

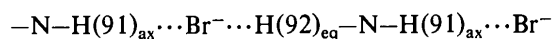
Fig. 1. View of the molecule showing the atom numbering.

piperazinium molecules (*e.g.* Vanier & Brisse, 1982) have much narrower CNC angles in the range 110 to 114°.

The $C(7)_{ax} \cdots C(8)_{ax}$ distance of 3.205 (11) Å is the shortest yet observed in 2,2,6,6-tetramethylpiperidine molecules and is consistent with a trend showing increasing $C_{ax} \cdots C_{ax}$ distance with increasing bulk of the 4-substituent; *e.g.* (I) (ethynyl) 3.214 (5) Å; (III) (vinyl) 3.264 (6) Å; (IV) (methyl) 3.271 (7) Å; (V) (*tert*-butyl) 3.383 (5) Å. Non-bonded H \cdots H contacts between the axial methyl groups are particularly short with $H(1) \cdots H(4) = 1.99$ Å and $H(2) \cdots H(8) = 2.34$ Å. Such interactions cause a significant flattening of the ring at nitrogen but leave the two C—C—C—C dihedral angles near the fully puckered values of $\pm 60^\circ$ (Table 2).

The near perfect mirror symmetry of the cation is broken only by the different conformations of the two equatorial methyl groups caused by interactions between the bromide ion and the methyl hydrogen on

C(7). Molecular packing is dominated by the hydrogen-bonded chains



with $Br \cdots H_{ax} = 2.52$ (6) and $Br \cdots H_{eq} = 2.49$ (6) Å.

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The Structure of *N*-[3-(3-Ammoniopropylammonio)propyl]succinamic Acid Sulfate, $C_{10}H_{23}N_3O_3^{2+} \cdot SO_4^{2-}$

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Abstract. $M_r = 329.37$, $P2_1/c$, $a = 17.693$ (2), $b = 9.453$ (1), $c = 8.958$ (1) Å, $\beta = 90.42$ (2)°, $V = 1498.2$ Å³, $Z = 4$, $F(000) = 704$, $D_m = 1.460$, $D_x = 1.457$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu(\text{Cu } K\alpha) = 22.25$ cm⁻¹, $T = 298$ K, $R = 0.042$ for

2278 reflections. The backbone chain in the cation consists of four short segments which are in the extended conformation. The N-terminus segment is six atoms in length and it is followed by two five-atom segments [N(2)C(7)C(6)C(5)N(1) and C(5)N(1)C(4)C(3)C(2)] and one four-atom segment [C(3)C(2)C(1)O(1)]. The chain changes direction abruptly at the three junctions between segments. The

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structure analysis proves unequivocally that selective acylation of 3,3'-diaminodipropylamine with succinic anhydride takes place at the primary and not the secondary amino group.

Introduction. The title compound is an intermediate in the synthesis of biotinylated insulins in which the biotin is separated from the insulin by a spacer arm based on 3,3'-diaminodipropylamine. In this connection it was important to establish the structure of a reaction product obtained by selective acylation of 3,3'-diaminodipropylamine with succinic anhydride. The crystal structure of $C_{10}H_{23}N_3O_3^{2+} \cdot SO_4^{2-}$ (I) was determined to demonstrate unambiguously whether the primary or the secondary amino group underwent acylation.

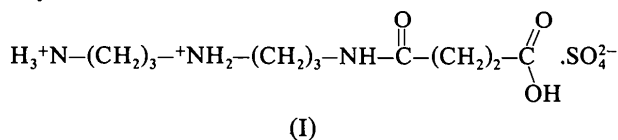


Table 1. Fractional atomic coordinates (and e.s.d.'s) of non-hydrogen atoms ($\times 10^4$) and hydrogen atoms ($\times 10^3$)

For non-hydrogen atoms, the isotropic equivalents of the anisotropic thermal factors are given: $B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$.

