Studies on the formation of pyridine base—*n*-butanol complexes

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Intermolecular interactions occurring in pyridine base—*n*-butanol—benzene systems were investigated by the Job's method of continuous variations. Dielectric constants, densities, and refractive indices of the solutions were determined. The densities and refractive indices were additive properties of the examined systems. Deviations of the dielectric constants $\Delta\varepsilon$ from the additivity were due to the formation of the hydrogen-bonded complexes. It is shown that there is a relation between $\Delta\varepsilon$ values of the solutions, in which 1   1 complexes are exclusively formed, and pK_a values of the corresponding pyridine bases.

The formation of hydrogen-bonded complexes by pyridine bases has been investigated by various methods involving spectral [1, 2], dielectric [3—12], and calorimetric determinations [13, 14]. The investigations were carried out to elucidate the nature of hydrogen bonding between the components of the complexes and to obtain information regarding the electronic structure and steric properties of *N*-heteroaromatic compounds. In all these studies the starting point was the determination of the composition of the complexes and of their structure. The composition can be determined by the dielectric version of the Job's method [15], *i.e.* the so-called dielectric titrations [4—6, 8—12]. By means of this method it has been shown that pyridine forms 1   1 complexes with phenols [8], *o*-chlorobenzoic and 2-chloro-5-nitrobenzoic acids [6] in benzene solutions, whereas the composition of its complexes with acetic [10] and dichloroacetic acids in benzene depends on total concentration of the solutions. At low total concentrations 1   1 complexes are present, but in more concentrated solutions complexes having higher acid to pyridine molar ratios are formed. In chlorobenzene and benzylidene fluoride solutions pyridine forms 1   1 and 1   2 complexes with acetic acid, but only 1   1 complexes with valeric acid [5]. It has been shown by means of dielectric titrations [4] that in *n*-heptane, chlorobenzene, and benzylidene fluoride solutions pyridine forms 1   1 complexes with alcohols and that in the presence of an excess of alcohol the complexes having higher alcohol to pyridine molar ratios are formed.

For these reasons the elucidation of the effect of nature and position of substituents in pyridine ring on the composition and polarity of pyridine base—*n*-butanol complexes in benzene solutions was of interest. In the present work the complexes formed by *n*-butanol with pyridine, 2-, 3-, and 4-methylpyridines, 2,4- and 2,6-dimethylpyridines, quinoline, isoquinoline, and 2-, 3-, and 4-cyanopyridines were investigated by the Job's method of continuous variations, in which dielectric constants, densities, and refractive indices of the solutions were determined.

Experimental

Purifications of materials

Pyridine, methylpyridines, dimethylpyridines, quinoline, and isoquinoline were re-distilled before the preparation of the solutions. 2-Cyanopyridine was crystallized from petroleum ether and 3- and 4-cyanopyridines from benzene. n-Butanol was distilled from its mixture with magnesium shavings through a fractionating column described in [16]. Benzene was purified according to [16].

Determinations

In the Job's method an arbitrarily chosen intensive physical property of a ternary system consisting of substances A and B forming a complex and an inert solvent is determined as a function of molar concentration of A or B. In every solution used in this method the sum of molar concentrations of components A (c_A) and B (c_B) is kept constant ($c_A + c_B = c = $ const), whereas the contributions of c_A and c_B to the total concentration are variable. The percent concentration of component A

$$\left(\frac{c_A}{c_A + c_B} \times 100\% = \left(1 - \frac{c_B}{c_A + c_B} \right) \times 100\% \right)$$

varies from 0 to 100%.

Thus the extreme solutions have molar concentrations equal to the sum of concentrations of A and B in the remaining solutions.

For each examined pair of n-butanol (A)—pyridine base (B) we prepared a series of 9 ternary and 2 binary solutions in benzene (S). In the binary solutions $c_A = c_B = c$. In the ternary solutions the percent contributions of n-butanol concentrations to the total concentrations were: 10, 20, 30, 40, 50, 60, 70, 80, and 90%. The solutions were prepared by mixing suitable amounts (measured by a burette) of the binary solutions. Then the dielectric constants ε, refractive indices for sodium light n_D, and densities ϱ of the solutions were determined.

