

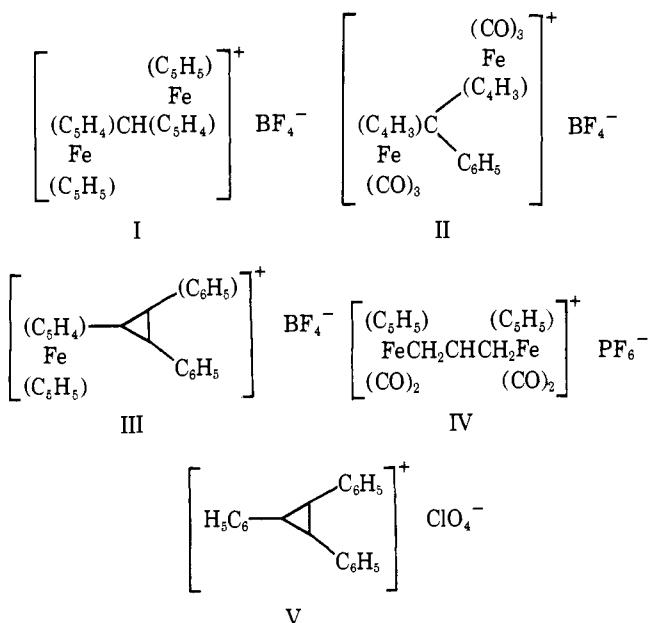
Determination of the Crystal Structure of α,α -Diferrocenylmethylum Tetrafluoroborate, a Stable Carbenium Ion Salt, and a Comparison of Its Structure with Those of Other Organometallic Carbenium Cations¹

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Abstract: The crystal structure of the monoclinic polymorph of α,α -diferrocenylmethylum tetrafluoroborate ($a = 15.99$, $b = 12.75$, $c = 9.365$ Å, $\beta = 90.6^\circ$, space group $P2_1/a$, 4 formula units per cell) has been determined by standard methods using 2648 (222 with $I_{\text{obsd}} = 0$) intensities measured on a Weissenberg diffractometer using graphite-monochromated Mo $K\alpha$ radiation. The final R factor was 9.3%. The cation has a transoid conformation, similar to that found for diferrocenyl ketone; the BF_4^- ions are orientationally disordered over three groups of sites. The ferrocenyl rings are bent at the α -carbon atoms so as to reduce the distances between the two Fe atoms and the exocyclic carbon atom to 2.69 and 2.81 Å. Analogous distortions have been reported in the bis[(cyclopentadienyl)dicarbonyliron]propylenium cation ($\text{Fe} \cdots \text{C}^+$ distances 2.57, 2.72 Å) and to a lesser extent in other organometallic cations. We conclude that both metal-exocyclic carbon atom interaction, with resulting geometrical distortion of the cation, and delocalization of the positive charge over suitable regions of the cation lead to stabilization of organometallic carbenium cations.

The exceptional stability of ferrocenylcarbenium ions has been considered a major factor governing the course of reaction in much of the organic chemistry of the ferrocenyl system leading to an intensive search for the sources of such stability.³ Success has not yet been achieved. In the hope that particular features of the geometry of such carbenium ions hold the clue to their stabilization, we have determined the crystal structure of the stable carbenium ion salt α,α -diferrocenylmethylum tetrafluoroborate (I). The results have been briefly reported.⁴



The other organometallic carbenium ion salts whose crystal structures have been reported are bis(α -cyclobutadienetricarbonyliron)phenylcarbenium tetrafluoroborate (II),⁵ ferrocenyldiphenylcyclopropenium tetrafluoroborate (III),^{6a} and bis[(cyclopentadienyl)dicarbonyliron]propylenium hexafluorophosphate⁷(IV). Intercomparison of all these results suggests that there are two interrelated factors which stabilize organometallic moiety in the delocalization of the positive charge, the other is the ability of the molecule to undergo geometrical changes which result in greater bonding interac-

tion between the metal atom and the formally positive ligand moiety.

