

Reactions of $\text{RO}_2\cdot + \text{R}\cdot$ could lead to RO_2R excited by about 71 kcal. which is far in excess of the 37 kcal. needed to break the O-O bond. In solution this would not be important, and one would expect the excited RO_2R to thermalize far faster than the rate of bond rupture. In the gas phase, however, this is not the case, and we should expect a fair amount of rupture into $2\text{RO}\cdot$, depending on pressure, effectiveness of energy transfer, and the complexity of R.³⁰ For R more complex than C_2H_5 at temperatures below 100° , redissociation should be unimportant. On the other hand, disproportionation of $\text{RO}_2\cdot + \text{R}\cdot$ to give $\text{RO}_2\text{H} + \text{olefin}$ may be expected to be important although

(30) Thus in the simplest case of $\text{CH}_3\text{O}_2\text{CH}_3$, using classical RRK theory of unimolecular reactions with 16 effective internal oscillators (see ref. 11, p. 231), we would expect about 50% redissociation of the excited species at 0.5 atm. pressure. For this calculation, we have used an A value of $10^{15} \text{ sec.}^{-1}$. For more complex R, the per cent will be lower.

there are, unfortunately, no experimental data for comparison.

In the discussion thus far, except for the termination reactions, we have made no explicit distinctions between gas phase and solution reactions. In general, in nonpolar solvents, first-order Arrhenius parameters do not appear to differ greatly between gas phase and solution.¹¹ However, for "slow" second-order reactions, one expects A factors to be about an order of magnitude larger in solution than in the gas phase, reflecting essentially a free volume effect but is subject to so many uncertainties and corrections³¹ that the expectation is not very strong for complex molecules. In fact, for these it is likely that the A factors should be about the same.

(31) The chief uncertainty is that in forming $(\text{A-B})^\ddagger$ from $\text{A} + \text{B}$, one may replace free rotations of $(\text{A-B})^\ddagger$ by hindered rotations in solution and this could well outweigh the translation factors.

The Crystal Structure of Tetracyano-1,4-dithiin

W. A. Dollase

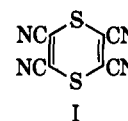
Contribution from the Crystallographic Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts. Received October 17, 1964

A crystal structure determination carried out on tetracyano-1,4-dithiin showed a folded molecule with approximate C_{2v} symmetry and a dihedral angle of 124° . All the atoms lie on one or the other of the dihedral planes. The interleaving of the molecules produces intermolecular distances as short as 3.1 \AA .

A recently synthesized group of completely cyano-substituted, sulfur-containing heterocyclic compounds, containing only carbon, nitrogen, and sulfur, present several interesting structural problems. Their molecular configurations may be inferred by comparison with their parent heterocyclic compounds, but the exact details, such as the effect of the cyano group substitution, must be obtained from crystal structure analysis. A second, and generally more neglected, problem concerns the intermolecular structure of these compounds. A large number of structure determinations of molecular crystals containing hydrogen has shown that, in most cases, the formation of intermolecular hydrogen bonds strongly affects the intermolecular arrangement. The thiocyanocarbons, however, as members of the rather small number of hydrogen-free molecular compounds, provide a means of uncovering other factors which affect intermolecular structure but which are normally masked by the presence of hydrogen bonding.

With these problems in mind, the thiocyanocarbon tetracyano-1,4-dithiin (I) was chosen for a crystal structure analysis. The preparation and some of the properties of this compound are given by Simmons, *et al.*¹

(1) H. E. Simmons, R. D. Vest, D. C. Blomstrom, J. R. Roland, and T. L. Cairns, *J. Am. Chem. Soc.*, **84**, 4746 (1962).



Experimental

The crystals are frequently elongated, yellow, transparent prisms.² Weissenberg photographs established the space group as $P2_1/n$, c unique. A least-squares refinement³ of back-reflection Weissenberg film measurements gave the cell dimensions: $a = 6.953 \pm 0.002$, $b = 7.024 \pm 0.002$, $c = 18.498 \pm 0.005 \text{ \AA}$, $\gamma = 90.52 \pm 0.02^\circ$.⁴ The specific gravity was established by flotation as 1.59. This determined that there were four formula units/unit cell and suggested that the molecule was in the general position.

