ABSOLUTE CONFIGURATION OF (*S*)-(+)-3-ETHYL-5-METHYLADAMANTANE-1-CARBOXYLIC ACID AND (*S*)-(+)-1-AMINO-3-ETHYL-5-METHYLADAMANTANE*

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The absolute configuration of (*S*)-(+)-3-ethyl-5-methyladamantane-1-carboxylic acid (*Ia*) and (*S*)-(+)-1-amino-3-ethyl-5-methyladamantane (*IIa*) has been determined by comparison of CD curves of the corresponding (+)-N-methylthioamide *IId* and salicylideneimino derivative *IIe* with curves of the analogous derivatives of (*S*)-(+)-2-methylbutyric acid and (*S*)-(+)-2-aminobutane, resp. The absolute configuration has been proved by degradation of the (*S*)-(+)-acid *Ia* to the amine *IIa* and comparison of CD curves of its salicylidene derivative *IIe*.***

The molecule of adamantane represents a highly symmetric system (T_d symmetry). The appropriate substitution of this system may lead to compounds of two chirality types. Thus, by substitution at $C_{(2)}$ and $C_{(6)}$ carbon atoms a system is formed possessing the axial chirality; 2,6-dichloroadamantane-1,3,5,7-tetracarboxylic acid is the first substance of this type, prepared in the optically active form[1]. Appropriate substitution at $C_{(1)}$, $C_{(3)}$, $C_{(5)}$, and $C_{(7)}$ carbon atoms of the adamantane ring system results in substances of a central chirality, as shown for the first time by von Schleyer[2]. The first attempts in this respect to resolve the acids *Ia*, *Ib*, and *Ic* (Stěpanov and Baklan[3]) or to prepare the optically active acid *Id* (Malfer[4]) were unsuccessful. Later on, the acid *Id* was resolved with the use of dehydroabietylamine (Mc Kervey[5]); the thus-obtained acid, though inactive at the D line, afforded by degradation the optically active 1-methyl-7-methylenebicyclo[3.3.1]nonan-3-one. When resolved with quinine[6,7], the optical rotation of the acid *Id* at the D line was $[\alpha]_D^{20} - 0{\cdot}36°$ (chloroform). In the recent time, (+)-1-amino-3-ethyl-5-methyladamantane has been prepared[8].

In the present paper we wish to report determination of the absolute configuration

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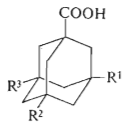
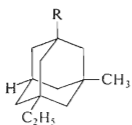
*** All the adamantane derivatives prepared in the present work were inactive at the sodium D line but afforded monotonous positive ORD curves in the region of shorter wavelengths. On the basis of this effect, the absolute configuration is ascribed to these derivatives.

of (+)-3-ethyl-5-methyladamantane-1-carboxylic acid (*Ia*) and (+)-1-amino-3-ethyl--5-methyladamantane (*IIa*).



Ia; $R^1 = C_2H_5$, $R^2 = CH_3$, $R^3 = H$
Ib; $R^1 = CH_2Br$, $R^2 = CH_3$, $R^3 = H$
Ic; $R^1 = CH_2Br$, $R^2 = C_2H_5$, $R^3 = CH_3$
Id; $R^1 = Br$, $R^2 = CH_3$, $R^3 = H$



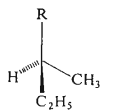
IIa, R = NH_2
IIb, R = H
IIc, R = Br
IId, R = $CSNHCH_3$
IIe, R = $N{:}CHC_6H_4OH(o)$
IIf, R = $CONH_2$

