

surrounded by ten I(2) atoms, two I(1) atoms and three U atoms, and I(2) by six I(2) atoms, five I(1) atoms and three U atoms.

The atomic packing tends to become more compact on going from UF₃ to UI₃. The efficiency of packing, as indicated by the ratio $(\frac{4}{3}\pi r^3)/\text{volume per halogen atom in the crystal (corrected for U volume)}$, is 0.55 for UF₃, 0.72 for UCl₃, 0.62 for UBr₃ and 0.89 for UI₃. Large channels, such as those occurring parallel to [001] in UCl₃ (Taylor & Wilson, 1974) and UBr₃, the latter having the UCl₃ structure-type, do not occur in UI₃.

The triangular edges of the prism are 3.679 (18) (2 \times) and 4.291 (15) (4 \times) Å; thus the prism is distorted from regularity. In addition, the uranium atom is removed from a central position in the prism. The centroid of the prism has coordinates [0.2366 (4), 0, $\frac{1}{4}$], and deviates from the uranium position [0.2562 (7) 0, $\frac{1}{4}$] by 0.275 (9) Å. These deviations from regularity are a consequence of the withdrawal of the third capping atom.

As seen in Fig. 2, the UI₃ structure is layered, the layers being parallel to the [100] face. Probably the bonding between layers is mainly due to van der

Waals attractions between iodine atoms. Anti-parallel rows of prisms occur in the layers, adjacent prisms being separated in the direction [100] by $b/2$, or half the prism height. The UCl₃ structure-type has a similar motif. In UCl₃, however, the prisms are arranged in a hexagonal pattern whereas in UI₃ the pattern is orthogonal.

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The Crystal Structures of the Barbitol Salts of 2-Ethoxyethylamine and 2-Dimethylaminoethylamine

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The crystal data for 2-ethoxyethylammonium 5,5-diethylbarbiturate [C₄H₁₂NO]⁺[C₈H₁₁N₂O₃]⁻ are: triclinic, space group *P*1; $a = 6.767$ (2), $b = 10.228$ (3), $c = 12.290$ (3) Å, $\alpha = 64.29$ (2), $\beta = 79.14$ (2), $\gamma = 75.51$ (2)°, with two formula units per cell. The crystal data for 2-dimethylaminoethylammonium 5,5-diethylbarbiturate [C₄H₁₃N₂]⁺[C₈H₁₁N₂O₃]⁻ are: orthorhombic, space group *Pna*2₁; $a = 20.419$ (3), $b = 11.137$ (2), $c = 6.777$ (2) Å, with four formula units per cell. The crystal structure determinations were based on 3045 and 1725 integrated X-ray intensities measured on a four-circle computer-controlled diffractometer using graphite-monochromated Cu *K* α radiation. The final *R* indices were 0.067 and 0.049. Similarities in these crystal structures include their modes of hydrogen bonding, and the occurrence of cation disordering with respect to two rotameric forms. The *syn* conformation is observed for the C–C bond in the NH₃⁺–CH₂–CH₂–O and NH₃⁺–CH₂–CH₂–N < moieties.

Introduction

Solution studies of the interactions of the drug-active barbiturates with phospholipids have been reported by Blaustein & Goldman (1966) and Novak & Swift

(1972). We have been unable to obtain suitable crystals of barbiturate/phospholipid complexes for study of the structural aspects of these interactions. However, we have obtained crystal complexes of 5,5-diethylbarbituric acid or barbital (Fig. 1) with molecules containing selected functional groups of the phospholipids. Thus, the crystal structure of the hexamethylphosphoramide/barbital complex (Hsu & Craven, 1974*a*) showed strong hydrogen bonding between barbital and a phosphoryl oxygen atom. We now report the crystal-

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structure determination of the barbital salt of 2-ethoxyethylamine* (Fig. 1). The cation in this complex contains the $\text{NH}_3^+-\text{CH}_2-\text{CH}_2-\text{O}$ fragment which is present in the phosphatidylethanolamines.

The crystal-structure determination of the barbital salt of 2-dimethylaminoethylamine* (Fig. 1), which we also report, was undertaken so as to compare the structures of the two cations. We find not only that the $\text{NH}_3^+-\text{CH}_2-\text{CH}_2-\text{O}$ - and $\text{NH}_3^+-\text{CH}_2\text{CH}_2\text{N}<$ fragments both have a *syn* conformation with respect to the C-C bond, but that the two crystal structures have similarities in the mode of hydrogen bonding and in the disordering of the cations.

Experimental

(i) The 2-ethoxyethylammonium salt

Crystals of the salt were obtained as triclinic needles elongated on *c*, by slow evaporation of a 1:1 mixture of 2-ethoxyethanolamine and barbital dissolved in absolute methanol. The crystals decomposed within several hours on exposure to air, so that it was necessary to mount a crystal in a thin-walled Lindemann-glass capillary in order to collect the X-ray data. This crystal had dimensions $0.1 \times 0.3 \times 0.6$ mm. The lattice parameters and X-ray intensities were obtained with a

* The abbreviations EEA and DMEA will be used for the 2-ethoxyethylammonium and 2-dimethylaminoethylammonium cations.

