quence of differences in the interaction of RS^- and of RO^- with solvating water molecules. It is known that RO^- is less stable in DOR than in HOR by a factor of about 2,[17] and there is evidence for a similar difference in the stability of the lyoxide ion in deuterium oxide and water.[14,18] These differences, at least in the case of the alkoxide ion, may be attributed to changes in the O–H stretching frequencies of one or more solvent molecules hydrogen bonded to the RO^- ion[14] and/or to changes in lower frequency librations.[19] The fact that the difference in the isotope effect on the ionization constants of ROH and RSH is *less* than that attributable to ROH and RSH themselves means that the sum of these frequencies must be smaller for molecules solvating RS^- than for those solvating RO^- anions of similar basicity. Both the hydrogen-bonding ability and the basicity of sulfur compounds are less than those of comparable oxygen compounds because of the large size and small electron density of sulfur, but *for a given basicity* there are indications that sulfur may cause a greater frequency shift of a hydrogen-bonded O–H group than oxygen: (i) for a given $-\Delta H$ (or K_{eq}) for hydrogen bond formation with phenol, the shift in ν_{OH} is considerably larger for sulfur than for oxygen or nitrogen as electron donors[20] and (ii) although oxygen and sulfur anions of the same basicity have similar effectiveness as general base catalysts for reactions with a large β value, sulfur anions are relatively more effective for reactions with a low β value, in which the transition state would be expected to resemble a hydrogen bond between RS^- and a proton donor.[21] Both of these observations may reflect the high polarizability of sulfur. Although the libration frequencies of water molecules in the neighborhood of a sulfur anion are not known, librational frequencies are known to decrease with increasing size and "structure-breaking" character of anions,[19] so that a decrease in these frequencies might be expected in the presence of the large sulfur anion. Thus, although direct experimental evidence is not yet available, there is reason to believe that either or both of these frequency shifts may be larger for RS^- than for RO^- and will provide the additional factor needed to account quantitatively for the observed differences in the isotope effects for the ionization of thiol and oxygen acids. The unusually large increase of 2.59-fold in the activity coefficient of SO_3^{2-} in deuterium oxide compared to water[22] may reflect a similar influence of lone pair electrons of the sulfur atom on stretching and/or librational frequencies of solvent molecules.

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The Structure of Binor-S Established from the Dione Derivative. The Crystal and Molecular Structure of Decahydro[1,2,4:5,6,8]dimetheno-*s*-indacenedione

F. Peter Boer,*[1a] Melvin A. Neuman,[1a] Ronald J. Roth,[1b] and Thomas J. Katz[1b]

Chemical Physics Research Laboratory, The Dow Chemical Company,
Midland, Michigan 48640, and Department of Chemistry,
Columbia University, New York, New York 10027.

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Abstract: The Binor-S-dione (decahydro[1,2,4:5,6,8]dimetheno-*s*-indacene-3,7-dione) was synthesized *via* the catalytic dimer of 7-*tert*-butoxynorbornadiene and its structure has been determined by a single-crystal X-ray diffraction study. This substance, $C_{14}H_{12}O_2$, crystallizes in space group $P2_1/c$ ($a = 7.914$, $b = 12.932$, $c = 9.641$ (Å), $\beta = 100.27°$) with four molecules per unit cell. The intensities of 1659 reflections were measured on a Picker automatic diffractometer using Cu Kα radiation. The structure was solved by exploiting the Σ_2 relationship. Full-matrix least-squares refinement assuming anisotropic thermal parameters for C and O atoms and isotropic parameters for H converged at a conventional R factor $R_1 = 4.9\%$ for the 1550 reflections above background. This study establishes that the caged hydrocarbon known as Binor-S is the syn isomer. Bond angles indicate the presence of considerable strain in the nortricyclanone subunits. Bond distances from the carbon atoms directly bonded to the cyclopropyl rings to the ring atoms are significantly shorter than the distances from these carbons to the remaining (apex) carbon atoms.

The caged hydrocarbon known as Binor-S is obtained when norbornadiene is dimerized in the presence of certain multicenter catalysts containing cobalt, rhodium, and iridium.[2-4] Because the mechanism of catalysis, believed to involve the concerted union of norbornadi-

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(1) (a) Dow Chemical Co., (b) Columbia University.

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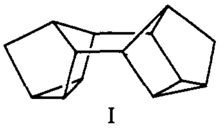
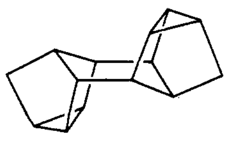
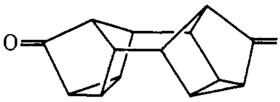
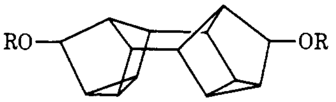
ene molecules fixed on proximate metal atoms,[2-4] depends on the configuration[5] (I or II) of the product, proof of the Binor-S structure by X-ray diffraction is


I


II


III


IVa, R = *tert*-Bu
b, R = $COCH_3$
c, R = H

desirable. Unfortunately, even though reproducible X-ray data on Binor-S can be obtained by standard methods (see Appendix) and the determination of its structure would appear in principle to be straightforward, we have been unable to derive a satisfactory solution.

We are reporting below the molecular and crystal structure of a derivative of Binor-S, the dione III, which unequivocally establishes the structure of the parent hydrocarbon to be I.

Experimental Section

Preparation of IVa. The procedure below is modeled on one that gives Binor-S.[2a] We were unsuccessful in isolating $Zn[Co(CO)_4]_2$, but the following variant of the published procedure[8] should have generated it in solution.