Determinations of the physical properties

The apparatus used for the determinations of ε and n_D was described in the previous communication [17]; the densities were determined by means of a pycnometer described in paper [18]. All the determinations of ε, n_D, and ϱ were carried out at 25°C.

Infrared spectra were obtained on a UR-10 (Zeiss, Jena) spectrophotometer.

## Results

We carried out the determinations for all the examined pyridine bases at the total concentration $c = 1$ mole/dm³, for unsubstituted pyridine also at $c = 0.1$, 0.5, 1.5, and 2.0 moles/dm³, and for isoquinoline at $c = 0.5$ mole/dm³. The results of determinations of ε are shown in Figs. 1—11 as the relation between $\Delta\varepsilon$ and the percent contribution of n-butanol concentration to the total concentration (dielectric titration curves). $\Delta\varepsilon$ Values, i.e. the differences between measured ε values and additive ε_{add} values were calculated by two methods.

Fig. 1. Dielectric titration curves for the
pyridine—n-butanol—benzene system.
$\Delta_1\varepsilon$ — full line; $\Delta_2\varepsilon$ — dashed line.
Total molar solute concentration: *1.* 0.1;
2. 0.5; *3.* 1.0; *4.* 1.5; *5.* 2.0 moles/dm³.
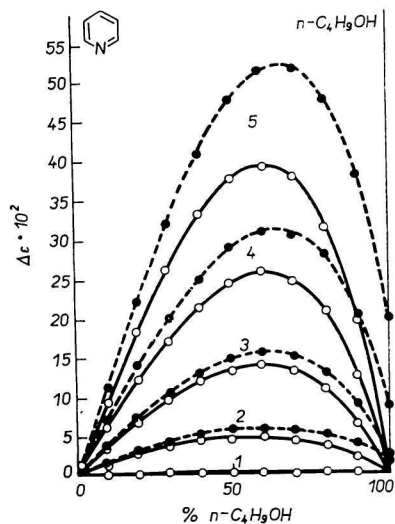
$$\varepsilon_{\text{add},1} = \varepsilon_2 + (\varepsilon_3 - \iota_2) \cdot \frac{c_A}{c_A + c_B}, \tag{1}$$

where ε_2 and ε_3 are the determined dielectric constants of pyridine base and n-butanol
solutions in benzene respectively.

$$_{,2} = \varepsilon_2 + (\varepsilon_{3,\text{calcd}} - \varepsilon_2) \cdot \frac{c_A}{c_A + c_B}, \tag{2}$$
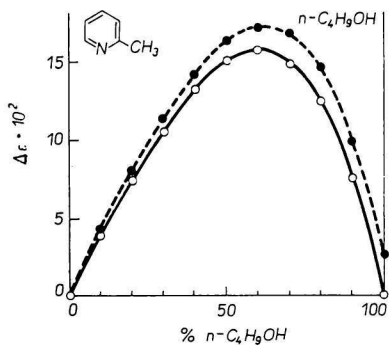

Fig. Dielectric titration curves for the
2-methylpyridine—n-butanol—benzene
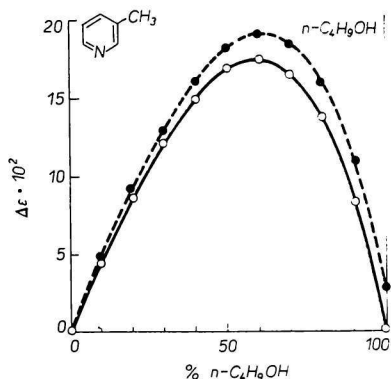system.
$c = 1$ mole/dm³.

Fig. 3. Dielectric titration curves for the
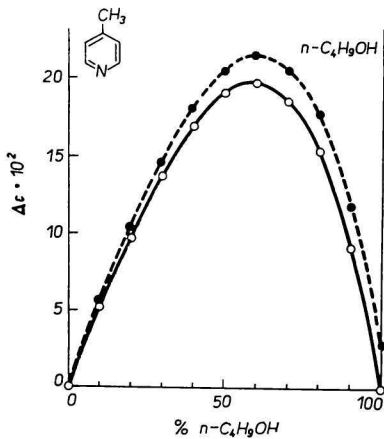3-methylpyridine—n-butanol—benzene
system.
$c = 1$ mole/dm³.

