# The Crystal and Molecular Structure of N-Formylaminomethylferrocene, [(C₅H₅)Fe(C₅H₄)]CH₂NHCHO*

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The crystal structure of N-formylaminomethylferrocene, [(C₅H₅)Fe(C₅H₄)]CH₂NHCHO, was determined by X-ray analysis based on data recorded with an automatic diffractometer and niobium-filtered Mo radiation. The space group is $P2_1/c$, with $a=8\cdot9161$ (7), $b=14\cdot3329$ (6), $c=16\cdot6763$ (8) Å, $\beta=90\cdot758$ (6)°, $Z=8$. The final indices $R(F)$ and $R(F^2)$ are 0·052 and 0·041. The standard errors of bond lengths C–C, C–N, and C–O range from 0·003 to 0·005 Å. Some differences among the C–C bond lengths in the unsubstituted rings appear to be significant. Average bond lengths (with estimated standard deviations from the averages in brackets) are: Fe–C, 2·033 [7]; C–C, 1·414 [6] Å in substituted rings and 1·395 [15] Å in unsubstituted rings; C–CH₂, 1·497 [1]; CH₂–NH, 1·460 [5]; NH–CHO, 1·322 [9]; CH–O, 1·213 [3] Å. In each of the two molecules in the asymmetric unit the rings are nearly perfectly planar and the heavy atoms of the side chain are in a nearly plane configuration also; the rings are nearly in the totally eclipsed conformation. Two different N–H···O hydrogen bonds, both 2·90 Å in length, link the two distinct molecules in alternating head-to-tail fashion into infinite chains parallel to a.
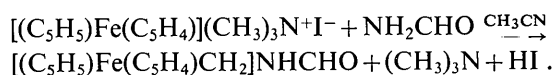
## Introduction

We have determined the crystal and molecular structure of N-formylaminomethylferrocene (FAMF) as a contribution to the growing body of structural data on metallocenes [for a recent review, see Wheatley (1967)]. In this particular ferrocene derivative the geometry of the amide side chain and the hydrogen bonding are structural features of interest in addition to those relating to the ferrocene moiety.

## Experimental

### Preparation

N-Formylaminomethylferrocene is prepared‡ (Freeman, 1966) in essentially 100% yield by the action of trimethyl)ferrocenylmethyl)ammonium iodide directly on formamide in acetonitrile:

[(C₅H₅)Fe(C₅H₄)](CH₃)₃N⁺I⁻ + NH₂CHO $\xrightarrow{\text{CH}_3\text{CN}}$

[(C₅H₅)Fe(C₅H₄)CH₂]NHCHO + (CH₃)₃N + HI .

The product is easily recrystallized from aqueous methanol, producing stout amber needles.

### Unit cell and space group

From preliminary X-ray precession films approximate unit-cell parameters were obtained, and the space

group $P2_1/c$ was indicated by the systematic extinction of reflections 0k0 for odd $k$ and h0l for odd $l$. Precise values of the unit-cell parameters, with standard errors,* were derived by the method of least squares from angle data recorded at about 23°C with the Oak Ridge automatic computer-controlled X-ray diffractometer (Busing, Ellison, Levy, King & Roseberry, 1968) for nine Cu $K\alpha_1$ reflections in the range 150–160° $2\theta$ (wavelength assumed to be 1·54051 Å): $a=8\cdot9161$ (7), $b=14\cdot3329$ (6), $c=16\cdot6763$ (8) Å, $\beta=90\cdot758$ (6)°. The reasonable value 1·516 g.cm⁻³ was calculated for the density on the assumption of eight molecules of FAMF per cell, or two molecules per asymmetric unit; the density was not experimentally determined.

### Reflection data

For intensity measurements a crystal specimen about 0·4 mm long was cut from a needle approximately 0·2 × 0·2 mm in cross section and mounted with the needle axis (crystal direction c) approximately parallel to the spindle axis of the automatic diffractometer. A total of 5500 intensity observations were recorded using niobium-filtered Mo $K\alpha$ radiation to the limit 51·5° in $2\theta$; these observations included some replicate and equivalent observations, as well as periodic observations of reference reflections. Measurements in the range 0° to 27° $2\theta$ were made with an ω-scan technique devised in this laboratory (Levy, 1966); measurements above 27° $2\theta$ were made with the $\theta$–$2\theta$ technique. Different scale-factor identifiers were assigned to the data

sets from the $\omega$ and $2\theta$ scans for subsequent use in least-squares adjustment of the scale factors.

Absorption corrections were applied using the calculated absorption coefficient 14·2 cm⁻¹; the range of correction factors was from 1·36 to 1·47. By averaging the data for equivalent and replicate reflections a set of structure-factor squares $F_o^2$ and statistical standard errors $\sigma_c(F_o^2)$ was derived for the 4089 independent reflections. Negative values of $F_o^2$ were replaced by zeros. The approximate scale factor on the $F_o^2$ data and the value 3·06 Å² for the over-all isotropic temperature factor were obtained by the method of Wilson (1942).

Details of procedure in the collection and processing of data not specifically mentioned here were nearly identical with those described in a recent paper from this laboratory (Brown, 1969), which also lists the computer programs used in this work.

## Solution and refinement

The solution for the structure was found by the heavy-atom method, with the iron atoms in the role of the heavy atoms. The identification of the Fe(1)–Fe(1) and Fe(2)–Fe(2) peaks in the Harker line and section of a three-dimensional sharpened Patterson map and of the peak Fe(1)–Fe(2) in the general part of the map established the coordinates of the two iron atoms, except for the ambiguity as to how to combine the two $y$ coordinates deduced with the two pairs of $x$ and $z$ coordinates. The ambiguity was resolved by structure-

### Table 1. *Parameters of the crystal structure of N-formylaminomethylferrocene*

The entries $X$, $Y$, and $Z$ are the fractional coordinates multiplied by $10^5$. For each non-hydrogen atom the entries $\beta_{ij}$ are the unique elements of the symmetric matrix $\beta$ in the anisotropic temperature factor exp $[-\mathbf{h}^T\beta\mathbf{h}]$, where $\mathbf{h}$ is the column matrix of reflection indices; for each hydrogen atom the entry $\beta_{11}$ is the parameter of the isotropic temperature factor exp $[-\beta_{11}\lambda^{-2}\sin^2\theta]$. The non-hydrogen atoms are designated as in the molecular drawings of Fig. 1. Atom H(2) is the hydrogen atom on C(2), H(1') is on C(1'), etc.