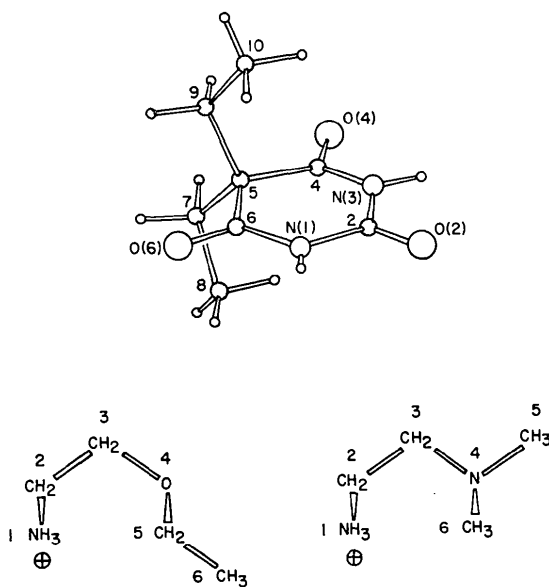


Fig. 1. Molecular structures of 5,5-diethylbarbituric acid or barbital (top), the 2-ethoxyethylammonium cation (EEA) (bottom left) and the 2-dimethylaminoethylammonium cation (DMEA) (bottom right). In the barbital molecule, balls of decreasing size represent oxygen, nitrogen, carbon and hydrogen atoms. In the EEA and DMEA salts, barbital anions are formed by deprotonation at nitrogen atom N(3).

computer-controlled four-circle diffractometer and graphite-monochromated $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418$ Å). The crystal was oriented with *c** along the diffractometer φ axis.

The lattice parameters are $a = 6.767$ (2), $b = 10.228$ (3), $c = 12.290$ (3) Å, $\alpha = 64.29$ (2), $\beta = 79.14$ (2), $\gamma = 75.51$ (2)°, corresponding to a primitive cell which contains 2 formula units $[\text{C}_4\text{H}_{12}\text{NO}]^+[\text{C}_8\text{H}_{11}\text{N}_2\text{O}_3]^-$. The observed crystal density (1.24 g cm^{-3} , measured by flotation in a bromoform/hexane mixture) agrees with the calculated value (1.23 g cm^{-3}). The space group was assumed to be $P\bar{1}$, and this was later confirmed by determination of time- and space-averaged crystal structure. The intensity data were measured for reflections with $2\theta \leq 130^\circ$ using $\theta:2\theta$ scans. Of a total of 3045 reflections, 550 were observed to have integrated intensities (*I*) less than $2\sigma(I)$. These reflections were assigned intensities of $\sigma(I)/2$. No corrections were applied for X-ray absorption or extinction.

The phase problem was solved by a combination of direct and Patterson methods. The *MULTAN* procedure (Germain, Main & Woolfson, 1971) gave a recognizable barbital molecule in the correct orientation, but in a position incompatible with intermolecular hydrogen bonding. The Langs (1973) translation function was used to determine the correct position of the molecule, and thereafter the non-hydrogen atoms of the cation were found by the usual Fourier methods. Atomic parameters were refined by a full-matrix least-squares procedure in order to minimize $\sum w\Delta F^2$ where $w^{-1} = 0.15 + 0.003|F|^2$.

After refinement to an *R* value of 0.09* a difference Fourier synthesis revealed all hydrogen atoms except those bonded to C(5) and C(6) of the cation. The latter hydrogen atoms were assigned fixed parameters corresponding to C-H bond lengths of 1.0 Å and tetrahedral bond angles. Thermal parameters for all hydrogen atoms were assigned the same values as those of the atoms to which they are bonded. These parameters were not subsequently refined.

The two highest peaks in the difference Fourier were consistent with a disordering of atoms C(5) and C(6) in the terminal ethyl group of the cation. For the major sites C(5) and C(6), occupancy factors of 0.67 were assumed and the previously derived values of the anisotropic thermal parameters were retained. Alternative sites C(5') and C(6') were assumed to have occupancy factors of 0.33 and isotropic temperature factors of 6.0 Å². In the final full-matrix least-squares refinement the atomic form factors were those of Cromer & Waber (1965) for C, N and O and of Stewart, Davidson & Simpson (1965) for H. Convergence was obtained at $R = 0.067$ for all reflections or $R = 0.052$ for reflections with non-zero weight. The latter included weak reflections with $I < 2\sigma(I)$ and nine reflections with small scattering angles, large $|F_{\text{meas}}|$

* $R = \frac{\sum | \Delta F |}{\sum | F_{\text{meas}} |}$ where $\Delta F = | F_{\text{meas}} | - | F_{\text{calc}} |$.

and with $|F_{\text{meas}}| < |F_{\text{calc}}|$.^{*} The final atomic parameters are in Table 1.[†]

(ii) *The 2-dimethylaminoethylammonium salt*

The experimental procedure was similar to that followed for the other salt.

^{*} These reflections are 001, 002, 003, 01 $\bar{3}$, 01 $\bar{2}$, 01 $\bar{1}$, 02 $\bar{2}$, 02 $\bar{1}$, 020.

[†] A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30779 (26 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The crystals were orthorhombic needles (m.p. 117°C) elongated on *c*. The X-ray data were measured using a crystal of dimensions 0.13 × 0.13 × 0.55 mm which was coated with lacquer to prevent deterioration on exposure to air. The crystal was mounted with the *c* axis at an angle of 5° from the diffractometer ϕ axis. The lattice parameters are $a = 20.419$ (3), $b = 11.137$ (2), $c = 6.777$ (2) Å with four formula units $[\text{C}_4\text{H}_{13}\text{N}_2]^+[\text{C}_8\text{H}_{11}\text{N}_2\text{O}_3]^-$ in the unit cell. These gave a calculated crystal density (1.174 g cm⁻³) in agreement with the density (1.167 g cm⁻³) measured by flotation in a carbon tetrachloride/hexane mixture. The systematic spectral absences were consistent with the space group $Pna2_1$. This space group was confirmed by the

Table 1. *Atomic parameters and their e.s.d.'s for the EEA salt*

Positional parameters are given as fractional coordinates × 10³ for hydrogen atoms and × 10⁴ for other atoms. Anisotropic thermal parameters (× 10⁴) are given according to the expression $T = \exp(-\sum_i \sum_j \beta_{ij} h_i h_j)$. The e.s.d.'s given in parentheses refer to the least significant digits of the parameter values.

