Redetermination of the Crystal Structure of Lactoylcholine Iodide

BIRTHE JENSEN

Royal Danish School of Pharmacy, Department of Chemistry BC, Universitetsparken 2, DK-2100 Copenhagen, Denmark

The crystal structure of lactoylcholine iodide, $CH_3CHOHCOOCH_2CH_2N^+(CH_3)_3, I^-$, has been determined by Chotia and Pauling,[1] but unfortunately neither coordinates nor any description of the crystal packing was published. The lactoylcholine ion is, in contrast to most other choline ester ions, a potential hydrogen bond donor. The redetermination of the crystal structure was undertaken as part of solid state studies of choline ester salts, in which hydrogen bonding of the choline ester ion cannot *a priori* be excluded.
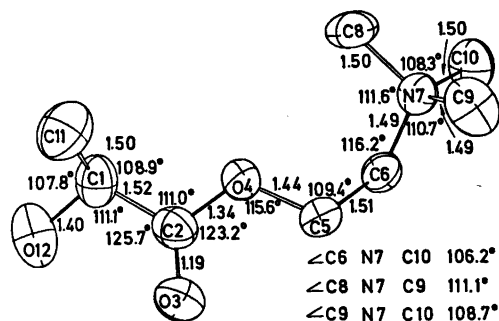

Fig. 1. (S)-Form of the lactoylcholine ion. The torsion angles are: $C11-C1-C2-O4$ $-86.0°$; $C1-C2-O4-C5$ $177.4°$; $C2-O4-C5-$ $C6$ $158.8°$; $O4-C5-C6-N7$ $82.6°$; $C5-C6-$ $N7-C8$ $-61.2°$. The estimated standard deviations on bond lengths and angles are about 0.01 Å and $0.7°$, respectively. The drawings were produced by ORTEP.[8]

Bond lengths and angles calculated from the final parameters (Table 1) are shown in Fig. 1 and are in general agreement with accepted values. A stereo view of the crystal packing is given in Fig. 2. O12 seems to be hydrogen bonded to $I^-_{(1-x, y-\frac{1}{2}, \frac{1}{2}-z)}$. The distance $O12..I^-$ is $3.45(1)$ Å, and the angle $O12-$ $H12..I^-$ is $146(7)°$. As in the crystal structures of acetylcholine β-resorcylate[2] and of two salts of GABA-choline ester[3] no hydrogen bonding involves the ester oxygen atoms O3 and O4.

Experimental. (R,S)-Lactoylcholine iodide was prepared according to published directions.[4] Yellow elongated prisms were obtained by recrystallization from ethanol and preliminary X-ray diffraction photographs showed these crystals to be identical with those investigated earlier.[1]

Crystal data. (R,S)-Lactoylcholine iodide, $C_8H_{18}NO_3I$, $M = 303.14$, m.p. $120.0 - 120.5$ °C. Space group $P2_1/c$, $a = 9.878(4)$, $b = 12.254(5)$, $c = 10.134(5)$ Å, $\beta = 90.50(4)°$, $V = 1227$ Å³. $D_m = 1.64$ g cm⁻³, $Z = 4$, $D_c = 1.64$ g cm⁻³. Linear absorption coefficient for X-rays $[\lambda (MoK\alpha) = 0.7107$ Å$]$, $\mu = 26.2$ cm⁻¹. $F(000) = 600$. The unit-cell parameters were refined by least-squares techniques from the θ angles measured for 22 reflections on a NONIUS three-circle automatic diffractometer. The density was measured by flotation in a mixture of bromobenzene and ethyl iodide. The melting point was determined on a Leitz hot stage microscope.

Intensity data were collected on the diffractometer from a crystal with dimensions $0.12 \times 0.18 \times 0.36$ mm using MoKα radiation and omega scan. 2163 reflections in the range $2.5 \le \theta \le 25.0°$ were measured twice and symmetry-related reflections were averaged. Out of these 1543 had $I_{net} \ge 3.0\sigma(I)$, where $\sigma(I)$ is the standard deviation from counting statistics. No absorption corrections have been made.

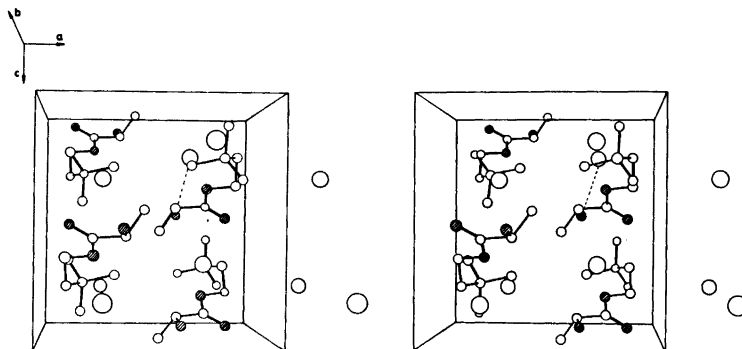The structure was solved by the heavy atom method and refined by full matrix least-

