Acta Cryst. (1975). B31, 1576

The Crystal and Molecular Structure of the Analgesic [*S*(*R*,*R*)]-Viminol; [α*S*(*R*,*R*)]-α-[(Di-s-butylamino)methyl]-1-(2-chlorobenzyl)-1*H*-2-pyrrolemethanol *p*-Hydroxybenzoate

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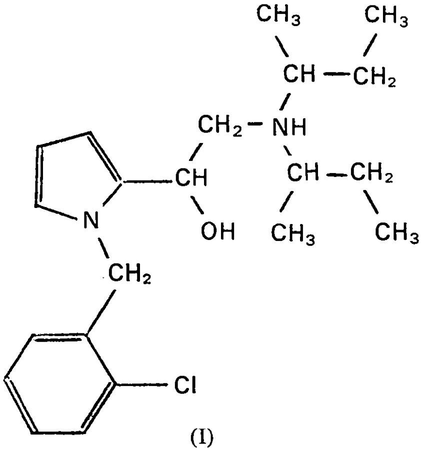
(*Received* 13 *November* 1974; *accepted* 20 *January* 1975)

Viminol, $(C_{21}H_{32}ClN_2O)^+.(C_7H_5O_3)^-$, is a narcotic analgesic or antagonist depending on stereochemistry. [*S*(*R*, *R*)]-viminol crystallizes in space group $P2_12_12_1$ with four formula units per cell. The cell dimensions are $a = 9{\cdot}5224$ (5), $b = 14{\cdot}3723$ (7), $c = 19{\cdot}4260$ (9). X-ray data were collected by an automatic diffractometer. The structure was solved by the calculation of structure invariants and has been refined to $R = 0{\cdot}029$ based on 2387 observed reflections. The absolute configuration was determined. The crystal is composed of chains of hydrogen-bonded anions with cations attached by two hydrogen bonds.

Introduction

Della Bella, Ferrari, Frigeni & Lualdi (1973) reported the properties of a new analgesic viminol or α-[(di-s-butylamino)methyl]-1-(2-chlorobenzyl)-1*H*-2-pyrrolemethanol (I) *p*-hydroxybenzoate.



(I)

While the stereochemistry of the s-butyl groups was essentially known from the synthetic method, nothing was known of the third asymmetric center, the carbon atom with the hydroxyl group. Pharmacologically there are two interesting stereo-isomers which, in terms of known stereochemistry and optical activity, are designated (−)*RR* and (−)*SS*. The first isomer is a narcotic analgesic of similar potency and addictivity to morphine and the second is an antagonist which depresses the activity of the first. The (−)*SS* isomer makes withdrawal symptoms in morphinized monkeys more severe but its clinical utility lies in its use in the racemate where it completely suppresses addiction liability in animals and men. The racemate is currently undergoing clinical trials (Della Bella, 1974).

The crystallographic study of viminol was undertaken to determine the stereochemistry of the unknown center, to confirm the structure and stereochemistry of the molecule and to obtain stereochemical information which may contribute to an understanding of the mode of action of narcotic analgesics since, among such compounds, viminol is one whose molecular formula cannot be manipulated to reproduce any significant part of the morphine skeleton. While both viminol and morphine possess a quaternary nitrogen atom and a benzene ring, the groups are not positioned similarly; the aromatic ring in viminol, unique among analgesics, has a chlorine substituent and the two properties do not together represent a criterion for analgesic activity.

Experimental

The crystal and experimental data are given in Table 1. Since preparation of crystals of a suitable size was somewhat difficult, X-ray work was commenced on the (−)*RR* isomer which first gave usable crystals. It was later possible to make crystals of the (−)*SS* isomer and the crystal data for this stereoisomer will be discussed later. Absorption corrections were not applied or deemed necessary since azimuthal scans of several reflections gave intensity variations of less than 5%.