Fig. 4. Dielectric titration curves for the
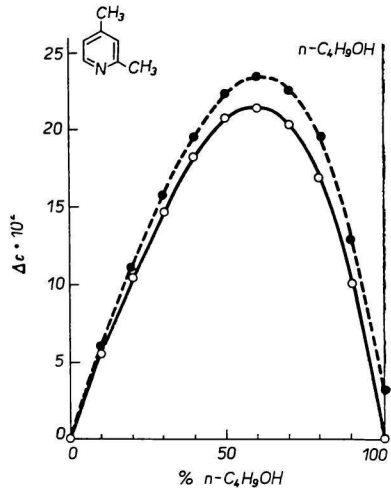4-methylpyridine — n-butanol — benzene
system.
$c = 1$ mole/dm³.

Fig. 5. Dielectric titration curves for the
2,4-dimethylpyridine — n-butanol —
— benzene system.
$c = 1$ mole/dm³.

where $\varepsilon_{3,\text{calcd}}$ is the dielectric constant of n-butanol in benzene calculated from the formula

$$\varepsilon_{3,\text{calcd}} = \varepsilon_1 + a_\varepsilon \cdot w_A,$$

where ε_1 is the dielectric constant of benzene, w_A is the weight fraction of n-butanol, and a_ε is the slope of the straight line expressing the relation between ε of the solution and w_A for small values of w_A; $a_\varepsilon = 4.060$ according to [19].
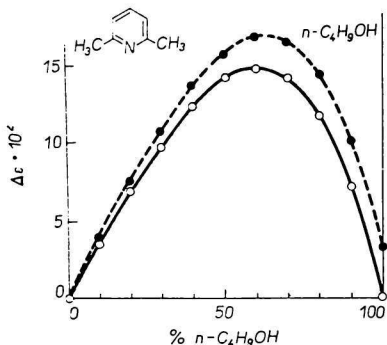

Fig. 6. Dielectric titration curves for the
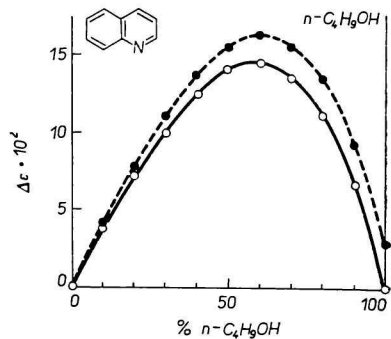2,6-dimethylpyridine — n-butanol —
— benzene system.
$c = 1$ mole/dm³.

Fig. 7. Dielectric titration curves for the
quinoline — n-butanol — benzene system.
$c = 1$ mole/dm³.

From the two ε_{add} values we calculated (by means of formulae $\Delta_1\varepsilon = \varepsilon - \varepsilon_{add,1}$ and $\Delta_2\varepsilon = \varepsilon - \varepsilon_{add,2}$) two different values of deviation of the dielectric constant from the additivity. $\Delta_2\varepsilon$ is a measure of all the possible kinds of the associations taking place in the considered solutions, i.e. the formation of $A-B$ complexes and multimerization, whereas $\Delta_1\varepsilon$ reflects first of all the complex formation processes.
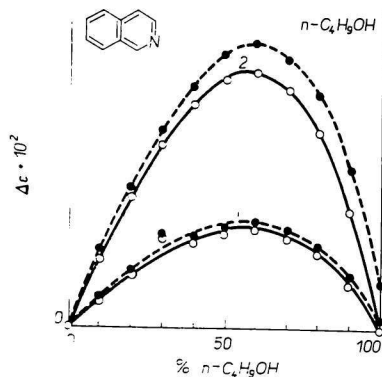

Fig. 8. Dielectric titration curves for the isoquinoline—n-butanol—benzene system.
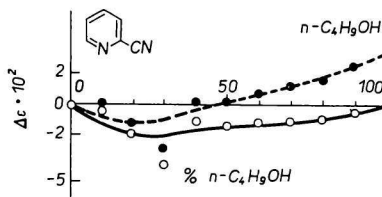Total molar solute concentration: 1. 0.5; 2. 1.0 mole/dm³.

Fig. 9. Dielectric titration curves for the 2-cyanopyridine—n-butanol—benzene system.
$c = 1$ mole/dm³.

