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## Chromatographic study of methylcyclopentadiene dimers and iso-dimers and determination of their boiling points

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### SUMMARY

The Kováts retention indices ( $I_R$ ) of a family of mono- and polycycloolefins with one or more endo- or exocyclic double bonds on stationary phases of different polarity are related to their boiling points, molar volume, molar refractivity and first-order molecular connectivity. The boiling points of methylcyclopentadiene dimers and their iso-dimers containing an exocyclic double bond were estimated from the relationships between  $I_R$  (on squalane at 100°C), boiling point and molecular connectivity obtained from a group of cycloolefins selected at random.

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### INTRODUCTION

Close relationships to exist between the chromatographic behaviour of solutes and some of their physico-chemical properties, and in previous papers we have reported empirical relationships for several families of hydrocarbons<sup>1–3</sup>. Recently, Rohrbaugh and Jurs<sup>4</sup> have applied these relationships to the study of linear, branched and cyclic monoolefins. These relationships may be suitable for calculating approximate values of solute properties, such as the boiling point ( $t_b$ )<sup>5,6</sup> and the molar refractivity<sup>2</sup>, although little use of this has been made so far. Nevertheless, the method seems to be interesting when one is dealing with compounds in complex mixtures which can only be resolved by gas chromatography (GC).

Kováts retention indices of a group of cycloolefins including dimethyldicyclopentadiene isomers were determined by GC on capillary columns loaded with stationary phases of polarity ranging between 0 and 1550 (McReynolds' scale<sup>7</sup>), and the relationships between  $I_R$  and  $t_b$ , the molar refractivity, ( $M_R$ ), the molar volume ( $V_M$ ) and the first-order molecular connectivity ( $\chi$ ) were established. Boiling points of methylcyclopentadiene dimers and iso-dimers were estimated from these relationships.

### EXPERIMENTAL

The mixture of methylcyclopentadiene (MCPD) dimer was supplied by Fluka (technical grade). Mixtures containing the iso-dimer compounds (peaks referred to as

numbers 8 and 10) were prepared in the laboratory by reaction with hydrogen chloride at room temperature<sup>8</sup>. Other solutes were supplied by Fluka, Aldrich and Merck.

GC analyses were carried out with Hewlett-Packard 5830 and Perkin-Elmer 8320 gas chromatographs equipped with flame ionization detectors. The capillary columns and operating conditions used are summarized in Table I. Preparative GC was performed on a Perkin-Elmer F 21 gas chromatograph. The commercial mixture of MCPD dimers was fractionated using a series of three stainless-steel U-shaped columns (1 m × 8 mm I.D.) packed with 10% silicone E 301 on Chromosorb P NAW (60–80 mesh). The flow-rate of the carrier gas (nitrogen) was kept at 160 ml min<sup>-1</sup>. Isothermal operation at 100°C was used for the fractionation with injector and detector temperatures of 150°C.

TABLE I  
CAPILLARY COLUMNS AND EXPERIMENTAL CONDITIONS

Parameter	Column					
	1 <sup>a</sup>	2 <sup>b</sup>	3 <sup>b</sup>	4 <sup>b</sup>	5 <sup>a</sup>	6 <sup>b</sup>
Stationary phase	Squalane	OV-101	SE-54	OV-1701	Ucon LB 550X	OV-215
Length (m)	45	25	25	25	50	25
Inside diameter (mm)	0.50	0.23	0.22	0.22	0.25	0.22
Carrier gas (N <sub>2</sub> )	1.30	1.00	1.50	1.00	1.00	0.85
Splitter (ml min <sup>-1</sup> )	1:91	1:150	1:53	1:120	1:92	1:194
Detector and injector temperature (°C)	170 275 <sup>c</sup>	170 275 <sup>c</sup>	170 275 <sup>c</sup>	170 275 <sup>c</sup>	170 275 <sup>c</sup>	170 275 <sup>c</sup>
McReynolds' polarity <sup>d</sup>	0	229	337	789	996	1545
Number of theoretical plates	78 000	95 000	95 000	118 000	76 500	94 000

<sup>a</sup> Stainless-steel capillary columns.

<sup>b</sup> Fused-silica capillary columns.

<sup>c</sup> For determinations of Kováts retention indices the injector and detector temperatures were kept at 275°C.

