model under the least strain but even so we would consider that the distance between the hydrogen atoms on C(11) and C(5) and the distance between the hydrogen atoms on C(11) and the β-methyl group are smaller than would be normally acceptable. However, bond-angle measurements show that these close contacts are relieved in the crystal by increasing the C(11)–C(6)–O angle from the normal trigonal value to 124·4°.

In summary, there would seem to be good reasons for supposing that the conformation of OMBEM TM1, as described by the four torsional angles discussed above, is determined primarily by intramolecular forces. This would lead us to expect that the molecule would adopt a very similar conformation *in vivo*. In support of this view it has been found that molecules of β-methylphenylcholine ether in crystals of the bromide have an almost identical structure (manuscript in preparation). Moreover, both these compounds adopt a conformation in which the atoms C(5)–O–C(6)–C(7) are coplanar or very nearly so, and the hypothesis of Clark & Williams (1967) that their lack of pharmacological activity arises because they cannot adopt such a conformation now seems untenable.

We wish to thank Dr E. R. Clark for suggesting the problem and for valuable discussions, Mr D. Akrigg

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The Crystal Structure of β-Methylphenylcholine Ether Bromide

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β-Methylphenylcholine ether bromide, $C_{12}H_{20}ON^+Br^-$, crystallizes as the hemihydrate in the orthorhombic space group $Pna2_1$ with 8 molecules in the unit cell (two molecules per asymmetric unit). The cell parameters are $a = 14·500$ (2), $b = 28·388$ (4) and $c = 6·829$ (1) Å. The structure was solved by three-dimensional Patterson and Fourier syntheses using 2505 independent reflexions collected on a computer-controlled four-circle diffractometer. It was refined by block-diagonal least-squares calculations to a final R index of 0·081. Both molecules in the asymmetric unit adopt a conformation in which the N–C–C–O system is positive synclinal (*gauche*) and the remaining torsional angles are close to 180°, although there are small differences in detail between the two molecules.

Introduction

A number of phenylcholine ether bromides are currently under investigation in our laboratory. These include two highly potent ganglion stimulants, phenylcholine ether bromide (TM1) and o-methylphenylcholine ether bromide (OME TM1), and two β-substituted derivatives which show no such activity, β-methylphenylcholine ether bromide (BEM TM1) and o-methyl β-methylphenylcholine ether bromide (OMBEM TM1) (Hey,

1952; Clark & Jana, 1966; Clark, Dawes & Williams, 1968).

It is hoped that these structural studies will help towards an understanding of why these compounds have such different pharmacological properties. X-ray intensity data have been collected for all these compounds and the structure of OMBEM TM1 has already been solved (see previous paper). The structures for BEM TM1 described below are similar to OMBEM TM1 although there are differences in detail.

Experimental

Crystal data

$C_{12}H_{20}ON^+Br^-.\frac{1}{2}H_2O$; M.W. 283.

Source: Dr E. R. Clark; recrystallized by slow evaporation from an undried mixture of propan-1-ol and carbon tetrachloride at room temperature.

Crystal system: orthorhombic.

Space group: $Pna2_1$; $a=14\cdot500$ (2), $b=28\cdot388$ (4), $c=6\cdot829$ (1) Å; $V=2811$ Å^3, $Z=8$, $D_c=1\cdot338$, $D_m=1\cdot314$ g cm^{-3} (density measured by flotation in a mixture of carbon tetrachloride and ethyl acetate).

Radiation: Graphite-monochromatized Cu $K\alpha$, $\lambda=1\cdot54051$ Å.

Three-dimensional intensity data were measured by the moving-crystal moving-counter technique in the range $3°\le\theta\le70°$. The crystal was mounted with its c axis coincident with the φ axis of an Enraf–Nonius CAD-4 diffractometer. After correction of the intensity data for Lorentz and polarization effects, a statistical analysis (Wilson, 1942) was carried out to determine a mean temperature factor and an absolute scale factor. No absorption corrections were made.