The solution of the phase problem did not prove to be routine. A sharpened Patterson map allowed the deduction of a probable position for the chlorine atom (later shown to be correct) but none of the various attempts to phase the rest of the structure factors by means of the chlorine contribution gave a recognizable map. Standard symbolic addition (Karle & Karle, 1966) produced similar results as did attempts to extend the set phased by the chlorine atom using the tangent formula (Karle & Hauptman, 1956). The problem was finally solved *via* the MDKS formula of Hauptman (1971) which allowed the deduction of

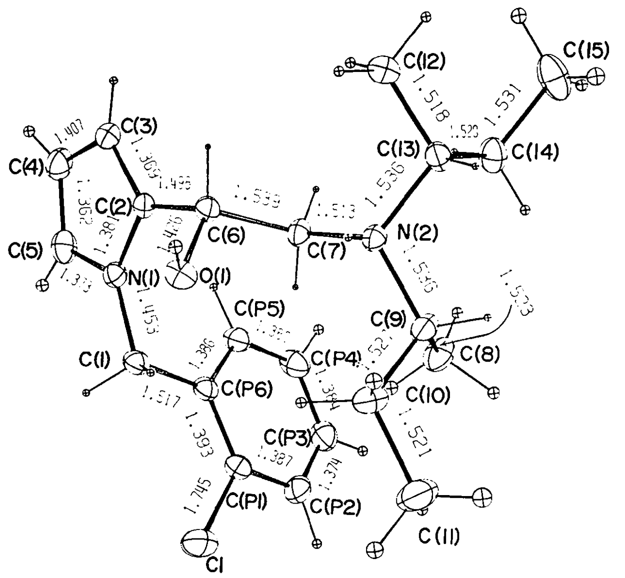


Fig. 1. The viminol cation in its crystal conformation. All lengths have e.s.d.'s in the range 0·002 to 0·004 Å. Thermal ellipsoids indicate 50% probability for heavier atoms. [*ORTEP* drawing (Johnson, 1965), also Figs. 2, 4, 5].

Table 1. *Crystal and experimental data*

[*S*(*R*,*R*)]-Viminol
Molecular formula: $(C_{21}H_{32}ON_2Cl)^+ . (C_7H_5O_3)^-$
Asymmetric unit weight = 501·1 Daltons
Habit: Orthorhombic prismatic (elongation; *a*)
Radiation: Cu $K\alpha$ (graphite monochromated $\lambda = 1{\cdot}5418$ Å)
Space group: $P2_12_12_1$ (No. 19)
Cell dimensions: From LS refinement of $\pm\theta$ data
$a = 9{\cdot}5224\ (5)$ Å
$b = 14{\cdot}3723\ (7)$
$c = 19{\cdot}4260\ (9)$
$V = 2658{\cdot}6$ Å^3
$Z = 4$
$D_m = 1{\cdot}24$ g cm^{-3}
$D_x = 1{\cdot}252$ g cm^{-3}
Temperature: *ca* 23 °C
$\mu = 15{\cdot}6$ cm^{-1}
Crystal size: sphere, $r = 0{\cdot}15$ mm
$\mu r = 0{\cdot}24$
Reflections: 2558 (171 unobserved: 1σ)
Maximum $\sin\theta/\lambda$: 0·61 Å^{-1}
Diffractometer: Enraf–Nonius CAD-4
LS weighting: After Peterson & Levy (1957): coefficient of I^2: 0·0004
R (observed reflexions only) = 0·029
Absolute configuration: [*S*(*R*,*R*)]
R value with [*R*(*S*,*S*)] configuration = 0·042
Unweighted *R* value ratio = 1·48 (weighted ratio identical)

Table 2. *Atomic parameters for the heavier atoms*

All values are multiplied by 10^4 except for *x*,*y*,*z* for chlorine which are multiplied by 10^5. E.s.d.'s refer to the last one or two figures, as appropriate. The temperature factor used had the form $\exp[-2\pi^2(\sum_i\sum_j U_{ij}a_ia_jh_ih_j)]$.