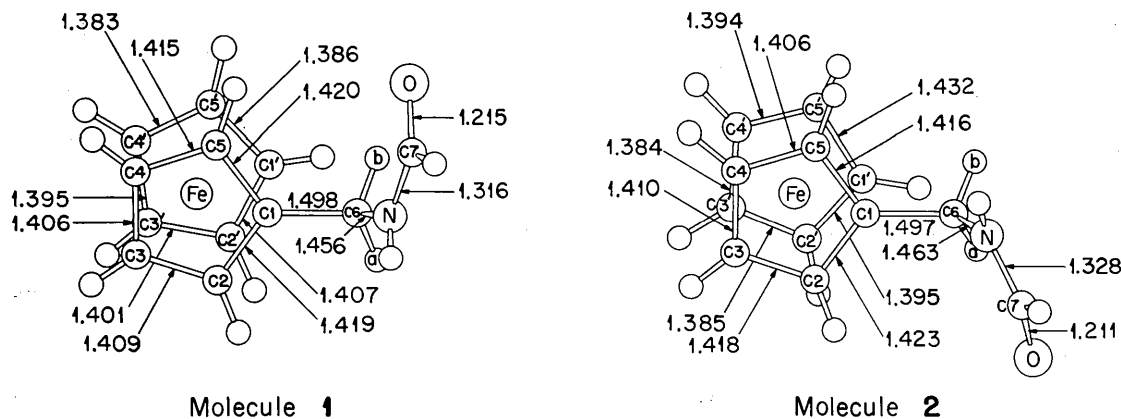| | | MOLECULE 1 | | | | | | | | | MOLECULE 2 | | | | | | | |
| ATOM | X | Y | Z | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ | X | Y | Z | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Fe | 50493(3) | 68590(2) | 43943(2) | 919(5) | 342(2) | 251(2) | -57(2) | -39(2) | -3(1) | 1256(3) | 88486(2) | 21109(2) | 927(5) | 464(2) | 233(2) | -9(2) | 93(2) | -12(1) |
| C(1) | 64946(22) | 76418(15) | 50621(12) | 810(27) | 366(12) | 264(8) | -102(16) | -22(12) | -4(9) | -13339(23) | 94311(16) | 28983(13) | 723(28) | 479(14) | 250(9) | -32(16) | 61(12) | -4(9) |
| C(2) | 72703(25) | 68960(17) | 46921(14) | 853(30) | 471(14) | 331(10) | 14(18) | 46(14) | -26(10) | -3472(25) | 88028(18) | 33026(14) | 902(31) | 542(15) | 243(9) | -2(18) | 85(14) | 44(10) |
| C(3) | 66310(28) | 60509(18) | 49515(15) | 1212(36) | 358(14) | 394(11) | 93(19) | -87(16) | -14(10) | -5199(30) | 79083(19) | 29506(16) | 1322(39) | 456(15) | 415(12) | 41(21) | 206(18) | 75(11) |
| C(4) | 54693(27) | 62650(17) | 54829(14) | 1230(36) | 419(14) | 304(10) | -165(19) | -54(15) | 77(10) | -16102(29) | 79800(20) | 23332(18) | 1270(39) | 526(17) | 468(13) | -225(21) | 189(18) | -112(12) |
| C(5) | 53868(25) | 72466(17) | 55656(13) | 931(31) | 438(14) | 265(9) | -65(16) | 36(14) | -3(9) | -21154(26) | 89084(20) | 23057(15) | 914(33) | 631(17) | 316(10) | -30(20) | -15(15) | -24(11) |
| C(1') | 39537(46) | 77204(26) | 36247(22) | 2971(78) | 500(20) | 505(16) | -12(32) | -699(30) | 87(15) | 13980(38) | 98613(23) | 16094(20) | 2128(58) | 568(20) | 469(14) | -173(28) | 548(24) | 62(14) |
| C(2') | 48435(38) | 70846(33) | 31992(17) | 1748(55) | 1373(36) | 248(11) | -470(37) | -106(19) | 125(16) | 23274(31) | 91867(24) | 19578(18) | 1105(39) | 789(22) | 395(12) | -118(24) | 209(18) | 41(14) |
| C(3') | 43463(36) | 61838(27) | 33848(18) | 1706(50) | 767(23) | 408(13) | 119(30) | -249(21) | -238(15) | 20230(36) | 83349(25) | 15987(21) | 1611(50) | 735(23) | 535(16) | 112(28) | 467(24) | -84(16) |
| C(4') | 31597(34) | 62822(23) | 39155(18) | 1509(46) | 646(21) | 470(14) | -340(26) | -318(21) | 44(14) | 9102(43) | 84559(32) | 10218(20) | 2055(61) | 1090(31) | 353(13) | -180(37) | 351(23) | -210(17) |
| C(5') | 29201(33) | 72192(26) | 40648(19) | 1315(44) | 916(26) | 410(13) | 285(28) | -233(20) | -88(15) | 4996(40) | 93940(34) | 10153(19) | 1723(55) | 1253(36) | 297(13) | 143(37) | 149(21) | 260(18) |
| C(6) | 67965(29) | 86596(17) | 49389(15) | 1078(35) | 388(14) | 362(11) | -100(18) | 22(16) | 8(10) | -15173(27) | 104515(17) | 30601(15) | 945(34) | 479(15) | 313(10) | 25(18) | 0(15) | 15(10) |
| C(7) | 71344(29) | 94956(18) | 62034(17) | 939(36) | 507(16) | 496(13) | -107(20) | -74(18) | -101(12) | -21782(27) | 109312(16) | 44266(16) | 1023(35) | 402(14) | 373(11) | 104(18) | 149(16) | -20(10) |
| N | 77050(22) | 90589(14) | 55842(13) | 626(26) | 428(12) | 479(11) | -90(15) | 25(13) | -61(9) | -25842(22) | 106397(14) | 36995(13) | 733(27) | 448(12) | 396(10) | 22(15) | 16(13) | -63(9) |
| O | 58102(19) | 96382(15) | 63151(12) | 858(26) | 997(15) | 667(11) | 9(16) | 100(13) | -288(11) | -9111(18) | 11053(13) | 46512(10) | 889(32) | 819(13) | 394(8) | 17(15) | -48(10) | -115(8) |
| H(2) | 8067(24) | 6991(15) | 4323(13) | 3.8(5) | | | | | | 279(25) | 8980(15) | 3731(14) | 4.0(5) | | | | | |
| H(3) | 6894(24) | 5445(17) | 4796(13) | 4.1(6) | | | | | | 133(24) | 7391(17) | 3112(14) | 4.7(6) | | | | | |
| H(4) | 4877(23) | 5849(16) | 5746(13) | 3.5(5) | | | | | | -1941(26) | 7478(19) | 1976(15) | 5.8(7) | | | | | |
| H(5) | 4661(21) | 7601(15) | 5874(13) | 3.3(5) | | | | | | -2779(26) | 9180(17) | 1937(14) | 4.6(6) | | | | | |
| H(1') | 4031(32) | 8371(23) | 3600(17) | 7.2(9) | | | | | | 1348(29) | 10499(20) | 1809(16) | 6.0(7) | | | | | |
| H(2') | 5656(33) | 7226(22) | 2878(19) | 8.2(9) | | | | | | 3096(28) | 9272(18) | 2376(15) | 5.3(7) | | | | | |
| H(3') | 4695(31) | 5620(22) | 3197(18) | 7.1(9) | | | | | | 2425(35) | 7733(25) | 1753(20) | 9.3(1,1) | | | | | |
| H(4') | 2597(30) | 5766(20) | 4120(16) | 6.3(8) | | | | | | 310(36) | 8012(26) | 680(21) | 10.1(1,1) | | | | | |
| H(5') | 2168(29) | 7507(20) | 4416(17) | 7.0(8) | | | | | | -125(31) | 9700(22) | 748(17) | 6.5(9) | | | | | |
| H(6a) | 7313(25) | 8751(15) | 4418(14) | 4.2(5) | | | | | | -493(25) | 10752(15) | 3193(13) | 4.0(5) | | | | | |
| H(6b) | 5864(23) | 9024(14) | 4906(12) | 2.8(5) | | | | | | -1889(24) | 10783(16) | 2570(14) | 4.3(6) | | | | | |
| H(7) | 7901(24) | 9717(14) | 6605(13) | 3.4(5) | | | | | | -3025(25) | 10994(15) | 4798(14) | 4.1(5) | | | | | |
| H(N) | 8584(25) | 8990(15) | 5591(13) | 3.1(5) | | | | | | -3488(28) | 10512(18) | 3587(15) | 4.8(6) | | | | | |

Molecule 1

Molecule 2

Fig. 1. Views of the two crystallographically independent molecules of *N*-formylaminomethylferrocene, showing lengths (Å) of bonds between C, N and O atoms. The view direction in each case is 11·5° from the normal to the substituted ring S.