Systematic absences found on Weissenberg photographs were consistent with the space groups $Pna2_1$ or $Pnam$. A study of the Harker lines and sections of the three-dimensional Patterson synthesis and the statistical averages of the intensity data (Table 1) indicated that the crystal was non-centrosymmetric and the space group $Pna2_1$ was chosen. This space group requires four equivalent positions whereas there are eight molecules in the unit cell and thus two molecules per asymmetric unit.

Table 1. *Statistical averages and distributions of* $|E|$
(Karle, Dragonette & Brenner, 1965)

	Experimental	Centro-symmetric	Non-centro-symmetric
$\langle|E|\rangle$	0·874	0·798	0·886
$\langle|E^2|\rangle$	0·783	0·968	0·736
$\langle|E^2|\rangle$	1·009	1·000	1·000
$\%|E|>3$	0·0	0·3	0·01
$\%|E|>2$	2·9	5·0	1·8
$\%|E|>1$	34·8	32·0	36·8

Structure determination and refinement

The positions of the two bromine atoms in the asymmetric unit were found from a study of the Patterson–Harker section $P(U,V,\frac{1}{2})$, and lines $P(U,\frac{1}{2},\frac{1}{2})$ and $P(\frac{1}{2},V,0)$. A three-dimensional Fourier synthesis was computed on the Leeds University 1906A computer by a modified version of a program originally written by Cruickshank, Pilling, Bujosa, Lovell & Truter

Table 2. *Fractional positional parameters of non-hydrogen atoms and their estimated standard deviations* $(\times 10^5)$

|	x/a	y/b	z/c
Molecule A			
Br	16614 (08)	38158 (05)	0
O	43270 (56)	35298 (28)	74216 (215)
N	37416 (50)	41449 (25)	40486 (133)
C(1)	28395 (65)	40478 (45)	50983 (224)
C(2)	39723 (79)	37410 (35)	27463 (233)
C(3)	36179 (87)	45810 (37)	29118 (313)
C(4)	44771 (61)	42453 (29)	55379 (159)
C(5)	49022 (113)	38315 (52)	65920 (252)
C(6)	45843 (78)	30955 (33)	81128 (200)
C(7)	39422 (84)	29089 (40)	93527 (236)
C(8)	41271 (108)	24813 (47)	2418 (199)
C(9)	49634 (98)	22538 (41)	99323 (246)
C(10)	55873 (92)	24486 (40)	86768 (246)
C(11)	54295 (79)	28538 (38)	77888 (223)
C(12)	55996 (103)	40298 (56)	80357 (266)
Molecule B			
Br	15436 (07)	3369 (04)	27441 (30)
O	35679 (41)	13081 (20)	49106 (124)
N	38813 (50)	6703 (29)	85422 (120)
C(1)	28725 (63)	7199 (37)	80509 (213)
C(2)	40967 (94)	9217 (52)	4745 (176)
C(3)	40824 (88)	1379 (39)	88788 (210)
C(4)	45150 (57)	8311 (35)	68948 (153)
C(5)	43531 (64)	13324 (33)	62197 (146)
C(6)	30557 (65)	17121 (29)	45702 (142)
C(7)	23315 (64)	16357 (35)	32962 (174)
C(8)	17776 (77)	20262 (40)	28363 (238)
C(9)	19708 (89)	24752 (45)	35110 (225)
C(10)	26868 (83)	25322 (34)	48212 (233)
C(11)	32627 (73)	21531 (35)	53101 (195)
C(12)	52005 (73)	14914 (43)	51239 (227)
Water molecule			
O	35791 (56)	99240 (35)	39468 (211)
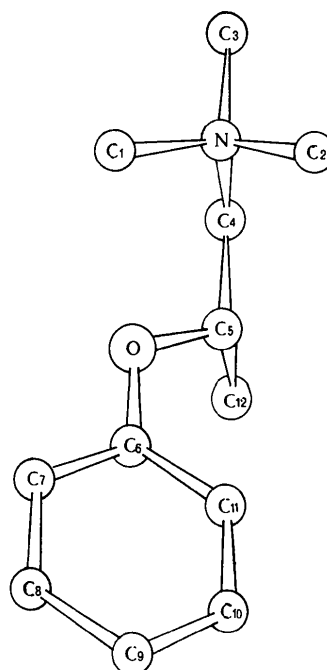
Fig. 1. Perspective view of the molecule showing the numbering of the atoms.

