for Crystal Structure Illustrations", Report ORNL-3794, Revised, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965, p 70.
(14) J. A. Kafalas and J. M. Longo, *Mater. Res. Bull.*, **3**, 501 (1968).
(15) J. M. Longo and J. A. Kafalas, *J. Appl. Phys.*, **40**, 1601 (1969).
(16) J. M. Longo and J. A. Kafalas, *J. Solid State Chem.*, **1**, 103 (1969).
(17) J. M. Longo, J. A. Kafalas, N. Menyuk, and K. Dwight, *J. Appl. Phys.*, **42**, 1561 (1971).
(18) J. M. Longo and J. A. Kafalas, *J. Solid State Chem.*, **3**, 429 (1971).
(19) B. Bleaney, *Philos. Mag.*, **42**, 441 (1951).
(20) B. Bleaney and D. J. E. Ingram, *Proc. R. Soc. London, Ser. A*, **205**, 336 (1951).
(21) B. R. McGarvey, *J. Phys. Chem.*, **71**, 51 (1967).
(22) H. Koga, K. Horai, and O. Matumura, *J. Phys. Soc. Jpn.*, **15**, 1340 (1960).
(23) T. P. P. Hall, W. Hayes, and F. I. B. Williams, *Proc. Phys. Soc., London*, **78**, 833 (1961).
(24) I. Y. Chan, D. C. Doetschman, C. A. Hutchison, Jr., B. E. Kohler, and J. W. Stout, *J. Chem. Phys.*, **42**, 1048 (1965).
(25) H. G. Hoeve and D. O. Van Osteburg, *Phys. Rev.*, **167**, 245 (1968).
(26) T. Iri and G. Kuwabara, *J. Phys. Soc. Jpn.*, **24**, 127 (1968).
(27) K. K. Cahn and L. Shields, *J. Chem. Soc. A*, 2700 (1970).
(28) G. L. McPherson, T. J. Kistenmacher, and G. D. Stucky, *J. Chem. Phys.*, **52**, 815 (1970).

Contribution from the Departments of Chemistry, University of Alabama, University, Alabama 35486, and University of New Orleans, New Orleans, Louisiana 70122

Crystal Structure and Mössbauer Spectrum of [2]Ferrocenophanethiazine 1,1-Dioxide

R. A. ABRAMOVITCH,*[1a] J. L. ATWOOD,*[1a] M. L. GOOD,*[1b] and B. A. LAMPERT[1a]

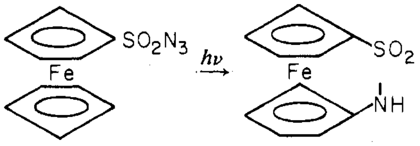
Received May 12, 1975

AIC503273

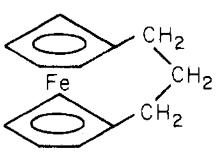
The cyclopentadienyl rings of the title compound are tilted by 23°. A comparison of its Mössbauer spectrum with those of ferrocene derivatives in which the rings are less tilted or parallel and antiprismatic supports the hypothesis that a large degree of ring tilt can occur without its affecting the bond energy. $(C_5H_4)Fe(C_5H_4)SO_2NH$ crystallizes in the monoclinic space group $P2_1/c$ [C_{2h}^5; No. 14] with unit cell dimensions a = 10.566 (7) Å, b = 11.802 (7) Å, c = 7.671 (6) Å, β = 93.35 (5)°, and Z = 4. Full-matrix least-squares refinement has led to a final R value of 0.051 based on 978 independent observed reflections collected by counter techniques. The Fe–C bond lengths range from 1.962 (8) to 2.096 (8) Å, and the bond lengths and angles involving the bridging groups are normal; there is no evidence of delocalization of ring electron density into the bridge.

Introduction

Photolysis of ferrocenesulfonyl azide (I) in hydrocarbon solvents using 3500-Å radiation yielded [2]ferrocenophanethiazine 1,1-dioxide (II) in good yield.[2] The structure of II was established on the basis of its microanalysis and spectral properties. In particular, the NMR spectrum exhibited two sets of A_2B_2 patterns associated with the two monosubstituted cyclopentadienyl rings, as did the N-methylated product.



I II



III

Molecular models clearly indicated that in II the two rings could not be parallel and that the molecule would have to have a prismatic conformation (as opposed to ferrocene itself which is antiprismatic and has parallel cyclopentadienyl rings). Ballhausen and Dahl[3] suggested that in protonated ferrocene the cyclopentadienyl rings are no longer parallel and calculated that the bonding of the rings to the metal atom is relatively insensitive to the value of the angle between the radius vectors from the metal atom to the centers of the rings. Considerable splaying of the rings could thus occur without any significant loss in bond energy.

