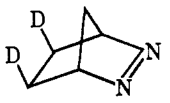
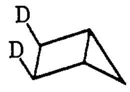
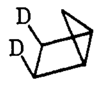


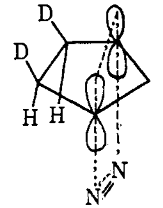
IV



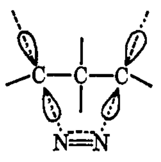
Va



Vb



VI



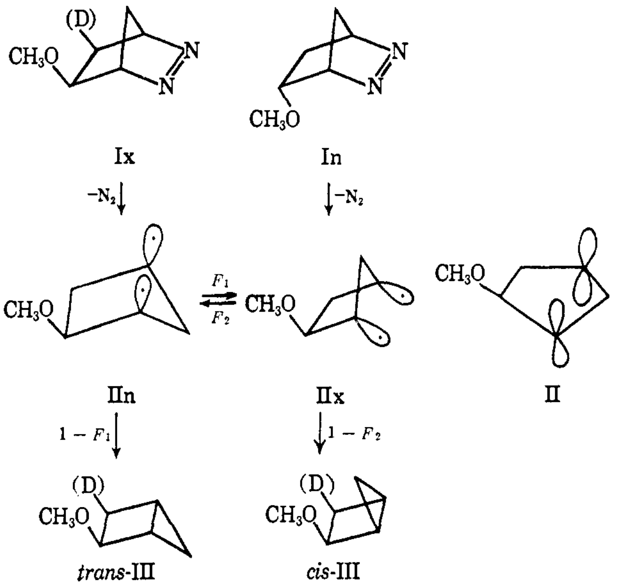
end view

VI

The Ix–In system provides a test of the above mechanism. Consideration of steric interaction between an *exo*-methoxyl group and C-7 hydrogen implies that Ix should show more inversion than IV. An *endo*-methoxyl group should cause hindrance to departure of nitrogen, and less inversion is predicted for In. These expectations are not realized. While the rate increases with Ix, inversion is substantially less. For In the rate decreases, but inversion is significantly greater.

A more plausible mechanism which accounts for the results may be formulated as shown in Scheme I. We propose that structurally inverted pyramidal diradicals IIn and IIx arise directly upon nitrogen elimination for Ix and In, respectively.[14–16] This inversion is thought to be a consequence of recoil from energy released by C–N bond breaking.[17] The excess product of inverted structure indicates that ring closure occurs before IIn or IIx fully equilibrate. The magnitude of decomposition rate differences strongly suggests that little product of retained structure results by direct formation of structurally retained diradicals from Ix or In.

Scheme I



It is instructive to evaluate the mole fraction of nonplanar diradicals which invert (F) or close to product ($1 - F$). This is accomplished by adjusting the values with successive approximations until both experimental product ratios are reproduced. The best values are $F_1 = 0.672$, $(1 - F_1) = 0.328$, $F_2 = 0.174$, and $(1 - F_2) = 0.826$. These fractions require that IIn and IIx be very short-lived. As calculated from eq 1, the per cent product, P, arising from diradicals which close directly

$$P = 100[(1 - F_1) + F_1(1 - F_2)] = 100[(1 - F_2) + F_2(1 - F_1)] \quad (1)$$

or invert only once and then close is 88.3%. A similar analysis of the *exo*-5,6-d_2-IV data shows 89.0% product formation before the nonplanar intermediates can invert more than once. This correspondence of values serves as a check of Scheme I since the diradicals from the Ix–In system and IV should have comparable lifetimes.

Evan L. Allred, Richard L. Smith
Department of Chemistry, University of Utah
Salt Lake City, Utah 84112

Received July 13, 1967

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[14] At present it is not clear whether a planar intermediate, II, also is involved, or if such a conformation only represents a transition state. It seems likely that II will be of higher energy than IIn or IIx because of strain imposed by planar 1,3-carbons in a five-membered ring.

[15] There is precedent for a short-lived nonplanar alkyl radical: P. D. Bartlett, R. E. Pincock, J. H. Rolston, W. F. Schindel, and L. A. Singer, *J. Am. Chem. Soc.*, 87, 2590 (1965).

