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169. Preparation of Neutral Ionophores for Alkali and Alkaline Earth Metal Cations and their Application in Ion Selective Membrane Electrodes

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(9. IV. 75)

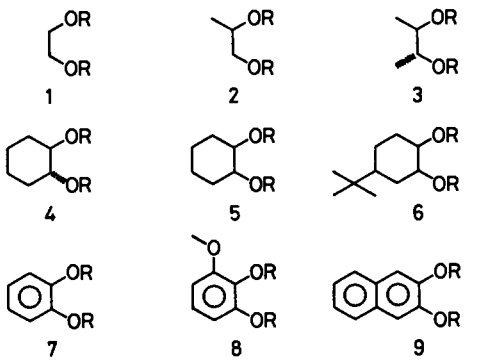
Summary. The preparation of a series of non-cyclic, uncharged ligands able to selectively complex alkali and alkaline earth metal cations is described. These molecules are designed to be used as carriers for cations through membranes. Some of the compounds show high Ca^{2+} and Na^{+} selectivity, respectively, in liquid membrane electrodes.

1. Introduction. – Certain uncharged, lipophilic complexing agents for cations behave as carriers for these ions through membranes [1] [2] and are therefore attractive components for ion selective liquid membrane electrodes [2] [3]. Although quite a number of such cyclic compounds has been described [2–6] only few are potentially useful components in liquid membrane electrodes [3] [7]. A series of non cyclic synthetic ligands showing high ion selectivity as well as carrier properties for

cations through bulk membranes [8] were utilised in ion sensors [7]. We report here on the preparation and properties of related compounds in view of correlating the structure with the ion selectivity and obtaining ligands of high selectivity for Ca^{2+} with respect to other alkaline earth as well as alkali metal cations.

2. Results and Discussion. – It has been shown earlier [9] that compound **1B** (see *Scheme 1*) complexes Ca^{2+} rather selectively and is able to transport this cation through bulk membranes by a carrier mechanism [8]. This ligand is therefore an ionophore for Ca^{2+} [10]. Since at least one of the ether oxygen atoms in **1** participates in the complex formation [11], structural changes in their neighbourhood should strongly influence the ion selectivity [3] [9]. Therefore compounds **2–9** (see *Scheme 1*) have been prepared. The ^{13}C-NMR. spectra of these ligands clearly show that the ester carbonyl groups in the series B do not participate in the coordination of the metal cation when used in liquid membrane electrodes of the type described below. This is the reason why there are only minor differences in the ion selectivities between corresponding molecules of the series A and B.

Scheme 1



The side chain in the series B, however, increases strongly the lipophilicity and the mobility of ligand and complex remains satisfactory; this ensures high life time of the corresponding membrane systems.

The potentiometric selectivity factors K_{NM}^{Pot} obtained by the separate solution technique [12] in 0.01M aqueous solutions of the chlorides of different cations and membrane solvents of high (*o*-nitro-phenyl *n*-octyl ether (*o*-NPOE), $\varepsilon \approx 24$ [7]) and low (dibutyl sebacate (DBS), $\varepsilon \approx 4$ [13]) dielectric constant are given in Tables 1 and 2 respectively. The factor K_{NM}^{Pot} is a measure for the preference of cation M relative to cation N by the membrane electrode. It is obvious from Tables 1 and 2 and especially from Fig. 1 that an increase in the dielectric constant of the membrane phase leads to a preference of the divalent relative to monovalent cation of a given size. This was predicted on the basis of model calculations [3] [7] [14][1]). Fig. 1 also demonstrates the

Table 1. *Selectivity factors* K^{Pot}_{CaM} (membrane solvent: *o*-NPOE) *obtained by EMF.-measurements in 0.01*M *aqueous solutions of the different metal chlorides*

Ion M	*o*-NPOE	Ligands																	
		1A	**1B**	**2A**	**2B**	**3A**	**3B**	**4A**	**4B**	**5A**	**5B**	**6A**	**6B**	**7A**	**7B**	**8A**	**8B**	**9A**	**9B**
Li^+	4	0.03	0.1	0.03	0.02	0.04	0.02	0.03	0.1	0.02	0.03	0.04	0.04	2	2	10	8	10	20
Na^+	26	0.01	0.2	0.04	0.03	0.02	0.01	0.06	0.08	0.02	0.05	0.03	0.05	300	90	80	40	2000	500
K^+	39	0.01	0.1	0.04	0.009	0.01	0.006	0.02	0.1	0.01	0.03	0.009	0.008	40	30	7	20	200	200
Rb^+	75	0.008	0.1	0.02	0.01	0.006	0.01	0.03	0.08	0.01	0.03	0.02	0.02	3	3	2	10	10	30
Cs^+	5	0.008	0.06	0.02	0.006	0.03	0.009	0.01	0.04	0.01	0.02	0.06	0.06	0.5	0.4	0.8	2	0.8	3
Mg^{2+}	0.3	0.0003	0.0004	0.0005	0.0002	0.0002	0.0002	0.0003	0.0004	0.0001	0.0003	0.0003	0.0002	0.002	0.2	0.01	0.2	0.001	0.04
Ca^{2+}	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Sr^{2+}	1	0.02	0.1	0.01	0.01	0.02	0.008	0.009	0.008	0.007	0.008	0.008	0.008	3	2	4	0.6	3	2
Ba^{2+}	0.4	0.02	0.8	0.004	0.01	0.003	0.001	0.0009	0.003	0.0006	0.001	0.001	0.001	6	6	100	10	7	2

Table 2. *Selectivity factors* K^{Pot}_{NaM} (membrane solvent: DBS) *obtained by EMF.-measurements in 0.01*M *aqueous solutions of the different metal chlorides*

Ion M	DBS	Ligands																	
		1A	**1B**	**2A**	**2B**	**3A**	**3B**	**4A**	**4B**	**5A**	**5B**	**6A**	**6B**	**7A**	**7B**	**8A**	**8B**	**9A**	**9B**
Li^+	0.8	0.5	0.3	0.9	0.7	1	2	2	1	0.9	0.9	1	1	0.3	0.2	0.6	0.5	0.1	0.2
Na^+	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
K^+	2	1	0.8	1	0.8	0.9	0.7	0.1	0.7	0.3	0.5	0.4	0.4	0.6	0.5	0.5	1	0.4	0.5
Rb^+	2	0.7	0.5	1	0.3	0.8	0.4	0.09	0.6	0.2	0.5	0.2	0.2	0.5	0.2	0.3	1	0.1	0.2
Cs^+	2	0.5	0.2	0.8	0.2	0.4	0.2	0.08	0.5	0.1	0.3	0.1	0.1	0.4	0.07	0.2	0.5	0.05	0.09
Mg^{2+}	0.1	0.03	0.003	0.02	0.005	0.09	0.02	0.005	0.1	0.006	0.05	0.01	0.01	0.05	0.003	0.005	0.1	0.0008	0.003
Ca^{2+}	0.1	0.07	0.04	0.04	0.1	0.08	0.2	0.05	0.3	0.1	1	0.09	0.1	0.05	0.01	0.008	0.1	0.003	0.007
Sr^{2+}	0.2	0.05	0.04	0.03	0.09	0.07	0.1	0.02	0.1	0.04	0.1	0.06	0.09	0.06	0.01	0.01	0.4	0.009	0.01
Ba^{2+}	0.3	0.08	0.1	0.04	0.1	0.08	0.09	0.02	0.1	0.05	0.1	0.05	0.07	0.07	0.02	0.02	0.3	0.006	0.01

