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ADAMANTANE AND ITS DERIVATIVES

XVI. THE GAS CHROMATOGRAPHIC CHARACTERIZATION OF ADAMANTANE DERIVATIVES

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SUMMARY

The KOVÁTS indices of 85 adamantane compounds, including hydrocarbons, hydroxy derivatives, ketones, halogen derivatives and esters, were determined. The elution data were obtained by means of capillary columns with a polar and a non-polar stationary phase. Besides ΔI values, so-called H values were also calculated: the latter were investigated with regard to the structure of the compounds involved. From all these data, increments and rules were derived, permitting at least an estimate of the values of the elution indices of unknown adamantane compounds.

INTRODUCTION

Adamantane chemistry has developed rapidly in recent years. The number of synthesized adamantane compounds has now reached several hundred. Gas chromatography can be used with advantage to determine the composition of the reaction mixtures, to study the course of the reactions and to ascertain the reaction products, provided of course that standards are available or that the elution data of the respective compounds are known. Very few data have so far been published in the literature in respect of elution times of adamantane compounds[1,2].

At present, the tabulation of chromatographic data in the form of KOVÁTS indices is considered to be one of the most suitable means of characterising the chromatographic behaviour of chemical compounds[3]. Besides a simple arrangement of the elution data, this method also has the advantage of allowing certain functional relationships to be derived from the accumulated data with the possibility of forecasting either the elution values of compounds from their structural formulas or judging the possible structure of an unknown compound from the known elution data. We assumed that this potentiality will be specially marked in the case of adamantane and its derivatives because adamantane is a perfectly symmetrical hydrocarbon with a practically rigid skeleton. It would therefore be expected that the contributions of the functional groups would not be influenced by the hydrocarbon proper to any substantial degree.

The relationships between the structure and retention indices of adamantane hydrocarbons will be published separately[4].

In the present communication the chromatographic elution characteristics of adamantane derivatives, in the main, are described. The KOVÁTS indices were measured for 85 adamantane compounds of different types (hydrocarbons, ketones, halogen derivatives, hydroxy derivatives and esters). Bearing the various types of compound in mind, the silicone elastomer SE-30 was chosen as the nonpolar stationary phase and Carbowax-20M as the polar phase. The stability of the phase at elevated temperatures was likewise a decisive factor in the selection of the phases. Although the set of substances measured was not intentionally selected from gas chromatographic aspects, and it consists only of substances which were prepared in the authors' laboratory for other reasons, some relationships which are in part known from other studies could be derived from the data obtained[5–9]; some of these relationships apply specifically to adamantane compounds.

EXPERIMENTAL

Elution data were measured with the CHROM III instrument (Laboratorní přístroje, Prague), fitted with a flame ionisation detector. The carrier gas was nitrogen. The temperature in the thermostat was kept constant to ± 0.2°. The capillaries employed were of stainless steel, inside diameter 0.25 to 0.30 mm, 50 m long. One of the capillaries was coated with the silicone phase SE-30 (5% solution in benzene) by the conventional technique. The other was coated with Carbowax 20M by the method described by METCALFE AND MARTIN[10] (0.05% trioctadecyl methylammonium bromide solution in chloroform, 7% Carbowax 20M solution in benzene).

The KOVÁTS indices were measured with the SE-30 phase at 145, 160, 175 and 190° and with the Carbowax 20M at 145, 160 and 175°. Samples measured included several adamantane compounds together with the respective *n*-paraffins. For the calculations, elution distances were used; this was measured from the point of emergence of methane which was injected before each new sample. Elution distances were measured with a precision of ± 0.1 mm. The I values were calculated for each sample and their average taken. The number of determinations varied between 3–5. For the majority of the determinations the I values differed by 2 to 3 units. In the cases where the difference was greater, the extreme values were eliminated. The average value was rounded-off to whole units. Non-rounded KOVÁTS index values

TABLE I

THE KOVÁTS INDICES OF ADAMANTANE COMPOUNDS ON SE-30 AND CARBOWAX 20 M

Compound	*SE-30*					*Carbowax-20 M*			
	I				*δI/10°*	*I*			*δI/10°*
	145	*160*	*175*	*190*		*145*	*160*	*175*	
Adamantane	1118	1132	1143	1153	7.8	1320	1339	1363	14.4
1-Methyladamantane	1137	1151	1162	1171	7.6	1313	1325	1348	11.8
1-Ethyladamantane	1260	1274	1286	1301	9.1	1448	1469	1491	14.4
1-Propyladamantane	1347	1361	1373	1388	9.0	1529	1552	1572	14.2
1-Isopropyladamantane	1358	1374	1386	1401	9.7	1561	1583	1605	14.8
1-Butyladamantane	1443	1457	1469	1479	8.0	1623	1644	1664	13.6
3-(1-Adamantyl)pentane	1539	1552	1568	1581	9.3	1744	1767	1787	14.4