(a) The non-hydrogen atoms

(i) The 2-ethoxyethylammonium cation

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11} or $B(\text{Å}^2)$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N(1)	-2112 (2)	5107 (2)	4177 (1)	141 (3)	141 (2)	101 (1)	-24 (2)	-6 (2)	-81 (1)
C(2)	-2781 (3)	6630 (3)	3289 (2)	247 (5)	182 (3)	116 (2)	9 (3)	-48 (3)	-68 (2)
C(3)	-1539 (4)	7664 (2)	3287 (2)	445 (8)	128 (3)	115 (2)	-24 (3)	-15 (3)	-58 (2)
O(4)	554 (3)	7295 (2)	2948 (1)	428 (6)	185 (2)	104 (1)	-126 (3)	26 (2)	-73 (1)
C(5)	788 (12)	7802 (10)	1659 (4)	362 (18)	359 (14)	94 (4)	-93 (13)	0 (5)	-71 (5)
C(6)	2953 (7)	7751 (6)	1223 (4)	352 (14)	333 (10)	122 (4)	-82 (9)	37 (5)	-112 (5)
C(5')	1728 (25)	7170 (13)	1860 (10)	5.0 (3)	Site factors	C(5)	0.71 (2)	C(6)	0.70 (1)
C(6')	1413 (27)	8658 (19)	910 (17)	11.6 (7)		C(5')	0.26 (2)	C(6')	0.35 (2)

(ii) The 5,5-diethylbarbiturate anion

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N(1)	5250 (2)	2790 (1)	2846 (1)	96 (3)	127 (2)	80 (1)	-14 (2)	-9 (1)	-63 (1)
C(2)	3821 (2)	3543 (1)	3446 (1)	109 (3)	104 (2)	70 (1)	-17 (2)	-8 (1)	-50 (1)
O(2)	4488 (2)	4126 (1)	3967 (1)	138 (3)	179 (2)	122 (1)	-30 (2)	-12 (1)	-110 (1)
N(3)	1799 (2)	3633 (1)	3467 (1)	98 (3)	117 (2)	82 (1)	-14 (2)	-5 (2)	-61 (1)
C(4)	1117 (2)	2982 (1)	2900 (1)	106 (3)	96 (2)	66 (1)	-23 (2)	-10 (1)	-37 (1)
O(4)	-747 (2)	3151 (1)	2867 (1)	108 (2)	180 (2)	126 (1)	-31 (2)	-15 (1)	-9 (1)
C(5)	2560 (2)	2014 (1)	2307 (1)	140 (3)	96 (2)	66 (1)	-20 (2)	-17 (1)	-43 (1)
C(6)	4802 (2)	1986 (2)	2315 (1)	135 (3)	100 (2)	63 (1)	-3 (2)	-12 (1)	-43 (1)
O(6)	6169 (2)	1287 (1)	1870 (1)	169 (3)	167 (2)	113 (1)	12 (2)	-7 (1)	-99 (1)
C(7)	2090 (3)	2598 (2)	977 (1)	194 (4)	151 (2)	72 (1)	-26 (2)	-32 (2)	-54 (1)
C(8)	2597 (4)	4117 (2)	178 (2)	278 (6)	166 (3)	80 (2)	-33 (3)	-28 (2)	-20 (2)
C(9)	2158 (3)	424 (2)	3007 (2)	234 (4)	100 (2)	108 (2)	-43 (2)	-18 (2)	-51 (2)
C(10)	2690 (4)	-319 (2)	4309 (2)	335 (7)	123 (2)	100 (2)	-46 (3)	-16 (3)	-10 (2)

(b) The hydrogen atoms

Thermal parameters for the hydrogen atoms were assigned to be equal to those of the atoms to which they are covalently bonded.

(i) The 2-ethoxyethylammonium cation

	<i>x</i>	<i>y</i>	<i>z</i>
H(11)	-231 (3)	495 (2)	497 (2)
H(12)	-74 (3)	477 (2)	405 (2)
H(13)	-289 (3)	440 (2)	418 (2)
H(21)	-415 (4)	692 (3)	358 (2)
H(22)	-279 (3)	673 (3)	247 (2)
H(31)	-222 (4)	871 (2)	272 (2)
H(32)	-159 (4)	756 (2)	416 (2)
H(51)*	35	712	138
H(52)*	5	882	121
H(61)*	330	790	20
H(62)*	369	684	174
H(63)*	327	862	126

(ii) The 5,5-diethylbarbiturate anion

	<i>x</i>	<i>y</i>	<i>z</i>
H(1)	654 (3)	285 (3)	280 (2)
H(71)	293 (3)	183 (2)	65 (2)
H(72)	60 (3)	258 (2)	98 (2)
H(81)	412 (4)	405 (2)	8 (2)
H(82)	178 (4)	485 (3)	53 (2)
H(83)	216 (3)	447 (2)	-70 (2)
H(91)	304 (3)	-41 (2)	262 (2)
H(92)	64 (3)	46 (2)	295 (2)
H(101)	196 (4)	24 (2)	480 (2)
H(102)	422 (4)	-40 (2)	434 (2)
H(103)	236 (4)	-128 (3)	464 (2)

* Atoms not found in a difference Fourier synthesis. The positional parameters are predicted values.

subsequent determination of the time- and space-averaged crystal structure.

