Acta Chemica Scandinavica B 30 (1976) 643—650

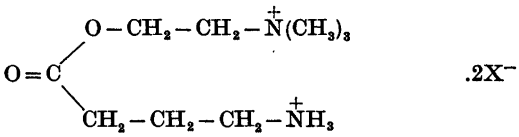
# The Crystal Structures of $\gamma$-Aminobutyric Acid Choline Ester Diiodide and $\gamma$-Aminobutyric Acid Choline Ester (±)-Tartrate

BIRTHE JENSEN

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

The crystal structures of $\gamma$-aminobutyric acid (GABA) choline ester diiodide, GAKOLI, and of GABA choline ester (±)-tartrate, GAKTRA, have been determined from diffractometer collected three-dimensional X-ray data and refined by full-matrix least-squares techniques to $R$ values of 0.049 and 0.075 for GAKOLI and GAKTRA, respectively. The conformations of the GABA-moieties in the two crystal structures differ from one another, while the conformations of the choline moieties are almost the same. No hydrogen bonding involves the ester oxygen atoms.

The crystal structures of the diiodide and the (±)-tartrate of $\gamma$-aminobutyric acid choline ester, GABA choline ester



$$O=C\begin{cases} O-CH_2-CH_2-\overset{+}{N}(CH_3)_3 \\ CH_2-CH_2-CH_2-\overset{+}{N}H_3 \end{cases} .2X^-$$

have been determined as part of conformational studies of choline esters in the solid state. Of special interest to the author are compounds in which hydrogen bonding of the choline ester ion cannot *a priori* be excluded.

The biological activity of GABA choline ester has been studied by several groups, and it has been concluded,[1,2] that the compound has little acetylcholine-like activity and only weak GABA-like activity.

## EXPERIMENTAL

*GABA choline ester diiodide, GAKOLI.* GABA choline ester dichloride was prepared from GABA and choline chloride according to directions of Daiichi Seizaku Co., Ltd.[3] GAKOLI was prepared by mixing saturated ethanolic solutions of GABA choline ester dichloride and potassium iodide. The instantaneously precipitated potassium chloride was filtered off, and upon standing colourless needleshaped crystals of GAKOLI were formed in the solution. Preliminary Weissenberg- and precession photographs showed the crystals to be monoclinic, space group $P2_1/c$. The unit cell parameters were refined by least-squares techniques from diffractometer measured $2\theta$-angles (Mo$K\alpha$ radiation, $\lambda = 0.7107$ Å) for 25 independent reflections. The density of the crystals was measured by flotation in a mixture of bromobenzene and methyliodide. The melting points given in this paper were determined on a Leitz hot stage microscope. Table 1 lists the unit cell parameters and other crystal data.

Three-dimensional diffraction data were measured at room temperature on a Nonius

*Table 1. Crystal data.*

| | GAKOLI | GAKTRA |
|---|---|---|
| Stoichiometry | $C_9H_{22}N_2O_2I_2$ | $C_{13}H_{26}N_2O_8$ |
| Formula weight | 444.10 | 338.36 |
| $Z$ | 4 | 4 |
| F(000) | 848 | 728 |
| Space group | $P2_1/c$ | $Pna2_1$ |
| $a$ (Å) | 11.660(1) | 11.487(2) |
| $b$ (Å) | 14.384(1) | 15.271(3) |
| $c$ (Å) | 9.499(1) | 9.419(1) |
| $\beta$ (°) | 101.37(1) | |
| Cell volume (Å$^3$) | 1561.9 | 1652.2 |
| $D_X$ (g cm$^{-3}$) | 1.89 | 1.36 |
| $D_m$ (g cm$^{-3}$) | 1.90(1) | 1.36(1) |
| $\mu$(Mo$K\alpha$) (cm$^{-1}$) | 41 | 1.2 |
| $\mu$(Cu$K\alpha$) (cm$^{-1}$) | | 9.8 |
| *M.p.* (°C) | 188.5 – 191.5 (decomp.) | 153.5 – 155.0 (decomp.) |