<sup>d</sup> Ref. 7.

Kováts retention indices of solutes were calculated by the "exact calculated method"<sup>9</sup>, using a mixture of C<sub>5</sub>–C<sub>15</sub> *n*-alkanes as a standard.

The input values of the physico-chemical properties required for the correlation were obtained from different sources<sup>10–14</sup>. The first-order molecular connectivity was calculated from the molecular structure<sup>15,16</sup>. An HP 1000 computer was used for the calculations with a multilinear regression program.

## RESULTS AND DISCUSSION

In order to assess the optimum experimental conditions for the chromatographic separation of the isomers and the accuracy of the separation of all components, the test mixture was run on six stationary phases of different polarity at 80 and 100°C<sup>8</sup>. The same seven chromatographic peaks with a molecular mass of 160 u were always

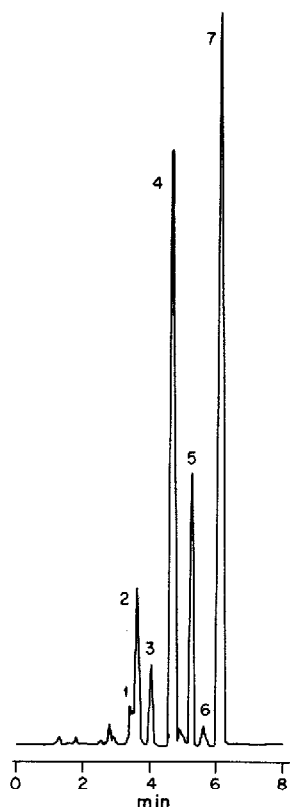


Fig. 1. Chromatogram of a commercial mixture of MCPD dimers on OV-215 at 80°C. The numbered peaks (1-7) belong to isomers of methylcyclopentadiene dimers. Analytical conditions as in Table I.

obtained. The dimers were retained differently by the tested stationary phases without the elution order being altered. Fig. 1, which is a chromatogram of MCPD dimers on OV-215 at 80°C, shows the complete separation of the seven components.

Table II shows the quantitative composition of the mixture obtained from

TABLE II

COMPOSITION (IN AREA %) OF THE COMMERCIAL MIXTURE OF METHYLCYCLOPENTADIENE DIMERS CHROMATOGRAPHED ON DIFFERENT STATIONARY PHASES AT 100°C

For chromatographic conditions see Table I.

Peak No. <sup>a</sup>	<i>Squalane</i>	<i>SE-54</i>	<i>OV-1701</i>	<i>Ucon LB 550X</i>	<i>OV-215</i>
1	2.33	2.42	1.74	1.88	1.72
2	7.09	7.42	8.17	7.08	8.40
3	3.98	4.09	4.06	4.85	4.02
4	28.85	28.73	29.53	28.41	28.27
5	14.97	14.81	13.76	14.98	15.01
6	1.13	1.25	1.29	1.23	1.25
7	41.65	41.30	41.45	41.56	41.33

<sup>a</sup> Peaks numbered relative to Fig. 1.

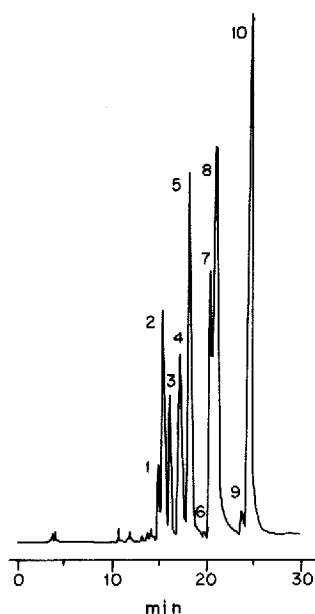
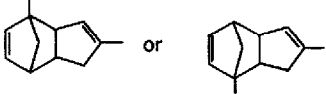
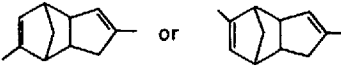
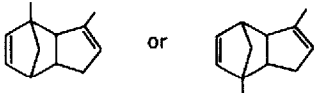
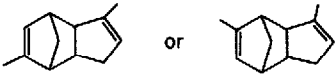
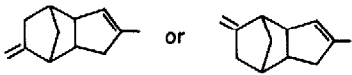
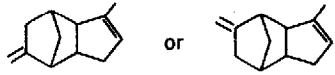


Fig. 2. Chromatogram of a mixture of MCPD dimers and their iso-dimers on squalane at 100°C. Peaks 1–7 as in Fig. 1; 8 and 10, isomers of 4 and 7 (iso-dimers). Analytical conditions as in Table I.