The integrated X-ray intensities were measured by $\theta:2\theta$ scans for a total of 1725 non-symmetry-related reflections with $2\theta \leq 150^\circ$. There were 350 reflections for which the intensity (I) was less than $2\sigma(I)$. These reflections were assigned intensities of $\sigma(I)/2$.

The phase problem was solved by use of the *MULTAN* procedure (Germain, Main & Woolfson, 1971). Atomic parameters for non-hydrogen atoms were refined by using full-matrix least-squares, as described for the other salt, but with weights $w^{-1} = 0.15 + 0.002|F|^2$. A difference Fourier synthesis revealed all

hydrogen atoms, although peaks corresponding to hydrogens of the terminal methyl groups of both ions were not clearly distinguished from the background in the map. Three of the four largest peaks in the difference map were not consistent with hydrogen-atom positions, but rather suggested a disordering of the atoms C(3), C(5) and C(6) which are bonded to the tertiary nitrogen atoms N(4) of the cation. In subsequent refinement alternative sites for these atoms, C(3'), C(5') and C(6'), were introduced with initial values of 0.15 for site factors and 6.0 \AA^2 for isotropic temperature factors. Limitation in computer facilities prevented a full-matrix refinement of all structure pa-

Table 2. Atomic parameters and their e.s.d.'s for the DMEA salt

Positional parameters are given as fractional coordinates. Anisotropic thermal parameters are given according to the expression $T = \exp(-\sum_i \sum_j \beta_{ij} h_i h_j)$. The e.s.d.'s given in parentheses refer to the least significant digits of the parameter values.

(a) The non-hydrogen atoms

(i) The 2-dimethylaminoethylammonium cation

	<i>x</i>	<i>y</i>	<i>z</i>	$\beta_{11} \times 10^5$ or $B(\text{\AA}^2)$	$\beta_{22} \times 10^4$	$\beta_{33} \times 10^4$	$\beta_{12} \times 10^5$	$\beta_{13} \times 10^5$	$\beta_{23} \times 10^4$
N(1)	0.45289 (9)	0.0224 (2)	0.6075 (3)	208 (4)	124 (2)	124 (3)	-136 (7)	0 (11)	9 (3)
C(2)	0.42210 (19)	0.1415 (3)	0.6269 (5)	394 (9)	152 (3)	224 (7)	102 (15)	294 (22)	-21 (5)
C(3)	0.41992 (16)	0.2087 (3)	0.4302 (6)	261 (9)	113 (4)	265 (9)	119 (14)	51 (20)	-4 (5)
N(4)	0.48265 (11)	0.2240 (2)	0.3431 (4)	278 (5)	119 (2)	283 (6)	22 (8)	-14 (15)	36 (3)
C(5)	0.4762 (3)	0.2633 (6)	0.1384 (8)	429 (20)	161 (8)	272 (15)	31 (27)	86 (35)	62 (7)
C(6)	0.5258 (3)	0.3074 (5)	0.4409 (13)	444 (17)	147 (6)	662 (34)	-15 (2)	-518 (54)	3 (9)
C(3')	0.4668 (9)	0.238 (2)	0.560 (3)	5.1 (6)					
C(5')	0.520 (2)	0.296 (3)	0.246 (6)	10 (1)					
C(6')	0.414 (1)	0.236 (2)	0.238 (4)	5.1 (7)					
Site factors	C(3)	0.81 (1)	C(5)	0.74 (2)	C(6)	0.86 (2)			
	C(3')	0.15 (1)	C(5')	0.21 (3)	C(6')	0.15 (1)			

(ii) The 5,5-diethylbarbiturate anion

	<i>x</i>	<i>y</i>	<i>z</i>	$\beta_{11} \times 10^5$	$\beta_{22} \times 10^4$	$\beta_{33} \times 10^4$	$\beta_{12} \times 10^5$	$\beta_{13} \times 10^5$	$\beta_{23} \times 10^4$
N(1)	0.32014 (8)	-0.1462 (2)	0.0269 (4)	199 (4)	126 (2)	72 (3)	-134 (8)	-40 (11)	1 (3)
C(2)	0.37160 (10)	-0.0877 (2)	0.1201 (4)	164 (5)	95 (2)	105 (4)	-60 (8)	17 (13)	-4 (3)
O(2)	0.41070 (7)	-0.0320 (2)	0.0152 (3)	203 (3)	123 (2)	133 (3)	-143 (6)	68 (11)	5 (2)
N(3)	0.37792 (9)	-0.0923 (2)	0.3169 (4)	217 (5)	128 (5)	91 (3)	-161 (8)	-45 (11)	-5 (2)
C(4)	0.33311 (12)	-0.1499 (3)	0.4282 (4)	244 (6)	125 (3)	98 (4)	-167 (11)	-41 (13)	2 (3)
O(4)	0.33901 (11)	-0.1484 (3)	0.6090 (4)	421 (6)	245 (4)	80 (3)	-474 (13)	-36 (14)	16 (3)
C(5)	0.27594 (11)	-0.2195 (2)	0.3419 (4)	225 (6)	108 (3)	116 (5)	-138 (10)	26 (13)	12 (3)
C(6)	0.27325 (10)	-0.2134 (2)	0.1172 (4)	192 (5)	100 (2)	127 (4)	-114 (9)	-37 (14)	-8 (3)
O(6)	0.23120 (8)	-0.2633 (2)	0.0233 (4)	283 (4)	153 (2)	178 (4)	-288 (8)	-101 (14)	-15 (3)
C(7)	0.2820 (2)	-0.3527 (3)	0.4015 (5)	413 (10)	129 (3)	221 (8)	-99 (16)	-38 (24)	45 (4)
C(8)	0.3467 (3)	-0.4095 (5)	0.3501 (8)	613 (16)	148 (5)	336 (14)	261 (23)	-41 (39)	17 (7)
C(9)	0.2111 (2)	-0.1705 (4)	0.4243 (5)	262 (7)	160 (4)	177 (6)	-106 (13)	113 (18)	-6 (4)
C(10)	0.1940 (3)	-0.0463 (5)	0.3596 (8)	630 (20)	162 (5)	332 (13)	280 (27)	258 (41)	-20 (7)