Bromination of 1-ethyl-3-methyladamantane (*IIb*) obtained on isomerisation of perhydrofluorene[9] or perhydrobenzo[1,2-e]indane in the presence of a complex of aluminium chloride and tert-butyl chloride (note the perhydrobenzo[1,2*e*]indane to be an intermediate in perhydrofluorene isomerisation[10]) afforded (±)-1-bromo--3-ethyl-5-methyladamantane (*IIc*) from which (±)-3-ethyl-5-methyladamantane--1-carboxylic acid (*Ia*) was prepared by carboxylation according to Koch and Haaf[11]. Resolution of the racemate with quinine in aqueous acetone afforded the corresponding (+)-enantiomer which was converted *via* the carboxylic acid chloride into (+)-N-methyl-3-ethyl-5-methyladamantane-1-carbothioamide (*IId*), $[\Theta]_{340}^{20}$ +2·4° (*c* 6·18; methanol). The Ritter reaction[8] of the bromo derivative *IIc* afforded (±)-1--amino-3-ethyl-5-methyladamantane (*IIa*), the resolution of which with (2*R*,3*R*)--(+)-*o*-nitrotartranilic acid in aqueous ethanol led to the (+)-enantiomer of the amine *IIa*; condensation of the latter compound with salicylaldehyde gave (+)-1--(2-hydroxybenzylideneimino)-3-ethyl-5-methyladamantane (*IIe*), $[\Theta]_{399}^{25}$ +36·5° (*c* 3·49; methanol). The (+)-acid *Ia* afforded the amide *IIf* which was converted by the Hofmann degradation into the (+)-amine *IIa* and finally into the Schiff base *IIe*, $[\Theta]_{399}^{25}$ +43° (*c* 3·42; methanol).

For the sake of comparison of CD curves, (*S*)-(+)-2-methylbutyric acid, $[\alpha]_D^{20}$ +19·26° (*in substancia*) was converted into (*S*)-(+)-N-methyl-2-methylbutyrothioamide[12] (*IIIb*), $[\alpha]_D^{20}$ +49·4° (*c* 1·21, chloroform), $[\Theta]_{331}^{20}$ +412° (*c* 0·17; methanol). (*S*)-(+)-2-aminobutane (*IIIc*), $[\alpha]_D^{20}$ +7·47° (*in substancia*) was converted into (*S*)-(+)-2-(2-hydroxybenzylideneimino)butane[13] (*IIId*), $[\alpha]_D^{20}$ +85·2° (*c* 1·34; methanol), $[\Theta]_{396}^{25}$ +639° (*c* 0·026; methanol).

It may be inferred from the present theories of optical rotation that a greater distance of substituents attached to the asymmetric carbon atom, from the center of asymmetry results in a decreased rotation. The rotation of 1-cyano-3-bromo-5-

-methyladamantane was calculated by means of the theory of pair interactions[6,7]. The rotatory power may be lowered up to one hundreth of that of the corresponding model compound. Such a decrease causes difficulties in measurements of rotations at the D line or in measurements of ORD and CD curves particularly when the substances are not optically pure[5].



IIa, R = COOH
IIb, R = $CSNHCH_3$
IIc, R = NH_2
IId, R = $N{:}CHC_6H_4OH(o)$

The absolute configuration of substituted adamantanes was determined on the basis of a comparison of CD spectra of suitable derivatives[14] with those of model substances of the known absolute configuration. From the same sign of the Cotton effect of the (+)-N-methylthioamide *IId*, $[\Theta]_{340}^{20}$ +2·4°, and the (*S*)-(+)-N-methylthioamide *IIIb*, $[\Theta]_{331}^{20}$ +412°, the (*S*)-configuration of (+)-3-ethyl-5-methyladamantane-1-carboxylic acid may be inferred. Similarly, the same sign of the Cotton effect of the salicylidene derivative *IIe*, $[\Theta]_{399}^{25}$ +36·5°, and of (*S*)-(+)-2-aminobutane (*IIIc*), $[\Theta]_{396}^{25}$ +639°, made possible that (+)-1-amino-3-ethyl-5-methyladamantane (*IIa*) was ascribed the configuration *S*. These determinations of absolute configuration were supported by degradation of the (*S*)-(+)-acid *Ia* to the (+)-amine *IIa* and conversion to the Schiff base *IIe* of the molecular elipticity $[\Theta]_{399}^{25}$ +43°, indicating thus the absolute configuration *S* for the (+)-amine *IIa*.