TABLE III

STRUCTURES OF ISOMERS OF METHYLCYCLOPENTADIENE DIMERS CONTAINED IN THE COMMERCIAL MIXTURE AND THEIR ISO-DIMERS

Peak No.	Structure	Nomenclature
2		<i>endo</i> -1,4-(or 4,7)-dimethyltricyclo[5.2.1.0 <sup>2,6</sup> ]deca-3,8-diene
4		<i>endo</i> -4,8-(or 4,9)-dimethyltricyclo[5.2.1.0 <sup>2,6</sup> ]deca-3,8-diene
5		<i>endo</i> -1,3-(or 3,7)-dimethyltricyclo[5.2.1.0 <sup>2,6</sup> ]deca-3,8-diene
7		<i>endo</i> -3,8-(or 3,9)-dimethyltricyclo[5.2.1.0 <sup>2,6</sup> ]deca-3,8-diene
8		<i>endo</i> -4-methyl-8-(or 9)-methylenetricyclo[5.2.1.0 <sup>2,6</sup> ]dec-3-ene
10		<i>endo</i> -3-methyl-8-(or 9)-methylenetricyclo[5.2.1.0 <sup>2,6</sup> ]dec-3-ene

chromatograms on different stationary phases at 100°C. The similarity of the results indicates that only seven isomers of MCPD dimers are present in the mixture, compounds 2, 4, 5 and 7 (see Fig. 1) being the major constituents.

The treatment of the mixture of isomers with an acidic solvent converted compounds 4 and 7 into two new compounds, 8 and 10 (iso-dimers), as shown in Fig. 2. This conversion could be an isomerization because the new compounds have slightly longer retention times than those of the dimers and the same molecular mass (160 u).

By preparative GC, isomer 7 was isolated as well as a mixture of 4 and 5, in which 4 is the main constituent (67%), and the conversion of compounds 4 and 7 into 8 and 10, respectively, was corroborated. The structures of the dimers and iso-dimers (Table III) were established mainly by relating the  $^1\text{H}$  NMR signals of olefinic and methyl hydrogens to the changes caused by the isomerization<sup>8</sup>. The longer retention times of the iso-dimers are in accordance with the formation of a more polar exocyclic double bond.

Some physico-chemical properties of MCPD dimers and iso-dimers can be calculated from their experimental  $I_R$  values by using equations that relate  $I_R$  to these properties<sup>1-6</sup>. These equations were derived from eqn. 1 assuming that the solute vapour pressure,  $P^0$ , at the column temperature is proportional to its boiling point and that some solute physico-chemical (or structural) properties responsible for the solute-stationary phase interactions account for the activity coefficient of the solute in the stationary phase at infinite dilution,  $\gamma^\infty$ .

$$V_g = \frac{273 R}{\gamma^\infty P^0 M_1} \quad (1)$$

where  $V_g$  is the specific retention volume,  $R$  is the gas constant and  $M_1$  is the molecular weight of the stationary phase.

In this way, the following equations were obtained for the calculation of Kováts retention indices:

$$I_R = I_R^0 + pP + qQ + \dots = a + bt_b + pP + qQ + \dots \quad (2)$$

where  $P, Q, \dots$ , represent independent solute parameters which account for the different solute-stationary phase interaction mechanisms, such as dispersion, induction or orientation; the coefficients  $p, q, \dots$  describe the sensitivity of the retention process to the different interaction mechanisms;  $I_R^0$  is the hypothetical retention index of a solute which forms ideal solutions with the phases ( $\gamma^\infty = 1$ ). In such an ideal process, the solute chromatographic retention only depends on its vapour pressure,  $I_R^0$  therefore being proportional to the boiling point. Hence  $P, Q, \dots$ , are solute-independent parameters whereas  $t_b$  account for the chromatographic retention in an ideal process.

The Kováts retention indices of the dimers and iso-dimers on several stationary phases of different polarity at 80 and 100°C are given in Table IV.