(b) The hydrogen atoms

(i) The 2-dimethylaminoethylammonium cation

	<i>x</i>	<i>y</i>	<i>z</i>	$B(\text{\AA}^2)$
H(11)	0.433 (1)	-0.016 (2)	0.503 (5)	4.0 (5)
H(12)	0.496 (1)	0.023 (2)	0.593 (4)	4.0 (5)
H(13)	0.445 (2)	-0.021 (3)	0.721 (6)	6.8 (8)
H(21)	0.442 (2)	0.179 (4)	0.713 (7)	8 (1)
H(22)	0.371 (2)	0.132 (3)	0.670 (6)	10 (1)
H(31)	0.393 (1)	0.158 (3)	0.314 (5)	6.4 (7)
H(32)	0.402 (2)	0.300 (3)	0.456 (6)	10 (1)
H(51)	0.445 (2)	0.202 (4)	0.074 (8)	9 (1)
H(52)	0.452 (2)	0.338 (4)	0.146 (7)	10 (1)
H(53)	0.504 (4)	0.283 (5)	0.056 (13)	14 (2)
H(61)	0.496 (2)	0.382 (4)	0.479 (8)	9 (1)
H(62)	0.530 (4)	0.299 (7)	0.58 (2)	19 (3)
H(63)	0.567 (3)	0.325 (4)	0.314 (10)	11 (2)

(ii) The 5,5-diethylbarbiturate anion

	<i>x</i>	<i>y</i>	<i>z</i>	$B(\text{\AA}^2)$
H(1)	0.319 (1)	-0.138 (2)	-0.083 (5)	3.7 (5)
H(71)	0.278 (2)	-0.371 (3)	0.534 (6)	8.4 (9)
H(72)	0.244 (1)	-0.406 (2)	0.339 (5)	4.9 (6)
H(81)	0.362 (2)	-0.389 (3)	0.212 (6)	6.4 (8)
H(82)	0.351 (3)	-0.496 (4)	0.377 (8)	10 (1)
H(83)	0.389 (2)	-0.345 (4)	0.419 (9)	12 (1)
H(91)	0.179 (1)	-0.236 (2)	0.387 (4)	4.9 (6)
H(92)	0.215 (2)	-0.189 (3)	0.581 (7)	9.0 (9)
H(101)	0.191 (2)	-0.047 (4)	0.227 (9)	10 (1)
H(102)	0.203 (3)	0.016 (6)	0.405 (10)	18 (2)
H(103)	0.149 (3)	-0.016 (4)	0.395 (8)	10 (1)

rameters. Parameters for the cation and anion (Table 2) were refined separately in alternate cycles until convergence was obtained. The final R value was 0.049 for all reflections, or 0.035 for reflections excluding those with $I < 2\sigma(I)$, which were given zero weight in the refinement. The list of observed and calculated structure factors is available.*

Discussion

The molecular species in both crystal structures are ions, as shown in each case by the determination of the hydrogen atom position in the $\text{NH}\cdots\text{N}$ hydrogen bond between barbital and amine. In each case, barbital atom N(3) is deprotonated and the primary amino nitrogen atom N(1) is protonated. Further evidence for ionic character comes from a comparison with other crystal structure determinations, which show that barbital and its ion differ significantly in bond lengths and angles, particularly at the deprotonation site N(3). These differences were discussed by Berking

(1972). Barbital anion bond lengths and angles in the EEA and DMEA salts agree well with each other and with values reported for the barbital anion in three other barbital salts (Table 3 and references cited therein). Berking (1972) also points out that although the pyrimidine ring in the barbital anion is nearly planar,

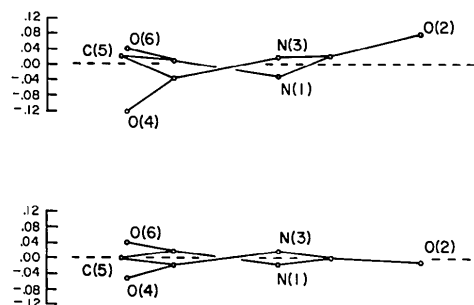


Fig. 2. Ring puckering of barbital anions in the salts with EEA (top) and DMEA (bottom). The dashed line represents the trace of the best least-squares plane through the six ring atoms. The vertical scale (Å) is 10 times greater than the horizontal scale.

* See footnote on p. 884.

Table 3. Bond lengths (Å) and angles (°) for the barbital anions in the two salts

Values in parentheses are e.s.d.'s referred to the least significant digit in the corresponding parameter.