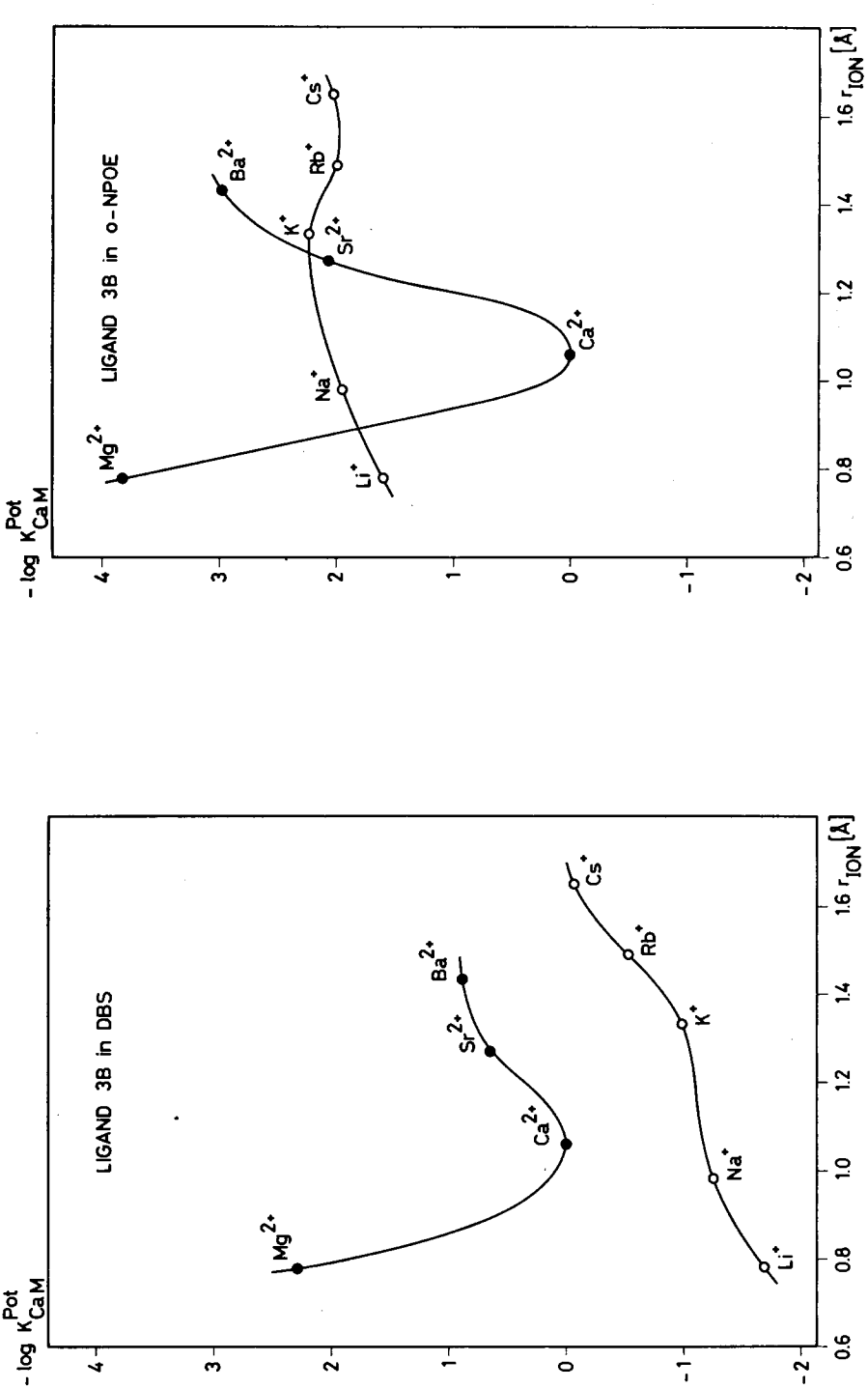


Fig. 1. *Influence of the membrane solvent on the selectivity of the corresponding neutral carrier liquid membrane electrodes*

remarkable Ca^{2+}-selectivity with respect to all other alkali- and alkaline earth metal cations of ligand **3B** when using *o*-NPOE as membrane component.

In Fig. 2 selectivity factors for a number of compounds are plotted in the order of decreasing polarity (decreasing with the expected polar substituent constant) [15] of the substituents attached to the carbon atoms carrying the two ether oxygen atoms[2]). For the molecules studied this order involves a change from a syn-periplanar to a synclinal arrangement of the ether oxygen atoms. According to model calculations [3] [16] [17], an increase of the dipole moment of the ligand groups[1])[2]) is expected to result in a selectivity enhancement for divalent relative to monovalent cations when the two are of the same radius (*e.g.* Ca^{2+}, Na^{+}) and for small relative to large cations of the same charge (*e.g.* Ca^{2+}, Ba^{2+}); these trends are obvious from Fig. 2.

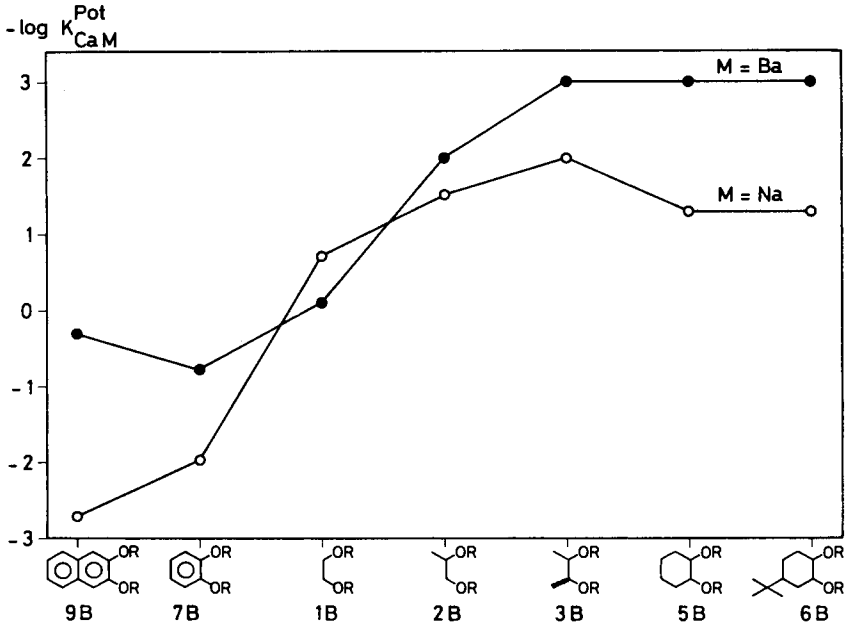


Fig. 2. *Influence of the structure of ion carriers on the selectivity of the corresponding liquid membrane electrodes*

Taking the specific molecular structures into account, the above can be amplified as follows: Ligands with a high preference for Ca^{2+} over Na^{+} and Ba^{2+} should conform either to one or to both of two specifications, *i.e.* small polar substituent constant or synclinal arrangement of the ether oxygen atoms (**3B**, Fig. 1). Conversely high polar substituent constant respectively syn-periplanar arrangement (**7B**) produces preference for Na^{+} and Ba^{2+} over Ca^{2+} [7].

The deviations from this trend of the experimental data near both ends of the scale in Fig. 2 (**9B**, **7B**, **5B**, **6B**) may be due to the bulkiness of those ligands, as measured by the average thickness of the ligand layer around the complexed metal

[1]) This holds only for a given complex stoichiometry.

[2]) It might be expected that the basicities of the ether oxygen atoms of the compounds shown in Fig. 2 increase from left to right [18].

cation; this characteristic in itself shifts selectivities to favor monovalent over divalent cations of the same size (*cf.* Fig. 3 and [3] [5]).