An 8-g sample of 30 mesh Zn was activated with $Cu(OAc)_2 \cdot H_2O$ in a 500-ml Morton flask[9] fitted with a high-speed mechanical stirrer, stopcock, reflux condenser, and nitrogen inlet.[10] A 4-g sample of $Hg[Co(CO)_4]_2$[11] and 40 ml of toluene were added and the mixture was stirred for 90 min at room temperature. *tert*-Butoxynorbornadiene[12] (13.2 g, 0.080 mol) was added. After stirring at 100° for 3.5 hr, the reaction mixture was cooled to room temperature, filtered, washed with 5% HCl, and dried over 3A Molecular Sieves. Distillation gave a mixture of dimers, bp 165° (0.1 mm) (7.6 g, 57% yield), of which 4.6 g, 61%, was (by glpc) IVa. Chromatography on silica gel with 50:50 hexane–chloroform separated IVa from its isomers: nmr ($CDCl_3$) τ 6.32 (0.98 H, broad singlet), 7.44 (0.92 H, broad singlet), 8.07 (1.08 H, broad singlet), 8.50–8.75 (1.85 H, multiplet), 8.85 (11.2 H, sharp methyl singlet superimposed on a multiplet); mass spectrum (75 eV), *m/e* (relative intensity, %) parent ion 328 (0.2), major fragments 216 (33), 134 (27), 133 (20), 117 (20), 91 (21), 57 (100), 41 (30).

Preparation of IVc. IVa was converted into IVb by the procedure of Story.[13] A solution of 25 ml of acetic acid and 6 ml of acetic anhydride was added to 1.25 g of IVa (3.8 mmol) After standing at room temperature for 40 min, and cooling in an ice bath, 3 ml of 70% perchloric acid was added The mixture was swirled for 1.5 min, poured onto 120 ml of ice water, and extracted with methylene chloride. The solution was washed with saturated aqueous $NaHCO_3$ and water and dried over 3A Molecular Sieves, and the solvent was stripped. Bulb-to-bulb distillation at *ca.* 120° (0.1 mm) gave IVb in 57–85% yield.

Crude IVb was reduced by refluxing for 1 hr in ether with $LiAlH_4$. Excess $LiAlH_4$ was destroyed by adding 15% NaOH. The sample was filtered, extracted with ether, washed with brine, and dried over $MgSO_4$, and the solvent was stripped. Sublimation gave IVc in 54–72% yields; ir (KBr) (cm^{-1}) 3263 (s) (OH), 2898 (s), 1356 (m), 1348 (m), 1103 (s), 1088 (m), 1071 (m), 1050 (m), 828 (m), and 810 (m) (cyclopropyl).

Preparation of III. IVc (394 mg, 1.82 mmol) was oxidized to III (300 mg, 78% crude yield) with Jones reagent.[14] Recrystallization from 95% ethanol followed by sublimation gave pure III: mp 227–229°; ir (KBr, cm^{-1}) 2935 (s), 1755 (s), and 1740 (s) (C=O), 832 (cyclopropyl); nmr ($CDCl_3$, 100 MHz) τ 7.3 (4.04 H, singlet), 7.73 (3.9 H, doublet), 8.41 (2.05 H, triplet), 8.60 (1.98 H, singlet); mass spectrum (75 eV), *m/e* (relative intensity, %) parent ion 212 (38), major fragments 131 (55), 106 (26), 78 (100), 77 (23), 52 (34), 51 (42), 39 (61).

Anal. Calcd for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70. Found: C, 79.23; H, 5.77.

Wolff–Kishner Reduction of III to I. The procedure was modeled on a preparation of barbaralane.[15] A mixture of the dione (III, 111 mg), 85% hydrazine hydrate (1.5 g), KOH (1 g), and diethylene glycol (1.5 ml) was heated at 100° for 1 hr. The temperature was raised to 195° by distilling out some water, and the mixture was heated for 3 hr. After the addition of water, extraction (*n*-pentane), drying (molecular sieves), and removal of solvent, the hydrocarbon was distilled from bulb to bulb. The yield was 21 mg (21%), and it was identified as Binor-S by comparing its ir and nmr spectra with those of the hydrocarbon prepared by dimerizing norbornadiene.

X-Ray Data Collection. Crystals of Binor-S-dione, $C_{14}H_{12}O_2$, commonly grow as needles elongated on *c*, but most of the crystals of this habit examined showed an undesirable amount of mosaicity. The crystal used in our study was an irregular prism which gave a sharp diffraction pattern. This crystal was sealed in a 0.3 mm i.d. thin-walled glass capillary and aligned on a precession camera with a^* parallel to the spindle. A preliminary photographic survey showed reciprocal lattice symmetry C_{2h} and the systematic absence of $h0l$ reflections for l odd and $0k0$ reflections for k odd, which established the space group $P2_1/c$ (C_{2h}^5). The crystal was then carefully centered on a Picker four-circle goniostat and the lattice constants were calculated by least-squares refinement of the setting angles of ten reflections (Cu Kα radiation, λ 1.5418 Å). The unit cell dimensions, $a = 7.914 \pm 0.008$, $b = 12.932 \pm 0.011$, $c = 9.641 \pm 0.009$ Å, and $\beta = 100.27 \pm 0.03°$, give a calculated density of 1.452 g cm^{-3} for mol wt 212.25 and $Z = 4$. All data were obtained at room temperature, 28°.

The intensities of 1659 independent reflections were measured using the θ–2θ scan mode of the diffractometer and nickel-filtered Cu Kα radiation. The X-ray tube was set at a 3° take-off angle and a detector aperture 6.0 mm square was placed 300 mm from the crystal. Scan angles from 2.0 to 2.6° were employed over the range (0–132°) of 2θ examined. Attenuators were used to prevent the count rate from exceeding 12,000/sec; attenuator factors up to 17.9 were required. The scan speed was 2°/min. Background counts of 10 sec were taken at each end of the scan by the stationary crystal–stationary counter technique. The (1.7.0) reflection was monitored after every 50 measurements and showed good stability with a ratio of 0.97 between the minimum and maximum readings. An error $\sigma(I) = [(0.02I)^2 + N_0 + k^2N_b]^{1/2}$ was assigned to the net intensity $I = N_0 - kN_b$ in order to establish the weights $w = 4F^2/\sigma^2(F^2)$ for subsequent least-squares refinement. Here N_0 is the gross count, k is the ratio of scan time to background time, and the F^2 are the intensities I corrected for Lorentz and polarization effects. The 109 reflections for which the conditions $I > 0$ or $\sigma(I)/I \leq 0.5$ were not met were denoted absent and were not used in refining the structure. The linear absorption coefficient for this material, μ(Cu Kα) = 7.84 cm^{-1}, is quite low. For this reason, and because the ratio of minimum and maximum intensities for the "ϕ-independent" (1.0.0) reflection was 0.97, absorption corrections were not applied.

