

Short communication

## Prediction of gas chromatographic retention indices of 2,4-dinitrophenylhydrazones

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### Abstract

Kováts retention indices ( $I$ ) of  $C_1$ – $C_8$  aldehydes and ketones and their 2,4-dinitrophenylhydrazones (DNPHs) were determined. The temperature gradient of the retention indices of keto hydrazones is higher than that of aldehyde hydrazones, hence the separation of certain co-eluting hydrazones is possible by changing the elution temperature. The retention index difference between the  $E$ - and  $Z$ -isomers increases with increasing asymmetry in the groups attached to the hydrazo carbon atom. The slope  $a$  in the equation  $I_{\text{DNPH}} = aI_{\text{oxo}} + b$  is near unity for not heavily branched aldehyde DNPHs, whereas for keto  $E$ -isomers it is less than unity and changes with the structure.

### Introduction

As volatile aldehydes and ketones are present in low concentrations in some matrices (e.g., automobile exhaust, foods and beverages, atmospheric air), their preconcentration is necessary before analysis. Derivatization to 2,4-dinitrophenylhydrazones (DNPHs) and subsequent determination by GC [1–5] and HPLC [6–10] is a generally used method.

The DNPHs of aldehydes and asymmetric ketones have  $E$  and  $Z$  stereoisomeric forms. The  $E$ -isomer is the form in which atoms or groups attached to the two ends of the  $C=N$  double bond and preferred to the sequence rule are on the opposite sides [11] (Fig. 1). The  $R_1$  is a group preferred over  $R_2$ ;  $R_1 = H$  in aldehydes. For DNPH isomers,  $R_3 = H$  and  $R_4 = C_6H_3(NO_2)_2$ . The DNPHs are generally, syn-

thesized in acidic medium [12–15] with the formation of both  $E$  and  $Z$ -isomers.

Kováts retention indices of DNPHs were measured on a slightly polar packed column [16], where, owing to the insufficient resolving power of the column, the  $E$  and  $Z$ -isomers could not be separated. On a more efficient capillary column, however, this separation problem was avoided [1–3, 17]. A retention index system using the *anti*

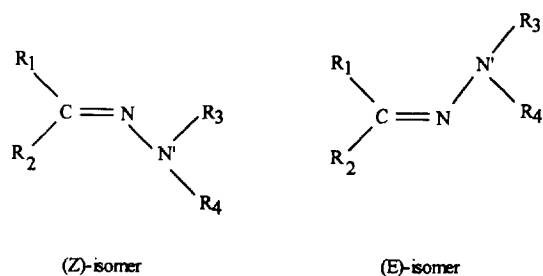


Fig. 1. Structural formulae of ( $Z$ )- and ( $E$ )-2,4-dinitrophenylhydrazone.

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isomers of the DNPHs of linear alkanals as reference components has been proposed; the retention indices were determined on an SE-30 column [17].

Physico-chemical data, such as boiling point, refractive index, dipole moment and Van der Waals volume, and topological indices are generally used for the prediction of retention indices [18–20]. In this case, owing to the complicated nature of the molecule and the lack of physical data, the only attempt was a qualitative correlation of the retention indices of the DNPHs with the carbon numbers of the starting oxo compounds [16].

This paper reports the Kováts retention indices of some aldehydes and ketones and their DNPH isomers, together with the temperature gradients measured on an apolar column. We have made an attempt to estimate the retention indices of DNPHs from the experimental retention indices of the aldehydes and ketones via an empirical equation, i.e., to check the validity of an additivity rule, and to find an explanation for the difference in GC behaviour of the (*E*)- and (*Z*)-DNPH isomers.

## 2. Experimental

### 2.1. Materials

The DNPHs were synthesized by the literature method [21]. The aldehydes, ketones and reference  $C_{20}$ – $C_{28}$  hydrocarbons were purchased from Fluka (Buchs, Switzerland) and Aldrich-Chemie (Steinheim, Germany).

### 2.2. Gas chromatography

The retention indices of DNPH isomers were determined on a 25 m  $\times$  0.32 mm I.D. dimethylpolysiloxane column (film thickness 0.25  $\mu$ m, FSOT; Supelco), whereas those of aldehydes and ketones were determined on a 50 m  $\times$  0.32 mm I.D. column (0.52  $\mu$ m, fused-silica open tubular; Hewlett-Packard). The retention indices were measured with a Hewlett-Packard Model 5890 Series II gas chromatograph with an

HP 3365 Series II ChemStation. A flame ionization detector and nitrogen carrier gas were used. The injector temperature was 240°C and it was used in split mode, with a splitting ratio of 1:40.

The Kováts retention indices were calculated as described previously [22]; the fitting parameters and the statistics were calculated by means of PSI-PLOT (Polysoft International). The temperature gradients of the retention indices of the DNPHs were calculated from the data obtained in the range 180–230°C and those of oxo compounds from the data measured at 40–90°C (for some low-boiling compounds, 30–80°C). In both instances, measurements were made at 10°C intervals. The boiling points of aldehydes and ketones were taken from Ref. [23].