[16] Recent results afford ample evidence that thermolysis of other 1-pyrazolines leads to nitrogen-free intermediates.[2a–c]

[17] A referee has suggested that orbital symmetry considerations may offer an explanation for the "direct" formation of inverted diradicals. We had considered this unlikely; a similar opinion has been reached by R. Hoffmann (private communication).

Circular Dichroism and the Absolute Configuration of the Chiral Disulfide Group[1]

Sir:

The S–S group has long been known to prefer a skewed, asymmetric spatial arrangement, whether in H_2S_2,[2] in allotropic forms of elemental sulfur,[3] in some inorganic polythio compounds,[4] or in various organic compounds whose structures have been determined by X-ray and other physical methods. Skewed configurations were predicted[5] for the general case of compounds containing atoms, $-\underset{..}{\overset{..}{A}}-\underset{..}{\overset{..}{B}}-$, with unshared electrons on adjacent atoms.

The energy barrier to rotation about the sulfur–sulfur bond has been variously estimated at 3–14 kcal/mole.[6] Enantiomeric forms of simple disulfides would not be expected to be resolvable at room temperature. The presence, however, of a fixed asymmetric center near a disulfide group in a molecule creates the possibility for unequal distribution of diasteroisomeric forms by a kind of asymmetric induction.[7] Fredga[8] has described a number of examples of large optical rotations observed even in the visible region for compounds having a disulfide group near an asymmetric carbon atom.[8]

ORD[9] and CD[10] spectra for cystine and certain cyclic

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[1] Publication No. 1519 of the Department of Chemistry, Indiana University.

[2] F. Fehér and M. Baudler, *Z. Elektrochem.*, 47, 844 (1941).

[3] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 134–136.

[4] O. Foss, *Advan. Inorg. Chem. Radiochem.*, 2, 237 (1960).

[5] W. G. Penney and G. B. B. M. Sutherland, *J. Chem. Phys.*, 2, 492 (1934).

[6] U. Schmidt, P. Grafen, and H. W. Goedde, *Angew. Chem. Intern. Ed. Engl.*, 4, 846 (1965).

[7] E. E. Turner and M. M. Harris, *Quart. Rev.* (London), 1, 299 (1947).

[8] A. Fredga, *Acta Chem. Scand.*, 4, 1307 (1950).

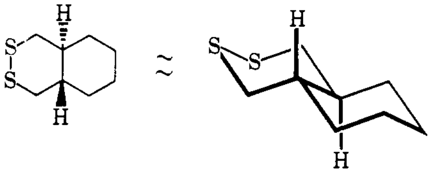
[9] J. A. Schellman in "Optical Rotatory Dispersion. Applications to Organic Chemistry," C. Djerassi, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1960, Section 15-4; *cf.* also Section 14-6.

[10] L. Velluz and M. Legrand, *Angew. Chem. Intern. Ed. Engl.*, 4, 838 (1965).

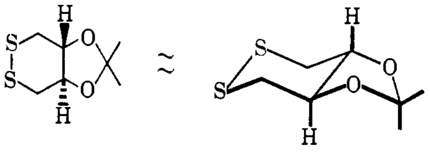
disulfides[11] have Cotton effects in the absorption region characteristic of disulfide groups between 250 and 330 mμ.

Beychok[12] has recently called attention to the potential usefulness of CD observations in this region for the study of phenomena involving the disulfide groups in biologically important proteins, but has pointed out the absence of direct evidence to permit the determination of the "screw sense" from circular dichroism data.

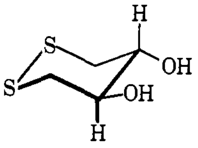
We wish to report on the results of our circular dichroism studies of several model compounds specifically synthesized to contain asymmetric carbon centers of known absolute configuration in which the helical sense of the disulfide groups can be predicted with reasonable certainty. Compound **1**, (9*S*,10*S*)(−)-*trans*-2,3-dithiadecalin, was synthesized from (+)-*trans*-cyclohexane-1,2-dicarboxylic acid, whose absolute configuration has been shown to be *S*,*S*.[13] Compound **2**, (4*R*,5*R*)(+)-4,5-isopropylidenedioxy-1,2-dithiane, was synthesized[14] from D$_s$(+)-tartaric acid; thus, the absolute configuration of its dithiane ring is established as opposite to that of **1**. Acidic hydrolysis of **2** gave the monocyclic **3**.