It seemed to us that ferrocenophane (II) would provide a good model for testing such a hypothesis since the angle between the two rings appeared (in Drieding models) to be larger than in [3]ferrocenophane (III) and 6-keto[3]ferrocenophane (8.8°).[4] We now report the crystal structure and Mössbauer spectrum of II.

Table I. Crystal Data

Compd	$(C_5H_4)Fe(C_5H_4)SO_2NH$
Mol wt	263.1
Linear abs coeff	17.99
Obsd density	1.82 (2)
Calcd density	1.83
Max crystal dimensions	0.08 × 0.08 × 0.70 mm
Space group	$P2_1/c$
Molecules/unit cell	4
Cell constants,[a] a	10.566 (7) Å
b	11.802 (7)
c	7.671 (6)
β	93.35 (5)°
Cell vol	955.0 Å^3

[a] Mo Kα radiation, λ 0.71069 Å. Ambient temperature of 22°.

Experimental Section

X-Ray Data Collection and Structure Determination. Single crystals of the red-orange air-stable substance were sealed in thin-walled glass capillaries. Final lattice parameters as determined from a least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 12 reflections ($\theta > 20°$) accurately centered on the diffractometer are given in Table I. The space group was uniquely determined to be $P2_1/c$ [C_{2h}^5; No. 14] from the systematic absences in $0k0$ for $k = 2n + 1$, and in $h0l$ for $l = 2n + 1$. The density was measured by flotation methods, and it indicated that there are four formula units per unit cell.

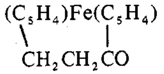
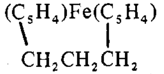
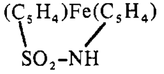
Data were taken on an Enraf-Nonius CAD-4 diffractometer with graphite crystal monochromated molybdenum radiation. The diffracted intensities were collected by the ω–2θ scan technique with a takeoff angle of 3.0°. The scan rate was variable and was determined by a fast (20° min^{-1}) prescan. Calculated speeds based on the net intensity gathered in the prescan ranged from 7 to 0.6° min^{-1}. Moving-crystal, moving-counter backgrounds were collected for 25% of the total scan width at each end of the scan range. For each intensity

Table II. Final Fractional Coordinates and Anisotropic Thermal Parameters[a] for [2]Ferrocenophanethiazine 1,1-Dioxide

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe	0.2270 (1)	0.4194 (1)	0.2988 (1)	0.0056 (1)	0.0126 (1)	0.0124 (2)	0.0013 (1)	−0.0020 (1)	−0.0012 (2)
S	0.2581 (2)	0.6328 (3)	0.0857 (3)	0.0104 (2)	0.0146 (3)	0.0153 (4)	−0.0007 (2)	−0.0018 (2)	−0.0009 (3)
O1	0.1956 (7)	0.7392 (7)	0.0720 (10)	0.0205 (10)	0.0123 (7)	0.0335 (19)	0.0020 (8)	−0.0108 (12)	0.0022 (10)
O2	0.3318 (6)	0.5977 (8)	−0.0567 (8)	0.0135 (8)	0.0290 (13)	0.0173 (13)	−0.0025 (8)	0.0054 (8)	0.0028 (11)
N	0.3503 (7)	0.6382 (7)	0.2699 (10)	0.0112 (8)	0.0122 (9)	0.0214 (16)	−0.0018 (7)	−0.0061 (9)	0.0018 (11)
C1	0.4159 (7)	0.4313 (10)	0.2853 (11)	0.0056 (7)	0.0166 (13)	0.0161 (16)	0.0026 (8)	−0.0003 (9)	−0.0008 (13)
C2	0.3909 (9)	0.3395 (9)	0.3953 (13)	0.0114 (11)	0.0127 (12)	0.0216 (21)	0.0048 (9)	−0.0071 (12)	−0.0050 (13)
C3	0.3257 (8)	0.3813 (10)	0.5367 (12)	0.0105 (10)	0.0145 (13)	0.0158 (18)	0.0012 (9)	−0.0052 (11)	0.0021 (12)
C4	0.3078 (8)	0.4961 (10)	0.5103 (11)	0.0100 (9)	0.0166 (13)	0.0104 (14)	0.0033 (9)	−0.0007 (10)	−0.0012 (11)
C5	0.3641 (7)	0.5310 (8)	0.3525 (11)	0.0070 (8)	0.0113 (10)	0.0142 (15)	0.0005 (7)	−0.0012 (9)	−0.0036 (11)
C6	0.1661 (9)	0.4109 (10)	0.0457 (11)	0.0124 (11)	0.0136 (12)	0.0153 (17)	0.0025 (10)	−0.0049 (11)	−0.0038 (13)
C7	0.0886 (12)	0.3400 (10)	0.1384 (18)	0.0153 (15)	0.0118 (14)	0.0336 (31)	−0.0024 (11)	−0.0146 (18)	0.0013 (17)
C8	0.0317 (9)	0.3967 (15)	0.2677 (18)	0.0072 (10)	0.0234 (21)	0.0338 (32)	−0.0042 (12)	−0.0046 (14)	0.0094 (22)
C9	0.0681 (8)	0.5095 (11)	0.2567 (12)	0.0066 (8)	0.0193 (15)	0.0180 (18)	0.0044 (9)	0.0013 (10)	0.0003 (14)
C10	0.1536 (7)	0.5218 (7)	0.1186 (10)	0.0071 (7)	0.0093 (8)	0.0116 (14)	0.0012 (6)	−0.0001 (8)	−0.0015 (9)
H1	0.469	0.427	0.179[b]						
H2	0.410	0.256	0.378						
H3	0.299	0.338	0.640						
H4	0.257	0.547	0.589						
H6	0.221	0.388	−0.050						
H7	0.075	0.257	0.116						
H8	−0.031	0.363	0.353						
H9	0.045	0.572	0.325						