A crystal $0.020 \times 0.025 \times 0.025 \text{ cm.}$ was selected for intensity measurements; 850 integrated intensities were measured on a single crystal equi-inclination diffractometer employing $\text{Cu K}\alpha$ radiation and a geiger tube detector. The intensities were corrected for background, absorption, Lorenz, and polarization factors.

Examination of the Patterson function⁵ gave the locations of two nonequivalent, relatively heavy sulfur atoms, verifying the general position of the molecule.

(2) A crystalline sample was kindly provided by Dr. H. E. Simmons.

(3) The calculations were performed with the aid of a computer program, LCLSQ, written by C. W. Burnham. (For this and other computer program references see "International Union of Crystallography, World List of Crystallographic Computer Programs," I.U.C.R. Commission on Crystallographic Computing, 1962.)

(4) It should be noted that the cell is very nearly dimensionally tetragonal which probably led to the incorrect preliminary X-ray results given by Simmons, *et al.*¹

(5) All Fourier summations were made with ERFR2; W. G. Sly, D. P. Shoemaker, and J. H. Van den Hende.

With the inversion peaks corresponding to these two nonequivalent sulfur atoms as image points, two M_2 minimum functions⁶ were mapped in three-dimensions and then combined to form a three dimensional M_4 function. The trial model suggested by the final minimum function was refined by alternation between full-matrix, least-squares refinement⁷ and difference Fourier maps to a final R factor of 11.7% with isotropic temperature factors, there being over 14 observations per variable. The final electron density and difference Fourier maps showed no anomalies and allowed definite distinction between the carbon and nitrogen atoms.

Results

Table I lists the final atomic positional and thermal

Table I. Final Atomic Parameters

	x	y	z	B
S(1)	1.12828 ^a	0.86637	0.38321	1.96
S(2)	0.69162	0.87199	0.43700	2.26
C(1)	0.81627	0.65762	0.42583	1.80
C(2)	1.00138	0.65682	0.40402	2.06
C(3)	0.76401	0.98015	0.35580	1.72
C(4)	0.94632	0.97578	0.33248	1.90
C(5)	0.71673	0.48242	0.44073	2.14
C(6)	1.10018	0.47957	0.39289	2.19
C(7)	0.61445	1.05608	0.31141	2.00
C(8)	1.00005	1.05644	0.26499	2.29
N(1)	0.64328	0.34112	0.45504	3.01
N(2)	1.17862	0.33685	0.38939	3.19
N(3)	0.49649	1.12137	0.27535	3.79
N(4)	1.04361	1.11883	0.20957	4.23
δ_{S^b}	0.00024	0.00021	0.00015	0.08
$\delta_{C,N}$	0.00093	0.00088	0.00054	0.21

^a The positional parameters are in fractions of cell edges. ^b The estimated standard deviations are the average values for the subscript species.

parameters along with their averaged estimated standard deviations. The atom designations refer to Figure 1 which shows the molecule in perspective. The molecule is best described as folded or dihedral, consisting of two planes of atoms meeting along the sulfur-sulfur axis. The dihedral angle⁸ is 124°. The deviations of the atoms from their respective planes are given in Table II. The planes are those determined by a least-squares fit⁹ using the atomic weights as weighting factors. The deviations are generally small and atom C(3), whose deviation is more than several positional e.s.d. units, is the only atom which is significantly extraplanar, and that only by 0.06 Å.

Table III gives the pertinent individual intramolecular distances and angles, and their e.s.d. values. Table IV lists the averaged, chemically equivalent bond lengths and angles and the maximum deviations from the average. Since these maximum deviations are similar in magnitude to the e.s.d. values given in Table III, the molecule taken by itself closely approximates C_{2v} symmetry.

(6) M. J. Buerger, "Vector Space," John Wiley and Sons, Inc., New York, N. Y., 1959, p. 239.

(7) SFLSQ3; C. T. Prewitt.

(8) For tetracyano-1,4-dithiin in dioxane solution, from the measured dipole moment of 4.0 ± 0.5 D., Simmons, *et al.*,¹ calculated a remarkably similar model—a boat-form heterocyclic ring with a dihedral angle of 130°.

(9) MGEOM; J. S. Wood, unpublished.