three-circle automatic diffractometer using graphite monochromated Mo$K\alpha$ radiation. The $\omega$ scan technique with a scan speed of 1.2° min$^{-1}$ was employed, and the scan angle was 1.0°. Background counts were taken for half the scanning time at each of the scan range limits. One standard reflection was measured after every 40 reflections. The intensity of this reflection diminished approximately 10 % during the measurement of the first *ca.* 3000 reflections, and a linear rescale factor was applied. During the measurement of the remaining reflections no systematic change in the intensity of the standard reflection was observed. All the data were measured from a single crystal with approximate dimensions $0.08 \times 0.08 \times 0.27$ mm. The crystal was sealed in a glass capillary and mounted with its elongated dimension, which was parallel to the crystallographic $a$-axis, along the $\phi$-axis of the goniostat. Each of the 2865 independent reflections in the range $2.5 \leq \theta \leq 25.0°$ was measured twice. 3645 of the 5725 reflections ($hk \pm l$ and $h-k \pm l$) had $I_{\text{net}} \geq 2.5\sigma(I)$, where $\sigma(I)$ is the standard deviation from counting statistics. These were regarded as observed reflections, whereas the remaining reflections were regarded as unobserved and excluded from the refinement procedure. The reflections from both quadrants were used independently in the refinement. Lorentz and polarization corrections were applied, but no absorption corrections were made.

The trial structure was obtained by the heavy atom method.

*GABA choline ester (±)-tartrate, GAKTRA.* Freshly precipitated silver oxide (2 mmol) was suspended in an aqueous solution of (±)-tartaric acid (1 mmol) and an aqueous solution of GABA choline ester dichloride (1 mmol) was added. After stirring for 1 h the precipitate was filtered off and the solution evaporated *in vacuo.* Colourless flat elongated prismatic crystals were obtained from a solution of GAKTRA in dimethylformamide and a few drops of water, standing in a desiccator containing phosphorus pentaoxide. Preliminary Weissenberg- and precession photographs showed the crystals to be orthorhombic. The systematically absent reflections are $h0l$ when $h$ is odd and $0kl$ when $k+l$ is odd, indicating that the space group is $Pnam$ or $Pna2_1$, but from considerations concerning the formula and the density of the compound, the centrosymmetric space group could be ruled out. The unit cell parameters were refined by least-squares techniques from diffractometer measured $2\theta$-angles (Mo$K\alpha$ radiation and/or Cu$K\alpha$-radiation, $\lambda = 1.5418$ Å) for 30 reflections. The density of the crystals was measured by flotation in a mixture of chlorobenzene and bromobenzene. The crystal data are listed in Table 1.

Two sets of intensity data have been measured, both at room temperature. Due to difficulties in growing and cutting appropriate crystals a tiny specimen was first examined and only a very low percentage of observed reflections was obtained. As better crystals were later obtained, another data set was collected.

The first set of data (I) was obtained from a single crystal with approximate dimensions $0.04 \times 0.08 \times 0.3$ mm using graphite monochromated Mo$K\alpha$-radiation and the second set (II) from a single crystal with dimensions $0.16 \times 0.26 \times 0.64$ mm using graphite monochromated Cu$K\alpha$-radiation. The crystals were sealed in glass capillaries and mounted with the elongated dimension, which was parallel to the crystallographic $c$-axis, along the $\phi$-axis of the goniostat. The $\omega$ scan technique with a scan speed of 0.6° min$^{-1}$ was employed, and the scan angles were 1.4 and 1.2° for measurement (I) and (II), respectively. One standard reflection was measured after every 25 reflections, showing no systematic decrease in intensity during the measurements. Using the first crystal, the reflections in the range $2.5 \leq \theta \leq 22.0°$ were measured once. From the second crystal the reflections in the range $2.5 \leq \theta \leq 50.0°$ were measured twice, and equivalent reflections were averaged. For data set I 477 of the 1089 independent reflections and for data set II 750 of the 918 independent reflections had $I_{\text{net}} \geq 2.5\sigma(I)$ and were regarded as observed. Lorentz and polarization corrections were applied, but no absorption corrections were made.

The trial structure was obtained from data set II by use of the 1974-version of MULTAN.[4] 15 of the highest peaks in the first calculated $E$-map were postulated to correspond to atomic positions. A refinement of this partial structure using the iterative tangent refinement procedure[5] gave a new $E$-map, from which the positions of 20 atoms were found. Out of these 20 atoms 12 were part of the mentioned partial structure. The positions of the remaining three atoms in the asymmetric unit [C(8), C(9) and C(10)] could be postulated from a subsequent Fourier synthesis.