(1961) with the phase angles specified by the bromine atoms. The resultant synthesis revealed the positions of the remaining light atoms with the exception of the oxygen atom of the water molecule. Six cycles of structure-factor block-diagonal least-squares (SFLS) isotropic refinement gave a residual $R=0.172$. Six
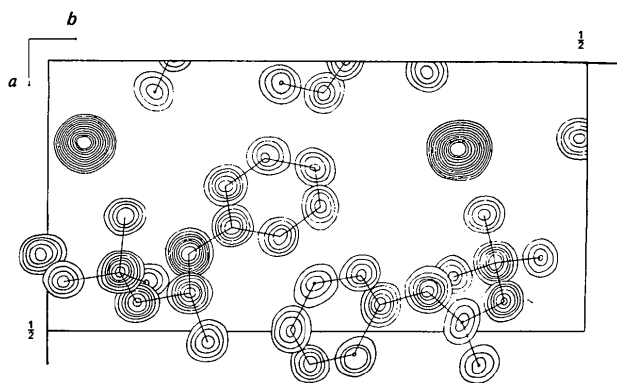

Fig. 2. Composite electron-density map of the asymmetric unit down the c axis.

more cycles of SFLS refinement using anisotropic temperature factors reduced the R value to 0·112.

At this stage a three-dimensional difference Fourier synthesis and a three-dimensional Fourier synthesis were computed in order to establish the positions of the hydrogen atoms. Both revealed a peak that was assumed to be the oxygen atom of one molecule of water of crystallization per asymmetric unit. This atom was introduced and three cycles of SFLS anisotropic refinement reduced the R value to 0·085. A three-dimensional difference Fourier map was computed and the positions of those hydrogen atoms not attached to the phenyl ring were found from this map. The positions of the hydrogen atoms attached to the phenyl ring were calculated assuming a C–H bond length of 1·0 Å. Three more cycles of SFLS refinement with anisotropic temperature factors for the non-hydrogen atoms, and isotropic for the hydrogen atoms gave an R value of 0·081.

The coordinates of the non-hydrogen atoms are given in Table 2 together with their estimated standard deviations. The anisotropic temperature factors are given in Table 3, and the positions and isotropic

Table 3. U_{ij}'s with standard deviations ($\times 10^4$)

Allowance was made for anisotropic vibration with

$$\exp\{-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+2klb^*c^*U_{23}+2lhc^*a^*U_{31}+2hka^*b^*U_{12})\}.$$

