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RETENTION BEHAVIOUR OF CONJUGATED AND ISOLATED *n*-ALKA-DIENES

IDENTIFICATION OF *n*-NONA- AND *n*-DECADIENES BY CAPILLARY GAS CHROMATOGRAPHY USING STRUCTURE–RETENTION CORRELATIONS AND MASS SPECTROMETRY

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SUMMARY

The isomerization products of *n*-C_8–C_{10} α,ω-alkadienes were separated on a high-efficiency squalane column (195 m × 0.25 mm I.D.) with 500,000 effective plates. Of the 102 possible *n*-C_8–C_{10} dienes with isolated and conjugated double bonds, only nine groups of isomers were not separated.

All isomers, except those with cumulated double bonds, were identified (23 octadienes, 33 nonadienes and 46 decadienes). The *n*-octadienes were identified by matching measured and published retention data. Because of the lack of standards, retention data and mass spectra of *n*-nona- and decadienes, and because the previously reported identification method for *n*-dienes up to C_8 was succesful, the problem of the identification of C_9–C_{10} *n*-alkadienes was solved similarly by using structure–retention correlations and combined capillary gas chromatography–mass spectrometry. Based on these results, the retention behaviour of the conjugated and isolated *n*-alkadienes, on squalane stationary phase, is generalized.

INTRODUCTION

The problem of identifying *n*-heptadienes and *n*-octadienes in complex mixtures has been discussed previously[1]. For the separation and structure–retention correlations for characterization, high-efficiency gas chromatography (GC) was used. The identification of *n*-alkadienes with more than eight carbon atoms in the chain is complicated because of the large number of possible isomers: 37 *n*-nonadienes and 50 *n*-decadienes with isolated, cumulated and conjugated double bonds. Only a few retention data on *n*-alkadienes were found in the literature (two for nonadienes on squalane[2], six for nonadienes and five for decadienes on silicone oil DC 200 and polypropylene glycol[3]). With few exceptions, reference materials and mass spectra

also are not available. Therefore, the *n*-nona- and -decadienes were identified by extrapolating the known information on molecular structure–retention correlations for the lower *n*-alkadienes.

The correlations applied are based on the retention index system. Specifically, use was made of the dependence of the "homomorphy factors", *H*, on the number of carbon atoms for the various homologous series of *n*-alkadienes. *H* is defined here as the difference between the retention index of an *n*-alkadiene (or a *n*-alkene) and that of the *n*-alkane with the same number of carbon atoms.

The prediction of retention indices for *n*-alkadienes is based on the concept of additivity. For a given number of carbon atoms, the *H* values of two *n*-alkene isomers add up to the *H* value of the structurally corresponding *n*-alkadiene[1]. Systematic deviations from the additivity rule, caused by the effects of conjugation and hyperconjugation, and by the "propyl effect"[4], are used to correct the predicted retention indices. Moreover, the temperature dependence of the retention indices, dI/dT, which varies with the position and geometry of the double bonds and with the number of carbon atoms, is taken into account.

The tentative identification of the *n*-alkadienes, as based on these correlations, was verified and in several instances adjusted by data obtained from combined capillary gas chromatography–mass spectrometry (GC–MS). Mass spectral data will be published elsewhere.

EXPERIMENTAL

Model mixtures of C_8–C_{10} *n*-alkadiene isomers were prepared by catalytic isomerization[5] of 1,7-octa-, 1,8-nona- and 1,9-decadienes with subsequent purification by column adsorption chromatography with fluorescent indicator adsorption[6]. The reaction of 1,*trans*- and *trans,trans*-conjugated *n*-alkadienes with maleic anhydride was effected by heating for 30 min at 50°C.

GC was carried out with a Carlo Erba GI 452 instrument, equipped with a flame-ionization detector. A glass capillary column, 195 m × 0.25 mm I.D., coated with 0.08 μm of squalane as stationary phase was used. Measurements were made at temperatures between 30 and 80°C. Hydrogen was used as the carrier gas, at an inlet pressure of 0.3 MPa and an average linear flow-rate of $\bar{u}$ = 25 cm/sec. The theoretical and effective plate numbers were 700,000 and 500,000, respectively, for *cis*-2,*cis*-4-decadiene with a capacity ratio of 5.6 at 70°C. The repeatability of the retention index measurements is characterized by a standard deviation of 0.14 index unit (i.u.).

RESULTS

The identification of C_9–C_{10} *n*-alkadienes was based on the dependence of the retention of *n*-alkadienes with certain structural features on the number of carbon atoms in the molecule. These relationships were extrapolated from the retention data for the lower *n*-alkadiene isomers. Because the squalane column used for the separation of C_9–C_{10} *n*-alkadienes had slightly different characteristics to the column previously used[1] (notably a thinner stationary phase film), the retention data of the *n*-octadienes were also measured on this column. The chromatogram of *n*-octadienes at 40°C is given in Fig. 1. The 23 theoretically possible isomers with isolated and
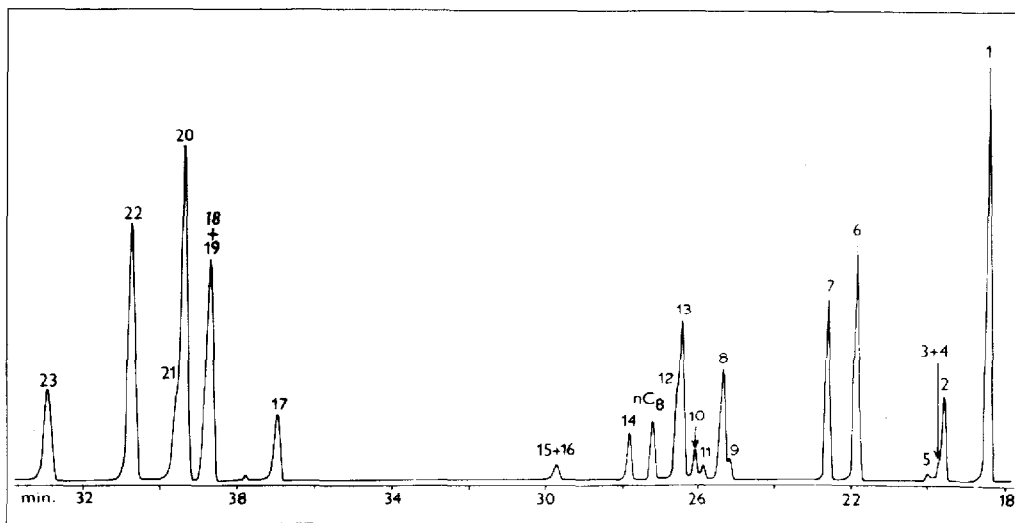
Fig. 1. Chromatogram of a mixture of *n*-octadienes separated on the squalane column at 40°C. For identification, see Table I. Column length, 195 m; hydrogen carrier gas linear flow-rate, 27 cm/sec.

conjugated double bonds were separated into 21 peaks. The 1,3-geometrical isomers and 1,*trans*-4- + 1,*cis*-5-octadiene remained unseparated up to 70°C. Compared with previous results[1], the separation of *trans*-2,*trans*-4- and *trans*-3,*trans*-5-octadiene was achieved by the higher efficiency of the squalane column used. Also, the elution of 1,*trans*-5-octadiene was found to occur before 1,*trans*-4-octadiene.

Fig. 2 shows a chromatogram for the *n*-nonadienes, separated at 70°C. The 33 theoretically possible isomers, with isolated and conjugated double bonds, were separated into 26 peaks. Seven pairs of isomers could not be separated: 1,*cis*-6- + 1,*cis*-4-; *trans*-2,*trans*-6- + *trans*-3,*cis*-6-; 1,*cis*-7- + *trans*-2,*cis*-6-; *cis*-2-,*cis*-6- + *trans*-2,*cis*-5-; *cis*-3,*trans*-5- + *trans*-3,*cis*-5-; *trans*-3-,*trans*-5- + *trans*-2,*cis*-4-; and 1,*cis*-3- + 1,*trans*-3-nonadienes. The separation of the geometrical 1,3-isomers was accomplished by lowering the temperature to 50°C. The separation of *trans*-3,*trans*-5- + *trans*-2,*cis*-4-; *trans*-2,*trans*-6- + *trans*-3,*cis*-6- and 1,*cis*-7- + *trans*-2,*cis*-6- was achieved at 40°C.

