ISOMERIC METHYLENE-BIS(1-AZA-2-CYCLOHEPTANONES) AND THEIR INFRARED SPECTROSCOPY

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Depending upon the method of synthesis, four isomers of methylene-bis(1-aza-2-cycloheptanone) were obtained. By the Schmidt reaction with 2,2′-methylene-bis(cyclohexanone) two stereoisomeric 7,7′-isomers can be obtained, the Beckmann rearrangement of the corresponding dioxime yields positional isomers 7,7′-, 3,3′-, 3,7′-. The structures of these isomers were analysed by means of infrared spectroscopy.

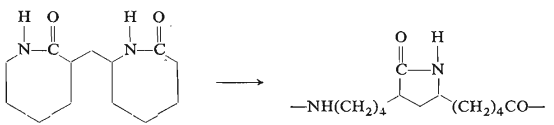
In relation to a study of cross-linked polyamides we have been concerned with the synthesis of several types of bislactams, among them methylene-bis(1-aza-2-cycloheptanone).

Birkofer and coworkers[1] prepared this bislactam by the Schmidt reaction of 2,2′-methylene-bis(cyclohexanone). The crude product was divided by crystallisation into two isomers of melting points 219—220°C and 236—237°C, to which, on the basis of an analogy to methylene-bis(1-aza-2-cyclohexanone), *meso*- and racemic structures were attributed. In the patent literature[2,3] the preparation of methylene-bis(1-aza-2-cycloheptanone) is described using the Beckmann rearrangement of the 2,2′-methylene-bis(cyclohexanone) dioxime. The product had a melting point of 175—200°C and was considered to be a mixture of positional isomers.

More detailed study of these bislactams has now shown that the occurrence of isomers depends upon the method of preparation. Whereas the Schmidt reaction gives rise to two diastereoisomers *Ia* (m.p. 235—236°C) and *Ib* (m.p. 195—197°C) the Beckmann rearrangement gives isomers *Ia*, *II* (m.p. 247°C) and *III* (m.p. 174—182°C). The Schmidt reaction in sulphuric acid gave[1] crude bislactam in a 35% yield. We found it possible to increase the yield up to 57% using hydrochloric acid and with the use of polyphosphoric acid the yield increased to 80%. Crude bislactam was divided by crystallisation from 2-propanol into isomers *Ia* and *Ib*. Both isomers occurred in approximately a 1 : 1 ratio without regard to the acid used or to the diastereoisomeric composition of the original diketone (2,2′-methylene-bis(cyclohexanone) in *meso* and racemic forms[4]). The Beckmann rearrangement of the 2,2′-methylene-bis(cyclohexanone) dioxime in sulphuric acid was not very successful. A maximum yield of 25% was obtained when the dioxime was extracted with chloroform into

sulphuric acid. Again the best results were obtained with polyphosphoric acid, with an 80% yield. From the crude product of the Beckmann rearrangement we first isolated isomer *Ia* as a portion insoluble in ethyl acetate. From the ethyl acetate solution we got a crystalline mixture of isomers *Ia* and *III*, which yielded pure isomer *III* on chromatography on silica gel. Isomer *II* was obtained from the last fraction of this chromatography.

Some information on the structure of compounds *I*—*III* was given by hydrolysis to isomeric methylene-bis(aminocaproic acids) and by heating them or the corresponding amino acids to a temperature just over melting point. With isomers *Ia*, *Ib* and *II* we could isolate after heating the original lactams and heating of the corresponding amino acids gave polycondensates with a *trans*-amide group, corresponding spectrally to polycaprolactams. On the contrary, the IR spectrum of product obtained by heating of *III* contained in addition to the *trans*-amide II band (I 560 cm^{-1}) and a *trans*-amide I band at 1675 cm^{-1} an absorption band in the region of 1700 cm^{-1}, indicating the presence of a *cis*-amide bond, *e.g.* a five-membered pyrrolidinone ring[5]. Such a ring can be closed only if isomer *III* has a 3,7′ structure (equation (*A*)).