Table 2. *Observed and calculated structure factors for N-formylaminomethylferrocene*

For each reflection, identified by the indices $H$ and $K$ of a subheading and the running index $L$, the values of $F_o \times 10$ and $F_c \times 10$ are given (OBS and CAL). The standard error ($\times 10$) of $F_o$ (see text) is given under the heading SG, except that for each reflection marked $W$, for which $F_o^2 \le \sigma(F_o^2)$, the standard error ($\times 1$) of $F_o^2$ is given instead. The three reflections marked $X$ were omitted in the final refinement cycles because they appear to show extinction error.

factor calculations including only the iron atoms; the combination yielding a discrepancy index $R(F) = 0.40$ was chosen over the one yielding $R(F) = 0.47$. A Fourier map with coefficients phased by the iron atoms and weighted by the Woolfson (1956) method showed the positions of all of the other atoms except the hydrogen atoms. After several cycles of least-squares refinement all 26 hydrogen atoms of the asymmetric unit were

Table 2 (*cont.*)

[Table of observed and calculated structure factors, with columns L, OBS, CAL, SG repeated across the page.]

Table 2 (*cont.*)

| L | OBS | CAL | SG | L | OBS | CAL | SG | L | OBS | CAL | SG | L | OBS | CAL | SG |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *** | 8 | 3 L | *** | 9W | 23 | 34 | 19 | 6W | 33 | -47 | 20 | 5 | 72 | -83 | 16 |
| 1 | 219 | -216 | 6 | 10W | 0 | -20 | 19 | 7W | 13 | -32 | 21 | 6W | 0 | -3 | 21 |
| 2W | 27 | -13 | 17 | 11 | 133 | -123 | 9 | 8 | 191 | -195 | 8 | 7 | 74 | 59 | 15 |
| 3 | 204 | -195 | 7 | 12 | 72 | 70 | 16 | 9 | 67 | 54 | 16 | 8 | 196 | 194 | 8 |
| 4 | 100 | 102 | 10 | *** | 8 | 5 L | *** | 10 | 140 | -151 | 10 | 9W | 0 | 9 | 23 |
| 5 | 51 | -26 | 16 | 1 | 372 | 377 | 7 | 11W | 31 | 28 | 21 | 10 | 156 | 156 | 9 |
| 6 | 142 | 141 | 8 | 2 | 99 | 102 | 10 | *** | 8 | 7 L | *** | *** | 8 | 9 L | *** |
| 7 | 368 | 374 | 8 | 3 | 62 | 61 | 15 | 1 | 71 | -74 | 14 | 1 | 205 | -200 | 7 |
| 8 | 62 | -56 | 16 | 4 | 165 | 164 | 7 | 2 | 210 | -202 | 7 | 2 | 86 | 74 | 13 |
| 9 | 118 | 99 | 8 | 5W | 24 | -49 | 20 | 3W | 20 | 45 | 19 | 3 | 124 | -129 | 10 |
| 10 | 88 | 71 | 12 | 6 | 71 | 86 | 14 | 4 | 166 | -163 | 8 | 4 | 209 | 221 | 8 |
| 11 | 195 | 189 | 8 | 7 | 89 | -89 | 11 | 5W | 0 | 3 | 20 | 5 | 54 | 57 | 19 |
| 12 | 130 | -119 | 9 | 8 | 101 | 104 | 11 | 6 | 272 | -259 | 7 | 6 | 172 | 182 | 8 |
| 13 | 70 | -55 | 16 | 9 | 316 | -307 | 7 | 7W | 24 | 41 | 20 | 7 | 113 | -113 | 11 |
| *** | 8 | 4 L | *** | 10 | 100 | -85 | 11 | 8W | 41 | -25 | 20 | 8W | 0 | -3 | 21 |
| 1 | 259 | 250 | 6 | 11W | 38 | -4 | 19 | 9 | 151 | 154 | 8 | *** | 8 | 10 L | *** |
| 2 | 270 | 273 | 7 | 12W | 0 | -1 | 21 | 10 | 66 | -60 | 16 | 1 | 189 | 204 | 9 |
| 3 | 88 | 89 | 10 | *** | 8 | 6 L | *** | 11W | 31 | -52 | 24 | 2W | 29 | 30 | 21 |
| 4 | 199 | -203 | 7 | 1 | 281 | -279 | 7 | *** | 8 | 8 L | *** | 3W | 33 | 19 | 20 |
| 5 | 326 | 320 | 7 | 2 | 271 | 270 | 7 | 1 | 81 | -66 | 13 | 4 | 57 | 58 | 19 |
| 6 | 123 | 118 | 9 | 3 | 60 | 11 | 14 | 2 | 382 | -380 | 8 | 5 | 157 | 148 | 8 |
| 7 | 294 | 292 | 7 | 4 | 57 | -8 | 16 | 3 | 89 | 58 | 11 | 6 | 59 | -50 | 18 |
| 8W | 42 | -50 | 22 | 5 | 422 | -421 | 8 | 4 | 78 | 97 | 15 | 7 | 71 | -42 | 15 |

| L | OBS | CAL | SG | L | OBS | CAL | SG | L | OBS | CAL | SG | L | OBS | CAL | SG |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *** | 8 | 11 L | *** | 11W | 28 | -12 | 22 | 10 | 118 | 122 | 11 | *** | 9 | 6 L | *** |
| 1 | 154 | 168 | 9 | *** | 9 | 2 L | *** | *** | 9 | 4 L | *** | 1 | 134 | -137 | 9 |
| 2 | 99 | -66 | 11 | 1 | 192 | 198 | 7 | 1 | 92 | 94 | 12 | 2 | 103 | -97 | 11 |
| 3 | 85 | 109 | 15 | 2W | 0 | -40 | 19 | 2 | 142 | 129 | 8 | 3 | 377 | 381 | 8 |
| 4 | 113 | -118 | 11 | 3 | 114 | -105 | 10 | 3 | 270 | -264 | 7 | 4 | 255 | -266 | 8 |
| 5W | 43 | -24 | 21 | 4 | 197 | 190 | 7 | 4 | 254 | -249 | 7 | 5W | 0 | 10 | 21 |
| *** | 9 | 0 L | *** | 5 | 373 | 375 | 8 | 5 | 204 | -193 | 7 | 6W | 34 | 43 | 23 |
| 2 | 406 | -403 | 8 | 6 | 69 | -97 | 17 | 6 | 128 | 128 | 10 | 7 | 171 | 178 | 8 |
| 4 | 409 | 410 | 8 | 7 | 92 | -84 | 11 | 7 | 282 | -290 | 7 | 8 | 89 | 96 | 14 |
| 6 | 96 | 86 | 12 | 8 | 138 | -149 | 9 | 8 | 51 | -56 | 22 | *** | 9 | 7 L | *** |
| 8 | 254 | 273 | 7 | 9W | 0 | -25 | 20 | 9W | 44 | -24 | 20 | 1 | 59 | 0 | 18 |
| 10 | 90 | 91 | 13 | 10 | 144 | -147 | 9 | 10 | 64 | -50 | 16 | 2 | 112 | 112 | 10 |
| *** | 9 | 1 L | *** | 11W | 0 | 4 | 22 | *** | 9 | 5 L | *** | 3 | 86 | 71 | 13 |
| 1 | 68 | -79 | 15 | *** | 9 | 3 L | *** | 1 | 82 | -63 | 13 | 4 | 125 | 119 | 10 |
| 2 | 58 | 56 | 15 | 1 | 325 | 322 | 7 | 2 | 90 | -93 | 12 | 5 | 64 | 12 | 16 |
| 3 | 185 | -174 | 7 | 2 | 116 | -119 | 10 | 3W | 29 | -43 | 22 | 6W | 44 | 33 | 21 |
| 4 | 190 | 197 | 7 | 3 | 205 | 199 | 7 | 4 | 180 | -177 | 8 | 7 | 112 | -101 | 11 |
| 5W | 0 | -11 | 20 | 4 | 59 | -103 | 20 | 5 | 90 | -41 | 11 | *** | 9 | 8 L | *** |
| 6 | 358 | 361 | 8 | 5W | 42 | -35 | 20 | 6 | 91 | -82 | 12 | 1 | 121 | -107 | 9 |
| 7 | 52 | -29 | 19 | 6 | 126 | 127 | 10 | 7 | 190 | 184 | 8 | 2 | 121 | 112 | 10 |
| 8W | 0 | 27 | 20 | 7 | 68 | -79 | 16 | 8W | 29 | 38 | 22 | 3 | 131 | 114 | 9 |
| 9 | 209 | 202 | 7 | 8W | 0 | -27 | 22 | 9W | 0 | -15 | 22 | 4 | 218 | 209 | 8 |
| 10W | 41 | 35 | 19 | 9 | 203 | -187 | 7 |  |  |  |  | 5 | 86 | -41 | 12 |