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
Molecule A						
Br	654 (06)	998 (08)	981 (09)	211 (17)	−394 (15)	−264 (11)
O	737 (47)	745 (46)	1662 (107)	705 (136)	−869 (141)	−446 (76)
N	478 (38)	467 (36)	611 (47)	−74 (73)	−81 (77)	36 (61)
C(1)	467 (49)	1055 (79)	781 (74)	−275 (155)	149 (123)	−98 (99)
C(2)	765 (67)	637 (54)	822 (76)	−233 (145)	−127 (148)	226 (96)
C(3)	894 (75)	555 (54)	1122 (107)	61 (167)	−424 (185)	95 (101)
C(4)	504 (45)	441 (42)	637 (60)	−220 (84)	−30 (87)	−95 (70)
C(5)	1242 (117)	1051 (98)	955 (108)	717 (173)	−1397 (201)	−792 (171)
C(6)	773 (64)	456 (45)	859 (85)	−70 (104)	−457 (129)	7 (86)
C(7)	693 (65)	728 (68)	1140 (114)	−924 (157)	−35 (143)	−129 (103)
C(8)	1305 (118)	936 (82)	522 (65)	−20 (135)	161 (154)	−541 (161)
C(9)	1163 (99)	695 (62)	823 (83)	−19 (143)	−747 (176)	−234 (130)
C(10)	778 (71)	623 (60)	1151 (110)	−389 (143)	−397 (163)	202 (108)
C(11)	738 (62)	754 (60)	713 (66)	149 (144)	−159 (145)	−84 (99)
C(12)	1015 (96)	1188 (101)	1030 (117)	202 (192)	−1125 (190)	−964 (170)
Molecule B						
Br	696 (05)	630 (05)	882 (07)	−158 (13)	33 (14)	−63 (09)
O	587 (33)	438 (29)	698 (43)	26 (65)	−377 (82)	57 (47)
N	458 (37)	659 (44)	490 (42)	16 (75)	59 (70)	−114 (68)
C(1)	475 (46)	714 (57)	891 (85)	61 (127)	−25 (115)	−199 (83)
C(2)	922 (85)	1165 (95)	462 (60)	54 (131)	20 (120)	−658 (147)
C(3)	830 (75)	663 (62)	746 (75)	227 (122)	10 (134)	123 (108)
C(4)	369 (40)	723 (56)	504 (50)	6 (93)	43 (79)	40 (76)
C(5)	511 (47)	572 (49)	488 (51)	68 (85)	−168 (83)	−125 (78)
C(6)	594 (48)	479 (42)	479 (53)	154 (81)	−16 (88)	101 (75)
C(7)	467 (45)	670 (55)	745 (74)	−104 (99)	−177 (97)	36 (83)
C(8)	705 (61)	790 (64)	761 (72)	180 (150)	−176 (143)	265 (101)
C(9)	742 (68)	763 (68)	968 (93)	249 (139)	−2 (148)	534 (116)
C(10)	878 (71)	486 (47)	932 (84)	−3 (122)	237 (160)	242 (96)
C(11)	668 (57)	585 (52)	692 (71)	62 (109)	−97 (114)	−1 (87)
C(12)	619 (56)	893 (71)	768 (76)	71 (143)	−13 (132)	−283 (104)
Water molecule						
O	613 (46)	1004 (64)	1415 (99)	−164 (146)	−139 (118)	−82 (84)

temperature factors of the hydrogen atoms in Table 4.*
The numbering of the atoms is shown in Fig. 1. The
bond lengths, bond angles and related e.s.d.'s were cal-
culated by a program written by Dr W. S. McDonald
and the results are shown in Tables 5 and 6. A com-
posite electron density map along the c axis is shown in
Fig. 2. The displacements of the phenyl ring atoms
from the plane of best fit are shown in Table 7.

Table 4. *Parameters of hydrogen atoms* ($\times 10^4$)

	x/a	y/b	z/c	U_{iso}
Molecule A				
H(C1)	2811	3775	5592	583
H'(C1)	2773	4241	5484	1196
H''(C1)	2312	3948	3984	600
H(C2)	3976	3311	3085	1574
H'(C2)	3258	3764	1562	943
H''(C2)	4573	3831	2039	1019
H(C3)	3111	4566	1706	827
H'(C3)	4059	4662	1613	1099
H''(C3)	3576	4890	3973	429
H(C4)	4384	4492	7088	1283
H'(C4)	5042	4337	4794	654
H(C5)	4902	3765	5380	801
H(C7)	3285	3093	9660	125
H(C8)	4058	2359	1224	965
H(C9)	4796	1972	1118	330
H(C10)	6235	2252	8399	753
H(C11)	5623	3193	6748	437
H(C12)	5379	4152	8523	1332
H'(C12)	6000	4099	7077	1029
H''(C12)	5361	3567	8829	857
Molecule B				
H(C1)	2672	465	6742	470
H'(C1)	2898	1020	7974	551
H''(C1)	2655	654	9294	469
H(C2)	3749	1117	1372	1409
H'(C2)	3973	571	1093	562
H''(C2)	4686	1006	1564	1499
H(C3)	4786	47	9730	685
H'(C3)	3505	50	9800	729
H''(C3)	3771	9964	7639	544
H(C4)	5101	869	7774	343
H'(C4)	4305	656	5460	841
H(C5)	4179	1532	7315	258
H(C7)	2174	1280	2721	581
H(C8)	1149	2000	1908	299
H(C9)	1532	2772	3077	523
H(C10)	2849	2886	5354	370
H(C11)	3874	2181	6263	496
H(C12)	5173	1597	4248	1052
H'(C12)	5306	1056	4640	1467
H''(C12)	5644	1533	6064	455
Water molecule				
H(W)	3345	9580	5024	877
H'(W)	3067	89	4046	1237

Atomic scattering factors were taken from *Interna-
tional Tables for X-ray Crystallography* (1962). The

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* The table of structure factors has been deposited with the
British Library Lending Division as Supplementary Publica-
tion No. SUP 30306 (50 pp., 1 microfiche). Copies may be
obtained through the Executive Secretary, International Union
of Crystallography, 13 White Friars, Chester CH1 1NZ,
England.