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl(1)	79322 (7)	−64342 (5)	−6842 (3)	789 (4)	828 (4)	514 (3)	−41 (4)	−150 (3)	−38 (3)
N(1)	7288 (1)	−5858 (1)	−2921 (1)	519 (10)	340 (8)	433 (8)	51 (8)	76 (8)	−3 (7)
N(2)	9341 (1)	−8763 (1)	−2941 (1)	380 (8)	338 (8)	386 (8)	32 (7)	18 (7)	32 (7)
O(1)	102 (1)	−6794 (1)	−2862 (1)	379 (7)	538 (8)	492 (8)	−11 (7)	26 (7)	−80 (7)
C(1)	7474 (2)	−5978 (1)	−2184 (1)	509 (12)	437 (10)	408 (10)	−25 (9)	81 (9)	−83 (8)
C(2)	7959 (2)	−6337 (1)	−3443 (1)	461 (10)	277 (9)	380 (9)	−30 (9)	44 (9)	9 (7)
C(3)	7447 (2)	−6004 (1)	−4053 (1)	662 (14)	401 (10)	427 (10)	−39 (10)	−45 (11)	53 (9)
C(4)	6440 (2)	−5314 (1)	−3909 (1)	720 (16)	478 (12)	658 (15)	29 (12)	−147 (14)	142 (12)
C(5)	6372 (2)	−5234 (1)	−3212 (1)	589 (14)	397 (11)	759 (16)	116 (11)	24 (13)	26 (11)
C(6)	9037 (2)	−7081 (1)	−3332 (1)	433 (10)	347 (9)	370 (10)	−3 (9)	61 (8)	−14 (8)
C(7)	8325 (2)	−7971 (1)	−3065 (1)	418 (10)	328 (9)	458 (10)	53 (9)	53 (9)	58 (9)
C(8)	7804 (2)	−9288 (1)	−1935 (1)	672 (15)	693 (16)	670 (14)	−4 (14)	210 (14)	209 (13)
C(9)	9291 (2)	−9148 (1)	−2204 (1)	558 (12)	457 (11)	452 (11)	101 (11)	59 (10)	123 (9)
C(10)	159 (2)	−8497 (1)	−1751 (1)	782 (17)	707 (16)	390 (11)	−26 (14)	−6 (12)	21 (11)
C(11)	285 (3)	−8834 (2)	−1011 (1)	1056 (23)	946 (21)	470 (13)	205 (19)	−41 (15)	128 (14)
C(12)	9597 (2)	−9086 (1)	−4194 (1)	647 (15)	545 (13)	435 (11)	−15 (12)	−7 (11)	−62 (10)
C(13)	9336 (2)	−9525 (1)	−3495 (1)	485 (11)	358 (10)	494 (11)	32 (9)	−74 (11)	−36 (9)
C(14)	8049 (2)	9848 (1)	−3476 (1)	639 (15)	480 (12)	754 (16)	−112 (12)	−30 (14)	1 (12)
C(15)	8129 (3)	9088 (2)	−4027 (1)	906 (22)	561 (15)	1332 (27)	−164 (16)	−127 (22)	−294 (18)
C(*B*1)	6051 (1)	−3271 (1)	−957 (1)	359 (9)	431 (10)	289 (8)	36 (8)	−31 (8)	−11 (8)
O(*B*1)	7794 (1)	−3559 (1)	−1802 (1)	442 (7)	537 (8)	429 (7)	25 (7)	78 (6)	−81 (6)
O(*B*2)	7549 (1)	−2104 (1)	−1422 (1)	437 (7)	485 (8)	439 (7)	−24 (7)	50 (7)	−32 (6)
C(*B*2)	5206 (2)	−2634 (1)	−610 (1)	420 (10)	367 (10)	435 (10)	23 (9)	46 (9)	−3 (8)
O(*B*3)	3068 (1)	−4192 (1)	452 (1)	609 (9)	476 (8)	443 (7)	−62 (8)	143 (7)	12 (6)
C(*B*3)	4195 (2)	−2932 (1)	−149 (1)	409 (10)	399 (10)	431 (10)	34 (9)	67 (9)	−36 (8)
C(*B*4)	4024 (2)	−3870 (1)	−12 (1)	403 (10)	445 (11)	316 (9)	−20 (9)	−15 (8)	9 (8)
C(*B*5)	4825 (2)	−4514 (1)	−368 (1)	629 (13)	373 (10)	407 (10)	−6 (10)	65 (10)	6 (9)
C(*B*6)	5821 (2)	−4210 (1)	−835 (1)	546 (12)	426 (10)	378 (10)	72 (10)	47 (10)	−57 (9)
C(*B*7)	7205 (1)	−2959 (1)	−1431 (1)	336 (9)	484 (11)	311 (8)	34 (9)	−57 (8)	−20 (8)
C(*P*1)	6529 (2)	−6868 (1)	−1164 (1)	590 (13)	443 (11)	411 (10)	40 (11)	44 (10)	−76 (9)
C(*P*2)	5586 (2)	−7464 (1)	−845 (1)	825 (17)	521 (13)	474 (12)	37 (13)	141 (13)	48 (11)
C(*P*3)	4478 (2)	−7820 (1)	−1215 (1)	759 (17)	550 (14)	648 (15)	−119 (14)	207 (14)	−32 (12)
C(*P*4)	4321 (2)	−7583 (1)	−1901 (1)	630 (14)	720 (15)	655 (15)	−215 (14)	71 (13)	−130 (13)
C(*P*5)	5268 (2)	−6982 (1)	−2211 (1)	560 (13)	577 (13)	443 (11)	−94 (11)	46 (10)	−81 (10)
C(*P*6)	6398 (2)	−6614 (1)	−1853 (1)	484 (11)	402 (10)	391 (10)	11 (9)	78 (9)	−80 (9)