| L | OBS | CAL | SG | L | OBS | CAL | SG | L | OBS | CAL | SG | L | OBS | CAL | SG | L | OBS | CAL | SG |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 6 | 91 | -78 | 12 | 2W | 0 | -42 | 23 | 2 | 73 | -45 | 14 | *** | -10 | 4 L | *** | 0 | 99 | 91 | 8 |
| *** | 9 | 9 L | *** | 1 | 114 | 126 | 10 | 3 | 299 | -295 | 8 | 7 | 52 | 55 | 22 | *** | 10 | 5 L | *** |
| 1 | 80 | -64 | 14 | 0 | 97 | -100 | 8 | 4 | 67 | 64 | 16 | 6 | 85 | -65 | 13 | 1 | 190 | 192 | 8 |
| 2 | 128 | -112 | 10 | *** | 10 | 1 L | *** | 5W | 0 | 8 | 21 | 5 | 103 | 110 | 13 | 2W | 25 | 25 | 22 |
| 3W | 0 | 31 | 25 | 1W | 0 | -27 | 21 | 6W | 37 | 5 | 21 | 4W | 19 | 10 | 22 | 3 | 156 | 153 | 9 |
| 4 | 134 | -124 | 10 | 2 | 115 | -116 | 9 | 7 | 178 | -175 | 8 | 3 | 216 | 206 | 8 | 4 | 94 | 101 | 13 |
| *** | -10 | 0 L | *** | 3 | 50 | -65 | 21 | *** | -10 | 3 L | *** | 2 | 66 | 53 | 18 | 5 | 58 | 25 | 19 |
| 8 | 261 | -254 | 8 | 4 | 211 | -213 | 7 | 7 | 149 | 149 | 9 | 1 | 139 | 139 | 10 | *** | -10 | 6 L | *** |
| 6W | 0 | -9 | 21 | 5 | 65 | 66 | 17 | 6 | 178 | 170 | 8 | 0 | 161 | -162 | 6 | 4W | 8 | -21 | 23 |
| 4 | 189 | -204 | 8 | 6 | 88 | -89 | 12 | 5 | 51 | -13 | 19 | *** | 10 | 4 L | *** | 3W | 32 | -41 | 24 |
| 2 | 81 | 43 | 13 | 7 | 168 | -163 | 9 | 4W | 0 | 10 | 23 | 1 | 70 | 78 | 16 | 2 | 55 | 65 | 21 |
| 0 | 183 | 187 | 6 | *** | -10 | 2 L | *** | 3 | 145 | 163 | 10 | 2 | 95 | 92 | 12 | 1 | 158 | -140 | 8 |
| *** | 10 | 0 L | *** | 8 | 69 | 91 | 18 | 2 | 211 | 218 | 8 | 3W | 0 | -9 | 21 | 0 | 123 | 137 | 11 |
| 2W | 0 | 30 | 26 | 7 | 79 | 63 | 14 | 1 | 166 | -170 | 9 | 4 | 240 | -245 | 7 | *** | 10 | 6 L | *** |
| 4 | 201 | 218 | 8 | 6 | 133 | 120 | 9 | 0 | 57 | 32 | 12 | 5 | 185 | 192 | 8 | 1 | 169 | -162 | 9 |
| 6 | 279 | -262 | 7 | 5 | 254 | -257 | 7 | *** | 10 | 3 L | *** | 6 | 102 | 72 | 11 | 2 | 172 | 173 | 9 |
| *** | -10 | 1 L | *** | 4 | 84 | 65 | 13 | 1 | 131 | -115 | 9 | *** | -10 | 5 L | *** | 3 | 82 | 68 | 14 |
| 8 | 66 | 18 | 16 | 3 | 143 | -128 | 9 | 2W | 0 | -23 | 21 | 6W | 40 | -35 | 23 | 4W | 28 | -14 | 22 |
| 7 | 138 | -142 | 9 | 2 | 72 | -45 | 15 | 3 | 111 | -76 | 9 | 5 | 178 | -178 | 8 | *** | -10 | 7 L | *** |
| 6 | 59 | 45 | 17 | 1 | 91 | -107 | 13 | 4 | 48 | -10 | 22 | 4 | 135 | 103 | 9 | 1W | 38 | -56 | 25 |
| 5 | 98 | 85 | 11 | 0 | 98 | -99 | 8 | 5 | 75 | 43 | 14 | 3 | 156 | 163 | 10 | 0W | 28 | 1 | 24 |
| 4 | 314 | -306 | 7 | *** | 10 | 2 L | *** | 6 | 115 | 124 | 12 | 2 | 84 | -94 | 15 |  |  |  |  |
| 3 | 153 | -159 | 9 | 1 | 206 | 208 | 8 | 7 | 127 | 121 | 11 | 1 | 75 | 85 | 16 |  |  |  |  |

located in a difference map; their coordinates and isotropic thermal parameters were then refined along with the coordinates and anisotropic thermal parameters of the heavy atoms and the two scale factors. The full-matrix least-squares method was used with the quantities $F_o^2$ as observations, and the weighting scheme was the one usually employed in this laboratory:

$$\sigma^2(F_o^2)=\sigma_c^2(F_o^2)+(0{\cdot}03\ F_o^2)^2$$
$$w\,(F_o^2)=1/\sigma^2(F_o^2)\,.$$

The correction term $(0{\cdot}03\ F_o^2)^2$ is added to the purely statistical variance $\sigma_c^2(F_o^2)$ to make some allowance for deficiencies in the model and for instability in the generator and counter circuitry (Peterson & Levy, 1957). The three reflections of highest intensity, apparently affected by extinction, were given zero weights. For 3512 of the total 4089 reflections $F_o^2$ was greater than the corresponding $\sigma(F_o^2)$, and for 3182 reflections $F_o^2$ was greater than $2\sigma(F_o^2)$. The full-matrix refinement converged with the following values of the usual measures of goodness of fit:* $R(F)=0{\cdot}052$, $R(F^2)=0{\cdot}041$, $R_w(F^2)=0{\cdot}066$, $\sigma_1=1{\cdot}18$. For the hydrogen and non-hydrogen parameters, respectively, the most significant shifts were only one tenth and one sixth of the corresponding standard errors.

The scattering factors used for the hydrogen atoms were from Table 2 of Stewart, Davidson & Simpson (1965); those for the other atoms were from the compilation of Ibers (1962). The constant $\Delta f'=0{\cdot}4$ (Templeton, 1962) was used to correct the scattering factor of iron for anomalous dispersion.†

The final positional and thermal parameters are listed in Table 1. The observed and calculated structure factors are given in Table 2. The standard error $\sigma(F_o)$, computed as $\sigma(F_o^2)/2F_o$, is given for each reflection for which $F_o^2>\sigma(F_o^2)$; the error $\sigma(F_o^2)$ is given for each reflection for which $F_o^2\le\sigma(F_o^2)$. The value of $F(000)$ is 1008.