[a] Anisotropic thermal parameters defined by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Hydrogen atoms are in calculated positions which were not refined. All hydrogen atoms were assigned an isotropic temperature factor of 5.5 Å^2.

Table III. Mossbauer Data for Ring-Substituted and/or Bridged Ferrocenes

	Mössbauer data[a]			Structural data	
Compd	δ,[b] mm/sec	E_Q, mm/sec	Ref	Structure	Ref
$(C_5H_5)_2Fe$	0.52	2.41	28	Rings are planar and parallel in staggered configuration; small rotational barrier	29-31
	0.53	2.40	24		
$[(C_5H_5)FeC_5H_4C(H)(OH)(C_6H_5)]$	0.51	2.41	28	Ferrocene structure expected	
$(C_5H_4Cl)_2Fe$	0.48	2.35	24	Ferrocene structure expected	
$[(C_5H_5)FeC_5H_4(C_6H_5)]$	0.51	2.34	24	Ferrocene structure expected	
$[(C_5H_5)FeC_5H_4(CN)]$	0.50	2.32	24	Ferrocene structure expected	
$[(CN)C_5H_4]_2Fe$	0.55	2.29	24	Ferrocene structure expected	
$(C_5H_4COOH)_2Fe$	0.49	2.16	28	Rings are planar and almost eclipsed (twist 1° 36′; rings are tilted by 1° 17′; substituents are cis and hydrogen bonded to nearest neighbor	32
$(C_5H_4CHO)_2Fe$	0.51	2.16	28	Structure has eclipsed rings with trans substituents	32
$[(C_5H_5)Fe(C_5H_4)]_2SO_2$	0.49	2.40	24	Expect almost eclipsed rings with little or no tilt. Compare with diferrocenyl ketone[33]	
 $(C_5H_4)Fe(C_5H_4)$ CH_2CH_2CO	0.48	2.20	28	Rings are tilted by 8.8° and twisted by 11.8°	14
 $(C_5H_4)Fe(C_5H_4)$ $CH_2CH_2CH_2$ (III)	0.49	2.30	28	Same as 6-keto[3]ferrocenophane above	14
	0.51	2.30	23		
 $(C_5H_4)Fe(C_5H_4)$ SO_2-NH (II)	0.49	2.33	28	Ring almost eclipsed and tilted 23°	

[a] All Mossbauer data reported are for experiments with absorber temperatures of 77 or 80 K. [b] Isomer shift is given relative to NBS standard iron foil absorber.

the scan width was determined by the equation

$$\text{scan range} = A + B \tan \theta$$

where A = 1.00° and B = 0.23°. Aperture settings were determined in a like manner with A = 4 mm and B = 4 mm. Other diffractometer parameters have been described previously.[5] As a check on the stability of the instrument and the crystal, three reflections, the (111), (1$\bar{1}$1), and (020), were measured after every 25 reflections; in no case was a variation of greater than ±2% noted.

The integrated intensity of a reflection, I, and its estimated standard deviation, $\sigma(I)$, were calculated with the equations

$$I = [C - 2(B_1 + B_2)]/S$$
$$\sigma(I) = [C + B_1 + B_2 + 0.03^2(C + B_1 + B_2]^{1/2}$$

where C is the counts collected during the scan and B_1 and B_2 are the background counts. S is an integer which is proportional to the total scan time.