(*A*)

Evidence for the structure of the four isomers was obtained from physical methods, mainly infrared spectroscopy. The position of the attached methylene bridge of isomers *I*—*III* was suggested by comparison with model substances 3-methyl-1-azacycloheptanone (*IV*) and its 7-methyl isomer *V*. The first of these substances shows in dilute tetrachloromethane solution a stretching vibration of free N—H bonds at a wavenumber of 3428 cm^{-1}, isomer *V* on the other hand at 3412 cm^{-1} (the analogous substance *VI* at 3410 cm^{-1}). The results of measurement of infrared spectra of substances *I*—*VI* are shown in Table. I. By comparison with model substances the constitution of substances *I*—*III* came out clearly from these results.

An isomer with melting point 247°C has a band of stretching vibration of a free N—H group at 3426 cm^{-1} and therefore corresponds to structure *II*. In agreement with this is the NMR spectrum (Table II). Two further isomers (m.p. 235—236°C and 195—197°C) show a stretching vibration of free N—H bonds at a clearly lower wavenumber of 3 406 cm^{-1}, and both correspond to structure *I*, again in agreement with NMR spectral data (Table II). They are, therefore, two diastereoisomers. Assignment of the relative configuration on $C_{(7)}$ and $C_{(7')}$ is not possible on the basis of the existing experimental data. In the region of the N—H stretching vibration of the more soluble diastereoisomer *Ib* there is an obviously marked association above a threshold concentration (about $2 . 10^{-4}$M) in tetrachloromethane, and this

is manifest by two separated bands. The band at 3213 cm^{-1} corresponds to the wavenumber of the band belonging to a cyclic dimer of a *cis*-amide. The second band (at 3295 cm^{-1}) is considered from the combination frequency on the one hand of a band of an associated ν(N—H), on the other hand of a low-lying band of a hydrogen bond H···O (*cf.*[6]). In chloroform both bands of associated N—H groups disappear. The remaining isomer (m.p. 174–182°C) has in the region of the stretching vibra-

TABLE I

Wavenumbers of the ν(N—H) Bands

Compound[a]	Molarity	ν(NH) free	ν(NH) bound	
Ia	[b]	3 406·3		
Ib	[c]	3 406·4	3 295	3 213
II	$2{\cdot}5 \cdot 10^{-4}$	3 426·5	3 331[d], 3 286[d]	3 223·5[d]
III	$2{\cdot}5 \cdot 10^{-4}$	3 424, 3 406[e]	3 295	3 221
IV	$4{\cdot}0 \cdot 10^{-4}$	3 428·3	3 339[d]	3 217[d]
V	$4{\cdot}0 \cdot 10^{-4}$	3 412	3 334,5[d]	3 212[d]
VI	$4{\cdot}0 \cdot 10^{-4}$	3 410·6	3 330	3 210

[a] Measured in CCl_4, instrument PE 621; [b] saturated solution of very low concentration; [c] saturated solution; [d] low intensity; [e] values after separation by Elliot 503 computer.

TABLE II

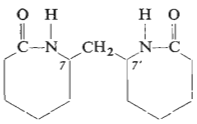
NMR Data

Measured on Varian HA-100 instrument in trifluoroacetic acid, chemical shift in δ (p.p.m.); s singlet, t triplet, m center of an unresolved multiplet, broad signal.