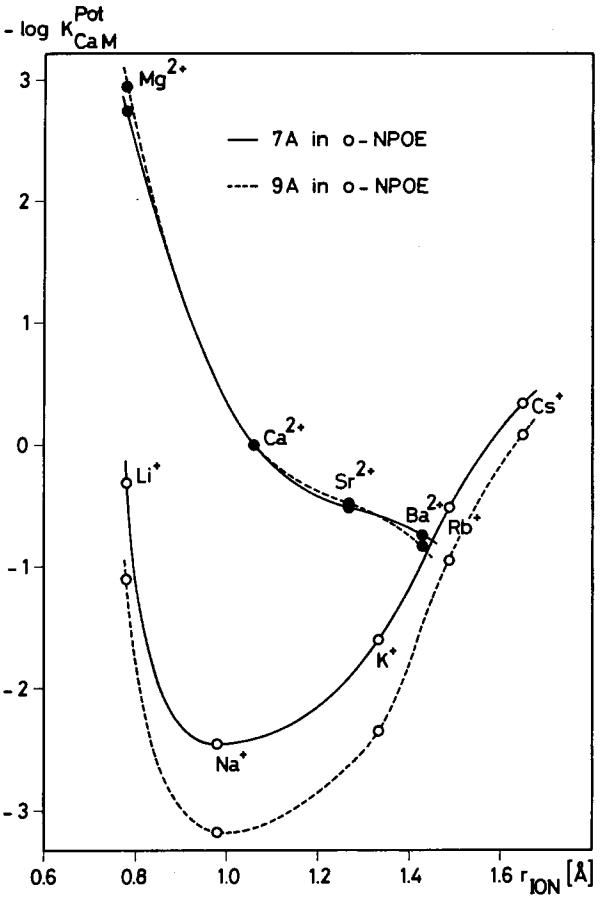


Fig. 3. *Influence of the average thickness of the ligand layer around the metal cation on the ion selectivity of liquid membrane electrodes*

Experimental Part

EMF.-Measurements. – The preparation of the PVC membranes and the measuring technique have been described in detail elsewhere [19] [20][21]. Throughout, cells of the type Hg; Hg_2Cl_2, KCl(satd.) / electrolyte bridge / sample solution // membrane // internal filling solution, AgCl; Ag with double junction reference electrodes and electrode bodies *Philips* IS-560 for mounting the membranes have been used at 25°. The internal filling solutions were always aqueous 0.01M $CaCl_2$. Throughout, the separate solution technique and 0.01M sample solutions were used to determine the selectivity factors, which are given by

$$\log K^{Pot}_{NM} = \frac{(EMF_M - EMF_N)z_N F}{2.303 \cdot RT} - \log a_M^{z_N/z_M} + \log a_N$$

R: gas constant
T: absolute temperature
F: Faraday constant
a: ion activities
z_N: charge of the reference ion
z_M: charge of the interfering ion

EMF_M: EMF of the cell assembly, the sample being a solution of the chloride of the interfering cation

EMF_N: EMF of the cell assembly, the sample being a solution of the chloride of the reference cation (Ca^{2+} or Na^+).

As activity standards the fundamental values set forth by *Bates* [22] were employed. For all alkaline earth metal cations the activity coefficients γ_{Ca} for Ca^{2+} were used and found to be related to the ionic strength I as

$$\log \gamma_{Ca} = \frac{-2.04\sqrt{I}}{1 + 1.55\sqrt{I}} + 0.2\,I.$$

The activity coefficients proposed by *Bates* for Na^+ are described by

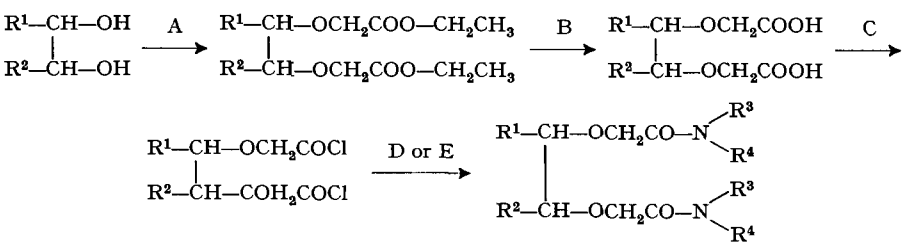
$$\log \gamma_{Na} = \frac{-0.51\sqrt{I}}{1 + 1.30\sqrt{I}} + 0.06\,I$$

and were used for all other alkali metal cations.

Syntheses. – *General remarks.* Most of the solvents used were dried by distillation over phosphorus pentoxide, calcium hydride, lithium aluminium hydride or molecular sieve. Organic solutions were dried over magnesium sulfate. ^{1}H-NMR. spectra were recorded on *Varian* A-60A or *Hitachi Perkin Elmer* R24 spectrometers at 60 MHz and on *Varian* HA-100 at 100 MHz using tetramethylsilane (TMS) as internal standard. Chemical shifts are reported in δ (ppm) coupling constants J in Hz. For each signal the multiplicity (with the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br. = broad), the relative intensity, and the assignment is given in parenthesis. ^{13}C-NMR.-spectra were recorded on a *Bruker-Spectrospin* HFX-90/B-SC-FFT-12 spectrometer at 22.6 MHz. Chemical shifts are reported in δ (ppm) relative to TMS as internal reference. Mass spectra were taken on *Hitachi*-RMU-6M (at Prof. Dr. *J. Seibl*, ETHZ) or *CEC* 21–492 mass spectrometers. The most important ions are reported as m/e values and relative intensities (% base peak, in parenthesis). IR. spectra were recorded on *Perkin Elmer* Infracord 157 G, 467 or 300 spectrophotometers in the indicated manner. The ν_{max} are given in cm^{-1}. UV. spectra were taken on a *Perkin Elmer* 402 spectrophotometer in 95% ethanol unless otherwise indicated. λ_{max} is given in nm with the ε value in parenthesis. Microanalyses were done by *W. Manser* (ETHZ) or *Galbraith Laboratories*, Knoxville, Tenn. Gas chromatograms (GC.) were done on a *Varian* A-700 gas chromatograph under the indicated conditions. GC./MS. spectra were run at 30 eV on a *Finnigan* Quadrupole Mass Spectrometer by *Vinca Parmakovitch* at Columbia University. Melting points (m.p.) were taken on a *Thomas Hoover* 'Unimelt' apparatus and are uncorrected, as are the boiling points. *Eastman Kodak* silica gel and alumina thin layer (TLC.) and *Merck* 'precoated PLC.-plates silica gel F-254' thick layer chromatography plates were used. The solvent was diethyl ether/chloroform/triethylamine 1:1:1 (solvent A), diethyl ether/benzene/triethylamine 1:1:1 (solvent B), benzene/acetone 1:2 (solvent C), or as indicated. The optical rotation was determined with a *Carl Zeiss* photo-electric precision polarimeter.

General procedures. The ligands 1 to 5 were generally prepared in the following manner (*Scheme 2*):

Scheme 2



If not otherwise indicated, the following general procedures were used.

A. *Conversion of glycols to the corresponding bis(ethoxycarbonyl-methyl)ethers* [23]. To an ice-cooled solution of ethyl diazoacetate (2 equiv., generally 9 g (0.079 mol)) and a diol (1 equiv.) in dry methylene chloride (60 ml) (under nitrogen) boron trifluoride diethyl etherate (0.4 ml) was added slowly under magnetic stirring. After the addition stirring was continued at room temperature for 1 h, then at 45° for 1 h. The solvent was then evaporated under vacuum to give the bis(ethoxy-carbonyl-methyl) ether of the diol.

B. *Hydrolysis of the diester.* The diester was hydrolyzed with KOH in a water/methanol mixture 1:2 by refluxing for 1 h (3.5 molKOH per mol diester). The methanol was then evaporated under vacuum, and the residue acidified with HCl. The extraction of the aqueous phase with ether yielded the diacid.

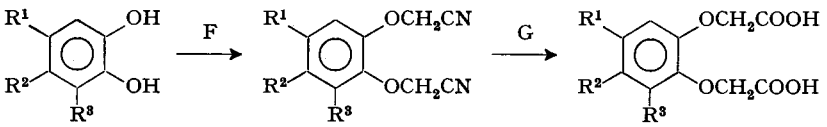
C. *Preparation of the acid chlorides.* To a solution of 10 drops N,N-dimethylformamide and 1 g of the dicarboxylic acid (1 equiv.) in dry benzene (25 ml), thionyl chloride (4 equiv.) was added. Thereafter stirring was continued at room temperature for 24 h. The benzene was then evaporated under vacuum to leave the acid chloride.

