

Fig. 3. The torsion angles ($^{\circ}$) about the (a) N—C(15), (b) N'—C'(15), (c) C(15)—C(16), and (d) C'(15)—C'(16) bonds in *N*-benzylphenothiazine.

cule *B*; however, the two planes make an angle of 15° in molecule *A*. The packing of the molecules in the crystal is determined by the van der Waals interaction. The closest intermolecular distances are 3.56 and 3.60 Å between C(8) and C(15) and between C(9) and C(15) respectively.

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Ferrocenylmethylpyridinium Iodide*

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Abstract. $(C_5H_5)Fe(C_5H_4)CH_2(NC_5H_5)^+I^-$, monoclinic, $P2_1/c$, $a = 10.125(3)$, $b = 12.713(3)$, $c = 12.231(3)$ Å, $\beta = 98.24(2)^{\circ}$, $D_c = 1.727$ g cm $^{-3}$, $Z = 4$ [$23.5 \pm 1.0^{\circ}C$, $\lambda(Mo K\alpha) = 0.7107$ Å]. The cyclopentadienyl rings are within 1.2° of parallelism and about 4.2° from eclipse. The iodide ion is 3.73 Å from the N atom and 3.58 Å from an α -C atom of the pyridinium ring, in a position almost the same as that

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of the iodide ion relative to the pyridinium ring in 1-methylnicotinamide iodide.

Introduction. A crystal specimen of the dark amber material‡ with dimensions about $0.06 \times 0.5 \times 0.6$ mm was used to obtain all diffraction data. From the Laue symmetry, $2/m$, and the systematic absences, $h0l$ for odd l and $0k0$ for odd k , the space group was uniquely established to be $P2_1/c$. The cell parameters were calculated by the method of least squares from angle data for 12 Mo $K\alpha$ reflections in the 2θ range 35 to

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40°. The Oak Ridge computer-controlled diffractometer (Busing, Ellison, Levy, King & Roseberry, 1968) was used to record intensities for a total of 3602 symmetrically independent reflections in the 2θ range 0 to 55°. The recording technique, which involved both ω and 2θ scans, and the preliminary data processing were essentially as described by Hall & Brown (1971). Absorption correction factors calculated by the Busing & Levy (1957) method were applied ($\mu = 29.9 \text{ cm}^{-1}$; minimum correction factor for $F_o^2 = 1.19$, maximum = 4.46). The variances of the F_o^2 data were corrected empirically by the addition of the term $(0.03 F_o^2)^2$ to the variance from the counting statistics (Peterson & Levy, 1957). The weights used later in least-squares refinement were the reciprocals of these corrected variances.

The structure determination, by the heavy-atom method, was straightforward, as was the subsequent refinement by Fourier and least-squares methods. At an advanced stage of the refinement, the 16 H atoms were included in the structure factor calculations in chemically sensible computed positions with reasonable isotropic thermal parameters (4 to 7 Å²), but their parameters were never adjusted.* In the final refinement cycles all 23 reflections with $\theta \leq 5^\circ$ were omitted

* At the suggestion of a referee, we add the following information. Each of the 14 H atoms on the three rings was placed 0.97 Å from a C atom along the external extension of the bisector of the C—C—C angle at that C atom. The other two H atoms were placed 0.99 Å from C(11) to complete the tetrahedron around that atom, with a H—C—H angle of 109° 28' and with the four C—C—H and N—C—H angles equal. The distances 0.97 and 0.99 Å were chosen consistent with the apparently short C—H distances usually found in precise X-ray crystal-structure analyses.

as having unreliable F_o^2 values resulting from improperly determined backgrounds, and all 518 reflections with $\theta \geq 25.24^\circ$ and F_o^2 values less than 2σ were also omitted. The final measures of goodness of fit* for the 3061 reflections included were: $R(F) = 0.072$; $R(F^2) = 0.050$; $R_w(F^2) = 0.077$; $\sigma_1 = 1.21$ (standard deviation of an observation of unit weight). For the 2511 F_o^2 values included which were greater than $\sigma(F_o^2)$, $R(F)$ was 0.054. There was no indication of extinction. The scattering factors used were: $f(\text{I}^-)$ from Cromer & Waber (1965); $f(\text{Fe})$, $f(\text{N})$, and $f(\text{C})$ from Hanson, Herman, Lea & Skillman (1964); $f(\text{H})$ from Stewart, Davidson & Simpson (1965); $\Delta f'$ and $\Delta f''$ for I⁻ and Fe from Cromer & Liberman (1970). The final parameters of the 19 atoms of the asymmetric unit other than H atoms are given in Table 1.†