Experimental Section

The (air-stable) title compound (see Figure 2 for crystallographic numbering) was synthesized by adaption of techniques developed by Cais and Eisenstadt⁸ and recrystallized from methanol. A number of salts were studied and the tetrafluoroborate was found to be the most stable and to give the best crystals for diffraction.⁴ Two polymorphs were found, one monoclinic reported here in detail (Table I) and one orthorhombic ($a = 18.27$ (1), $b = 11.88$ (1), $c = 8.98$ (2) Å, $V = 1944$ Å³, $d_{\text{calcd}} = 1.59$ g cm⁻³ for $Z = 4$, $d_{\text{meas}} = 1.55$ g cm⁻³). Unfortunately the orthorhombic crystal used for photography was lost before the space group was determined, and other orthorhombic crystals have not been found. The crystal structure determination was therefore carried out on the monoclinic polymorph.

Data Collection. The intensities of 2648 reflections were measured on a Stoe Weissenberg semiautomatic diffractometer with graphite-monochromated Mo $K\alpha$ radiation (layer lines $h0l$ to $h8l$, maximum $\sin \theta/\lambda$ 0.66 Å⁻¹, 222 reflections were unobserved); the ω - 2θ method was used (scan speed 2° 2θ min⁻¹ and scan width 2.4° in 2θ ; background count for 30 s at each of the scan extremities). Intensities were corrected for geometrical and absorption effects⁹ (maximum and minimum values of the absorption correction were 1.25 and 1.18, respectively); because of rather poor crystal quality high accuracy was not achieved.

Structure Determination and Refinement. The positions of the two iron atoms were obtained from a three-dimensional Patterson synthesis, and the other atoms were added progressively from a series of difference syntheses and least-squares calculations (SHELX-76 program system;^{10a} atomic scattering factors and dispersion corrections from Tables 2.2B and 2.3.1 of Volume IV of "International Tables for X-Ray Crystallography";^{10b} unit weights were used and the function minimized was $\sum w(F_o - F_c)^2$). The principal difficulties experienced in the refinement arose from large thermal motion of the cyclopentadienyl rings and tetrafluoroborate ion, together with orientational disorder of the anion. These difficulties were greatly alleviated by exploiting a number of features of the SHELX-76 program. The tetrafluoroborate ion and the four cyclopentadienyl rings were treated as rigid bodies of standard dimensions; difference syntheses in the region of the BF_4^- ion were interpreted in terms of an approximately equal distribution of the ion over three orientations. Each of the three fractional ions was rotated independently of the others about a dummy pivot atom placed at the position of the boron atom, until all 12 fluorine atoms (each weighted $1/3$) took up optimal positions and isotropic Debye-Waller factors, the standard geometry of BF_4^-

Table I. Crystal Data for α,α -Diferrocenylmethylium Tetrafluoroborate^a

monoclinic	$C_{21}H_{19}Fe_2BF_4$
$a = 15.99 (2) \text{ \AA}$	mol wt 469.88
$b = 12.75 (1) \text{ \AA}$	space group $P2_1/a$
$c = 9.365 (2) \text{ \AA}$	$F(000) = 952$
$\beta = 90.63 (1)^\circ$	$d_{\text{meas}}^b = 1.62 (1) \text{ g cm}^{-3}$
$V = 1909.2 \text{ \AA}^3$	$d_{\text{calcd}} = 1.64 \text{ g cm}^{-3}$ for
	$Z = 4$
	$\mu (\text{Mo K}\alpha) = 15.89 \text{ cm}^{-1}$

^aCell dimensions were determined on the Weissenberg diffractometer. Numbers in parentheses here and throughout this paper are the estimated standard deviations in units of the least significant digit. ^bDensity measured by suspension in toluene-tetrabromoethane mixture.

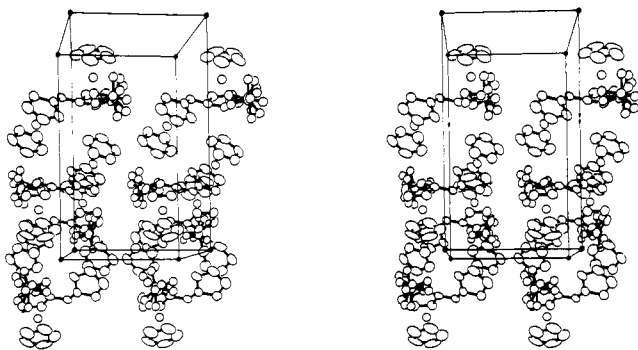


Figure 1. ORTEP¹¹ stereoview of unit cell of diferrocenylmethylium tetrafluoroborate. The origin is at the rear lower left-hand corner of the cell, with a toward the top of the page, b toward the observer, and c to the right. The reference asymmetric unit (coordinates given in Table II) is in the lower left-hand part of the diagram, outside the boundaries of the cell.

