The Crystal Structure of 2,2-Dicyanovinylferrocene

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2,2-Dicyanovinylferrocene, $C_5H_5FeC_5H_4CH=C(CN)_2$, crystallizes in the monoclinic space group $P2_1/c$. Four molecules are in the unit cell: $a=11\cdot33$, $b=7\cdot85$, $c=13\cdot46\pm0\cdot015$ Å, $\beta=94\cdot1\pm0\cdot1°$. A least-squares refinement based on 884 observed film intensities converged at an R value of $7\cdot3\%$. The almost parallel cyclopentadienyl rings are separated by $3\cdot28$ Å and deviate by $7°$ from the eclipsed conformation. The substituent vinyl group is turned $13°$ away from the ring plane. Close intermolecular $C\cdots C$ approaches of $3\cdot28$ and $3\cdot39$ Å are found.

As part of a program to characterize organic materials having potentially useful electrical or photoconductive properties, we have determined the crystal structure of 2,2-dicyanovinylferrocene (DCF). There was interest in ascertaining if DCF exhibits a weak form of the donor–acceptor bonding found in the molecular complex between ferrocene and tetracyanoethylene (TCNE) (Adman, Rosenblum, Sullivan & Margulis, 1967). In another dicyanomethylene derivative, such 'self-complexing' is postulated as giving rise to enhanced photoconductivity (Silverman, Krukonis & Yannoni, 1968).

Well-formed ruby-red crystals of DCF, $[C_5H_5FeC_5H_4CH=C(CN)_2]$, are monoclinic, space group $P2_1/c$ with $Z=4$. Cell dimensions determined from precession photographs are $a=11\cdot33$, $b=7\cdot85$, $c=13\cdot46\pm0\cdot015$ Å, $\beta=94\cdot1\pm0\cdot1°$. Density by flotation is $1\cdot45$ g.cm^{-3}; the calculated value is $1\cdot457$ g.cm^{-3}. In-

tensities were measured by densitometry of integrated precession camera films taken with Zr-filtered Mo $K\alpha$ radiation. 1280 overlapping data points taken about three axes, $0kl–4kl$; $h0l–h3l$; $2k,k,l–(2k+2),k,l$, reduced to 884 independent observations upon cross-correlation by a least-squares program (Reeke, 1966). Lorentz and polarization corrections were applied. The prismatic crystal of average cross section $0\cdot03$ cm ($\mu=12\cdot66$ cm^{-1} for Mo) is estimated to have (neglected) absorption effects of about 6% in relative values of F_o for unfavourable cases. The structure was solved by the heavy atom method. Refinement based on observed reflections only was by a full-matrix least-squares program (Busing, Martin & Levy, 1962) which minimizes $W(|F_o|-K|F_c|)^2$. Unit weights initially used were retained on the basis of statistical analysis of final cycles. Scattering factors are from Hanson, Herman,
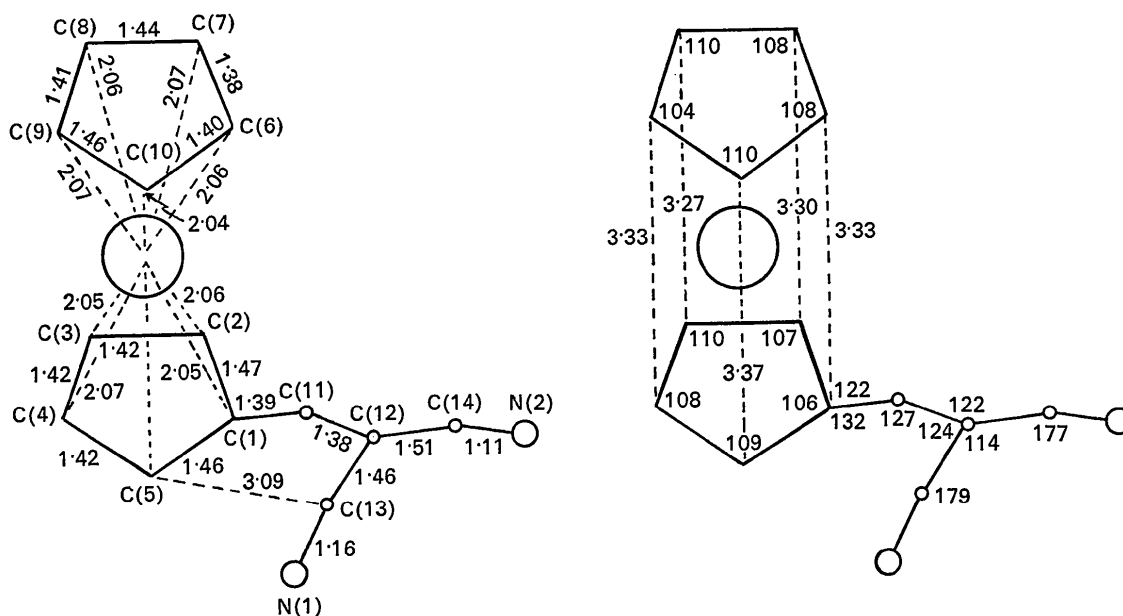

Fig. 1. Crystallographic numbering and molecular dimensions of DCF.