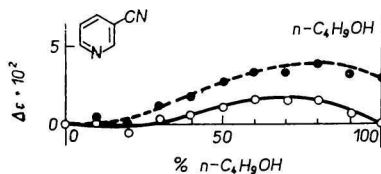Fig. 10. Dielectric titration curves for the 3-cyanopyridine—n-butanol—benzene system.
$c = 1$ mole/dm³.
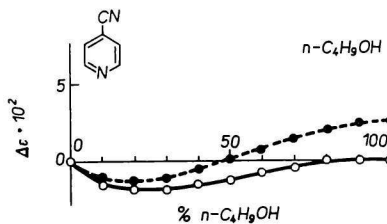
Fig. 11. Dielectric titration curves for the 4-cyanopyridine—n-butanol—benzene system.
$c = 1$ mole/dm³.

The density was a linear function (within the experimental error limits) of the percent contribution of n-butanol to the total concentration. With the exception of certain systems (containing quinoline, dimethylpyridines, and pyridine at higher total concentrations) in which the deviations from the additivity were slightly greater than the experimental error, n_D was also additive. All the determinations were carried out twice.

## Discussion

The lack of deviations of $\Delta\varrho$ and n_D from additivity and considerable values of $\Delta\varepsilon$ observed in the examined solutions indicate that the sensitivity of ε to intermolecular interactions is much higher than that of ϱ and n_D. This result of our investigation is in agreement with the observations reported by other authors [10, 20]. For this reason we will consider association processes taking place in the examined systems on the basis of dielectric titration curves (Figs. 1—11).

The dielectric titration curve for the system containing unsubstituted pyridine and having the total concentration $c = 0.1$ mole/dm³ has the simplest shape. In this case the $\Delta\varepsilon$ values are positive, the maximum corresponds to the solution containing equimolar amounts of pyridine and n-butanol, and the curve is symmetrical. This relation between $\Delta\varepsilon$ and the composition of the solution indicates that:

1. pyridine and n-butanol form the 1 1 (AB) complex,
2. the dipole moment of the complex μ_{AB} is greater than the square root of the sum of squares of dipole moments of n-butanol, μ_A and pyridine, μ_B

$$\mu_{AB} > \sqrt{\mu_A^2 + \mu_B^2}.$$

The probable structure of the complex is represented by the following formula

$$C_5H_5N \cdots H-O \diagdown$$
$$n\text{-}C_4H_9$$
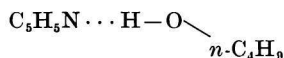
Since $\Delta\varepsilon$ values for the system having $c = 0.1$ mole/dm³ are low, we carried out measurements for higher total concentrations ($c = 0.5, 1.0, 1.5$, and 2.0 moles/dm³). As expected, $\Delta\varepsilon$ increased with increasing c, but at the same time the symmetry of the dielectric titration curves decreased (Fig. 1). The increase of c was accompanied by the shift of a maximum of $\Delta\varepsilon$ in the direction of solutions containing higher concentrations of n-butanol. This could be rationalized by postulating that in concentrated solutions of n-butanol the formation of the 1 1 (AB) complex is accompanied by the formation of complexes having higher n-butanol to pyridine molar ratios (A_nB). The formation of such complexes increases the polarity of the solution even more effectively than the formation of the 1 1 complexes. The probable structure of these complexes could be represented by

$$n\text{-}C_4H_9$$
$$/$$
$$C_5H_5N \cdots H-O$$

$$H$$
$$\diagdown$$
$$O-n\text{-}C_4H_9$$

$$H$$
$$/$$
$$-O$$
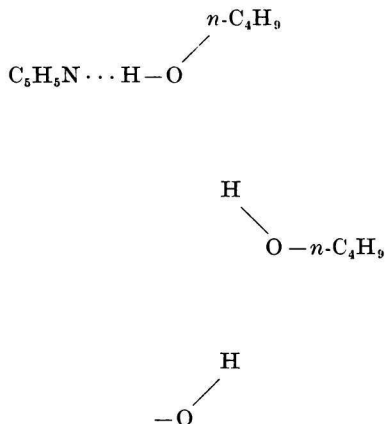
The fact that $\varDelta_1\varepsilon \neq \varDelta_2\varepsilon$ indicates that in the examined solutions multimerization of n-butanol $(mA \rightarrow A_m)$ takes place. Since the numerical values of $\varDelta_2\varepsilon$ are higher than those of $\varDelta_1\varepsilon$ it appears that multimerization of n-butanol increases the polarity of the system in the case of benzene solutions [19, 21], whereas it decreases it in the case of solutions in carbon tetrachloride and saturated hydrocarbons [22−25].