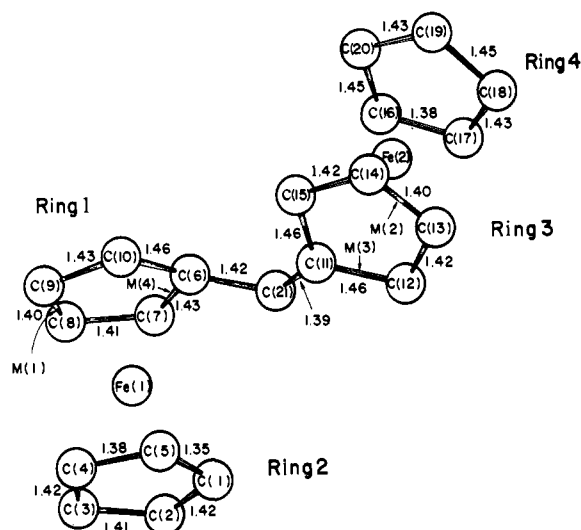


Figure 2. Diferrocenylmethylium cation: (a) numbering of atoms and midpoints of various bonds, e.g., M(1) is the midpoint of C(8)–C(9); (b) interatomic distances (\AA), $\sigma(\text{C}–\text{C}) \approx 0.01 \text{ \AA}$.

being preserved. Release of the rigid body constraints of the BF_4^- resulted in serious distortion of the regular tetrahedra because of the large correlation between the various orientations and the constraints were therefore retained. The boron atom was treated separately and included in the anisotropic refinement. The rigid-body constraints for the cyclopentadienyl rings were lifted in the penultimate stage of the refinement, and the atoms allowed to take on optimal positions and Debye–Waller factors. The shifts were small. Also 65 reflections with appreciable errors of measurements were excluded at this stage. The hydrogens of the rings were introduced at appropriate calculated positions and a final cycle of refinement was carried out. The ring

Table II. Fractional Atomic Coordinates of Nonhydrogen Atoms ($\times 10^4$) and Hydrogen Atoms ($\times 10^3$)^a

Atom	x	y	z
Fe(1)	–2849 (1)	1566 (1)	–2061 (1)
Fe(2)	–668 (1)	1893 (1)	2396 (1)
C(1)	–3724 (9)	2217 (17)	–749 (15)
C(2)	–4111 (7)	1416 (14)	–1578 (23)
C(3)	–4010 (8)	1718 (16)	–3007 (19)
C(4)	–3557 (9)	2673 (14)	–3026 (17)
C(5)	–3389 (9)	2944 (15)	–1623 (22)
C(6)	–1821 (5)	1049 (10)	–1045 (10)
C(7)	–2273 (6)	190 (9)	–1661 (10)
C(8)	–2306 (7)	346 (13)	–3145 (12)
C(9)	–1893 (7)	1279 (13)	–3476 (10)
C(10)	–1589 (5)	1765 (10)	–2191 (10)
C(11)	–1644 (6)	2248 (9)	1071 (9)
C(12)	–1839 (6)	2477 (11)	2560 (10)
C(13)	–1247 (9)	3209 (14)	3092 (13)
C(14)	–700 (7)	3497 (12)	2001 (14)
C(15)	–927 (6)	2919 (11)	764 (11)
C(16)	–332 (8)	298 (11)	2228 (13)
C(17)	–569 (7)	529 (10)	3598 (11)
C(18)	–61 (7)	1347 (11)	4180 (11)
C(19)	537 (6)	1657 (11)	3115 (14)
C(20)	346 (7)	1008 (11)	1909 (12)
C(21)	–1968 (5)	1372 (9)	383 (9)
B	–1501 (8)	4960 (15)	–3022 (13)
F(1)	–944	4606	–3984
F(2)	–1398	4448	–1782
F(3)	–2284	4819	–3532
F(4)	–1366	6003	–2809
F(1)'	–1158	4068	–3539
F(2)'	–1209	5087	–1670
F(3)'	–2342	4899	–3037
F(4)'	–1260	5792	–3834
F(1)''	–706	4687	–3325
F(2)''	–1651	479	–1601
F(3)''	–2035	4397	–3829
F(4)''	–1606	6002	–3315
H(1)	–369	222	45
H(2)	–442	72	–116
H(3)	–423	125	–391
H(4)	–339	307	–401
H(5)	–306	367	–131
H(7)	–252	–45	–105
H(8)	–260	–20	–389
H(9)	–183	160	–455
H(10)	–126	247	–211
H(12)	–233	210	313
H(13)	–124	351	419
H(14)	–19	404	209
H(15)	–63	296	–27
H(16)	–59	–26	149
H(17)	–107	14	419
H(18)	–9	167	524
H(19)	99	223	320
H(20)	68	104	89