## Discussion

The general conformations of the two molecules are shown in Fig. 1, which also shows the bond lengths C–C, C–N, and C–O. Table 3 shows all of the various kinds of intramolecular distances and angles with their standard errors computed from the least-squares covariance matrix; it also shows averages for most of the molecular parameters which might be expected to be the same, or nearly the same, in the isolated FAMF molecule. The number in square brackets associated with each average specifies the standard error $\sigma_{\rm int}$ of an individual bond length or angle estimated from the internal consistency in the group averaged.*

The average C–C distances are not significantly different from those found in other ferrocene derivatives (Laing & Trueblood, 1965; Wheatley, 1967). There are rather striking variations, however, among the apparent C–C bond lengths of the unsubstituted rings (rings *U*). The extreme difference in bond lengths around ring *U* of molecule **2** is from 1·3838 (47) to 1·4320 (47) Å, or about 7·3 times the standard error of the difference ($\sigma_d$). For ring *U* of molecule **1** the range of lengths is from 1·3830 (42) Å to 1·4065 (48) Å, about 3·7 $\sigma_d$. Between the two rings *U* the largest difference, between lengths C(4')–C(5') in **1** and C(5')–C(1') in **2**, equals 7·8 $\sigma_d$. Since the conformations of the rings are not greatly different (see below), we may identify pairs of corresponding bonds between molecules **1** and **2**. The within-pair difference for the rings *U* is largest for bond C(5')–C(1'), amounting to 6·2 $\sigma_d$.

Among crystallographers a difference of $3\sigma_d$ between two bond lengths or angles has often been taken as the minimum difference to be considered signifi-

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* The discrepancy indices $R(F^k)$ are defined by the equation $R(F^k)\equiv\Sigma\|F_o{}^k|-S^k|F_c{}^k\|/\Sigma|F_o{}^k|$, and the index $R_w(F^2)$ is defined by $R_w(F^2)\equiv[\Sigma w(F_o{}^2-S^2F_c{}^2)^2/\Sigma wF_o{}^4]^{1/2}$, where $S$ is the scale factor on $F_c$. The quantity $\sigma_1$ is the standard deviation of an observation of unit weight, defined by the equation $\sigma_1\equiv[\Sigma w(F_o{}^2-S^2F_c{}^2)^2/(n-p)]^{1/2}$, where $w$ is the weight of an observation $F_o{}^2$, $n$ is the total number of observations, and $p$ is the number of parameters fitted to the data. Unit value is expected for $\sigma_1$ at convergence when the observational errors are randomly distributed and correctly estimated and the model is correct. The measures of goodness of fit quoted above include contributions from all of the reflections except the three given zero weights. Since some workers exclude as unobserved those reflections for which $F_o{}^2$ is less than $\sigma(F_o{}^2)$ or less than $2\sigma(F_o{}^2)$, it is appropriate for purposes of comparison to note that our $R(F)$ values calculated with such exclusions are 0·039 and 0·033, respectively.

† The constant $\Delta f''=1{\cdot}0$ should also have been included in the structure-factor calculations, but it was omitted, unfortunately.

* For example, if $n$ individual bond lengths $L_i$ average to $L$, then

$$\sigma_{\rm int}=[\sum_{i=1}^{n}(L-L_i)^2/(n-1)]^{1/2}.$$

cant.* Somewhat arbitrarily, but in keeping generally with what we believe to be a consensus among crystallographers that least-squares estimates of standard errors are usually unrealistically low because of systematic errors (Hamilton, 1965, 1969; Harker, 1965; Zachariasen, 1969), we prefer to take $6\sigma_d$ as the minimum difference to be considered significant. We would then conclude that there is apparently a significant difference between the bond lengths C(5')–C(1') of the

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* In applying this criterion one is actually applying Student's *t* test and taking the probability $P = 0.0025$ as the significance point. Strictly, the *t* test is not properly used in this manner (see Hamilton, 1964, 1969).

two rings *U*, though we ignore the other variations. We also ignore the variations among the bond lengths of the rings *S*, noting that the extreme value of these variations is $3.6\ \sigma_d$.

The atoms of the unsubstituted rings show more thermal motion than those of the substituted rings, as is shown in Table 4 and in the stereoscopic drawings of Fig. 2, which shows the 50% probability thermal ellipsoids (Johnson, 1965). The greater motion is probably the reason that the average C–C bond in the unsubstituted rings appears to be slightly shorter than the average for the other rings. However, there is no reason to suppose that correction of the bond lengths in the rings *U*, if it were possible,

Table 3. *Intramolecular distances* (Å) *and valence angles* (degrees), *both uncorrected for effects of thermal motion*

The full least-squares covariance matrix was used in calculating the standard errors appearing in the parentheses. The bracketed numbers next to the averages specify the estimated standard deviations from the averages. Rings *S* and *U* are the substituted and unsubstituted cyclopentadienyl rings, respectively. The key to the system of atomic designations is contained in Fig. 1 and the caption of Table 1.

DISTANCES (Å)

| | MOLECULE 1 | | MOLECULE 2 | |
|---|---|---|---|---|
| | RING S | RING U | RING S | RING U |
| C(1)–C(2) | 1.4188(30) | 1.4065(48) | 1.4225(30) | 1.3951(41) |
| C(2)–C(3) | 1.4092(33) | 1.4010(47) | 1.4176(34) | 1.3850(42) |
| C(3)–C(4) | 1.4059(34) | 1.3954(43) | 1.4103(36) | 1.3838(46) |
| C(4)–C(5) | 1.4153(33) | 1.3830(42) | 1.4055(37) | 1.3935(50) |
| C(5)–C(1) | 1.4204(28) | 1.3853(44) | 1.4160(31) | 1.4320(47) |
| AVERAGES | 1.4139[62] | 1.3944[98] | 1.4144[66] | 1.3979[197] |
| | 1.4141[60] | | | 1.3962[148] |
| | | 1.4052[206] | | |
| C(1)–H(1) | | 0.936(31) | | 0.974(27) |
| C(2)–H(2) | 0.956(22) | 0.929(30) | 0.935(22) | 0.979(25) |
| C(3)–H(3) | 0.937(23) | 0.922(30) | 0.978(23) | 0.968(34) |
| C(4)–H(4) | 0.913(21) | 0.959(27) | 0.976(27) | 1.003(35) |
| C(5)–H(5) | 0.977(21) | 0.987(28) | 0.933(23) | 0.834(27) |
| AVERAGES | 0.946[27] | 0.947[27] | 0.956[26] | 0.952[66] |
| | 0.946[21] | | 0.954[50] | |
| | | 0.950[39] | | |
| C(1)–C(6) | 1.4981(31) | | 1.4967(32) | |
| C(6)–N | 1.4556(30) | | 1.4633(29) | |
| C(6)–H(6a) | 0.997(23) | | 1.032(22) | |
| C(6)–H(6b) | 0.983(20) | | 0.999(23) | |
| N–C(7) | 1.3156(32) | | 1.3282(30) | |
| N–H(N) | 0.790(21) | | 0.845(24) | |
| C(7)–O | 1.2150(28) | | 1.2115(27) | |
| C(7)–H(7) | 1.002(22) | | 0.987(22) | |
| Fe–C(1) | 2.0301(20) | 2.0229(29) | 2.0394(21) | 2.0295(27) |
| Fe–C(2) | 2.0358(22) | 2.0251(27) | 2.0379(23) | 2.0413(26) |
| Fe–C(3) | 2.094(24) | 2.0337(28) | 2.0321(25) | 2.0425(28) |
| Fe–C(4) | 2.0354(24) | 2.0308(28) | 2.0243(25) | 2.0344(29) |
| Fe–C(5) | 2.0459(22) | 2.0359(27) | 2.0304(23) | 2.0190(29) |
| AVERAGES | 2.0373[58] | 2.0297[55] | 2.0328[61] | 2.0333[96] |
| | 2.0335[67] | | 2.0331[76] | |
| | | 2.0333[70] | | |
| C(1)–C(1) | 3.2783(34) | | 3.3274(33) | |
| C(2)–C(2) | 3.2880(35) | | 3.3406(32) | |
| C(3)–C(3) | 3.2971(36) | | 3.2759(36) | |
| C(4)–C(4) | 3.3062(35) | | 3.2293(39) | |
| C(5)–C(5) | 3.3077(33) | | 3.2686(37) | |
| AVERAGES | 3.2955 | | 3.2884 | |
| | | 3.2920 | | |