(a) Bond lengths

	EEA salt	DMEA salt	Range* Barbital (anion)	Range* Barbital (acid)
C(6)–N(1)	1.363 (2)	1.360 (3)	1.343–1.355	1.355–1.372
C(2)–N(1)	1.387 (2)	1.388 (3)	1.376–1.405	1.362–1.379
C(2)–N(3)	1.344 (2)	1.341 (3)	1.323–1.345	1.371–1.387
C(4)–N(3)	1.351 (2)	1.349 (3)	1.332–1.349	1.354–1.376
C(2)–O(2)	1.243 (2)	1.236 (3)	1.228–1.251	1.204–1.215
C(4)–O(4)	1.235 (2)	1.231 (3)	1.238–1.254	1.213–1.228
C(6)–O(6)	1.218 (2)	1.205 (3)	1.216–1.229	1.203–1.223
C(4)–C(5)	1.529 (2)	1.518 (3)	1.512–1.542	1.510–1.522
C(6)–C(5)	1.512 (2)	1.526 (3)	1.495–1.520	1.519–1.530
C(7)–C(5)	1.544 (2)	1.542 (4)	1.539–1.568	1.538–1.551
C(9)–C(5)	1.542 (2)	1.537 (4)	1.541–1.549	1.536–1.552
C(7)–C(8)	1.520 (3)	1.506 (6)	1.504–1.531	1.503–1.528
C(9)–C(10)	1.514 (3)	1.491 (6)	1.469–1.525	1.507–1.518
N(1)–H(1)	0.88 (2)	0.75 (3)	0.87–0.91	0.84–0.90

(b) Bond angles

C(6)–N(1)–C(2)	125.1 (1)	125.9 (2)	123.8–125.5	125.4–126.9
N(1)–C(2)–N(3)	121.4 (1)	120.5 (2)	120.6–122.6	115.6–116.8
C(2)–N(3)–C(4)	120.1 (1)	120.6 (2)	119.2–120.6	125.5–127.0
N(3)–C(4)–C(5)	122.6 (1)	123.3 (2)	122.3–123.8	118.2–119.2
C(4)–C(5)–C(6)	113.4 (1)	112.9 (2)	111.9–113.1	113.3–114.3
C(5)–C(6)–N(1)	116.9 (1)	116.6 (2)	116.7–118.0	117.6–119.5
N(1)–C(2)–O(2)	117.2 (1)	117.6 (2)	116.0–119.0	122.0–123.1
N(3)–C(2)–O(2)	121.4 (1)	121.9 (2)	118.4–122.8	121.1–122.2
N(3)–C(4)–O(4)	119.2 (1)	118.9 (2)	118.9–120.9	119.1–120.7
N(1)–C(6)–O(6)	120.5 (1)	121.2 (2)	119.7–121.1	120.0–120.6
C(7)–C(5)–C(9)	109.5 (1)	108.4 (2)	108.2–111.5	109.0–110.3
C(5)–C(7)–C(8)	113.8 (2)	114.5 (3)	113.2–115.1	114.4–115.8
C(5)–C(9)–C(10)	115.0 (2)	115.1 (3)	114.1–115.0	113.7–115.4

* The ranges of bond lengths and angles are those which have been determined for the six independent barbital anions in the crystal structures of sodium barbital (Berking & Craven, 1971), calcium barbital trihydrate (Berking, 1972) and guanidinium barbital dihydrate (McClure & Craven, 1973); and for nine barbital acid molecules in the hydrogen-bonded complexes with caffeine (Craven & Gartland, 1974), hexamethylphosphoramide (Hsu & Craven, 1974a), acetamide (Hsu & Craven, 1974b), imidazole (Hsu & Craven, 1974c), urea (Gartland & Craven, 1974), 2-aminopyridine (Hsu & Craven, 1974d), and *N*-methylpyridone (Hsu & Craven, 1974e).

there is usually a slight puckering in a mode which appears to depend on the nature of the molecular environment. Slight ring puckering also occurs in both

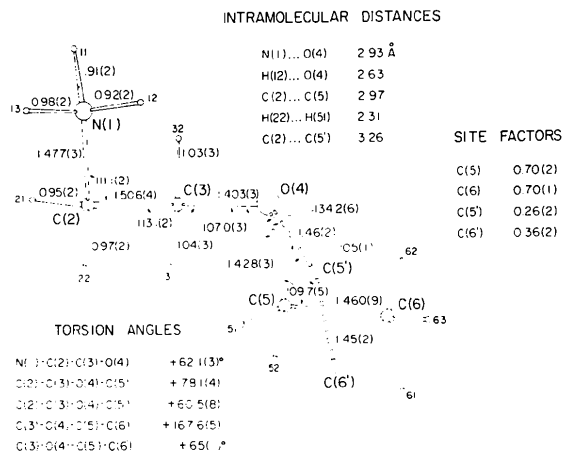


Fig. 3. The 2-ethoxyethylammonium cation, projected on the bisector of the C(2)-C(3)-O(4) bond angle.

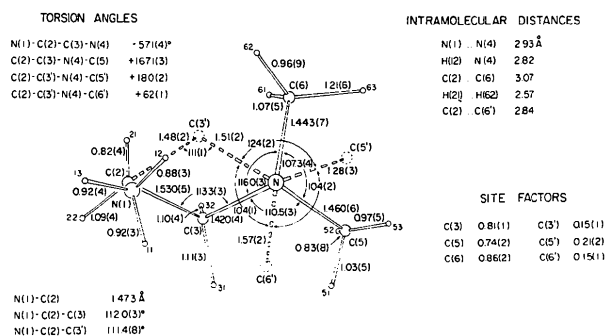


Fig. 4. The 2-dimethylaminoethylammonium cation, projected on the normal to the plane of atoms C(3), C(5) and C(6).