Discussion. The intramolecular distances and angles, shown in Fig. 1(a),(b), are normal and need not be discussed in detail. The average C—C bond length in the substituted five-ring is 1.412 Å (r.m.s.d. 0.007 Å), and the average in the other five-ring is 1.389 (r.m.s.d. 0.011) Å, the difference being consistent with the greater thermal motion of the second ring (see the thermal ellipsoids of Fig. 2).

* These measures of fit are explicitly defined by Hall & Brown (1971) and elsewhere.

† A table of the fixed parameters used for the H atoms and a list of structure factors have been deposited with the British Library Lending division as Supplementary Publication No. SUP 32101 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Fractional coordinates and thermal parameters, β_{ij} , (all $\times 10^5$) for the crystal structure of ferrocenylmethylpyridinium iodide

H atom parameters are not included. The temperature factor is of the form:
 $\exp(-h^2\beta_{11} - k^2\beta_{22} - l^2\beta_{33} - 2hk\beta_{12} - 2hl\beta_{13} - 2kl\beta_{23}) \times 10^{-5}$.

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
I	15238 (04)	26815 (03)	47973 (02)	2122 (07)	749 (03)	804 (03)	-111 (03)	528 (03)	-82 (02)
Fe	62202 (06)	11764 (04)	20368 (05)	936 (08)	482 (04)	816 (05)	-46 (04)	383 (05)	-24 (03)
C(1)	48035 (46)	692 (32)	15946 (33)	1227 (62)	611 (30)	830 (35)	-211 (37)	382 (37)	-119 (26)
C(2)	60576 (53)	-4154 (32)	18453 (43)	1439 (71)	516 (30)	1333 (51)	30 (39)	810 (49)	-60 (31)
C(3)	65768 (46)	-1657 (37)	29494 (45)	1019 (61)	771 (37)	1305 (51)	212 (39)	391 (46)	360 (34)
C(4)	56306 (44)	4685 (32)	33786 (34)	934 (55)	714 (32)	793 (34)	-47 (36)	193 (36)	132 (27)
C(5)	45368 (39)	6302 (28)	25469 (31)	817 (50)	497 (26)	692 (30)	-49 (30)	289 (33)	42 (22)
C(6)	62769 (68)	21379 (41)	7252 (42)	2040 (97)	746 (39)	1063 (45)	-213 (52)	506 (53)	131 (33)
C(7)	75267 (65)	17140 (39)	10426 (52)	1641 (84)	758 (39)	1437 (58)	-63 (49)	1039 (58)	-24 (38)
C(8)	79559 (54)	19971 (44)	21201 (59)	1191 (75)	907 (45)	1741 (70)	-326 (46)	439 (59)	94 (44)
C(9)	69685 (81)	26225 (41)	24790 (50)	2543 (116)	735 (41)	1284 (57)	-705 (60)	827 (68)	-275 (39)
C(10)	59094 (64)	27054 (38)	16070 (65)	1644 (85)	504 (31)	1940 (74)	75 (44)	915 (67)	242 (42)
C(11)	33081 (41)	12368 (31)	26645 (33)	922 (51)	622 (30)	859 (34)	19 (33)	307 (33)	46 (25)
N	22289 (33)	5128 (23)	29062 (27)	771 (41)	542 (23)	776 (28)	36 (25)	265 (28)	69 (20)
C(12)	12395 (49)	2821 (38)	21290 (38)	977 (59)	844 (38)	993 (42)	-19 (41)	104 (42)	77 (31)
C(13)	2573 (51)	-4076 (44)	23392 (50)	1041 (68)	960 (45)	1610 (63)	-209 (47)	-82 (50)	8 (43)
C(14)	3277 (57)	-8564 (38)	33603 (60)	1251 (75)	623 (35)	1861 (71)	78 (48)	750 (61)	208 (42)
C(15)	13456 (59)	-5967 (38)	41505 (43)	1504 (75)	781 (39)	1139 (47)	83 (46)	691 (50)	208 (34)
C(16)	22950 (45)	997 (33)	39162 (34)	1263 (62)	681 (33)	831 (37)	118 (37)	346 (38)	148 (27)