Binor-S-dione is a strong scatterer, as indicated by the Wilson plot scale factor[16] for relative F's of 17.89, one of the largest values in

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Table I

Quantity	Found	Theoretical (centric)
$\langle\lvert E\rvert\rangle$	0.795	0.798
$\langle E^2\rangle$	1.000	1.000
$\langle\lvert E^2 - 1\rvert\rangle$	0.975	0.968
Per cent > 1	31.28	32.00
Per cent > 2	4.10	5.00
Per cent > 3	0.42	0.30

Table II. Atomic Parameters[a,b]

Atom	x	y	z	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
C(1)	1.0974 (2)	0.2844 (2)	0.2581 (2)	110 (3)	53 (1)	117 (3)	6 (2)	13 (2)	4 (1)
C(2)	0.9989 (2)	0.3429 (2)	0.3554 (2)	116 (3)	53 (1)	83 (2)	2 (2)	−2 (2)	0 (1)
C(3)	0.9449 (3)	0.4478 (1)	0.2888 (2)	119 (3)	42 (1)	102 (2)	−15 (2)	10 (2)	−6 (1)
C(4)	0.9291 (2)	0.4124 (2)	0.1343 (2)	124 (3)	51 (1)	87 (2)	−2 (2)	22 (2)	11 (1)
C(5)	0.8015 (2)	0.3225 (1)	0.1355 (2)	110 (3)	49 (1)	73 (2)	4 (2)	15 (2)	−11 (1)
C(6)	0.9063 (2)	0.2635 (2)	0.2584 (2)	118 (3)	40 (1)	105 (2)	−2 (1)	24 (2)	−2 (1)
C(7)	1.0942 (2)	0.3528 (2)	0.1345 (2)	112 (3)	57 (1)	103 (2)	−15 (2)	20 (2)	−8 (1)
C(8)	0.4860 (3)	0.4217 (2)	0.3589 (2)	132 (3)	51 (1)	96 (2)	3 (2)	34 (2)	9 (1)
C(9)	0.6800 (3)	0.4124 (1)	0.4079 (2)	147 (4)	46 (1)	76 (2)	3 (2)	21 (2)	−6 (1)
C(10)	0.7683 (2)	0.4864 (1)	0.3185 (2)	138 (3)	36 (1)	98 (2)	−4 (2)	16 (2)	−9 (1)
C(11)	0.6286 (3)	0.4810 (2)	0.1847 (2)	136 (4)	46 (1)	90 (2)	9 (2)	20 (2)	7 (1)
C(12)	0.6252 (2)	0.3626 (1)	0.1624 (2)	103 (3)	48 (1)	74 (2)	4 (1)	8 (2)	−7 (1)
C(13)	0.5893 (2)	0.3343 (1)	0.3088 (2)	117 (3)	41 (1)	84 (2)	−3 (1)	21 (2)	−4 (1)
C(14)	0.4674 (3)	0.4999 (2)	0.2457 (2)	133 (4)	44 (1)	113 (3)	7 (2)	17 (2)	−10 (1)
O(1)	1.1922 (2)	0.3564 (1)	0.0512 (2)	138 (3)	82 (1)	126 (2)	−8 (1)	50 (2)	−4 (1)
O(2)	0.3573 (2)	0.5649 (1)	0.2135 (2)	173 (3)	63 (1)	171 (3)	38 (2)	25 (2)	6 (1)
				B^c					
H(1)	1.1848 (28)	0.2357 (17)	0.2899 (21)	3.48 (45)					
H(2)	1.0300 (34)	0.3331 (18)	0.4576 (26)	4.82 (56)					
H(3)	1.0355 (28)	0.4992 (16)	0.3207 (22)	3.42 (44)					
H(4)	0.9090 (33)	0.4623 (19)	0.0720 (27)	5.33 (66)					
H(5)	0.7758 (28)	0.2830 (16)	0.0391 (22)	3.50 (45)					
H(6)	0.8645 (29)	0.1966 (19)	0.2864 (23)	4.12 (51)					
H(8)	0.4040 (25)	0.4104 (16)	0.4282 (19)	2.97 (43)					
H(9)	0.7334 (26)	0.3936 (15)	0.5066 (21)	3.03 (42)					
H(10)	0.7798 (38)	0.5555 (23)	0.3611 (28)	6.36 (69)					
H(11)	0.6400 (28)	0.5257 (18)	0.1029 (21)	3.78 (48)					
H(12)	0.5307 (25)	0.3405 (14)	0.0924 (19)	2.40 (38)					
H(13)	0.5766 (26)	0.2602 (16)	0.3403 (20)	3.26 (42)					

[a] Standard errors given in parentheses referred to the last significant digit. [b] Anisotropic temperature factors are in the form $\exp(-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23}))$. [c] Isotropic temperature factor.

our experience for an organic crystal. The overall temperature factor[16] was 3.803 Å^2.