One independent quadrant of data was measured out to 2θ = 50°; a slow scan was performed on a total of 978 unique reflections. Since these data were scanned at a speed which would yield a net count of 4000, the calculated standard deviations were all very nearly equal. No reflection was subjected to a slow scan unless a net count of 10 was obtained in the prescan. Based on these considerations, the data set of 978 reflections (used in the subsequent structure determination and refinement) was considered observed and consisted in the main of those for which $I > 2\sigma(I)$. The intensities were corrected for Lorentz, polarization, and absorption effects[6] (the transmission factors varied from 0.55 to 0.68).

Fourier calculations were made with the ALFF[7] program. The full-matrix, least-squares refinement was carried out using the Busing and Levy program ORFLS.[8] The function $w(|F_o| - |F_c|)^2$ was minimized. No corrections were made for extinction. Neutral atom scattering factors for Fe, S, O, N, and C were taken from Cromer and Waber,[9] and the scattering for iron was corrected for the real and imaginary components of anomalous dispersion using the values of Cromer and Liberman.[10] Scattering factors for hydrogen were from ref 11. Final bond distances, angles, and errors were computed with the aid of the

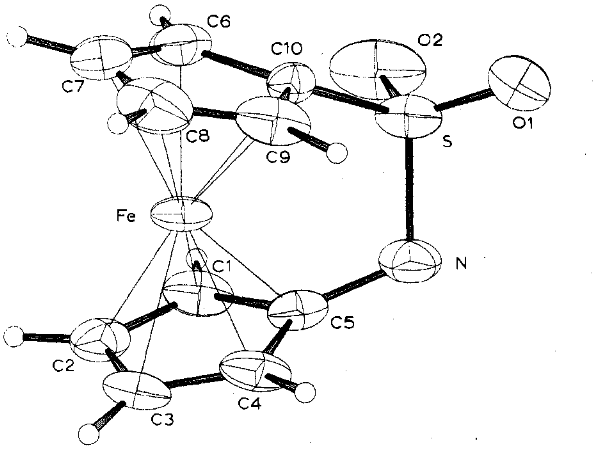


Figure 1. Molecular structure of [2]ferrocenophanethiazine 1,1-dioxide with the atoms represented by their 50% probability ellipsoids for thermal motion.

Busing, Martin, and Levy ORFFE program.[12] Crystal structure illustrations were obtained with the program ORTEP.[13]

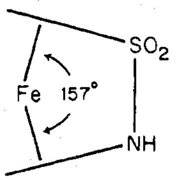
The position of the iron atom was revealed by inspection of a Patterson map, and a Fourier map phased on the iron atom afforded the coordinates of all nonhydrogen atoms. Isotropic least-squares refinement led to a discrepancy factor of $R_1 = \sum(|F_o| - |F_c|)/|F_o| = 0.095$. The hydrogen atoms of the cyclopentadienyl rings were then placed at calculated positions 1.00 Å from the bonded carbon atoms. Subsequent anisotropic refinement of all nonhydrogen atoms led to final values of $R_1 = 0.051$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2} = 0.050$. A final difference Fourier showed no feature greater than 0.4 e/Å^3; the hydrogen atom bonded to the nitrogen atom could not be located. Attempts to place the hydrogen atom in either of the two calculated positions or to half-weight it in both positions resulted in a slight increase in the R factors ($R_1 = 0.052$; $R_2 = 0.051$), and its contribution is therefore not included. The largest parameter shifts in the final cycle of refinement were less than 0.01 of their estimated standard deviations. The standard deviation of an observation of unit weight was 1.31. No systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional and thermal parameters are given in Table II.[14]

Mössbauer Spectrum Determination. A Mössbauer spectrometer (Austin Science Associates) operating in the conventional transmission and constant acceleration mode was made. Data were accumulated in a Nuclear Data Multichannel Analyzer, Series 2200, operating in the multiscaling mode. Data reduction was carried out using a conventional least-squares Lorentzian line shape program on a PDP-10 computer.[15] Precision of δ (isomer shift) and ΔE_Q (quadrupole splitting) values is greater than 0.01 mm/sec based on consecutive runs and error analysis of individual runs.

Samples were finely ground to provide randomly oriented, polycrystalline absorbers. Sample sizes of 15–25 mg/cm^2 were used with the absorber cooled to 77°K (liquid N_2 temperature) and the source at room temperature. Calibration of the spectrometer was accomplished by laser interferometry (via an Austin Science Associates laser system) and isomer shifts were referenced to an NBS certified iron foil standard absorber at room temperature. No second-order Doppler correction was made on the sample data to account for the fact that source and absorber were at different temperatures.[16] This correction is generally quite small and the other literature data to be compared (see Table III) also do not include this correction.

Results and Discussion

The molecular structure illustration (Figure 1) clearly shows the tilt of the cyclopentadienyl rings. The angle made by the normals to the $C_5H_4^-$ groups is 157 (1)°, i.e.