Each cyclopentadienyl ring displays essentially ideal D_{5h} symmetry to the precision of this determination. No atom of either ring is displaced more than 0.006 Å from the least-squares best plane through the ring. C(11) is displaced 0.029 Å from the best plane through C(1), C(2), ... C(5), on the side opposite the Fe. The two ring planes are inclined at 1.2° to each other, and the rings are twisted from the eclipsed conformation by about 4.2° around the axis through their centroids (see Fig. 1). The slight departure from eclipse, along with similar results from this laboratory for *N*-formylaminomethylferrocene (Hall & Brown, 1971) and for 1,1'-diethoxyoctachloroferrocene (Brown, 1971; Brown, Hedberg & Rosenberg, 1972), supports the conclusion (Palenik, 1970; Krukonis, Silverman &

Yannoni, 1972) that the eclipsed form is energetically preferred for unbridged ferrocene molecules.

Because pyridinium iodides show charge-transfer bands in their electronic spectra [for references see Mackay & Poziomek (1972), Freeman & Bugg (1974)], the spatial relationships of the iodide ions to the pyridinium ions are additional features of interest in this structure, beyond those connected with the ferrocenyl moiety. The packing of the ions in the crystal is shown in the stereoscopic Fig. 3. Details of the closest contacts of I ions with atoms of the pyridinium ion are shown in Fig 4. The normal projection of the I ion on the ring best plane lies well outside the ring. The position of the I ion relative to the pyridinium ion is almost the same as in 1-methylnicotinamide iodide (Freeman & Bugg, 1974), where the $N \cdots I$ and $C_\alpha \cdots I$ distances are 3.739 and 3.537 Å and the displacement of the I ion from the plane is 3.42 Å, to be compared with our distances 3.73, 3.58, and 3.36 Å (Fig. 4). The $C_\alpha \cdots I$ distances in the two pyridinium iodides may suggest ef-

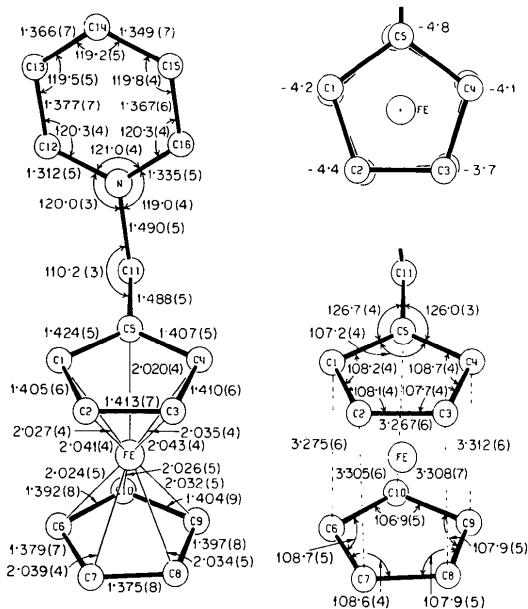


Fig. 1. The structure of the ferrocenylmethylpyridinium cation. Interatomic distances (Å) and angles ($^\circ$), and conformation angles ($^\circ$) (Klyne & Prelog, 1962) for pairs of C atoms about the axis through the centroids of the two five-carbon rings.