^aThe numbering of the atoms is shown in Figure 2. The fluorine atoms have occupancies of $1/3$. The hydrogen positions are calculated positions and were not refined.

hydrogens were not refined in this cycle and the methylum hydrogen was not included at any stage in the analysis. The final R factor was 9.3%.

Atomic coordinates are given in Table II; structure factors and anisotropic temperature factors are given as supplementary material. See paragraph at end of paper.

Results

Molecular Structure A. The Cation. A stereoscopic view¹¹ is shown in Figure 1 and detailed interatomic distances and angles are given in Figures 2 and 3. The transoid conformation of the cation is remarkably similar to that found for diferro-

Table III. Deviations (in Units of 10^{-2} Å) of Atoms from Various Planes in Cation 1^a

plane 1:	through ring 1 (C(6) through C(10)); $-0.8618x + 0.4979y + 0.1066z - 3.081 \text{ Å} = 0$ deviations: C(11) 72; C(21) 54; Fe(1) 163
plane 2:	through ring 2 (C(1) through C(5)); $-0.8597x + 0.5102y + 0.0351z - 6.528 \text{ Å} = 0$ deviations: Fe(1) -166
plane 3:	through ring 3 (C(11) through C(15)); $-0.6113x + 0.7394y - 0.2754z - 3.459 \text{ Å} = 0$ deviations: C(6) -42; C(21) -34; Fe(2) -164
plane 4:	through ring 4 (C(16) through C(20)); $+0.6459x - 0.6806y + 0.3387z - 0.098 \text{ Å} = 0$ deviations: Fe(2) -167
plane 5:	through atoms C(6), C(11), C(21); $-0.7830x + 0.5384y - 0.3028z - 3.279 \text{ Å} = 0$ deviations: ring 1: C(1) 310; C(2) 327; C(3) 376 C(4) 385; C(5) 343
ring 2:	C(7) 15; C(8) 72; C(9) 94; C(10) 53
ring 3:	C(12); C(13) -41; C(14) -59; C(15) -35
ring 4:	C(16) -331; C(17) -324; C(18) -348; C(19) -372; C(20) -358 Fe(1) 193; Fe(2) -184; M(1) 83; M(2) -50

^aPlanes through the atoms listed were determined by standard methods;¹³ these atoms did not deviate from the planes given by more than 0.01 Å. M(1) is at the center of C(8)-C(9) and M(2) is at the center of C(13)-C(14). Planes were defined with respect to the *crystal* axes in the form $lx + my + nz - d = 0$ where x, y, z are the atomic coordinates in Å, l, m, n are the direction cosines of the plane normal with respect to the crystal axes, and d is the origin to plane distance.

cenyl ketone;¹² however, the latter molecule has true C_2 -2 symmetry whereas this is only approximately true for the cation, the two ferrocenyl moieties being related by a pseudo-twofold axis bisecting C(6)-C(21)-C(11).

