JOURNAL OF THE CHEMICAL SOCIETY

Chemical Communications

Number 14
1985

Shape Similarity Effect on the Strength of Weak Interactions of a Phenyl Group with Unsaturated Hydrocarbons and Ethers

Tadashi Endo,* Masato M. Ito, and Takao Namiki
College of Science and Engineering, Aoyama Gakuin University, Chitosedai, Setagaya-ku, Tokyo 157, Japan

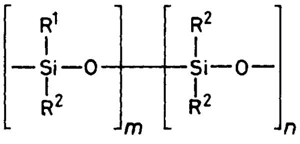
Gas chromatographic studies for pairs of six-membered-ring (cyclic) and straight-chain hydrocarbons and ethers have shown that the weak interactions of the phenyl group in a stationary liquid are more attractive with the cyclic hydrocarbons and ethers, which are similar in shape to the phenyl group, than with the straight-chain hydrocarbons and ethers, each pair containing the same number of π-electrons or oxygen atoms.

Recently, we have suggested the importance of three-dimensional shape similarity between interacting groups of reacting molecules in specific molecular recognition.[1] This 'similarity recognition hypothesis' led us to examine the correlation of shape similarity between interacting groups with the strength of weak interactions between them, since shape-specific weak interactions have been suggested to be responsible for specific molecular recognition.[2] We have studied the retention time in gas–liquid partition chromatography for various hydrocarbons containing different numbers of π-electrons or oxygen atoms, and report here that the weak interactions of a phenyl (Ph) group are more attractive with the six-membered-ring (cyclic) hydrocarbons, which are similar in three-dimensional shape to the Ph group, than with the corresponding straight-chain hydrocarbons.

As stationary liquid phases we used a pair of silicone oils [(**1**) and (**2**)]† with and without a Ph group. The samples employed were a variety of cyclic (**3**) and straight-chain (**4**) hydrocarbons and ethers, each having a different number of π-electrons or oxygen atoms. The relative retention (α_x) was defined as the ratio of the retention time‡ for (**3**) or (**4**) to that for n-hexane (**4f**) as the reference, where $x = 1$ or 2, depending on the nature [(**1**) or (**2**)] of the stationary liquid phase employed.

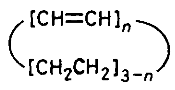
The α_1 and α_2 values were measured at various temperatures. Plots of ln α_x against T^{-1} showed a straight line for each sample pair examined. Since the relationship $\ln \alpha_x = -\Delta\Delta H_x/RT + C$ holds, where $\Delta\Delta H_x$ is the difference in molar heat of solution between samples (**3**) or (**4a**—**e**) and (**4f**) in liquid x,[3,4] the slope of the plots yields $-\Delta\Delta H_x/R$. Though the $\Delta\Delta H_x$ itself involves the difference in heat of vaporisation between samples (**3**) or (**4a**—**e**) and (**4f**), the difference is cancelled by subtracting $\Delta\Delta H_1$ from $\Delta\Delta H_2$.[3] Thus, the $\Delta\Delta H^{\mathrm{t}}$ ($= \Delta\Delta H_2 - \Delta\Delta H_1$) can be regarded as a measure of the difference in the weak interactions of the Ph group in (**2**) between (**3**) or (**4a**—**e**) and (**4f**).[3]

Figure 1 plots the $\Delta\Delta H^{\mathrm{t}}$ values for cyclic (**3a**—**c**) and straight-chain unsaturated hydrocarbons (**4a**—**c**), together with those for (**3f**)[3] and (**4f**), against the number of π-electrons in the samples. The $\Delta\Delta H^{\mathrm{t}}$ values are negative for all the



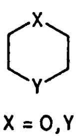
$$\left[-\overset{R^1}{\underset{R^2}{\mathrm{Si}}}-\mathrm{O}-\right]_m\left[-\overset{R^2}{\underset{R^2}{\mathrm{Si}}}-\mathrm{O}-\right]_n$$

(**1**) $R^1 = R^2 = Me$
(**2**) $R^1 = Me, R^2 = Ph$ ($m:n = 1:1$)



$H[CH{=}CH]_n[CH_2CH_2]_{3-n}H$

(**3a**) $n = 1$	(**4a**) $n = 1$
(**3b**) $n = 2$	(**4b**) $n = 2$, *trans*
(**3c**) $n = 3$	(**4c**) $n = 3$, *trans*
(**3f**) $n = 0$	(**4f**) $n = 0$