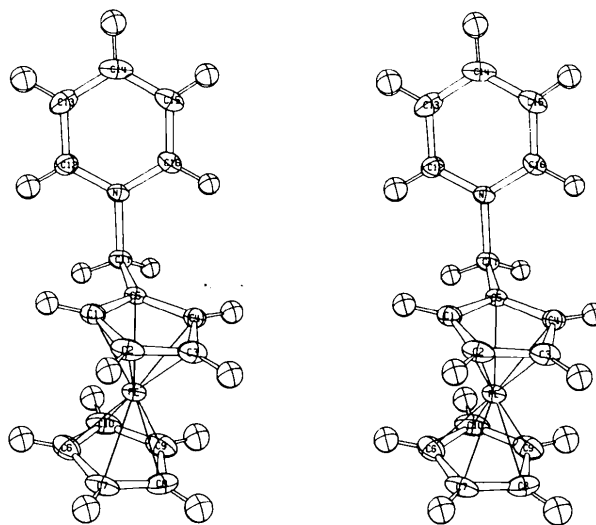


Fig. 2. Stereoscopic view of the cation in ferrocenylmethylpyridinium iodide, showing the ellipsoids of 20% probability (Johnson, 1970).

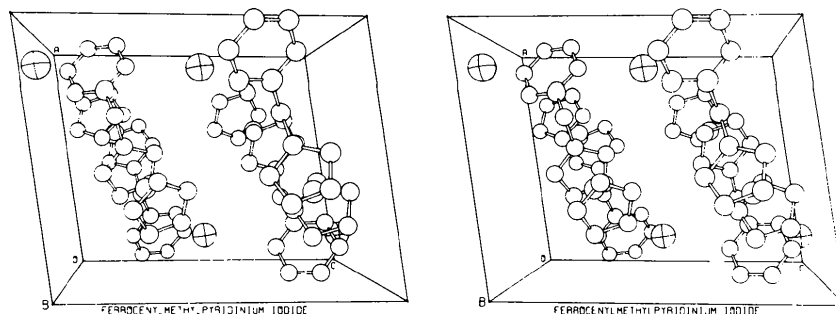


Fig. 3. Stereoscopic view of the crystal structure of ferrocenylmethylpyridinium iodide. Fe-C bonds and H atoms are omitted for clarity. I ions are represented by large circles with crossed arcs.

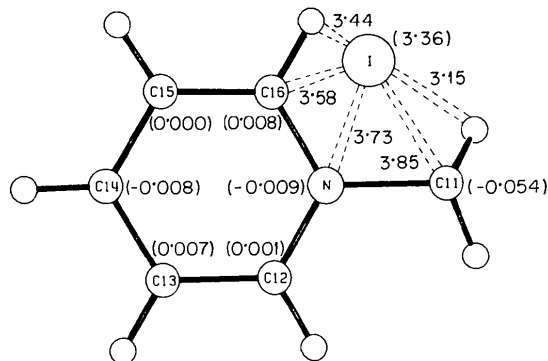


Fig. 4. Closest approaches (Å) of the I ion to atoms of the pyridinium cation. Numbers in parentheses are displacements (Å) of atoms from the least-squares best plane through the six-ring atoms.

fects of charge transfer, since the normally expected van der Waals separation is about 3.85 Å; however, a distance C...I of 3.57 Å has been found in tri(*p*-iodophenyl)amine (Freeman, Brown & Levy, 1969*a,b*; Freeman, 1970), where charge transfer is not involved. Freeman & Bugg's (1974) remark relative to 1-methylnicotinamide iodide that 'it is likely that the observed geometrical arrangement of iodide relative to pyridinium ion is dictated primarily by classical Coulombic and van der Waals forces' seems equally applicable to ferrocenylmethylpyridinium iodide.

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3-Thiocyanato-2-thiocyanatomethyl-1-propen

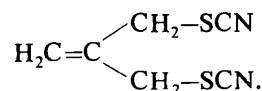
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Abstract. C₆H₆S₂N₂, *M_r* = 170.3, monoclinic, *P*2₁/*c* (No. 14), *a* = 7.994 (4), *b* = 9.676 (5), *c* = 11.336 (6) Å, β = 101.91 (1)°; *Z* = 4, *U* = 866.1 Å³, *D_m* = 1.28 (1), *D_x* = 1.30 g cm⁻³; μ(Cu Kα) = 48.8 cm⁻¹, *F*(000) = 352; m.p. 65–66°C. The structure was solved by Patterson and Fourier syntheses. An *R* value of 0.09 was obtained for 713 independent reflexions

after block-diagonal least-squares refinement. The structural formula of the molecule is:



The most important feature of the structure is the