In Fig. 3, the chromatogram of the *n*-decadiene mixture, separated at 70°C, is shown. The 46 theoretically possible conjugated and isolated isomers were separated into 43 peaks. The 1,9- and 1,*trans*-5-isomers, and the pairs *trans*-2,*trans*-6- + *cis*-3,*cis*-6- and *cis*-3,*trans*-6- + *trans*-3,*cis*-6-decadienes could not be separated, even with temperature changes. The pair *trans*-2,*cis*-5- + *cis*-2,*cis*-7-decadiene was separated at 60°C.

DISCUSSION

The characterization of C_9–C_{10} *n*-alkadienes was carried out as with *n*-alkenes[7] and alkylbenzenes[8], on the basis of structure–retention correlations. These correlations are based on the dependence of H on the number of carbon atoms, N, for the homologous series of C_5–C_8 *n*-alkadienes and for the first members of the
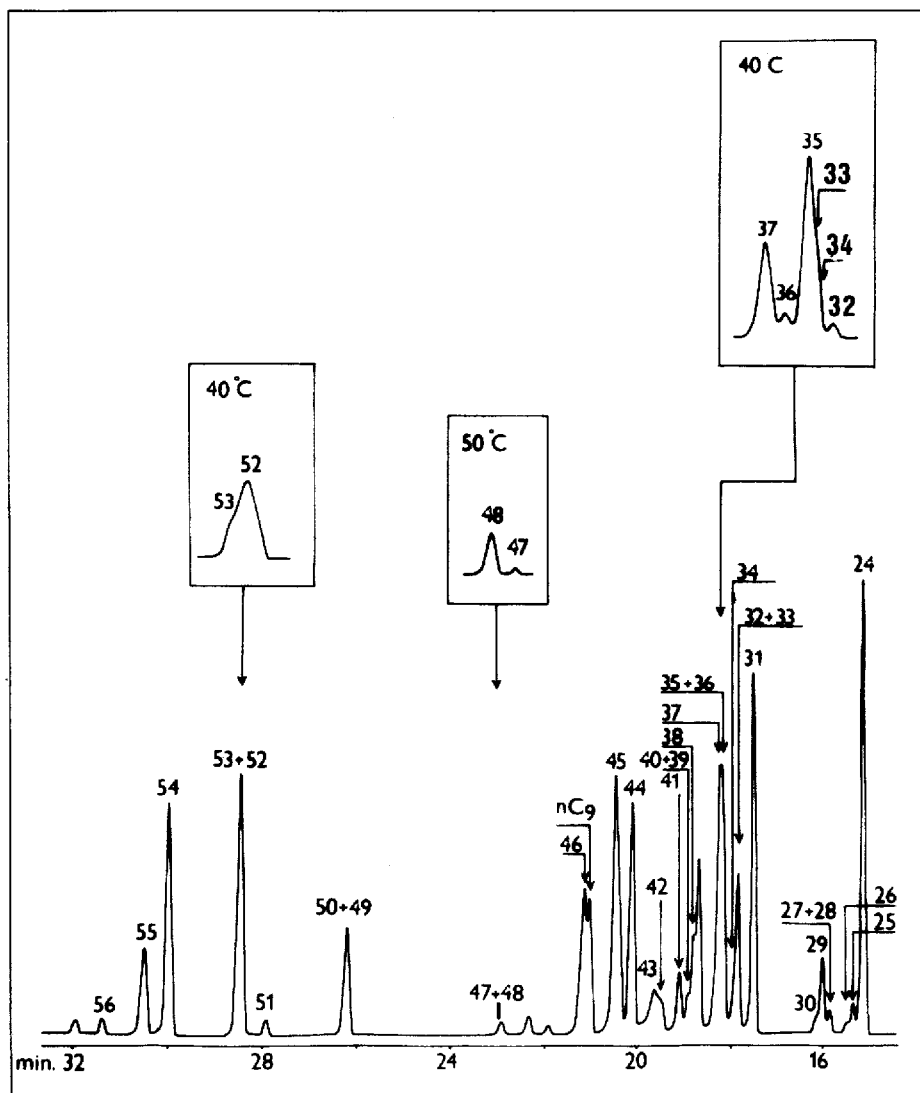
Fig. 2. Chromatogram of a mixture of n-nonadienes separated on the squalane column at 70°C. For identification, see Table I. Column length, 195 m; hydrogen carrier gas linear flow-rate, 25 cm/sec.

homologous series of C_5–C_8 n-alkadienes. By extrapolation of the individual relationships $H = f(N)$ for the homologous series up to nine and ten carbon atoms, respectively, H values for all C_9 and C_{10} n-alkadiene isomers were obtained. These H values were compared with those measured for candidate peaks in the chromatograms. Incorporating refinements with respect to other retention characteristics, such as dI/dT, ΔI_{CH_2}, δI, δH and $\delta I_{calc.\,-meas.}$ values, mass spectra and chemical reactions on the one hand and molecular structures of the C_5–C_{10} n-alkadienes on the other hand, a preliminary identification of the studied C_9–C_{10} n-dienes was made.
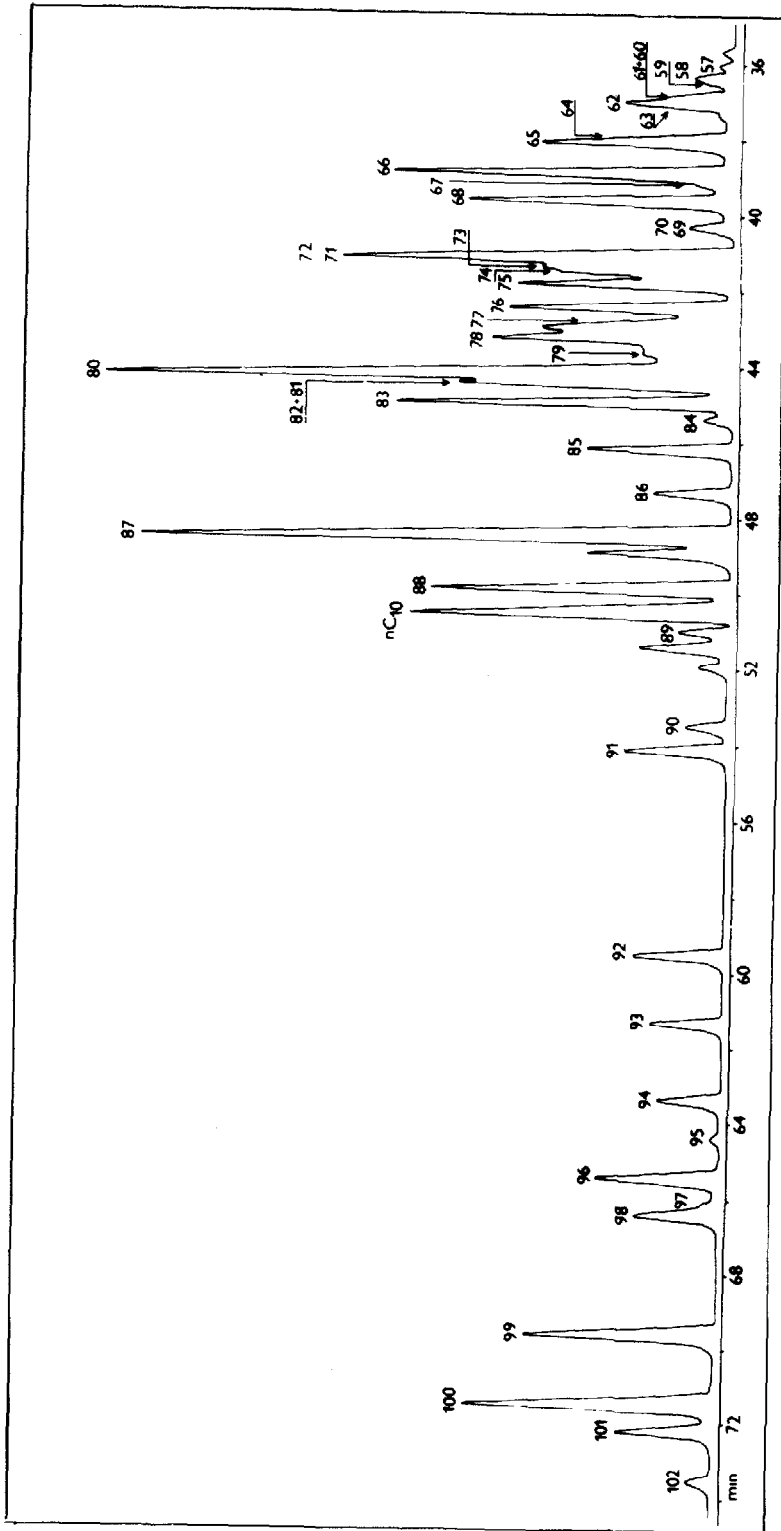
Fig. 3. Chromatogram of a mixture of *n*-decadienes separated on the squalane column at 70°C. For identification, see Table I. Column length, 195 m; hydrogen carrier gas linear flow-rate, 25 cm/sec.