Fig. 12. Infrared spectra of the pyridine−n-butanol−benzene system. Total molar concentration $c = 0.1$ mole/dm³.
1. pyridine in benzene; *2.* pyridine−−n-butanol (9 : 1) in benzene; *3.* pyridine−n-butanol (8 2) in benzene; *4.* pyridine−n-butanol (7 3) in benzene; *5.* pyridine−n-butanol (6 : 4) in benzene; *6.* pyridine−n-butanol (5 : 5) in benzene; *7.* pyridine−n-butanol (4 : 6) in benzene; *8.* pyridine−n-butanol (3 7) in benzene; *9.* pyridine−n-butanol (2 8) in benzene; *10.* pyridine−n-butanol (1 9) in benzene; *11.* n-butanol in benzene.
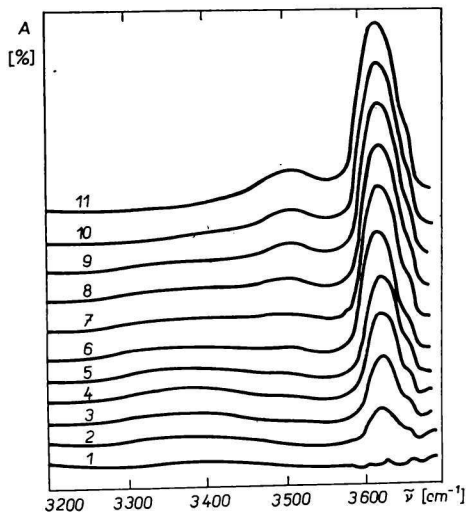
The infrared spectra of pyridine−n-butanol−benzene system obtained for $c = 0.1$, 0.5, and 1.0 mole/dm³ (Figs. 12−14) show that multimerization and complex formation can be regarded as competitive processes. In the region of OH stretching frequencies we observed the bands corresponding to: 1. the "free" OH group vibration in n-butanol molecule ($\bar{\nu}_f = 3617$ cm⁻¹); 2. the vibration of the OH group H-bonded to pyridine nitrogen atom ($\bar{\nu}_c = 3355$ cm⁻¹); 3. the vibration of the OH group H-bonded to oxygen atom of another n-butanol molecule. In the last case the position of the band(s) ($\bar{\nu}_m$) depends on the composition and structure of the associates formed. As a consequence the absorption of the $-O-H\cdots O<$ group was observed in the wide spectral range of 3300−3540 cm⁻¹. The shift of the $\bar{\nu}_f$ band to lower frequencies (as compared with that observed in the gas phase or in solutions in neutral solvents [23, 26]) indicates that there is an interaction between n-butanol and benzene molecules. The bands $\bar{\nu}_c$ and $\bar{\nu}_m$ were largely overlapping. The ratio (I_c/I_m) of their intensities increases with increasing pyridine concentration. As seen from Fig. 14 at $c = 1.0$ mole/dm³ in solutions containing no more than 20% n-butanol the formation of the 1 1 complexes takes place almost exclusively.

For this reason for such solutions $\varDelta_1\varepsilon$ values (which in this case are almost equal to $\varDelta_2\varepsilon$) are a measure of the strength and degree of the 1 1 complex formation.