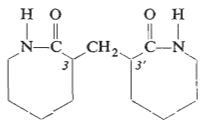
Compound	>NH	—CH—N<	—CH—CO—	Other protons[a]
Ia	8·83 bs (2 H), $W_{1/2}$ = 10·5 Hz	3·90 b (2 H)	2·79 m (4 H)	1·20—2·40 (14 H)[b]
Ib	8·84 bs (2 H), $W_{1/2}$ = 12 Hz	3·90 b (2 H)	2·83 m (4 H)	1·30—2·40 (14 H)[b]
II	9·18 bm (2 H), $W_{1/2}$ = 25 Hz	3·65 m (4 H)	3·07 m (2 H)	1·50—2·35 (14 Hg)
III	9·75 bs (1 H)	3·96 m (1 H)	2·85 m (1 H)	1·30—2·50 (14 H)
	8·91 b (1 H)	3·58 m (2 H)	3·17 bt (1 H)	
VI[c]	8·62 m (1 H)	3·80 m (1 H)	2·88 bt (2 H)	1·40—2·30 (9 H)

[a] Envelops; [b] spectra of compounds *Ia*, *Ib* were practically identical except for small differences in the region 1·30—2·40 p.p.m.; [c] protons of a geminal dimethyl group form a doublet at 0·9 p.p.m. 6 H, J = 6 Hz.

tions of N—H bonds 4 different bands. Two with higher wavenumbers belong to vibrations of nonassociated N—H bonds: the band at 3406 cm^{-1} can be associated with the free N—H group neighbouring the methylene bridge, the band at 3424 cm^{-1} has practically the same wavenumber as the band of lactam *IV* and corresponds to the



I



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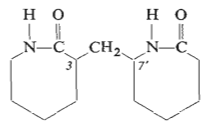
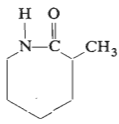
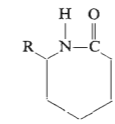


III



IV



V, R = CH_3
VI, R = $CH_2CH(CH_3)_2$

vibrations of a free N—H group more distant from the methylene bridge in structure *III*. Assignment of constitution is again in agreement with the results of NMR measurements (Table II). In the region of vibrations of bound N—H groups there is a band with a low wavenumber conditioned by vibrations of structures similar to intermolecular dimers of *cis*-lactams (3221 cm^{-1}). To the band with a higher wavenumber (3295 cm^{-1}) there is a contribution, in addition to vibrational modes referred to with substance *Ib*, mainly from the vibration of N—H groups involved in intramolecular hydrogen bonds, which for steric reasons is possible only between N—H and CO groups in the neighbourhood of the methylene bridge in isomer *III*. In agreement with this interpretation the band of the associated dimer system disappears from the spectrum of substance *III* in chloroform solution, but the band of the intramolecular hydrogen bond at 3283 cm^{-1} remains. Characteristic is also the behaviour of the bands of free N—H groups. The band at 3406 cm^{-1}, attributed to the N—H group in the proximity of the methylene bridge, has in tetrachloromethane a lower intensity (34%) than the band of the second free N—H group (100%) since it is to a large extent involved in the intramolecular hydrogen bond. In chloroform this bond is partially split and the intensity of the band, the wavenumber of which decreased to 3399 cm^{-1} due to a solvent effect, is increased (56% in relation to the second band). Supporting this interpretation is the temperature dependence of a solution of substance *III* in tetrachloroethylene between 20 and 110°C. In the region of stretching vibrations of N—H groups there are again 4 bands. The band about

3200 cm^{-1} disappears with increasing temperature, as would be expected for a band conditioned by intermolecular association. The band at about 3300 cm^{-1} on the other hand remained even at 110°C. An intramolecular hydrogen bond remains in existence therefore for the most part even at high temperature. With increasing temperature there is an increased intensity of the weak band of the free N—H group originally involved in the intramolecular hydrogen bond in comparison with the band of the second free group (at 3424 cm^{-1}) which with increasing temperature decreases, so that the extinction coefficient decreases with increasing temperature. At the band 3408 cm^{-1} the decrease in extinction coefficient is overbalanced by the increased population of the free N—H group by gradual dissociation of the intramolecular hydrogen bond. With increasing temperature (at about 90°C) a further small band begins to appear at 3452 cm^{-1} which does not disappear when the temperature falls again. This is due to decomposition products of isomer *III* (see below).

