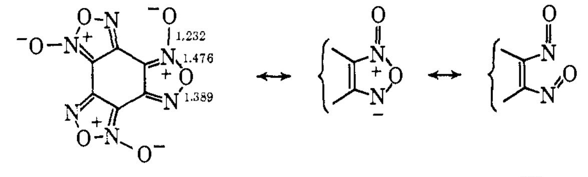
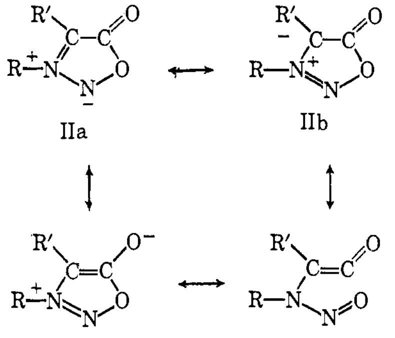


IIIa IIIb IIIc

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]

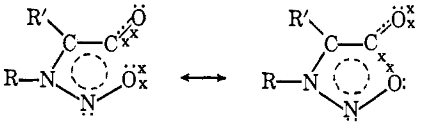


IIa IIb IIc IId

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.

Acknowledgments. Financial support of this research by the National Science Foundation (NSF GP-6635) is gratefully acknowledged. We are indebted to Professor John I. Brauman for helpful discussions.

---

(14) B. Bak, D. Christensen, W. B. Dixon, L. Hansen-Nygaard, J. Rastrup-Andersen, and M. Schottländer, *J. Mol. Spectry.*, **9**, 124 (1962).

(15) I. L. Karle and J. Karle, *Acta Cryst.*, **20**, 555 (1966).

(16) J. Gaultier and C. Hauw, *ibid.*, **20**, 646 (1966).

(17) This contributor, first mentioned by Earl, Leake, and Le Fevre[18] was summarily dismissed by Baker, Ollis, and Poole[5] on the ground that the C–C–O system in the sydnone cannot be linear as it is in the ground state of ketene. The geometry of a resonance hybrid is, of course, not limited to the hypothetical ground state geometry of one of the contributors, benzene being an obvious example.

(18) J. C. Earl, E. W. Leake, and R. J. W. Le Fevre, *Nature*, **160**, 366 (1947).

(19) Corresponding bond angles about the two carbonyl groups agree with each other to within 1°, even though one of the carbonyl oxygen atoms is involved in a relatively close (2.98 A) intermolecular contact with a neighboring chlorine while the other carbonyl oxygen is free of such contact.

(20) H. H. Cady, A. C. Larson, and D. T. Cromer, *Acta Cryst.*, **20**, 336 (1966).

(21) I. M. Levine, *J. Chem. Phys.*, **38**, 2326 (1963).

(22) W. J. O. Thomas, *Chem. Ind.* (London), 533 (1955).

(23) (a) G. J. Palenik, *Acta Cryst.*, **19**, 47 (1965); (b) T. Sakurai, M. Sundaralingam, and G. A. Jeffrey, *ibid.*, **16**, 354 (1963); (c) G. Gafner and F. H. Herbstein, *ibid.*, **15**, 1081 (1962).

(24) L. H. Kaplan, *Dissertation Abstr.*, **19**, 3130 (1959).

W. E. Thiessen, Håkon Hope
Department of Chemistry, University of California
Davis, California 95616

Received August 7, 1967

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.

---

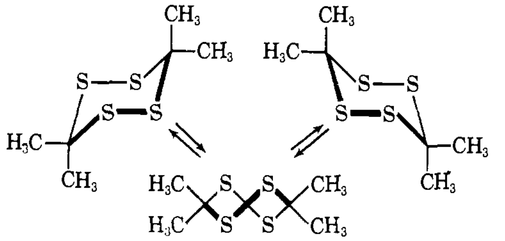
(1) F. R. Jensen, D. S. Noyce, C. H. Sederholm, and A. J. Berlin, *J. Am. Chem. Soc.*, **84**, 386 (1962); F. A. L. Anet and A. J. R. Bourn, *ibid.*, **89**, 760 (1967); F. A. L. Anet and M. Z. Haq, *ibid.*, **87**, 3147 (1965); F. R. Jensen and C. H. Bushweller, *ibid.*, **87**, 3285 (1965).

