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THE GAS CHROMATOGRAPHIC CHARACTERIZATION OF 2-THIAADAMANTANE DERIVATIVES

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SUMMARY

The Kováts indices of 2-thiaadamantane and its 4-mono- and 4,8-disubstituted homologues were determined at 190, 200 and 210° for all of the solutes used. Capillary columns with Apiezon L (non-polar phase) and polyphenyl ether 6 P5E (medium polar phase) were used.

INTRODUCTION

In 1932, an interesting tricyclic hydrocarbon, adamantane, was isolated by Landa and Macháček[1] from Hodonín crude oil, and 20 years later, in 1952, a similar compound having the CH_2 group of the adamantane structure substituted by sulphur was isolated by Birch and co-workers[2,3] from Iranian crude oil. The latter substance has been named 2-thiaadamantane. Similarly, as further homologues of adamantane were isolated from petroleum fractions[4,5], the occurrence of 2-thiaadamantane homologues in sulphurous crude oils may be postulated.

A series of 2-thiaadamantane homologues was prepared[6,7] as standards, and their properties were studied. Recently, the Kováts retention indices[8] have been widely used for the characterization of various substances in gas chromatographic analyses. The use of retention indices facilitates the identification of individual compounds in mixtures and are also of help in choosing a suitable stationary phase and analysis conditions. The retention indices are reproducible values and the occurrence of further derivatives in analysed mixtures can be established without the need to use standards. In published papers involving Kováts retention indices, the data relate mainly to hydrocarbons and their derivatives[9].

Further attention was paid even to oxygenated substances[10] (ethers, ketones, aldehydes and alcohols) and, to a certain extent, even to nitrogen-containing substances[11], but up to now no studies on sulphur-containing substances have been reported.

EXPERIMENTAL

The measurements of retention values of the 2-thiaadamantane homologues were carried out with a Chrom IV gas chromatograph (Laboratorní přístroje, Prague, Czechoslovakia) equipped with a flame ionization detector. The temperature of the thermostat was maintained at the required value to within ± 0.2° (measured on the column). The temperature of the sample inlet was 320° in all instances. Two 50 m × 0.2 mm I.D. stainless-steel capillary columns were used. Nitrogen was used as the carrier gas with a stream-splitter adjusted for a ratio 1:200. One of the columns was coated with Apiezon L (non-polar stationary phase) and the other with polyphenyl ether 6 P5E (medium polar stationary phase).

The Kováts retention indices of all of the compounds were measured on both columns at temperatures of 190, 200 and 210° with the addition of standard *n*-paraffins. Before the introduction of each sample, the retention distance of methane was determined, and this value was subtracted from the retentions of the analysed samples. The measurements of the retention distances were carried out with an accuracy of ± 0.05 mm. Every sample was measured three times and the mean values were rounded off to whole numbers (Tables I and II).

RESULTS AND DISCUSSION

As no data of retention indices measurements of 2-thiaadamantanes were found in the literature, no comparison of the obtained results with other data could be made, and therefore agreement or differences between them could not be discussed.

The presence of sulphur in the molecules of the thiaadamantane series causes certain complications, as the presence of the sulphur heteroatom permits the existence of stereoisomers. As for the adamantane series, stereoisomers are known only for some ditopic derivatives. Two stereoisomers (a and b) are possible with monotopic thiaadamantane derivatives (4-alkyl-2-thiaadamantane, for example) and they do exist. Ditopic thiaadamantane derivatives (4,8-dialkyl-2-thiaadamantane, for example) have three stereoisomers (c, d and e) when both alkyl groups are the same, and when the alkyl groups are different four stereoisomers are possible. All these considerations apply to alkylation on the secondary carbon atoms. At present, the conformation of these stereoisomers is still being studied, so in this paper their denomination has to be limited to the letters a, b, c, d and e only, which refer to the increase in the elution times of single stereoisomers.

For methylene-2-thiaadamantane and 4,8-dimethylene-2-thiaadamantane, the existence of stereoisomers is not possible.

Tables I and II give the results for all the measured saturated 2-thiaadamantane homologues and show that, with the exception of 4-ethyl-2-thiaadamantane, they can be separated satisfactorily, including the single stereoisomers. The same applies to the series of alkene 2-thiaadamantane homologues.