Table II. Deviations of the Atoms from Their Respective Least-Squares Planes

Atom	Plane	Dev., Å.
S(1)	A	0.000
S(2)	A	0.001
C(1)	A	-0.004
C(2)	A	0.013
C(5)	A	-0.023
C(6)	A	-0.033
N(1)	A	0.017
N(2)	A	0.022
S(1)	B	-0.025
S(2)	B	-0.001
C(3)	B	0.062
C(4)	B	0.032
C(7)	B	0.000
C(8)	B	0.020
N(3)	B	-0.025
N(4)	B	-0.014

Table III. Interatomic Distances and Angles

Bond	Distance, Å.	Dev., Å.
S(1)-C(2)	1.752	0.006
S(1)-C(4)	1.758	0.007
S(2)-C(1)	1.756	0.006
S(2)-C(3)	1.755	0.009
C(1)-C(2)	1.349	0.009
C(3)-C(4)	1.340	0.009
C(1)-C(5)	1.433	0.009
C(2)-C(6)	1.442	0.009
C(3)-C(7)	1.432	0.011
C(4)-C(8)	1.420	0.014
N(1)-C(5)	1.143	0.009
N(2)-C(6)	1.147	0.009
N(3)-C(7)	1.155	0.011
N(4)-C(8)	1.154	0.014
Angle	Degrees	Dev.
C(2)-S(1)-C(4)	97.2	0.5
C(1)-S(2)-C(3)	97.4	0.4
S(2)-C(1)-C(2)	121.1	0.7
S(1)-C(2)-C(1)	122.4	0.8
S(2)-C(3)-C(4)	122.2	0.5
S(1)-C(4)-C(3)	121.5	0.6
S(2)-C(1)-C(5)	118.4	0.6
S(1)-C(2)-C(6)	117.0	0.8
S(2)-C(3)-C(7)	116.5	0.7
S(1)-C(4)-C(8)	117.1	0.5
C(2)-C(1)-C(5)	120.5	0.9
C(1)-C(2)-C(6)	120.6	0.9
C(4)-C(3)-C(7)	121.0	0.5
C(3)-C(4)-C(8)	121.3	0.8
C(1)-C(5)-N(1)	176.9	1.1
C(2)-C(6)-N(2)	175.0	0.9
C(3)-C(7)-N(3)	178.3	0.8
C(4)-C(8)-N(4)	178.8	0.9

The expected van der Waals distances for the atoms concerned here are about 3.4 Å. Almost all the intermolecular distances were found to equal or exceed this value and will not be further discussed. There are, however, eight distances, all involving atoms N(3) or N(4), which are less than this, and these are listed in Table V and shown in Figure 2. Figure 2 is a projection of the structure along the axis a . The dashed lines indicate the short intermolecular contacts between the shaded central molecule and a molecule one-half a translation above it. The individual short contacts, together with their symmetry equivalents, form a

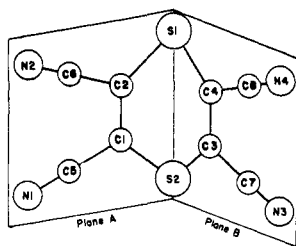


Figure 1. Perspective view of the tetracyano-1,4-dithiin molecule.

continuous network normal to the c axis, but the levels of this network are not continuously connected in the direction of the c axis.

Table IV. Averaged Interatomic Distances and Angles

Bond	Distance, Å.	Dev., Å.
S-C	1.755	0.003 ^a
C-C (in ring)	1.344	0.005
C-C (out of ring)	1.432	0.012
C-N	1.150	0.007
Angle	Degrees	Dev.
C-S-C	97.3	0.2
S-C-C (in ring)	121.8	0.7
S-C-C (out of ring)	117.2	1.1
C-C-C	120.8	0.5
C-C-N	177.2	2.2

^a Maximum deviation from the average.

Table V. Intermolecular Distances Less Than 3.4 Å.

Bond	Distance, Å.	Location
N(4)-C(7)	3.13	a ^a
N(4)-C(1)	3.15	b
N(4)-C(5)	3.18	c
N(4)-C(3)	3.19	d
N(3)-C(8)	3.15	e
N(3)-C(4)	3.21	f
N(3)-C(2)	3.33	g
N(3)-C(6)	3.35	h

^a The letters show the locations of these contacts in Figure 2.

In Figure 2 the dihedral planes are seen nearly end-on. The partial interleaving of the planes and their stacking, approximately parallel to (001), give each molecule 12 close neighbors.