## REFINEMENT OF THE STRUCTURES

The trial structures were refined by full-matrix least-squares techniques. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$ where weights were initially taken as unity. For GAKOLI the following weighting scheme was used during the last cycles of refinement: $w = 1/\{1 + [(F_o - B)/A]^2\}$ where $A = 20.0$ and $B = 45.0$. 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 nitrogen and oxygen atoms were treated as uncharged. All hydro-

*Table 2.* Final positional and thermal parameters for non-hydrogen atoms. The estimated standard deviations, referring to the last significant figure, are given in parentheses. Thermal parameters are × 10². The temperature factor is defined by: exp $[-2\pi^2(U_{11}h^2a^{*2}+\cdots+2U_{12}hka^*b^*+\cdots)]$

| Atom | $x/a$ | $y/b$ | $z/c$ | $U$ or $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| GAKOLI | | | | | | | | | |
| $I^-(1)$ | .49856(4) | .15571(4) | .62418(5) | 4.26(3) | 5.08(3) | 5.16(3) | 0.59(2) | 0.67(2) | −0.35(3) |
| $I^-(2)$ | −.07120(4) | .15678(4) | −.26431(5) | 4.20(3) | 3.85(3) | 6.26(3) | −0.34(2) | −0.15(2) | −0.13(3) |
| N(13) | .2893(6) | −.2257(5) | −.4145(7) | 5.0(2) | | | | | |
| C(12) | .3123(7) | −.1368(5) | −.3344(8) | 4.8(2) | | | | | |
| C(11) | .2039(7) | −.0904(6) | −.3078(8) | 4.8(2) | | | | | |
| C(1) | .2332(7) | .0018(5) | −.2249(8) | 4.6(2) | | | | | |
| C(2) | .2893(6) | −.0104(5) | −.0748(5) | 4.0(2) | | | | | |
| O(3) | .3122(6) | −.0836(4) | −.0122(7) | 6.7(2) | | | | | |
| O(4) | .3111(4) | .0710(3) | −.0047(5) | 4.5(1) | | | | | |
| C(5) | .3716(7) | .0706(5) | .1422(8) | 4.6(2) | | | | | |
| C(6) | .2946(6) | .0555(5) | .2494(7) | 4.0(2) | | | | | |
| N(7) | .2006(5) | .1276(4) | .2552(6) | 3.5(1) | | | | | |
| C(8) | .1046(8) | .1198(6) | .1280(9) | 5.6(2) | | | | | |
| C(9) | .2514(7) | .2234(6) | .2639(9) | 5.3(2) | | | | | |
| C(10) | .1535(8) | .1112(6) | .3880(9) | 5.4(2) | | | | | |
| GAKTRA | | | | | | | | | |
| N(13) | −.0468(9) | .3521(7) | .3854(22) | 3.4(7) | 3.5(7) | 3.9(8) | 0.1(6) | −0.0(7) | −0.8(7) |
| C(12) | .0366(15) | .2798(10) | .3509(26) | 6.9(12) | 4.6(11) | 4.5(11) | −0.2(10) | −1.0(11) | −1.6(9) |
| C(11) | .1556(16) | .2990(11) | .4110(22) | 5.5(13) | 6.7(11) | 3.1(10) | 0.8(9) | −0.1(10) | −2.1(9) |
| C(1) | .1590(15) | .2925(11) | .5735(−) | 5.6(12) | 6.3(12) | 3.7(10) | −1.1(9) | −1.6(9) | −0.5(9) |
| C(2) | .2829(18) | .3184(11) | .6286(26) | 7.5(16) | 5.3(12) | 2.3(12) | 2.0(10) | −1.1(11) | −0.2(10) |
| O(3) | .3623(11) | .3408(9) | .5616(22) | 5.0(8) | 10.7(11) | 4.7(8) | −1.0(8) | 1.1(7) | −0.3(8) |
| O(4) | .2823(9) | .3058(7) | .7703(21) | 6.7(9) | 5.2(7) | 4.7(9) | 0.8(6) | −0.2(7) | −1.3(6) |
| C(5) | .3985(16) | .3185(12) | .8436(27) | 6.1(13) | 7.0(13) | 6.2(12) | 0.9(11) | −2.7(12) | −1.0(11) |
| C(6) | .4175(15) | .4130(11) | .8819(28) | 5.6(12) | 5.8(12) | 6.6(14) | −0.7(10) | 0.5(11) | −2.7(11) |
| N(7) | .3470(11) | .4456(8) | 1.0047(21) | 5.1(9) | 5.2(8) | 3.9(8) | 0.3(6) | 0.3(8) | −0.6(8) |
| C(8) | .2179(14) | .4403(13) | .9775(28) | 3.4(10) | 12.0(15) | 9.0(18) | −0.5(10) | 1.0(11) | −5.1(15) |
| C(9) | .3763(21) | .3982(12) | 1.1452(28) | 14.0(20) | 5.2(12) | 6.1(15) | 0.1(13) | 1.2(15) | 1.1(11) |
| C(10) | .3810(16) | .5421(10) | 1.0212(26) | 9.9(14) | 4.0(11) | 5.6(13) | −0.9(10) | −0.6(13) | −1.5(10) |
| O(011) | .4689(10) | −.0059(8) | .7313(20) | 8.1(9) | 4.6(8) | 4.0(8) | 2.3(7) | 1.6(7) | −0.0(6) |
| O(012) | .3916(10) | .1260(7) | .6833(20) | 7.0(8) | 4.5(7) | 2.9(6) | 1.2(6) | 0.2(6) | 0.9(6) |
| C(01) | .4207(14) | .0644(12) | .7643(24) | 4.5(10) | 4.4(11) | 3.8(10) | −0.6(10) | 1.0(10) | −1.0(11) |
| C(02) | .3920(15) | .0765(11) | .9284(25) | 5.2(13) | 6.4(12) | 2.5(10) | 0.6(10) | 1.1(9) | −0.1(9) |
| O(02) | .4129(9) | −.0056(6) | .9981(19) | 7.7(7) | 4.3(6) | 2.5(6) | 1.9(6) | −0.7(6) | 0.4(6) |
| C(03) | .2633(14) | .1039(10) | .9498(23) | 5.4(12) | 4.5(10) | 2.1(10) | 0.4(9) | 1.1(8) | −0.7(8) |
| O(03) | .1881(9) | .0331(7) | .9058(21) | 4.8(7) | 6.3(8) | 4.6(7) | −0.9(6) | −0.3(6) | −1.9(7) |
| C(04) | .2501(17) | .1254(12) | 1.1099(23) | 5.0(12) | 5.5(12) | 3.3(11) | 1.1(11) | 0.2(10) | 0.5(11) |
| O(041) | .3064(9) | .1860(7) | 1.1564(20) | 6.1(8) | 5.8(7) | 2.8(7) | −0.3(7) | −0.8(6) | −1.4(6) |
| O(042) | .1781(11) | .0753(8) | 1.1734(20) | 10.1(11) | 8.2(9) | 4.8(8) | −1.5(8) | 4.0(8) | 0.8(8) |