TABLE I *(continued)*

Compound	SE-30					Carbowax 20 M			
	I				*δI/10°*	*I*			*δI/10°*
	145	*160*	*175*	*190*		*145*	*160*	*175*	
2-Methyladamantane	1196	1209	1224	1234	8.6	1400	1420	1442	14.1
2-Ethyladamantane	1284	1299	1310	1323	8.7	1482	1505	1525	14.2
2-Propyladamantane	1371	1384	1396	1408	8.3	1559	1581	1601	14.1
2-Isopropyladamantane	1349	1360	1374	1386	8.1	1540	1561	1582	14.1
2-Butyladamantane	1465	1478	1489	1499	7.7	1651	1672	1692	13.6
2-Isobutyladamantane	1416	1429	1440	1453	8.3	1581	1604	1623	13.8
1,3-Dimethyladamantane	1151	1163	1174	1184	7.5	1296	1310	1331	11.4
1,2-Dimethyladamantane	1236	1249	1264	1275	8.7	1424	1449	1468	14.6
$1^{e},4^{e}$-Dimethyladamantane*	1205	1216	1230	—	8.4**	1373	1395	1414	13.8
$1^{e},4^{a}$-Dimethyladamantane*	1211	1221	1235	—	7.9**	1382	1404	1423	13.6
2,2-Dimethyladamantane	1269	1281	1296	1309	8.8	1479	1500	1523	14.7
1,3,5-Trimethyladamantane	1163	1173	1185	1194	7.0	1274	1292	1310	12.0
1-Ethyl-3,5-dimethyladamantane	1279	1291	1303	1313	7.6	1406	1421	1441	11.7
2-(1-Adamantyl)propene	1362	1374	1389	1402	8.9	1618	1643	1666	16.0
3-(1-Adamantyl)pentene-2	1559	1571	1587	1600	9.0	1811	1834	1854	14.3
2-Methyleneadamantane	1160	1173	1181	1197	8.2	1388	1407	1429	13.7
2-Ethylideneadamantane	1267	1279	1289	1300	7.4	1487	1508	1526	12.7
2-Propylideneadamantane	1339	1350	1361	1373	7.6	1540	1557	1577	12.2
2-Isopropylideneadamantane	1349	1359	1371	1381	7.1	1554	1574	1593	13.1
2-(2-Adamantyl)propene	1382	1394	1409	1422	8.8	1643	1667	1691	16.0
2-Butylideneadamantane	1432	1444	1454	1466	7.6	1630	1648	1668	12.6
2-Isobutylideneadamantane	1370	1381	1391	1402	7.1	1534	1554	1570	12.0
Spiro[adamantane-2,1′-cyclopropane]	1257	1272	1284	1299	9.4	1477	1502	1525	16.1
2′-Methylspiro[adamantane-2,1′-cyclopropane]	1332	1346	1358	1373	9.0	1542	1567	1588	15.4
Adamantanone	1320	1344	1357	1370	11.1	1867	1895	1918	17.0
Methyl-(1-adamantyl) ketone	1443	1463	1476	1491	10.7	1939	1964	1995	18.4
Ethyl-(1-adamantyl) ketone	1529	1547	1560	1574	10.0	—	2022	2047	16.7***
Propyl-(1-adamantyl) ketone	1609	1629	1641	1657	10.6	—	2085	2110	16.4***
Methyl-(2-adamantyl) ketone	1445	1458	1474	1487	9.3	1939	1964	1987	16.1
1-Adamantanol	1268	1292	1301	1313	10.1	1844	1862	1882	12.8
3-Methyl-1-adamantanol	1283	1305	1317	1331	10.7	1827	1845	1863	12.1
3-Ethyl-1-adamantanol	1408	1429	1442	1461	11.9	1969	1988	2008	13.1
3-Propyl-1-adamantanol	1495	1517	1532	1550	12.3	—	2069	2089	13.6***
3-Isopropyl-1-adamantanol	1506	1528	1539	1556	11.1	—	—	2122	—
3-Butyl-1-adamantanol	1595	1613	1626	1641	10.1	—	—	2182	—
3,5-Dimethyl-1-adamantanol	1295	1315	1333	1345	11.1	1807	1824	1840	11.1
3,5,7-Trimethyl-1-adamantanol	1304	1322	1335	1344	9.0	1785	1801	1816	10.3
3-Ethyl-5,7-dimethyl-1-adamantanol	1421	1440	1454	1466	10.0	1909	1932	1948	13.1
2-Adamantanol	1329	1348	1366	1381	11.5	1944	1962	1983	13.1
2-Methyl-2-adamantanol	1348	1366	1381	1394	10.1	1878	1899	1920	14.1
2-Ethyl-2-adamantanol	1446	1464	1478	1496	11.2	1953	1974	1996	14.2
2-Propyl-2-adamantanol	1526	1543	1556	1572	10.4	—	2036	2058	14.6***
2-Butyl-2-adamantanol	1620	1637	1650	1665	10.1	—	—	2143	—
2-Isobutyl-2-adamantanol	1570	1588	1602	1618	10.6	—	2042	2061	12.9***
1-Hydroxymethyladamantane	1402	1423	1436	1455	11.7	—	2053	2072	12.5***
2-Methyl-1-hydroxymethyladamantane	1490	1504	1520	1536	10.2	—	—	2167	—