EXPERIMENTAL

Melting points and boiling points are uncorrected. Analytical samples were dried at 20°C/0·1 Torr for 8 h. Optical rotations were measured on a Zeiss Opton apparatus. The ORD curves were taken on a JASCO ORD/UV 5 spectropolarimeter of Japan Spectrometric Company. The CD curves were measured on a Roussel - Jouan Dichrograph II.

1-Ethyl-3-methyladamantane (*IIb*)

A. To an agent prepared from aluminium chloride (22 g; 165 mmol) and tert-butyl chloride (3·4 ml; 32·4 mmol) there was added perhydrofluorene (141 g; 791 mmol) and the whole mixture was heated at 100°C under stirring. The course of isomerisation was checked by gas chromatography. When the reaction mixture contained 59% of 1-ethyl-3-methyladamantane, 25% of 1,3,5--trimethyladamantane, and 10% of perhydrophenalene (the residue was formed by nonidentified hydrocarbons), the isomerisation was stopped. After cooling, the mixture was washed with 10% aqueous sodium hydroxide (500 ml), the hydrocarbon layer separated, and distilled. The fraction (110 g) boiling in the range of 100—133°C/15 Torr was rectified at 80 Torr on a NFA-100 type Nester-Faust column at the rate of 1 ml of the distillate per 9 min. Yield, 65·1 g (46·1%) of compound *IIb*, b.p. 142°C/80 Torr; reported[11], b.p. 107°C/20 Torr.

B. Catalytic hydrogenation of 3a,8,9,9a-tetrahydrobenzo[1,2-e]indane (b.p. 125—128°C/14 Torr) on Raney nickel W 2 in cyclohexane at 210°C/130 at afforded perhydrobenzo[1,2-*e*]indane, b.p. 123—126°C/14·5 Torr; reported[15], b.p. 128—130°C/17 Torr. Perhydrobenzo[1,2-*e*]indane (30 g; 168 mmol) was isomerised at 100°C with a mixture of aluminium chloride (6 g) and tert-butyl chloride (1·5 ml). The composition of the resulting mixture of products was analogous to that obtained by isomerisation of perhydrofluorene in paragraph *A*. 1-Ethyl-3-methyladamantane was also isolated analogously to paragraph *A*.

1-Bromo-3-ethyl-5-methyladamantane (*IIc*)

To 1-ethyl-3-methyladamantane (*IIb*; 80 g; 0·448) there was added tetrachloromethane (90 ml) and bromine (450 ml), the whole mixture refluxed for 8 h, and the excess bromine distilled off. The residue was diluted with tetrachloromethane (250 ml) and washed with saturated aqueous sodium pyrosulfite (200 ml). The organic layer was dried and distilled under diminished pressure to afford 93·1 g (85·1%) of the bromo derivative *IIc*, b.p. 141—143°C/15·5 Torr; reported[11], b.p. 133—134°C/9 Torr.

(±)-3-Ethyl-5-methyladamantane-1-carboxylic Acid (*Ia*)

To an emulsion of the bromo derivative *IIc* (24·3 g; 94·5 mmol) in 100% sulfuric acid (600 ml) there was added dropwise under stirring at 10°C anhydrous formic acid (*87*·5 ml) over 3 h. The stirring was continued for 2 h, the mixture poured onto ice (2 kg) and extracted with ether. The ethereal solution was filtered, the filtrate shaken with 4% aqueous sodium hydroxide (160 ml), the aqueous layer washed with ether, and acidified with 20% aqueous sulfuric acid. The oil was extracted with ether, the extract dried over anhydrous magnesium sulfate, and distilled to afford 16·9 g (80·3%) of the racemic compound *Ia*, b.p. 153°C/8 Torr, m.p. 56—58°C (methanol–light petroleum); reported[11], m.p. 57—58°C. For $C_{14}H_{22}O_2$ (254·3) calculated: 75·63% C, 9·98% H: found: 75·70% C, 10·00% H.