TABLE I

RETENTION INDICES, *I*, AND d*I*/d*T* VALUES FOR *n*-OCTA-, *n*-NONA- AND *n*-DECADIENES, MEASURED ON A SQUALANE COLUMN AT 70°C

Peak No.	Compound	I_{70}^{SQ}	d*I*/d*T*
1	1,7-Octadiene	763.5	0.045
2	1,*trans*-5-	768.3	0.015
3	1,*trans*-4-	769.0	0.020
4	1,*cis*-5-	769.2	0.040
5	1,*cis*-4-	771.6	0.050
6	1,*trans*-6-	779.3	0.035
7	1,*cis*-6-	783.5	0.055
8	*trans*-2,*trans*-6-	792.3	−0.010
9	*trans*-2,*cis*-5-	792.7	0.025
10	*trans*-2,*trans*-5-	795.2	−0.020
11	*cis*-2,*cis*-5-	796.5	0.060
12	*cis*-2,*trans*-5-	797.8	0.015
13	*trans*-2,*cis*-6-	798.0	0.030
14	*cis*-2,*cis*-6-	804.0	0.065
15	1,*trans*-3-	810.5	0.050
16	1,*cis*-3-	810.5	0.065
17	*trans*-3,*cis*-5-	830.6	0.030
18	*cis*-3,*cis*-5-	835.9	0.040
19	*trans*-2,*cis*-4-	835.9	0.040
20	*trans*-2,*trans*-4-	837.9	0.055
21	*trans*-3,*trans*-5-	838.1	0.055
22	*cis*-2,*trans*-4-	840.6	0.045
23	*cis*-2,*cis*-4-	846.3	0.060
24	1,8-Nonadiene	862.7	0.050
25	1,*trans*-5-	864.5	0.040
26	1,*cis*-5-	865.6	0.070
27	1,*cis*-6-	868.0	0.070
28	1,*cis*-4-	868.1	0.070
29	1,*trans*-6-	869.1	0.030
30	1,*trans*-4-	869.9	0.020
31	1,*trans*-7-	879.1	0.020
32	*trans*-3,*cis*-6-	881.4	0.030
33	*trans*-2,*trans*-6-	881.6	−0.010
34	*cis*-3,*cis*-6-	882.0	0.040
35	1,*cis*-7-	883.6	0.060
36	*trans*-2,*cis*-6-	883.6	0.040
37	*trans*-3,*trans*-6-	884.0	0.025
38	*cis*-2,*trans*-6-	887.2	0.035
39	*cis*-2,*cis*-6-	887.9	0.070
40	*trans*-2,*cis*-5-	887.9	0.040
41	*trans*-2,*trans*-5-	889.2	0.000
42	*cis*-2,*cis*-5-	891.6	0.050
43	*cis*-2,*trans*-5-	892.4	0.035
44	*trans*-2,*trans*-7-	895.0	0.020
45	*trans*-2,*cis*-7-	897.0	0.040
46	*cis*-2,*cis*-7-	900.6	0.080
47	1,*cis*-3-	909.5	0.080
48	1,*trans*-3-	909.7	0.060
49	*cis*-3,*trans*-5-	925.0	0.030
50	*trans*-3,*cis*-5-	925.0	0.030

TABLE I (*continued*)

Peak No.	Compound	I_{70}^{SQ}	dI/dT
51	*cis*-3,*cis*-5-	932.3	0.055
52	*trans*-3,*trans*-5-	934.5	0.050
53	*trans*-2,*cis*-4-	934.5	0.060
54	*trans*-2,*trans*-4-	940.5	0.070
55	*cis*-2,*trans*-4-	942.6	0.050
56	*cis*-2,*cis*-4-	945.8	0.060
57	1,*cis*-5-Decadiene	961.4	0.065
58	1,*trans*-6-	962.3	0.030
59	1,*cis*-6-	962.5	0.070
60	1,9-	964.0	0.030
61	1,*trans*-5-	964.0	0.030
62	1,*cis*-4-	964.5	0.045
63	1,*trans*-4-	965.5	0.035
64	1,*cis*-7-	967.1	0.065
65	1,*trans*-7-	967.8	0.030
66	*trans*-3,*cis*-7-	970.1	0.010
67	*cis*-3,*cis*-7-	970.9	0.040
68	*trans*-3,*trans*-7-	972.3	0.035
69	*trans*-3,*cis*-6-	974.0	0.035
70	*cis*-3,*trans*-6-	974.0	0.035
71	*trans*-2,*trans*-6-	976.4	0.015
72	*cis*-3,*cis*-6-	976.4	–
73	1,*trans*-8-	977.1	0.035
74	*trans*-3,*trans*-6-	977.9	0.030
75	*trans*-2,*cis*-6-	978.5	0.035
76	*trans*-2,*cis*-7-	980.1	0.045
77	1,*cis*-8-	981.1	0.060
78	*cis*-2,*trans*-6-	982.3	0.050
79	*cis*-2,*cis*-6-	983.3	0.070
80	*trans*-2,*trans*-7-	984.6	0.015
81	*cis*-2,*cis*-7-	985.3	0.075
82	*trans*-2,*cis*-5-	985.3	0.030
83	*cis*-2,*trans*-7-	986.8	0.045
84	*cis*-2,*cis*-5-	988.1	0.070
85	*trans*-2,*trans*-5-	990.0	−0.005
86	*cis*-2,*trans*-5-	992.9	0.035
87	*trans*-2,*trans*-8-	995.4	−0.005
88	*trans*-2,*cis*-8-	998.7	0.040
89	*cis*-2,*cis*-8-	1001.4	0.080
90	1,*cis*-3-	1007.2	0.055
91	1,*trans*-3-	1008.5	0.050
92	*trans*-4,*cis*-6-	1019.4	0.050
93	*trans*-3,*cis*-5-	1022.8	0.035
94	*cis*-3,*trans*-5-	1026.6	0.040
95	*cis*-4,*cis*-6-	1028.3	0.075
96	*trans*-4,*trans*-6-	1030.2	0.085
97	*cis*-3,*cis*-5-	1031.4	0.070
98	*trans*-2,*cis*-4-	1032.0	0.055
99	*trans*-3,*trans*-5-	1037.4	0.075
100	*trans*-2,*trans*-4-	1040.5	0.075
101	*cis*-2,*trans*-4-	1041.7	0.055
102	*cis*-2,*cis*-4-	1043.8	0.070

The measured retention indices and corresponding dI/dT values for C_8–C_{10} *n*-alkadienes are given in Table I.

The "homomorphy factors", H_{70}^{SQ}, calculated from the measured retention indices of *n*-alkadienes up to C_{10}, are plotted as a function of the number of carbon atoms for homologous series of *n*-alkadienes in Fig. 4. The *H*-values decrease with increasing number of carbon atoms. For the higher members of the homologous series (sixth and higher), *H* becomes nearly constant.

The decrease in the *H*-values is higher for *cis*-isomers (maximum for *cis,cis*-isomers). The regularity of the dependence of *H* on the number of carbon atoms is broken in those instances where the propyl effect is apparent. The propyl effect[4], a cyclic conformation of a propyl group adjacent to a double bond, is shown by all hydrocarbons with a 4-pentenyl moiety in the *trans*-configuration. In Fig. 4, arrows indicate the predictable deviation of the measured *H*-values ($-$ 2–3 i.u.), pointing to the predicted values when neglecting this contribution.

The retention of *trans*-4,*trans*-6-decadiene was expectedly influenced by a double propyl effect[4] (about -5 i.u.). The significance of the corrections of the *H*-values for the propyl effect is evident, for example, for the *cis*-2,*trans*-4- and the 1,*trans*-3- homologous series. Neglect of the propyl effects could, for instance, falsely lead to the prediction of reversed retention orders for *cis*-2,*trans*-4- and *trans*-2,*trans*-4-octadiene, and for 1,*trans*-3- and *trans*-2,*cis*-5-heptadiene, respectively. When the propyl effects are taken into account, the retention behaviour of the higher members of the various homologous series can be exactly predicted. About 15% of all the possible isomers up to C_{11} exhibit propyl effects in the molecules. Geometrical 1,*cis*-, *trans,cis*- and *cis,cis-n*-alkadiene isomers can also show propyl effects, albeit very weak. In the range C_6–C_{10}, it can be observed only with *cis*-2,*cis*-4- and *trans*-2,*cis*-4-octadienes.