Solution and Refinement of the Binor-S-dione Structure. A set of normalized structure factors (E's) was computed.[16] Their distribution is indicated in Table I, after rescaling to the condition $\langle E^2\rangle = 1$. The structure was solved by application of the σ-2 relationship using the program MAGIC by Dewar and Stone.[16] A set of 219 E's was given phases in accord with the most probable sign combination. The 14 largest peaks in an E map calculated[17a] with these phases gave the positions of the carbon and oxygen atoms; there were only three false peaks with heights greater than two-thirds the height of the weakest carbon atom. An initial structure factor calculation[17b,18] gave $R_1 = \Sigma\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\Sigma\lvert F_o\rvert = 0.298$ and $R_2 = \{\Sigma w[F_o - F_c]^2/\Sigma wF_o^2\}^{1/2} = 0.425$. After one cycle of full-matrix least-squares refinement[17b] on atomic positions followed by one cycle on positions and isotopic temperature factors, these quantities were reduced to $R_1 = 0.137$ and $R_2 = 0.186$. Since at this stage all distances and temperature factors appeared normal, the 12 hydrogens were introduced at calculated positions. Seven additional cycles of isotropic refinement gave convergence of all parameters at $R_1 = 0.106$ and $R_2 = 0.134$. An examination of the observed and calculated structure factors suggested that a moderate number of high intensity reflections might be affected by secondary extinction. The Zachariasen correction $F_o^{\text{corr}} = F_o(1 + c\beta I_{\text{obsd}})$ was applied to 40 reflections, with $c = 0.163 \times 10^{-6}$ (the scale factor at this stage was 15.687). Refinement was then completed assuming anisotropic thermal parameters for the carbon and oxygen atoms, and isotropic temperature factors for hydrogen. After five cycles R_1 and R_2 had converged from their starting values after the extinction correction (0.089 and 0.124, respectively) to their final values of 0.049 and 0.066 for the 1550 reflections above background. The parameter shifts in the final cycle were, for the heavy atoms, 0.005σ (average) and 0.03σ (maximum), and for hydrogen 0.02σ (average) and 0.11σ (maximum). A final difference map[17a] contained no positive density above 0.22 electron/Å^3 and no negative regions below −0.30 electron/Å^3. Atomic parameters and their standard deviations as calculated in the final least-squares cycle are listed in Table II, while Table III gives root-mean-square components of thermal displacement along the principal axes,[17c] as defined by the anisotropic thermal parameters. The directions of these axes may be inferred from the computer-produced stereoview of the molecule[17d] (Figure 1), where the thermal motion is represented by 50% probability ellipsoids. Most of the ellipsoids are seen to be spheroidal and of fairly uniform size. There is, however, significant anisotropy in the atoms of the carbonyl groups, especially

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(16) Program MAGIC and auxiliary links, R. B. K. Dewar and A. L. Stone, University of Chicago.

(17) (a) J. Gvildys, "Two- and Three-Dimensional Crystallographic Fourier Summation Program," Based on MIFRI, Program Library B-149, Argonne National Laboratory, Applied Mathematics Division, Argonne, Ill., April 13, 1965; (b) J. Gvildys, "A Fortran Crystallographic Least-Squares Refinement Program," based on OR FLS, Program Library 14E7043, Argonne National Laboratory, March 31, 1967; (c) J. Gvildys, "ANL FFE, A Fortran Crystallographic Function and Error Program," based on OR FFE, Program Library B 115, Argonne National Laboratories, Sept 17, 1964; (d) C. K. Johnson, "OR TEP: A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations," Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., June 1965; (e) J. Gvildys, "Least-Squares Plane and Line Fitter," see V. Shomaker, J. Waser, R. E. Marsh, and G. Bergman, *Acta Crystallogr.*, **12**, 600 (1959); Program Library B-125, Argonne National Laboratory, May 18, 1965.

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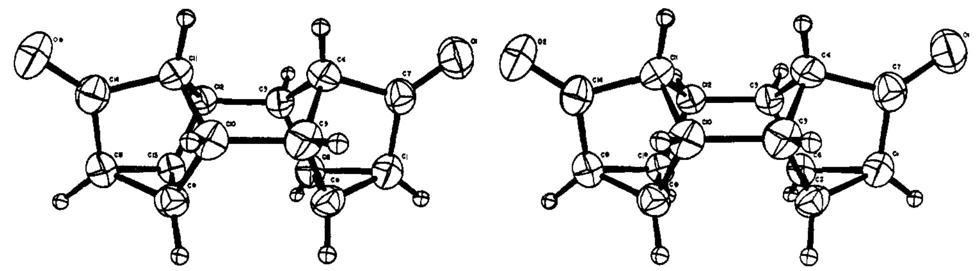

Figure 1. Three-dimensional view of a molecule of decahydro [1,2,4:5,6,8]dimetheno-*s*-indacenedione. The ellipsoids represent the anisotropic thermal motion of the carbon and oxygen atoms, while hydrogens are drawn as uniform spheres.

the oxygen atoms, which shows fairly large components in the planes in directions approximately perpendicular to the carbon–oxygen bonds. Table IV lists bond distances and angles.[17c] The standard deviations given in Tables III and IV were computed[17c] from the variance–covariance matrix generated during the final least-squares cycle. A table of observed and calculated structure factors is available on request.[19] We note that the numbering system for atoms was chosen arbitrarily and bears no relation to the accepted nomenclature.

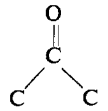

Table III. Root-Mean-Square Amplitudes of Thermal Motion[a] (Ångströms)

Atom	Axis 1	Axis 2	Axis 3
C(1)	0.181 (3)	0.213 (3)	0.235 (3)
C(2)	0.175 (3)	0.211 (3)	0.215 (3)
C(3)	0.167 (3)	0.210 (3)	0.221 (3)
C(4)	0.182 (3)	0.197 (3)	0.219 (3)
C(5)	0.172 (3)	0.185 (3)	0.213 (3)
C(6)	0.183 (3)	0.190 (3)	0.219 (3)
C(7)	0.176 (3)	0.211 (3)	0.233 (3)
C(8)	0.182 (3)	0.208 (3)	0.223 (3)
C(9)	0.179 (3)	0.203 (3)	0.214 (3)
C(10)	0.169 (3)	0.207 (3)	0.217 (3)
C(11)	0.185 (3)	0.203 (3)	0.215 (3)
C(12)	0.169 (3)	0.189 (3)	0.207 (3)
C(13)	0.183 (3)	0.187 (3)	0.200 (3)
C(14)	0.184 (3)	0.204 (3)	0.236 (3)
O(1)	0.188 (2)	0.244 (2)	0.267 (2)
O(2)	0.185 (2)	0.270 (2)	0.281 (2)

[a] Ordered on increasing magnitude.

Discussion

The solution of its crystal structure proves that the Binor-S-dione is in fact the syn isomer III, with a molecular geometry in the solid that conforms closely, but not exactly, to C_{2v} symmetry. Because the dione is convertible to Binor-S by Wolff–Kishner reduction, the syn configuration of Binor-S[2] is established unequivocally. The small deviations from ideal C_{2v} symmetry are believed to originate in packing forces and will be described in detail below.