(*S*)-(+)-3-Ethyl-5-methyladamantane-1-carboxylic Acid (*Ia*)

The racemic acid *Ia* (5·0 g; 22·5 mmol) was added to a solution of (—)-quinine (7·2 g; 22·5 mmol) in acetone (20 ml), the resulting solution heated to the boiling point, treated with 20% aqueous acetone (50 ml), and the whole allowed to cool gradually (5°C/h) under stirring. The salt was collected with suction at 40°C; m.p. 135·5—139°C. A similar threefold recrystallisation from 50% aqueous acetone afforded 2.6 g of a salt, m.p. 139—141·5°C, $[\alpha]_D^{20}$ —111·3° (*c* 3·6; 1 : 1 acetone–methanol). The organic acid was liberated with mineral acid, extracted with ether, the extract dried over anhydrous magnesium sulfate, and distilled to afford the enantiomer *Ia*, m.p. 53—55°C, $[\alpha]_D^{20}$ 0·0° (*c* 0·6; methanol). A smooth ORD curve (*c* 6·0; ethanol): $[\alpha]_{300}^{26}$ +0·84°, $[\alpha]_{218}^{25}$ +1·67°.

(*S*)-(+)-N-Methyl-3-ethyl-5-methyladamantanecarboxamide (*IIf*)

A mixture of the (*S*)-(+)-acid *Ia* (650 mg; 2·92 mmol) and thionyl chloride (2 ml) was refluxed for 2 h, the excess thionyl chloride distilled off, and the residue distilled under diminished pressure to afford 571 mg of the corresponding chloride, b.p. 100—120°C/5 Torr (bath temperature). This chloride (530 mg; 2·2 mmol) was added to a solution of methylamine (3 g) in benzene (15ml), the whole kept at room temperature for 24 h, and then diluted dith water (70 ml). The benzene layer was separated, dried, and distilled to afford 420 mg of the amide *IIf*, b.p. 160—175°C/0·12 Torr (bath temperature).

(*S*)-(+)-N-Methyl-3-ethyl-5-methyladamantanecarbothioamide (*IId*)

To the (*S*)-(+)-N-methylamide *IIf* (320 mg) in xylene (3 ml) there was added a mixture of phosphorus pentasulfide (300 mg) and potassium polysulfide (235 mg) and the whole heated at 80°C for 90 min with stirring. The xylene solution was separated and the residue extracted at about °C with four 3 ml portions of xylene. The xylene solution and extracts were combined, evaporated, and the residue chromatographed on a thin layer of silica gel HF_{254} in 9 : 1 benzene–chloroform. Distillation of the eluate afforded 165 mg (47·5%) of the (*S*)-(+)-thioamide *IId* as a viscous oil; a smooth positive ORD curve, $[\Theta]_{340}^{20}$ +2·4° (*c* 6·18; methanol). For $C_{15}H_{25}NS$ (251·4) calculated: 71·65% C, 10·02% H, 5·57% N; found: 71·93% C, 10·21% H, 5·37% N.

(±)-1-Amino-3-ethyl-5-methyladamantane (*IIa*)

The bromo derivative *IIc* (62 g; 241 mmol) was treated with acetonitrile (460 ml) and then 99% sulfuric acid (93 ml) was added dropwise under stirring. The mixture was stirred at 45°C for 24 h, cooled down, and poured into water (2000 ml). The resulting amine acetyl derivative was hydrolysed by refluxing with powdered potassium hydroxide (90 g) in diethylene glycol (750 ml) for 5·5 h. The mixture was cooled down, diluted with water (1 300 ml), the oil extracted with ether, the extract dried, and saturated with hydrogen chloride. The resulting hydrochloride was recrystallised from a 1 : 8 mixture of ethanol and light petroleum to afford 30·4 g (54·8%) of the *IIa* hydrochloride, m.p. 247—249°C. For $C_{13}H_{24}ClN$ (229·8) calculated: 6·09% N, 15·43% Cl; found: 6·30% N, 15·45% Cl. The base was liberated with aqueous sodium hydroxide, extracted with ether, the extract dried over solid potassium hydroxide, and distilled; b.p. 114·5—117°C/17 Torr. For $C_{13}H_{23}N$ (193·3) calculated: 80·76% C, 11·99% H, 7·25% N; found: 81·14% C, 12·15% H. 7·20% N.