In order to calculate the boiling points of these compounds, a large group of cycloolefins with similar structures was used to obtain eqns. 2 by regression analysis. The  $I_R$  values were determined using the same columns and operation conditions as used for MCPD dimers (Table I). The  $I_R$  values obtained are given in Table IV. The physico-chemical and structural properties accountable for the chromatographic



Ethylidene-cyclohexane	861.8	865.9	868.8	873.4	878.0	899.7	899.7	895.6	914.0
5-Vinyl-2-norbornene	864.7	868.6	881.2	886.8	892.7	899.7	899.7	934.7	940.4
<i>cis</i> -5-Ethylidene-2-norbornene*	891.8	895.4	910.1	915.2	922.6	928.4	928.4	948.9	952.6
<i>trans</i> -5-Ethylidene-2-norbornene	900.6	906.5	916.5	920.7	928.5	934.8	934.8	958.0	962.2
<i>exo</i> -Dicyclopentadiene	996.6	1003.3	1006.8	1015.2	1022.4	1032.8	1032.8	1075.5	1086.9
<i>endo</i> -Dicyclopentadiene	1003.3	1005.0	1016.4	1025.3	1032.4	1043.2	1043.2	1082.2	1093.6
Bicyclo[4.3.0]nona-3,6(1)-diene	1031.5	1037.5	1038.8	1046.6	1056.6	1066.4	1066.4	1136.6	1146.6
1,4-(or 4,7-)Dimethyl-DCPD <sup>b</sup>	1079.5	1086.7	1099.3	1107.6	1111.1	1121.4	1121.4	1147.9	1162.0
4,8-(or 4,9-)Dimethyl-DCPD <sup>b</sup>	1100.2	1107.6	1124.5	1133.9	1136.8	1146.4	1146.4	1173.2	1187.0
1,3-(or 3,7-)Dimethyl-DCPD <sup>b</sup>	1108.3	1115.8	1124.5	1133.9	1136.8	1148.5	1148.5	1180.2	1199.5
<i>cis</i> -Cyclodecene*	1111.3	1121.4	1126.5	1122.5	1126.5	1139.1	1139.1	1168.6	1181.3
3,8-(or 3,9-)Dimethyl-DCPD <sup>b</sup>	1130.4	1138.4	1149.6	1159.9	1163.5	1174.0	1174.0	1203.9	1215.5
4-Methyl-8-(or 9-)methylene-DCP <sup>c</sup>	1134.7	1142.0	1156.0	1165.1	1173.5	1183.7	1183.7	1210.7	1222.8
3-Methyl-8-(or 9-)methylene-DCP <sup>c</sup>	1161.6	1169.6	1176.2	1186.3	1176.2	1206.3	1206.3	1236.6	1250.1
<i>trans,cis</i> -1,5,9-cyclododecatriene	1270.4	1283.2	—	1296.7	1303.3	1317.2	1317.2	1365.2	1382.0
$\alpha$ -Cedrene <sup>d,*</sup>	1379.1	1392.3	—	1392.6	1388.5	1403.3	1403.3	1452.5	1471.8

<sup>a</sup> Standards for the simplified calculation of  $t_b$  are marked with asterisks.

<sup>b</sup> DCPD = tricyclo[5.2.1.0<sup>2,6</sup>]deca-3,8-diene.

<sup>c</sup> DCP = tricyclo[5.2.1.0<sup>2,6</sup>]deca-3-ene.

<sup>d</sup> (1*S*, 2*R*, 5*S*)-2,6,6,8-Tetramethyltricyclo[5.3.1.0<sup>1,5</sup>]undeca-8-ene.