gen atoms in the GAKOLI structure were located in a difference Fourier-map calculated during the later stages of refinement, while a corresponding difference Fourier-map calculated for the GAKTRA structure only gave very weak indications of the positions of the hydrogen atoms. The final cycles of refinement of the GAKOLI structure included the positional parameters for all atoms and the thermal parameters for all non-hydrogen atoms (anisotropic for the iodide ions and isotropic for carbon, nitrogen, and oxygen atoms). The temperature parameters of the hydrogen atoms were fixed at arbitrary values. For the GAKTRA structure the final cycles of refinement included the positional and anisotropic thermal parameters for all non-hydrogen atoms. No hydrogen atoms were introduced in the calculations. Although anisotropic refinement hardly can be justified in

*Table 3.* GAKOLI. Final positional parameters for hydrogen atoms and the thermal parameters ($\times 10^3$) used. The estimated standard deviations (referring to the last significant figure) are given in parentheses.

| Atom | $x/a$ | $y/b$ | $z/c$ | $U$ |
|---|---|---|---|---|
| H(131) | .247(6) | −.249(5) | −.370(7) | 5.1 |
| H(132) | .254(7) | −.198(5) | −.504(8) | 5.1 |
| H(133) | .352(7) | −.242(5) | −.419(7) | 5.1 |
| H(121) | .352(7) | −.158(5) | −.235(8) | 5.1 |
| H(122) | .344(6) | −.107(5) | −.385(8) | 5.1 |
| H(111) | .156(7) | −.072(5) | −.401(8) | 5.1 |
| H(112) | .162(7) | −.126(5) | −.258(8) | 5.1 |
| H(11) | .287(6) | −.033(5) | −.259(8) | 5.1 |
| H(12) | .161(6) | .028(5) | −.224(7) | 5.1 |
| H(51) | .418(6) | .019(5) | .169(7) | 5.1 |
| H(52) | .421(7) | .137(5) | .149(8) | 5.1 |
| H(61) | .254(7) | −.007(5) | .223(8) | 5.1 |
| H(62) | .329(6) | .052(5) | .339(7) | 5.1 |
| H(81) | .136(7) | .139(5) | .050(8) | 5.1 |
| H(82) | .070(6) | .052(5) | .129(8) | 5.1 |
| H(83) | .044(7) | .165(5) | .163(8) | 5.1 |
| H(91) | .291(6) | .225(5) | .344(8) | 5.1 |
| H(92) | .267(6) | .234(5) | .169(8) | 5.1 |
| H(93) | .192(6) | .267(5) | .266(7) | 5.1 |
| H(101) | .119(6) | .048(5) | .373(8) | 5.1 |
| H(102) | .201(7) | .126(5) | .469(8) | 5.1 |
| H(103) | .089(7) | .153(5) | .372(8) | 5.1 |