apparently reliable phase equations and the evaluation of about 100 phases in terms of one arbitrary symbol (restricted to 90° or 270°). After extension of the sets of phases by the tangent formula, the two *E* maps were calculated. The map corresponding to the solution with the higher consistency index gave a large peak incompatible with the Patterson map but the map from the solution with lower index was compatible and allowed recognition of the two benzene rings of the asymmetric unit and part of the remainder of the cation up to the pyrrole ring.

Later, after refinement of the model, the invariants were calculated by Hauptman's (1971) triple-product formula which, in several cases, contradicted those calculated as large values by the MDKS method. Thus, had it been possible to follow Hauptman's (1973) advice to use both formulae, a better map might have been obtained since, although according to the MDKS calculation all the invariants used had cosines corresponding to angles less than 26°, some of the angles were as large as 60° and at least one was 90°. The worst deviations were indicated by the triple-product calculation.

Given the starting model, deduction of the rest of the molecule followed and the absolute configuration of the molecule was determined unambiguously (Table 1). The structure was refined to convergence by full-matrix least-squares methods. Because of computer size limitations, the normal-equations matrix was blocked to refer to sets of parameters corresponding to hydrogen atoms, anion, chlorobenzene and the remainder of the cation respectively. The isomer on which the X-ray work was carried out is thus [*S*(*R*,*R*)]. The atomic parameters for the heavier atoms are given in Table 2 and those for the hydrogen atoms in Table 3.* Most of the calculations used the X-RAY 72 system of Stewart, Kruger, Ammon, Dickinson & Hall (1972) except for the direct methods, where a combination of our own programs and those of the Hauptman group was employed. The bond lengths are given in Figs. 1 and 2, and bond angles in Fig. 3. Relevant torsion angles are given in Table 4.* All bond lengths have e.s.d.'s less than 0·003 Å except for one or two of the highly vibrating terminal methyl bonds where the e.s.d.'s are less than 0·004 Å. All bond angles have e.s.d.'s less than 0·2°. Scattering factors used for the heavier atoms were taken from *International Tables*

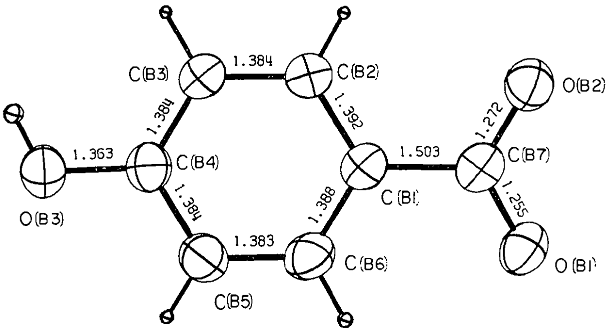


Fig. 2. Bond lengths in *p*-hydroxybenzoate anion. All lengths have e.s.d.'s less than 0·003 Å.