(continued on p. 210)

TABLE I (*continued*)

Compound	*SE-30*					*Carbowax 20 M*			
	I				$\delta I/10°$	*I*			$\delta I/10°$
	145	*160*	*175*	*190*		*145*	*160*	*175*	
4^{e}-Methyl-1^{e}-hydroxymethyladamantane*	1472	1484	1501	1514	9.5	—	—	2139	—
4^{a}-Methyl-1^{e}-hydroxymethyladamantane*	1482	1495	1512	1524	9.4	—	—	1252	—
3,5-Dimethyl-1-hydroxymethyladamantane	1425	1445	1459	1471	10.3	—	2017	2032	10.1***
2-(1-Adamantyl)-2-propanol	1515	1535	1550	1566	11.5	—	2059	2083	16.1***
5,7-Dimethyl-1,3-adamantanediol	1438	1451	1461	1484	10.3	—	—	—	—
1-Fluoroadamantane	1159	1174	1184	1196	8.3	1512	1534	1557	15.0
2-Fluoroadamantane	1182	1197	1210	1223	9.0	1521	1544	1566	15.1
1-Chloroadamantane	1298	1315	1331	1341	9.5	1689	1713	1741	17.2
2-Chloroadamantane	1342	1361	1376	1392	11.0	1738	1765	1791	18.0
1-Chloromethyladamantane	1404	1423	1440	1455	11.3	1791	1818	1844	17.6
1-Bromoadamantane	1382	1403	1419	1436	11.8	1809	1837	1871	20.4
2-Bromoadamantane	1426	1447	1464	1482	12.3	1861	1891	1922	20.3
1-Bromomethyladamantane	1488	1508	1526	1543	12.2	1916	1941	1971	18.3
3,5-Dimethyl-1-bromoadamantane	1401	1417	1432	1448	10.5	1762	1788	1815	17.4
5,7-Dimethyl-1,3-dibromoadamantane	1606	1627	1642	1660	11.9	—	—	—	—
Esters of adamantane-1-carboxylic acid									
Methyl ester	1449	1465	1474	1486	8.4	1892	1914	1937	15.0
Ethyl ester	1508	1523	1532	1545	8.3	1917	1939	1960	14.4
Propyl ester	1603	1617	1629	1642	8.8	—	2027	2046	12.3***
Isopropyl ester	1532	1546	1557	1568	8.0	1894	1916	1934	13.2
Butyl ester	1699	1714	1723	1737	8.6	—	—	2138	—
Isobutyl ester	1658	1675	1685	1699	9.0	—	2060	2082	15.0***
sec.-Butyl ester	1631	1646	1658	1670	8.6	1994	2015	2036	14.1
tert.-Butyl ester	1556	1571	1582	1595	8.5	1875	1896	1915	13.4
Esters of adamantane-2-carboxylic acid									
Methyl ester	1467	1482	1494	1507	8.9	1921	1944	1965	14.9
Ethyl ester	1529	1542	1555	1566	8.1	1954	1976	1999	15.1
Methyl esters of									
2-Methyladamantane-1-carboxylic acid	1512	1524	1537	1550	8.3	1951	1974	1996	15.0
4^{e}-Methyladamantane-1^{e}-carboxylic acid*	1512	1524	1537	1550	8.3	1951	1974	1996	15.0
4^{a}-Methyladamantane-1^{e}-carboxylic acid*	1525	1538	1551	1563	8.4	1968	1990	2013	15.0
3-Ethyladamantane-1-carboxylic acid	1579	1594	1604	1618	8.8	—	2028	2051	15.7***
3,5-Dimethyladamantane-1-carboxylic acid	1467	1482	1490	1501	7.6	1850	1869	1888	12.7
Dimethylester of 5,7-dimethyladamantane-1,3-dicarboxylic acid	1769	1777	1784	1795	5.7	—	—	—	—

* The symbols a and e denote the axial and equatorial positions, respectively, in respect to that ring of the adamantane skeleton on which the two substituents are bound.