The cyclopentadienyl rings of the two ferrocenyl moieties are essentially planar (Table III) and their interatomic distances and angles do not differ significantly from standard values. There is an angle of 4.2° between rings 1 and 2 and 5.7° between rings 3 and 4; rings 1 and 2 are mutually rotated away from the eclipsed conformation by 11.0° while rings 3 and 4 are fully eclipsed but mutually displaced by ~ 0.1 Å. The iron atoms are not significantly displaced from the lines joining appropriate ring centers. The Fe-C distances and the ring-ring separations do not differ significantly from the values found in neutral ferrocenes. The angle at the exocyclic carbon (C(6)-C(21)-C(11)) is $127(1)^\circ$. The conformation of the cation is conveniently described (Figure 2) with respect to the plane through atoms C(6), C(21), and C(11) (plane 5). This also provides a convenient reference for a later comparison with the conformation of diferrocenyl ketone (see Discussion). Ring 1 is bent out of plane 5 by 24.1° such that M(1) (opposite C(6) in the pentagon) deviates from this plane by 0.83 Å in the direction of Fe(1). There is an additional but considerably smaller twist of this ferrocenyl moiety roughly about the C(9)-M(4) axis. The second ferrocenyl moiety is bent out of plane 5 by 5.3° (for ring 3) such that M(2) deviates from this plane by 0.50 Å in the direction of Fe(2). The axis of bending is close to the C(11)-C(12) line, and there is an additional but small twist roughly about C(14)-M(3). As a result of these bends and twists the distances C(21)-Fe(1) and C(21)-Fe(2) are 2.69 and 2.87 Å, respectively, appreciably less than the corresponding distance (3.12 Å) in diferrocenyl ketone where there is twisting but no bending.

B. The Anion. The dimensions of the anion (tetrahedral, $d(\text{B-F}) = 1.35$ Å) have been based on those reported earlier^{6a} and were not determined independently here. The disorder found here is orientational only, whereas Hodgson and Ibers^{14,15} have found both orientational and positional disorder

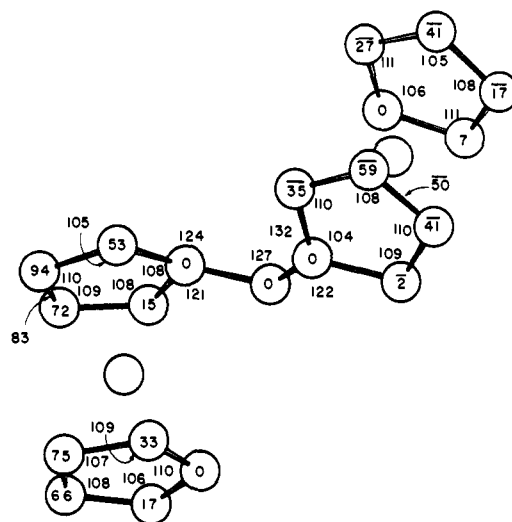


Figure 3. Diferrocenylmethyl cation. (a) Bond angles (deg), $\sigma(\text{C}-\text{C}-\text{C}) \sim 1^\circ$. (b) Deviations from the plane through atoms C(6), C(21), C(11), in units of 10^{-2} Å; for rings 2 and 4, the deviations of atoms C(1) and C(16), analogous to C(6) and C(11), have been set to zero and the deviations of the other atoms in these rings have been expressed with respect to these reference atoms; deviations below the C(6), C(21), C(11) plane (i.e., toward the lower end of the page) are given as positive.

of BF_4^- ions in the compounds they studied. The large Debye-Waller factors reported by Sime and Sime^{6a} suggest disorder in their compound as well but this appears not to have been explored by them.

Crystal Structure. A stereoscopic drawing of the unit cell contents is shown in Figure 1. The distances between the ionic moieties are unexceptional and are not reproduced in detail. Both ionic and dispersion interactions contribute to the cohesion of the crystal.

Discussion

Are there any geometrical features peculiar to organometallic carbenium cations which can be related to their special stability? Models considered in the past have the following geometrical features: (a) higher metal-ligand bond order through displacement of the $\eta^5\text{-C}_5\text{H}_5\text{Fe}$ group toward the exocyclic carbon atom of the substituted cyclopentadienyl ring;¹⁶ (b) resonance stabilization in the fully planar fulvene moiety of the ferrocenyl carbenium ion and no bonding interaction between the ion and the exocyclic carbon atom;¹⁷ (c) a nonplanar fulvene ligand in which folding across the carbon atoms α to the substituted position would bring the exocyclic carbon atom nearer to the iron atom to permit better overlap between ligand and metal orbitals and consequently increased stabilization;^{3a,b} (d) a nonplanar fulvene ligand in which the exocyclic carbon atom is displaced from the plane of the substituted cyclopentadienyl ring toward the iron atom, with concomitant tilting of the ring.¹⁸

We pursue the search for special geometrical features, in particular those proposed in the various models, both by comparing individual cations with closely related neutral molecules on a pairwise base, and by considering the organometallic carbenium cations as a group. Particular attention will be directed to those aspects of the geometry of the α,α -diferrocenylmethyl cation which appear unusual.