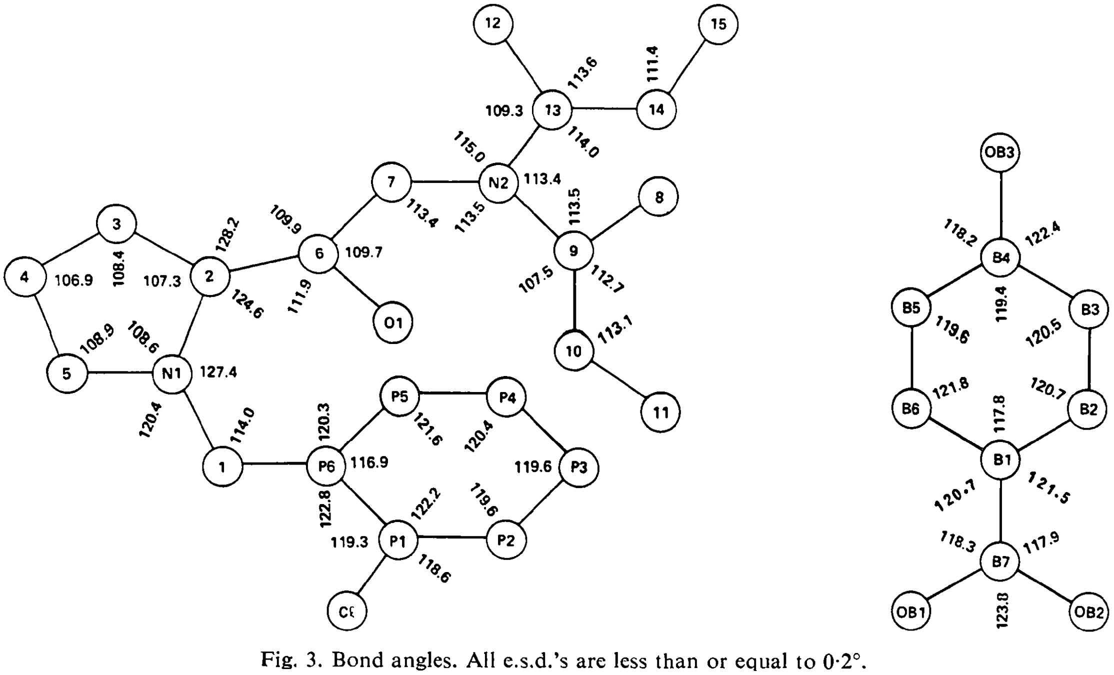


Fig. 3. Bond angles. All e.s.d.'s are less than or equal to 0·2°.

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* A list of structure factors and Table 4 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30892 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

for X-ray Crystallography (1962) and, for hydrogen, from Stewart, Davidson & Simpson (1965). Anomalous dispersion corrections for chlorine were also taken from *International Tables for X-ray Crystallography* (1962).

Discussion

C–H bond lengths in general have e.s.d.'s of *ca* 0·03 Å, aliphatic C–H and aromatic C–H lengths have averages of 1·01 and 0·97 Å respectively with no significant deviations from the means. The apparently short bonds in the s-butyl groups of the cation can be accounted for by thermal vibration but, since correction would neither be greatly relevant to the problem nor simple because of the flexibility of the structure, no attempts have been made to adjust the bond lengths for thermal motion. The N(2)–C bonds are longer than the value quoted by Sutton (1965) but the lengths are consistent with the fact that salt-forming nitrogen atoms, as Birnbaum (1967) discussed, usually have bond lengths considerably longer than the standard trivalent value of 1·47 Å. That N(2) is the ionized nitrogen atom is also consistent with chemical reasoning, its possession of a hydrogen atom and its association with the *p*-hydroxybenzoate ion. Other bond lengths and angles in the cation, apart from the pyrrole moiety, are as might be expected. The lack of symmetry of the pyrrole ring is only marginally significant but the bond lengths show deviations from the microwave results of Nygaard, Neilsen, Kirchheiner, Maltesen, Rastrup-Andersen & Sorensen (1969) for unsubstituted pyrrole, although only C(4)–C(5) and C(2)–C(3) differ by more than three standard deviations from the corresponding

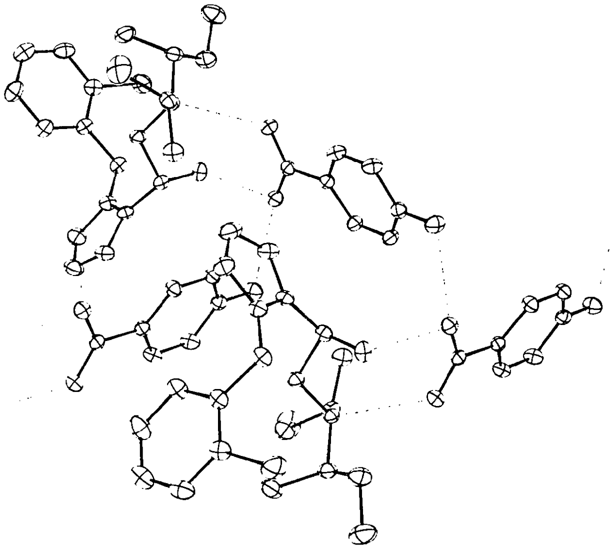

Fig. 4. Hydrogen bonding showing the chains of acid anions related by the *a* screw axis (horizontal) and the attached cations.