From the above presentation it would appear that isomer *Ia*, with melting point 235–236°C, and isomer *Ib*, with melting point 195–197°C, are diastereoisomers of 7,7′-methylene-bis(1-aza-2-cycloheptanone), isomer *II*, with melting point 247°C, is the 3,3′-derivative and isomer *III* (m.p. 174–182°C) is the 3,7′-derivative of methylene-bis(1-aza-2-cycloheptanone). In the case of the 7,7′-derivative *I*, as opposed to the other derivatives, both diastereoisomers could be isolated due to their solubility differences. Birkofer[1] was able to isolate in pure form only isomer *Ia*. The presented[1] lower melting isomer (219–220°C) is probably only a mixture of isomers *Ia* and *Ib*. In isomers *II* and *III* one cannot from spectral data decide whether they are individual stereoisomers or mixtures. A study of the stereoisomerism of the initial dioximes was also unsuccessful in this respect.

Palsky and coworkers[7] present the argument that from the *meso*-form of 2,2′-methylene-bis-(cyclohexanone) they prepared a dioxime of melting point 191°C, whereas from the racemic form of the diketone they derived a dioxime of melting point 130°C. In our own experiments we were not able to prepare dioximes with these melting points from separate isomers of 2,2′-methylene-bis(cyclohexanone). From the *meso*- and racemic form, resp., of the diketone we always got a dioxime with a melting range from 120 to 150°C. Fractions obtained by extraction were separated and subjected to a Beckmann rearrangement. From analysis of the infrared spectra of the products it would appear that from the low-melting fraction of dioximes (124–128°C and 128–132°C) we got a product rich in isomer *III*, from the higher-melting fraction (179–183°C) we got a product rich in isomer *Ia*, whereas from the middle fraction (m.p. 159–164°C) or the crude dioxime (m.p. 120–150°C) we got a mixture of isomers *Ia* and *III* in approximately a 1 : 1 ratio.

The results of these experiments suggest that the above fractions of dioximes differ not in terms of diastereoisomerism at the C atom, but in geometric isomerism. Three different isomers of this type can exist, of which each could result in a different positional isomer of a bislactam: isomer *Z*, *Z* corresponds with *II*, isomer *E*, *Z* corresponds with *III* and *E*, *E* corresponds with *I*. A fraction with a low melting point would therefore correspond with a mixture of isomers, enriched by isomer *Z*, *E*, whereas the fraction with the highest melting point a mixture enriched with isomer

E, *E* and the middle fraction a mixture of all three isomers. Under the conditions of preparation of the dioximes there is isomerisation at the C atom, with the formation of one of both forms (*meso* or racemate) being preferred. At the same time there may be isomerisation of the oxime group.

The dioxime of 2,2′-methylene-bis(cyclohexanone), under conditions of the Beckmann rearrangement, gives by cyclisation 1,2,3,4,5,6,7,8-octahydroacridine (in polyphosphoric acid 13%, in sulphuric acid 20%). Colonge and coworkers[8] prepared octahydroacridine using HCl with the given dioxime with a 66% yield. Methylene-bis(1-aza-2-cycloheptanone) with its constitutional isomerism and diastereoisomerism forms an exception in the series of bislactams derived from 2,2′-alkylene-bis(cyclohexanones), since the other prepared bislactams were isolated in the single form of 7,7′-derivatives as products of the Schmidt reaction, as well as of the Beckmann reaction.

EXPERIMENTAL

Melting points (uncorrected) were determined on a Koffer block.