1



2



3

Because of the close structural relationship of **1** to *trans*-decalin and to 1,2-dithiane, which have been shown on the basis of dipole moment data[15] to prefer the chair conformation, it seems reasonable to assign chair conformations to the dithiane rings of both **1** and **2**. In the chair,chair form, **1** has a left-handed (M)[16] helix and **2** has a right-handed (P)[16] helix.

The ultraviolet and circular dichroism parameters are listed in Table I. Compound **1** has a negative CD band at 290 mμ while compound **2** has a positive band at 287 mμ.

Table I. Ultraviolet and Circular Dichroism Parameters[a]

Parameters	**1**	**2**	**3**	**3**
Solvent	Isooctane	Isooctane	CH_2Cl_2	H_2O
Uv, λ_1, mμ	290	287	286	281
ϵ	404	335	435	326
Δ,[b] mμ	27	28	27	27
CD, λ_1, mμ	290	287	288	282
$[\theta]$, deg	−16,700	+12,000	+13,200	+11,500
Δ,[b] mμ	28	28	27	27
$R \times 10^{40}$ [c]	−19.9	+14.4	+15.2	+13.6
g[d]	0.0125	0.0108	0.0092	0.0107
Uv, λ_2, mμ	240	238	240 (sh)	...
ϵ	144	179	212	...
CD, λ_2, mμ	241	238	241	238
$[\theta]$, deg	15,300	−18,800	−9820	−6670
Δ,[b] mμ	13	13	12	11
$R \times 10^{40}$ [c]	10.2	−12.6	−6.03	−3.80
g[d]	0.0322	0.0318	...	...

[a] Measurements were made at 26°. [b] Δ is the half-band width. [c] R is rotational strength expressed in erg cm.[3] [d] $g = (\epsilon_l - \epsilon_r)/\epsilon$ where $(\epsilon_l - \epsilon_r) = [\theta]/3300$.

On the assumption that the preferred forms in solution have chair conformations, one can conclude that *in simple 1,2-dithiane ring systems a positive CD band corresponding to the lowest frequency ultraviolet absorption band of the disulfide group (in the case of 1,2-dithianes in the range 280–290 mμ) is associated with a right-handed (P) screw sense of the helix containing the atoms C–S–S–C, and a negative CD band is associated with a left-handed (M) screw sense of the helix.* This rule is seen to parallel the rule developed for skewed dienes.[17]

A second band was observed around 240 mμ. Its spectral parameters suggest that it is related to the transition observed around 245 mμ in some cyclic sulfides.[18] This band also appears to reflect the chirality of the disulfide, but is, in the examples we have studied, opposite in sign to the first band at longer wavelengths. The large dependence of [θ] and ε on small variations in the chemical structure around the disulfide function and upon solvent variations suggests that assignment based on this band be undertaken with caution.

Both electronic transitions appear to be magnetic dipole allowed as indicated by the values for *g*.[19] The values for [θ] appear to be directly proportional to the extraneous electric moment. The greater variation in [θ] and ε for the 240-mμ band with respect to the 290-mμ band reflects the greater allowedness of the latter.

Molecular models show that it is possible for the dithiane rings in both **1** and **2** to assume twist-boat conformations which have opposite chirality to the chair forms and thus would have opposite signs of rotation. Values of [θ] and ε were found to decrease by 3–5.5% going from 0 to 60° after correction for solvent expansion. This indicates that the extent of conformational change is too small to cause ambiguity in the use of the sign of the lowest frequency CD band for assignment of chirality.

Application of this rule to open-chain disulfides should be undertaken with caution since the magnitude of the rotational strength expected for the isolated, dissymmetric disulfide is unknown. The possibility exists that this magnitude could be of the same order as vicinal contributions. Work is currently in progress in an

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[11] C. Djerassi, H. Wolf, and E. Bunnenberg, *J. Am. Chem. Soc.*, **84**, 4552 (1962).

[12] S. Beychok, *Science*, **154**, 1288 (1966); *cf.* especially p 1295.