ANGLES (DEGREES)

| | MOLECULE 1 | | MOLECULE 2 | |
|---|---|---|---|---|
| | RING S | RING U | RING S | RING U |
| C(5)–C(1)–C(2) | 107.60(20) | 108.34(32) | 106.94(21) | 106.72(32) |
| C(1)–C(2)–C(3) | 108.22(21) | 107.66(30) | 108.25(22) | 108.60(31) |
| C(2)–C(3)–C(4) | 108.07(22) | 106.96(31) | 107.84(24) | 108.95(35) |
| C(3)–C(4)–C(5) | 108.45(22) | 109.42(31) | 108.08(24) | 108.19(35) |
| C(4)–C(5)–C(1) | 107.64(21) | 107.61(31) | 108.88(23) | 107.55(33) |
| AVERAGES | 108.00[37] | 108.00[93] | 108.00[71] | 108.00[89] |
| | | 108.00[69] | | |
| C(5)–C(1)–C(6) | 126.63(21) | | 126.08(22) | |
| C(5)–C(1)–H(1) | | 126.1(2.0) | | 130.4(1.7) |
| C(2)–C(1)–C(6) | 125.77(21) | | 126.98(21) | |
| C(2)–C(1)–H(1) | | 125.5(2.0) | | 122.5(1.7) |
| C(1)–C(2)–H(2) | 122.9(1.4) | 126.8(2.1) | 123.3(1.4) | 128.0(1.6) |
| C(3)–C(2)–H(2) | 128.9(1.4) | 125.4(2.1) | 128.4(1.4) | 123.3(1.6) |
| C(2)–C(3)–H(3) | 127.4(1.4) | 128.6(1.9) | 120.7(1.4) | 127.0(2.1) |
| C(4)–C(3)–H(3) | 124.5(1.4) | 124.5(1.9) | 131.2(1.4) | 123.8(2.1) |
| C(3)–C(4)–H(4) | 126.6(1.4) | 123.5(1.7) | 126.2(1.5) | 133.4(2.1) |
| C(5)–C(4)–H(4) | 124.9(1.4) | 127.0(1.7) | 125.7(1.5) | 118.0(2.1) |
| C(4)–C(5)–H(5) | 127.1(1.2) | 128.4(1.7) | 128.1(1.6) | 133.3(2.2) |
| C(1)–C(5)–H(5) | 125.1(1.3) | 124.0(1.7) | 122.7(1.6) | 119.1(2.2) |
| AVERAGES | 126.0[1.8] | 126.0[1.4] | 125.9[3.3] | 125.9[5.2] |
| | | 126.0[3.3] | | |
| C(1)–C(6)–N | 112.38(20) | | 112.65(20) | |
| C(1)–C(6)–H(6a) | 109.4(1.3) | | 110.4(1.2) | |
| C(1)–C(6)–H(6b) | 111.8(1.2) | | 110.6(1.3) | |
| N–C(6)–H(6a) | 109.5(1.3) | | 110.4(1.3) | |
| N–C(6)–H(6b) | 107.1(1.2) | | 107.3(1.3) | |
| H(6a)–C(6)–H(6b) | 106.4(1.7) | | 105.1(1.8) | |
| C(6)–N–C(7) | 123.38(22) | | 123.45(21) | |
| C(6)–N–H(N) | 120.2(1.6) | | 115.2(1.7) | |
| C(7)–N–H(N) | 116.3(1.6) | | 121.2(1.7) | |
| N–C(7)–O | 125.94(26) | | 126.07(23) | |
| N–C(7)–H(7) | 114.0(1.2) | | 113.6(1.3) | |
| O–C(7)–H(7) | 120.0(1.2) | | 120.3(1.3) | |

would alter the pattern of bond-length variations appreciably.

Table 4. *Atomic root-mean-square displacements*
(Å, × 1000) *in principal-axis directions*

ROOT–MEAN–SQUARE DISPLACEMENTS

| ATOM | MOLECULE 1 P.A. 1 | P.A. 2 | P.A. 3 | MOLECULE 2 P.A. 1 | P.A. 2 | P.A. 3 |
|---|---|---|---|---|---|---|
| Fe | 176(1) | 189(1) | 203(1) | 168(1) | 204(1) | 221(1) |
| C(1) | 167(3) | 194(3) | 207(3) | 164(3) | 193(3) | 234(3) |
| C(2) | 183(3) | 213(3) | 226(4) | 169(3) | 201(3) | 240(3) |
| C(3) | 186(4) | 214(4) | 247(3) | 196(4) | 216(4) | 271(4) |
| C(4) | 180(4) | 203(3) | 250(3) | 195(4) | 218(4) | 293(4) |
| C(5) | 185(3) | 196(3) | 218(3) | 191(4) | 211(3) | 257(4) |
| C(1') | 182(4) | 235(5) | 394(5) | 169(4) | 254(4) | 342(4) |
| C(2') | 180(4) | 244(4) | 396(5) | 179(4) | 257(4) | 290(4) |
| C(3') | 183(4) | 255(4) | 329(5) | 178(4) | 282(4) | 323(5) |
| C(4') | 182(4) | 248(4) | 317(4) | 178(4) | 288(5) | 362(5) |
| C(5') | 190(4) | 249(4) | 329(4) | 174(5) | 262(4) | 377(5) |
| C(6) | 187(4) | 220(4) | 226(3) | 194(4) | 209(3) | 225(4) |
| C(7) | 179(4) | 228(4) | 277(4) | 174(4) | 215(4) | 243(3) |
| N | 154(3) | 209(3) | 264(3) | 171(3) | 206(3) | 245(3) |
| O | 182(3) | 254(3) | 366(3) | 187(3) | 225(2) | 301(2) |

In diferrocenyl ketone (Trotter & Macdonald, 1966), in α-keto-1,5-tetramethyleneferrocene (Fleischer & Hawkinson, 1967), and in ferrocene itself (Dunitz, Orgel & Rich, 1956) such apparent differences as were observed in the ring bonds were not considered significant. In contrast, Macdonald & Trotter (1964) considered significant the apparent differences of 0·1 Å (2·3 σd) which they found among C–C bond lengths in both the substituted and unsubstituted rings of biferrocenyl. However, since their structure was not a

highly refined one [R(F) = 1·16, calculated with isotropic thermal parameters and without hydrogen atoms], it is questionable to regard these differences as significant.

Wheatley (1967) has discussed critically the correlations of 'possible' distortions in unsubstituted cyclopentadienyl rings that has been attempted by R. Mason and co-workers (Bennett, Churchill, Gerloch & Mason, 1964; see Wheatley (1967) for additional references to specific compounds) for a number of π-complexes with transition elements. Wheatley concludes that the correlation is not convincingly successful. We judge that the variations in apparent bond lengths involved give at best no more than a marginal indication of significance, such as we have ignored for the bonds of the substituted rings in FAMF.

It is, at any rate, apparent that there is a somewhat more positive indication of significance for variations in the apparent C–C bond lengths in the unsubstituted rings of FAMF than has been found in other cyclopentadienyl complexes. It is worth noting that our apparent standard errors from the least-squares refinement are no more than one third as large as those reported in the best of the other determinations. Our analysis is the only one in which corrections for absorption were applied.