** $\delta I^{145-175°}/10°$.

*** $\delta I^{160-175°}/10°$.

TABLE II

ΔI VALUES AND $\delta\Delta I/10°$ ON SE-30 AND CARBOWAX 20 M (t = 175°)

Compound	$\Delta I_{175°}^{Carbowax\ 20M-SE-30}$	$\delta\Delta I/10°$
Adamantane	223	6.7
1-Methyladamantane	186	4.2
1-Ethyladamantane	205	5.3
1-Propyladamantane	199	5.3
1-Isopropyladamantane	219	5.1
1-Butyladamantane	195	5.7
3-(1-Adamantyl)pentane	220	5.1
2-Methyladamantane	218	5.6
2-Ethyladamantane	215	5.5
2-Propyladamantane	205	5.8
2-Isopropyladamantane	209	5.9
2-Butyladamantane	202	5.9
2-Isobutyladamantane	182	5.5
1,3-Dimethyladamantane	157	4.0
1,2-Dimethyladamantane	204	5.9
$1^e,4^e$-Dimethyladamantane*	184	5.4
$1^e,4^a$-Dimethyladamantane*	188	5.7
2,2-Dimethyladamantane	227	5.9
1,3,5-Trimethyladamantane	125	4.8
1-Ethyl-3,5-dimethyladamantane	139	4.3
2-(1-Adamantyl)propene	277	7.1
3-(1-Adamantyl)pentene-2	286	5.3
2-Methyleneadamantane	248	5.5
2-Ethylideneadamantane	236	5.4
2-Propylideneadamantane	216	4.6
2-Isopropylideneadamantane	222	6.0
2-(2-Adamantyl)propene	282	7.2
2-Butylideneadamantane	213	5.1
2-Isobutylideneadamantane	179	4.9
Spiro[adamantane-2,1'-cyclopropane]	241	6.7
2'-Methylspiro[adamantane-2,1'-cyclopropane]	231	6.5
Adamantanone	561	5.9
Methyl-(1-adamantyl) ketone	519	7.8
Ethyl-(1-adamantyl) ketone	487	6.6
Propyl-(1-adamantyl) ketone	468	5.7
Methyl-(2-adamantyl) ketone	513	6.8
1-Adamantanol	581	2.9
3-Methyl-1-adamantanol	546	1.4
3-Ethyl-1-adamantanol	566	1.2
3-Propyl-1-adamantanol	558	1.3
3-Isopropyl-1-adamantanol	583	—
3-Butyl-1-adamantanol	556	—
3,5-Dimethyl-1-adamantanol	508	0.0
3,5,7-Trimethyl-1-adamantanol	481	1.3
3-Ethyl-5,7-dimethyl-1-adamantanol	482	3.1
2-Adamantanol	617	1.6
2-Methyl-2-adamantanol	539	4.0
2-Ethyl-2-adamantanol	518	2.9
2-Propyl-2-adamantanol	502	4.2
2-Butyl-2-adamantanol	494	—
2-Isobutyl-2-adamantanol	459	2.3
1-Hydroxymethyladamantane	636	0.8
2-Methyl-1-hydroxymethyladamantane	632	—

(continued on p. 212)

TABLE II (*continued*)

Compound	$\Delta I^{Carbowax\ 20\ M-SE\text{-}30}_{175°}$	$\delta\Delta I/10°$
4^e-Methyl-1^e-hydroxymethyladamantane*	624	—
4^a-Methyl-1^e-hydroxymethyladamantane*	628	—
3,5-Dimethyl-1-hydroxymethyladamantane	573	−0.2
2-(1-Adamantyl)-2-propanol	533	4.6
1-Fluoroadamantane	373	6.7
2-Fluoroadamantane	356	6.1
1-Chloroadamantane	409	7.7
2-Chloroadamantane	416	6.9
1-Chloromethyladamantane	404	6.3
1-Bromoadamantane	452	8.6
2-Bromoadamantane	440	8.0
1-Bromomethyladamantane	445	6.2
3,5-Dimethyl-1-bromoadamantane	383	6.9
Esters of adamantane-1-carboxylic acid		
Methyl ester	462	6.6
Ethyl ester	428	6.1
Propyl ester	417	3.5
Isopropyl ester	377	5.2
Butyl ester	415	—
Isobutyl ester	397	6.0
sec.-Butyl ester	378	5.5
tert.-Butyl ester	333	4.9
Esters of adamantane-2-carboxylic acid		
Methyl ester	471	6.0
Ethyl ester	444	7.0
Methyl esters of		
2-Methyladamantane-1-carboxylic acid	459	6.7
4^e-Methyladamantane-1^e-carboxylic acid*	459	6.7
4^a-Methyladamantane-1^e-carboxylic acid*	462	6.6
3-Ethyladamantane-1-carboxylic acid	448	6.8
3,5-Dimethyladamantane-1-carboxylic acid	397	5.1

* The symbols a and e denote the axial and equatorial positions, respectively, in respeto to that ring of the adamantane skeleton on which the two substituents are bound.

were used to calculate the $\delta I/10°$, $\Delta I^{Carbowax\ 20M\ -\ SE\text{-}30}$ values, and the homomorphic factors H; and only after the results were obtained were these values rounded off.