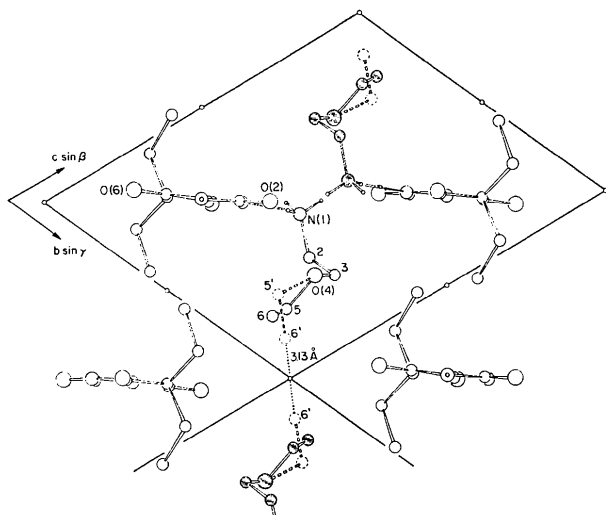


Fig. 5. The crystal structure of the EEA salt, projected on the *a* axis.

the EEA and DMEA salts (Fig. 2). The ring puckering in the EEA structure is the more pronounced, and is in a different mode from any which has previously been observed for a barbituric anion. However, this puckering is similar to that observed for several 5,5-dialkylbarbituric acid molecules such as amobarbital (Craven, Cusatis, Gartland & Vizzini, 1973).

In the EEA crystal structure, the cation is disordered with respect to two rotameric forms which occur with probabilities of about 70% and 30%, as indicated by the values of the least-squares atomic site factors (Table 1 and Fig. 3). There is also disorder in the DMEA structure, where the rotamers occur with probabilities of about 80% and 20% (Table 2 and Fig. 4). The alternative sites C(3) or C(3'), C(5) or C(5') and C(6) or C(6') are resolved in the electron-density difference maps, the shortest intersite distance being 0.77 Å for C(5) and C(5') in EEA. Difference Fourier syntheses gave no indication that atoms O(4) in EEA and N(4) in DMEA might also be at different sites in each rotamer. The maximum r.m.s. amplitudes of vibration derived from the thermal parameters for these atoms, assuming them to be ordered, are 0.33 Å for O(4) and 0.29 Å for N(4). These values are intermediate between those of C(3) and C(5), which are 0.32 and 0.34 Å in EEA and 0.28 and 0.34 Å in DMEA. Thus, if O(4) and N(4) are disordered, the sites are too close to give unusually large apparent thermal parameters. The bond lengths and angles (Figs. 3 and 4) have not been corrected for the effects of anisotropic thermal vibration or for possible disordering of O(4) and N(4) with respect to sites which may well be separated by an unresolvably small distance, such as 0.05 Å. Thus, differences in O(4)-C bond lengths in EEA, and N(4)-C bond lengths in DMEA are not considered to be real, although they are significant in terms of their apparent e.s.d.'s.

In both cations, the conformation is *syn* with respect to the bond C(2)-C(3) (Figs. 3 and 4) and is thus consistent with the conformation observed in related molecules containing the $^+\text{NH}_3\text{-CH}_2\text{-CH}_2\text{-X}^-$ moiety, where X=O or N. These include the $^+\text{NH}_3\text{C-C-O}$ group in 1,2-dilauroyl-(±)-phosphatidylethanolamine (Hitchcock, Mason, Thomas & Shipley, 1974), *O*-L-glycerylphosphorylethanolamine (DeTitta & Craven, 1971, 1973), and 2-aminoethanol phosphate (Kraut, 1961), and in the $(^+\text{NH}_3\text{-CH}_2\text{-CH}_2)_3\text{-N}$ groups in 2,2',2''-triaminotriethylamine trihydrochloride (Rasmussen & Grønabæk, 1963; Grønabæk-Hazell & Rasmussen, 1968).* Sundaralingam (1968) has explained the short $\text{N}^+\cdots\text{O}$ intramolecular distances in molecules containing the $\text{N}^+\text{-C-C-O}$ system in terms of a Coulombic attraction, rather than intramolecular hydrogen bonding. In the EEA cation the short intramolecular N(1) \cdots O(4) distance (2.93 Å; cf. 2.83 Å in glycerylphosphorylethanolamine) does not represent

* The *anti* configuration is reported for the C-C bond in crystal structure of ethylenediamine (Jamet-Delcroix, 1973).

a hydrogen bond, since the corresponding H(12)···O distance (2.63 Å) is too long. This is a normal H···O van der Waals distance. Similarly, in the DMEA cation, there is a short N(1)···N(4) intramolecular distance (2.93 Å; cf. 2.95 Å in the triaminotriethylammonium ion) but the H(12)···N(4) distance is too long (2.82 Å) for hydrogen bonding.

It is of interest that both rotamers of the EEA cation also have a *syn* conformation with respect to the bond C(3)–O(4) (Fig. 3). The torsion angles for the bond C(3)–O(4) differ by 18° in the two rotamers. In the rotamer which occurs with 70% probability, the *syn* conformation leads to a short intramolecular non-bonded distance C(2)···C(5) of 2.97 Å. In the *anti* conformation, this short distance would be avoided. It may be significant that when the configuration at the C(3)–O(4) is *syn*, as observed, rather than *anti*, the region presumably occupied by O(4) lone pairs of electrons is closer to the ammonium group. The conformation at the bond O(4)–C(5) is *anti* in the rotamer which occurs with 70% probability and *syn* in the other. This difference could be due to crystal packing effects.