2,2′-Methylene-bis(cyclohexanone) dioxime

A mixture of 100 g (0·48 mol) of 2,2′-methylene-bis(cyclohexanone)[9], 500 ml of methanol 105 g (1,15 mol) $NaHCO_3$ and 80 g (1·15 mol) of hydroxylamine hydrochloride was refluxed for 8 h. After cooling water was added; the dioxime which separated out had a m.p. 120—150°C or 127—160°C (methanol). For $C_{13}H_{22}N_2O_2$ (238·3) calculated: 65·60% C, 9·25% H, 11·78% N found: 65·80% C, 9·43% H, 11·78% N. The crude dioxime was extracted gradually with methanol at 20, 40 and 60°C, and finally five times at the boiling point of methanol. The separate extracts were gradually concentrated so that they yielded three crystalline fractions. Of a total of 29 fractions most melted in the range 159—164°C. In addition, about 1% showed a m.p. of 124—128°C and 2% a m.p. of 128—132°C, the latter from complete concentration of the filtrate of the last two fractions. The insoluble remnant and the first crystalline fraction, extruded from the last extraction, had a m.p. of 179—183°C (total of 6·5%).

The Schmidt Reaction of 2,2′-Methylene-bis(cyclohexanone)

a) 384 ml of concentrated hydrochloric acid were saturated for 1·5 hours with HCl gas at 2—5°C, then under mixing and bubbling of HCl at 15—20°C a solution of 36·8 g (0·176 mol) of 2,2′-methylene-bis(cyclohexanone) in 72 ml chloroform was added with simultaneous addition of sodium azide (total 25 g, 0·384 mol). HCl gas was bubbled for a further 30 min, the reaction mixture was diluted (under cooling) with 300 ml water and the chloroform layer was separated off. The aqueous layer was cooled and neutralised with 25% aqueous ammonium hydroxide and then extracted with chloroform. After distilling off the chloroform, a few milliliters of acetone were added and the mixture was left standing several days at 0°C. The yield of bislactam I was 24 g (57%), m.p. 190—215°C. *b*) To an homogenised mixture of 175 ml of 85% phosphoric acid and 125 g P_2O_5 at 15°C under mixing, 20·8 g (0·1 mol) 2,2′-methylene-bis(cyclohexanone) and 13·4 g (0·206 mol) sodium azide were added gradually. The mixture was stirred for 3 h and after 24 h standing at room temperature was further worked up in the same manner as in *a*) above for the aqueous layer. The yield was 19 g (80%) of bislactam *I*, m.p. 195—217°C.

Isomer separation: 52·7 g of bislactam *I* in 500 ml 2-propanol was heated to boiling. The insoluble fraction (27·6 g, 52·4%) yielded after repeated crystallisation from water isomer *Ia* (21 g,

39·9%), m.p. 235—236°C. After concentrating the filtrate and repeated crystallisation from toluene, saturated with water at 20°C, isomer *Ib* was isolated in a yield of 18·9 g (35·8%), m.p. 195 to 197°C. For $C_{13}H_{22}N_2O_2$ (238·3) calculated: 65·60% C, 9·25% H, 11·78% N; found for isomer *Ia*: 65·79% C, 9·39% H, 11·61% N; found for isomer *Ib*: 65·76% C, 9·40% H, 11·73% N.