[13] D. E. Applequist and N. D. Werner, *J. Org. Chem.*, **28**, 48 (1963).

[14] M. Carmack and C. J. Kelley, to be published.

[15] H. T. Kalef and E. Havinga, *Rec. Trav. Chim.*, **81**, 282 (1962).

[16] R. S. Cahn, C. Ingold, and V. Prelog, *Angew. Chem. Intern. Ed. Engl.*, **5**, 385 (1966); see especially pp 391 and 406.

[17] A. Moscowitz, E. Charney, U. Weiss, and H. Ziffer, *J. Am. Chem. Soc.*, **83**, 4661 (1961).

[18] P. Laur, H. Hauser, J. E. Gurst, and K. Mislow, *J. Org. Chem.*, **32**, 498 (1967).

[19] See S. F. Mason, *Quart. Rev.* (London), **17**, 20 (1963); *cf.* especially p 33 ff.

attempt to determine the applicability of this rule to open-chain compounds and other sized rings.

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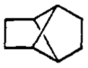
Marvin Carmack, Leonard A. Neubert
Department of Chemistry, Indiana University
Bloomington, Indiana 47401
Received July 17, 1967

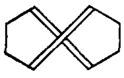
trans,trans-1,5-Cyclooctadiene[1]

Sir:

Irradiation of *cis,cis*-1,5-cyclooctadiene in an ether solution containing copper(I) chloride yields tricyclo-$[3.3.0.0^{2,6}]$octane (**1**).[2] The mechanism of this reaction is still unclear;[2] however, the fact that the carbon skeleton of **1** can in principle be derived in a simple manner from the racemic conformation of *trans,trans*-1,5-cyclooctadiene (**3a**) makes the properties of this latter hydrocarbon under the conditions of the photochemical reaction of interest. We wish to report the isolation of both *cis,trans*-[3] and *trans,trans*-1,5-cyclooctadienes from an irradiated pentane suspension of bis[chloro(*cis,cis*-1,5-cyclooctadiene)copper(I)] (**2**).[4]



1



3a

3b

The crystalline complex **2**, when suspended in pentane, dissociates partially to free cyclooctadiene and a solid nonstoichiometric cyclooctadiene–copper(I) chloride complex containing excess copper(I) chloride. A stirred suspension of **2** (0.5 g, 1.2 mmoles) in 70 ml of degassed pentane was irradiated for 24 hr in a quartz vessel, using a Rayonet reactor equipped with low-pressure mercury lamps. The resulting mixture was filtered, and the solid was washed thoroughly with pentane. The filtrate was shown by vpc to contain **1** (19%, based on the cyclooctadiene originally present in the complex **2**), *cis,cis*-1,5-cyclooctadiene (52%), and small quantities of several other components.[5] The remainder of the olefinic material was bound in the pentane-insoluble copper(I) chloride residue.

The solid residues from several irradiations were combined and treated with aqueous sodium cyanide solution to displace the remaining olefins from their copper(I) complexes. The pentane extract of the resulting mixture contained *cis,cis*-1,5-cyclooctadiene (10% based on **2**), *cis,trans*-1,5-cyclooctadiene (13%; vpc retention time and infrared spectrum identical with those of an authentic sample[3]), and a new compound, **3** (1.5%).[6]

Compound **3** polymerized rapidly in the presence of oxygen or acid, or in concentrated solution, but could be isolated by preparative vpc[6] and stored in dilute pentane solution at −20° for several hours. Its infrared spectrum (CCl_4 or CS_2) showed bands at 1615 (olefin) and 985 cm^{-1} (*trans* olefin), but no bands in the region 750–650 cm^{-1} (*cis* olefin).[7] Its mass spectrum showed a clearly defined molecular ion at *m/e* 108 ($C_8H_{12}^+$) and a fragmentation pattern very similar to that of *cis,cis*- and *cis,trans*-1,5-cyclooctadienes,[8] but easily distinguishable from that of *cis,cis*-1,3- and *cis,cis*-1,4-cyclooctadienes.[9] The nmr spectrum of **3** (1:1 TMS–CCl_4, −20°) showed structureless peaks at δ 4.88 (olefinic hydrogen) and 2.43 (allylic hydrogen), with relative areas 1:2. Ozonolysis of **3** and oxidation of the ozonide gave succinic acid in approximately 85% yield, as determined by vpc analysis of its dimethyl ester following esterification with diazomethane. No (<0.5%) glutaric or adipic acid could be detected in the ozonolysis mixture.