The difference between the Kováts retention indices of the 2-thiaadamantane homologues on the two stationary phases is related to the polarity of the particular

TABLE I

KOVÁTS RETENTION INDICES (*I*) OF 2-THIAADAMANTANE COMPOUNDS ON APIEZON L

Compound	*Isomer*	*Temperature, T (°C)*			$10\left(\frac{\delta I}{\delta T}\right)$
		190	*200*	*210*	
2-Thiaadamantane		1429	1439	1449	10
4-Methyl-2-thiaadamantane	a	1493	1505	1517	12
	b	1505	1518	1531	13
4-Ethyl-2-thiaadamantane	a	1573	1585	1598	12.5
	b	1591	1604	1617	13
4,8-Dimethyl-2-thiaadamantane	c	1559	1571	1582	11.5
	d	1570	1582	1593	11.5
	e	1581	1593	1604	11.5
4,8-Diethyl-2-thiaadamantane	c	1718	1730	1743	12.5
	d	1732	1745	1757	12.5
	e	1746	1759	1772	13
4,8-Dipropyl-2-thiaadamantane	c	1871	1882	1894	11.5
	d	1889	1900	1912	11.5
	e	1906	1918	1930	12
4,8-Dibutyl-2-thiaadamantane	c	2057	2070	2082	12.5
	d	2080	2092	2104	12
	e	2103	2115	2128	13
4-Methylene-2-thiaadamantane		1462	1473	1484	11
4-Ethylidene-2-thiaadamantane	a	1556	1563	1574	9
	b	1569	1577	1588	9.5
4,8-Dimethylene-2-thiaadamantane		1487	1498	1509	11
4,8-Diethylidene-2-thiaadamantane	c	1645	1658	1670	12.5
	d	1654	1667	1679	12.5
	e	1663	1677	1689	13
4,8-Dipropylidene-2-thiaadamantane	c	1787	1799	1810	11.5
	d	1802	1814	1825	11.5
	e	1817	1828	1839	11
4,8-Dibutylidene-2-thiaadamantane	c	1962	1973	1983	10.5
	d	1985	1995	2005	10
	e	2010	2020	2030	10

molecule. In comparison with adamantane, the sulphur heteroatom in the thiaadamantane molecule causes an increase in the Kováts retention index and this effect takes place even in the case of homologues in the thiaadamantane series. A comparison of Kováts retention indices of 4-alkyl-2-thiaadamantane and of the corresponding adamantanes substituted in the 2-position is shown in Table III. For adamantane hydrocarbons, only results for Carbowax 20M and SE-30 have been published[12] and therefore in Table III the values obtained on Apiezon L at 190° are compared with the published values obtained on SE-30. However, the polarities of these two phases are similar; the slight difference between them may result in different absolute values, but the agreement of relative values is very good, as can be seen in Table III.

TABLE II

KOVÁTS RETENTION INDICES (*I*) OF 2-THIAADAMANTANE COMPOUNDS ON POLYPHENYL ETHER 6 P5E

Compound	*Isomer*	*Temperature, T (°C)*			$10\left(\frac{\delta I}{\delta T}\right)$
		190	*200*	*210*	
2-Thiaadamantane		1667	1682	1700	16.5
4-Methyl-2-thiaadamantane	a	1723	1735	1751	14
	b	1741	1753	1770	14.5
4-Ethyl-2-thiaadamantane	a	1800	1811	1825	12.5
	b	1828	1839	1853	12.5
4,8-Dimethyl-2-thiaadamantane	c	1774	1789	1801	13.5
	d	1792	1807	1819	13.5
	e	1810	1825	1837	13.5
4,8-Diethyl-2-thiaadamantane	c	1919	1932	1944	12.5
	d	1944	1958	1971	13.5
	e	1971	1985	1998	13.5
4,8-Dipropyl-2-thiaadamantane	c	2052	2063	2074	11
	d	2087	2098	2109	11
	e	2121	2133	2144	11
4,8-Dibutyl-2-thiaadamantane	c	2214	2226	2237	11.5
	d	2260	2273	2284	12
	e	2307	2318	2331	12
4-Methylene-2-thiaadamantane		1724	1737	1753	14.5
4-Ethylidene-2-thiaadamantane	a	1814	1828	1841	13.5
	b	1833	1848	1861	14
4,8-Dimethylene-2-thiaadamantane		1768	1780	1793	12.5
4,8-Diethylidene-2-thiaadamantane	c	1922	1934	1945	11.5
	d	1936	1948	1960	12
	e	1949	1961	1974	12.5
4,8-Dipropylidene-2-thiaadamantane	c	2053	2063	2075	11
	d	2075	2085	2099	11.5
	e	2097	2107	2120	11.5
4,8-Dibutylidene-2-thiaadamantane	c	2216	2227	2238	11
	d	2249	2260	2272	11.5
	e	2284	2295	2307	11.5