Table 1. Final positional and thermal parameters. The estimated standard deviations, referring to the last figure, are given in parentheses. Thermal parameters are $\times 10^2$. The temperature factor is defined by:

$$\exp[-2\pi^2(U_{11}h^2a^{*2}\cdots + 2U_{12}hka^*b^* + \cdots)].$$

ATOM	X/A	Y/B	Z/C	U11	U22	U33	U12	U13	U23
I-	.27466(6)	.45031(5)	.31466(6)	6.49(4)	7.65(4)	5.45(4)	-1.36(3)	0.44(2)	0.62(3)
O12	.6416(9)	.0887(6)	.4701(7)	12.0(6)	6.4(4)	6.3(4)	-1.7(4)	1.8(4)	0.3(3)
C11	.5507(10)	.2537(10)	.5460(11)	7.3(6)	9.2(7)	8.1(7)	-0.3(6)	1.6(5)	-0.9(6)
C 1	.6297(9)	.1998(8)	.4386(8)	7.0(5)	6.6(6)	4.5(4)	-1.5(4)	0.0(4)	0.4(4)
C 2	.7676(8)	.2535(7)	.4301(8)	5.8(5)	5.7(5)	4.7(4)	1.0(4)	0.4(4)	0.6(4)
O 3	.8677(7)	.2239(6)	.4857(8)	6.3(4)	9.7(5)	10.4(5)	0.9(4)	-0.7(4)	5.0(5)
O 4	.7630(5)	.3420(5)	.3526(5)	4.8(3)	5.2(3)	6.1(3)	-0.3(3)	-0.3(2)	1.5(3)
C 5	.8881(8)	.4023(7)	.3422(9)	4.1(4)	5.4(5)	7.1(6)	-0.1(4)	-0.3(4)	0.8(4)
C 6	.8850(7)	.4703(6)	.2182(8)	4.3(4)	5.2(5)	5.2(4)	0.2(3)	1.1(3)	0.1(3)
N 7	.8132(6)	.5774(5)	.2270(6)	4.7(3)	4.8(4)	4.0(3)	-0.2(3)	0.2(3)	0.1(3)
C 8	.6663(8)	.5627(8)	.2599(10)	4.8(4)	7.4(6)	6.9(5)	2.1(4)	0.9(4)	0.5(5)
C 9	.8818(10)	.6506(8)	.3243(8)	9.8(7)	5.8(5)	4.8(5)	-0.2(5)	-0.7(5)	-0.7(4)
C10	.8219(10)	.6282(8)	.0924(8)	8.1(6)	7.6(6)	4.2(4)	-1.0(5)	-0.2(4)	1.4(4)
H12	.694 (9)	.076 (7)	.385 (10)	6.3					

Fig. 2. A stereo view of the packing of lactoylcholine iodide. The possible hydrogen bond $O12 \ldots I^-_{(1-x, y-\frac{1}{2}, \frac{1}{2}-z)}$ is indicated by a broken line. Oxygen atoms are shaded.

squares techniques to a final R value of 0.05, using the X-RAY-system.[5] All hydrogen atoms bonded to carbon atoms were found in a difference fourier map at the calculated positions (distance C−H equal to 1.0 Å) and were introduced in the final refinement as a fixed contribution ($U = 6.3$). Also the position of the hydroxyl hydrogen atom H12 was suggested in the difference fourier map, and the positional parameters of this atom have been refined. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\{1 + [(F_o - B)/A]^2\}$, $B = 25.0$ and $A = 20.0$. The X-ray atomic scattering factors used for hydrogen were those of Stewart, Davidson and Simpson[6] and for all other atoms those of Cromer and Mann.[7] All atoms but I^- were treated as uncharged. The final list of structure factors is available on request.

1. Chotia, C. and Pauling, P. *Nature (London)* **219** (1968) 1156.
2. Jensen, B. *Acta Chem. Scand. B* **29** (1975) 531.
3. Jensen, B. *Acta Chem. Scand. B* **30** (1976) 643.
4. Rama Sastry, B. V., Lasslo, A. and Pfeiffer, C. C. *J. Org. Chem.* **23** (1958) 2005.
5. Stewart, J. M., Kruger, G. J., Ammon, H. L., Dickinson, C. and Hall, S. R. *The X-Ray System — Version of June 1972.* Technical Report TR-192 of The Computer Science Center, University of Maryland, June 1972.
6. Stewart, R. F., Davidson, E. R. and Simpson, W. T. *J. Chem. Phys.* **42** (1965) 3175.
7. Cromer, D. and Mann, J. *Acta Crystallogr. A* **24** (1968) 321.
8. Johnson, C. K. *ORTEP, A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations*, Oak Ridge 1965.

Propellicene or
Bi-2,13-pentahelicenylene

BENGT THULIN and OLOF WENNERSTRÖM

Department of Organic Chemistry, Chalmers University of Technology and University of Göteborg, Fack, S-402 20 Göteborg, Sweden

Aromatic compounds having structures with interesting topologies, *e.g.* the helicenes,[1,2] cyclophanes,[3-5] and circulenes[6-9] have long fascinated the synthetic chemists. We now wish to report the synthesis of a new hydrocarbon, $C_{44}H_{24}$, which has the geometry of a two-bladed propeller. The compound, which we would like to call propellicene or bi-2,13-pentahelicenylene[12] is built from two pentahelicene units, with the terminal rings linked together at C_2 and C_{13} by single bonds (Fig. 1).

We recently described a procedure, using the Wittig reaction, whereby various [2.2.2.2]-cyclophanes and related compounds can be prepared.[10,11] Such compounds may serve as precursors for topologically interesting compounds like those mentioned above.
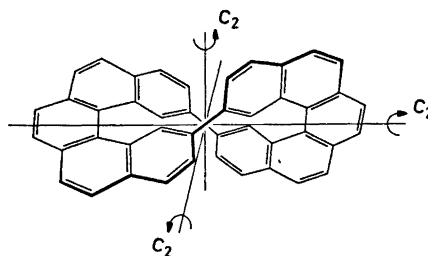

Fig. 1. Proposed structure of propellicene or bi-2,13-pentahelicenylene with the three symmetry axes.