## 3. Results and discussion

The Kováts retention indices of the aldehydes and ketones studied and their DNPHs are listed together with their temperature gradients in Table 1.

At 200°C (a characteristic temperature for the separation of small- and medium-sized DNPHs), 2-propanone and 2-propanal were not separated, but, as a consequence of their different temperature gradients, a baseline separation was possible at 160°C.

The ketone DNPHs have higher temperature gradients (aldehyde DNPHs,  $10.4 \pm 0.7$  i.u. (index unit) per 10°C,  $n = 14$ ; ketone DNPHs,  $11.7 \pm 0.5$  i.u. per 10°C,  $n = 12$ ; the exceptionally high value of cyclohexane DNPH was not included in the calculations). This behaviour may give a possibility for the separation of closely eluting compounds.

The retention index of the (*Z*)-DNPH isomer was always lower than that of the *E*-isomer (Table 1). This behaviour was explained earlier by the more exposed nature of the *Z*-isomer [17,24].

The difference between the retention indices of the stereoisomers is largely dependent on the difference in the substitution patterns of the alkyl chains of  $R_1$  and  $R_2$ , i.e., the greater the difference in the carbon numbers of  $R_2$  and  $R_1$

Table 1  
Kováts retention indices ( $I$ ) and their temperature gradients  $[(dI/dT) \cdot 10]$  for aldehydes and ketones and their DNPH derivatives

Compound	DNPH isomers			Oxo compounds		$dI^c$
	$I^a$	$(dI/dT) \cdot 10$	$I_E - I_Z$	$I^b$	$(dI/dT) \cdot 10$	
Formaldehyde	1905	10.5	–			
Acetaldehyde	2035	10.9	21	365.3	–0.3	1674
2-Propanone	2121	11.8	–	471.9	–0.4	1654
2-Propenal	2121	10.3	–	466.9	–0.2	1657
Propanal	2129	10.7	32	474.6	–0.3	1658
2-Methylpropanal	2173	9.8	33	542.2	0.1	1629
2,2-Dimethylpropanal	2202	9.2		584.6	0.6	1610
2-Butanone	2207	11.4	16	577.0	–0.1	1631
Butanal	2223	9.6	39	573.3	0.3	1646
3-Methyl-2-butanone	2260	11.8		642.3	0.3	1613
3-Methylbutanal	2275	10.2	39	637.1	0.7	1629
2-Methylbutanal	2277	11	60	647.6	0.6	1621
3-Pentanone	2279	12.1	–	676.9	0.1	1601
2-Butenal	2288	12.0	–	628.9	1.0	1647
2-Pentanone	2294	12.5	30	667.1	0.1	1624
Pentanal	2325	10.6	45	676.5	0.4	1643
4-Methyl-2-pentanone	2331	11.4	22	721.9	0.4	1604
3-Hexanone	2350	11.7	12	765.4	0.3	1581
2,4-Dimethyl-3-pentanone	2356	10.9	–	779.5	1.0	1563
2-Hexanone	2388	11.6	37	768.8	0.2	1616
3-Heptanone	2443	11.4	20	866.3	0.4	1572
5-Methyl-2-hexanone	2449	11.5	42	837.3	0.5	1604
2-Heptanone	2483	11.3	45	869.1	0.4	1609
Hexanal	2426	10.6	48	778.6	0.6	1640
2-Furancarboxaldehyde	2486	13.1	36	816.4	0.6	1661
Cyclohexanone	2545	18.4	–	868.0	3.5	1632
Octanal	2626	10.4	58	981.1	0.8	1634

<sup>a</sup>  $I_{(E)-DNPH}$  at 200°C.

<sup>b</sup> Measured at 70°C.

<sup>c</sup>  $I_{(E)-DNPH} - I(\text{analogous oxo compound, extrapolated})$  at 200°C.

(dC), the greater is the difference in the retention indices of the *E*- and *Z*-isomers (Fig. 2). Branching at the carbon atom next to the C=N double bond has the most significant effect on the retention behaviour and formation of the *Z*-isomer (see the great difference in the retention indices of (*E*)- and (*Z*)-2-methylbutanal DNPH; formation of the thermodynamically and kinetically unfavourable (*Z*)-2,2-dimethylpropanal, (*Z*)-2,2-dimethyl-3-butanone [17] and (*Z*)-3-methyl-2-butanone DNPHs was not observed).

In the *Z*-isomers, the larger group  $R_2$  is *cis* to N-( $R_3, R_4$ ), so there may be a non-bonded interaction between these groups. This effect was

observed for the *NN*-dimethylhydrazones [25] and *N*-methyl-*N*-phenylhydrazones [26] but not for the *N*-methylhydrazones [27] and hydrazones ( $R_1, R_2 = H$ ) [28]. As a consequence, the aldehyde *N,N*-dimethyl- and *N*-methylhydrazones show no detectable isomerization around the C=N double bond [25,26]; they exist in the *E* form.