Table 3. *Hydrogen atom parameters* ($\times 10^3$)

E.s.d.'s refer to the last one or two figures as appropriate. Atom designations indicate attachments.

	x/a	*y/b*	*z/c*	*U*
O3	280 (2)	−374 (1)	72 (1)	79 (8)
*B*2	530 (2)	−198 (1)	−70 (1)	52 (6)
*B*3	358 (2)	−247 (1)	6 (1)	50 (6)
*B*5	466 (2)	−512 (1)	−28 (1)	57 (7)
*B*6	635 (2)	−466 (1)	−108 (1)	64 (7)
*P*2	574 (2)	−760 (1)	−36 (1)	76 (8)
*P*3	377 (2)	−825 (1)	−99 (1)	85 (9)
*P*4	351 (3)	−790 (1)	−216 (1)	89 (9)
*P*5	512 (2)	−677 (1)	−269 (1)	67 (7)
O1	95 (3)	−684 (1)	−306 (1)	95 (9)
N2	21 (2)	−850 (1)	−297 (1)	48 (6)
1	737 (2)	−537 (1)	−198 (1)	53 (6)
1′	843 (2)	−620 (1)	−211 (1)	56 (6)
3	767 (2)	−616 (1)	−448 (1)	63 (7)
4	595 (3)	−496 (1)	−424 (1)	93 (9)
5	578 (3)	−485 (2)	−291 (1)	102 (10)
6	945 (2)	−719 (1)	−379 (1)	38 (5)
7	783 (2)	−783 (1)	−263 (1)	42 (5)
7′	760 (2)	−819 (1)	−339 (1)	46 (5)
8	714 (2)	−956 (1)	−223 (1)	86 (9)
8′	742 (3)	−871 (2)	−169 (1)	109 (10)
8″	786 (3)	−981 (1)	−156 (1)	92 (9)
9	969 (2)	−979 (1)	−223 (1)	53 (6)
10	121 (3)	−856 (2)	−192 (1)	113 (11)
10′	967 (2)	−779 (1)	−177 (1)	76 (8)
11	107 (3)	−835 (2)	−72 (1)	116 (11)
11″	923 (3)	−886 (1)	−81 (1)	84 (8)
11′	53 (4)	−946 (2)	−95 (1)	136 (13)
12	42 (2)	−863 (1)	−419 (1)	70 (7)
12′	983 (2)	−957 (1)	−453 (1)	71 (7)
12″	879 (2)	−875 (1)	−432 (1)	76 (8)
13	15 (2)	−985 (1)	−337 (1)	46 (6)
14	721 (2)	−976 (1)	−355 (1)	58 (6)
14′	792 (2)	−42 (1)	−300 (1)	74 (7)
15	813 (3)	−62 (2)	−455 (1)	116 (11)
15′	901 (4)	−127 (2)	−395 (1)	135 (13)
15″	730 (3)	−126 (2)	−396 (1)	95 (9)

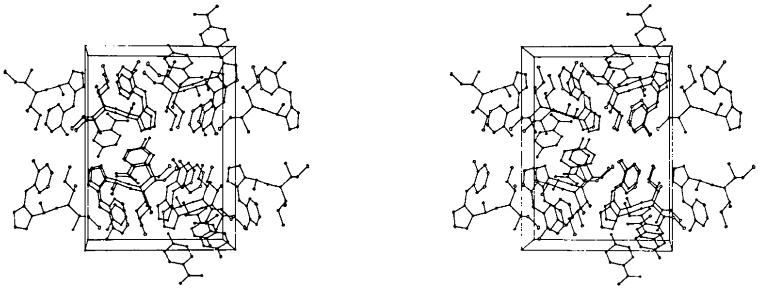

Fig. 5. Packing diagram. The projection is down **a**.

spectroscopic value [1·382 (4) Å]. Accurate X-ray studies of pyrrole compounds with all carbon atoms substituted, by Bonnett, Hursthouse & Neidle (1972*a*, *b*), have average values for corresponding bond lengths very close to the microwave results but show considerable individual variation. Since the structure of viminol represents the first accurate X-ray study of an *N*-substituted pyrrole, it will be interesting to see if the trends observed are confirmed in future studies.