Lea & Skillman (1964). Plausible peaks for hydrogen atoms were found in difference maps among an equal number of comparable apparently spurious peaks. Refinement of these hydrogen positions was not satis-

Table 1. *Comparison of observed and calculated structure factors*

factory. In final cycles, we introduced idealized and fixed hydrogen atom positions with isotropic thermal parameters corresponding to their attached carbon atoms as well as anisotropic thermal values for the heavy atoms. Convergence to a point of negligible shifts in parameters was rapid and gave final R values of $R_w = 8.5$ and $R = 7.3\%$. Table 1 presents the observed and calculated structure factors.

Table 2 lists final positional and thermal parameters; Fig. 1 illustrates the crystallographic numbering and the molecular dimensions. The mean value for the 10 C–C bond lengths in the cyclopentadienyl rings is 1.427 ± 0.009 Å; for the 10 Fe–C bonds, 2.056 ± 0.004 Å; and for the internal ring angles, $108.0 \pm 0.6°$. (Standard deviations from the inverted least-squares matrix are 0.02–0.03 Å for individual C–C bonds, about 0.016 Å

(a)

(b)

Fig. 2. Views in projection perpendicular to the appropriate mean planes of: (a) The ferrocene moiety with the plane of projection passing through the iron atom. Averaged positions of ring centers are indicated. (b) The substituted cyclopentadienyl rings related by the center at $\frac{1}{2},0,0$. Closest intermolecular approaches as well as the distance of each atom from the plane of projection (passed through the symmetry center) are shown in Å.

for Fe–C bonds and about 1·6° for C–C–C angles. At this level of accuracy, no deviations among the related individual values are significant and the standard deviations given for the mean values are internal statistical estimates based on the individual scatter.) These averages agree very closely with those from the gas phase structure of ferrocene (Bohn & Haaland, 1966) as well as with those from recent X-ray results on ferrocene derivatives. [An extensive list of ferrocene structure work is cited by Churchill & Wormald (1969), Table 8, to which the recent work of Hirotsu, Higuchi & Shimada (1968), Palenik (1969, 1970), Allen, Trotter & Williston (1970), Hall & Brown (1971) may be added.] We note that the bond angle enlargements at C(11) to 127° and at C(12) to 124·4° work in conjunction with the rotation of the substituent out-of-plane (vide infra) to relieve the intramolecular steric strain between atoms C(5)···C(13) and H [on C(5)]···C(13) by increasing the final interatomic distances to 3·09 and 2·4 Å respectively. The two five-membered rings are each planar to within ±0·015 Å and are offset by 2·3° from parallelism. The closest C···C contacts between rings range from 3·27 to 3·37 Å. The iron atom is found at 1·675 and 1·65 Å from each plane. A view of the ferrocene moiety in projection is shown in Fig. 2(a). As defined by angles made between the lines from almost eclipsed carbon atoms to the midpoint of the opposite sides of the rings (Fleischer & Hawkinson, 1967), estimates of the deviations from the eclipsed conformation range from 5·8 to 7·7°; the average is 7·0°. Superimposed on this rotation is a slight lateral translation of the rings leaving their centers about 0·044 Å apart in projection. While the individual atomic shifts in question are only about 2·6σ, the fact that reestablishing the coincidence of the ring centers leaves the rings in almost perfect rotational alignment, attests to the reality of the effect. A similar translation of about 0·09 Å is noted and referred to as a 'deformation shift' in diferrocenyl (Kaluski, Struchkov & Avoyan, 1964) and in its diethyl derivative (Kaluski & Struchkov, 1965). The dicyanovinyl substituent is planar to ±0·02 Å. It makes a dihedral angle of 167° to the C(1)–C(5) ring, largely due to rotation about the C(1)–C(11) bond [in the sense which moves N(1) further from the iron atom].

The present configuration lends further weight to Palenik's (1970) observation that recent results indicate that the eclipsed form is the norm for ferrocene derivatives. The tendency in the literature to invoke packing forces whenever a nearly eclipsed configuration is found, a viewpoint stemming from the staggered conformation found in crystalline ferrocene (Dunitz, Orgel & Rich, 1956), has persisted even after electron diffraction results had demonstrated that the free ferrocene molecule is eclipsed with a 0·9 kcal.mole⁻¹ barrier to free rotation (Bohn & Haaland, 1966; Haaland & Nilsson, 1968). In fact leaving aside ferrocene and ferrocene/TCNE (both are possibly disordered at room temperature) as well as bridged ferrocenes where intramolecular steric constraints are operative, one finds in surveying available conformation angles in the solid that 15 out of 17 are ≤17° and 13 out of 17 are ≤10° (0°=eclipsed and 36°=staggered). Surveyed conformations are from Table 8 of Churchill & Wormald (1969, updated by the references cited above and DCF). Hence while the barrier is low enough to be 'traded off' for improved packing up to a point, its overall influence on these conformations is evident. The tendency for uncrowded nitro group substituents on aromatic rings to remain within about 10° of their isolated (planar) form (Silver-