As the structural systematics of caged hydrocarbons[20–22] are still of considerable interest, some of the geometric features of III merit further discussion. Binor-S-dione consists of two nortricyclanone subunits, each of which contains a three-membered ring and three five-membered rings. The subunits are in turn linked by a pair of C–C bonds to form in addition a six-membered and an eight-membered ring, both in boat conformations. In the following discussion, we shall refer to the cyclopropyl carbons of the nortricyclanone subunits C(1), C(2), C(6), C(8), C(9), and C(13) as the *base* carbons; C(3), C(5), C(7), C(10), C(12), and C(14) will be termed the *bridging* carbons; and C(4) and C(11) will be referred to as the *apex* carbons. Bond distance and angles cited in text will, unless otherwise stated, be average values assuming C_{2v} molecular symmetry. Individual values are available in Table IV.

The five-membered rings in the nortricyclanone moieties show evidence of severe strain. The largest deviations from normal bond angles occur at the bridging carbons where the internal angles are 101.3° at the carbonyl bridge, or 19° less than the normal value for an sp^2 hybridized carbon atom, and 96.5° at the saturated bridge atoms (C(3), C(5), C(10), and C(12)), or 13° less than the tetrahedral angle. At the apex carbons the CCC bond angles are also substantially less than the normal tetrahedral value. The two angles which also form part of the six-membered ring (of the type C(3)–C(4)–C(5)) average 98.9° while the angles between the carbonyl and saturated bridges (type C(3)–C(4)–C(7)) are slightly larger, 101.9°. The internal angles in the five-membered rings at the base carbons are of three different kinds: type C(3)–C(2)–C(6), 106.3°; type C(2)–C(1)–C(7), 104.5°; and type C(1)–C(2)–C(3), 108.2°. Although these values are not far removed from the tetrahedral angle of 109.5°, they represent a significant distortion from the average value of 119.5° for twelve analogous exocyclic bond angles in an unstrained cyclopropane derivative.[23]

Most of the internal angles in the six- and eight-membered rings are close to the tetrahedral value. For example, the angles at the ends of the eight-membered boat (type C(3)–C(2)–C(6)) average 106.3°, while those

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(19) Listings of structure factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D.C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

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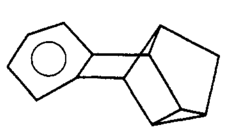
Table IV. Bond Distances and Angles[a]

A. Distances grouped according to C_{2v} symmetry			
C(1)–C(2)	1.524 (3)	C(8)–C(9)	1.529 (3)
C(1)–C(6)	1.537 (3)	C(8)–C(13)	1.523 (3)
C(2)–C(6)	1.491 (3)	C(9)–C(13)	1.485 (3)
C(2)–C(3)	1.528 (3)	C(9)–C(10)	1.537 (3)
C(5)–C(6)	1.524 (3)	C(12)–C(13)	1.533 (3)
C(3)–C(4)	1.543 (3)	C(10)–C(11)	1.544 (3)
C(4)–C(5)	1.541 (3)	C(11)–C(12)	1.545 (3)
C(4)–C(7)	1.517 (3)	C(11)–C(14)	1.517 (3)
C(1)–C(7)	1.480 (3)	C(8)–C(14)	1.476 (3)
C(3)–C(10)	1.557 (3)	C(5)–C(12)	1.553 (2)
C(7)–O(1)	1.213 (2)	C(14)–O(2)	1.211 (2)
C(1)–H(1)	0.945 (22)	C(8)–H(8)	1.021 (19)
C(2)–H(2)	0.980 (24)	C(9)–H(9)	1.000 (20)
C(6)–H(6)	0.981 (24)	C(13)–H(13)	1.015 (20)
C(3)–H(3)	0.986 (21)	C(10)–H(10)	0.981 (29)
C(5)–H(5)	1.048 (21)	C(12)–H(12)	0.957 (19)
C(4)–H(4)	0.876 (25)	C(11)–H(11)	0.996 (22)
Intramolecular H···H contacts			
H(2)···H(9)	2.596 (23)	H(6)···H(13)	2.562 (29)
H(3)···H(10)	2.249 (34)	H(5)···H(12)	2.221 (29)
H(4)···H(11)	2.349 (32)		
B. Angles, deg			
C(2)–C(1)–C(6)	58.3 (1)	C(9)–C(8)–C(13)	58.2 (1)
C(2)–C(1)–C(7)	105.1 (2)	C(9)–C(8)–C(14)	104.2 (2)
C(2)–C(1)–H(1)	123.8 (13)	C(9)–C(8)–H(8)	120.4 (13)
C(6)–C(1)–C(7)	103.3 (2)	C(13)–C(8)–C(14)	105.2 (2)
C(6)–C(1)–H(1)	123.1 (13)	C(13)–C(8)–H(8)	122.7 (13)
C(7)–C(1)–H(1)	124.4 (13)	C(14)–C(8)–H(8)	126.3 (13)
C(1)–C(2)–C(3)	108.5 (2)	C(8)–C(9)–C(10)	108.1 (2)
C(1)–C(2)–C(6)	61.3 (1)	C(8)–C(9)–C(13)	60.7 (1)
C(1)–C(2)–H(2)	119.3 (15)	C(8)–C(9)–H(9)	123.0 (12)
C(3)–C(2)–C(6)	106.1 (2)	C(10)–C(9)–C(13)	106.2 (2)
C(3)–C(2)–H(2)	122.6 (14)	C(10)–C(9)–H(9)	121.9 (12)
C(6)–C(2)–H(2)	123.2 (14)	C(13)–C(9)–H(9)	121.3 (12)
C(2)–C(3)–C(4)	96.4 (2)	C(3)–C(10)–C(9)	114.6 (2)
C(2)–C(3)–C(10)	113.6 (2)	C(3)–C(10)–C(11)	111.4 (2)
C(2)–C(3)–H(3)	109.5 (12)	C(3)–C(10)–H(10)	110.5 (18)
C(4)–C(3)–C(10)	110.6 (2)	C(9)–C(10)–C(11)	96.4 (2)
C(4)–C(3)–H(3)	115.4 (13)	C(9)–C(10)–H(10)	110.5 (17)
C(10)–C(3)–H(3)	110.7 (13)	C(11)–C(10)–H(10)	113.0 (16)
C(3)–C(4)–C(5)	99.0 (1)	C(10)–C(11)–C(12)	98.8 (1)
C(3)–C(4)–C(7)	103.2 (2)	C(10)–C(11)–C(14)	101.3 (2)
C(3)–C(4)–H(4)	114.6 (16)	C(10)–C(11)–H(11)	118.9 (13)
C(5)–C(4)–C(7)	100.5 (2)	C(12)–C(11)–C(14)	102.7 (2)
C(5)–C(4)–H(4)	121.4 (17)	C(12)–C(11)–H(11)	117.8 (13)
C(7)–C(4)–H(4)	115.3 (17)	C(14)–C(11)–H(11)	114.5 (3)
C(4)–C(5)–C(6)	96.7 (1)	C(5)–C(12)–C(11)	111.1 (2)
C(4)–C(5)–C(12)	111.0 (2)	C(5)–C(12)–C(13)	113.2 (1)
C(4)–C(5)–H(5)	112.6 (12)	C(5)–C(12)–H(12)	113.2 (11)
C(6)–C(5)–C(I2)	114.7 (1)	C(11)–C(12)–C(13)	96.3 (1)
C(6)–C(5)–H(5)	116.0 (11)	C(11)–C(12)–H(12)	112.7 (11)
C(12)–C(5)–H(12)	105.8 (12)	C(13)–C(12)–H(13)	109.2 (11)
C(1)–C(6)–C(2)	60.4 (1)	C(8)–C(13)–C(9)	61.1 (1)
C(1)–C(6)–C(5)	108.1 (2)	C(8)–C(13)–C(12)	108.2 (2)
C(1)–C(6)–H(6)	122.3 (14)	C(8)–C(13)–H(13)	121.2 (12)
C(2)–C(6)–C(5)	106.3 (2)	C(9)–C(13)–C(12)	106.4 (2)
C(2)–C(6)–H(6)	125.9 (13)	C(9)–C(13)–H(13)	120.8 (11)
C(5)–C(6)–H(6)	119.5 (13)	C(12)–C(13)–H(13)	123.0 (12)
C(1)–C(7)–C(4)	101.3 (2)	C(8)–C(14)–C(11)	101.3 (2)
C(1)–C(7)–O(1)	129.4 (2)	C(8)–C(14)–O(2)	129.6 (2)
C(4)–C(7)–O(1)	129.2 (2)	C(11)–C(14)–O(2)	129.0 (2)