The measured elution indices, their temperature increments and the $\Delta I^{Carbowax\ 20M\ -\ SE\text{-}30}_{175°}$ values are given in Tables I and II.

RESULTS AND DISCUSSION

The details concerning the elution characteristics of the saturated adamantane hydrocarbons will not be dealt with here as they are reported in a different study[4], and the published relationships applying to squalan (or Apiezon L) tetrakis-o-(2-cyanoethyl)-pentaerythrite also apply to the combination SE-30–Carbowax 20M. The two only differ in the specific values of the different quantities.

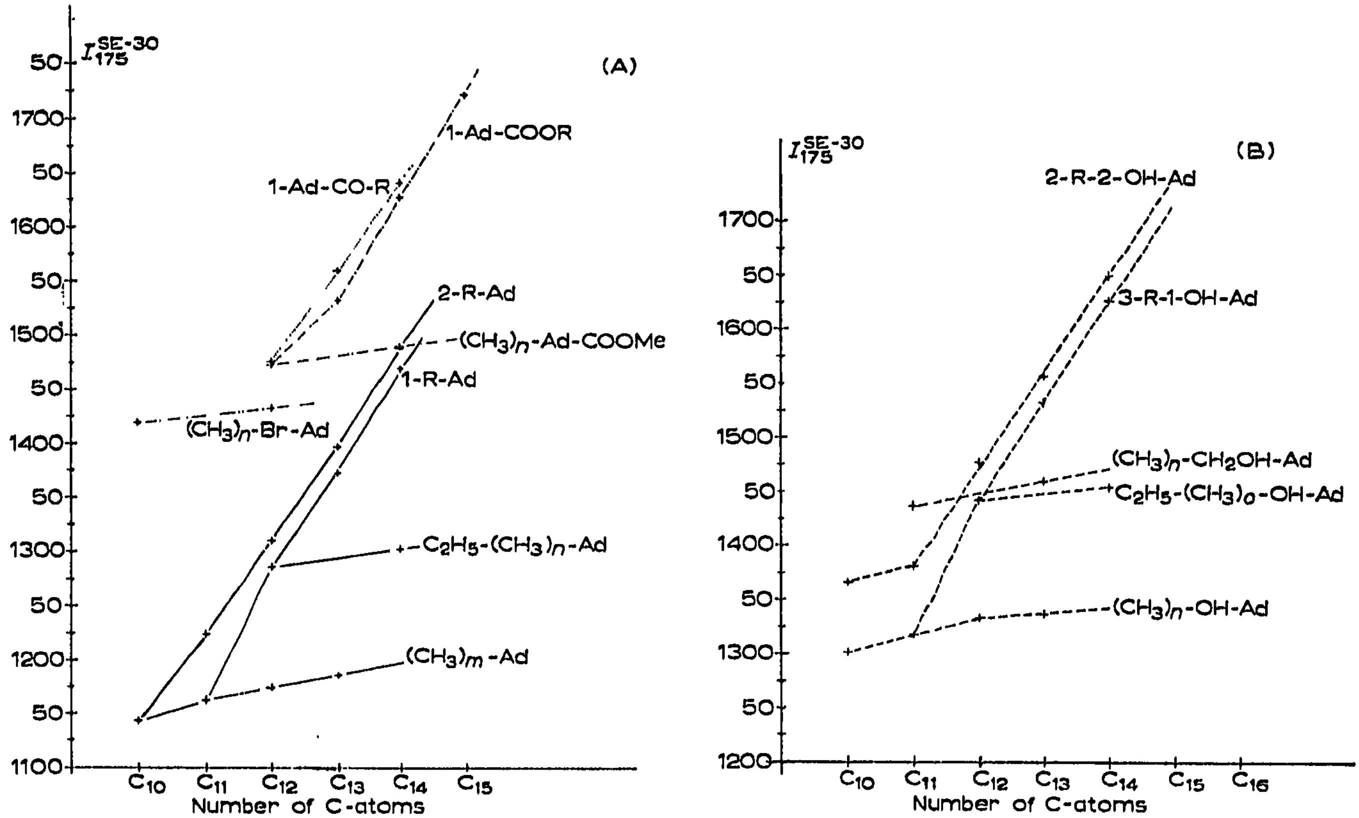

Fig. 1. Dependence of the magnitude of the retention indices on the number of C-atoms in homologous series (SE-30, $t = 175°$). R = n-alkyl-, Ad = adamantyl-. $m\ \varepsilon < 0.4 >$; $n\ \varepsilon < 0.3 >$; $o\ \varepsilon < 0.2 >$. Hydrocarbons ———; ketones · · · · ·; hydroxy derivatives— — — —; halogen derivatives —· ·—· ·; esters —·—·—.