For the characterization of those isomers which cannot be correlated from the relationships shown in Fig. 4, *i.e.*, isomers with "new" structural features (new homologous series of *n*-alkadienes, starting at higher numbers of carbon atoms) the dependence $H = f(N)$ for the first members of new homologous series was used, as shown in Fig. 5. These dependences are characteristic. The prediction of the retention indices of isomers with new structural features is possible by extrapolating these dependences.

1,*trans*-5-Heptadiene, *trans*-2,*cis*-6-octadiene and *trans*-2,*trans*-6-octadiene have lower retentions than predicted from the characteristic dependences of the functions $H = f(N)$ for the first members of homologous series (Fig. 5). Inspection of molecular models showed that an intramolecular interaction between both double bonds (σ overlap of p-orbitals) is possible, resulting in a cyclic conformation with a distance between the double bonds of 2.5 Å. For all other positional and geometrical isomers, this distance is more than 3.5 Å and the formation of a cyclic conformer is not possible because of the non-bond interactions in the molecules. This conformational effect is a function of the geometrical configuration. It is large for *trans,trans*- and 1,*trans*-isomers, but *cis,cis*- and 1,*cis*-isomers are not able to adopt a cyclic conformation. This effect reduces the surface contact between solute and solvent and lowers the polarizability of the molecules. Hence these compounds show lower retention characteristics. All positional isomers with the same "distance" (two carbon atoms) between the double bonds can be expected to show this effect.
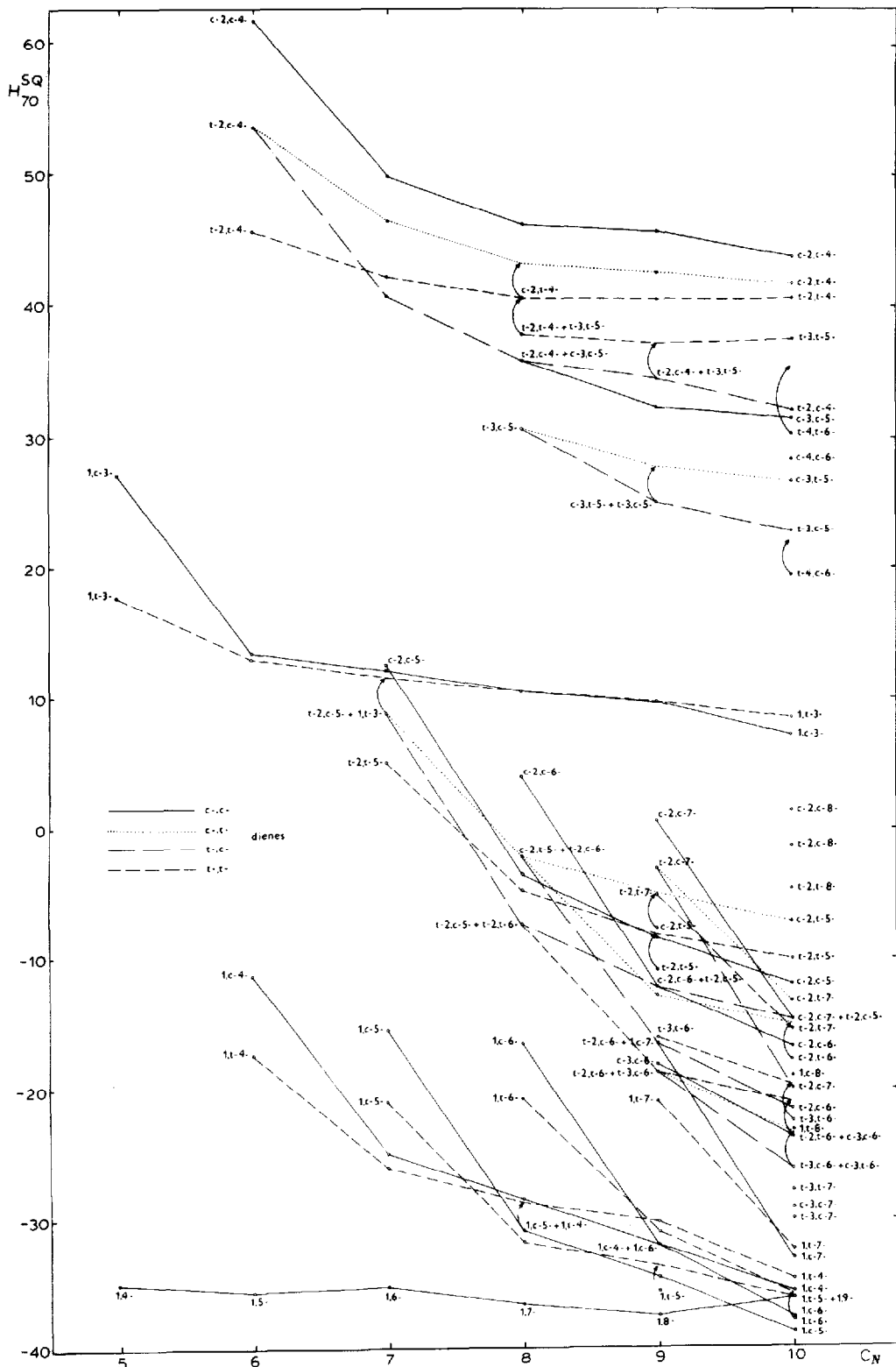
Fig. 4. Dependence of the homomorphy factors, H, for C_5–C_{10} *n*-alkadienes, on the number of carbon atoms; *c*- = *cis*-, *t*- = *trans*-isomers.
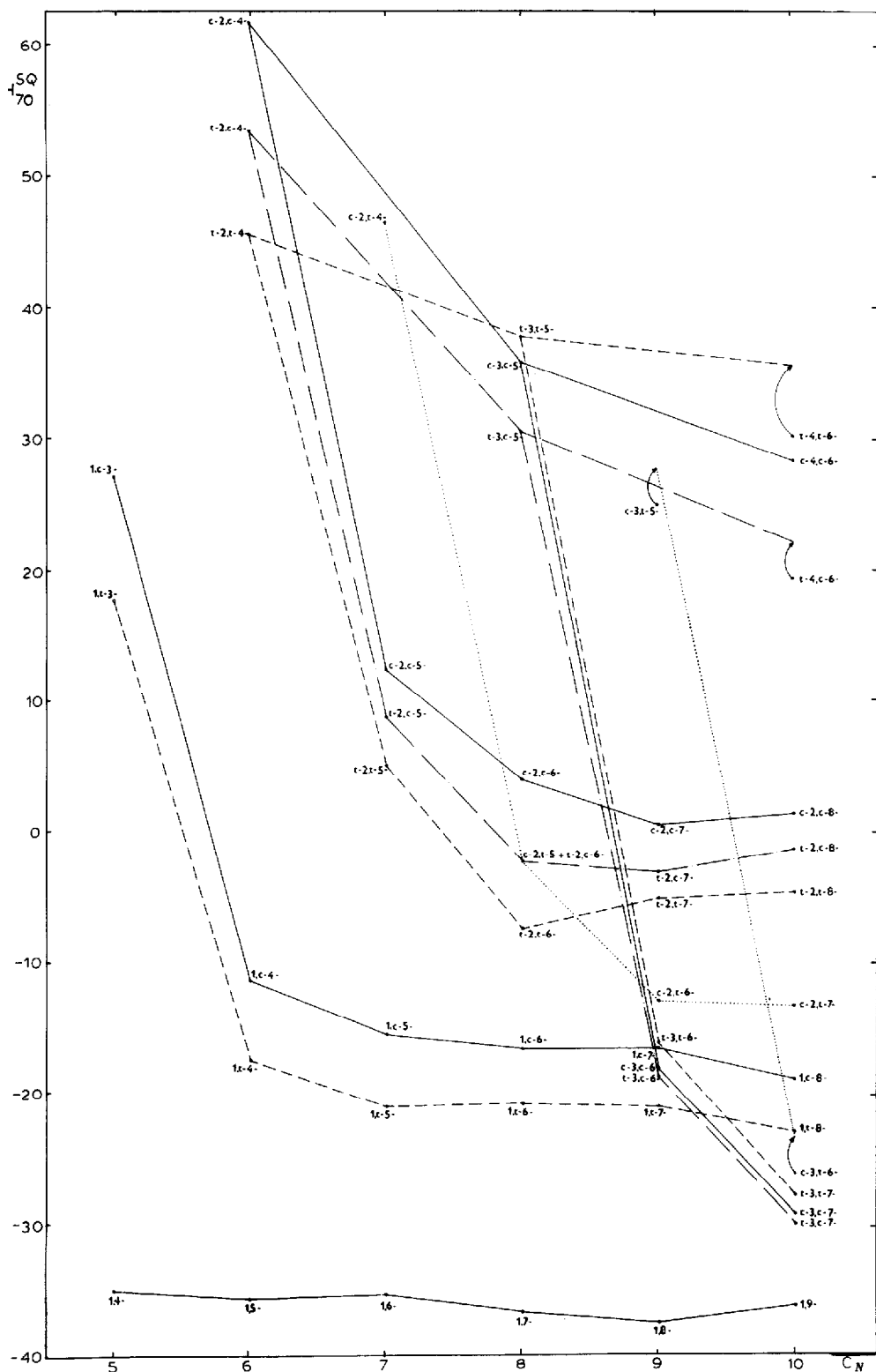
Fig. 5. Dependence of the homomorphy factors, H, for C_5–C_{10} *n*-alkadienes on the number of carbon atoms for the first members of homologous series; c- = *cis*-, t- = *trans*-isomers.
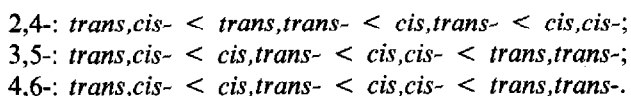
A similar effect was found for α,ω-alkadienes. In this homologous series the alternation of H values (relatively higher retention for homologues with an even position of the second double bond) is reversed from 1,8-nonadiene onwards. It was found that all α,ω-alkadienes up to C_8 (1,5-C_6, 1,6-C_7, 1,7-C_8) are able to adopt a cyclic conformation in which the distance between the double bonds is about 2.5 Å. All higher α,ω-alkadienes are not able to do this, and the distance between their double bonds is more than 3.5 Å for all positions of the molecules. From this point of view, the homologous series of α,ω-dienes can be divided into two groups. The first group includes the C_4–C_8 α,ω-alkadienes and the second group is formed by the higher members of this homologous series, with a reversed course of alternation.