Table 5. *Bond lengths and estimated standard deviations*
(*in parentheses* $\times 10^3$)

	Molecule A	Molecule B
C(1)—N	1·517 (13) Å	1·507 (12) Å
C(2)—N	1·489 (14)	1·532 (15)
C(3)—N	1·472 (16)	1·556 (14)
C(4)—N	1·501 (12)	1·523 (12)
C(4)—C(5)	1·509 (17)	1·514 (14)
C(5)—C(12)	1·520 (18)	1·508 (15)
C(5)—O	1·323 (18)	1·449 (11)
C(6)—O	1·372 (13)	1·386 (10)
C(6)—C(7)	1·365 (20)	1·381 (14)
C(7)—C(8)	1·384 (20)	1·404 (14)
C(8)—C(9)	1·390 (22)	1·384 (19)
C(9)—C(10)	1·364 (23)	1·380 (20)
C(10)—C(11)	1·320 (18)	1·402 (15)
C(11)—C(6)	1·422 (16)	1·383 (14)

Table 6. *Bond angles and standard deviations*
(*in parentheses*)

	Molecule A	Molecule B
C(6)—C(7)—C(8)	118·71 (1·06)°	116·85 (0·87)°
C(7)—C(8)—C(9)	120·66 (1·15)	122·46 (0·97)
C(8)—C(9)—C(10)	119·07 (1·09)	118·43 (0·96)
C(9)—C(10)—C(11)	121·81 (1·12)	120·82 (0·97)
C(10)—C(11)—C(6)	119·89 (1·10)	118·58 (0·92)
C(11)—C(6)—C(7)	119·80 (0·97)	122·51 (0·79)
C(11)—C(6)—O	127·92 (0·97)	124·85 (0·75)
C(7)—C(6)—O	112·12 (0·98)	112·53 (0·72)
C(6)—O—C(5)	123·90 (1·03)	119·02 (0·65)
O—C(5)—C(12)	112·42 (1·21)	110·38 (0·81)
O—C(5)—C(4)	116·79 (1·03)	105·36 (0·65)
C(12)—C(5)—C(4)	107·02 (1·02)	107·82 (0·77)
C(5)—C(4)—N	117·75 (0·73)	114·40 (0·70)
C(4)—N—C(1)	109·09 (0·81)	113·15 (0·75)
C(4)—N—C(3)	106·51 (0·78)	106·69 (0·75)
C(4)—N—C(2)	113·03 (0·71)	111·94 (0·71)
C(1)—N—C(3)	107·27 (0·87)	107·78 (0·74)
C(1)—N—C(2)	109·64 (0·79)	110·24 (0·86)
C(3)—N—C(2)	111·10 (1·05)	106·67 (0·88)

Table 7. *Least-squares planes referred to standard
orthogonal axes and displacements of atoms from the
planes*

Phenyl ring A: $0·4125X + 0·4899Y + 0·7680Z = 11·3023$

	Displacement (Å)
C(6)	−0·0003
C(7)	0·0064
C(8)	−0·0113
C(9)	0·0102
C(10)	−0·0042
C(11)	−0·0008

Phenyl ring B: $0·5960X + 0·1866Y − 0·7809Z = 1·1157$

	Displacement (Å)
C(6)	0·0051
C(7)	−0·0079
C(8)	0·0186
C(9)	−0·0263
C(10)	0·0234
C(11)	−0·0128

weighting scheme used in the final stages of refinement
was:

$$\sqrt{w} = \left[1 + \left(\frac{|F_o| - P_2}{P_1}\right)^2\right]^{-1/2} \text{(Mills \& Rollett, 1961)}$$

where $P_1 = |F\text{max}|/10$, $P_2 = |F\text{max}|/40$.