D. and E. *Conversion of the acid chlorides to the corresponding diamides.* Procedure D: The acid chloride (1 equiv., generally 1g), in dry benzene (15 ml), was added to a solution of the amine (2 equiv.) plus triethylamine (4 equiv.) in benzene (15 ml) to give the amide, which was purified by TLC. (solvent C).

Procedure E: The acid chloride (1 equiv.) was reacted with the amine, respectively the hydrochloride of the amine (2 equiv.) and triethylamine, in methylene chloride at 4–6° (ice bath) over 30–50 min with stirring. Stirring was continued for 1–2.5 h; the solvent was evaporated under vacuum and triethylamine hydrochloride was precipitated with diethyl ether. Concentration of the filtrate gave the product which was treated as described.

The aryl-dioxydiacetic acids were prepared in the following manner (*Scheme 3*):

Scheme 3



(R^1, R^2, R^3 as indicated below)

The following general procedures were used [24]:

F. *Preparation of the arenedioxyacetonitrile.* A solution of an arylic diol (1.0 equiv.), chloracetonitrile (2.0 equiv., 61 g (0.81 mol)), potassium carbonate (1.2 equiv., 67 g (0,48 mol)) and potassium jodide (0.12 equiv., 8 g (0.048 mol)) in acetone (320 ml) was refluxed for 7 h. After cooling the solution to room temperature the inorganic salts were filtered off and the solvent was evaporated under vacuum. The residue was recrystallized from ethanol.

G. *Hydrolysis of the dinitrile.* The diacetonitriles were hydrolyzed in methanol water 1:1.8 with KOH at 90° for 18 h. Thereafter the solution was acidified with conc. HCl to pH 1 to give the solid diacides.

Ethyl 12-methylamino-laurat. To 1 g of 12-methylamino-lauric acid (0.0044 mol) in ethanol (100 ml) HCl-gas was admitted until all material went into solution. The mixture was then refluxed for 72 h. The ethanol was evaporated under vacuum. The residue was dissolved in chloroform and washed with 0.1N NaOH. The chloroform was evaporated under vacuum to yield 860 mg of ethyl 12-methylamino-laurat (77%). – IR. (neat): 1735. – ^{1}H-NMR. ($CDCl_3$): 1.1–1.8 (*m*, 21, CH_3CH_2 and $(CH_2)_9$); 2.3 (*t*, 2, CH_2CO); 2.45 (*s*, 3, CH_3N); 2.6 (*t*, 2, CH_2N); 4.15 (*q*, 2, CH_2CH_3). – MS.: M^+ 257 (5), 212 (10), 170 (9), 57 (13), 44 (100), 41 (12), 28 (24).

3,6-Dioxaoctanedioyl dichloride (93% from 3,6-dioxaoctanedioic acid [25] and $SOCl_2$ by procedure C) was converted with dipropylamine by procedure D to *N,N,N,N-Tetrapropyl-3,6-dioxaoctane diamide* (**1A**, 90%). – IR. (neat): 1645. – ^{1}H-NMR. ($CDCl_3$): 0.9 (*t*, 12, CH_3CH_2); 1.5 (*m*, 8, CH_2CH_3); 3,2 (*m*, 8, CH_2N); 3.7 (*s*, 4, OCH_2CH_2O); 4.2 (*s*, 4, OCH_2CO). – MS.: M^+ 344 (6), 216 (7), 186 (61), 158 (30), 128 (33), 114 (12), 100 (55), 86 (28), 72 (22), 58 (25), 43 (100).

$C_{18}H_{36}N_2O_4$ (344.50) Calc. C 62.77 H 10.53 N 8.13% Found C 62.57 H 10.50 N 7.98%

N,N'-Di[(11-ethoxycarbonyl)undecyl]-N,N'-dimethyl-3,6-dioxaoctane diamide (**1B**, 32%, obtained from 3,6-dioxaoctanedioyl dichloride and ethyl 12-methylamino-laurat by procedure D). – IR. (neat): 1725, 1640. – ^{1}H-NMR. ($CDCl_3$): 1.2–1.8 (*m*, 42, CH_3CH_2, $(CH_2)_9$); 2.3 (*t*, 4, CH_2CO); 2.95 (*s*, 6, CH_3N); 3.25 (*t*, 4, CH_2N); 3.75 (*s*, 4, OCH_2CH_2O); 4.15 (*q*, 4, CH_2CH_3); 4.2 (*s*, 4, OCH_2CO). – MS.: M^+ 656 (11), 612 (11), 611 (29), 343 (31), 342 (100), 284 (35), 268 (35), 256 (40), 238 (13), 210 (11), 86 (11), 84 (11), 83 (13), 74 (27), 59 (13), 58 (13), 57 (21), 55 (11), 44 (55), 43 (11).

$C_{36}H_{68}N_2O_8$ (656.96) Calc. C 65.82 H 10.43 N 4.26% Found C 65.58 H 10.15 N 4.19%

Diethyl 4-methyl-3,6-dioxaoctane-1,8-dioat (97%) was obtained from propylene glycol and ethyl diazoacetate by procedure A. – ^{1}H-NMR. ($CDCl_3$): 1.3 (*m*, 9, CH_3CH_2 and CH_3CH); 3.6 (*m*, 3, CH_2CH); 4.2 (*q*, 4, CH_2CH_3); 4.2 (*s*, 4, OCH_2CO). The hydrolysis of this diester by procedure B gave 4-methyl-3,6-dioxaoctanedioic acid (34%). – IR. (neat): 1725. – ^{1}H-NMR. (CD_3OD): 1.15 (*d*, 3, CH_3CH); 3.6 (*m*, 3, CH_2CH); 4.2 (*d*, 4, OCH_2CO).

From this diacid 4-methyl-3,6-dioxaoctanedioyl dichloride (90%) was obtained by procedure C: IR. (neat): 1805.

4-Methyl-N,N,N,N-tetrapropyl-3,6-dioxaoctane diamide (**2A**, 75%) obtained by procedure D from the above acid chloride and dipropylamine. – IR. (neat): 1645. – ^{1}H-NMR. ($CDCl_3$): 0.9 (*t*, 12, CH_3CH_2); 1.15 (*d*, 3, CH_3CH); 1.55 (*m*, 8, CH_2CH_3); 3.2 (*m*, 8, CH_2N); 3.6 (*m*, 3, CH_2CH); 4.2 (*d*, 4, OCH_2CO). – MS.: M^+ 358 (7), 230 (7), 216 (7), 200 (36), 186 (16), 172 (8), 158 (25), 142 (16), 128 (32), 114 (14), 100 (63), 86 (28), 72 (18), 58 (18), 43 (100).

$C_{19}H_{38}N_2O_4$ (358.53) Calc. C 63.65 H 10.68 N 7.81% Found C 63.54 H 10.74 N 7.73%

N,N'-Di[(11-ethoxycarbonyl)undecyl]-N,N'-dimethyl-3,6-dioxaoctane diamide (**2B**, 72%) obtained from the corresponding acid chloride and ethyl 12-methylamino-laurat by procedure D. – IR. (neat) 1735, 1660, 1650. – ^{1}H-NMR. ($CDCl_3$): 1.3 (*m*, 45, CH_3CH, $-(CH_2)_9-$ and CH_3CH_2); 2.2 (*m*, 4, CH_2CO); 2.9 and 3.0 (2 *s*, 6, CH_3N); 3.25 (*m*, 4, CH_2N); 3.6 (*m*, 3, CH_2CH); 4.1 (*q*, 4, CH_2CH_3); 4.2 (*s*, 4, OCH_2CO). – MS.: M^+ 670 (2), 625 (1), 583 (0.5), 486 (21), 458 (8), 441 (12), 413 (5), 374 (15), 356 (22), 342 (17), 328 (10), 314 (13), 299 (9), 284 (41), 268 (24), 256 (24), 212 (16), 172 (35), 114 (37), 86 (47), 69 (25), 57 (41), 55 (41), 44 (100).