Discussion

The two likely¹⁰ configurations for a six-membered heterocyclic ring with two *para* oxygen, sulfur, or selenium atoms are the chair form, which features the greatest possible separation of the heteroatoms, and the boat form, which features the formation of two planes

(10) A planar configuration would require a C-S-C bond angle of about 120° compared to the C-S-C bond angles of about 100° in non-cyclic, supposedly unstrained compounds.

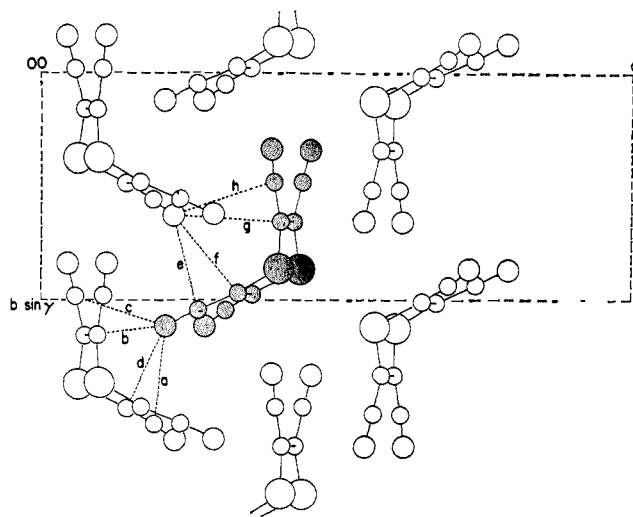
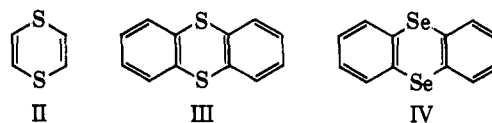


Figure 2. Projection of the structure along the a axis.

of atoms intersecting along the heteroatom axis. In the solid state all the dioxanes, dithianes, diselenanes, mixed heterocycles, and charge-transfer adducts of these compounds studied to date have the chair form. On the other hand, tetracyano-1,4-dithiin (I), its parent heterocycle (II),¹¹ thianthrene (III),¹² and selenanthrene (IV),¹³ which to date have been the only unsaturated analogs of the first group studied,¹⁴ all have the boat form. It appears likely that the normal



electrostatic repulsion between the heteroatoms, leading to the chair form in the saturated compounds, is overcome in the unsaturated compounds by the formation of delocalized π -bonding systems over the two planes of the boat form. In cases I, III, and IV the boat form is further stabilized by extension of the π -bonding systems over the substituents which tends to make them coplanar with the ring "halves." A small, but real, participation of the heteroatoms in the π -bonding is suggested by the decrease of the calcogen-carbon atom bond lengths found in the unsaturated compounds relative to the saturated. In tetracyano-1,4-dithiin, the average S-C bond length of 1.755 Å. is about 0.05 Å. less than that of the "pure" single-bond distance.

The shorter-than-expected intermolecular distances are apparently forced upon the crystal by the close packing. The densest packing of dihedral molecules requires some amount of interleaving of the planes. From Figure 2 it can be seen that this interleaving brings the terminal atoms of one plane of the molecule [N(3) and N(4)] into the concave openings of two neighboring molecules. These adjacent molecules are,

(11) P. A. Howell, R. M. Curtis, and W. N. Lipscomb, *Acta Cryst.*, 7, 498 (1954).

(12) I. Rowe and B. Post, *ibid.*, 11, 372 (1958).

(13) R. G. Wood and G. Williams, *Nature*, 150, 321 (1942).

(14) The configuration of the 1,4-dioxin molecule in the liquid state was the subject of an electron diffraction study but was assumed to be planar by the investigator and cannot be considered as known: cf. J. Y. Beach, *J. Chem. Phys.*, 9, 54 (1941).

more or less, wrapped around the plane of N(3) and N(4), producing the shorter van der Waals contacts. In contrast to this, the terminal atoms N(1) and N(2) always lie on the convex side of neighboring molecules and are not involved in any intermolecular distances less than 3.4 Å.