(*S*)-(+)-1-Amino-3-ethyl-5-methyladamantane (*IIa*)

To a hot solution of *o*-nitrotartranilic acid, $[\alpha]_D^{23}$ +98·8° (*c* 0·8; ethanol), m.p. 191—195·5°C (11·98 g; 51·75 mmol) in ethanol (100 ml) there was added the (±)-amine *IIa* (10 g; 51·75 mmol), the mixture shortly refluxed, concentrated to half of the original volume, and cooled down. The resulting salt was dissolved at 70°C in 50% aqueous ethanol and the solution allowed to cool gradually (5°C per hour). At 45°C, the solution began to deposit the salt. The mixture was stirred at 40°C for 5 h and collected with suction at the same temperature; m.p. 92—96°C. Two recrystallisations from 50% aqueous ethanol afforded 2·6 g of the salt, m.p. 89—90·5°C, $[\alpha]_D^{25}$ +45° (*c* 1·3; ethanol); reported[8], m.p. 78—79°C, $[\alpha]_D^{20}$ +70° (*c* 1·2; methanol). The base was liberated with 1% aqueous sodium hydroxide, extracted with ether, the ethereal *o*-nitroaniline-containing extract of the base dried over anhydrous magnesium sulfate, and saturated with carbon dioxide to deposit the amine carbonate. The base was liberated with aqueous sodium hydroxide, extracted with ether, the extract dried, and distilled to afford the (*S*)-(+)-amine *IIa*, $[\alpha]_D^{24}$ +0·0° (*c* 8·7; methanol); a smooth ORD curve (*c* 3·8; methanol): $[\Theta]_{300}^{25}$ +0·53°, $[\Theta]_{230}^{25}$ +0·84°. Hydrochloride, m.p. 243—246°C.

(*S*)-(+)-1-(2-Hydroxybenzylideneimino)-3-ethyl-5-methyladamantane (*IIe*)

The (*S*)-(+)-amine *IIa* (460 mg; 2·38 mmol) was added to salicylaldehyde (290 mg; 2·38 mmol in methanol (3 ml), the whole mixture refluxed for 30 min, and cooled down. The oily product separated on standing. The methanol was evaporated and the residue distilled to afford 676 mg (90·2%) of the Schiff base, yellow oil, b.p. 150—154°C/0·05 Torr; a smooth positive ORD curve,

$[\Theta]_{399}^{25}$ +36·5° (*c* 3·49; methanol). For $C_{20}H_{27}NO$ (297·4) calculated: 80·76% C, 9·15% H, 4·71% N; found: 80·73% C, 9·21% H, 5·02% N.

(*S*)-(+)-3-Ethyl-5-methyladamantanecarboxamide (*IIf*)

A mixture of the (*S*)-(+)-acid *Ia* (1·35 g; 6·07 mmol) and thionyl chloride (3·4 g) was refluxed for 2 h and the excess agent was distilled off under diminished pressure. The residue was stirred in conc. aqueous ammonia (11 ml) for 30 min, the oil extracted with ether, the extract washed with water, dried over anhydrous magnesium sulfate, and distilled to afford 1·03 g (78·8%) of the oily (*S*)-(+)-amide *IIf*, b.p. 160–170°C/0·1 Torr (bath temperature), which solidified on standing; m.p. 50–53°C.