The pyrrole and the chlorobenzene rings are flat and substituents are coplanar except for the chlorine atom which is 0·013 Å from the benzene-ring mean plane. The deviation of the chlorine atom can be partially accounted for by the fact that the shift tends to increase the fairly short C(1)–Cl distance (3·02 Å). The deviation also increases the distance of the chlorine atom from hydrogen atoms attached to C(*P*2) and C(1).

The system of hydrogen bonds which is a major influence on the crystal structure is shown in Fig. 4 and a packing diagram is given as Fig. 5. Chains of anions extending throughout the crystal, with the components related by the *a* screw axis, are formed by hydrogen bonds, of length 2·696 Å, between the hydroxyl oxygen atom, O(*B*3), and the acid oxygen atom O(*B*2), in the next ion. A cation is attached to each *p*-hydroxybenzoate anion by two hydrogen bonds from O(1) and N(2) of lengths 2·670 and 2·788 Å respectively. The last hydrogen bond may be complicated by ionic attraction and it is also the only such bond in the crystal which is significantly bent: the OHN angle is 152°.

There are small but significant distortions from planarity of the *p*-hydroxybenzoate ion which, since they are in a sense which tends to reduce the lengths of the hydrogen bonds, may be attributable to such bonding. C(*B*7) and O(*B*3) are significantly out of the benzene ring plane with deviations of 0·10 and 0·05 Å respectively and the plane of the acid group is also twisted by 13° from the ring plane. The benzene ring itself is distorted to a slightly 'boat' form. The angles between the planes [C(*B*4), C(*B*3), C(*B*5)] and [C(*B*2), C(*B*1), C(*B*6)] to the plane of the central four atoms are 2·5° and 1·7° respectively which represent significant distortions. The two acid group bond lengths C(7)–O(*B*1) and C(7)–O(*B*2) are significantly different at 1·255 and 1·272 Å respectively and the difference is consistent with the fact that O(*B*2) forms two hydrogen bonds and O(*B*1) only one.

Little is known about the nature of the active site for morphinoid analgesic activity and, indeed, one cannot be certain that there is a single active site. Clinically useful narcotic analgesics, as indicated by Jacobson, May & Sargent (1970), seem to possess the following characteristics: (*a*) a quaternary carbon atom, (*b*) a benzene nucleus linked to (*a*), (*c*) a tertiary nitrogen atom two saturated carbon atoms away from (*a*), and (*d*) a phenolic hydroxyl group *m* to (*a*) if (*c*) is part of a six-membered ring. It can be seen that viminol bears very little relationship to the above description. The capability of narcotic analgesics to form two simultaneous hydrogen bonds, which De Camp & Ahmed (1972) have correlated with analgesic activity in the case of promedol alcohol (a morphinoid analgesic), is probably a significant factor but obviously the etiology of analgesic or antagonistic activity is more complicated. The differences in molecular architecture between the [*S*(*S*,*S*)] antagonist (it is assumed from preparative chemistry and optical activity that the absolute configuration of the third center is the same as in the present structure) and the [*S*(*R*,*R*)] analgesic are relatively small if one assumes that the activity is associated with the two atoms which form hydrogen bonds. The only difference between the isomers with respect to these atoms is that, as models indicate, the s-butyl groups can be manipulated to produce somewhat less interference with potential hydrogen bonding in the cation of the [*S*(*R*,*R*)] analgesic. The rather small difference is consistent with the fact that the crystals of the [*S*(*S*,*S*)] salt are nearly isomorphous with those of the [*S*(*R*,*R*)] salt [$a=9{\cdot}51$ (1), $b=14{\cdot}79$ (1), $c=19{\cdot}41$ (2)], and the increase in cell volume is only 2·7 %. Since viminol, as stated previously, bears no simple relationship to morphine, theories of analgesic mechanisms will have to take its structure into account but discussion of the interaction between the viminol isomers and the analgesic active site must await further biochemical and physiological investigations.