The apparent significant difference between the two bonds C(5')–C(1') is a puzzling feature; if there is a real physical difference, it must be a packing effect. It is not easy to see from the packing of the two molecules why there should be any such effect. Nor is it clear how such an effect can be traced indirectly to
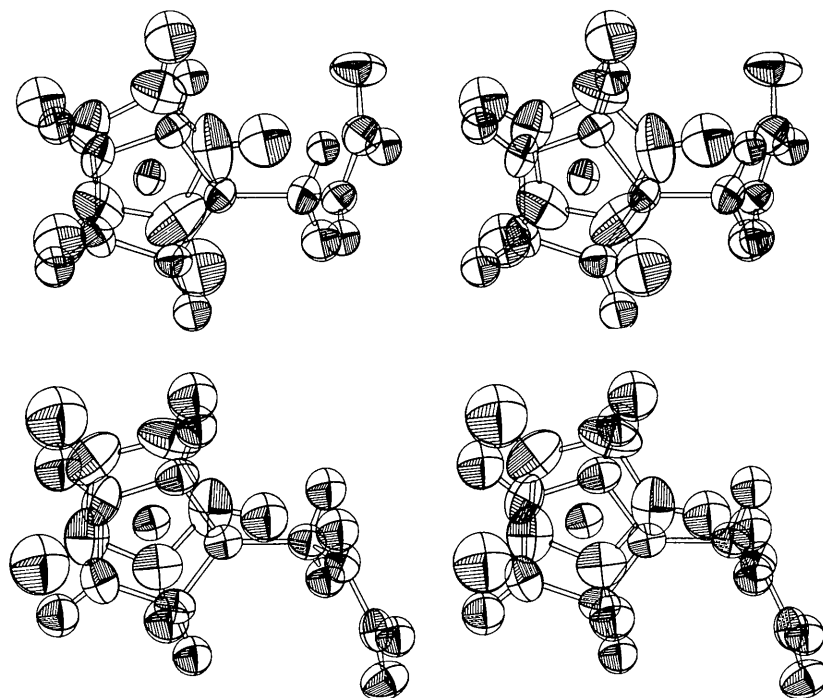


Fig. 2. Stereoscopic views of the two molecules, oriented as in Fig. 1, showing the 50% probability thermal ellipsoids.

packing in the sense that it may somehow be related to the slight difference in geometry between the two molecules (see below).

Consistent with the variations among the C–C bonds, there are some variations among the C–C–C angles (Table 3) within the cyclopentadienyl rings, the extreme variation being from 106·7° to 109·4°. For each of the four rings the average interior angle is 108·0°, consistent with the fact that the carbon atoms of each ring are almost exactly coplanar (see Table 5).

Table 5. *Distances of atoms from least-squares best planes of the five atoms of each ring and from the least-squares best planes of the four non-hydrogen atoms of each side chain.*

Standard errors of positions of atoms along the plane normals appear in parentheses. Best planes were computed with units weights for all atoms. In the equations *X*, *Y*, and *Z* are fractional coordinates and the last term is the distance in Å from the origin to the plane.

EQUATIONS FOR MOLECULE 1

| | | |
|---|---|---|
| RING S | $5.7375X - 0.4317Y + 12.6119Z$ | $= 9.7874$ Å |
| RING U | $5.6708X - 0.5464Y + 12.7115Z$ | $= 6.4275$ Å |
| SIDE CHAIN | $0.5707X + 12.3753Y - 8.3585Z$ | $= 6.9782$ Å |

EQUATIONS FOR MOLECULE 2

| | | |
|---|---|---|
| RING S | $-6.4509X - 3.0982Y + 11.0916Z$ | $= 1.1574$ Å |
| RING U | $6.2793X + 2.6567Y - 11.5827Z$ | $= 1.6337$ Å |
| SIDE CHAIN | $-0.8348X + 13.5465Y - 5.1984Z$ | $= 12.6976$ Å |

DISTANCES OF ATOMS FROM BEST PLANES (Å)

| | MOLECULE 1 | | MOLECULE 2 | |
|---|---|---|---|---|
| | RING S | RING U | RING S | RING U |
| C(1) | -0.0067(20) | 0.0003(38) | -0.0043(21) | -0.0001(34) |
| C(2) | 0.0038(23) | -0.0014(31) | 0.0023(23) | 0.0006(29) |
| C(3) | 0.0006(25) | 0.0019(31) | 0.0005(27) | -0.0009(34) |
| C(4) | -0.0049(24) | -0.0017(30) | -0.0032(28) | 0.0008(37) |
| C(5) | 0.0071(22) | 0.0009(31) | 0.0046(24) | -0.0004(35) |
| C(6) | -0.0329(25) | | -0.0225(25) | |
| H(1) | | -0.022(29) | | -0.094(27) |
| H(2) | -0.009(22) | 0.044(30) | 0.019(23) | 0.022(25) |
| H(3) | -0.018(22) | -0.008(29) | -0.081(22) | -0.087(33) |
| H(4) | 0.005(21) | -0.032(27) | -0.030(25) | -0.099(34) |
| H(5) | -0.033(20) | 0.054(27) | -0.060(24) | -0.023(29) |
| Fe(1) | -1.6444(03) | 1.6469(03) | -1.6385(03) | -1.6491(03) |
| | SIDE CHAIN | | SIDE CHAIN | |
| C(6) | -0.0020(25) | | -0.0035(24) | |
| N | 0.0046(20) | | 0.0081(20) | |
| C(7) | -0.0050(26) | | -0.0089(23) | |
| O | 0.0025(21) | | 0.0044(18) | |
| H(N) | -0.036(22) | | -0.031(25) | |
| H(7) | -0.023(21) | | -0.047(22) | |

The average of the 18 different values of the apparent C–H bond lengths (Table 3) for H atoms on the rings is 0·950 [39]; the only bond length which deviates significantly from the average is C(4)–H(4) in molecule 2, which is 0·834 (25) Å. The external angles C–C–H are all close to the value 126° expected for a symmetrical cyclopentadienyl ring; there is a somewhat larger range of values for these angles in mole-

cule 2 than in molecule 1. There is one puzzling aspect of the apparent positions of the ring hydrogens; namely, that every deviation of an H atom from its ring plane greater than $\sigma$ is in the direction of the opposite ring of the molecule (see Table 5). The deviations of the two atoms C(6), which are small but significant, also have this same sense. The angle between the C(1)–C(6) bond and the best plane of the substituted ring in molecule 1 is 1·0°; the corresponding angle in molecule 2 is 0·7°.

In each molecule the two five-membered rings are in a nearly totally eclipsed conformation (see Fig. 3), similar to the conformations found in biferrocenyl (Macdonald & Trotter, 1964), diferrocenyl ketone (Trotter & Macdonald, 1966), α-keto-1,5-tetramethylene ferrocene (Fleischer & Hawkinson, 1967), and 1,1′-diacetylferrocene (Palenik, 1967). For a more quantitative description of the conformations we compute for each pair of atoms such as C(1) and C(1′) within a molecule a signed torsion angle (Klyne & Prelog, 1960) about the line connecting the centroids of the two rings of carbon atoms. The torsion angles are given in Fig. 3, which shows for each molecule a view of the ferrocene moiety along the line connecting the ring centroids. The average of the five torsion angles is −7·8° in molecule 1 and +4·2° in molecule 2. Of course the torsion angles of the enantiomorphs of 1 and 2, which are also present in the
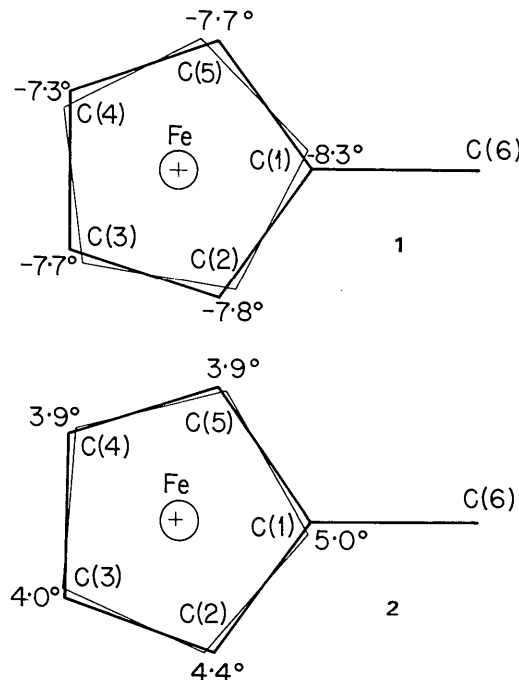


Fig. 3. Views of the two ferrocene moieties showing relative conformations of cyclopentadienyl rings. The direction of view in each case is along the axis through the centroids of the two sets of five carbon atoms. The axis in each molecule is marked by a cross within the circle representing the iron atom. The torsion angle about this axis for each pair of atoms C(1)–C(1′), *etc.*, is given.

centrosymmetric cell, have signs opposite to those given.