$C_{37}H_{70}N_2O_8$ (670.98) Calc. C 66.23 H 10.52 N 4.17% Found C 66.08 H 10.40 N 4.19%

Diethyl (R,R)*-4,5-dimethyl-3,6-dioxaoctanedioate* (73%) obtained from D(−)2,3-butanediol (absolute configuration: (−)-(*R,R*) [26]) by procedure A. – ^{1}H-NMR. ($CDCl_3$): 1.3 (*t*, 12, CH_3CH_2 and CH_3CH); 3.65 (*m*, 2, CH); 4.2 (*s*, 4, OCH_2CO); 4.2 (*q*, 4, CH_2CH_3). Hydrolysis by procedure B gave the corresponding (*R,R*)-diacid (92%). – ^{1}H-NMR. ($CDCl_3$): 1.2 (*m*, 6, CH_3CH); 3.5 (*m*, 2, CH); 4.2 (*s*, 4, OCH_2CO).

(R,R)*-4,5-Dimethyl-3,6-dioxaoctanedioyl dichloride* (95%) from the diacid by procedure C. – IR. (neat): 1795.

(−)-(R,R)*-4,5-Dimethyl-N,N,N,N-tetrapropyl-3,6-dioxaoctane* diamide (**3A**, 80%) was obtained from the above acid chloride and dipropylamine by procedure D. – IR. (neat): 1640. – ^{1}H-NMR. ($CDCl_3$): 0.9 (*t*, 12, CH_3CH_2); 1.2 (*d*, 6, CH_3CH); 1.6 (*m*, 8, CH_2CH_3); 3.2 (*m*, 8, CH_2N); 3.6 (*m*, 2, $CHCH_3$); 4.2 (*s*, 4, OCH_2CO). – MS.: M^+ 372 (9), 244 (7), 230 (11), 214 (27), 186 (100), 160 (77), 143 (25), 142 (27), 128 (27), 114 (32), 100 (89), 86 (32), 72 (59), 58 (39), 43 (70), 41 (41); $[\alpha]_{546}^{22} = -3.63$ ($c = 1{,}3775$, EtOH).

(−)-(R,R)*-N,N'-Di[(11-ethoxycarbonyl)undecyl]-N,N',4,5-tetramethyl-3,6-dioxaoctane diamide* (**3B**, 73%) prepared from the corresponding acid chloride and ethyl 12-methylamino-laurat by procedure D. – IR. (neat): 1735, 1650. – ^{1}H-NMR. ($CDCl_3$): 1.3 (*m*, 48, CH_3CH_2, CH_3CH and $(CH_2)_9$); 2.2 (*m*, 4, CH_2CO); 2.9 and 3.0 (2 *s*, 6, CH_3N); 3.4 (*m*, 6, CH_2N, $CHCH_3$); 4.2 (*q*, 4, OCH_2CH_3); 4.2 (*s*, 4, OCH_2CO). – MS.: M^+ 684 (0.02), 398 (0.1), 370 (0.2), 342 (6), 299 (11), 298 (12), 284 (20), 256 (12), 240 (21), 212 (20), 198 (30), 142 (16), 128 (14), 115 (19), 100 (17), 87 (31), 72 (100), 55 (37), 44 (72). – $[\alpha]_{589}^{22} = -4{,}213$ ($c = 1.78$, EtOH).

$C_{38}H_{72}N_2O_8$ (685.01) Calc. C 66.63 H 10.60 N 4.09% Found C 66.36 H 10.61 N 4.04%

Diethyl trans-1,2-cyclohexanedioxydiacetate (60%) was prepared from *trans*-1,2-cyclohexanediol by procedure A: b.p.: 133–134°/0.15 Torr; TLC.: (same as for the *cis*-diester) Rf 0.31. – IR. (neat) 1740. – ^{1}H-NMR. (CCl_4): 1.25 (*t*, 6, CH_3); 1.0–2.0 (*m*, 8, CH_2); 3.25 (*m*, 2, CH—O); 4.15 (*q*, 4, CH_2CH_3); 4.2 (*s*, 4, CH_2O). – GC.: (175° on 20% SE-30) 6.2 min.

The hydrolysis of this diester by procedure B gave trans-*1,2-cyclohexanedioxydiacetic acid* (97%): m.p.: 114.5–116.5°. – IR. (nujol): 1720, 1760. – ^{1}H-NMR. ($CDCl_3$): 1.2–2.1 (*m*, 8, CH_2); 3.3 (*m*, 2, CH—O); 4.2 (*m*, 4, CH_2O).

$C_{10}H_{16}O_6$ (232.24) Calc. C 51.70 H 6.95% Found C 51.76 H 6.92%

This diacid was converted to trans-*1,2-cyclohexanedioxydiacetyl dichloride* (84%) by procedure C: b.p.: 123°/0.2 Torr. – IR. (neat): 1800. – ^{1}H-NMR. (CCl_4): 1.2–2.1 (*m*, 8, CH_2); 3.3 (*m*, 2, CH—O); 4.6 (*s*, 4, CH_2O).

trans-*N,N,N,N-Tetrapropyl-1,2-cyclohexanedioxydiacetamide* (**4A**, 97%) was obtained from the above acid chloride and dipropylamine by procedure E. It was distilled from a micro still, bath temp. 165°/0.05 Torr, for analysis. Larger amounts were purified by shaking a solution of the substance in ether with silica gel: TLC. (solvent B): Rf 0.46. – IR. (neat): 1640. – ^{1}H-NMR. (CCl_4): 0.9 (*t*, 12, CH_3); 1.2–1.8 (*m*, 16, CH_2); 3.2 (*m*, 10, CH_2N and CH); 4.2 (*s*, 4, CH_2—O). – MS.: M^+ 398 (19), 397 (1), 383 (1), 298 (2), 270 (10), 256 (38), 240 (27), 160 (100), 142 (27), 128 (15), 114 (15), 100 (60).

$C_{22}H_{42}N_2O_4$ (398.59) Calc. C 66.30 H 10.62 N 7.03% Found C 66.10 H 10.66 N 6.94%

trans-*N,N'-Di[(11-ethoxycarbonyl)undecyl]-N,N'-dimethyl-1,2-cyclohexanedioxydiacetamide* (**4B**, 92%) was prepared from the corresponding acid chloride and ethyl 12-methylamino-laurat by procedure E: TLC. (solvent B): Rf 0.43. – IR. (neat): 1730, 1640. – ^{1}H-NMR. (CCl_4): 1.3 (*t*, 6, CH_3); 0.9–2.1 (*m*, 44, CH_2); 2.2 (*t*, 4, CH_2CO); 2.9 and 3.0 (2 *s*, 6, CH_3N); 3.4 (*m*, 4, CH_2N); *ca.* 3.6 (*m*, 2, CH); 4.1 (*q*, 4, CH_2CH_3); 4.1 (*s*, 4, OCH_2CO). – MS.: M^+ 710 (18), 665 (15), 623 (3), 426 (8), 412 (40), 396 (20), 315 (100), 298 (20), 284 (35), 270 (48), 256 (33), 227 (12), 213 (61), 199 (13), 185 (14), 171 (20), 157 (14), 143 (20), 129 (20), 115 (34).

Hydrogenation of 1,2-phenylenedioxydiacetic acid (see below) in glacial acetic acid with 5% Rh/Al_2O_3 for 26 h, at 25° and 2.6 atü in a *Parr* shaker gave a viscous oil cis-*1,2-cyclohexanedioxydiacetic acid* (76%). – IR. (neat): 1730, 3700–2200. – ^{1}H-NMR. ($CDCl_3$): 1.1–1.9 (*m*, 8, CH_2); 3.65 (*m*, 2, CH); 4.20 and 4.22 (2 *s*, 4, CH_2O); 9.5 (*s*, 2, COOH). Without destillation of the acid chloride the sample contained an impurity (^{1}H-NMR.: 4.18). The acid chloride was prepared by procedure C (85%): b.p.: 133°/0.6 Torr. – IR. (neat): 1800. – ^{1}H-NMR. (CCl_4): 1.6 (*m*, 8, CH_2); 3.7 (*m*, 2, CH); 4.5 (*s*, 4, OCH_2CO).