view of the limited amount of data, this approach has been used. The reason for this is, that independent refinements using the two data sets give the same overall picture of the anisotropic thermal motions. The final $R$ index $(\sum||F_o|-|F_c||/\sum|F_c|)$ is 0.049 for GAKOLI and for GAKTRA 0.086 and 0.075 for data set I and II, respectively.

The calculations were performed on an IBM 1130 computer and an IBM 360/75 computer, using INDIFF,[8] a local version of *The N.R.C. 2A Picker Data Reduction Program*,[9] an updated version of *The X-Ray System*,[10], and *ORTEP*.[11] The observed and calculated structure factor data are available from the author on request.

## RESULTS AND DISCUSSION

Tables 2 and 3 list final parameters and estimated standard deviations for non-hydrogen atoms and for hydrogen atoms, respectively. Unless otherwise stated the figures given for GAKTRA are based on data set II. The calculated bond lengths and angles involving only non-hydrogen atoms are given in Table 4. The atomic numbering used is shown in Fig. 1.

### Packing arrangements

*GAKOLI.* The crystal packing is illustrated in Fig. 2. The iodide ions are situated in two layers, one rather puckered around $x=0$ and one nearly planar around $x=\frac{1}{2}$. Between these

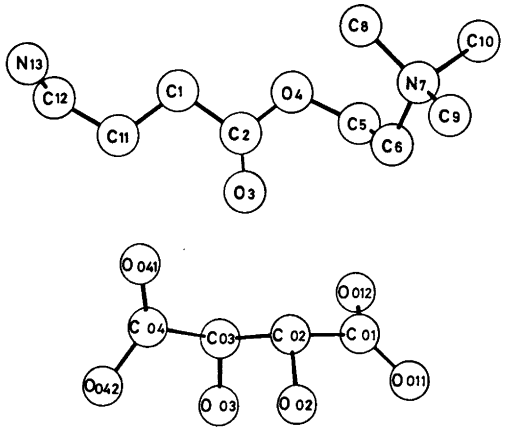


*Fig. 1.* The atomic numbering used for carbon, nitrogen, and oxygen atoms of GAKOLI and GAKTRA. The distances O(4)···C(8) and O(4)···N(7) are 3.01(1) and 3.11(1) Å for GAKOLI and 2.93(3) and 3.16(2) Å for GAKTRA.

*Table 4.* Bond lengths (Å) and angles (°) involving only non-hydrogen atoms and their estimated standard deviations, referring to the last significant figure, in parentheses.