The following discussion on the retention behaviour of *n*-alkadiene isomers is based on the dependence $H = f(N)$ as illustrated in Figs. 4 and 5. The significantly different retentions of alkadienes with conjugated compared with isolated double bonds are evidently characteristic.

n-Alkadienes with conjugated double bonds

Because of the high polarizability and the limited mobility of the carbon atoms in a conjugated system, strong dispersal forces occur by intermolecular interactions. Therefore, conjugated dienes are retained more than those with isolated double bonds; they are eluted after the *n*-alkanes with the same number of carbon atoms. There is a characteristically different retention behaviour of 1,3-alkadienes compared with the other conjugated *n*-alkadienes, because there is a significant difference in the polarizability of the conjugated system at terminal and inner positions of the carbon chain. Generally, the retention of positional isomers of non-terminal conjugated *n*-alkadienes up to C_{10} increases with the shift of the double bonds towards the end of the carbon chain (*i.e.*, to the 2,4-position). However, 1,3-*n*-alkadienes have the lowest retention of all conjugated *n*-alkadienes: 1,3- ≪ 4,6- < 3,5- < 2,4-. For positional isomers with a given geometry, the retention increases in the same order: *cis*-4,*cis*-6- < *cis*-3,*cis*-5- < *cis*-2,*cis*-4-; *trans*-4,*trans*-6- < *trans*-3,*trans*-5- < *trans*-2,*trans*-4-; *trans*-4,*cis*-6- < *trans*-3,*cis*-5- < *trans*-2,*cis*-4-; *cis*-4,*trans*-6- < *cis*-3,*trans*-5- < *cis*-2,*trans*-4-.

The exceptional behaviour of *trans*-2,*trans*-4-octadiene, which co-elutes with *trans*-3,*trans*-5-octadiene, is well explained by the propyl effect. Geometrical conjugated *n*-alkadiene isomers show a retention order as a function of the positional isomers:

2,4-: *trans,cis-* < *trans,trans-* < *cis,trans-* < *cis,cis-*;
3,5-: *trans,cis-* < *cis,trans-* < *cis,cis-* < *trans,trans-*;
4,6-: *trans,cis-* < *cis,trans-* < *cis,cis-* < *trans,trans-*.

This order is valid for symmetrical isomers, *i.e.* for the first members of the homologous series with three geometrical isomers, and also for asymmetrical isomers, *i.e.*, for the second and higher members of the homologous series with four geometrical isomers. The 2,4-hexadienes, which have the retention order *trans,trans-* < *trans,cis-* < *cis,cis-*, behave differently. The retention order of 2,4-hexadienes is also found with all symmetrical isomers, $CH_3CH = CH(CH_2)_mCH = CHCH_3$ ($m \geqslant 0$). These compounds have a higher electron polarizability of the molecule as a result of the position of the methyl group adjacent to the double bond (effect of "hyperconjugation").

Because of the lower polarizability of 1,3-n-alkadienes, compared with conjugated dienes with double bonds within the carbon chain, they are less retained. The retention behaviour of both geometrical isomers, 1,cis-3- and 1,trans-3-, is almost identical. Their retention order is reversed when the number of carbon atoms increases. Up to C_7 the 1,trans-3-diene is eluted first, but subsequently ($N > 9$), the 1,cis-3-diene is eluted before the 1,trans-3-isomer.

n-Alkadienes with isolated double bonds

A generalization of the retention behaviour of n-alkadienes with isolated double bonds is considerably more complicated than for conjugated alkadienes. The n-alkadienes with isolated double bonds have a large number of isomers and some of them show very similar characteristics. Moreover, the regularity of the structure–retention dependences is influenced by the effects of hyperconjugation, the propyl effect, the possibility of σ overlap of the p-orbitals and the non-bond interactions of the π-electrons in $-C = C-C-C = C-$ substructures for many n-alkadiene isomers.

The n-alkadienes with isolated double bonds elute, with few exceptions, such as 2,5-heptadienes, before the corresponding n-alkanes. The lower retention is, of course, correlated with the geometry of the molecules and hence with a different charge distribution. With 2,5-heptadienes, the non-bond interactions of the π-electrons ("homoconjugation") and the double effect of electron polarizability in the molecule as a result of the position of the methyl groups adjacent to the double bonds (double effect of hyperconjugation) play a role. This explains why the 2,5-heptadienes elute after n-heptane, with a retention close to those of the conjugated 1,3-heptadienes. The effect of hyperconjugation is apparent in the retention behaviour of all alkadiene isomers with one double bond in the 2-position, and of other isomers with a methyl group adjacent to a double bond.

The effect of hyperconjugation thus causes a higher retention. These effects are more pronounced with 1,cis-, cis,cis- and trans,cis-isomers and less with 1,trans-, trans,trans- and cis,trans-isomers.

Generalizing the retention behaviour of geometrical isomers, the retention order of the positional isomers is as given in Table II.

From Table II and Fig. 4 it is possible to distinguish three groups of isolated n-alkadienes according to their retention behaviour: (i) isomers with terminal double bonds (α,ω-alkadienes); (ii) isomers with one double bond at the end of the molecule and the other one within the carbon chain (1-positional isomers); and (iii) isomers with both double bonds within the carbon chain (2-, 3-, etc., positional isomers).

n-Alkadienes with one or both double bonds at terminal positions. n-Alkadienes with both double bonds at the ends of the carbon chain (α,ω-alkadienes) are eluted up to C_9 before the other isomers. With increasing number of carbon atoms, the retention behaviour of these compounds approaches that of those isomers with one double bond in the 1-position. At C_{10}, 1,9-decadiene is eluted after the 1,trans-6-, 1,cis-6- and 1,trans-5-decadienes. With increasing number of carbon atoms, the H-values of the 1-positional n-dienes decrease and some positional isomers elute before the corresponding α,ω-dienes.

Of the isomers with one double bond at the end of the molecule (1-positional isomers), those with a hyperconjugation effect significantly have the highest retention,

TABLE II

AVERAGE RETENTION ORDERS OF POSITIONAL ISOMERS OF ISOLATED C_6–C_{10} *n*-AL-KADIENES

The retention order was obtained by using average values of retention.