	x	y	z	$B_{eq}(\text{\AA}^2)$ or B_{iso}
S	4020.6 (3)	884 (1)	3012.9 (5)	1.7
OS(1)	4112 (1)	361 (2)	4564 (2)	2.5
OS(2)	4490 (1)	2146 (2)	2807 (2)	2.7
OS(3)	4212 (1)	-215 (2)	1948 (2)	3.2
OS(4)	3216 (1)	1326 (2)	2811 (2)	2.6
O(1)	-2265 (1)	5026 (2)	3882 (2)	3.7
O(2)	-1979 (2)	3619 (3)	2022 (3)	6.7
O(3)	-107 (2)	4463 (2)	2617 (4)	7.4
N(1)	349 (1)	2378 (2)	1962 (2)	2.6
N(2)	3018 (1)	4022 (2)	1618 (2)	2.0
N(3)	4545 (1)	7396 (3)	4592 (2)	2.4
C(1)	-1862 (1)	4021 (3)	3267 (3)	2.7
C(2)	-1288 (1)	3397 (3)	4321 (3)	3.1
C(3)	-735 (1)	2410 (3)	3574 (3)	2.9
C(4)	-139 (1)	3179 (3)	2677 (3)	3.1
C(5)	954 (1)	2936 (3)	1042 (3)	2.8
C(6)	1657 (1)	3335 (3)	1920 (3)	2.5
C(7)	2283 (1)	3741 (3)	854 (3)	2.5
C(8)	3021 (1)	5295 (3)	2591 (3)	2.6
C(9)	3789 (1)	5575 (3)	3264 (3)	2.4
C(10)	3789 (1)	6979 (3)	4060 (3)	2.5
H(O1)	-260 (2)	545 (3)	322 (3)	3.2
H1(C2)	-161 (2)	286 (3)	510 (3)	3.2
H2(C2)	-104 (2)	415 (3)	487 (3)	3.2
H1(C3)	-100 (2)	176 (3)	297 (3)	3.2
H2(C3)	-48 (2)	182 (3)	430 (3)	3.2
H(N1)	34 (2)	158 (3)	207 (3)	3.2
H1(C5)	75 (2)	374 (3)	57 (3)	3.2
H2(C5)	112 (2)	222 (3)	34 (3)	3.2
H1(C6)	180 (2)	251 (3)	249 (3)	3.2
H2(C6)	155 (2)	404 (3)	247 (3)	3.2
H1(C7)	236 (2)	299 (3)	20 (3)	3.2
H2(C7)	218 (2)	460 (3)	33 (3)	3.2
H1(N2)	338 (2)	411 (3)	92 (3)	3.2
H2(N2)	318 (2)	320 (3)	215 (3)	3.2
H1(C8)	267 (2)	517 (3)	327 (3)	3.2
H2(C8)	287 (2)	613 (3)	197 (3)	3.2
H1(C9)	414 (2)	555 (3)	256 (3)	3.2
H2(C9)	391 (2)	480 (3)	391 (3)	3.2
H1(C10)	360 (2)	775 (3)	345 (3)	3.2
H2(C10)	348 (2)	696 (3)	483 (3)	3.2
H1(N3)	471 (2)	694 (3)	528 (3)	3.2
H2(N3)	488 (2)	725 (3)	396 (3)	3.2
H3(N3)	459 (2)	822 (3)	479 (3)	3.2

Experimental. Transparent rectangular crystals from aqueous methanol, $0.08 \times 0.14 \times 0.72$ mm, density measured by flotation in mixture of xylene and carbon tetrachloride, Picker FACS-1 diffractometer, graphite-monochromatized $Cu K\alpha$, lattice parameters from 12 reflections with $54^\circ < 2\theta < 77^\circ$, 2409 independent reflections with $4.5^\circ < 2\theta < 126.0^\circ$, 2278 with $I > 3\sigma(I)$, Lp correction, absorption correction with max. 1.69 and min. 1.19; complete molecule except for the H atoms obtained by direct methods and refined by full-matrix least squares on F_o , all H-atom positions located from difference Fourier map, fixed isotropic temperature factor of 3.2 \AA^2 for all H's, $R_w = 0.056$, w determined from an analysis of variance (Lalancette, Cefola, Hamilton & Laplaca 1967), $w = [\sigma^2(F_o)]^{-1}$, $\sigma(F_o) = -0.018|F_o| + 4.4$ for $0 \leq F_o < 70.6$, $\sigma(F_o) = 0.024|F_o| + 1.4$ for $70.6 < F_o \leq 280.4$ and $\sigma(F_o) = 0.068|F_o| - 10.84$ for $280.4 < F_o$, $S = 1.44$, all $\Delta/\sigma < 0.1$, final difference map with no $\Delta\rho$ excursions $> 0.5 \text{ e \AA}^{-3}$ or $< -0.6 \text{ e \AA}^{-3}$, scattering factors from *International Tables for X-ray Crystallography* (1974), computer programs: *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), absorption-correction program by L. Templeton (Based on the analytical method of Alcock, 1970), *QWKREF* (Furey, Wang & Sax, 1982), *APFOUR* (Furey, Wang & Sax, 1982) and *ORTEP* (Johnson, 1976).