There were 413 reflexions which were accessible but too weak to be measured. These were assigned an intensity equal to one half of the minimum measured intensity and a calculation of the structure factors including these reflexions gave a residual $R = 0.086$.

Discussion

The two molecules (A and B) in the asymmetric unit have approximately the same conformation and a perspective view of one of the mirror image forms of the conformation is shown in Fig. 1. This structure is conveniently described by the torsional angles $\tau_0 [C(7)-C(6)-O-C(5)]$, $\tau_1 [C(6)-O-C(5)-C(4)]$, $\tau_2 [O-C(5)-C(4)-N]$, and $\tau_3 [C(5)-C(4)-N-C(3)]$. These are listed in Table 8 and compared with the corresponding angles in OMBEM TM1 and β-methylacetylcholine iodide (Chothia & Pauling, 1969).

The group of atoms O-C(5)-C(4)-N adopts the *gauche* conformation but the value of τ_2 of 51.6° in BEMTM1(A) is one of the lowest yet observed in acetylcholine-like compounds. $N^+ \rightarrow O$ distances of 3.01 Å (A) and 3.10 Å (B) might indicate that this *gauche* conformation is stabilized by electrostatic forces (Sundaralingam, 1968). In molecule B the C(1) $\rightarrow$ O distance of 2.90 Å possibly suggests a hydrogen bond and the difference Fourier maps show a hydrogen atom to be in a good position for the formation of such a bond. This is not the case for molecule A [C(1) $\rightarrow$ O = 3.05 Å]. The C(6)-O bond lengths of 1.372 Å (A) and 1.386 Å (B) indicate partial double-bond character of this bond, which is confirmed by the near planarity of the Ph-O-C(5) system and a tendency towards sp^2 hybridization of the oxygen atom [C(6)-O-C(5) = 123.9° in molecule A and 119.0° in molecule B]. The torsional angle τ_1 is $-167.5°$ in molecule A and $-158.3°$ in molecule B. These values are reasonably close to those found in acetyl β-methylcholine and OMBEM TM1 but different from those found in non-β-substituted derivatives. This is no doubt due to steric interference of the β-methyl group (Chothia & Pauling, 1969). It would appear that the tendency towards planarity of the Ph-O-C(5) system has resulted in some close contacts which have been relieved by increasing the C(11)-C(6)-O angle from the normal trigonal value to 127.9° in molecule A and 124.9° in molecule B.

Although there are only small structural differences

between molecules A and B these are perhaps worth some discussion since they seem to follow a consistent pattern. Apart from the aromatic ring and the bonds C(5)-C(12) and C(1)-N, all bonds in molecule A are shorter than the corresponding bonds in molecule B (by an average of 0.05 Å or $\sim 3\sigma$). Moreover, in molecule A the bond angles O-C(5)-C(4) = 116.8° and C(5)-C(4)-N = 117.8° suggest a tendency towards the trigonal form for the atoms C(5) and C(4). Thus, there would appear to be some electron delocalization along the whole chain of molecule A. The largest difference in bond lengths occurs between atoms C(5) and O [C(5)-O = 1.323 Å (A) and 1.449 Å (B)]. Manual attempts to place C(5) of molecule A in the expected position corresponding to that of C(5) in molecule B were unsuccessful. The refinement procedure always brought this atom back to the position given in Table 2.

In an attempt to find an explanation for these small structural differences the near-environment of each molecule was examined. The most obvious differences would appear to be the relationship of the N atom in each molecule to its neighbouring six bromine ions and one water molecule; in particular, the water molecule is much closer to N(B) (N $\rightarrow$ O = 3.81 Å) than to N(A) (N $\rightarrow$ O = 5.27 Å).