C_6:	1,5* < 1,4**
C_7:	1,6* < 1,4 < 1,5** < 2,5***
C_8:	1,7* < 1,5 < 1,4 < 1,6** < 2,5 < 2,6***
C_9:	1,8* < 1,5 < 1,6 < 1,4 < 1,7** < 3,6 < 2,6 < 2,5 < 2,7***
C_{10}:	1,6§ < 1,5 < 1,9* < 1,4 < 1,7 < 3,7 < 3,6 < 1,8** < 2,6 < 2,7 < 2,5 < 2,8***

    * *n*-Alkadiene with terminal double bonds (α,ω-alkadiene).
   ** 1-Alkadiene with hyperconjugation effect.
  *** 2-Alkadiene with double hyperconjugation effect.
    § *n*-Alkadiene with propyl effect (marked only when the retention order is influenced).

e.g., the 1,*cis*- and 1,*trans*-isomers with a methyl group in a position adjacent to the double bond, *i.e.*, the first members of homologous series. For other 1-alkadiene isomers it is observed that their retention increases with approach of the double bonds to the 1,4-position. This relationship can be stated more accurately when retention data of higher *n*-alkadienes are available. However, because the characteristics of these isomers are very similar, the hyperconjugation and propyl effects markedly influence the retention order of this type of *n*-alkadiene isomers. For example, comparison of the retention behaviour of the pairs 1,*cis*-5- and 1,*cis*-4-hepta- and -octadienes, respectively, shows that loss of the hyperconjugation effect causes a change in retention order. The retention order of the geometrical isomers of 1-alkadienes is the same in the range of 7–10 carbon atoms, with one exception: 1,*trans*-6-decadiene has a lower retention than 1,*trans*-5-decadiene because the former compound exhibits the propyl effect (Table III).

    The retention order of geometrical 1-alkadiene isomers up to C_8 is 1,*trans*- < 1,*cis*- (Table IV). However, with higher numbers of carbon atoms, 1,*cis*-isomers are eluted before the corresponding 1,*trans*-isomers. The change in retention order of the geometrical isomers of 1-alkadienes depends on the number of carbon atoms and on the position of the second double bond.

TABLE III

RETENTION ORDERS OF POSITIONAL ISOMERS WITH THE SAME GEOMETRY OF 1-POSITIONAL C_7–C_{10} *n*-ALKADIENES

C_7:	1,*cis*-4- < 1,*cis*-5-
	1,*trans*-4- < 1,*trans*-5-
C_8:	1,*cis*-5- < 1,*cis*-4- < 1,*cis*-6-
	1,*trans*-5- < 1,*trans*-4- < 1,*trans*-6-
C_9:	1,*cis*-5- < 1,*cis*-6- = 1,*cis*-4- < 1,*cis*-7-
	1,*trans*-5- < 1,*trans*-6- < 1,*trans*-4- < 1,*trans*-7-
C_{10}:	1,*cis*-5- < 1,*cis*-6- < 1,*cis*-4- < 1,*cis*-7- < 1,*cis*-8-
	1,*trans*-6-* < 1,*trans*-5- < 1,*trans*-4- < 1,*trans*-7- < 1,*trans*-8-

   * *n*-Alkadiene with propyl effect (marked only when the retention order is influenced).

TABLE IV

RETENTION ORDERS OF GEOMETRICAL ISOMERS OF 1-POSITIONAL C_6–C_{10} *n*-ALKA-DIENES

C_6:	1,*trans*-4- < 1,*cis*-4-
C_7:	1,*trans*-5- < 1,*cis*-5-; 1,*trans*-4- < 1,*cis*-4-
C_8:	1,*trans*-6- < 1,*cis*-6-; 1,*trans*-5- < 1,*cis*-5-; 1,*trans*-4- < 1,*cis*-4-
C_9:	1,*trans*-7- < 1,*cis*-7-; 1,*trans*-6- > 1,*cis*-6-; 1,*trans*-5-* < 1,*cis*-5-; 1,*trans*-4- > 1,*cis*-4-
C_{10}:	1,*trans*-8- < 1,*cis*-8-; 1,*trans*-7- > 1,*cis*-7-; 1,*trans*-6-* < 1,*cis*-6-; 1,*trans*-5- > 1,*cis*-5-; 1,*trans*-4- > 1,*cis*-4-

* *n*-Alkadiene with propyl effect (marked only when the retention order is influenced).

At 70°C, the elution order of conjugated 1,3-dienes is reversed at the sixth members of the homologous series (at C_{10}); for 1,4-isomers the reversal occurs at the fourth members of the homologous series. With 1,5-dienes, the change in retention order might have occurred at the third members of the homologous series, but because 1,*trans*-5-nonadiene has an anomalous behaviour (propyl effect), the reversal is actually observed from the fourth member. Beginning from 1,6-isomers, all higher positional isomers (1,6-, 1,7-, 1,8-, etc.) show a change in retention order of geometrical isomers at the second members of the homologous series. For example, 1,*trans*-4-hexadiene elutes before 1,*cis*-4-hexadiene (first members), and 1,*trans*-4-nonadiene after 1,*cis*-4-nonadiene (fourth members of the homologous series). 1,*trans*-6-Octadiene elutes before 1,*cis*-6-octadiene, but starting with the nonadienes, this retention order is reversed: 1,*trans*-6-nonadiene elutes after 1,*cis*-6-nonadiene (Tables III and IV and Fig. 4).

n-Alkadienes with non-terminal isolated double bonds. For all types of positional isomers of C_8–C_{10} *n*-alkadienes with one of the double bonds in the 2-position, the following retention order was found:

C_8: 2,5- < 2,6-;
C_9: 2,6- < 2,5- < 2,7-;
C_{10}: 2,6- < 2,7- < 2,5- < 2,8-.
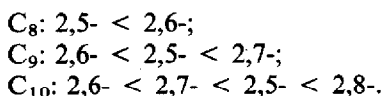
For isomers with the same geometry, the retention order parallels that found for conjugated *n*-alkadienes. For geometrical isomers of the symmetrical 2,5-hepta-, 2,6-octa-, 2,7-nona and 2,8-decadienes, which are the first members of homologous series, the retention order is *trans,trans*- < *trans,cis*- < *cis,cis*-. As pointed out before for conjugated *n*-alkadienes, this is a general rule for the retention order of symmetrical alkadienes with double hyperconjugation effects. The retention of these types of isomers is characteristically higher then that of other dienes with double bonds well within the molecule, because there is a double effect of "hyperconjugation".

For asymmetric *n*-alkadienes with non-terminal double bonds, the retention order found for their geometrical isomers was *trans,cis*- < *trans,trans*- ≈ *cis,cis*- < *cis,trans*-, except for 2,6-isomers, which had the retention order *trans,trans*- < *trans,cis*- < *cis,trans*- ≈ *cis,cis*-. The changes in the retention order of these isomers (Fig. 4) are related to the number of carbon atoms and the position of the double bonds in the molecule in a similar way to the 1-positional isomers discussed above. *n*-Alkadienes with isolated double bonds, one of them being in the 3-position, do not

show a hyperconjugation effect of a methyl group, but a weak effect of hyperconjugation of an ethyl group. The retention of positional isomers is very close, as can be seen by comparing the retentions of 3,6- and 3,7-decadienes. It can be stated that the retention order of the geometrical isomers of symmetrical and asymmetric compounds, with one of the double bonds in the 3- or 4-position, is the same as for the corresponding conjugated *n*-alkadienes: *trans,cis-* $\leqslant$ *cis,trans-* $<$ *cis,cis-* $<$ *trans, trans-*.

Differences between retention indices of positional n-alkadiene isomers with the same geometry: δI values

Neglecting the conjugation, hyperconjugation and propyl effects, the changes in the retention order of *n*-alkadienes, as a function of the number of carbon atoms, are in agreement with the rules for the retention behaviour of pairs of isomers[8]. The separation of the pairs 1,*cis*-5- + 1,*cis*-6-, *cis*-2,*cis*-5- + *cis*-2,*cis*-6-, *trans*-2,*trans*-5- + *trans*-2,*trans*-6-alkadienes is expressed as a function $H = f(N)$ in Fig. 6. For those pairs where the isomer whose homologous series begins at the lower number of carbon atoms elutes first (1,*cis*-5- at C_7), the δI values decrease with the number of carbon atoms (Fig. 6A). Fig. 6C shows that, if the isomer eluted first is the one whose homologous series begins at a higher number of carbon atoms (*trans*-2,*trans*-6- at C_8), the δI values increase with the number of carbon atoms. Fig. 6B shows the intermediate case. Because the difference between the H values of both homologous series is small (smaller than in Fig. 6A), a reversal of the retention order takes place with increasing numbers of carbon atoms: up to C_8 the *cis*-2,*cis*-5-isomer elutes first and from C_9 onwards the *cis*-2,*cis*-6-isomer does. The relationships described are similarly valid for all homologous series of *n*-alkadienes.