TABLE V  
PHYSICO-CHEMICAL PROPERTIES DATA OF STANDARD COMPOUNDS

Compound <sup>a</sup>	$t_b$ (°C)	$n$	$d$ ( $g\ ml^{-1}$ )	$M_R$ ( $ml\ mol^{-1}$ )	$V_M$ ( $ml\ mol^{-1}$ )	$\chi$	Ref.
1,3-Cyclopentadiene	40.0	1.4440	0.8021	21.890	82.409	1.8165	10
Cyclopentene	44.2	1.4225	0.772	22.440	88.250	2.1498	10
Methylenecyclopentane*	75.5	1.4360	0.780	27.538	105.320	2.5607	11
1-Methylcyclopentene	75.8	1.4320	0.778	27.362	105.281	2.5505	12
Cyclohexene	83.0	1.4465	0.8102	27.065	101.395	2.6498	10
2,5-Norbornadiene	89.5	1.4702	0.9064	28.378	101.677	2.8165	10
3-Methylcyclohexene*	104.0	1.4414	0.7990	31.809	120.363	3.0605	10
4-Methylcyclohexene	102.7	1.4414	0.7991	31.805	120.348	3.0437	10
1-Methylcyclohexene	110.0	1.4503	0.8102	31.917	118.699	3.0505	10
Vinylcyclohexane*	128.0	1.4420	0.804	36.266	137.065	3.5581	11, 13
4-Vinylcyclohexene	128.9	1.4639	0.8299	35.963	130.353	3.2079	10
<i>cis</i> -Bicyclo[3.3.0]oct-2-ene	134.0	1.437	0.889	31.600	121.586	3.6330	11
Ethylidenecyclohexane	136.0	1.4618	0.822	36.842	134.063	3.5731	12
<i>cis</i> -5-Ethylidene-2-norbornene*	147.3	1.4895	0.893	38.885	134.602	3.7330	13, 14
<i>endo</i> -Dicyclopentadiene	170.0	1.5120	1.0701	37.070	123.539	4.3000	10, 13
<i>cis</i> -Cyclodecene*	198.0	1.4854	0.873	45.215	157.651	4.6498	10, 12
1,4-(or 4,7-)Dimethyl-DCPD <sup>b</sup>	—	—	—	—	—	5.0563	—
4,8-(or 4,9-)Dimethyl-DCPD <sup>b</sup>	—	—	—	—	—	5.1109	—
1,3-(or 3,7-)Dimethyl-DCPD <sup>b</sup>	—	—	—	—	—	5.0662	—
3,8-(or 3,9-)Dimethyl-DCPD <sup>b</sup>	—	—	—	—	—	5.1210	—
4-Methyl-8-(or 9-)methylene-DCP <sup>c</sup>	—	—	—	—	—	5.1043	—
3-Methyl-8-(or 9-)methylene-DCP <sup>c</sup>	—	—	—	—	—	5.1143	—
<i>trans,cis,cis</i> -1,5,9-Cyclodecatriene	238.0	1.5140	0.907	53.865	178.919	4.9495	11
$\alpha$ -Cedrene <sup>d,*</sup>	262.5	1.5034	0.9342	64.709	218.754	5.8886	10, 12

<sup>a-d</sup> See Table IV.

retention<sup>17</sup> were available from different sources or could be calculated. They are given in Table V.

From the data in Tables IV and V, equations  $I_R = f(t_b)$  were obtained in order to establish the extent of the deviation from the ideal chromatographic process. As

TABLE VI  
EQUATIONS  $I_R = f(t_b)$  FOR DIFFERENT STATIONARY PHASES AT 100°C

$r$  = Correlation coefficient,  $s$  = standard deviation,  $N$  = number of experimental points.

Stationary phase	Equation	$r$	$s$	$N$
Squalane	$I_R = 331.42 + 3.98 t_b$	0.9985	12.0	14
OV-101	$I_R = 344.12 + 3.96 t_b$	0.9986	11.9	15
SE-54	$I_R = 367.81 + 3.89 t_b$	0.9973	17.6	15
OV-1701	$I_R = 371.76 + 3.99 t_b$	0.9982	15.6	9
OV-215	$I_R = 375.27 + 4.09 t_b$	0.9940	26.5	18



TABLE VII

EQUATIONS  $I_R = f(t_b, \theta)$  WHERE  $\theta$  IS  $M_R$ ,  $V_M$  OR  $\chi$ , FOR DIFFERENT STATIONARY PHASES AT 100°C $r$  = Correlation coefficient,  $s$  = standard deviation,  $N$  = number of experimental points.