This agrees with the 157° value[17] given for 6,6,7,7-tetramethyl[2]ferrocenophane, a molecule with a two-atom bridge, and is appreciably smaller than the values for the three-atom-bridged 6-keto[3]ferrocenophane (171°)[4] and its 10-methyl-8-phenyl derivative (170°).[18]

Table IV. Intramolecular Distances (Å) and Angles (deg) for [2]Ferrocenophanethiazine 1,1-Dioxide[a,b]

Atoms	Dist	Atoms	Dist
Fe–C1	2.008 (8)	Fe–C6	2.013 (8)
Fe–C2	2.070 (8)	Fe–C7	2.080 (9)
Fe–C3	2.096 (8)	Fe–C8	2.082 (10)
Fe–C4	2.005 (9)	Fe–C9	1.999 (9)
Fe–C5	1.983 (8)	Fe–C10	1.962 (8)
S–O1	1.420 (8)	S–C10	1.740 (9)
S–O2	1.439 (7)	S–N	1.671 (7)
N–C5	1.419 (11)		
C1–C2	1.407 (14)	C6–C7	1.395 (15)
C2–C3	1.407 (13)	C7–C8	1.365 (17)
C3–C4	1.380 (14)	C8–C9	1.389 (17)
C4–C5	1.439 (12)	C9–C10	1.439 (11)
C5–C1	1.408 (13)	C10–C6	1.431 (13)
	Nonbonded		
C1–C6	3.14 (1)	C1–C7	3.74 (1)
C1–C10	3.17 (1)	C1–C9	3.79 (1)
C2–C6	3.58 (1)	C2–C10	3.85 (1)
C2–C7	3.65 (1)	C2–C8	3.92 (1)
C3–C8	3.64 (1)	C3–C7	3.87 (1)
C3–C9	3.70 (1)	C3–C10	3.96 (1)
C4–C9	3.11 (1)	C4–C8	3.57 (1)
C4–C10	3.35 (1)	C4–C6	3.91 (1)
C5–C10	2.78 (1)	C5–C6	3.37 (1)
C5–C9	3.18 (1)	C5–C8	3.87 (1)
C5–C7	3.96 (1)		
C10–O2	2.54 (1)	C10–O1	2.63 (1)
N–C1	2.52 (1)	N–C4	2.55 (1)
N–C9	3.34 (1)	N–C6	3.67 (1)
N–O1	2.48 (1)	N–O2	2.55 (1)
N–C10	2.69 (1)	S–C5	2.58 (1)
S–C1	3.24 (1)	S–C4	3.65 (1)
S–C9	2.86 (1)	S–C6	2.80 (1)

Atoms	Angle	Atoms	Angle
O1–S–O2	117.9 (5)	O1–S–C10	112.4 (4)
O1–S–N	105.9 (5)	O2–S–C10	105.6 (5)
O2–S–N	109.7 (4)	N–S–C10	104.5 (4)
S–N–C5	112.5 (6)		
C2–C1–C5	109.5 (8)	C7–C6–C10	106.2 (9)
C1–C2–C3	108.0 (9)	C6–C7–C8	111.8 (11)
C2–C3–C4	107.5 (9)	C7–C8–C9	106.9 (11)
C3–C4–C5	110.2 (9)	C8–C9–C10	109.2 (10)
C4–C5–C1	104.9 (9)	C9–C10–C6	105.8 (9)

[a] Estimated standard deviations, given in parentheses, are calculated by considering all of the elements of the positional covariance matrix of the last cycle of refinement. Contributions from the errors in the unit cell parameters are included. [b] The bond lengths have not been corrected for the effects of thermal motion.

The configuration of the cyclopentadienyl rings is intermediate between the eclipsed and staggered extremes. The angle made by the normals to the planes defined by N–S–C10 and S–N–C5 is 29°; this is in agreement with the value of 25° found for the equivalent angle in 6,6,7,7-tetramethyl[2]ferrocenophane. The nature of the configuration is also illustrated by the data in Table IV: for example, the C1–C10 distance is 3.17 Å, while the C4–C10 separation is 3.35 Å.

The Fe–C lengths (Table IV), which range from 1.962 (8) to 2.096 (8) Å, are well within the values stated for other bridged ferrocenes.[4,12,18] The bond distances involving the sulfur atom also appear close to expected values: S–C = 1.740 (9) vs. 1.738 (5) Å for the equivalent hybridization situation in $C_{33}H_{47}NO_9S$;[19] S–O = 1.430 (7) vs. 1.418 (4) Å in $C_{33}H_{47}NO_9S$;[19] S–N = 1.671 (7) vs. 1.713 (6) Å in rubidium

