

Zakład Chemii Nieorganicznej. Instytut Chemii Podstawowych, Wydział Farmaceutyczny,
Akademia Medyczna w Lublinie
Kierownik: prof. dr Edward Soczewiński

Edward SOCZEWIŃSKI, Wojciech MARKOWSKI

Graphical Representation of Solvent Effects in the Investigation of Optical Activity: The Role of the Reference Compound

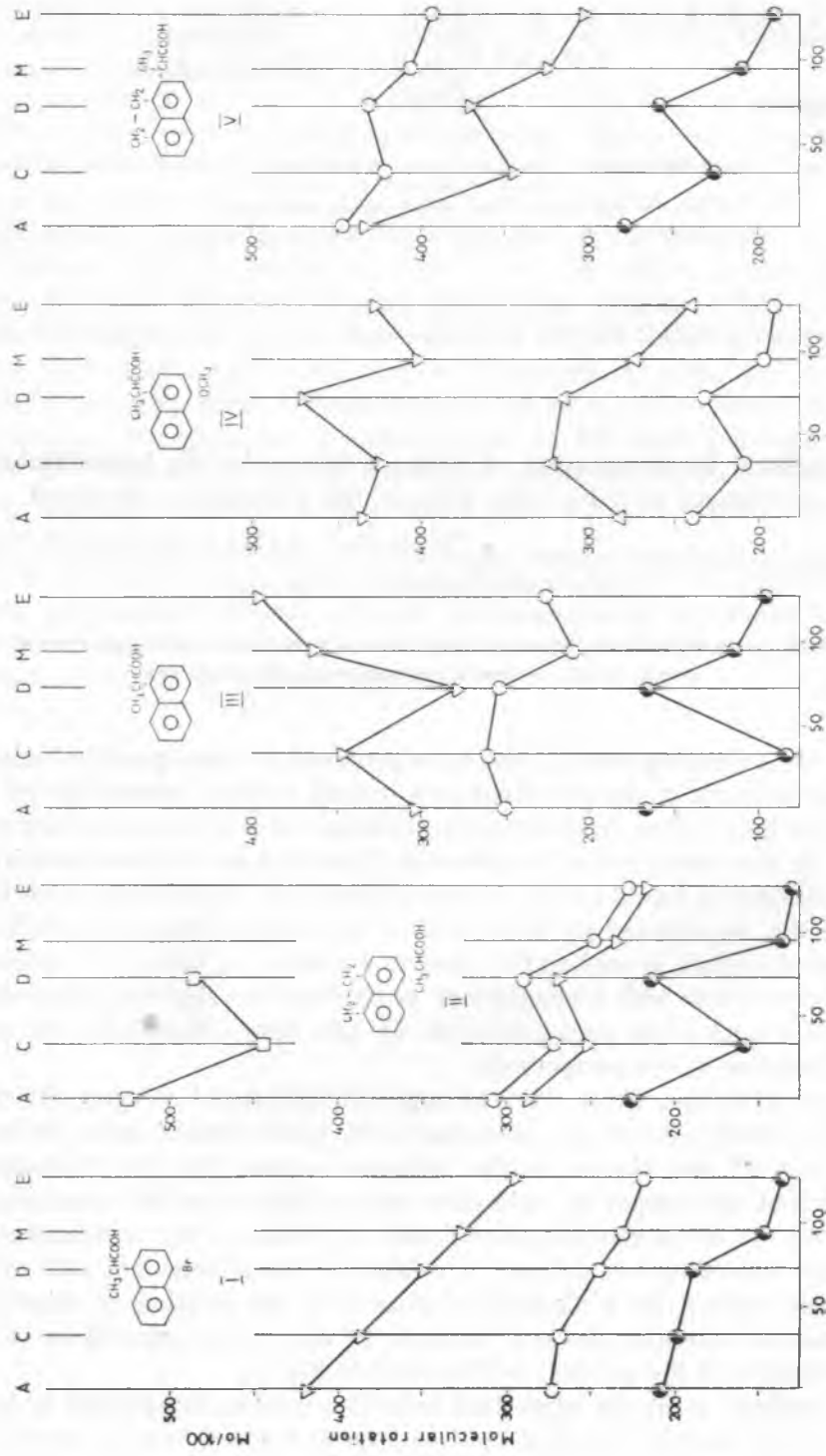
Graficzne przedstawienie wpływu rozpuszczalnika w badaniach aktywności optycznej:
rola wyboru substancji odniesienia

Графическое изображение влияния растворителя в исследованиях над оптической
активностью: значение выбора вещества отнесения