Stationary phase	Equation	$r$	$s$	$N$
Squalane	$I_R = 52.56 + 4.68 t_b + 6423.5/M_R$	0.9994	7.9	14
	$I_R = 220.70 + 4.23 t_b + 9811.9/V_M$	0.9987	11.0	14
	$I_R = 98.94 + 4.57 t_b + 517.1/\chi$	0.9992	8.5	14
OV-101	$I_R = -0.47 + 4.82 t_b + 7890.1/M_R$	0.9998	4.3	15
	$I_R = 132.46 + 4.43 t_b + 18717.1/V_M$	0.9994	7.6	14
	$I_R = 131.23 + 4.50 t_b + 466.8/\chi$	0.9992	8.8	15
SE-54	$I_R = 15.96 + 4.85 t_b + 7588.7/M_R$	0.9999	3.9	15
	$I_R = 75.40 + 4.60 t_b + 24393.8/V_M$	0.9996	7.1	15
	$I_R = 184.39 + 4.42 t_b + 363.9/\chi$	0.9989	11.2	15

expected, the statistical analysis (Table VI) showed that the solute-stationary phase interactions increase with increasing McReynolds' polarity of the stationary phase, which is reflected by the decrease in the correlation coefficient and the increase in the standard deviation. The existence of these interactions is also revealed by alterations in the elution order. The elution order on squalane is close to the increasing order of solute boiling points, whereas on stationary phases of higher polarity this relationship fails. Some examples of this are the change in the elution order of 1,3-cyclopentadiene and cyclopentene on OV-215 at 80 and 100°C, the gradual change of in the relative  $I_R$  values of methylenecyclohexane and 4-methylcyclohexene with polarity and similar changes for the pair formed by *cis*-bicyclo[3.3.0]oct-2-ene and ethylidenecyclohexane. The standard deviation of the equations  $I_R = f(t_b)$  is too high to be used in the calculation of  $t_b$ .

When low-polarity solutes are chromatographed on stationary phases of low and medium polarity, the interactions are mainly dispersive and can be corrected by introducing dispersive descriptors, such as  $M_R$ ,  $V_M$  or  $\chi$ , in the correlation. The equations  $I_R = f(t_b, \theta)$ , where  $\theta$  is  $M_R$ ,  $V_M$  or  $\chi$ , obtained with  $I_R$  on stationary phases of low and medium polarity at 100°C are shown in Table VII. It can be seen that the introduction of the new parameter improves the statistics, especially for OV-101 and SE-54 when  $M_R$  is used as the descriptor. The similar effect produced by these three parameters agrees with their high intercorrelation, which is shown in Table VIII.

TABLE VIII

CORRELATION COEFFICIENTS BETWEEN DIFFERENT SOLUTE PROPERTIES

Parameter	$t_b$	$1/M_R$	$1/V_M$	$1/\chi$
$t_b$	1.0000	0.9607	0.9419	0.9246
$1/M_R$		1.0000	0.9318	0.8573
$1/V_M$			1.0000	0.8591
$1/\chi$				1.0000

Unfortunately, the only parameter available for the calculation of  $t_b$  for methylcyclopentadiene dimers and iso-dimers is  $\chi$ , which can be calculated from their structures<sup>15,16</sup>. Nevertheless, from equation  $I_R = f(t_b, \chi)$  obtained from  $I_R$  values on squalane (Table VII), fairly good  $t_b$  values can be calculated, as shown in Table IX, where experimental and calculated  $t_b$  values are given. The standard deviation was less than  $\pm 2.0^\circ\text{C}$ , which may be considered as acceptable taking into account the poor precision of some of the experimental  $t_b$  values. Sometimes, two different  $t_b$  values were found in the literature for the same compound. It is to be expected that the values calculated for MCPD dimers and iso-dimers bear a similar error.

The general expression of the equations in Table VII closely remembers the following equation deduced by Kaliszan<sup>18</sup> for the calculation of  $I_R$  on polar stationary phases from those on non-polar phases:

$$I_P = k_1 + k_2 I_{NP} - k_3 D \quad (3)$$

TABLE IX  
EXPERIMENTAL AND CALCULATED  $t_b$  OF MCPD DIMERS AND OTHER CYCLOOLEFINS

Compound	$t_b$ ( $^\circ\text{C}$ )			
	Eqn. 1	Eqn. 2	Exptl.	Ref
1-Methylcyclopentene <sup>a</sup>	76.4	75.9	75.8	12
Cyclohexene <sup>a</sup>	84.5	84.2	83.0	10
2,5-Norbornadiene <sup>a</sup>	84.4	84.7	89.5	10
2-Norbornene	100.0	—	96.0	13
3-Methylcyclohexene <sup>a,b</sup>	103.0	104.6	104.0	10
Methylenecyclohexane	104.0	104.6	102–103 <sup>c</sup>	10
4-Methylcyclohexene <sup>a</sup>	104.1	104.7	102.7	10
1-Methylcyclohexene <sup>a</sup>	110.1	110.4	110.1	10
Vinylcyclohexane <sup>a,b</sup>	127.4	128.8	128.0	11, 13
4-Vinylcyclohexene <sup>a</sup>	124.6	124.8	128.9	10
<i>cis</i> -Bicyclo[3.3.0]oct-2-ene	134.1	135.3	134.0	11
Ethylidenecyclohexane <sup>a</sup>	136.2	137.0	136.0	12
5-Vinyl-2-norbornene	137.9	139.1	141.0	11
<i>cis</i> -5-Ethylidene-2-norbornene <sup>a,b</sup>	144.0	144.9	147.3	14
<i>trans</i> -5-Ethylidene-2-norbornene	146.4	—	148.5	14
<i>exo</i> -Dicyclopentadiene	171.6	172.5	—	—
<i>endo</i> -Dicyclopentadiene <sup>a</sup>	171.9	172.8	170.0	10
Bicyclo[4.3.0]nona-3,6(1)-diene	175.5	175.1	178.0	13
1,4-(or 4,7-)Dimethyl-DCPD <sup>d</sup>	193.8	194.9	—	—
4,8-(or 4,9-)Dimethyl-DCPD <sup>d</sup>	198.6	199.6	—	—
<i>cis</i> -Cyclodecene <sup>a</sup>	199.4	199.5	198.0	12
1,3-(or 3,7-)Dimethyl-DCPD <sup>d</sup>	200.2	201.0	—	—
3,8-(or 3,9-)Dimethyl-DCPD <sup>d</sup>	205.4	206.7	—	—
4-Methyl-8-(or 9-)methylene-DCP <sup>e</sup>	206.1	206.6	—	—
3-Methyl-8-(or 9-)methylene-DCP <sup>e</sup>	212.2	212.4	—	—
<i>trans,cis,cis</i> -1,5,9-cyclododecatriene <sup>a</sup>	236.4	234.9	238.0	11
$\alpha$ -Cedrene <sup>a,b,f</sup>	263.8	262.2	262.5	12

<sup>a</sup> Compounds used as standards for eqn. 1 ( $I_R = 98.94 + 4.57 t_b + 517.1/\chi$ ).

<sup>b</sup> Compounds used as standards for eqn. 2 ( $I_R = -0.99 + 4.84 t_b + 725.7/\chi$ ).

<sup>c</sup> At 764 mmHg.

<sup>d-f</sup> See footnotes *b-d* in Table IV.

where  $I_P$  and  $I_{NP}$  are the retention indices on polar and non-polar stationary phases, respectively, and  $D$  is a dispersive descriptor.

The similarity between the equations in Table VII and eqn. 3 is not surprising, as for low-polarity solutes there is a clear correlation between their  $I_R$  values on non-polar stationary phases ( $I_{NP}$ ) and the boiling points, as the equations in Table VI show.

In practice, the use of a large number of standards to obtain equations suitable for calculating  $t_b$  can be avoided. A small number of compounds selected at random with the only condition of covering the whole range of  $t_b$  may be sufficient. Thus, by choosing only the six cycloolefins marked with asterisks in Tables IV and V, the equation  $I_R = -0.99 + 4.84t_b + 725.7/\chi$  was obtained. This equation provides  $t_b$  values very similar to those calculated from the former equation. They are also given in Table IX.

The method described offers the advantage of requiring only  $I_R$  and  $\chi$  values of compounds for the calculation of their  $t_b$ . Although it is not as precise as those of Matukuma<sup>19</sup> and Sojak *et al.*<sup>20</sup>, it provides better values than those obtained by the methods proposed by Kamlet *et al.*<sup>21</sup> and Lydesen<sup>22</sup>.

## CONCLUSIONS

Relationships between  $I_R$  values on several stationary phases of polarity ranging from 0 to 1550 (McReynolds' scale) and the physico-chemical properties of cycloolefins have been established that permit the calculation of approximate  $t_b$  values for dimethyldicyclopentadiene dimers and their iso-dimers with an exocyclic double bond, whose  $t_b$  data are not available in the literature.

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