Acknowledgment is gratefully made to Professor Davide Della Bella (Zambon S.p.a., Bresso-Milan, Italy) for bringing this problem to our attention and for his continued interest, to W. D. Vincent and P. Kalkowski (NIH Computer Center) for programming assistance and to Dr C. A. Weeks (Medical Foundation of Buffalo) for provision of the programs of the Hauptman group.

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Acta Cryst. (1975). B**31**, 1581

A Reinvestigation of the Crystal Structure of Acetylcholine Bromide

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(*Received* 21 *January* 1975; *accepted* 23 *January* 1975)

A reinvestigation of the structure of acetylcholine bromide, $[C_7H_{16}O_2N]^+Br^-$, with X-ray diffraction intensities collected from two untwinned crystals has been carried out. The crystals are monoclinic, space group $P2_1/n$, with $a=10·966$ (4), $b=13·729$ (7), $c=7·159$ (4) Å, $\beta=108·18$ (7)°, $Z=4$. The structure was refined by full-matrix least-squares calculations with 1730 observed reflexions, and anisotropic temperature factors for all non-hydrogen atoms. The final R was 0·041. Atomic coordinates, thermal parameters, bond lengths and angles are compared with those from previous work on acetylcholine derivatives.

Introduction

An X-ray investigation of the structure of acetylcholine bromide was first reported by Sørum (1956, 1959). The structure was solved in space group $P2_1$ with two crystallographically different molecules in the asymmetric unit. From physiological considerations Canepa (1964) suggested that one of these molecular forms was incorrect, and Dunitz (1963), observing some unusual systematic absences, suggested that the crystal used was a twinned $P2_1/c$ rather than a single $P2_1$ specimen. Taking this into account, the structure was refined from the previous photographic intensities corrected for twinning by Canepa, Pauling & Sørum (1966), referred to hereafter as CPS, to a final R of 0·10. Because of the importance of acetylcholine as a synaptic transmitter, it seemed worth while to re-examine the structure with diffractometer data obtained from an untwinned crystal. It is also of interest to determine the positions of the H atoms.

Experimental

Crystal data

Crystals were kindly prepared by Dr T. Bruun of The Institute of Organic Chemistry of this University by recrystallization from acetone and HBr of a sample supplied from Koch-Light Laboratories Ltd. They are colourless and slightly hygroscopic. Weissenberg photographs of the $hk0$, $hk1$ and $hk3$ reciprocal-lattice planes showed none of the additional diffraction spots reported by Sørum (1956). Crystallographic data based on observations for two such untwinned specimens are summarized below.

Acetylcholine bromide, $[C_7H_{16}O_2N]^+Br^-$; F.W. 226·12; monoclinic; λ(Mo $K\alpha$)$=0·71069$ Å; μ(Mo $K\alpha$) $=42·106$ cm^{-1}. $a=10·966$ (4), $b=13·729$ (7), $c=7·159$ (4) Å, $\beta=108·18$ (7)°; $V=1024·2$ Å^3; $Z=4$. Systematic absences: $h0l$: $h+l=2n+1$; $0k0$: $k=2n+1$. Space group $P2_1/n$. $D_c=1·467$ g cm^{-3}.

Another choice of axes giving the space group $P2_1/c$ results in $a=11·069$ Å and $\beta=109·71$°, leaving b and c unchanged. These values may be compared with $a=11·057$, $b=13·690$, $c=7·153$ Å and $\beta=109·65$° obtained by Hjortås (1966) and $a=11·10$, $b=13·67$, $c=7·18$ Å and $\beta=110$° obtained by Sørum (1959). The cell dimensions found in the present work are mean values from repeated measurements for two crystals on an automatic diffractometer. The least-squares method was used to fit the settings for 12 high-angle reflexions. The estimated standard deviations are approximately 2·5 times larger than the e.s.d.'s from one measurement.

Data collection and processing

Intensities were collected for two plate-shaped crystals of dimensions 0·3 × 0·3 × 0·1 mm and 0·3 × 0·2 × 0·15 mm for specimen I and II respectively. As the crystals were hygroscopic they were mounted in glass capillaries with **c** approximately parallel to the φ axis of the goniometer. The crystal faces parallel to **c** were (110) planes. The intensities were collected on a Picker FACS-1 four-circle automatic diffractometer