biliverdin dimethyl ester. The =NH resonances were imperceptible in the HA-100 spectrum.[3] These were assigned by elimination and from the observation[2] that phycoerythrobilin possesses only one pyrrolenine (—N=) nitrogen. The vinyl group and the unsaturated ring A were assigned by comparison with biliverdin dimethyl ester and phycocyanobilin dimethyl ester, respectively. Specifically there were no resonances attributable to the CH_3– and –CH_2– of an ethyl group, nor any attributable to a third methine bridge.

Mass spectral analyses[6,7] gave a strong base peak at *m/e* 614, requiring the empirical formula $C_{35}H_{42}N_4O_6$. The mass spectrum also showed an intense peak at *m/e* 492. This would be consistent with cleavage of the pyrrole (D) ring at the methylene bridge.

Validation of this structure is provided by two simple isomerizations. Treatment of phycoerythrobilin with 12 *N* HCl under N_2 at room temperature yields phycocyanobilin (identified as dimethyl ester by visible, ultraviolet, and infrared absorption spectra and mixed chromatography). Phycoerythrobilin, boiled in 1 *N* KOH in methanol under reflux for 15 min, yields mesobiliverdin (identified as dimethyl ester by visible, ultraviolet, and infrared absorption spectra and mixed chromatography).

Assignment of the 7′ proton to the pyrrole ring substituted with the vinyl group is based on the prototropic isomerizations to phycocyanobilin and mesobiliverdin and the strong *m/e* 492 peak.

The *β* substituents of rings A and D may be interchanged in the structure proposed, but the mass spectra pattern and the visible–ultraviolet absorption spectrum would support the conjugated system present in the structure outlined. Enzymatic cleavage of C-phycoerythrin with the enzyme Nagarse[8] yields phycoerythrobilin, providing further support that it is the native chromophore.

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(8) H. W. Siegelman, D. J. Chapman, and W. J. Cole, *Arch. Biochem. Biophys.*, in press.

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Molecular Geometry and Bonding in the Sydnone Ring

Sir:

The sydnones, which have been taken as prototypes of the general class of "mesoionic" compounds,[1] have thus far evaded a satisfactory formulation for their bonding.[2]

The most commonly written formula, I, whose implied aromaticity would account for the weak basicity of the sydnones[3] and for their benzenoid electronic spectra,[5,6] is difficult to reconcile with the high frequency (1768 cm^{-1}) and intensity of the carbonyl stretching band observed for the 3-alkylsydnones.[7]

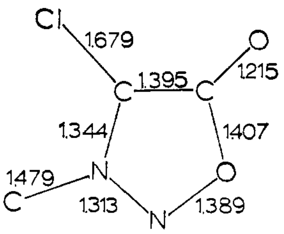


Figure 1.

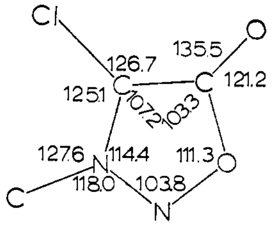
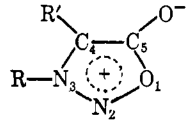


Figure 2.

A crystal structure determination of 3-*p*-bromophenylsydnone[8] indicated a molecular geometry which could not be interpreted in terms of structure I. It



I

was pointed out that the geometry of the sydnone ring might be influenced by a "charge transfer interaction" between the carbonyl oxygen and a neighboring bromine atom, and since the estimated standard deviations for bond distances were as high as 0.015 A, we felt that it was worthwhile to determine another sydnone structure. We chose for investigation 4,4′-dichloro-3,3′-ethylenebissydnone,[4] which crystallizes in the orthorhombic system, space group Pbca with eight molecules in the unit cell, thus permitting the determination of two crystallographically independent sydnone rings in the same crystal. The structure was determined by use of data collected with a Picker automatic diffractometer. The final *R* index for 1312 observed reflections was 0.042, and estimated standard deviations for bond lengths were about 0.004–0.005 A. Average bond distances and angles, corrected for anisotropic thermal motion effects,[9] are shown in Figures 1 and 2. The structure reported by Bärnighausen, *et al.*,[8] is in satisfactory agreement with ours, when due consideration is given to the standard deviations.