Increments in homologous series

The following homologous series could be distinguished on SE-30 as well as on Carbowax 20M: 2-n-alkyladamantanes (+ adamantane); 1-n-alkyladamantanes; 3-n-alkyladamantanols-1; 2-n-alkyladamantanols-2; n-alkyl-1-adamantyl ketones; n-alkyl esters of adamantane carboxylic-1 acid; and, probably, adamantane carboxylic-2 acid as well (see Figs. 1 and 2). The homologous increment is 80 to 90 units starting with the second member of the series. 2-Alkylideneadamantanes do not form a simple homologous series in chromatographic terms.

In addition, other series are also seen, their homologous increment is, however, considerably less[4]. They are: 1-methyladamantane to 1,3,5-trimethyladamantane; 1-ethyl to 1,3-dimethyl-5-ethyladamantane; adamantanol-1 to 3,5,7-trimethyladamantanol-1; 3-ethyladamantanol-1 to 3,5-dimethyl-7-ethyladamantanol-1; hydroxymethyladamantanes, bromoadamantanes and adamantane carboxylic-1 acid methyl esters, all substituents of which are bound to bridgehead carbon atoms of the adamantane skeleton. The increment for the methyl group is a positive value with SE-30 (Table III). Its value decreases with the increasing number of substituents. On Carbowax 20M this increment is negative and its absolute value, by comparison, rises with the rising number of substituents. The negative value of this increment on the polar phase may be explained by the fact that hydrogen atoms on bridgehead carbon atoms of the adamantane skeleton are polarised to a high degree. When such

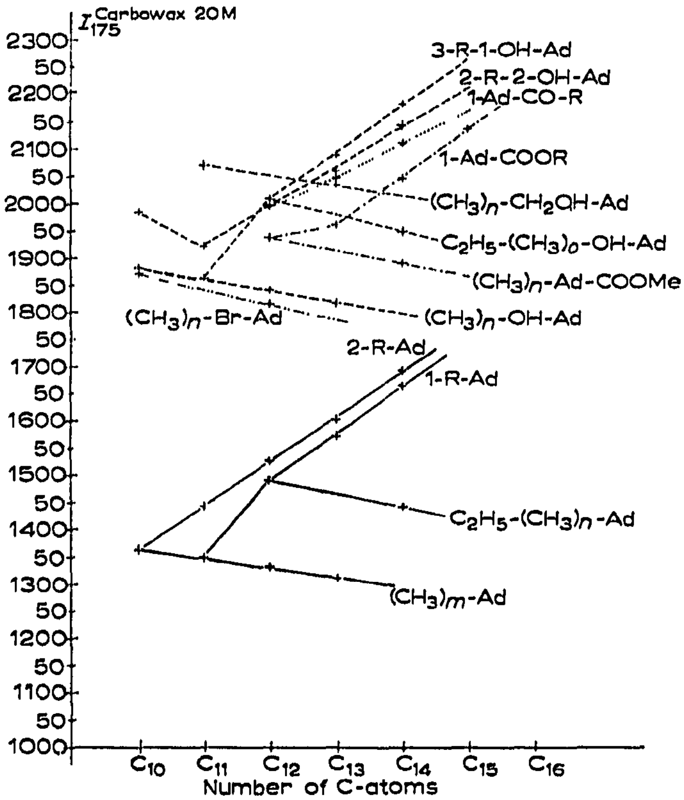

Fig. 2. Dependence of the magnitude of the retention indices on the number of C-atoms in homologous series (Carbowax 20 M, $t = 175°$). R = *n*-alkyl-, Ad = adamantyl-. m ε < 0.4 >; n ε < 0.3 >; o ε < 0.2 >. Hydrocarbons ———; ketones · · · · ·; hydroxy derivatives — — — —; halogen derivatives —· ·—· ·; esters —·—·—.

a hydrogen atom is replaced by a non-polar methyl group, the polarity of the compound decreases and the elution time decreases likewise[4].

Relationship between some derived quantities and the structure of the compound

Temperature coefficient. The temperature coefficient $\delta I/10°$ is higher with all compounds on the polar compared to the non-polar phase. Its magnitude depends