| | GAKOLI | GAKTRA | |
|---|---|---|---|
| | | Data set II | Data set I |
| N(13)–C(12) | 1.49(1) | 1.50(2) | 1.49(3) |
| C(12)–C(11) | 1.49(1) | 1.51(3) | 1.46(4) |
| C(11)–C(1) | 1.55(1) | 1.53(2) | 1.57(3) |
| C(1)–C(2) | 1.46(1) | 1.57(3) | 1.53(3) |
| C(2)–O(3) | 1.21(1) | 1.16(3) | 1.17(4) |
| C(2)–O(4) | 1.35(1) | 1.35(3) | 1.39(4) |
| O(4)–C(5) | 1.43(1) | 1.52(2) | 1.59(3) |
| C(5)–C(6) | 1.50(1) | 1.50(3) | 1.48(4) |
| C(6)–N(7) | 1.52(1) | 1.50(3) | 1.47(4) |
| N(7)–C(8) | 1.48(1) | 1.51(2) | 1.50(3) |
| N(7)–C(9) | 1.50(1) | 1.53(2) | 1.59(4) |
| N(7)–C(10) | 1.49(1) | 1.55(3) | 1.55(3) |
| ∠N(13)–C(12)–C(11) | 113.4(6) | 111(1) | 111(2) |
| C(12)–C(11)–C(1) | 111.1(6) | 113(2) | 114(2) |
| C(11)–C(1)–C(2) | 114.0(6) | 110(1) | 111(2) |
| C(1)–C(2)–O(3) | 126.6(7) | 127(2) | 128(3) |
| C(1)–C(2)–O(4) | 112.6(6) | 107(1) | 107(2) |
| O(3)–C(2)–O(4) | 120.7(6) | 126(2) | 125(3) |
| C(2)–O(4)–C(5) | 119.1(5) | 115(2) | 116(2) |
| O(4)–C(5)–C(6) | 114.5(6) | 111(1) | 110(2) |
| C(5)–C(6)–N(7) | 117.3(6) | 115(2) | 114(2) |
| C(6)–N(7)–C(8) | 110.7(6) | 113(2) | 116(2) |
| C(6)–N(7)–C(9) | 110.5(6) | 113(1) | 111(2) |
| C(6)–N(7)–C(10) | 108.2(5) | 109(1) | 104(2) |
| C(8)–N(7)–C(9) | 110.0(6) | 110(2) | 109(2) |
| C(8)–N(7)–C(10) | 109.5(6) | 109(1) | 110(2) |
| C(9)–N(7)–C(10) | 107.9(6) | 108(2) | 106(2) |
| O(011)–C(01) | | 1.25(2) | 1.23(3) |
| O(012)–C(01) | | 1.26(2) | 1.25(3) |
| C(01)–C(02) | | 1.59(3) | 1.64(4) |
| C(02)–O(02) | | 1.44(2) | 1.42(3) |
| C(02)–C(03) | | 1.55(2) | 1.56(3) |
| C(03)–O(03) | | 1.44(2) | 1.43(3) |
| C(03)–C(04) | | 1.55(3) | 1.59(4) |
| C(04)–O(041) | | 1.21(2) | 1.18(3) |
| C(04)–O(042) | | 1.28(2) | 1.29(3) |
| ∠O(011)–C(01)–O(012) | | 128(2) | 129(3) |
| O(011)–C(01)–C(02) | | 116(2) | 117(2) |
| O(012)–C(01)–C(02) | | 117(2) | 114(2) |
| C(01)–C(02)–O(02) | | 108(1) | 105(2) |
| C(01)–C(02)–C(03) | | 111(2) | 108(2) |
| O(02)–C(02)–C(03) | | 110(1) | 109(2) |
| C(02)–C(03)–O(03) | | 109(1) | 113(2) |
| C(02)–C(03)–C(04) | | 106(2) | 102(2) |
| O(03)–C(03)–C(04) | | 112(2) | 112(2) |
| C(03)–C(04)–O(041) | | 117(2) | 118(3) |
| C(03)–C(04)–O(042) | | 113(2) | 111(2) |
| O(041)–C(04)–O(042) | | 129(2) | 130(3) |

layers the GABA choline ester ions are arranged. Only one close contact between two of these ions is observed. The distance N(13)···$O(3)_{(x,-\frac{1}{2}-y,-\frac{1}{2}+z)}$ is 2.925(9) Å. This is, however, a polar rather than a hydrogen bonded contact. None of the three N–H···O contacts are even approximately linear as can be seen from Fig. 2 and Table 5, which lists some dimensions

*Table 5.* GAKOLI. Some dimensions describing the surroundings of N(13).

| A | B | A···B Å | ∠A−H···B° |
|---|---|---|---|
| N(13)−H(131) | $\cdots I^-(2)_{(-x,-\frac{1}{2}+y,-\frac{1}{2}-z)}$ | 3.730(7) | 173(6) |
| N(13)−H(132) | $\cdots I^-(2)_{(-x,-y,-1-z)}$ | 3.701(6) | 155(6) |
| N(13)−H(133) | $\cdots I^-(1)_{(1-x,-y,-z)}$ | 3.612(7) | 124(6) |
| N(13)−H(133) | $\cdots I^-(1)_{(1-x,-\frac{1}{2}+y,\frac{1}{2}-z)}$ | 3.734(6) | 115(6) |
| N(13)−H(131) | $\cdots O(3)_{(x,-\frac{1}{2}-y,-\frac{1}{2}+z)}$ | 2.925(9) | 81(5) |
| N(13)−H(132) | $\cdots O(3)_{(x,-\frac{1}{2}-y,-\frac{1}{2}+z)}$ | 2.925(9) | 63(4) |
| N(13)−H(133) | $\cdots O(3)_{(x,-\frac{1}{2}-,-\frac{1}{2}+z)}$ | 2.925(9) | 101(6) |

describing the surroundings of N(13). Four iodide ions form a rectangle. N(13) is situated 0.37 Å off the plane of these four iodide ions, and the four nitrogen-iodide distances are not very different. Two of these contacts, $N(13)\cdots I^-(2)_{(-x,-\frac{1}{2}+y,-\frac{1}{2}-z)}$ and $N(13)\cdots I^-(2)_{(-x,-y,-1-z)}$, may be described as rather weak hydrogen bonds. The iodide ions are also in close contact with the carbon atoms C(6) to C(10) of the quaternary ammonium group. This group is surrounded by six iodide ions, three of which are nested between the carbon atoms. The carbon-iodide distances are in the range 3.82 to 4.31 Å.