This acid chloride gave with dipropylamine by procedure E cis-*N,N,N,N-tetrapropyl-1,2-cyclohexanedioxydiacetamide* (**5A**, 97%), TLC. (solvent B): Rf 0.33. – IR. (neat): 1640. – ^{1}H-NMR. (CCl_4): 0.85 (*t*, 12, CH_3CH_2); 1.1–1.9 (*m*, 16, CH_2); 3.2 (br. *t*, 8, CH_2N); 3.5 (br. *d*, 2, CH); 4.1 (*s*, 4, OCH_2CO). – MS.: M^+ 398 (5), 298 (1), 270 (4), 256 (22), 240 (16), 160 (100), 142 (31), 128 (13), 100 (85).

cis-*N,N'-Di[(11-ethoxycarbonyl)undecyl]-N,N'-dimethyl-1,2-cyclohexanedioxydiacetic amide* (**5B**, 92%) from the corresponding acid chloride by procedure E: TLC. (solvent B): Rf 0.41. – IR. (neat): 1730, 1640. – ^{1}H-NMR. (CCl_4): 1.3 (*t*, 6, CH_3CH_2); 1.0–2.0 (*m*, 44, CH_2); 2.2 (*t*, 4, CH_2CO); 2.9 and 3.0 (2 *s*, 6, CH_3N); 3.3 (*m*, 4, CH_2N); 3.6 (*m*, 2, CH); 4.1 (*q*, 4, CH_2CH_3); 4.1 (*s*, 4, OCH_2CO). – MS.: M^+ 710 (2), 665 (2), 412 (6), 396 (4), 315 (17), 298 (37), 284 (50), 270 (27), 256 (18), 227 (10), 213 (100), 198 (18), 185 (24), 171 (29), 157 (28), 143 (42), 129 (32), 115 (69), 101 (59), 87 (91), 73 (68).

4-t-Butyl-1,2-phenylenedioxydiacetonitrile (87%) was prepared by procedure F from 4-*t*-butylcatechol: m.p.: 48–50°; TLC. (solvent: ether): Rf 0.6. – IR. (nujol): 2250. – ^{1}H-NMR. ($CDCl_3$): 1.3 (*s*, 9, CH_3); 4.65 and 4.75 (2 *s*, 4, CH_2); 7.1 (*m*, 3, aryl). – MS.: M^+ 244 (26), 229 (100), 204 (5), 188 (15), 176 (3), 162 (16), 134 (12).

$C_{14}H_{16}N_2O_2$ (244.30) Calc. C 68.83 H 6.60 N 11.47% Found C 68.90 H 6.52 N 11.30%

4-t-Butyl-1,2-phenylenedioxydiacetic acid (89%) obtained by procedure G: m.p.: 158–160°. – IR. (nujol): 3600–2200, 1700. – ^{1}H-NMR. (DMSO-d_6): 1.1 (*s*, 9, CH_3); 4.45 and 4.55 (2 *s*, 4, CH_2); 6.8 (*m*, 3, aryl); 7.5 (*s*, 2, OH).

4-t-Butyl-1,2-cyclohexanedioxydiacetic acid (89%). Hydrogenation of the above diacide (0.02 mol) in glacial acetic acid (200 ml) in presence of Rh/C (5%, 1.7 g) and sodium acetate (0.04 mol) for 45 h at 27° and 3.2 atü of hydrogen gave incomplete conversion. Addition of fresh catalyst (0.85 g) (after removal of the old catalyst) and continued hydrogenation for 45 h gave a mixture of the 3 isomeric 4-*t*-butyl-1,2-cyclohexanedioxydiacetic acid (see below). – IR. (neat):

3700–2380, 1730. – ^{1}H-NMR. (CCl_4): 0.9 (*s*, 9, CH_3); 0.8–2.2 (*m*, 7, ring CH_2 and CH); 3.35 and 3.9 (2 *m*, *ca.* 2, CH—O); 4.2 (*m*, 4, OCH_2CO); 11.0 (*s*, 2, COOH).

4-t-Butyl-1,2-cyclohexanedioxydiacetyl dichloride (87%) obtained from the above mixture of the diacides and thionyl chloride at 70° for 45 min. – IR. (neat): 1800. – ^{1}H-NMR. (CCl_4): 0.9 (2 *s*, 9, CH_3); 0.8–2.3 (*m*, 7, ring CH_2 and CH); 3.3 and 3.9 (2 *m*, 2, CH—O); 4.6 (*m*, 4, OCH_2CO).

For analysis of the mixture the corresponding dimethylester was prepared (93%) from the above diacid dichloride. – IR. (neat): 1700. – ^{1}H-NMR. (CCl_4): 0.9 (*s*, 9, CH_3); 0.8–2.3 (*m*, 7, ring CH_2 and CH); 3.3 and 3.9 (2 *m*, 2, OCH); 3.7 (*s*, 6, CH_3O); 4.2 (*m*, 4, OCH_2CO). – GC. (20% SE-30, 180°): 3 peaks in ratio 55:42:3 (retention times 11, 12, 14 min). – GC./MS. (OV I, 180°): 4 peaks: major peaks 1: M^+ 316 (0.1), 284 (0.3), 259 (5), 243 (0.3), 227 (1.5), 226 (2), 211 (6), 198 (1), 183 (3), 169 (100), 137 (35), 129 (26), 121 (15), 97 (83), 79 (56); major peak 2: 259 (8), 227 (2), 198 (0.5), 183 (10), 170 (30), 137 (54), 121 (53), 97 (62), 79 (100); minor peak 3: M^+ 316 (17), 284 (68), 219 (17), 175 (5), 165 (41), 148 (100), 147 (88); minor peak 4: 273 (7), 225 (5), 212 (1.3), 211 (2), 183 (83), 137 (100), 105 (72).

4-t-Butyl-N,N,N,N-tetrapropyl-1,2-cyclohexanedioxydiacetamide (crude yield 96%) from the corresponding acid chloride and dipropylamine by procedure E. Chromatography of 4.36 g crude diamides on silica gel (50 g on a 37 × 2 cm column) using diethyl ether as eluant gave a total of 1.99 g (overall yield 44%) of one isomer which was used in our studies (**6 A**): TLC. (solvent B): Rf 0.5. – IR. (neat): 1640. – ^{1}H-NMR. (100 MHz in $CDCl_3$): 0.7–1.0 (*m*, 21, CH_3); 1.1–2.0 (*m*, 15, ring CH and CH_2, CH_2CH_3); 3.3 (*m*, 8, CH_2N); 3.5 (*m*, 1, CHO axial); 3.95 (*m*, 1, CHO equatorial); 4.25 (*s*, 2, OCH_2CO); 4.3 and 4.4 (*AB*-System, J = 12.5, 2, OCH_2CO). – ^{13}C-NMR. ($CDCl_3$): 11.2 and 11.4 (CH_3CH_2), 20.6 (ring C(5)); 20.8 and 22.1 (CH_2CH_3 cisoid respectively transoid to carbonyl oxygen atom); 27.6 ($(CH_3)_3$- and ring C(3) or C(6)); 28.8 (ring C(6) or C(3)); 32.5 (C—$(CH_3)_3$); 46.7 (ring C(4)); 47.4 and 48.7 (CH_2N cisoid respectively transoid to carbonyl oxygen atom); 67.3 and 69.7 (OCH_2CO); 74.7 (ring C(1)); 81.5 (ring C(2)); 169.3 and 169.7 (CO). – MS.: M^+ 454 (8), 439 (3), 326 (2), 296 (12), 238 (25), 160 (100), 158 (7), 142 (18), 128 (8), 100 (50).