Methylene group increments: ΔI_{CH_2} values

Within the various individual homologous series, ΔI_{CH_2} values between 86.3 and 102.9 i.u. are found when the carbon chain is lengthened outside the double bond region. Values higher than 100 i.u. were found only when the propyl effect is involved.

Differences between measured and calculated retention indices of n-alkadienes: $\delta I_{meas.-calc.}$

Starting from the concept that an *n*-alkadiene molecule can be thought of as being constructed from two molecules of the corresponding *n*-alkenes, the retention indices of *n*-dienes were calculated by using the retention indices of the corresponding *n*-alkenes[1]. The retention indices of *n*-alkenes used for these calculations were measured on the same squalane column as used for the determination of the retention indices of *n*-dienes.

Good agreement between measured and calculated values of the retention indices ($\delta I_{\text{meas.}-\text{calc.}} = -0.5$ i.u. on average) was found for *n*-alkadienes with a distance between the double bonds in the molecule of three carbon atoms and more (Fig. 7). With the mutual approach of the double bonds, the agreement between measured and calculated values decreases and the δI values are increased. This effect is explained by the higher mutual interactions of the double bonds on approach. As is shown in Fig. 7, the δI value of 1,*trans*-4-decadiene is 2.3 i.u., whereas for 1,*trans*-3-decadiene it is 41.5 i.u.
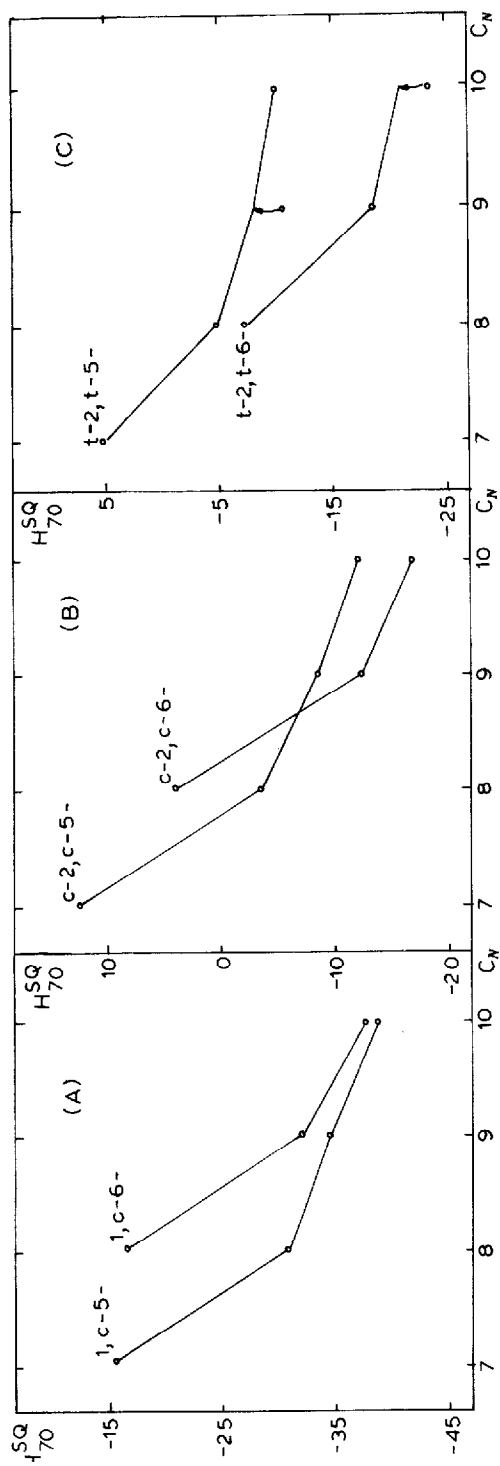
Fig. 6. Dependence of the homomorphy factors, H, on the number of carbon atoms for pairs of geometrical n-alkadiene isomers.

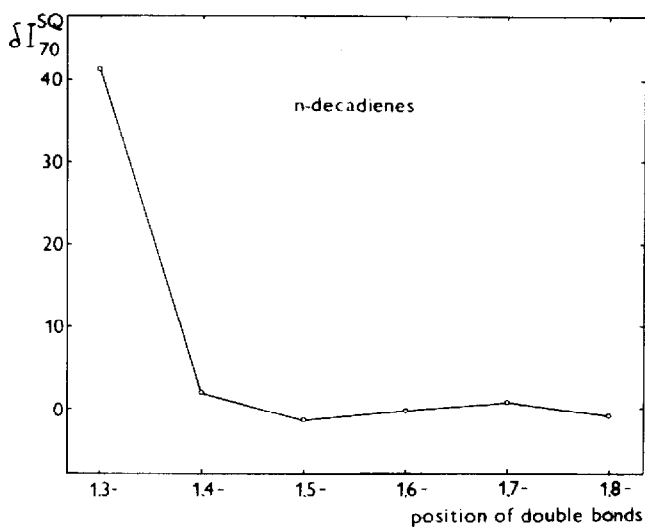Fig. 7. Dependence of $\delta I_{\text{meas.}-\text{calc.}}$ on the position of the double bonds for *n*-1, *trans-i*-decadienes at 70°C ($i = 3$–8).

The high δI value for 1,*trans*-3-decadiene confirms the influence of the con-jugation effect on the retention behaviour of these types of *n*-alkadienes compared with those with isolated double bonds. The unexpectedly high δI value (2.3 i.u.) for 1,*trans*-4-decadiene, however, is a result of the "homoconjugation" effect (non-bond intramolecular interaction between π-orbitals) in this type of molecule, similar to the homoconjugation effect in diphenylmethane. This homoconjugation effect causes higher retention characteristics. The negative δI value for 1,*trans*-5-decadiene con-firms the intramolecular cyclic conformation (with σ overlap of p-orbitals) described before.

The possibilities for the characterization of *n*-alkadienes on the basis of $\delta I_{\text{meas.}-\text{calc.}}$ values is demonstrated in Fig. 8, which shows the dependence of the δI values on the number of carbon atoms for the homologous series 1,3-, 1,4- and 1,5-*n*-alkadienes. Fig. 9A shows the characteristic dependence of the δI values on the position of the double bonds in *n*-decadienes with isolated double bonds of the type –C=C–C–C=C– (1,4-, 2,5-, 3,6-positions). Fig. 9B shows this relationship for decadienes with conjugated double bonds (1,3-, 2,4-, 3,5-, 4,6-positions).

