained when the latter is chromatographed on alumina; see ref. 1a.

(6) H. Rapoport and J. R. Tretter, *J. Org. Chem.*, **23**, 248 (1958).

(7) Satisfactory elemental analyses were obtained for all compounds reported herein.

(8) H. Rapoport and J. R. Tretter, *J. Am. Chem. Soc.*, **80**, 5574 (1958).