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Crystal Structure of (*S,S*)-Diphenylethanediammonium (*R,R*)-Tartrate

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Summary. The crystal structure of (−)-diphenylethanediammonium-(*R,R*)-tartrate was determined. From this structure determination, the (*S,S*) configuration was assigned to the (−)-diphenylethanediamine. The asymmetric unit of the crystal structure contains two units of the title compound plus one molecule of ethanol and one water molecule, which form an intricate network of 19 hydrogen bonds.

Keywords. (*S,S*)-(−)-1,2-Diphenylethylenediamine; (*S,S*)-(−)-1,2-Diamino-1,2-diphenylethane; Absolute configuration.

Die Kristallstruktur von (*S,S*)-Diphenylethandiammonium-(*R,R*)-tartrat

Zusammenfassung. Es wurde die Kristallstruktur von (−)-Diphenylethandiammonium-(*R,R*)-tartrat bestimmt. Aus dieser Strukturbestimmung ergab sich die Zuordnung der (*S,S*)-Konfiguration zum (−)-Diphenylethandiamin. Die asymmetrische Einheit der Kristallstruktur besteht aus zwei Formeleinheiten der Titelverbindung sowie einem Molekül Ethanol und einem Wassermolekül, welche ein komplexes Netzwerk von insgesamt 19 Wasserstoffbrücken bilden.

Introduction

(*R,R*) and (*S,S*)-Diphenyl-ethanediamine (*DPEDA*), which is now readily available as a racemate [1], can be separated into the enantiomers by simple crystallization with (*R,R*)- and (*S,S*)-tartaric acid. Optically pure *DPEDA* derivatives have been used recently not only as efficient controller for enantioselective Diels-Alder and Aldol reactions [1], but also for enantioselective allylation of aldehydes [2], for enantioselective vicinal hydroxylation of olefins [3], as manganese containing chiral catalyst for asymmetric epoxidation of unsubstituted olefins [4], as chiral auxiliary for an intramolecular asymmetric lactonization [5] and, most recently [6], as a chiral backbone for the synthesis of an efficient chiral stationary phase.

We decided to determine the crystal structure of the diastereomeric salt formed from (*R,R*)-tartaric acid and (−)-*DPEDA*, which we obtained from (*R,R*)-tartaric acid and racemic *DPEDA* in 96% ethanol, following the known procedure [7]. Our objective was to provide independent and unquestionable proof of the absolute configuration of (−)-*DPEDA*, which has been a matter of revision in the past:

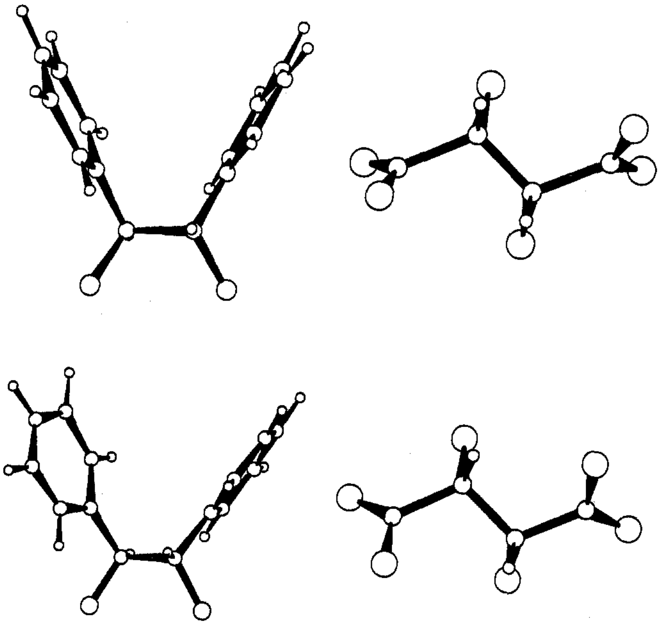

Fig. 1. Computer drawings of the two crystallographically independent molecules of *DPEDA* (left) and tartaric acid (right)

using anomalous dispersion data, Kuroda and Mason assigned the (*S*,*S*) configuration to the three (−)-*DPEDA* molecules of a Co(III)-complex [8]. Much earlier, similarity studies with ORD spectra of Cobalt complexes [9] and later with CD spectra of a zinc complex [10] had led to the same result. However, difficulties have been encountered in the interpretation of some complexes, and wrong absolute configurations were assigned [11].