A. Displacement of Exocyclic Carbon Atoms from the Planes of Cyclopentadienyl Rings in Ferrocene Derivatives. There is complete coplanarity in diferrocenyl ketone¹² and minor displacements of 0.02 Å toward the iron atom in 1,2-bis(ferrocenyl)ethane¹⁹ and of 0.03 Å away from the iron atom in 2,2-dicyanovinylferrocene.²⁰ In 1,1'-diacetylferrocene²¹ the displacements of the exocyclic carbons are 0.08 and 0.12 Å,

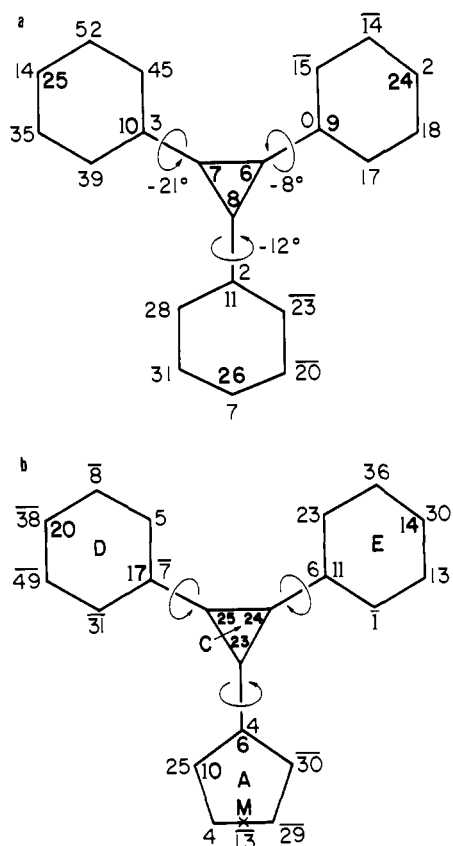


Figure 4. Comparison of molecular geometries of (a) *sym*-triphenylcyclopropenium (V) and (b) ferrocenyldiphenylcyclopropenium (III) cations. Numbers of some atoms (as given in the original papers) have been inserted within the rings (denoted by letters for III, as in ref 6a) for reference purposes. The deviations of certain atoms (in units of 10^{-2} Å) from the planes of the cyclopropenium rings are shown as well as torsion angles for V (signs according to the convention of Klyne and Prelog³²). These values agree well with those given by Sundaralingam and Jensen.²⁷ Although signs can be given to the torsion angles for III, physically meaningful numerical values are difficult to define and have been omitted. M is the midpoint of the C(8)–C(9) bond in the upper cyclopentadienyl ring of the ferrocenyl moiety. All six- and five-membered rings are planar within experimental error. The angle between the planes of the two pentadienyl rings of the ferrocenyl moiety is 2.7° .

respectively, both toward the iron atom, and similar displacements are found in 1-acetyl-1'-benzoylferrocene.²² We conclude that, in neutral ferrocene-type molecules, the exocyclic carbon atoms do not deviate by more than ~ 0.1 Å from the planes of the cyclopentadienyl rings to which they are bonded. Displacements of this size are generally ascribed to packing (i.e., intermolecular) effects. Pairwise comparison between the conformations of diferrocenyl ketone¹² and the diferrocenylmethylum cation reinforces this conclusion. For both moieties the conformations are transoid (compare their Figure 2b and our Figure 2). In diferrocenyl ketone the molecule has a crystallographic C_2 -2 axis (through the C=O group) and the two cyclopentadienyl groups are twisted (by 17°) out of the plane of the C=O group and the two rings atoms to which it is bonded, but not bent out of this plane. The diferrocenylmethylum cation has an approximate twofold axis in a position similar to that found in diferrocenyl ketone; however, in the cation the major displacement of the atoms of the rings 1 and 3 from the plane of C(6), C(11), C(21) is by bending, with only a minor component of twisting. Thus there is a significant geometrical difference between the coplanar exocyclic carbon atoms of the neutral ferrocene derivatives and the bending (toward the iron atom) of C(21) in the present carbenium ion by 0.54 Å out of the cyclopentadienyl plane (plane 1, Table III). As the steric interference from the hy-