In molecule **1** the best planes through the two five-membered rings are at an angle of 0·71° to each other; in molecule **2**, 2·69°. In each molecule the plane defined by the two ring normals is nearly parallel to the line connecting C(1) and C(4). The two tilt angles have opposite senses, however, so that the shortest inter-ring C–C distance is C(1)–C(1') in **1** and C(4)–C(4') in **2** (see Table 3). The average separation for such pairs of atoms is 3·29 Å.

The averages of the Fe–C distances are 2·0335 [67] and 2·0331 [76] Å in molecules **1** and **2** respectively. In molecule **1** the distances from the iron atom to the best planes through the substituted and unsubstituted rings are 1·644 and 1·647 Å; in molecule **2**, 1·639 and 1·649 Å. These distances are close to those found in other ferrocene derivatives (Laing & Trueblood, 1965; Wheatley, 1967).

The principal difference between the two side chains is the marked difference in conformation about the C(6)–N bonds, which in a rough sense makes the non-equivalent molecules **1** and **2** mirror images of each other. The bond lengths and valence angles (Fig. 1 and Table 3) of the two side chains agree well and also seem normal. The N–C(7) and C(7)–O lengths are in reasonable agreement with the corresponding values found by Ladell & Post (1954) in crystalline formamide at − 50°C, considering the larger standard errors of their determination. For comparison, we cite also the bond lengths for gaseous formamide determined by microwave spectroscopy (Dowling & Costain, 1960); C–N, 1·376 (10); C=O, 1·193 (20) Å.

Best-plane calculations (Table 5) show that the four heavy atoms of each side chain are nearly coplanar. The deviation from planarity is specified in another way by the dihedral angle between planes C(6)–N–C(7) and N–C(7)–O, which is 1·3 (0·4)° in **1** and 2·3 (0·4)° in **2**. The hydrogen atoms on atoms N and C(7) of the side chains do not appear to deviate significantly from the best planes of the heavy atoms. Thus, there is no indication from this work of non-coplanarity of the nitrogen valence bonds as reported for gaseous formamide by Dowling & Costain (1960), whose microwave study indicated for the two H atoms on nitrogen torsion angles around the C–N bond of 12° ±7° and − 7° ±5° from the plane configuration found for the remaining atoms in the molecule. On the other hand,
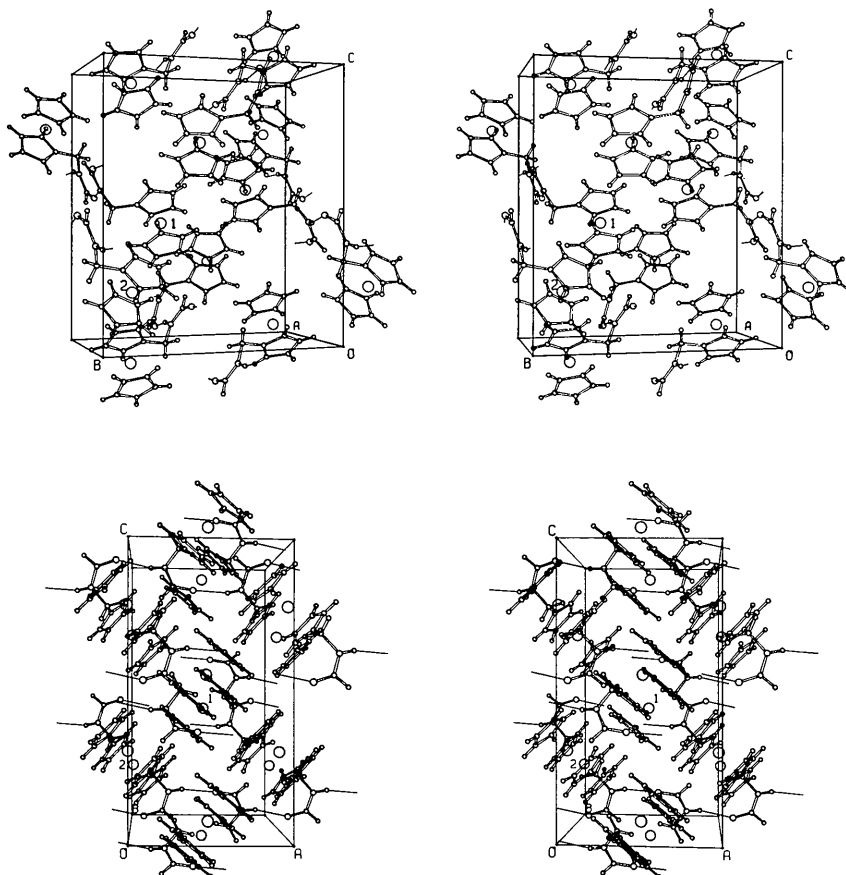


Fig. 4. Stereoscopic views of the crystal structure of *N*-formylaminomethylferrocene: (top) view direction 15° from **a**; (bottom) view direction along **b**.

the accuracy of our hydrogen determination hardly allows us to rule out the possibility of some departure from coplanarity.

Each molecule is connected by N–H$\cdots$O hydrogen bonds to two other molecules in head-to-tail fashion; molecules **1** and **2** alternate in the resulting infinite chains, which are parallel to **a**. The two sets of distance and angle parameters which describe the two different hydrogen bonds (Table 6) are not significantly different. Each N–H$\cdots$O bond departs significantly from linearity. The hydrogen bonding and other details of the arrangement of molecules are shown in the two stereoscopic views of Fig. 4.

Table 6. *Distance and angle parameters of the two hydrogen bonds*

|  | N(1)–H$\cdots$O(2) | N(2)–H$\cdots$O(1) |
|---|---|---|
| N$\cdots$O | 2·9001 (26) | 2·9035 (27) |
| N–H | 0·790 (21) | 0·845 (24) |
| H$\cdots$O | 2·123 (22) | 2·090 (25) |
| N–H$\cdots$O | 167·8 (2·2) | 161·5 (2·5) |

The interatomic distances associated with the van der Waals contacts are all in the normal range.

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# The Crystal Structure of the Carotenoidal Compound 1,14-Bis-(2',6',6'-trimethylcyclohex-1'-enyl)-3,12-dimethyl-tetradeca-1,3,5,7,9,11,13-heptaene-6,9-dinitrile

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The compound crystallizes in the triclinic space group $P\bar{1}$ with $Z=1$, $a=12·79$, $b=8·58$, $c=7·36$ Å, $\alpha=101·50$, $\beta=92·11$ and $\gamma=106·96°$. Three-dimensional intensity data were collected with an automatic single-crystal diffractometer. The structure was solved using an automatic Patterson search method, assuming the conformation of a part of the molecule to be known. A least-squares refinement yielded an $R_w$ index of 5·2%. The molecule is all-*trans* and almost straight and flat.

## Introduction

The compound, $C_{36}H_{46}N_2$, m.p. 207–208°C, is one of a series of carotenoidal compounds synthesized by condensation of polyenealdehydes with 1,4-dicyanobut-2-ene (Haeck & Kralt, 1966).

The aim of the investigation was to determine the molecular conformation, which proved to be all-*trans*.