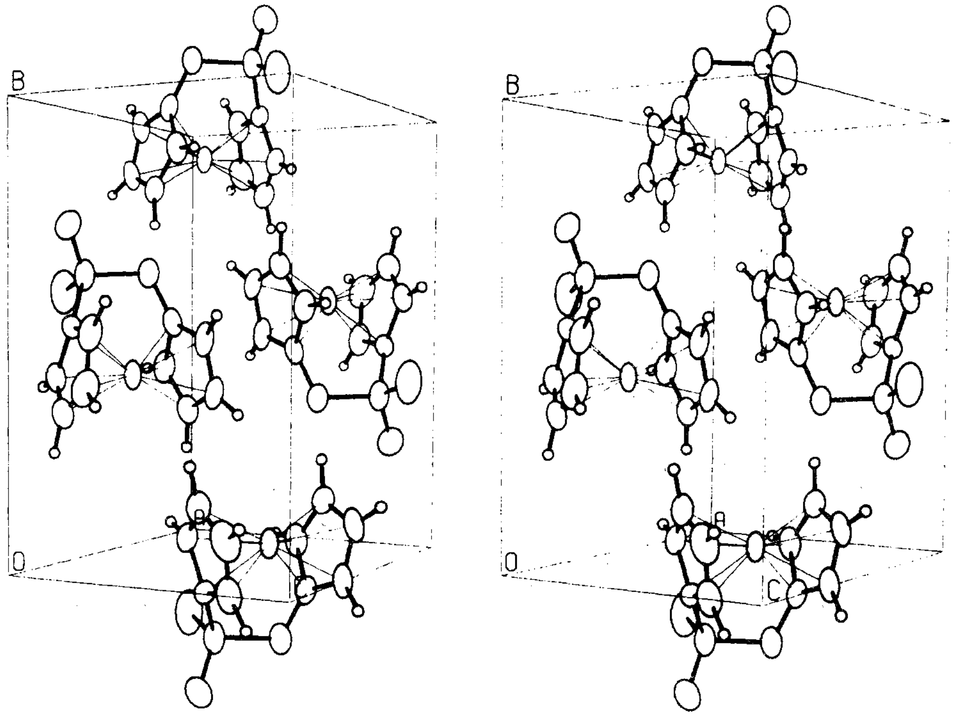


Figure 2. Stereoscopic drawing showing the packing of [2]ferrocenophanethiazine 1,1-dioxide in the unit cell.

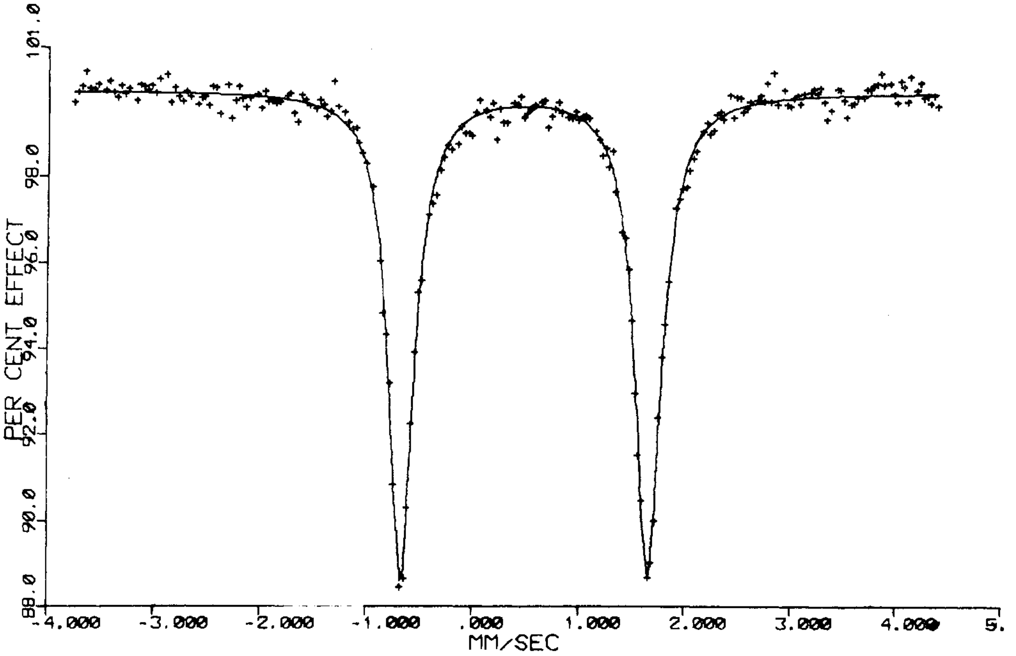


Figure 3. Mössbauer spectrum for [2]ferrocenophanethiazine 1,1-dioxide at 77 K. (Points are raw data from the multichannel analyzer and the smooth curve is the least-squares fit of Lorenztian line shape.)

hydroxylamine-*N*,*N*-disulfonate.[20] Although the N–C bond length (1.419 (11) Å) is shorter than the 1.472-Å standard given[21] for 3-covalent nitrogen in paraffinic and saturated heterocyclic systems, this difference is probably not significant in view of the 0.03-Å correction which must be made for sp^2 vs. sp^3 hybridization of the carbon atoms.