That these short contacts to only one side of the molecule have little or no effect on the over-all molecular structure is evidenced by the C_{2v} molecular sym-

metry and by the existence of a single $C\equiv N$ band in the infrared spectrum.¹

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Electronic Spectrum of Cyclononatetraenide

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The electronic spectrum of cyclononatetraenide ($C_9H_9^-$), a monocycle possessing a ninefold rotation axis, has been measured. The tetraethylammonium salt shows only two regions of absorption from -33 to 25° in acetonitrile: an intense, structureless absorption at $250 m\mu$ (ϵ 66,300) and a weaker, resolved system centered at $320 m\mu$ (ϵ 6700). Theoretical analysis of the spectrum expected for planar $C_9H_9^-$ (D_{9h}) shows good agreement with that obtained experimentally. The high-energy band is the only allowed transition (${}^1E_1'$) in the spectrum, but it can be shown that vibronic coupling imparts a transition moment of the observed magnitude to the low-energy band.

Introduction

Cyclononatetraenide¹ is an odd nonalternant monocycle of nine carbons and ten π -electrons. N.m.r. evidence favors a planar, nonagonal structure, although this implies 180° of classical angle strain in the σ -framework. The purpose of this paper is the consideration of the electronic spectrum of this molecule, which is shown to be in accord with theoretical expectation for the planar structure.

Since cyclononatetraenide bears a negative charge and is subject to destructive hydrolysis by amphiprotic solvents, its spectrum could be obtained only in aprotic organic solvents. Spectra of alkali metal and tetraethylammonium salts in tetrahydrofuran and acetonitrile solutions, respectively, revealed two regions of absorption: an intense, structureless band at $250 m\mu$ (ϵ 66,300) and a much weaker absorption at $320 m\mu$. The weak band was resolved for the tetraethylammonium salt in acetonitrile with major components at $317 m\mu$ (ϵ 6630) and $322 m\mu$ (ϵ 6750) (Figure 1).

Theory and Calculations

The theory of the electronic states of the even alternant monocycles containing $(4n + 2)$ π -electrons is well understood from the work of Platt² and Moffitt.³

(1) E. A. LaLancette and R. E. Benson, *J. Am. Chem. Soc.*, **85**, 2853 (1963); T. J. Katz and P. J. Garratt, *ibid.*, **85**, 2852 (1963).
(2) J. R. Platt, *J. Chem. Phys.*, **17**, 484 (1949).

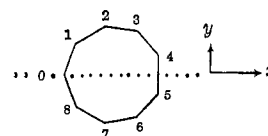
Odd nonalternant monocyclic systems have been studied less thoroughly, although from the original work of Hückel⁴ it was possible to predict that the $(4n + 2)$ ions, $C_3H_3^+$, $C_5H_5^-$, $C_7H_7^+$, $C_8H_8^{-2}$, and $C_9H_9^-$, would have closed-shell ground states and be potentially capable of synthesis. The C_3 - C_8 ions have been considered previously by Longuet-Higgins and McEwen.⁵

Planar $C_9H_9^-$ belongs to the D_{9h} -symmetry point group (character table given in Table I) and possesses the highest rotation axis yet encountered in a small molecule. The self-consistent molecular orbitals are determined fully by the C_9 subgroup and can be written in the form⁶

$$\psi_\xi = \sigma_\xi \sum_{m=0}^8 \omega^{m\xi} \phi_m \quad (\xi = 0, \pm 1, \pm 2, \pm 3, \pm 4) \quad (1)$$

$$\omega = \exp(2\pi i/9)$$

where the ϕ_m 's are carbon $2p\pi$ -AO's numbered as shown, and the σ_ξ are normalizing constants equal to



$1/\sqrt{9}$ for all ξ when overlap is neglected. Under D_{9h} the molecular orbitals transform as

$$\psi_0 \longrightarrow a_2''$$

$$\psi_{\pm|\xi|} \longrightarrow e_{|\xi|}'' \quad (\xi = 1, 2, 3, 4)$$

The closed-shell ground state (${}^1A_1'$) is given by the configuration

$$\text{ground state: } \psi_0^2 \psi_{+1}^2 \psi_{-1}^2 \psi_{+2}^2 \psi_{-2}^2$$

which with the neglect of overlap corresponds to the configurational wave function

(3) W. Moffitt, *ibid.*, **22**, 320 (1954).
(4) E. Hückel, *Z. Physik*, **70**, 204 (1931).
(5) H. C. Longuet-Higgins and K. L. McEwen, *J. Chem. Phys.*, **26**, 719 (1957).
(6) The subsequent notation conforms closely to that of Moffitt³ for comparison purposes.