It is clear that all of the ring distances except that of the C–O bond are between single and double, and compare with, for example, the aromatic distances in benzene (1.397 A),[10] the C=N distance in pyridine (1.340 A),[11] the N=N distance in tetrazine (1.321 A),[12] and the N=O distance in 1,2,5-oxadiazole (1.380 A).[13]

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(1) W. Baker and W. D. Ollis, *Quart. Rev.* (London), **11**, 15 (1957).

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(3) Sydnones crystallize from moderately concentrated mineral acid solutions.[4]

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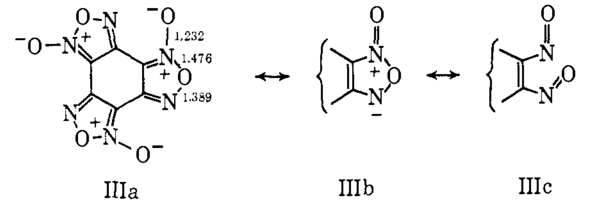
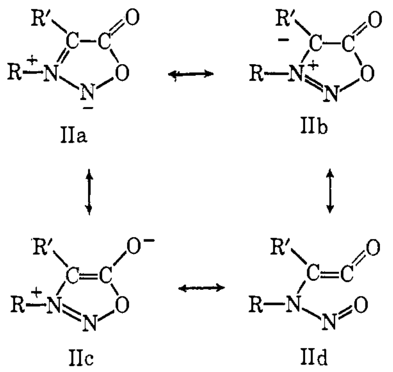


IIIa IIIb IIIc

Figure 3.

Disparity with formulation I arises in the C–O ring distance (1.407 A), which is longer than those of furan (1.362 A)[14] and the α,β-unsaturated lactones anemonin[15] and 4-hydroxycoumarin[16] (1.37 A). The exocyclic C=O bond is essentially double, being only slightly longer than those (1.19–1.20 A) found in anemonin and 4-hydroxycoumarin. This combination of bond lengths would seem to be best accommodated by postulating the noncharge-separated form IId as a significant contributor to the resonance hybrid II.[17]

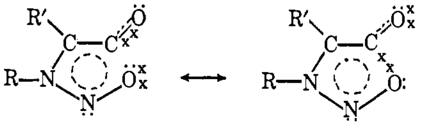


IIa IIb IIc IId

The striking deformation of the bond angles about the carbonyl group (Figure 2) is, then, directly attributable to the contribution of the ketene-like form IId.[19] The expected higher energy of such a bent ketene form must be counterbalanced by the coulombic work involved in charge separation in the other contributors.

Analogy for the foregoing proposal is found in the structure of benzotrifuroxan,[20] whose average bond lengths are given in Figure 3. These distances bespeak only a minor contribution from IIIa, a major contribution from IIIb, and a significant contribution from IIIc, since the 1.476-A distance is longer than any actual N–O single bond and is appreciably longer than the 1.44 A calculated for a pure single N–O bond.[21]

The bonding in sydnones can be viewed in the following way. Eight π electrons are distributed (as proposed by Thomas[22]) in orbitals perpendicular to the plane of the sydnone ring. These electrons are represented by dashes in structure IV. Four electrons, represented by x's, *in the plane* of the sydnone ring are appreciably delocalized over one carbon and two oxygen atoms. The extremes of this delocalization are represented by IVa and IVb.



IVa IVb

This delocalization appears to lend extra p character to the carbon orbital associated with the ring oxygen, thereby lengthening that bond, and to detract p character from the other two orbitals of that carbon, shortening those bonds and widening the angle between them.

The carbon–chlorine distance (Figure 1) found in this study is significantly shorter than the 1.74 A found in several aryl[23] and vinyl[24] chlorides. This may represent delocalization of the chlorine lone-pair electrons onto the relatively positive ring nitrogen atom.

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Conformational Analysis in Multisulfur Heterocycles. I. Chair–Boat Equilibration in Duplodithioacetone

Sir:

In the numerous reports of the measurement of the rate of chair–chair equilibration in various six-membered carbocycles,[1] the boat or twist-boat conformation has been postulated as a discrete intermediate. However, thermodynamic calculations[2] and a direct experimental technique[3] indicate that the boat forms of such six-membered carbocycles are of substantially higher energy (3–10 kcal/mole) than the corresponding chair conformations. The detection of such conformationally unstable species utilizing nuclear magnetic resonance (nmr) spectroscopy is essentially impossible.

This report concerns the observation of a conformationally stable twist-boat form of duplodithioacetone (tetramethyl-*s*-tetrathiane) as an intermediate in the equilibration of the *less stable* chair conformers.

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