(*S*)-(+)-1-(2-Hydroxybenzylideneimino)-3-ethyl-5-methyladamantane (*IIe*)

The (*S*)-(+)-amide *IIf* (1·01 g; 4·56 mmol) was added into methanolic sodium methoxide (from 0·34 g of sodium and 8·7 ml of methanol). Bromine (1·15 g) was then added dropwise with cooling, the mixture stirred at 55°C for 30 min, diluted with water (20 ml), the oil extracted with ether, the extract dried over anhydrous magnesium sulfate, and evaporated. To the crude urethane there was added powdered sodium hydroxide (3·1 g) and diethylene glycol (25 ml), the whole mixture refluxed for 6 h, cooled down, diluted with water (80 ml), extracted with ether, the extract dried over solid sodium hydroxide, and evaporated. Distillation of the residue under diminished pressure afforded 580 mg (65·8%) of the corresponding amine, b.p. 107–110°C/10 Torr. The Schiff base was prepared similarly as in the case of the amine obtained by resolution of the racemate; $[\Theta]_{399}^{25}$ +43° (*c* 3·42; methanol).

(*S*)-(+)-2-Aminobutane (*IIIc*)

Hydrogenation of methyl ethyl ketoxime (b.p. 150·5–151°C/740 Torr) over Raney nickel W 2 in methanol at 105°C/125 atm afforded 65·9% of (±)-2-aminobutane (b.p. 62–63°C) which was resolved with (+)-tartaric acid to yield after four recrystallisations from water the tartarate, m.p. 139–140°C, $[\alpha]_D^{22}$ +16·9° (*c* 3·1; water); reported[16], m.p. 139–140°C and $[\alpha]_D^{21}$ +16·8° (*c* 2·8; water). From this tartarate, there was liberated (*S*)-(+)-2-aminobutane (*IIIc*), b.p. 62–64°C, $[\alpha]_D^{20}$ +7·47° (*in substancia*); reported[16], $[\alpha]_D^{20}$ +7·48° (*in substancia*).

(*S*)-(+)-2-(2-Hydroxybenzylideneimino)butane (*IIId*)

(*S*)-(+)-2-Aminobutane (*IIIc*; 366 mg; 5 mmol) in methanol (2 ml) was added to 610 mg (5 mmol) of salicylaldehyde in methanol (3 ml), the mixture refluxed for 10 min and then kept at room temperature for 24 h. Evaporation of the methanol and distillation of the residue under diminished pressure afforded 836 mg (85·6%) of yellow oil, b.p. 108–110°C/0·1 Torr, $[\Theta]_{396}^{25}$ +639° (*c* 0·26; methanol).

(*S*)-(+)-N-Methyl-2-methylbutyrothioamide (*IIIb*)

The potassium permanganate oxidation of 2-methylbutanol, $[\alpha]_D^{24}$ −4·75° (*in substancia*), in an alkaline medium at 17°C afforded (*S*)-(+)-2-methylbutyric acid, b.p. 78°C/17 Torr, $[\alpha]_D^{20}$ +19·26° (*in substancia*). The chloride of (*S*)-(+)-2-methylbutyric acid, b.p. 113–117°C, $[\alpha]_D^{25}$ +14·05° (*in substancia*). (*S*)-(+)-N-Methyl-2-methylbutyroamide, m.p. 35–36°C, $[\alpha]_D^{23}$ +30·2° (*c* 2·4; chloroform); reported[12], m.p. 29°C and $[\alpha]_D^{25}$ +29° (*c* 2·4; chloroform).

To a solution of the N-methylamide (430 mg) in xylene (3·5 ml) there was added a mixture of potassium polysulfide (450 mg) and phosphorus pentasulfide (505 mg), the whole heated at 70°C for 1 h, and the xylene solution decanted. The residue was extracted with seven portions of hot xylene. The crude thioamide was purified by thin-layer chromatography on silica gel HF_{254} in 7 :1 benzene–ethyl acetate. Yield, 275 mg (56·1%) of an oil, b.p. 90—95°C/0·11 Torr, $[\alpha]_D^{20}$ +49·4° (*c* 1·2; chloroform), $[\Theta]_{331}^{20}$ 412° (*c* 0·17; methanol); reported[12], $[\alpha]_D^{26}$ +49° (*c* 1·14; chloroform) and $[\Theta]_{330}^{20}$ +427° (*c* 0·1; methanol).

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