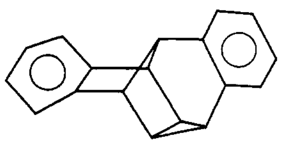
[a] Standard errors referred to the last significant digit are in parentheses.

associated with links between the nortricyclanone subunits, namely types C(2)–C(3)–C(10) and C(4)–C(3)–C(10), have values of 113.0 and 111.0°, respectively. We have already seen that the angles at the ends of the six-membered boat (type C(3)–C(4)–C(5), 98.9°) are an exception.

The planes of the two cyclopropyl rings are tilted at angles of approximately 13° with respect to a plane through the four atoms C(3), C(5), C(10), and C(12) forming the links between the nortricyclanone entities. The direction of tilt is such as to bring the extreme atoms C(1) and C(8) closer to the central plane (see also Figure 1). The 13° value is fairly close to an angle of 9° found[21] in another nortricyclane derivative, V. An angle of −6° (where the extreme carbon is more distant from the central plane) occurs in a homonortricyclane derivative, VI, in which an extra carbon is present in the outer bridge.[22]



V



VI

An interesting feature of the structure is the increased length of bonds formed by the bridging carbons to the apex carbons as compared to those formed to the cyclopropyl carbons. Thus, at the carbonyl bridges the two bonds of type C(7)–C(4) average 1.517 Å *vs.* 1.478 Å for the C(7)–C(1) bonds, a difference of 0.039 Å. For the saturated bridges the difference is smaller but is believed to be significant; these distances are C(3)–C(4), 1.543 Å and C(3)–C(2), 1.530 Å. Part of this effect may be attributed to a shortening of the C–C bonds to the base atoms caused by increased s character in the exocyclic bonds of cyclopropyl carbons. The s character in these bonds may be further enhanced by the opening of the exocyclic CCH bond angles due to strain in the five-membered rings. These external angles average 125.4° at C(1) and C(7) and 121.8° at C(2), C(6), C(9), and C(13). By comparison the average of the corresponding external angles in an unstrained cyclopropane derivative[23] is only 110.5°. On the other hand the reduced CCC angles at C(4) and C(7) should increase the p character in the C–C bonds to the apex carbons and tend to lengthen these bonds. Similar differences in bond lengths to the apex and base carbons have been observed in the structures of the related compounds V and VI.[21,22]

The two bonds connecting the nortricyclanone subunits, C(3)–C(10) and C(5)–C(12), average 1.555 Å or 0.02 Å longer than a standard C–C single bond. Allen, Kraut, and Traylor have given a detailed analysis of the variations in the C–C single bond lengths in some bisbridgehead caged alkanes.[20a] They attributed the observed deviations from normal values to two principal causes: (1) an orbital hybridization effect acting to decrease the C single bond radius with increasing s character in the bond, and (2) repulsions between nonbonded atoms resulting in increased bond distances. The net change may clearly reflect the balance between two opposite components. Both kinds of forces will act in the present case, but the available evidence suggests that neither will be as strong as in the more severe cases discussed by these authors. Thus, the bond angles external to the nortricyclanone subunits, namely C(4)–C(3)–C(10) 111.0°, C(2)–C(3)–C(10) 113.0°, and C(10)–C(3)–H(3) 110.0°, are on average only about 2° greater than the tetrahedral angle, whereas in 1-biapocamphane,[20a] where a bond shortening of 0.034 Å is inferred, the external angles (114.8°, 115.0°, 119.6°) average nearly 7° greater than the tetrahedral angle. On this basis, orbital hybridization effects in Binor-S-