Experimental

Crystals were obtained from ethanol/water: $(C_{14}H_{18}N_2 \cdot C_4H_4O_6)_2$. C_2H_5OH. H_2O ($= C_{38}H_{52}N_4O_{14}$) MW = 788.8. Cell constants were determined by a least square fit to the setting angels of 49 reflections in the range $7° \leqslant 2\theta \leqslant 23°$: space group $P2_1$, $a = 12.650$ (3), $b = 9.604$ (4), $c = 17.035$ (4) Å, $\beta = 71.30$ (2)°, $V = 1960.4$ (6) Å^3, $Z = 2$, $d_{calc} = 1.336$ g/cm^3 (298 K), $d_{exp} = 1.323$ g/cm^3 (flotation method from toluene/chloroform at 298 K), $F(000) = 840$ e. Data were collected on a STOE 4-circle diffractometer with MoK$_\alpha$-radiation ($\lambda = 0.71069$ Å, graphite monochromator) at ambient temperature for two octans with $4.5° \leqslant 2\theta \leqslant 50°$ ($-15 \leqslant h \leqslant 15$, $0 \leqslant k \leqslant 11$, $0 \leqslant l \leqslant 20$); scan type: Ω-scan, scanwidth 0.8°, 3 reflections were periodically remeasured (every 100 reflections); their intensities fluctuated by ± 4%. 3454 reflections observed, of which 2918 unique and 1499 observed ($F_{obs} > 3\sigma(F_{obs})$); no absorption correction ($\mu = 0.96$ cm^{-1}); LP-correction.

Solution with direct methods; isotropic refinement of all non-hydrogen atoms; hydrogen atoms attached to carbon were included at calculated positions, with their isotropic temperature coefficients refined. Hydrogen atoms attached to N or O were neither observed nor calculated. $R = 0.0824$ (unit weights) for 257 parameters and 1663 observations. A terminal difference Fourier synthesis showed features up to 0.5 eÅ^{-3}; atomic coordinates and equivalent isotropic temperature coefficients for the non-hydrogen atoms in Table 1. Computer programs used are listed in [12].

Results

The result of the crystal structure determination (Fig. 1) corroborates the (*S*,*S*) configuration for (−)-*DPEDA*. In addition to the configuration assignment, the crystal structure shows several remarkable features.