In the case of methyl derivatives of pyridine, quinoline, and isoquinoline the dielectric titration curves (Figs. 2−8) indicate the presence of an association having the character similar to that observed in unsubstituted pyridine solutions. The more complex shapes of these curves in the case of cyanopyridine solutions (Figs. 9−11) are probably due to the following facts:
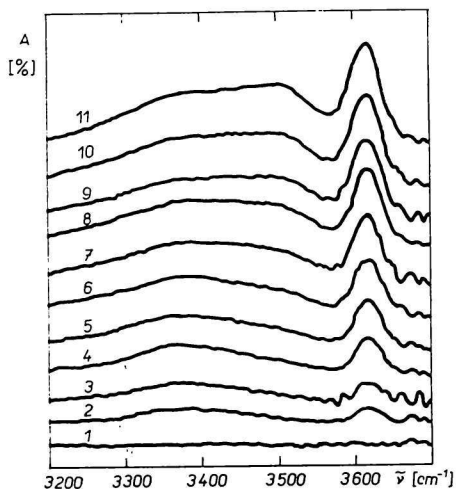
Fig. 13. Infrared spectra of the pyridine—*n*-butanol—benzene system.
$c = 0.5$ mole/dm³.
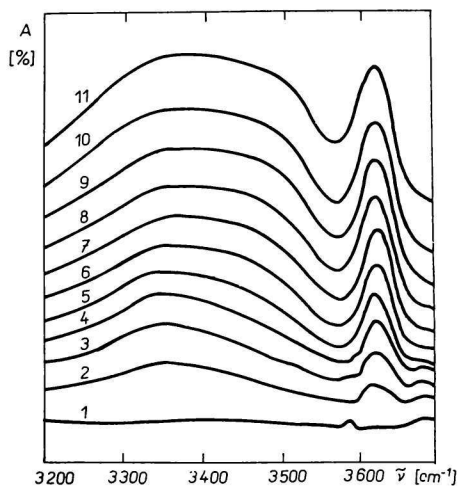The numbers indicate the spectra of the solutions with the same pyridine—*n*-butanol molar ratio as those shown Fig. 12.

Fig. 14. Infrared spectra of the pyridine—*n*-butanol—benzene system.
$c = 1.0$ mole/dm³.
The numbers indicate the spectra of the solutions with the same pyridine—*n*-butanol molar ratio as those shown Fig. 12.

1. cyanopyridines are weak bases (Table 1);
2. the formation of complexes decreases the polarity of the solutions;
3. the cyano group can also form hydrogen bonds with alcohol molecules [1].

In view of the physical sense of $\varLambda_1\varepsilon$ it could be expected that in the case of solutions in which the formation of the 1 1 complexes exclusively takes place $\varLambda_1\varepsilon$ could be corre-

Table 1

Comparison between the pK_a and $\varLambda_1\varepsilon$ values for the bases examined

Pyridine base	pK_a	$\varLambda_1\varepsilon \cdot 10^4$
Pyridine	5.17 [27]	695
2-Methylpyridine	5.97 [27]	747
3-Methylpyridine	5.68 [27]	854
4-Methylpyridine	6.02 [27]	974
2,4-Dimethylpyridine	6.72 [27]	1045
2,6-Dimethylpyridine	6.77 [27]	688
Quinoline	4.94 [28]	718
Isoquinoline	5.40 [29]	847
2-Cyanopyridine	—	−186
3-Cyanopyridine	1.45 [30]	− 45
4-Cyanopyridine	—	−167

lated with other physical properties determining the tendency of electron-donating compounds to hydrogen bonding, *e.g.* pK_a of acids conjugated with the considered bases. In Table 1 $\Delta_1\varepsilon$ values determined for 1.0 molar solutions of the examined pyridine bases containing 20% n-butanol are compared with the corresponding pK_a values.

Table 1 shows that as a rule $\Delta_1\varepsilon$ increases with increasing pK_a, but there are exceptions from this relationship. Thus on passing from 2-methylpyridine to 3-methylpyridine pK_a decreases whereas $\Delta_1\varepsilon$ increases; $\Delta_1\varepsilon$ for 2,6-dimethylpyridine, which is the most basic of the examined pyridine bases, exceeds only the $\Delta_1\varepsilon$ values of cyanopyridines. Those exceptions are probably due to the steric hindrance caused by substituents in the 2 and 6 positions, which bar the approach of n-butanol molecules to the ring nitrogen atom. This effect, decreasing the complex formation constant, is also observed in the cases of 2,4-dimethylpyridine and quinoline. The steric hindrance has no effect on the protonation of pyridine bases [31] owing to the small size of proton. $\Delta_1\varepsilon$ Values observed for quinoline and isoquinoline are slightly higher than those expected on the basis of comparison of the pK_a values corresponding to quinoline, isoquinoline, pyridine, and methylpyridines. This is probably due to increased stability of the complexes.

The results of this investigation show that dielectric titrations can provide interesting information regarding intermolecular association. However, when this method is used it is difficult to separate the effects caused by different kinds of molecular association.

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