TABLE III

HOMOMORPHIC FACTORS (*H*) OF 2-THIAADAMANTANES ON APIEZON L – SE-30

Compound		$H_{190} = I_{TA} - I_A$
TA	*A*	
2-Thiaadamantane	Adamantane	276
4-Methyl-2-thiaadamantane*	2-Methyladamantane	271
4-Ethyl-2-thiaadamantane*	2-Ethyladamantane	268
4-Methylene-2-thiaadamantane	2-Methyleneadamantane	265
4-Ethylidene-2-thiaadamantane*	2-Ethylideneadamantane	269

* b isomer.

TABLE IV

HOMOLOGOUS INCREMENTS OF KOVÁTS RETENTION INDICES FOR CH$_2$ GROUPS

Compound	*Isomer*	I_{CH_2} *(200°)*	
		Apiezon L	*Polyphenyl ether*
4-Methyl-2-thiaadamantane	a	66	53
	b	79	71
4,8-Dimethyl-2-thiaadamantane	c	65	53
	d	70	62
	e	76	71
4-Ethyl-2-thiaadamantane	a	73	64
	b	82	78
4,8-Diethyl-2-thiaadamantane	c	72	62
	d	76	69
	e	80	76
4,8-Dipropyl-2-thiaadamantane	c	74	63
	d	77	69
	e	79	75
4,8-Dibutyl-2-thiaadamantane	c	79	67
	d	81	74
	e	84	79

From the chromatographic point of view, both dialkylthiaadamantane and dialkenylthiaadamantane form simple homologous series, as shown in Fig. 1.

The difference between the Kováts retention indices of single stereoisomers (see Table IV) is almost double when polyphenyl ether is used as the stationary phase

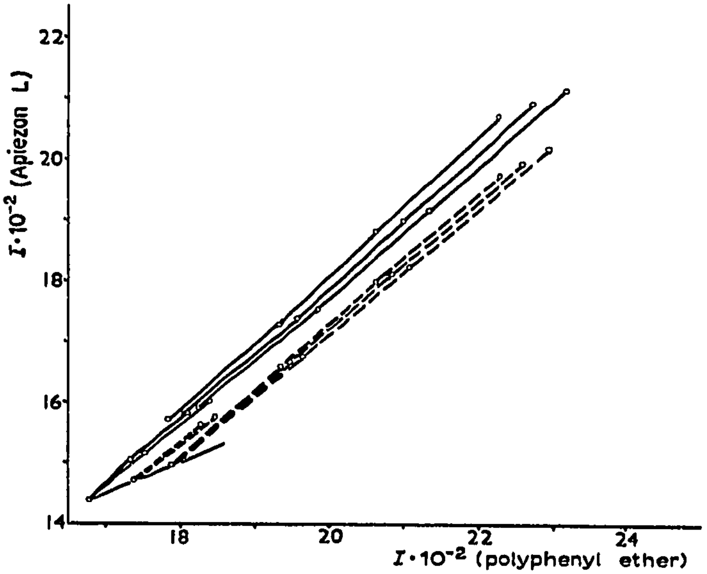

Fig. 1. Kováts retention indices of the 2-thiaadamantanes on Apiezon L and polyphenyl ether. Solid line, alkyl derivatives; broken line, alkylidene derivatives. Temperature, 200° C.

in comparison with the values when Apiezon L is used. These results represent the difference between the Kováts retention indices of alkyl-2-thiaadamantane and 2-thiaadamantane divided by the number of carbon atoms in the alkyl group. With an increase in the length of the alkyl chain, the value of the increment for the CH_2 group increases slightly and ascends uniformly in the case of both of the phases used.

CONCLUSION

We were successful in obtaining good results for the gas chromatographic behaviour of the 2-thiaadamantane, dialkenyl-2-thiaadamantane and dialkyl-2-thiaadamantane series on a non-polar and a medium polar phase. For the monotopic homologues, only two members of each series were available, so it is not possible to draw more general conclusions in this case.

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