Discussion. The molecular structure* is shown in Fig. 1 and the atomic coordinates, bond lengths and valence angles are listed in Tables 1 and 2. The crystal structure is composed of SO_4^{2-} anions and $C_{10}H_{23}N_3O_3^{2+}$ cations in which the two amino groups are protonated. The sulfate ions have an almost regular tetrahedral shape. The mean S—O distance of $1.47(1) \text{ \AA}$ and the mean O—S—O angle of $109(2)^\circ$ are in good agreement with earlier results (Taesler & Olovsson, 1969; Gustafsson, Lundgren & Olovsson, 1977). In the cationic moiety the mean bond length of $1.512(6) \text{ \AA}$ for $C(sp^3)-C(sp^3)$ is comparable to the limiting value for a pure σ bond (1.51 \AA). The dimensions and geometry of the acid amide group are normal. The conformation of the chain in the cation is described as follows. The segment of the chain that includes the six atoms from N(3) to C(7) is approximately in the extended form since the associated torsion angles are all near 180° (the *trans* conformation) [$N(3)-C(10)-C(9)-C(8) = -173.3(2)^\circ$, $C(10)-C(9)-C(8)-N(2) = 172.1(2)^\circ$, and $C(9)-C(8)-N(2)-C(7) = -176.7(2)^\circ$]. The chain direction then changes abruptly at bond $N(2)-C(7)$ where the torsion angle becomes $-66.9(3)^\circ$. This

* Lists of structure factors, anisotropic thermal parameters, least-squares planes, and hydrogen bonds have been deposited with the British Library Lending Division, as Supplementary Publication No. SUP 38838 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

point marks the beginning of a second short segment of extended chain consisting of the atoms from N(2) to N(1) inclusive. The torsion angles in this segment are $N(2)-C(7)-C(6)-C(5) = -174.7(2)^\circ$ and $C(7)-C(6)-C(5)-N(1) = 173.5(2)^\circ$. A second abrupt change in chain direction occurs at the $C(5)-N(1)$ bond where the torsion angle is $84.1(3)^\circ$. Here the third short segment of extended chain begins and it includes the five atoms from $C(5)$ to $C(2)$. The torsion angles are $C(5)-N(1)-C(4)-C(3) = 179.6(2)^\circ$ and $N(1)-C(4)-C(3)-C(2) = -178.2(2)^\circ$. The final change in chain direction occurs at the $C(3)-C(2)$ bond where the torsion angle is $75.6(3)^\circ$. The fourth and final short segment of extended chain contains atoms $C(3)-C(2)-C(1)-O(1)-H(O1)$. The torsion angle at $C(2)-C(1)$ is $-170.6(2)^\circ$. Atoms N(3), N(2), N(1), O(3) and O(1) participate in hydrogen bonding to either sulfate ions or symmetry-related cationic moieties. In the crystal sulfate groups are arranged such that they are near the centers of symmetry at $\frac{1}{2}00$, $\frac{1}{2}0\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}0$ and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. Therefore all the sulfates tend to cluster about the (200) plane (see Fig. 2). All S atoms lie on planes which are parallel to the (200) plane and separated by $\pm 1.733 \text{ \AA}$.

The sulfate clusters are flanked by layers or sheets of antiparallel cationic chains in which the amino groups in one chain and the OH group in the other are in close proximity to the anions. Every terminal amino group is surrounded by four neighboring sulfates and forms an $NH \cdots O$ hydrogen bond with each of them. One of the hydrogen bonds is bifurcated. The $N(3)H \cdots O$ distances range from $2.765(2) \text{ \AA}$ to $3.011(3) \text{ \AA}$. The hydroxyl group and secondary amino group also form hydrogen bonds to the anions. The $OH \cdots O$ distance is $2.570(2) \text{ \AA}$ and $N(2)H \cdots O$ distances are $2.742(2) \text{ \AA}$ and $2.784(3) \text{ \AA}$. The amide groups are involved in hydrogen bonds [$2.814(3) \text{ \AA}$] which link neighboring antiparallel chains.