The ^{1}H-NMR. spectrum shows one axial and one equatorial OCH ring proton (*cf.* [27]). Thus **6 A** has either a 1,2-*cis*-2,4-*cis*- or a 1,2-*cis*-2,4-*trans*-configuration. Using the chemical shifts of *cis*- and *trans*-4-*t*-butylcyclohexanol [28] and additive increments for the substituents [29] the chemical shifts of the ring carbons for these isomers were estimated. The experimental values are close to the estimated ones for the *cis-cis*-compound and shows larger deviations especially for C(4) and C(5) for the *cis-trans*-compound (see Table 3). Based on these results **6 A** was assigned to *1,2*-cis-*2,4*-cis-*4*-t-*butyl-N,N,N,N-tetrapropyl-1,2-cyclohexanedioxydiacetamide.*

4-t-Butyl-N,N'-di[(11-ethoxycarbonyl)undecyl]-N,N'-dimethyl-1,2-cyclohexanedioxydiacetamide (crude yield 94%), liquid, obtained from the corresponding acid chloride and ethyl 12-methylaminolaurat by procedure E. Chromatography as above of 3.58 g using tetrahydrofurane as eluant gave a fraction (**6 B**, 1.48 g, 36%). – TLC. (solvent B): Rf 0.5; IR. (neat): 1640, 1730. – ^{1}H-NMR. ($CDCl_3$): 0.9 (*s*, 9, $(CH_3)_3C$); 1.1–1.9 (*m*, 49, ring CH_2 and CH, – $(CH_2)_9$ and CH_3CH_2)); 2.3 (*t*, 4, CH_2CO); 2.9 (br. *s*, 3, CH_3N); 3.05 and 3.1 (2 *s*, 3, CH_3N); 3.2–3.5 (br. *m*, 5, CH_2N and CHO axial); 3.9 (br. *m*, 1, CHO equatorial); 4.1 (*q*, 4, CH_2CH_3); 4.2 and 4.3 (2 br. *s*, 4, OCH_2CO). – ^{13}C-NMR. ($CDCl_3$): 14.3 (CH_3CH_2); 20.5 (ring C(5)); 25.0 (CH_2CH_2COO); 26.9 ($CH_2CH_2CH_2N$); 27.1 (CH_2CH_2N cisoid to carbonyl oxygen atom); 27.6 ($(CH_3)_3C$), and ring C(3) or C(6)); 28.5 (CH_2CH_2N transoid to carbonyl oxygen atom); 29.3–29.5 ($NCH_2CH_2CH_2$—$(CH_2)_6CH_2CH_2COO$ and ring C(6) or C(3)); 32.5 (C—$(CH_3)_3$); 33.2 (CH_3N cisoid to carbonyl oxygen atom); 34.4 (CH_2COO and CH_3N transoid to carbonyl oxygen atom); 46.6 (ring C(4)); 48.0 and 49.3 (CH_2N cisoid respectively transoid to carbonyl oxygen atom); 60.1 (CH_2O—CO); 67.3, 67.7, 69.5 and 70.0 (OCH_2CO); 74.6 (ring C(1)); 81.5 (ring C(2)); 169.3 and 169.7 (CO—N); 173.8 (COO). – MS.: M^+ 766 (22), 751 (4), 721 (28), 679 (4), 482 (4), 470 (18), 468 (29), 452 (19), 394 (49), 314 (100), 298 (44), 284 (15), 270 (70), 256 (24), 227 (5), 213 (10).

$C_{44}H_{82}N_2O_8$ (767.17) Calc. C 68.89 H 10.77 N 3.65% Found C 69.15 H 11.05 N 3.70%

The chemical shifts of the OCH protons and ring C(4) and C(5) carbon atoms indicate that this compound has a 1,2-*cis*-2,4-*cis*-configuration (see also Table 3).

1,2-Phenylendioxydiacetonitrile (83%) was prepared by procedure F from catechol and chloracetonitrile: m.p.: 81–84° ([24]: m.p.: 85–86°). – IR. (KBr): 2250. – ^{1}H-NMR. ($CDCl_3$): 4.6 (*s*, 4, CH_2); 6.9 (*s*, 4, aryl). – MS.: M^+ 188 (81), 148 (100), 121 (35), 120 (19), 108 (20), 93 (37), 80 (68), 65 (19), 52 (35).

Table 3. *Estimation of the chemical shifts of the ring carbon atoms for 1,2-cis-2,4-trans- and 1,2-cis-2,4-cis-4-t-butyl-N,N,N,N-tetrapropyl-1,2-cyclohexanedioxydiacetamide*

Ring carbon atom	Estimated chemical shifts [ppm] for the		Assignment of observed chemical shifts
	1,2-*cis*-2,4-*trans*-compound	1,2-*cis*-2,4-*cis*-compound	
1	77.6	74.6	74.7
2	75.2	78.2	81.5
3	32.3	29.8	27.6 or 28.8
4	41.4	48.0	46.7
5	26.1	21.9	20.6
6	29.8	30.6	28.8 or 27.6

By hydrolysis of this dinitrile by procedure G *1,2-phenylendioxydiacetic acid* (90%) was obtained: m.p.: 175–178°, ([30]: m.p.: 177–178°). Recrystallization from diluted HCl gave m.p.: 180–181°. – ^{1}H-NMR. (DMSO-d_6): 4.5 (*s*, 4, CH_2); 6.7 (*s*, 4, aryl).

1,2-Phenylendioxydiacetyl dichloride (93%): a mixture of the above diacid and $SOCl_2$ was heated at reflux (85°) for 1 h with stirring. Most of the $SOCl_2$ was then distilled and the residue was crystallized from ether/petrolether in two fractions to give 1,2-phenylenedioxydiacetyl dichloride: m.p.: 47–50° ([31]: m.p.: 49–50°). – IR. (nujol): 1800. – ^{1}H-NMR. ($CDCl_3$): 5.0 (*s*, 4, CH_2); 7.0 (*s*, 4, aryl).

N,N,N,N-Tetrapropyl-1,2-phenylenedioxydiacetamide (**7 A**, 97%) obtained by procedure E: m.p.: 57.5–60° after distillation at bath temperature of 165°/0.05 Torr. – IR. (neat): 1640. – ^{1}H-NMR. (CCl_4): 0.9 (*t*, 12, CH_3); 1.2–2.0 (*m*, 8, CH_2CH_3); 3.1–3.5 (*m*, 8, CH_2N); 4.6 (*s*, 4, OCH_2CO); 6.9 (*s*, 4, aryl). – MS.: M^+ 392 (1), 292 (2), 262 (62), 250 (23), 222 (2), 142 (92), 128 (17), 100 (100), 72 (23). – UV.: 272 (1870).

$C_{22}H_{36}N_2O_4$ (392.55) Calc. C 67.32 H 9.24 N 7.14% Found C 67.40 H 9.28 N 6.87%

N,N'-Di[(11-ethoxycarbonyl)undecyl]-N,N'-dimethyl-1,2-phenylenedioxydiacetamide (**7 B**, 96%) was obtained by procedure E: TLC. (solvent A): Rf 0.35. – IR. (neat): 1650, 1720. – ^{1}H-NMR. ($CDCl_3$): 1.1–1.4 (*m*, 42, CH_3CH_2 and $(CH_2)_9$); 2.2 (*m*, 4, CH_2CO); 2.8 and 3.0 (2 *s*, 6, CH_3N); 3.3 (*m*, 4, CH_2N); 4.5 (*q*, 4, CH_2CH_3); 4.6 (*s*, 4, OCH_2CO); 6.9 (*s*, 4, aryl). – MS.: M^+ 704 (15), 659 (40), 631 (4), 617 (10), 420 (100), 406 (10), 390 (8), 298 (78), 284 (36), 270 (29), 256 (81), 227 (4), 213 (25), 199 (9), 185 (5), 171 (7), 157 (7), 143 (22), 129 (14), 115 (21), 101 (14), 87 (62). – UV.: 273 (1720).