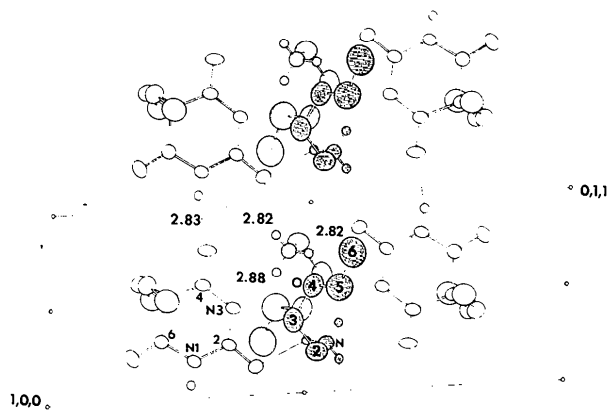
The disordering in the DMEA structure is with respect to DMEA rotamers which are nearly enantiomorphous. There is a pseudo mirror plane passing through the atoms N(1), C(2) and N(4) which are common to both rotamers. From an inspection of a crystal structure model, there appears to be room for interconversion from one rotamer to the other by concerted rotation about the bonds N(1)–C(3), C(2)–C(3) and C(3)–C(4), leaving the ammonium group anchored by means of its hydrogen bonding. However, it is impossible to determine whether such an interconversion is occurring from our diffraction study of the space- and time-averaged structure at only one temperature.

In Fig. 4, the DMEA cation is viewed almost along the bond N(1)–C(2). It can be seen that in the predominant rotamer, there is a staggered configuration of the substituents at N(2) and C(2), whereas in the other rotamer, there would be an eclipsed configuration.* The preference for a staggered conformation about N(1)–C(2) is consistent with the greater probability of this rotamer.

There are striking similarities in the molecular packing and hydrogen bonding in the crystal structures of the two salts (Figs. 5,6,7,8). In both cases, barbital anions form N(1)H(1)···O(4) hydrogen-bonded chains parallel to *c* (Figs. 6 and 8). These chains are cross-linked to form double ribbons by means of the three hydrogen bonds involving the ammonium group of the cation. In the EEA structure, the two barbital chains in a ribbon are anti-parallel. In the DMEA structure, these chains are parallel. In spite of this difference, the hydrogen bonding between chains is very similar.

* Alternative sites for H(21) and H(22) were not found in the difference Fourier map. This is not surprising, since the hydrogen atom site factors would be about 0.2. However, it is reasonable to assume that all bond angles at C(2) are approximately tetrahedral in both structures.

Thus, barbital oxygen atom O(2) accepts two hydrogen bonds, and each barbital nitrogen atom N(3) accepts one. The N⁺···O(2) distances are 2.82, 2.82, 2.86, 2.96 Å. The N(1)H···O(4) hydrogen bonds have N···O distances (2.83, 2.86 Å) which are within the range of distances observed for other NH···O hydrogen bonds in which barbiturates are both donor and acceptor. The NH···N hydrogen bonds have shorter N···N distances (2.88 and 2.80 Å) than in the only other reported NH···N hydrogen bond in which a barbital nitrogen atom is the acceptor (3.00 Å, guanidinium barbital dihydrate; McClure & Craven, 1973).



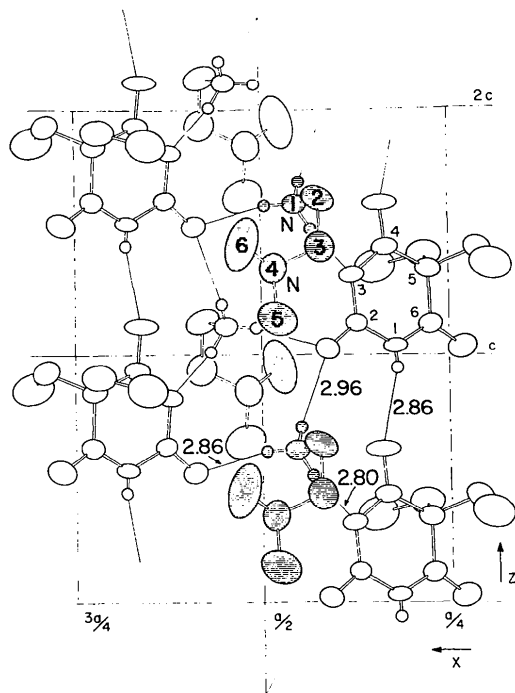


Fig. 8. The crystal structure of the DMEA salt projected down the b axis. The positive sense of the b axis is from the page to the viewer. As in Fig. 7, atoms C(3'), C(5') and C(6') are omitted.

It is of interest that neither the ether oxygen O(4) of the EEA cation nor the tertiary nitrogen N(4) of the DMEA cation are hydrogen bonded. From Figs. 6 and 8, it may appear as if these atoms are involved in bifurcated hydrogen bonds with the ammonium groups of neighboring cations. However, the $N \cdots O(4)$ and $N \cdots N(4)$ distances (3.49, 3.44 Å) correspond to normal van der Waals interactions.

There are no unusually short intermolecular distances within the ribbon structures except for the distance $C(5') \cdots N(3)$ of 3.28 (2) Å, in the EEA structure. This distance is about 0.2 Å shorter than the sum of van der Waals radii if these are assumed to be 2.0 Å for the methylene group and 1.5 Å for the barbiturate nitrogen atom.

The ribbons in each crystal structure are bordered by the ethyl groups of the barbital anions and have cations curled over on each side of the planes of barbiturate rings. Thus, the ribbon periphery is largely occupied by non-polar groups, and the packing together of ribbons appears to be dominated by the van der Waals interactions of these groups (Figs. 5 and 7). The atomic distances between ribbons are not unusual although in the EEA structure there appears to be a

very short distance $C(6') \cdots C(6')$ of 3.13 Å (Fig. 6). This short separation need not actually occur, because of the disordering of the cations.

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