The predictability of retention indices of DNPHs from physical data is very limited as most of these data are not available but, as the compounds studied differ only in the “oxo part” of the molecules, the retention index of the whole molecule can be characterized:

(a) by the *boiling point* of the analogous

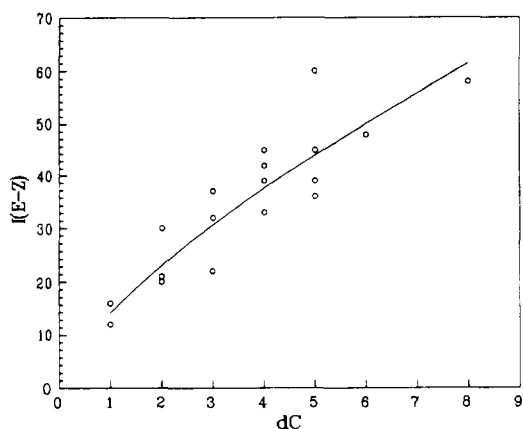


Fig. 2. Correlation between the retention index difference of the (*E*)- and (*Z*)-DNPH isomers and the difference in the carbon numbers of groups  $R_2$  and  $R_1$ .

aldehyde or ketone as the generally best descriptor of dispersive forces:

$$I_{(E)-DNPHs} = (3.51 \pm 0.12)b.p.(oxo) + (1945 \pm 13) \\ n = 27; r = 0.9866; s = 27 \quad (1)$$

where  $n$  is the number of data involved in the calculations,  $r$  is the correlation coefficient and  $s$  is the standard error of estimation;

(b) by the retention index of the aldehyde or ketone molecule from which the DNPH was formed:

$$I_{(E)-DNPHs} = aI_{oxo} + b \quad (2)$$

where  $a$  and  $b$  are expected to be constant for a given class of compounds. This additivity rule was observed to hold when the retention indices of amides were correlated with those of the amines from which they were formed [29].

Eq. 1 is expected to hold when new types of interactions are not formed in any of the molecules studied or between some solute and the stationary phase.

The difference between the  $I$  values of DNPHs and the analogous oxo compounds is  $1625 \pm 28$  at  $200^\circ\text{C}$  (Table 1). Substituting the measured retention indices into Eq. 2 (the  $I$  values of oxo compounds were extrapolated to  $200^\circ\text{C}$ ), we obtain

$$I_{(E)-DNPH} = (0.91 \pm 0.03)I_{oxo} + (1688 \pm 22) \\ n = 26; r = 0.9864; s = 24 \quad (3)$$

Inspection of the calculated  $dI$  values (Table 1) and the deviation of the slope  $a$  in Eq. 3 from unity shows that the  $I_{DNPH}$  vs.  $I_{oxo}$  function has different slopes for the investigated ketones and aldehydes (Fig. 3). The  $dI$  value gradually decreases with increasing asymmetry and branching in  $R_1$  and  $R_2$  (e.g. 2-butanone  $\rightarrow$  2-heptanone; pentanal  $\rightarrow$  2,2-dimethylpropanal); a larger effect was observed for the ketone hydrazones.

The slope of Eq. 2 is near unity for aldehydes and their DNPHs:

$$I_{(E)-DNPH} = (0.97 \pm 0.03)I_{ald} + (1662 \pm 21) \\ n = 13; r = 0.9939; s = 19 \quad (4)$$

whereas for ketones (the behaviour of cyclohexanone DNPH is similar to that of aldehyde DNPHs) the additivity does not seem to hold:

$$I_{(E)-DNPH} = (0.84 \pm 0.04)I_{ketone} + (1718 \pm 32) \\ n = 12; r = 0.9870; s = 18 \quad (5)$$

We assume that the small anomaly in Eq. 2 (Fig. 3) may be explained by the interactions present in ketone hydrazones, which are not significant in aldehyde hydrazones.

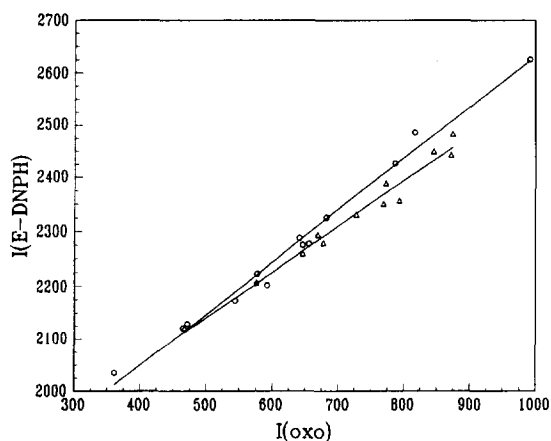


Fig. 3. Dependence of the retention indices of the (*E*)-DNPH (○) and the analogous aldehyde or ketone (△) at  $200^\circ\text{C}$ .

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