$MeXCH_2CH_2YMe$

(**3d**) $X = O, Y = CH_2$	(**4d**) $X = O, Y = CH_2$
(**3e**) $X = Y = O$	(**4e**) $X = Y = O$

---

† Silicone oils were used as the stationary liquid phases: (**1**), Silicone OV-101 (100% Me); (**2**), Silicone OV-25 (75% Ph and 25% Me). These were coated on acid-treated Celite 545 in a weight ratio of 1 to 5, and the stationary phases were packed in stainless-steel tubes (3 mm internal diameter × 2 m). The carrier gas was nitrogen with a flow rate of 20 ml min^{-1}.

‡ Retention time was measured from the methane peak to correct for the free space in the system.

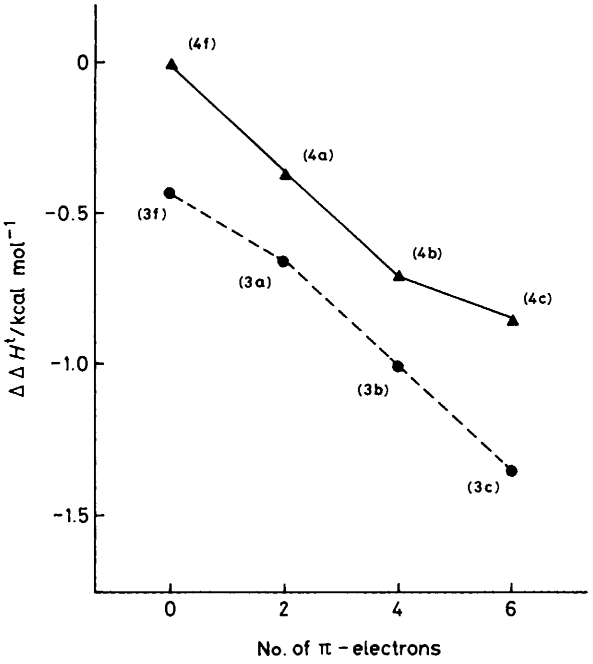


Figure 1. Plot of $\Delta\Delta H^t$ for cyclic (**3**) and straight-chain C_6 hydrocarbons (**4**) against their numbers of π-electrons. Samples used are cyclohexene (**3a**), hex-1-ene (**4a**), cyclohexa-1,3-diene (**3b**), hexa-1,3-diene (**4b**), benzene (**3c**), hexa-1,3,5-triene (**4c**), cyclohexane (**3f**),[3] and n-hexane (**4f**). The experimental errors (standard deviation) range from ±0.02 [for the pair (**3a**)–(**4f**)] to ±0.06 kcal mol^{-1} [for the pair (**3b**)–(**4f**)]. Temperature range: 70—120 °C.

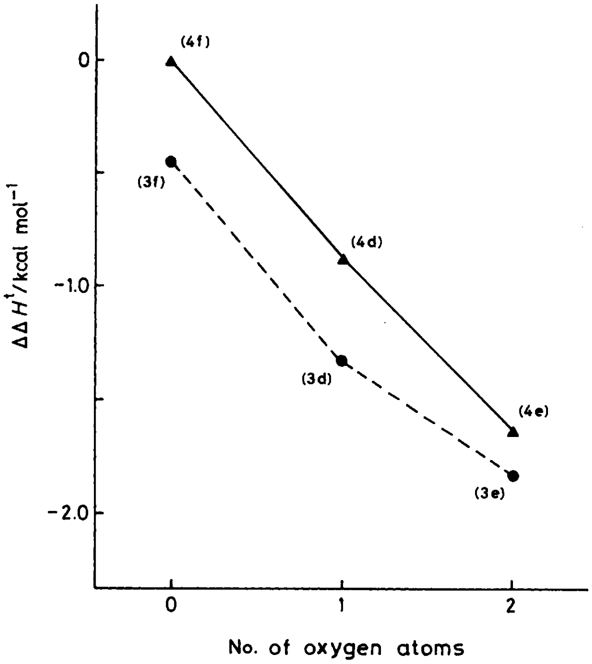


Figure 2. Plot of $\Delta\Delta H^t$ for cyclic (**3**) and straight-chain ethers (**4**) against their numbers of oxygen atoms. Samples used are tetrahydropyran (**3d**), 1-methoxybutane (**4d**), 1,4-dioxane (**3e**), 1,2-dimethoxyethane (**4e**), cyclohexane (**3f**),[3] and n-hexane (**4f**). The experimental errors (standard deviation) range from ±0.03 [for the pair (**3d**)–(**4f**)] to ±0.04 kcal mol^{-1} [for the pair (**4e**)–(**4f**)]. Temperature range: 70—120 °C.