(2) C. W. Beckett, K. S. Pitzer, and R. Spitzer, *ibid.*, **69**, 2488 (1947); C, W, Beckett, N. K. Freeman, and K. S. Pitzer, *ibid.*, **70**, 4227 (1948); R. B. Turner, *ibid.*, **74**, 211 (1952); K. E. Howlett, *J. Chem. Soc.*, 4353 (1957).

(3) W. S. Johnson, J. L. Margrave, V. J. Bauer, M. A. Frisch, L. H. Dreger, and W. N. Hubbard, *J. Am. Chem. Soc.*, **82**, 1255 (1960).

Examination of the nmr spectrum[4] of duplodithioacetone (15% by weight in $Cl_2C{=}CCl_2$) at 35° reveals a set of two broad resonances of unequal intensities at δ 2.00 and 1.66 ppm. Upon lowering the temperature, these resonances sharpened in the usual manner (Figure 1) into a set of three peaks consisting of two resonances of *equal area* at δ 1.53 and 2.03 ppm and a larger sharp singlet at δ 1.68 ppm. When the sample temperature was raised, the spectrum showed kinetic broadening characteristic of an intermediate exchange rate on the nmr time scale (Figure 1), and at 80°, the two broad resonances observed at 35° had coalesced into a singlet at δ 1.73 ppm. Upon again lowering the temperature, an identical sequence of spectral transitions was observed.

The above results would seem to be best rationalized by the presence of a thermodynamically stable twist-boat form of duplodithioacetone in equilibrium with the two chair conformers (eq 1).[5] At lower temperatures

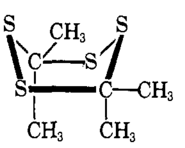


(1)

(−30°), the two peaks of equal area at δ 1.53 and 2.03 ppm (Figure 1) are assigned to the axial and equatorial methyl resonances of the chair conformers of duplodithioacetone (eq 1) and the sharp singlet at δ 1.68 ppm to the symmetrical twist-boat conformation (eq 1). The ratio of boat to chair conformers is 2.2:1.0, respectively, at 0° ($\Delta F° = -0.8$ kcal/mole).

The free energy of activation ($\Delta F^{\ddagger}$) for the chair to boat process is estimated to be 16 ± 1 kcal/mole at 50°.

Entropy considerations, the long carbon–sulfur and sulfur–sulfur bonds, and the complete lack of any Pitzer strain due to carbon–hydrogen bonds in the flexible twist-boat form apparently render it more stable than the rigid chair form of duplodithioacetone. Indeed, X-ray crystallographic studies[6] indicate that duplodithioacetone exists in a boat conformation with a sulfur atom at each prow position (I).



I

In acetone diperoxide, it is apparent that the shorter carbon–oxygen and oxygen–oxygen bond lengths play an important role in causing the chair form to be the most stable conformer.[7] It would be expected that lone-pair repulsions would be larger in acetone diperoxide than in duplodithioacetone. Indeed, a consideration of models indicates that the true boat form of acetone diperoxide is incapable of existence due to serious nonbonded compressions between methyl groups. However, the twist-boat conformer would appear to be relatively strain-free, although lone-pair repulsions are still probably serious.