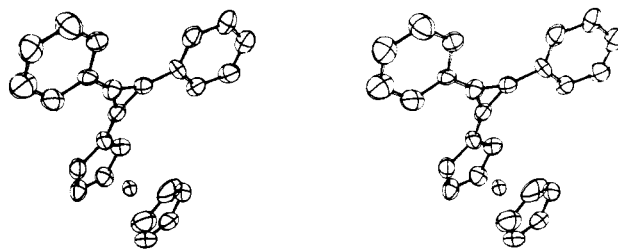


Figure 5. ORTEP stereoview of ferrocenyldiphenylcyclopropenium cation (coordinates from ref 6a).

drogen atoms (H(10), H(15) in our numbering) is much the same in both moieties, and because bending is energetically more expensive than twisting, we infer that the bending results from a cause other than the relief of steric interference.

The distances from the exocyclic carbon atom C(21) to the two ferrocenyl moieties are not significantly different (1.39 , 1.42 Å) nor does their mean differ significantly from the corresponding distance in diferrocenyl ketone (1.45 (2) Å). Thus there is no particular shortening of this distance in the carbenium cation.

The sense of the bending for both²³ ferrocenyl moieties is such as to decrease the distance between C(21) and the two iron atoms. A similar type of distortion to an analogous end is found in the neutral molecule tricarbonyl(1-5, α - η -diphenylfulvene)chromium [$((C_5H_4)CPh_2)Cr(CO)_3$],²⁴ where the exocyclic carbon atom is bent toward the chromium atom by 31° out of the plane of the cyclopentadiene ring, as a result of interaction of all the π electrons of the fulvene system with the chromium atom. The Cr...C(exocyclic) distance was found to be 2.53 Å. Dimethylfulvene itself is a strictly planar molecule.²⁵ Furthermore, comparison of the structures of the neutral molecule [$(\eta^5-C_5H_5)Fe(CO)_2(CH_2CH_2CH_2)$]²⁶ and the stable carbenium ion [$(\eta^5-C_5H_5)Fe(CO)_2(CH_2CHCH_2)^+$]⁷ (IV) shows that there are reductions of C–C–C bond angles in the carbenium ion such that the Fe...C⁺(CC) distances are 2.57 and 2.72 Å compared to 3.07 Å for the analogous distance in the neutral molecule.

It is not possible to carry out a similar comparison for bis(α -cyclobutadieneiron tricarbonyl)phenylcarbenium cation⁵ as coordinates have not been reported, nor is the structure of a corresponding neutral molecule known. However, Davis et al.⁵ note the following points: (1) The formally positive exocyclic carbon is coplanar with respect to the butadiene rings, which are twisted by small amounts (5° , 8°) out of the mean molecular plane. (2) The phenyl group is twisted by 43° out of the mean molecular plane and thus the major resonance stabilization comes from the butadiene rings; (3) The iron atoms are essentially above the centers of the butadiene rings. (4) The Fe...C⁺ distances are 2.85 and 2.94 Å, respectively.

Two other cations are available for discussion: ferrocenyldiphenylcyclopropenium tetrafluoroborate (III)^{6a} (for a stereoview see Figure 5) and *sym*-triphenylcyclopropenium perchlorate (V).²⁷ The crystal structures of analogous neutral molecules have not been reported but a comparison of these two cations should show whether substitution of phenyl by ferrocenyl has a significant effect and, in particular, whether there is distortion such as to reduce the distance between the iron atom and the formally positive carbon atom. The two structures are compared in Figure 4 in terms of the deviations of the substituent rings from coplanarity with the cyclopropenium rings. In V the principal deviations from coplanarity are due to concerted (propeller-like) twists of the phenyl rings about the bonds linking them to the cyclopropenium ring, with only slight out-of-plane displacements of each ring as a whole. In III both displacements and twists occur and the displacement of the ferrocenyl ring is actually smaller than those of the

two phenyl rings. For both moieties it seems reasonable to consider that the twists result from intramoiety interactions (steric hindrance) and that the displacements result from intermoiety interactions (packing forces).