The average C–C bond length of 1.406 Å compares well with the expected 1.43-Å value[22] when one considers that the librational motion of the ring has the effect of shortening the C–C lengths. Each ring is planar to within 0.01 Å, and the iron atom resides 1.64 Å out of the planes.

An examination of the unit cell packing (Figure 2) shows several intermolecular contacts of less than 3.50 Å: N–O1 $(x, 1^1/_2 - y, ^1/_2 + z)$ = 3.25 (1) Å; O2–C1 $(1 - x, 1 - y, z)$ = 3.29 (1) Å; C1–C4 $(1 - x, 1 - y, 1 - z)$ = 3.35 (1) Å; O1–C4 $(x, 1^1/_2 - y, -^1/_2 + z)$ = 3.39 (1) Å; N–O2 $(x, 1^1/_2 - y, ^1/_2 + z)$ = 3.40 (1) Å. Unfortunately, the failure to locate the H atom bonded to the N atom obscures any hydrogen-bond interpretation of the N–O distances.

A representative Mössbauer spectrum of II is shown in Figure 3. The specific Mössbauer parameters for this compound are as follows: isomer shift (δ) = +0.493 ± 0.001 mm/sec (reference Fe metal); quadrupole splitting (ΔE_Q) = 2.329 ± 0.002 mm/sec; line width at half-maximum (Γ) = 0.297 ± 0.004 mm/sec. A comparison of the data for this molecule and several representative substituted and bridged ferrocenes is made in Table III. Remembering that the isomer shift provides a measure of the s-electron density about the

Fe atom (for Fe, as the s-electron density increases, δ decreases) and the quadrupole splitting is a function of the magnitude of the electric field gradient about the iron atom, one can discern that substitution or ring bridging has little effect on the bonding between Fe and the ring substituents which are good electron-withdrawing groups such as cyanide or carboxylate. This influence appears to be more important than any concurrent structural deformations on the coplanarity of the rings. Note that the quadrupole splitting parameter is more sensitive to molecular changes than the isomer shift. The effects of ring substitutions on the Mössbauer parameters of ferrocenes were first discussed in some detail by Wertheim and Herber[23] and later by Nesmeyanov and coworkers.[24] These latter authors found a linear correlation between ΔE_Q and the induction constants of the substituents on ring-substituted ferrocenes. They concluded that the ring substituents affected the electron density near the iron atom only as they were able to affect the bonding MO's of the sandwich compound (assumed to be formed from the AO's of iron and the π-MO's of the ring). The ring substituent effect could only be transmitted through the ring by inductive polarization of the metal–ring bond. Thus the substituent effect on the electron density at the metal atom should be indirect and slight as evidenced by the small changes observed in the Mössbauer parameters.

A look at the data in Table III also indicates that the relative orientation of the cyclopentadienyl rings in bridged ferrocenes (ring tilt and eclipsed or staggered configuration) does not greatly affect the Mössbauer parameters. Again the quadrupole splitting is decreased slightly in the bridged species. It is interesting to note that the values for [3]ferrocenophane are the same as those observed for [2]ferrocenophanethiazine 1,1-dioxide, although the ring tilt increases from about 9 to 23°. These observations at first appear to be anomalous but they are adequately predicted by the detailed MO description of ferrocene systems. The MO's for ferrocene were first presented quantitatively by Shustorovich and Dyatkina[25] and Dahl and Ballhausen.[3,26] The utility of these MO approaches was demonstrated by Collins,[27] who observed that the sign of the electric field gradient in ferrocene and the collapse of the quadrupole splitting in the ferricenium ion could be predicted by calculations derived from these MO's. The small effect of ring tilt is indicated by Ballhausen and Dahl's calculation[3] of the total overlap of the 12 bonding electrons with the rings, in systems both where the rings are parallel and where they are tilted. The magnitude of the overlap, S, varied from 2.00 for the parallel ring case to 1.87 for a ring-tilt angle of 30°. Thus, the total changes in the electron density and the electric field gradient at the iron nucleus are expected to be small even when the rings are tilted by appreciable amounts. The observation of the small deviation in quadrupole splitting for the bridged ferrocene of this study (ring tilt 23°) is excellent justification for these theoretical results.