Temperature dependences of the retention indices of n-alkadienes: dI/dT

The dI/dT values depend on the position and geometry of the double bonds, and on the number of carbon atoms. The dI/dT values of *n*-decadienes, given in Tables I and V, are illustrative. They were determined in the temperature range 50–80°C. The dI/dT values were obtained from measurements of complex mixtures of *n*-alkadienes, with some peaks poorly separated. However, the data on unresolved peaks were excluded in this consideration. The dI/dT values of the *n*-alkadienes stud-ied range from -0.03 to 0.08 i.u./°C. The lowest dI/dT values of all were found for isolated *trans,trans*-isomers. These isomers have the smallest average molecular cross-section. Their dI/dT values approach those of *n*-alkanes. A general distinction be-
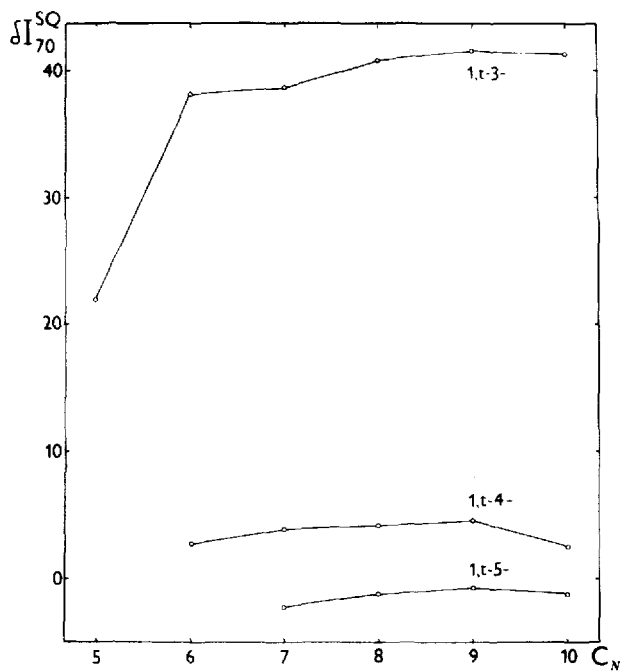
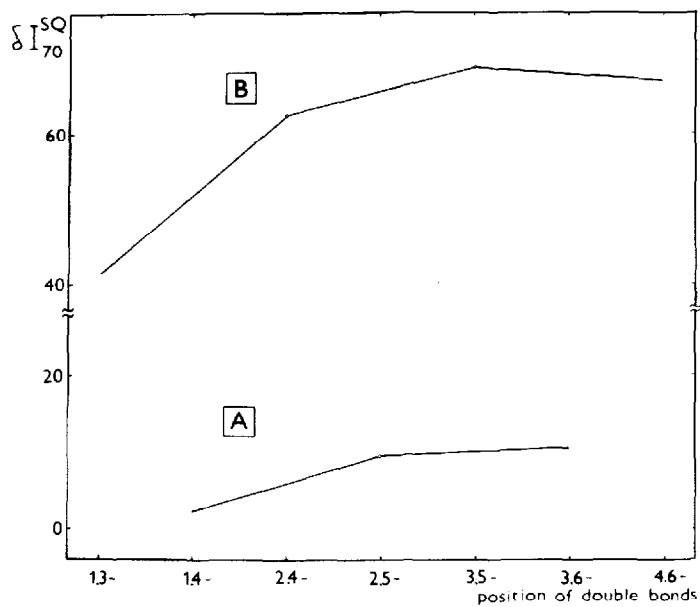Fig. 8. Dependence of $\delta I_{\text{meas.-calc.}}$ on the number of carbon atoms for n-1, i-alkadienes ($i = 3-5$).

Fig. 9. Dependence of $\delta I_{\text{meas.-calc.}}$ on the position of the double bonds in n-decadiene molecules for (A) isolated and (B) conjugated double bonds.

TABLE V

TEMPERATURE DEPENDENCES, dI/dT, OF RETENTION INDICES OF *n*-DECADIENES

Positional isomer	1,trans-			1,cis-
1,3-	0.050			0.055
1,4-	0.035			0.045
1,5-	0.030			0.065
1,6	0.030			0.070
1,7-	0.030			0.065
1,8-	0.035			0.060
1,9-		0.030		
	trans,trans-	trans,cis-	cis,trans-	cis,cis-
2,4-	0.075	0.055	0.055	0.070
2,5-	−0.005	0.030	0.035	0.070
2,6-	0.015	0.035	0.050	0.070
2,7-	0.015	0.045	0.045	0.075
2,8-	−0.005	0.040	0.040	0.080
3,5-	0.075	0.055	0.055	0.070
4,6-	0.085	0.050	0.050	0.075

tween *n*-alkadienes with conjugated and isolated double bonds is not possible on the basis of dI/dT values. Characteristically different are the dI/dT values of 1,*cis*- and 1,*trans*-isomers with isolated double bonds (about 0.03 i.u./°C; Table V). This is in a good agreement with the dI/dT values found for *cis*- and *trans*-*n*-alkenes[6]. For *n*-alkadienes with inner positions of the double bonds, the differences between dI/dT values of *cis,cis*- and *trans,trans*-isomers are doubled, while the dI/dT values of *cis, trans*- and *trans,cis*-isomers are very close and between those of *cis,cis*- and *trans, trans*-isomers. For conjugated 1,3-isomers, the dI/dT values of 1,*cis*-isomers are higher than those of 1,*trans*-isomers. These effects are less evident for *cis,cis*- and *trans-, trans*-isomers of conjugated dienes; the dI/dT values of *cis,trans*- and *trans,cis*-isomers are smaller and about equal. The dependence of the dI/dT values on the number of carbon atoms in the molecule is not characteristic for the range of alka-dienes studied. However, the relationships are analogous to the dependences for *n*-alkenes. Consequently, it can be expected that dI/dT values increase slightly in each homologous series.

Reaction of n-alkadienes with maleic anhydride

The characterizations of 1,*trans*-3-, *trans*-2,*trans*-4- and *trans*-3, *trans*-5-nona-dienes and decadienes and of *trans*-4,*trans*-6-decadiene were confirmed by the reac-tion of these compounds with crystalline maleic anhydride on heating for 30 min at 50°C[1]. Fig. 10 shows the chromatograms of conjugated decadienes before and after reaction.
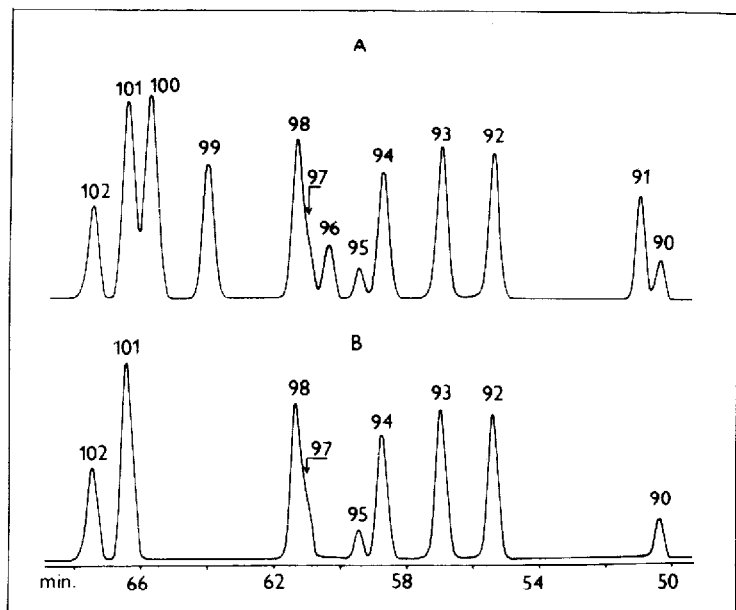
Fig. 10. Chromatogram of conjugated n-decadienes (A) before and (B) after reaction with crystalline maleic anhydride. For identification, see Table I.

CONCLUSION

With increasing chain length, the retention indices (I) of n-alkadienes, separated on apolar columns, decrease with respect to those of the corresponding n-alkanes with the same number of carbon atoms. The H-values ($H = I_{n\text{-alkadiene}} - I_{n\text{-alkane}}$) of the higher members of the various homologous series approach asymptotic values.

On mutual approach of the double bonds in the molecules, stronger intra- and intermolecular interactions cause increased GC retention. Alkadienes with isolated double bonds generally elute before the corresponding n-alkanes. Up to C_{10}, α,ω-dienes have the lowest retentions. 1-Positional isomers are eluted later, and dienes with non-terminal double bonds are retained most.

Alkadienes with conjugated double bonds are retained more than those with isolated double bonds. The conjugated dienes elute after the corresponding n-alkanes. 1,3-Isomers have the lowest retentions and 2,4-dienes the highest.

Of the lowest members of the various homologous series, cis-isomers are eluted after the corresponding trans-isomers. With increasing number of carbon atoms, the retention indices of cis-, particularly cis,cis-, isomers decrease more rapidly than those of the trans-isomers.

Molecular fine structures cause predictable deviations from the retention behaviour as calculated from primary structural features. "Propyl effects" lower the retention (about -2.5 i.u. at 70°C). Double propyl effects decrease the retention indices by about 5 i.u. Generally, compounds that are able to adopt cyclic conformations are retained less. This effect is especially noteworthy when the spatial dis-

tance between the double bonds can be as low as 2.5 Å. Evidently, this effect can occur with isolated *trans,trans-* and 1,*trans-*isomers, but (up to C_{11}) it is impossible with *cis,cis-* or 1,*cis-*isomers. The same conformational effects influence the course of alternation in the *H*-values of α,ω-isomers with odd and even numbers of carbon atoms. From C_9 onwards, this alternation is reversed.

While stereochemical cyclization possibilities decrease the retention of *n*-alkadiene isomers, electromeric stabilization effects increase their retention. In addition to the evident conjugation effects, "homoconjugation" plays a role. Also, methyl and ("weak") ethyl group hyperconjugation effects in 2- and 3-positional isomers, respectively, are apparent, particularly when these effects are doubled as in symmetrical *n*-alkadienes.

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