We calculate, from the coordinates given by Sime and Sime,^{6a} that $d(\text{Fe}\cdots\text{C}(23))$ is 2.96 Å and that the angle $\text{C}(23)\text{--C}(6)\text{--M}$ is 6.3° (M is the midpoint of $\text{C}(8)\text{--C}(9)$, using the numbering of ref 6a). $\text{C}(23)$ is displaced by 0.16 Å out of the plane of the cyclopentadienyl ring toward the iron atom; this displacement is much less than the displacement of 0.54 Å found here for I and is only slightly greater than the largest values found for neutral ferrocene derivatives (vide supra); concomitantly there is less bending²⁸ of $\text{C}(23)$ toward the iron atom of the ferrocenyl system than there is for the corresponding atoms of I. We conclude that the results of Sime and Sime^{6a} do not substantiate appreciable interaction of "iron d orbitals and empty orbitals of the cyclopropenium moiety". We suggest that in III the contribution of the diphenylcyclopropenium group to delocalization of the positive charge of the cation is much greater than that of the ferrocenyl moiety.^{6b} Consequently, the carbenium ion stabilization mechanism involves less interaction between the fulvene system and the iron atom d-orbital electrons, resulting in less bending of $\text{C}(23)$ toward the Fe atom. By the same argument it can be stated that the order of increasing $\text{Fe}\cdots\text{C}(\text{exocyclic})$ distance in the series of organometallic carbenium ions $\text{IV} < \text{I} < \text{II} < \text{III}$ is indicative of the degree of participation of the organometallic moiety in the delocalization of the positive charge. We venture to predict that in α -ferrocenyl carbenium ions with only one ferrocenyl moiety, instead of two as in I, the bending of the exocyclic carbon atom toward the iron atom should be greater than that found in I; indeed the bending may even approach that found in diphenylfulvenechromium tricarbonyl.²⁴

We note that in cations I, II, and V the two analogous $\text{Fe}\cdots\text{C}^+$ distances are different, despite the formal symmetry of the cation. Laing et al.⁷ ascribe this sort of difference to packing effects; more generally the problem is that of Buridan's ass, recently considered quantum mechanically.²⁹

B. The C–C–C Angle at the Formally Positive Carbon Atom in Carbenium Cations. The angle $\angle \text{C}(1)\text{--C}(21)\text{--C}(11)$ in diferrocenylmethyl cation is $127(1)^\circ$; that at the central (formally positive) carbon of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2(\text{C}_3\text{H}_5)^+$ is 126° ; no value was given for bis(cyclobutadienetricarbonyliron)methyl cation.⁵ In cations which do not contain metal atoms, these angles do not differ from 120° [(biphenyl-4,4'-bis(diphenylmethyl) dihexachloroantimonate $[\text{C}_{38}\text{H}_{28}^{2+}2(\text{SbCl}_6)^-]$ ³⁰ and tetra-*p*-anisylethylene bis(dichloriodate)³¹]; McKechnie and Paul³⁰ also give references to a number of earlier determinations of the structures of triphenylmethyl salts where the cation has threefold symmetry of one kind or another, and hence where the C–C–C angles at the formally positive carbon atom will be 120° . Thus a difference in the two sets of bond angles appears to be established; however, we do *not* ascribe this difference to the presence of metal atom, especially as we note that the analogous angle in diferrocenyl ketone is $126(1.5)^\circ$. The organometallic cations and diferrocenyl ketone have unsymmetrical arrangements of substituents about the exocyclic carbon atom, whereas the cations of the second group have symmetrically substituted formally positive carbon atoms. An unsymmetrical arrangement of substituents leads to a departure from pure sp^2 hybridization. In terms of the main thrust of the present paper, this is an essentially irrelevant effect.

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Supplementary Material Available: Anisotropic temperature factors and structure factors (15 pages). Ordering information is given on any current masthead page.

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