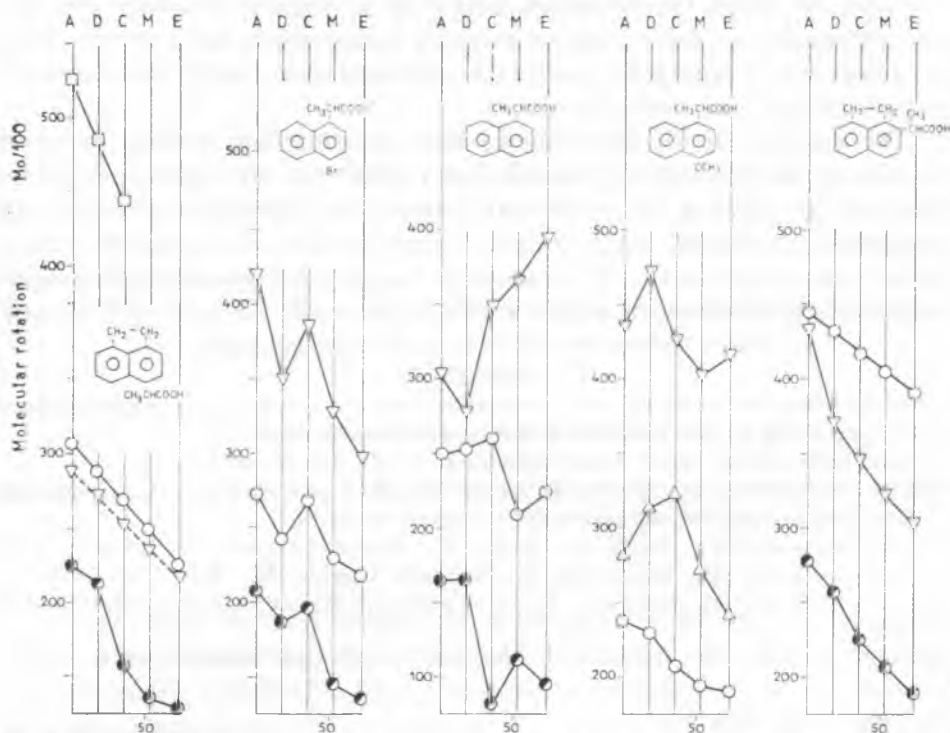
In the preceding note (1) one of us proposed to use a graphical method for the analysis of solvent effects on optical activity, arranging the solvents so that a linear correlation is obtained for a chosen reference solute, as in the classification of stationary liquids in gas chromatography (2) and solvents in liquid-liquid chromatography (3). The present note illustrates the importance of the choice of a suitable reference solute; the graphical method is applied this time to a number of carboxylic acids and their derivatives with acenaphthene or naphthalene skeleton, obtained by J a n c z e w s k i and co-workers (4—6), who also determined the molecular rotation of the compounds.

The substances show more strongly differentiated solvent effects on optical activity. As in the preceding note, p-nitrobenzyl ester of one of the acids (I) was chosen as the reference solute (Fig. 1). It should be noted that the choice of reference solute influences the regularity of "spectra" of the remaining solutes and, for instance, the arrangement of solvents subordinate to a linear correlation of the nitrobenzyl ester of acid II would reduce the irregularities caused by the position of chloroform between acetone and dioxane, however, at the cost of appearance of new irregularities in the spectra, as illustrated in Fig. 2.

It follows from the plots that even for related compounds it is not possible to arrange the solvents assuming a single reference solute. Ne-



vertheless, clear parallelism of the spectra is often apparent for the derivatives of a given acid (for instance, I, II, V); in some cases, the omission of one of the solvents (for instance, chloroform in Fig. 1, IV) would result in a more regular relationships, and in other cases parallel



Ryc. 2. Jak na ryc. 1; substancją odniesienia jest ester p-nitrobenzylowy kwasu II
Fig. 2. As in figure 1; the reference solute is p-nitrobenzyl ester of acid II

Ryc. 1. Rotacja molekularna pięciu prawoskrętnych kwasów (I—V) i ich pochodnych wykresiona jako funkcja różnicy rotacji molekularnych estru p-nitrobenzylowego kwasu I rozpuszczonego w acetonie ($M_0(A)/100$) i w czterech pozostałych rozpuszczalnikach ($M_0(i)/100$) w taki sposób, aby otrzymać dla substancji odniesienia linię prostą. Substancje oznaczono następująco: kwas $\circ$, amid $\bullet$, ester metylowy Δ , ester p-nitrobenzylowy ∇ , ester p-bromofenacylowy $\square$. Rozpuszczalniki oznaczono następująco: A-aceton, C-chloroform, D-dioksan, E-etanol, M-metanol

Molecular rotation of the dextrorotary acids (I—V) and their derivatives plotted against difference of molecular rotation of p-nitrobenzyl ester of acid I dissolved in acetone ($M_0(A)/100$) and in the four remaining solvents ($M_0(i)/100$), so that a straight line is obtained for the reference compound. The solutes are denoted as follows; acid $\circ$, amide $\bullet$, methyl ester Δ , p-nitrobenzyl ester ∇ , p-bromophenacyl ester $\square$. The solvents are denoted as follows; A-acetone, C-chloroform, D-dioxane, E-ethanol, M-methanol

changes for a pair of solvents is visible (e. g., for acetone and dioxane). These analogies are much more easily observed when the solvents are arranged after the proposed method, even for compounds of different types and the analysis of structural effects and solvation is thereby facilitated. Additional effects would be obtained by employing a series of mixed solvents, in which the solvation would be varied continuously and not discontinuously as for change of solvent; furthermore, for a series of binary solvents it would be possible to estimate more easily the accuracy and precision of the determinations.

The analysis of the plots shows that the graphical method provides promising results; further examples of regular parallel spectra could be obtained by plotting the molecular rotation of tetrahydroderivatives of compounds described in the former communication and prepared recently by J a n c z e w s k i (7). However, its application should be investigated on a larger number of solutes and solvents.

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STRESZCZENIE

Podano przykłady zastosowania metody graficznej w analizie wpływu rozpuszczalnika na skręcalność cząsteczkową związków organicznych. Rozpuszczalniki porządkowano w taki sposób, aby otrzymać prostą linię korelacyjną dla wybranej substancji wzorcowej. Zilustrowano wpływ wyboru odpowiedniej substancji wzorcowej dla regularnego przebiegu widm.

РЕЗЮМЕ

Предложенный Литтлевудом метод классификации стационарных фаз, применяемых в газовой хроматографии, был использован для анализа влияния растворителя на оптическую активность. Доказано, что этот метод может найти более широкое применение.