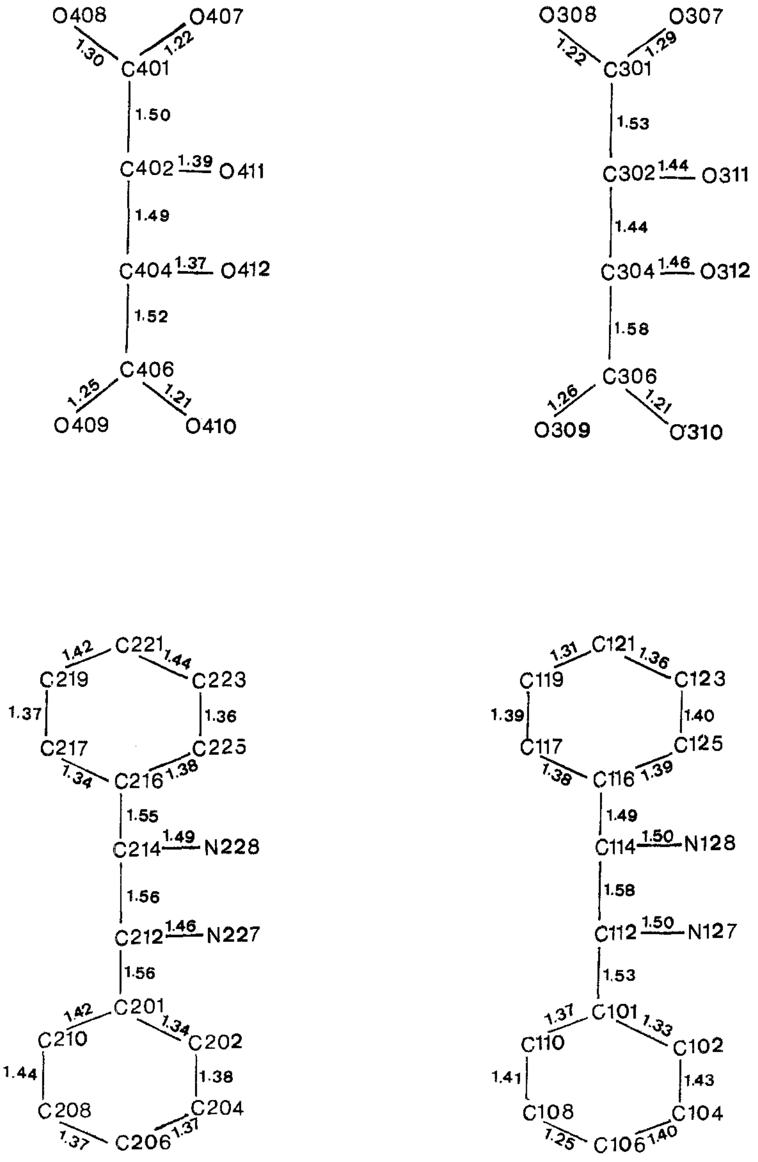

Fig. 2. Selected bond lengths and dihedral angles and the definition of the numbering scheme used to describe the crystal structure of the title compound. The estimated standard deviation for a C – C bond is 0.03 Å

The asymmetric unit contains two molecules of *DPEDA*, two molecules of tartaric acid, one molecule of ethanol and one molecule of water. Both, the two crystallographically independent *DPEDA* molecules and the two tartrates differ considerably in their conformation (Fig. 1). Although we did not directly observe hydrogen atoms, the bond lengths (Fig. 2) of the tartaric carboxyl groups (as well as the *pK* values of the constituents) are consistent with the formulation as diphenylethanediammonium tartrate. The six molecules of the asymmetric unit are connected by an intricate network of 19 intermolecular hydrogen bonds, which are listed in Table 2.

Table 1. Fractional atomic coordinates [$\times 10^4$] and isotropic temperature coefficients [Å $\times 10^4$] for the crystal structure of the title compound. Estimated standard deviations (in units of the last significant digit) in parentheses. The isotropic temperature factor has the form $T = \exp[-8\pi^2 U_{\mathrm{iso}} (\sin^2\theta/\lambda^2)]$