The Beckmann Rearrangement of 2,2'-Methylene-bis(cyclohexanone) Dioxime

a) To 6 ml of an 85% solution of H_2SO_4 with continuous mixing we added over 30 min 3 g (0·015 mol) of the dioxime (m.p. 120—150°C). The mixture was heated to 60°C and after solution of the dioxime further 6 ml of sulphuric acid and 3 g dioxime were added. The reaction mixture was slowly heated to 95°C, and the temperature then allowed to increase to 103°C. After cooling the mixture was neutralised and worked up in the same manner as in the Schmidt reaction. The yield was 1 g (16·7%) of bislactam, m.p. 164—175°C. *b*) In the flask of a Soxhlet extractor a mixture of 100 g 90% sulphuric acid and 505 ml chloroform was heated under stirring up to the boiling point. 50 g (0·21 mol) of the dioxime were introduced into the extraction capsule. The extraction lasted 6 h, following which the reaction mixture was maintained at the boiling temperature for a further 2 h and then worked up in the same manner as decribed in *a*) above. The yield was 12·5 g (25%) of the bislactam, m.p. 164—175°C. *c*) To a homogenised mixture of 100 ml 85% phosphoric acid and 250 g P_2O_5, 20 g (0·08 mol) of the dioxime were added under mixing at a rate which guaranteed solution of the latter. The reaction mixture was stirred for 1 h at a bath temperature of 100°C. Neutralisation and isolation of the crude product were carried out as above. The chloroform extract was, however, concentrated under reduced pressure and the concentrate was diluted with water. After steam distillation the distillate yielded 2·2 g (13%) of 1,2,3,4,5,6,7,8-octahydroacridine, m.p. 60—62°C. For $C_{13}H_{16}N$ (202·0) calculated 83·35% C, 9·17% H, 7·46% N; found: 83·49% C, 9·43% H, 7·48% N. The aqueous solution was extracted with chloroform and after evaporation of the latter and addition of acetone there separated out 15·9 g (79·5)% of bislactam, m.p. 164—173°C, which contained according to the infrared spectrum isomers *I* and *III* in approximately 1 : 1 ratio. The same ratio of isomers was obtained from the fraction of dioxime, with m.p. 159—164 and 127—160°C resp. From a fraction of dioxime with m.p. 128—132°C a product of m.p. 155—168°C, rich in isomer *III*, was obtained. From a fraction of dioxime with m.p. 179—183°C a product rich in isomer *I* was prepared.

Isomer separation: The crude product (from the rearrangement of the dioxime with m.p. 120—150°C) was dissolved in ethyl acetate at the boiling point. The insoluble remnant (42·0%) gave isomer *Ia* (33·6%) after repeated crystallisation from water, m.p. 235—236°C. Crystals which separated from ethyl acetate showed a m.p. of 172—178°C and were further crystallised from ethyl acetate until there was a constant m.p. of 176—178°C (44·7%). This product was separated chromatographically on a column of silica gel (60—120 μm) in a mixture of acetone–ethyl acetate–acetic acid (6 : 2 : 0·1). Fractions (100 ml) were evaporated under reduced pressure; acetic acid remnants were removed by 2 h of drying at 60°C at a pressure of 10 Torr. To the remainder acetone was added and after 2 h of standing at 0°C a crystalline product separated out which was collected by filtration. Fractions 1—7 (elution volume 4025—4750 ml for 4·3 g used for separation) were pooled (17·4%) and after crystallisation from ethyl acetate yielded isomer *III*, m.p. 174—182°C (14·0%). For $C_{13}H_{22}N_2O_2$ (238·3) calculated: 65·60% C, 9·25% H, 11·78% N; found: 65·23% C, 9·41% H, 11·92% N. In the further fractions isomer *III* was gradualy enriched with isomer *Ia*. The last fractions (elution volume 7740—10120 ml) were pooled and after crystallisation from 2-propanol there was a yield of 1·6% of isomer *II*, m.p. 247°C. For $C_{13}H_{22}N_2O_2$ (238·3) calculated: 65·60% C, 9·25% H, 11·78% N; found: 65·18% C, 9·64% H, 12·20% N.

Hydrolysis of Methylene-bis(1-aza-2-cycloheptanones)