Table 2. *Final positional parameters x,y,z in fractional coordinates* ($\times 10^4$), *anisotropic thermal parameters* β_{ij} ($\times 10^4$) *from the expression* $-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)$ *and r.m.s. displacements* u_i *in* 10^2 Å *along molecular axes*

u_1 is perpendicular to the ring planes, u_2 is approximately along the C(1)–C(11) bond parallel to these planes and u_3 also parallel completes an orthogonal system.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	u_1	u_2	u_3
Fe	1754(2)	1886(3)	−1154(1)	58(2)	115(4)	31(1)	18(4)	−1(1)	−0(3)	17	21	18
C(1)	3379(15)	0890(20)	−0721(10)	112(19)	130(34)	37(9)	−12(22)	−21(11)	−9(14)	22	23	20
C(2)	2663(15)	−0358(23)	−1309(12)	87(16)	149(35)	71(11)	40(23)	27(12)	38(18)	21	29	20
C(3)	1611(15)	−0642(21)	−0815(11)	93(17)	105(29)	60(11)	−9(23)	12(11)	−3(15)	22	23	22
C(4)	1650(14)	0323(24)	0079(11)	95(18)	213(40)	39(9)	3(24)	4(10)	−23(16)	21	24	24
C(5)	2723(14)	1274(21)	0142(10)	71(14)	199(37)	35(8)	2(20)	1(9)	−8(14)	21	22	21
C(6)	1983(17)	3887(28)	−2107(17)	79(19)	229(46)	107(17)	10(26)	0(15)	−99(25)	18	23	37
C(7)	1239(19)	2701(28)	−2578(11)	149(23)	280(56)	39(9)	37(30)	19(12)	−45(19)	20	32	27
C(8)	0230(14)	2502(24)	−1997(13)	63(16)	230(44)	74(12)	−8(21)	5(11)	−54(19)	21	21	31
C(9)	0347(18)	3573(26)	−1159(15)	100(20)	207(50)	97(16)	43(27)	3(15)	0(21)	23	29	28
C(10)	1472(24)	4443(27)	−1250(18)	187(35)	165(40)	99(18)	88(37)	49(20)	13(24)	19	40	27
C(11)	4434(14)	1532(22)	−1036(10)	89(15)	187(41)	34(8)	49(23)	1(9)	−22(15)	17	26	23
C(12)	5274(14)	2465(21)	−0475(9)	102(17)	214(39)	23(7)	71(22)	−3(9)	−44(13)	13	28	24
C(13)	5179(13)	2942(24)	0563(12)	69(14)	192(40)	60(10)	40(23)	−5(10)	−43(20)	17	23	28
C(14)	6380(17)	3112(32)	−0905(12)	94(18)	280(47)	56(10)	58(33)	−3(11)	−56(23)	18	27	30
N(1)	5114(13)	3343(24)	1386(11)	122(16)	300(43)	76(11)	12(26)	−7(11)	35(20)	31	30	24
N(2)	7224(14)	3523(30)	−1202(12)	62(13)	556(75)	102(13)	9(29)	−22(11)	−83(26)	31	22	40

man, Krukonis & Yannoni, 1968) is perhaps an analogous case.

The thermal motion breakdown shown in the last three columns of the table indicates a pattern noted in other ferrocenes (see for example Trotter & Macdonald, 1966) in which there is minimum motion perpendicular to the plane, greater overall movement in the unsubstituted ring, and a clear component of rotary motion in the plane of the cyclopentadienyl rings, especially evident in DCF for the C(6)–C(10) ring.

In the structure, intermolecular approaches are normal except for the short distances found between molecules related by symmetry centers at $\frac{1}{2},0,0$. The distances of 3·28 and 3·39 Å between C(13)···C(2) and C(12)···C(1) suggest a donor–acceptor interaction analogous to that found in the π-molecular complex, ferrocene/TCNE (Adman et al., 1967). However the overlap diagram [Fig. 2(b)] lacks a characteristic feature found in many aromatic hydrocarbon/TCNE complexes in which the central bond in TCNE [corresponding to C(11)–C(12) in DCF] is found within the hydrocarbon ring system in projection (see Figs. 12 and 17 in the review of Herbstein, 1971). Hence, these short distances could actually be repulsive contacts which allow more efficient overall packing. Each molecule is in contact with 8 others in a complicated herring-bone arrangement. This structure is one of several derivatives which along with ferrocene itself crystallizes in a monoclinic space group in which the unique axis lies between 7·4 and 7·9 Å.

Note added in proof: A lateral displlcement of 0·16 Å in the cyclopentadienyl rings in projection similar to that found in DCF is reported in 1′-acetyl-1-benzoylferrocene (Calvarin & Weigel (1971); compare their Fig. 3(a) with Fig. 2(a) of this paper).

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