TABLE III

HOMOLOGOUS INCREMENTS OF KOVÁTS INDICES FOR CH_3 GROUP

Compound	*$\Delta I/CH_3$ (175°)* SE-30	Carbowax 20 M
1-Methyladamantane — adamantane	+19	−15
1,3-Dimethyladamantane — adamantane	+15	−16
1,3,5-Trimethyladamantane — adamantane	+14	−18
3-Methyl-1-adamantanol — 1-adamantanol	+16	−19
3,5-Dimethyl-1-adamantanol — 1-adamantanol	+16	−21
3,5,7-Trimethyl-1-adamantanol — 1-adamantanol	+11	−22
1-Ethyl-3,5-dimethyladamantane — 1-ethyladamantane	+ 8	−25
3-Ethyl-5,7-dimethyl-1-adamantanol — 3-ethyl-1-adamantanol	+ 6	−30
3,5-Dimethyl-1-bromoadamantane — 1-bromoadamantane	+ 7	−28
3,5-Dimethyladamantane-1-carboxylic acid methyl ester — adamantane-1-carboxylic acid methyl ester	+ 8	−24
3,5-Dimethyl-1-hydroxymethyladamantane — 1-hydroxymethyladamantane	+12	−20

on the type of substituent (it is greatest with halogen derivatives on both phases). The number and position of substituents has no major influence on the $\delta I^{SE\text{-}30}/10°$ value. A greater influence was observed with the $\delta I^{Carbowax\ 20M}/10°$ value.

The difference in the KOVÁTS *indices on the polar and non-polar phases.* ($\Delta I^{Carbowax\ 20M\ -\ SE\text{-}30}_{170°}$, is denoted as ΔI in the following). This quantity reflects two main factors: the functional group (its type and position), and the number of substituents.

With 1-*n*-alkyladamantanes the value of this quantity is 190 to 200 units. With 2-*n*-alkyladamantanes, it is 200 to 220 units. Branching in the side chain may change this value by $\pm$ 20 units. Further substitution on the secondary carbon atom increases this value only slightly. In contrast, substitution on the bridgehead carbon atom decreases this value considerably. For example, 1,3-disubstituted hydrocarbons have ΔI values 30 to 40 units lower, and 1,3,5-trisubstituted ones 50 to 60 units lower compared to monosubstituted compounds. This decrease is perceptible with all types of compounds measured. The mean value is -34 units per one methyl group.

The ΔI value decreases somewhat in the homologous series with the rising number of carbon atoms (this does not apply solely to hydrocarbons). 2-*n*-Alkylideneadamantanes have ΔI values of about 210 to 250 units, with alkenyladamantanes this value is 275 to 285 units. Spiro-adamantane-cyclopropanes have about the same ΔI value as 2-alkylideneadamantanes. The magnitude of the ΔI values of *n*-alkyl-1-adamantantyl ketones varies from 470 to 520 units. This quantity is very suitable for elucidating the position of the hydroxyl group. Its magnitude rises in the series: *tert.*-OH $<$ *sec.*-OH $<$ *prim.*-OH (585, 617, 630 units, respectively). In the series of

TABLE IV

HOMOMORPHIC FACTORS (H) OF ADAMANTANOLS

Compound	$H = I_{ROH} - I_{RH}$	
	SE-30	*Carbowax 20 M*
1-Adamantanol	158	519
3-Methyl-1-adamantanol	155	515
3-Ethyl-1-adamantanol	156	517
3-Propyl-1-adamantanol	159	517
3-Isopropyl-1-adamantanol	153	517
3-Butyl-1-adamantanol	157	518
3,5-Dimethyl-1-adamantanol	159	509
3,5,7-Trimethyl-1-adamantanol	150	506
3-Ethyl-5,7-dimethyl-1-adamantanol	151	507
2-Adamantanol	223	620
2-Methyl-2-adamantanol	157	478
2-Ethyl-2-adamantanol	168	471
2-Propyl-2-adamantanol	160	466
2-Butyl-2-adamantanol	161	452
2-Isobutyl-2-adamantanol	162	439
1-Hydroxymethyladamantane	274	724
2-Methyl-1-hydroxymethyladamantane	256	700
4^e-Methyl-1^e-hydroxymethyladamantane	271	724
4^a-Methyl-1^e-hydroxymethyladamantane	277	729
3,5-Dimethyl-1-hydroxymethyladamantane	274	722
2-(1-Adamantyl)-2-propanol	164	478

TABLE V

HOMOMORPHIC FACTORS (H) OF ADAMANTYL KETONES

Compound	$H_{175}{}^{\circ} = I_{AdCOR} - I_{AdCH_2R}$	
	SE-30	*Carbowax 20 M*
Methyl-(1-adamantyl) ketone	190	503
Ethyl-(1-adamantyl) ketone	187	475
n-Propyl-(1-adamantyl) ketone	173	446
Methyl-(2-adamantyl) ketone	164	463

adamantanols-1 substituted on the bridgehead carbon atom, the ΔI value decreases with the number of substituents: 3-alkyladamantanols 550–560 units; 3,5-dialkyladamantanols 510 units; and 3,5,7-trialkyladamantanols 480 units.

In the case of halogen derivatives, the ΔI values rise with the increasing atomic weight of the halide. They also depend on the position of the halide. The dependency of the ΔI value of alkylated halogen derivatives on the number of alkyl groups is similar in this case to that of hydrocarbons and hydroxy derivatives.