A solution of 2·4 g (0·01 mol) of *Ia* in 100 ml conc. hydrochloric acid was boiled for 14 h. Hydrochloric acid was distilled off under reduced pressure and the dihydrochloride of 6,6'-methylene-bis(6-aminocaproic acid) which remained was dissolved in 1 l of water. This solution was poured through a column of Amberlite IR4B and then evaporated to dryness. The residue was dissolved in 10 ml water. The free acid separated out after addition of 50 ml ethanol and was recrystallised from a mixture of ethanol and water. The yield was 2·4 g (90%) of 6,6'-methylene-bis-(6-aminocaproic acid), m.p. 232—233°C (isomer A). For $C_{13}H_{26}N_2O_4$ (274·3) calculated: 56·91% C, 9·55% H, 10·21% N; found: 56·61% C, 9·73% H, 10·05% N. In a similar fashion isomer *Ib* was hydrolysed. Precipitation with methanol and crystallisation from a mixture of ethanol and water gave a yield of 86·5% of 6,6'-methylene-bis(6-aminocaproic acid), m.p. 191—192°C (isomer *B*) in the form of the monohydrate. For $C_{13}H_{26}N_2O_4 . H_2O$ (292·4) calculated: 53·40% C, 9·65% H, 9·58% N; found: 53·46% C, 9·78% H, 9·56% N. Hydrolysis of the product of m.p. 176—178°C (a mixture of isomers *Ia*, *II* and *III*), carried out in the same manner, yielded after precipitation in methanol or ethanol 11% of isomer *A*, m.p. 232—233°C. After separation of isomer A the solution was dehydrated by means of azeotropic distillation with benzene, then evaporated and the remnant was dissolved in methanol. After standing for several days at 0°C an amino acid separated out (15%), m.p. 189—191°C, corresponding to bislactam *III*. For $C_{13}H_{26}N_2O_4$ (274·3) calculated: 56·91% C, 9·55% H, 10·21% N; found: 56·29% C, 9·65% H, 10·17%N.

Hydrolysis of isomer II: A mixture of 0·77 g (0·0024 mol) of barium hydroxide octahydrate and several milliliters of water was heated in a boiling water bath, 0·5 g (0·0021 mol) of isomer *II* were added, the resulting suspension was heated for two h in a boiling water bath, diluted with water, neutralised with solid CO_2 and extracted with hot water. After separation of barium carbonate the filtrate was concentrated under reduced pressure, and after addition of ethanol the concentrate yielded 2,2'-methylene-bis(6-aminocaproic acid), m.p. 195—205°C in an amount of 0·45 g (78·2%).

The effect of increased temperature: A test tube containing the investigated isomer of bislactam or bisaminocaproic acid was heated under a stream of dry nitrogen gas in a bath at a temperature required for melting the isomer (200—250°C). After cooling the contents of the test tube (a glass-like mass) was ground to a powder and analysed by infrared spectroscopy.

Spectroscopic Measurements

Infrared spectra in the region of stretching vibrations of NH bonds were measured on a Perkin-Elmer model 621 instrument. The precision of the programme used was $\pm 0{\cdot}5\ cm^{-1}$. Calibration was made with NH_3. The cells had a 10 cm optical path length. Concentrations are given in Table I. Temperature dependence in the region of ν(NH) was measured on Unicam instrument model SP 100. The solvent used was tetrachloroethylene, the cells had a 2 cm optical path length, sample concentration was 0·0015M, temperature was measured with a thermocouple encased in glass and penetrating the cover of the cell. The thermocouple output was measured with a Zeiss Jena model 1 galvanometer. Other spectra were measured on a Zeiss Jena model UR 10 instrument. For quantitative determinations of individual constitutional isomers in mixtures we used solutions in chloroform at a concentration of 0·0015M. Under these conditions all the substances are in a nonassociated state. For appreciation of the degree to which various contents of diastereoisomers can influence quantitative determination, extinction coefficients of free NH of both stereoisomers *Ia* and *Ib* were measured. *Ia*: ν(NH) 3398·4 cm^{-1}, ε^a_{max} 185·2 ± ± 2 (102·1% in relation to the mean value of ε^a_{max} of both isomers); *Ib*, ν(NH) 3398·7 cm^{-1},

ε^{a}_{max} 177·8 ± 2 (97·9% in relation to mean values of ε^{a}_{max}). It is highly probable therefore, that varying content of diastereoisomers of individual constitutional isomers does not have a significant effect on the quantitative determination of separate constitutional isomers in mixtures.

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