sample pairs examined, and decrease with an increase in number of π-electrons. Of particular interest is the finding that, when the samples (**3**) and (**4**) have equal numbers of π-electrons, the $\Delta\Delta H^t$ values are more negative for cyclic hydrocarbons (**3**) than for straight-chain hydrocarbons (**4**) by *ca.* 0.3 kcal mol^{-1} [*e.g.*, −0.66 ± 0.02 kcal mol^{-1} for (**3a**) − (**4f**) and −0.35 ± 0.04 kcal mol^{-1} for (**4a**) − (**4f**)].§

Further, the data in Figure 2 clearly indicate that the $\Delta\Delta H^t$ values are more negative for cyclic ethers (**3d,e**) than for straight-chain ethers (**4d,e**) when (**3d,e**) and (**4d,e**) have equal numbers of oxygen atoms.

The weak interactions of the Ph group in liquid (**2**) with samples (**3**) and (**4**) become more attractive as the number of π-electrons increases (Figure 1), probably reflecting the π-electron interactions;¶ the increase in strength of the above interactions with increasing numbers of oxygen atoms in the samples (Figure 2) would be due to multipole–induced multipole interactions, as suggested by Stoddart *et al.*[5]|| Moreover, examination of Corey–Pauling–Koltun (CPK) molecular models indicates that a Ph group bears closer resemblance in three-dimensional shape to cyclic samples (**3**) than to straight-chain samples (**4**).

On the basis of the results and discussions presented here, we propose that the weak interactions of a Ph group become more attractive with a group which resembles the Ph group in three-dimensional shape. This 'shape similarity effect' on weak interactions is assumed to underlie the 'similarity recognition hypothesis.'[1]

Received, 26th March 1985; Com. 408

References

1 T. Endo, H. Tasai, K. Miyazawa, M. Endo, K. Kato, A. Uchida, Y. Ohashi, and Y. Sasada, *J. Chem. Soc., Chem. Commun.*, 1983, 636; T. Endo, 'The Role of Molecular Shape Similarity in Specific Molecular Recognition,' in 'Biomimetic and Bioorganic Chemistry,' Springer, Berlin, 1985.
2 T. Endo, Y. Takeda, T. Orii, T. Murata, M. Sakai, N. Nakagawa, and K. Nikki, *Chem. Lett.*, 1980, 1291.
3 T. Endo, M. M. Ito, Y. Yamada, H. Saito, K. Miyazawa, and M. Nishio, *J. Chem. Soc., Chem. Commun.*, 1983, 1430.
4 R. J. Laub and R. L. Pecsok, 'Physicochemical Applications of Gas Chromatography,' Wiley, New York, 1978.
5 J. F. Stoddart, *Chem. Soc. Rev.*, 1979, **8**, 85 and the references cited therein; S. E. Fuller, B. E. Mann, and J. F. Stoddart, *J. Chem. Soc., Chem. Commun.*, 1982, 1096.

---

§ 1 cal = 4.184 J.

¶ Considering that transfer of a benzene molecule from an environment of benzene molecules into an environment of saturated hydrocarbon molecules is suggested to be energetically unfavourable to an extent ranging up to *ca.* 1 kcal mol^{-1} (W. P. Jencks, 'Catalysis in Chemistry and Enzymology,' McGraw-Hill, New York, 1969, p. 415, and the references cited therein), the value of 0.93 ± 0.05 kcal mol^{-1} for the difference in $\Delta\Delta H^t$ between benzene (**3c**) and cyclohexane (**3f**) seems to be reasonable (Figure 1).

|| In this connection it is interesting to note that the interactions of a Ph group are no less attractive with 1,3-dioxane ($\Delta\Delta H^t$ = −1.86 ± 0.04 kcal mol^{-1}) than with its 1,4-isomer (**3e**) ($\Delta\Delta H^t$ = −1.82 ± 0.03 kcal mol^{-1}).