Atom	x/a	y/b	z/c	U_{iso}
C116	−2850 (15)	693 (26)	12872 (11)	228 (44)
C117	−3454 (22)	−469 (36)	13228 (17)	656 (76)
C119	−4308 (24)	−389 (37)	13987 (18)	708 (82)
C121	−4506 (25)	849 (39)	14326 (20)	794 (92)
C123	−4009 (25)	2086 (41)	14035 (20)	830 (96)
C125	−3133 (24)	1956 (38)	13283 (18)	747 (86)
C114	−1912 (15)	569 (28)	12073 (11)	287 (48)
C112	−1054 (18)	−582 (31)	12152 (14)	468 (62)
C101	−690 (15)	−209 (28)	12906 (12)	301 (48)
C102	−38 (17)	876 (28)	12929 (13)	336 (52)
C104	312 (24)	1192 (38)	13632 (19)	796 (88)
C106	−124 (22)	367 (38)	14344 (17)	697 (78)
C108	−744 (22)	−612 (35)	14270 (18)	732 (85)
C110	−1110 (19)	−1022 (30)	13600 (14)	447 (61)
N128	−2274 (12)	344 (25)	11322 (9)	304 (40)
N127	−43 (13)	−652 (24)	11385 (9)	311 (42)
C201	3803 (14)	1105 (27)	2175 (11)	207 (43)
C202	3241 (20)	2147 (32)	1955 (16)	555 (70)
C204	2805 (21)	3313 (35)	2423 (17)	625 (77)
C206	2991 (21)	3374 (35)	3175 (17)	639 (76)
C208	3531 (29)	2400 (46)	3500 (26)	1120 (125)
C210	3989 (24)	1249 (38)	2951 (18)	785 (90)
C212	4275 (19)	−189 (30)	1621 (14)	501 (64)
C214	3308 (17)	−1278 (28)	1793 (13)	344 (55)
C216	3115 (17)	−1942 (29)	2660 (13)	365 (53)
C217	2070 (16)	−1982 (28)	3193 (12)	341 (51)
C219	1827 (20)	−2520 (32)	3975 (15)	555 (70)
C221	2690 (20)	−3141 (32)	4226 (15)	550 (68)
C223	3791 (20)	−3167 (33)	3617 (14)	535 (68)
C225	3982 (15)	−2567 (27)	2855 (11)	261 (47)
N227	4774 (12)	230 (25)	754 (9)	297 (40)
N228	3559 (13)	−2381 (25)	1137 (10)	345 (42)
C301	6267 (16)	3381 (27)	1038 (12)	252 (46)
C302	5995 (15)	4941 (27)	1173 (12)	329 (51)
C304	6875 (17)	5841 (29)	673 (13)	352 (53)
C306	6528 (17)	7428 (29)	784 (13)	378 (56)
O307	5736 (12)	2760 (0)	606 (9)	472 (41)
O308	7016 (14)	2904 (28)	1269 (11)	726 (55)
O309	6293 (12)	8006 (23)	194 (9)	456 (40)
O310	6514 (11)	7887 (23)	1452 (9)	409 (38)
O311	4944 (11)	5233 (23)	1038 (8)	396 (36)
O312	7166 (10)	5412 (23)	−194 (8)	342 (35)
C401	735 (14)	2864 (29)	10402 (11)	253 (45)
C402	395 (17)	4282 (28)	10771 (12)	311 (50)
C404	1147 (15)	4855 (26)	11212 (12)	305 (49)
C406	694 (12)	6231 (25)	11642 (9)	93 (36)
O407	821 (10)	2634 (24)	9678 (8)	366 (36)
O408	954 (10)	1966 (23)	10899 (8)	311 (33)
O409	1343 (11)	7256 (22)	11525 (8)	365 (36)
O410	−298 (12)	6316 (23)	12002 (9)	451 (40)
O412	2250 (11)	5030 (23)	10740 (9)	448 (40)
O411	321 (11)	5235 (23)	10168 (9)	425 (37)
O501	2564 (34)	1016 (53)	7473 (27)	2422 (181)
C502	1213 (41)	−261 (61)	6103 (32)	1683 (193)
C506	2242 (45)	258 (65)	5442 (31)	1760 (203)
O509	2877 (55)	970 (85)	5875 (39)	3861 (348)

Table 2. The 19 hydrogen bonds observed in the crystal structure of the title compound

Donor [D]	Acceptor [A]	Distance D...A	Type
N227	O307	2.69 (2)	NH_3...O=C
N228	O307	2.82 (2)	NH_3...O=C
N128	O308	2.63 (3)	NH_3...O=C
N227	O309	2.83 (3)	NH_3...O=C
N128	O310	2.79 (3)	NH_3...O=C
N228	O311	2.86 (3)	NH_3...OH
N227	O311	2.96 (2)	NH_3...OH
O312	O408	2.74 (2)	OH...O=C
N227	O312	2.91 (2)	NH_3...OH
N127	O407	2.85 (3)	NH_3...OH
N127	O408	2.82 (3)	NH_3...O=C
N127	O409	2.73 (3)	NH_3...O=C
N228	O409	2.69 (2)	NH_3...O=C
N127	O410	3.08 (3)	NH_3...O=C
O501	O411	2.73 (5)	OH...O=C
N127	O411	2.91 (2)	NH_3...OH
N128	O411	2.92 (2)	NH_3...OH
O412	O309	2.80 (3)	OH...O=C
O501	O310	3.05 (5)	OH...O=C

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