Compound **3** could also be prepared, albeit in low yield (2.4%), by the low-temperature Hofmann degradation[10] of a mixture of *cis*- and *trans*-1,5-bis(dimethylamino)cyclooctane dimethiodides[11] with potassium amide in liquid ammonia. The only other hydrocarbon product detectable by vpc in this reaction was *cis,trans*-1,5-cyclooctadiene (1.2%).

These results show unambiguously that **3** is *trans,trans*-1,5-cyclooctadiene. That the *cis,trans*- and *trans,trans*-1,5-cyclooctadienes are found only in the solid residues from the irradiation, rather than free in solution, is consistent with the known high stability of complexes of cyclic *trans* olefins with silver(I).[12]

The ultraviolet spectrum of *trans,trans*-1,5-cyclooctadienes in both isooctane and ether solutions showed an unusual absorption at $\lambda_{\max}$ 246 mμ (ε ~1500). This transition must in some manner owe its low energy to the proximity of the π orbitals of the double bonds of **3**.[13] However, neither this observation, nor the other available spectroscopic data, can presently be interpreted to provide a clear answer to the chemically important question of the relative stabilities of the conformations **3a** and **3b**.

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(1) Supported in part by the U. S. Army Research Office (Durham), Grant ARO(D)-31-124-435, and by the National Science Foundation, Grant GP-6222.

(2) R. Srinivasan, *J. Am. Chem. Soc.*, **86**, 3318 (1964); I. Haller and R. Srinivasan, *ibid.*, **88**, 5084 (1966).

(3) A. C. Cope, C. F. Howell, J. Bowers, R. C. Lord, and G. M. Whitesides, *ibid.*, **89**, 4024 (1967).

(4) J. H. van der Hende and W. C. Baird, Jr., *ibid.*, **85**, 1009 (1963); H. L. Haight, J. R. Doyle, N. C. Baenziger, and G. F. Richards, *Inorg. Chem.*, **2**, 1301 (1963).

(5) See J. Meinwald and B. E. Kaplan, *J. Am. Chem. Soc.*, **89**, 2611 (1967), and ref 2 for discussions of the structures of these products.

(6) Vpc analyses were carried out using glass columns containing 4-nitro-4-methylpimelonitrile or 1,2,3-tris(2-cyanoethoxy)propane on Chromosorb P; injection and detector block temperatures of 80° were necessary to avoid thermal decomposition of **3**.

(7) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958, pp 34–57.

(8) The principal differences were small differences in peak intensities. Mass spectra of *cis* and *trans* olefins are usually almost identical (K. Bieman, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 151).

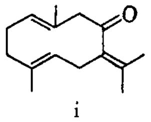
(9) The most intense peak in the mass spectra of **3** and the 1,5-cyclooctadienes occurred at *m/e* 54, attributable to butadiene molecular ion. There were no intense peaks in this region in the spectra of the other isomers.

(10) G. Wittig and R. Polster, *Ann. Chem.*, **612**, 102 (1958).

(11) Z. Jacura, Ph.D. Thesis, Massachusetts Institute of Technology, 1962. The amine was prepared in a straightforward manner from 1,5-cyclooctanedicarboxylic acid [A. C. Cope, E. S. Graham, and D. J. Marshall, *J. Am. Chem. Soc.*, **76**, 6159 (1954)].

(12) M. A. Bennett, *Chem. Rev.*, **62**, 611 (1962).

(13) The anomalous absorption displayed by germacrone (i) and its derivatives at 213 mμ (ε 12,600) provides some precedent for the spectrum of **3**: F. Sorm, *Pure Appl. Chem.*, **2**, 533 (1961). Although this transition was rationalized by an interaction between parallel double bonds, the endocyclic double bonds in the related germacatriene have been shown to possess the "crossed" conformation by X-ray crystallography of its silver nitrate complex: F. H. Allen and D. Rogers, *Chem. Commun.*, 588 (1967).



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