Conclusion

The considerable similarity between the overall structures of BEMTM1(A), BEMTM1(B), OMBEM TM1, and acetyl β-methylcholine would suggest that this conformation (designated *trans-trans-gauche-trans* or TTGT) lies in a deep minimum in the potential energy surface, especially since the crystal packing is entirely different in each case. It is interesting to note that the TTGT system is one of the four conformations calculated to lie in potential energy minima for acetylcholine (Liquori, 1968). These results for the phenylcholine ethers are confirmation of the currently-held belief that the TTGT system represents the *in vivo* structure for β-substituted acetylcholine-like compounds. The situation is not nearly so clear in non-β-substituted compounds where a variety of conformations have been observed. Our preliminary results for phenylcholine ether bromide indicate a TTTT structure similar to that in one of the molecules in the asymmetric unit of acetyl α-methylcholine iodide (Chothia & Pauling, 1969).

Table 8. *Torsional angles*

Molecule	τ_0 C(7)-C(6)-O-C(5)	τ_1 C(6)-O-C(5)-C(4)	τ_2 O-C(5)-C(4)-N	τ_3 C(5)-C(4)-N-C(3)
BEMTM1 (A)	−163.3	−167.5	51.6	166.0
BEMTM1 (B)	180.0	−158.3	80.7	−174.3
OMBEMTM1	179.3	−156.9	85.7	−174.7
Acetyl β-methylcholine iodide	175	−147	85	—

For ease of comparison with other molecules the angles listed above for BEMTM1 refer to the mirror-image forms of the molecules described by the coordinates given in Table 2.

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Note added in proof:- The structure of TM1 has been congrmed as TTTT. The structure of ome TM1 has recently been determined as TTGT (manuscripts in preparntion).

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The Structure of Bis-(3,5-dimethyl-1,2-dithiolium) Tetrachloroferrate(II): a Comparison of Structural Details Derived from Two Independent Diffractometer Analyses

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Results from two independent X-ray diffraction studies are discussed. Both analyses are based on three-dimensional diffractometer data with least-squares refinement of the scattering model. In other details the experimental and refinement techniques employed are substantially different. The mean difference between corresponding parameters derived from the two analyses is *ca.* $1 \cdot 2\sigma$. Terminal *R* values are 0·039 (MRR) and 0·061 (FMN), respectively. Similar agreement is observed between the two sets of $F_{obs} [R(F_o) = 0.069]$ and the two sets of $F_{calc} [R(F_c) = 0.054]$. The crystals are monoclinic, space group $C2/c (C_{2h}^6$, No. 15), with $a = 17.68$ (1), $b = 7.65$ (1), $c = 15.80$ (1) Å, $\beta = 122.0$ (1)° (mean values) and $Z = 4$. The structure comprises discrete 3,5-dimethyl-1,2-dithiolium $[= (SacSac)^+ = (C_5H_7S_2)^+]$ cations and $[FeCl_4]^{2-}$ anions. The tetrachloroferrate(II) ions lie on the twofold rotation axes and therefore have exact C_2 symmetry, but deviate markedly from the free ion (T_d) symmetry. Charge transfer, associated with close contacts between each $Fe^{II}Cl_4^{2-}$ ion and two pairs of dithiolium cations, results in the intense broad absorption band (centred at *ca.* 20 000 cm^{-1}) in the reflectance spectrum.

Introduction

At the time when the present work was initiated independently in Sheffield and Sydney, there was much interest in 'model' transition metal complexes for non-haem iron–sulphur proteins such as rubredoxin and the ferredoxins. In this context our preliminary results

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(Mason, McKenzie, Robertson & Rusholme, 1968; Freeman, Milburn, Nockolds, Hemmerich & Knauer, 1969) and related spectroscopic data (Heath, Martin & Stewart, 1969) were negative. They showed that there were no Fe–S bonds at all in a class of complexes which had been thought to contain thioacetylacetonato ligands bound to iron and to be related to the redox site in rubredoxin. Subsequently the structures of rubredoxin (*Peptococcus aerogenes*) and ferredoxin (*P. aerogenes*) were solved by Jensen and coworkers (Herriot, Sieker, Jensen & Lovenberg, 1970; Sieker, Adman & Jensen, 1972). The structural chemistry of these and related systems has recently been reviewed (Mason & Zubieta, 1973), and the present work turns out to be related in an unexpected way to the mechanisms of