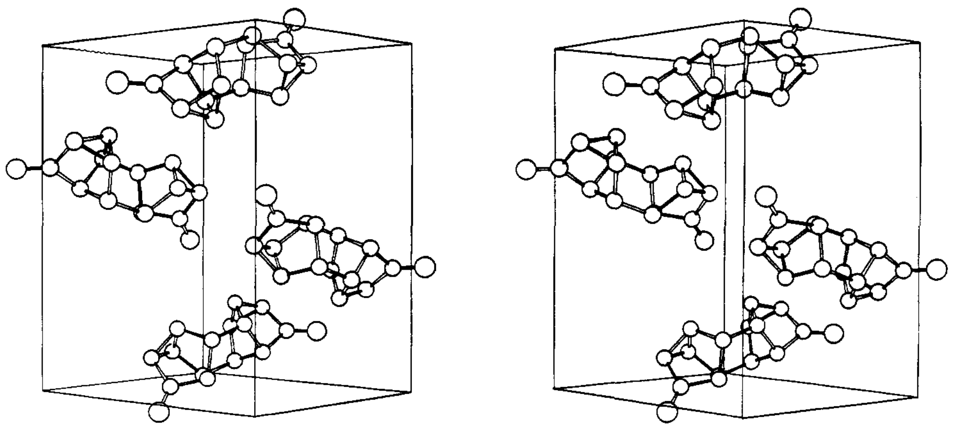


Figure 2. Three-dimensional view of the crystal packing in decahydro[1,2,4:5,6,8]dimetheno-*s*-indacenedione. The *y* axis is vertical while the *x* axis goes from the left front to right rear.

dione could shorten these bonds by at most 0.01 Å. There are five H···H contacts that can contribute to steric repulsions between the nortricyclanone fragments. As measured in the X-ray experiment, the shortest of these are between H(3) and H(10) and between H(5) and H(12), 2.24 Å (average). The flagpole hydrogens of the six-membered chair are 2.35 Å distant (Table IV), while the H(2)···H(9) and H(6)···H(13) distances average 2.58 Å. The closest contacts between carbon atoms that are 1,4 to each other are C(4)···C(11), 2.663 Å; C(2)···C(9), 2.808 Å; C(6)···C(13), 2.793 Å. The first value is slightly longer than the value of 2.559 Å calculated for a cyclohexane chair assuming bond angles of 109.5° and C–C distances of 1.535 Å.

Bond distances and angles in the cyclopropane ring appear to be unequal. The two transverse bonds C(2)–C(6) and C(9)–C(13) have an average length of 1.488 Å which is shorter than the average value 1.528 Å for the bonds of the C(1)–C(2) type. A similar difference occurs in the homonortricyclane derivative VI[22] which also contains a saturated bridging group and has a transverse cyclopropyl bond of 1.480 Å and distances of 1.516 and 1.517 Å on the remaining sides of the triangle. In the nortricyclane derivative V,[21] which contains only saturated bridging atoms, all three distances were found to be 1.51 Å.

The carbonyl C=O bond bisects the exterior angles at C(7) and C(14) nearly exactly, as shown by near equality of the angles C(1)–C(7)–O(1), 129.5° (average), and C(4)–C(7)–O(1), 129.1° (average). The average C=O bond length, 1.212 Å, is normal.

The results above must be considered in the context of the systematic and random errors present in the structure analysis. The most serious of these is the unknown correction to the bond lengths due to thermal motion in the crystal. This type of error may invalidate conclusions based on small differences in bond distances. However, because the overall temperature factor of the structure (B_0 = 3.8 Å^2) is not high and because, as we have seen, most of the thermal ellipsoids are near-spheres of fairly uniform size, these corrections should not be especially large and should for the most part be of similar magnitudes for most of the C–C bonds. The hydrogen positions are subject to a second type of systematic error arising from the bias of the electron density distribution toward the bonding region between the C and H nuclei, and are also affected by considerably larger random errors than the C and O positions. In view of these factors the C–H bonds, which range between 0.88 and 1.05 Å, appear fairly well behaved, as are the CCH and HCH bond angles which show reasonable consistency across the elements of molecular symmetry.

The deviations from ideal C_{2v} symmetry that are exhibited by the Binor-S-dione molecule in the crystalline state can be grouped into three classes: (1) variations in the displacements of atoms from the mirror planes of C_{2v}, (2) variations in bond angles related by these mirrors, and (3) variations in bond distances related by the mirrors. These classes are, of course, interrelated; variations of the first type, which in the present structure are moderately large, must be accomplished through changes of the second and/or third kinds as imposed by the packing forces arising in crystallization. The structural data in fact suggest that the observed variations in displacements from the mirrors arise by a series of subtle but significant changes in the bond angles, but that differences in bond distances are probably not significant. Consider the longitudinal mirror plane defined by C(1), C(4), C(8), and C(11). The equation of the least-squares plane[17e] through these atoms is $2.885x + 8.886y + 5.335z = 7.067$ and the calculated deviations from it are ±0.003 Å for C(1) and C(8), respectively, and ±0.006 Å for C(4) and C(11), respectively. These deviations are possibly significant but are certainly not large. However, the remaining heavy atoms expected to lie on this plane show much larger deviations: O(1), −0.187 Å; O(2), +0.122 Å; C(7), −0.058 Å; C(14), +0.035 Å. Thus the carbonyl groups appear to be bent in opposite directions and by unequal amounts from the longitudinal plane. Among the CCC bond angles, the maximum difference between symmetry related pairs is 2.7°, for C(3)–C(4)–C(7) and C(5)–C(4)–C(7). Actually four different angles of this type occur in the structure, and when these are averaged, the maximum deviation from the mean value is 1.4°, or six to seven times the standard error σ for an individual measurement. A number of other fairly large differences occurs. For example, there is a 1.5° difference between C(6)–C(5)–C(12) and C(5)–C(12)–C(13), and C(6)–C(1)–C(7) (103.3°) is significantly lower than the related angles C(13)–C(8)–C(14) (105.2°) and C(2)–C(1)–C(7) (105.1°). Among the bond distances, on the other hand, no individual value deviates more than 3σ