The fact that the quadrupole splitting of [2]ferrocenophanethiazine 1,1-dioxide is about the same as that for [3]ferrocenophane also indicates that the $-SO_2-NH-$ bridge does not provide for any significant electron delocalization from the ring. This is in contrast to the results obtained for cyanide, carboxylate, and acetyl substituents but is consistent with the values obtained for the $-SO_2$-bridged biferrocene (see Table III). This nondelocalization of ring electron density is consistent with the normal bond lengths observed for the S–C, S–O, S–N, and N–C bonds from the structural analysis.

Acknowledgment. M.L.G. wishes to acknowledge the partial financial support of the Mössbauer work by the National Science Foundation (Grant GP-38054X), and R.A.A., support from the same source (Grant GP-33361X2).

Registry No. II, 32964-64-0.

Supplementary Material Available. A listing of structure factor amplitudes and complete least-squares plane results will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th Street, N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number AIC503273-12-75.

References and Notes

(1) (a) University of Alabama. (b) University of New Orleans.
(2) R. A. Abramovitch, C. I. Azogu, and R. G. Sutherland, *Chem. Commun.*, 1439 (1969).
(3) C. J. Ballhausen and J. P. Dahl, *Acta Chem. Scand.*, **15**, 1333 (1961).
(4) N. D. Jones, R. E. Marsh, and J. H. Richards, *Acta Crystallogr.*, **19**, 330 (1965).
(5) J. L. Atwood and K. D. Smith, *J. Am. Chem. Soc.*, **95**, 1488 (1973).
(6) D. J. Wehe, W. R. Busing, and H. A. Levy, "ORABS, a Fortran Program for Calculating Single-Crystal Absorption Corrections", Report ORNL-TM-229, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.
(7) C. R. Hubbard, C. O. Quicksall, and R. A. Jacobson, USAEC Report IS-2625, Ames Laboratory, Iowa State University, Ames, Iowa, 1971.
(8) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, a Fortran Crystallographic Least-Squares Program", Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.
(9) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).
(10) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).
(11) "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, 1962, p 202.
(12) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, a Fortran Crystallographic Function and Error Program", Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.
(13) C. K. Johnson, "ORTEP, a Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations", Report ORNL-3794, Revised, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.
(14) Supplementary material.
(15) S. W. Marshall, J. A. Nelson, and R. M. Wilenzick, *Commun. ACM*, **8**, 313 (1965).
(16) N. N. Greenwood and T. C. Gibb, "Mossbauer Spectroscopy", Chapman and Hall, London, 1971, p 50.
(17) M. B. Laing and K. N. Trueblood, *Acta Crystallogr.*, **19**, 373 (1965). These values are often referred to as "ring tilt" and are thus given as the supplements of the dihedral angles.
(18) C. Lecomte, Y. Dusausoy, and J. Protas, *Acta Crystallogr., Sect. B*, **29**, 1127 (1973).
(19) F. R. Ahmed, *Acta Crystallogr., Sect. B*, **30**, 2558 (1974).
(20) R. J. Guttormson, J. S. Rutherford, B. E. Robertson, and D. B. Russell, *Inorg. Chem.*, **13**, 2062 (1974).
(21) L. E. Sutton, *Chem. Soc., Spec. Publ.*, **No. 18** (1965).
(22) M. R. Churchill and K. L. Kalra, *Inorg. Chem.*, **12**, 1650 (1973).
(23) G. K. Wertheim and R. H. Herber, *J. Chem. Phys.*, **38**, 2106 (1963).
(24) R. A. Stukan, S. P. Gubin, A. N. Nesmeyanov, V. I. Gol'danskii, and E. F. Makarov, *Teor. Eksp. Khim.*, **2**, 805 (1966).
(25) E. M. Shustorovich and M. E. Dyatkina, *Dokl. Akad. Nauk SSSR*, **128**, 1234 (1959).
(26) J. P. Dahl and C. J. Ballhausen, *K. Dan. Vidensk. Selsk., Mat.-Fys. Medd.*, **33**, No. 5 (1961).
(27) R. L. Collins, *J. Chem. Phys.*, **42**, 1072 (1965).
(28) Data taken in M. L. Good's laboratory at the University of New Orleans. A large collection of Mössbauer data for iron sandwich complexes is given in M. L. Good, J. Buttone, and D. Foyt, *Ann. N.Y. Acad. Sci.*, **239**, 193 (1974).
(29) J. Dunitz, L. E. Orgel, and A. Rich, *Acta Crystallogr.*, **9**, 373 (1956).
(30) R. K. Bohn and A. Haaland, *J. Organomet. Chem.*, **5**, 470 (1966).
(31) A. Haaland and J. Nilsson, *Chem. Commun.*, 88 (1968).
(32) G. J. Palenik, *Inorg. Chem.*, **8**, 2744 (1969).
(33) J. Trotter and A. C. McDonald, *Acta Crystallogr.*, **21**, 359 (1966).