*GAKTRA.* The crystal packing is illustrated in Fig. 3. Only few and weak contacts between the GABA choline ester ions are observed. The tartrate ions are linked together in chains along the screw-axes. Although the positions of the hydrogen atoms could not be determined it seems reasonable to postulate the existence of a hydrogen bond $O(02)-H\cdots O(011)_{(1-x,-y,\frac{1}{2}+z)}$. The O−O distance is 2.59(2) Å. No other close contacts between the tartrate ions are found. Most of the closer contacts in the crystal are found between the positively charged GABA choline ester ions and the negatively charged tartrate ions. Nine tartrate ions surround the GABA choline ester ion, and seven of these have van der Waals' or other contacts to the GABA choline ester ion. The existence of three hydrogen bonds N−H···O may be postulated, and these will be approximately linear, if the conformation around C(12)−N(13) is staggered in this crystal structure, as is approximately the case in the GAKOLI structure. The N···O distances are $N(13)\cdots O(12)_{(x-\frac{1}{2},\frac{1}{2}-y,z)}$, 2.91(3) Å, N(13)···

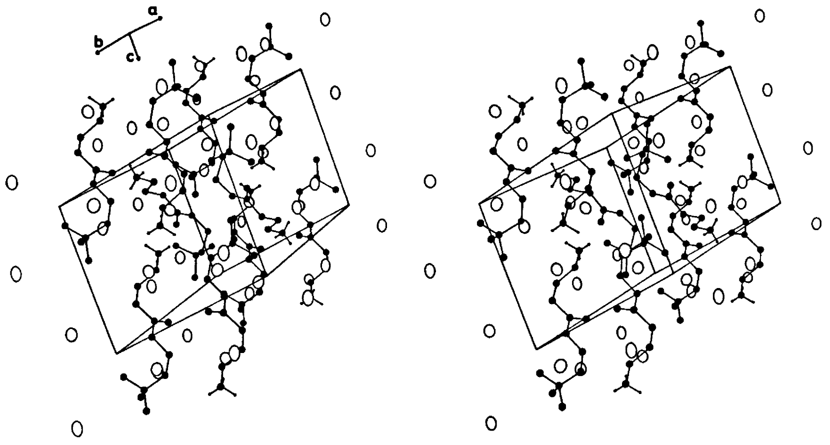


*Fig. 2.* Stereodiagram illustrating the packing of GAKOLI. All hydrogen atoms but the three bonded to N(13) have been omitted for clarity.

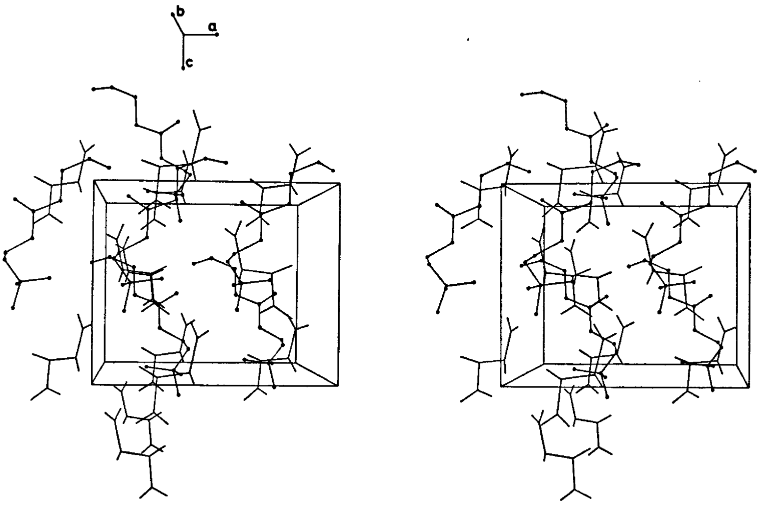


*Fig. 3.* Stereodiagram illustrating the packing of GAKTRA.