Table V. Molecular Packing

Atom 1	Atom 2	Distance, Å	Transform, atom 2
A. H···H Contacts Less than 2.6 Å			
H(2)	H(10)	2.54	$2 - x, 1 - y, 1 - z$
H(4)	H(4)	2.38	$2 - x, 1 - y, -z$
H(5)	H(9)	2.32	$x, {}^1/_2 - y, z - {}^1/_2$
H(5)	H(13)	2.32	$x, {}^1/_2 - y, z - {}^1/_2$
B. O···H Contacts Less than 3 Å			
O(1)	H(12)	2.64	$x + 1, y, z$
O(1)	H(11)	2.64	$2 - x, 1 - y, -z$
O(1)	H(4)	2.68	$2 - x, 1 - y, -z$
O(1)	H(1)	2.78	$x, {}^1/_2 - y, z - {}^1/_2$
O(1)	H(2)	2.84	$x, {}^1/_2 - y, z - {}^1/_2$
O(2)	H(6)	2.45	$1 - x, {}^1/_2 + y, {}^1/_2 - z$
O(2)	H(13)	2.65	$1 - x, {}^1/_2 + y, {}^1/_2 - z$
O(2)	H(9)	2.96	$1 - x, 1 - y, 1 - z$
C. O···O Contact			
O(1)	O(2)	3.269	$1 + x, y, z$
D. O···C Contacts Less than 3.6 Å			
O(1)	C(14)	3.201	$1 + x, y, z$
O(1)	C(1)	3.332	$x, {}^1/_2 - y, z - {}^1/_2$
O(1)	C(2)	3.394	$x, {}^1/_2 - y, z - {}^1/_2$
O(1)	C(12)	3.403	$1 + x, y, z$
O(1)	C(4)	3.527	$2 - x, 1 - y, -z$
O(1)	C(8)	3.529	$1 + x, y, z$
O(1)	C(11)	3.571	$2 - x, 1 - y, -z$
O(2)	C(6)	3.349	$1 - x, {}^1/_2 + y, {}^1/_2 - z$
O(2)	C(7)	3.445	$x - 1, y, z$
O(2)	C(13)	3.520	$1 - x, {}^1/_2 + y, {}^1/_2 - z$
E. C···C Contacts Less than 4.0 Å			
C(1)	C(8)	3.534	$1 + x, y, z$
C(1)	C(13)	3.889	$1 + x, y, z$
C(2)	C(7)	3.673	$x, {}^1/_2 - y, {}^1/_2 + z$
C(2)	C(5)	3.977	$x, {}^1/_2 - y, {}^1/_2 + z$
C(2)	C(8)	3.981	$1 + x, y, z$
C(4)	C(4)	3.758	$2 - x, 1 - y, -z$
C(4)	C(7)	3.974	$2 - x, 1 - y, -z$
C(5)	C(9)	3.771	$x, {}^1/_2 - y, z - {}^1/_2$
C(5)	C(13)	3.869	$x, {}^1/_2 - y, z - {}^1/_2$
C(6)	C(7)	3.962	$x. {}^1/_2 - y, {}^1/_2 + z$
C(7)	C(14)	3.516	$1 + x, y, -z$
C(7)	C(8)	3.563	$1 + x, y, z$
C(7)	C(13)	3.985	$1 + x, y, z$
C(8)	C(8)	3.366	$1 - x, 1 - y, 1 - z$
C(8)	C(9)	3.525	$1 - x, 1 - y, 1 - z$
C(8)	C(14)	3.897	$1 - x, 1 - y, 1 - z$
C(9)	C(14)	3.896	$1 - x, 1 - y, 1 - z$
C(11)	C(11)	3.806	$1 - x, 1 - y, -z$

from the average for all symmetry related bonds of that type, and the maximum difference between symmetry equivalent C–C distances is only 0.014 Å (see Table IV).

The arrangement of the molecule in the crystal is shown in three dimensions[17d] in Figure 2, and the closer intermolecular contacts are summarized in Table V. Several close contacts occur along the cell translation in the *a* direction between the two crystallographically distinct carbonyl groups. These include the shortest O···O (3.269 Å) and O···C (3.201 Å) contacts. The shortest intermolecular C···C distance (3.366 Å) is between two C(8) atoms related by the inversion center at ${}^1/_2$, ${}^1/_2$, ${}^1/_2$. A few fairly short intermolecular contacts occur between hydrogen atoms. H(5) forms two contacts of 2.32 Å with H(9) and H(13) of a neighboring molecule related by the *c* glide, and a distance of 2.38 Å occurs between two H(4) atoms across an inversion center. The H···H distances are, of course, subject to the errors affecting hydrogen positions listed above. None of the intermolecular distances appears to be unusually short.

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Appendix

Crystal Data for Binor-S. Single crystals of Binor-S, $C_{14}H_{16}$, were sealed in thin-walled glass capillaries and their diffraction pattern was surveyed on Weissenberg and precession cameras. The reciprocal lattice symmetry C_{4h} and the reflection conditions $hkl\,(h + k + l = 2n)$; $hk0$, $h = 2n\ (k = 2n)$; and $00l\ (l = 2n)$ establish the space group $I4_1/a$ (C_{4h}^6). A crystal was then aligned on its (112) axis on the Picker goniostat, and lattice parameters were calculated by least-squares refinement of the setting angles of 12 unique reflections (Cu Kα radiation). The cell constants, $a = 11.390 \pm 0.012$ and $c = 15.153 \pm 0.019$ Å, give a calculated density $\rho = 1.245$ g cm^{-3} for mol wt 184.28 and $Z = 8$. The requirement of eight formula units per unit cell constrains molecules of C_{2v} symmetry (structure I) to lie on the twofold axes (8e sites) of the space group. If structure II were correct, the 8c and 8d sites of symmetry I would be permitted in addition to the 8e positions.

The intensities of 842 unique reflections were measured under the experimental conditions described above; of this number 215 were absent by the prior criteria. The data were subsequently checked by measuring reflections in four redundant quadrants and showed excellent internal agreement. A Wilson plot[16] gave a relatively high overall temperature factor, 6.67 Å^2. The distribution of E's was fairly close to that expected for a centric crystal (*vide supra*): $\langle |E| \rangle$, 0.816; $\langle E^2 \rangle$, 1.000; $\langle |E^2 - 1| \rangle$, 0.920; $\% > 1$, 30.8; $\% > 2$, 4.3; $\% > 3$, 0.1. Attempts to solve the structure by a variety of methods have thus far been unsuccessful.