Table 2. Bond distances (\AA) and angles ($^\circ$) with *e.s.d.*'s

S-OS(1)	1.482 (2)	C(4)-N(1)	1.319 (3)
S-OS(2)	1.465 (2)	C(5)-N(1)	1.454 (3)
S-OS(3)	1.453 (2)	C(5)-C(6)	1.515 (3)
S-OS(4)	1.493 (2)	C(10)-N(3)	1.471 (3)
C(1)-O(1)	1.312 (3)	C(6)-C(7)	1.517 (3)
C(1)-O(2)	1.195 (3)	C(7)-N(2)	1.490 (3)
C(1)-C(2)	1.503 (4)	N(2)-C(8)	1.486 (3)
C(2)-C(3)	1.512 (4)	C(8)-C(9)	1.506 (3)
C(3)-C(4)	1.515 (4)	C(9)-C(10)	1.506 (3)
C(4)-O(3)	1.217 (3)		
OS(1)-S-OS(2)	109.4 (1)	O(3)-C(4)-C(3)	122.4 (2)
OS(1)-S-OS(3)	110.6 (1)	N(1)-C(4)-C(3)	116.3 (2)
OS(1)-S-OS(4)	107.7 (1)	O(3)-C(4)-N(1)	121.3 (2)
OS(2)-S-OS(3)	111.4 (1)	C(4)-N(1)-C(5)	123.7 (2)
OS(2)-S-OS(4)	107.3 (1)	N(1)-C(5)-C(6)	113.6 (2)
OS(3)-S-OS(4)	110.3 (1)	C(5)-C(6)-C(7)	109.7 (2)
O(1)-C(1)-O(2)	122.1 (2)	N(2)-C(7)-C(6)	113.3 (2)
O(1)-C(1)-C(2)	112.8 (2)	N(2)-C(8)-C(9)	112.1 (2)
O(2)-C(1)-C(2)	125.1 (2)	C(7)-N(2)-C(8)	114.4 (2)
C(1)-C(2)-C(3)	113.6 (2)	C(8)-C(9)-C(10)	110.0 (2)
C(2)-C(3)-C(4)	113.2 (2)	N(3)-C(10)-C(9)	112.7 (2)

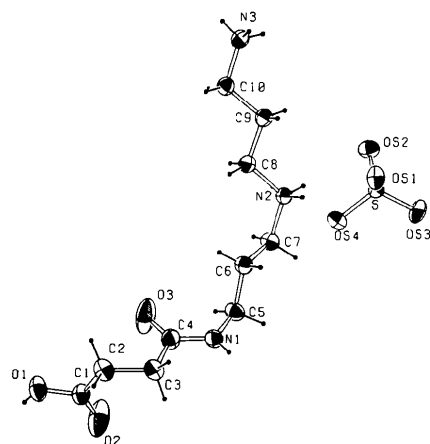


Fig. 1. ORTEP drawing (Johnson, 1976) of a molecule with the labelling scheme used. Thermal ellipsoids scaled to 50% probability; the H atoms are on an arbitrary scale.

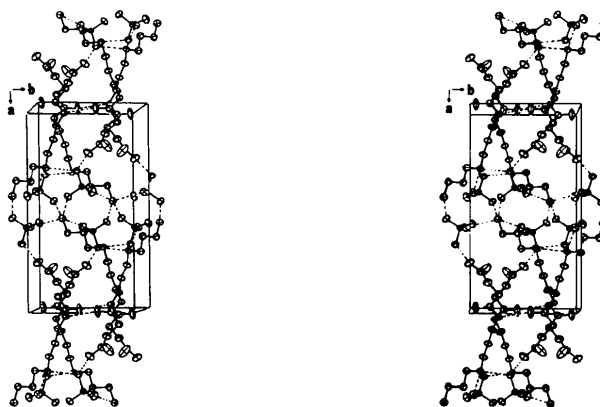


Fig. 2. Stereoview of the unit cell down the *c* axis. The ellipsoids correspond to 50% probability. Hydrogens are omitted. The broken lines indicate hydrogen bonds. (+*a* down, +*b* from left to right.)