The magnitude of the ΔI values of adamantane carboxylic acid esters depends on the position of the carboxylic group and the number of alkyl groups on the adamantane skeleton, similarly to the preceding cases. Here again, substitution on the secondary carbon atom has no marked influence on the ΔI value. The ΔI value

TABLE VI

HOMOMORPHIC FACTORS (H) OF ADAMANTANE CARBOXYLIC ACIDS METHYL ESTERS

Methyl ester	$H_{175}{}^{\circ} = I_{RCOOMe} - I_{RH}$	
	SE-30	*Carbowax 20 M*
Adamantane-1-carboxylic acid	331	574
Adamantane-2-carboxylic acid	351	602
2-Methyladamantane-1-carboxylic acid	313	554
4^{e}-Methyladamantane-1^{e}-carboxylic acid	313	554
4^{a}-Methyladamantane-1^{e}-carboxylic acid	327	571
3-Ethyladamantane-1-carboxylic acid	318	560
3,5-Dimethyladamantane-1-carboxylic acid	317	550

permits esters of primary, secondary or tertiary alcohols to be distinguished with adamantane carboxylic-1 acid esters.

The homomorphic factor H. It was found, that with different types of compounds, it is advantageous to define different homomorphic factors[8,9]. *E.g.*, with alcohols, the homomorphic factor $H = I_{ROH} - I_{RH}$, where R = adamantyl or the respective alkyladamantyl. The quantity thus defined (Table IV) enables us, in the case of the SE-30 phase, to find out whether a primary, secondary or tertiary alcohol is involved. With Carbowax 20M there is moreover the possibility of estimating from the value of this quantity, whether a 2-alkyladamantanol-2 or an adamantanol-1 substituted

TABLE VII

HOMOMORPHIC FACTORS (H) OF ADAMANTANE CARBOXYLIC-1 ACID ALKYL ESTERS

Ester of adamantane-1-carboxylic acid	$H_{175°} = I_{AdCOOC_nH_{2n+1}} - I_{n\text{-alkane } C_{n+11}}$	
	SE-30	*Carbowax 20 M*
Methyl ester	274	737
Ethyl ester	232	659
Propyl ester	229	646
Butyl ester	223	638
Isopropyl ester	157	534
sec.-Butyl ester	158	536
tert.-Butyl ester	82	415

on the bridgehead carbon atom is involved or whether the hydroxy group is bound to the tertiary carbon atom in the side chain.

With ketones, it is advantageous to define the homomorphic factor $H = I_{AdCOR} - I_{AdCH_2R}$ (Table V).

Similarly, with methyl esters of adamantane carboxylic acids, the homomorphic factor is suitably defined as $H = I_{RCOOMe} - I_{RH}$ (Table VI). From the value of this factor it may be judged whether the carboxyl group is bound to the bridgehead carbon atom or to a secondary carbon atom.

When the homomorphic factor $H = I_{AdCOO-C_nH_{2n+1}} - I_{n\text{-alkane } C_{n+11}}$ is defined in the case of adamantane carboxylic-1 acid alkyl esters (Table VII), we may judge from its value (similarly to the case of ΔI values), whether an ester of a primary, secondary or tertiary alcohol is involved.

The difference between 1- and 2-monosubstituted derivatives is not a particularly characteristic quantity (Table VIII). Much depends in this case on the type of

TABLE VIII

HOMOMORPHIC FACTORS (H) OF SOME ADAMANTANE DERIVATIVES IN POSITION 1 AND 2

Compound	$I_{2AdX} - I_{1AdX}$	
	SE-30	*Carbowax 20 M*
Methyladamantane	62	94
Ethyladamantane	24	33
Propyladamantane	23	29
Isopropyladamantane	−12	−22
Butyladamantane	20	28
Adamantylpropene	20	25
Adamantanol	64	101
Fluoroadamantane	27	9
Chloroadamantane	44	51
Bromoadamantane	45	51
Adamantane carboxylic acid methyl ester	20	29
Adamantane carboxylic acid ethyl ester	23	39

substituent involved, especially on the degree to which the substituent on the secondary carbon atom screens the vicinal hydrogen atoms on the bridgehead carbon atoms (in the case of hydrocarbons, for example, rather similar values are obtained, *i.e.* 20 units with SE-30 and 28 units with Carbowax 20M).

It is clear from the above discussion that the KOVÁTS indices can only be estimated fairly easily with derivatives substituted on bridgehead carbon atoms. In respect of derivatives substituted on secondary and bridgehead carbon atoms, or only on the secondary ones, the situation is more complicated. The problem of working out rules for deriving elution data from the formulae of the respective compounds is complicated in this case mainly by a lack of other experimental data.

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