3-Methoxy-1,2-phenylenedioxydiacetonitrile (81%) obtained from 3-methoxycatechol by procedure F: m.p.: 69–70. – IR. (nujol): 2250. – ^{1}H-NMR. ($CDCl_3$): 3.9 (*s*, 3, CH_3O); 4.7 and 4.8 (2 *s*, 4, CH_2); 6.9 (*m*, 3, aryl).

$C_{11}H_{10}N_2O_3$ (218.22) Calc. C 60.55 H 4.62 N 12.84% Found C 60.54 H 4.62 N 12.73%

3-Methoxy-1,2-phenylenedioxydiacetic acid (85%) was prepared by procedure G: m.p.: 142–145°. – IR. (nujol): 1770, 1740, 1710. – ^{1}H-NMR. (DMSO-d_6): 3.8 (*s*, 3, CH_3O); 4.5 and 4.7 (2 *s*, 4, CH_2); 6.9 (*m*, 3, aryl).

3-Methoxy-1,2-phenylendioxydiacetyl dichloride (98% crude yield) was obtained from the above diacid and $SOCl_2$ (30 min reflux). – IR. (neat): 1800. – ^{1}H-NMR. ($CDCl_3$): 3.8 (*s*, 3, CH_3O); 4.95 and 5.0 (2 *s*, 4, OCH_2CO), 6.5–7.2 (*m*, 3, aryl).

3-Methoxy-N,N,N,N-tetrapropyl-1,2-phenylendioxydiacetamide (**8 A**, 91%) was obtained as a liquid by procedure E: TLC. (solvent B): Rf 0.6. – IR. (neat): 1640. – ^{1}H-NMR. (CCl_4): 0.9 (*t*, 12, CH_3CH_2); 1.5 (*m*, 8, CH_2CH_3); 3.3 (*m*, 8, CH_2N); 3.8 (*s*, 3, CH_3O); 4.45 and 4.6 (2 *s*, 4, OCH_2CO); 6.6 (*m*, 3, aryl). – MS.: M^+ 422 (16), 421 (2), 407 (1), 393 (1), 294 (77), 280 (2), 252 (2), 142 (90), 128 (13), 100 (100).

N,N'-Di[(11-ethoxycarbonyl)undecyl]-N,N'-dimethyl-3-methoxy-1,2-phenylendioxydiacetamide (**8B**, 94%) was prepared from the above acid chloride and ethyl 12-methylamino-laurat hydrochloride by procedure E: TLC.: (solvent B): Rf 0.5. – IR. (KBr): 1640, 1730. – ^{1}H-NMR. ($CDCl_3$): 1.1–2.0 (*m*, 42, $-(CH_2)-_9$ and CH_3CH_2); 2.2 (*t*, 4, CH_2CO); 2.9 (2 *s*, 6, CH_3N); 3.2 (*m*, 4, CH_2N); 3.8 (*s*, 3, CH_3O); 4.0 (*q*, 4, CH_2CH_3); 4.5 and 4.65 (2 *s*, 4, OCH_2CO); 6.6 (*m*, 3, aryl). – MS.: M^+ 734

(11), 705 (5), 689 (17), 507 (11), 450 (100), 436 (13), 298 (36), 284 (17), 261 (30), 256 (40), 227 (14), 213 (35), 171 (19), 115 (21), 87 (53).

2,3-Naphthalenedioxydiacetonitrile (79%) was obtained as needles from 2,3-naphthalenediol by procedure F: m.p.: 115–117°. – IR. (nujol): 2250. – ^{1}H-NMR. ($CDCl_3$): 4.9 (*s*, 4, OCH_2CO); 7.3–7.85 (*m*, 6, aryl). – MS.: M^+ 238 (67), 198 (49), 170 (14), 152 (5), 143 (36), 130 (56), 115 (54), 102 (100).

$C_{14}H_{10}N_2O_2$ (238.25) Calc. C 70.57 H 4.23 N 11.76% Found C 70.29 H 4.17 N 12.02%

The hydrolysis of this dinitrile by procedure G gave *2,3-naphthalenedioxydiacetic acid* (85%): m.p.: 250° (contains some monopotassium salt). – IR. (nujol): 1700 (br.).

2,3-Naphthalenedioxydiacetyl dichloride (70%) was prepared from the above diacid and $SOCl_2$ by procedure C: m.p.: 119–125°. – IR. (nujol): 1790. – ^{1}H-NMR. ($CDCl_3$): 5.1 (*s*, 4, OCH_2CO); 7.0–7.9 (*m*, 6, aryl).

N,N,N,N-Tetrapropyl-2,3-naphthalenedioxydiacetamide (**9A**, 47%) was obtained as an off-white solid by procedure E: m.p.: 108.5–111.5°. – IR. ($CHCl_3$): 1645. – ^{1}H-NMR. (CCl_4): 0.9 (*t*, 12, CH_3CH_2); 1.5 (*m*, 8, CH_2CH_3); 3.2 (*t*, 8, CH_2N); 4.6 (*s*, 4, OCH_2CO); 6.9–7.8 (*m*, 6, aryl). – MS.: M^+ 442 (17), 441 (1), 413 (1), 342 (3), 314 (87), 300 (16), 284 (5), 272 (2), 172 (16), 142 (67), 128 (17), 114 (30), 100 (100), 72 (37).

$C_{26}H_{38}N_2O_4$ (442.61) Calc. C 70.56 H 8.65 N 6.32% Found C 70.49 H 8.77 N 6.27%

N,N'-Di-[(11-ethoxycarbonyl)undecyl]-N,N'-dimethyl-2,3-naphthalenedioxydiacetamide (**9B**, 100% crude yield) was prepared from the above acid chloride and ethyl 12-methylamino-laurat by procedure E. Chromatography on silica gel (solvent B) gave a clear liquid (79%). TLC. (solvent A): Rf 0.46. – IR (neat): 1730, 1650. – ^{1}H-NMR. (CCl_4): 0.8–1.9 (*m*, 42, CH_3CH_2, $(CH_2)_9$); 2.2 (*t*, 4, CH_2CO); 2.85 and 2.95 (2 *s*, 6, CH_3N); 3.2 (*m*, 4, CH_2N); 4.0 (*q*, 4, CH_2CH_3); 4.7 (*s*, 4, OCH_2CO); 7.0–7.7 (*m*, 6, aryl). – MS.: M^+ 754 (2), 709 (2), 541 (4), 498 (4), 470 (25), 456 (8), 386 (15), 298 (19), 270 (25), 256 (35), 213 (42), 199 (21), 185 (29), 171 (21), 157 (10), 143 (21), 129 (23), 115 (42), 101 (38), 87 (100).

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170. Comments on the Interpretation of NMR. Parameters in Some Platinum-Olefin Complexes

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(12. VI. 75)

Summary. ^{13}C- and ^{195}Pt-NMR. parameters for the complexes *trans*-[$PtCl_2(C_5H_{10}N)(CH_3CH{=}CHCH_3)$] are presented. It is suggested that conclusions, concerning metal olefin bond strengths, drawn from NMR. studies of nuclei not directly involved in the bonding can be misleading.

Although the *Chatt-Dewar* model explaining the nature of olefin bonding in square planar complexes of Pt(II) is widely accepted [1], the more subtle aspects of this type of bond are still the subject of numerous investigations mainly by NMR. spectroscopy [2]. Although this theory predicts an energy minimum when the plane of the olefin π-system is perpendicular to the plane defined by the metal and the remaining ligand atoms, X-ray studies have shown that distortions from perpendicularity may exist [3] and attempts have been made to correlate such distortions to changes in NMR. parameters [2]. For Pt(II) complexes of the type [$PtCl_2X(RCH{=}CH_2)$], X = Cl [2a], pyridine-N-oxide [2b], pyridine [2c] it is known that the values ^2J(Pt, H) may vary in magnitude by 15–25 Hz [2]. The factors inducing these differences are not completely understood although explanations stemming from structural distortions and/or differing metal-carbon bond strengths for the CH and CH_2 have been offerred [2].