We conclude that acylation occurs at one of the primary amino groups of 3,3'-diaminodipropylamine when it is reacted under controlled conditions with succinic anhydride. Details of the synthesis of *N*-[3-(3-ammoniopropylammonio)propyl]succinamic acid sulfate will be published elsewhere.

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The Structure of 4-Hydroxy-2,3,4-triphenyl-2-cyclopenten-1-one Benzene Solvate, $C_{23}H_{18}O_2 \cdot \frac{1}{2}C_6H_6$

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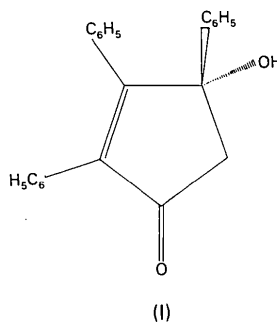
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Abstract. $M_r = 365.14$, triclinic, $P\bar{1}$, $a = 6.068$ (1), $b = 13.110$ (1), $c = 13.527$ (1) Å, $\alpha = 110.63$ (1), $\beta = 100.41$ (2), $\gamma = 82.62$ (2)°, $V = 988.09$ Å³, $Z = 2$, $D_m = 1.21$, $D_x = 1.23$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu(\text{Cu } K\alpha) = 5.53$ cm⁻¹, $F(000) = 386$. The structure was solved by direct methods and refined to a final R value of 0.075 for 2558 reflections collected with Cu $K\alpha$ radiation at 295 K. The five-membered ring is puckered in a half-chair conformation. The benzene molecule lies on the centre of symmetry.

Introduction. The title compound (I) belongs to the class of hydroxycyclopentenones which are important in the preparation of cyclopentadienes and related compounds (Freeman, Gagan & Lloyd, 1973). Moreover, the dehydration of compound (I) gives various interesting cyclopentadienone dimers (Conner, Dunston, Le Goff & Yates, 1971), which contain this molecule as the basic skeleton. The structural analysis was undertaken to study the effect of the substituents on the conformation of the five-membered ring and to compare it with the conformation in the dimers.

Experimental. Compound prepared by condensation of benzil with phenylacetone in the presence of alcoholic KOH (Koelsch & Geissman, 1939) and characterized by IR and NMR. Single crystals obtained by slow evaporation of the solution of the compound in benzene–petrol. Density measured by flotation in aqueous KI solution. Needle-shaped crystal, 0.15 × 0.125 × 0.45 mm elongated along *a*, CAD-4 diffractometer; cell parameters based on 15 centred reflections within the θ range 10–40°. Intensity data collected for



4252 reflections, $\omega/2\theta$ scan, $0 \leq h \leq 7$, $-15 \leq k \leq 15$, $-16 \leq l \leq 16$, $(\sin \theta/\lambda)_{\max} = 0.61$ Å⁻¹. Variation in two standard reflections (131 and 111) < 15%; reflections scaled by the use of standards. 3189 unique reflections ($R_{\text{int}} = 0.024$), 631 of which were considered unobserved [$I < 3\sigma(I)$]; Lp correction but not absorption. Direct methods, refinement by full-matrix least squares on F . H positions from a difference map but not refined (their temperature factors fixed at $U = 0.063$ Å²). 253 parameters refined. Final $R = 0.093$ for all data, $wR = 0.097$, $S = 3.27$; R for 2558 observed reflections is 0.075. $w = 2.974/[\sigma^2(F) + 0.00018F^2]$ where $\sigma(F)$ was derived from counting statistics. In the final cycle of refinement $(\Delta/\sigma)_{\max} = 0.13$, maximum and minimum $\Delta\rho$ excursions 0.10 and -0.15 e Å⁻³ respectively. Scattering factors from *International Tables for X-ray Crystallography* (1974). *MULTAN* (Germain, Main & Woolfson, 1971) used for structure determination, *SHELX 76* (Sheldrick, 1976) for refinement and *ORTEP* (Johnson, 1976) for diagrams.