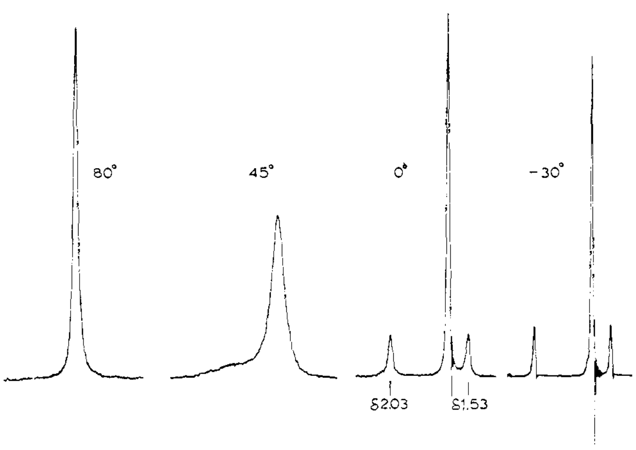


Figure 1. The nmr spectrum (60 Mc) of duplodithioacetone at various temperatures.

The barrier to conformational isomerism in duplodithioacetone is comparable to that in acetone diperoxide ($\Delta F^{\ddagger} = 15.4$ kcal/mole at 30°)[7] and substantially higher than in 1,1,4,4-tetramethylcyclohexane ($\Delta F^{\ddagger} = 11.4$–$11.6$ kcal/mole at −65°).[8] The barriers to chair–chair equilibration in 3,3,6,6-tetramethyl-1,2-dithiane ($\Delta F^{\ddagger} = 13.8$ kcal/mole at −2°) and 3,3,6,6-tetramethyl-1,2-dioxane ($\Delta F^{\ddagger} = 14.6$ kcal/mole at 12°) are of intermediate value.[9]

Duplodithioacetone was prepared according to the method of Magnusson.[10]

Our effort toward the conformational analysis of other multisulfur ring systems, as well as the measurement of the conformational enthalpy and entropy of chair ⇄ boat equilibria, is continuing.

---

[4] The nmr spectra were recorded on a Varian Associates A-60 nmr spectrometer using a V-6040 temperature controller. Temperature was measured using a methanol sample.

[5] The data as presented do not rule out unequivocally some kind of dissociative process for rendering all the methyl groups equivalent. However, the very sharp lines in the nmr spectrum observed at high temperatures (>80°) would seem to rule out the intervention of radicals in such a process. Experiments are in progress to test such a hypothesis.

[6] A. Fredga, *Acta Chem. Scand.*, **12**, 891 (1958).

[7] R. W. Murray, P. R. Story, and M. L. Kaplan, *J. Am. Chem. Soc.*, **88**, 526 (1966).

[8] R. W. Murray and M. L. Kaplan, *Tetrahedron*, **23**, 1575 (1967); W. Reusch and D. F. Anderson, *ibid.*, **22**, 583 (1966); H. Friebolin, W. Faisst, and H. S. Schmid, *Tetrahedron Letters*, 1317 (1966).

[9] G. Claeson, G. Androes, and M. Calvin, *J. Am. Chem. Soc.*, **83**, 4357 (1961).

[10] B. Magnusson, *Acta Chem. Scand.*, **13**, 1031 (1959).

C. Hackett Bushweller
Oxidation and Catalyst Research Section
Mobil Chemical Company, Edison, New Jersey 08817

Received August 28, 1967

The Far-Ultraviolet Cotton Effects and Conformation of Ribonuclease and Pepsin[1]

Sir:

The conformation of ribonuclease has been disclosed recently by high-resolution X-ray diffraction.[2,3] This

---

[1] This study was supported in part by Grant CA-01785 from the National Cancer Institute, National Institutes of Health, U. S. Public Health Service, and by Grant G-051 from the Robert A. Welch Foundation, Houston, Texas.

[2] G. Kartha, J. Bello, and D. Harker, *Nature*, **213**, 862 (1967).

[3] H. W. Wyckoff, K. D. Hardman, N. M. Allewell, T. Inagami, L. N. Johnson, and F. M. Richards, *J. Biol. Chem.*, **242**, 3984 (1967); H. W. Wyckoff, private communication.