$O(041)_{(\frac{1}{2}-x,\frac{1}{2}-y,z-1)}$, 2.80(2) Å, and $N(13)\cdots O(011)_{(\frac{1}{2}-x,\frac{1}{2}+y,z-\frac{1}{2})}$, 2.76 Å. The distance $N(13)\cdots O(02)_{(\frac{1}{2}-x,\frac{1}{2}+y,z-\frac{1}{2})}$ is 2.87(2) Å. From model studies it seems most reasonable to assume this last contact not to be a hydrogen bond.

In summary the three possible $\overset{+}{N}-H\cdots O$ hydrogen bonds are found, and so is one of the two possible $O-H\cdots O$ hydrogen bonds. No *inter*-molecular hydrogen bond involving O(03) is observed. Three of the four carboxylate oxygen atoms act as hydrogen bond acceptors. O(011) accepts two hydrogen bonds, O(012) and O(041) accept one each, while no hydrogen bonding involves O(042). No close contacts to the ester oxygen atoms are observed.

*The tartrate ion.* As the estimated standard deviations on the dimensions of the tartrate ion are very high, importance can hardly be attached to the deviations from the dimensions determined by Ambady[12] and others. The torsion angle C(01)–C(02)–C(03)–C(04) is ± 173(1)°. The distance from O(02) to the plane determined by O(011), O(012), C(01), and C(02) is 0.23 Å, while the deviation of O(03) from the plane through C(03), C(04), O(041), and O(042) is insignificant.

*The GABA choline ester ion.* The dimensions listed in Table 4 for GAKOLI are within the uncertainty in agreement with normally accepted values. The deviations between the corresponding figures for GAKOLI and GAKTRA are hardly significant.

The conformations of the GABA choline ester ion found in the two crystal structures are illustrated in Fig. 4, and torsion angles are listed in Table 6. The two conformations of the GABA-moiety are fundamentally different. In the crystal structures of GABA (zwitterion),[13] of GABA. HCl,[14] and of two

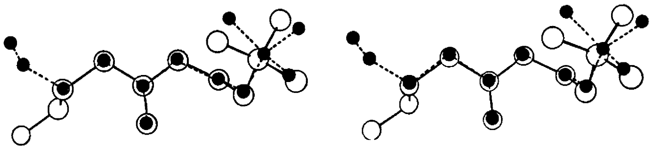


*Fig. 4.* A stereo view of the GABA choline ester ions of GAKOLI (○) and GAKTRA (●). The ions are viewed perpendicular to the plane of the ester group, and C(2) and the direction of C(1)–O(4) are defined to be common for both ions.

*Table 6.* Torsion angles of the GABA choline ester ion as found in GAKOLI and GAKTRA. The estimated standard deviations (referring to the last significant figure) are given in parentheses.

| | GAKOLI | GAKTRA |
|---|---|---|
| N(13) – C(12) – C(11) – C(1) | ±179.7(6) | ±70(3) |
| C(12) – C(11) – C(1) – C(2) | ∓71.8(9) | ∓177(2) |
| C(11) – C(1) – C(2) – O(4) | ∓178.5(7) | ∓176(2) |
| C(1) – C(2) – O(4) – C(5) | ∓176.8(7) | ±174(2) |
| C(2) – O(4) – C(5) – C(6) | ∓ 84.8(8) | ± 86(2) |
| O(4) – C(5) – C(6) – N(7) | ∓ 62.1(8) | ± 74(2) |
| C(5) – C(6) – N(7) – C(8) | ± 72.7(8) | ∓ 62(2) |

copper(II) complexes of GABA[15] a further variety of different conformations of GABA are found. This indicates that the conformation of GABA is highly dependent on the influence of the environment, and it falls in line with the results of NMR studies on a solution of GABA in $D_2O$, in which several different GABA conformers were found to coexist.[16] Theoretical studies especially on the effect of a solvent (water) on the relative stability of different conformers of GABA[17] also seem to indicate that a number of conformations with relatively small mutual energy differences are possible.

The conformation of the choline moiety is approximately the same in the two crystal structures. The torsion angles O(4) – C(5) – C(6) – N(7), ±62° in GAKOLI and ±74° in GAKTRA, are in the range found in most (but not all) crystal structures of compounds containing this atomic arrangement.[18–20] The torsion angle C(2) – O(4) – C(5) – C(6), for which much greater variations are found among the known crystal structures of choline esters,[18–20] is of the same size in GAKOLI and GAKTRA.

*Acknowledgement.* The author thanks Dr. Povl Krogsgaard-Larsen for the preparation of GABA choline ester chloride.

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Received December 15, 1975.