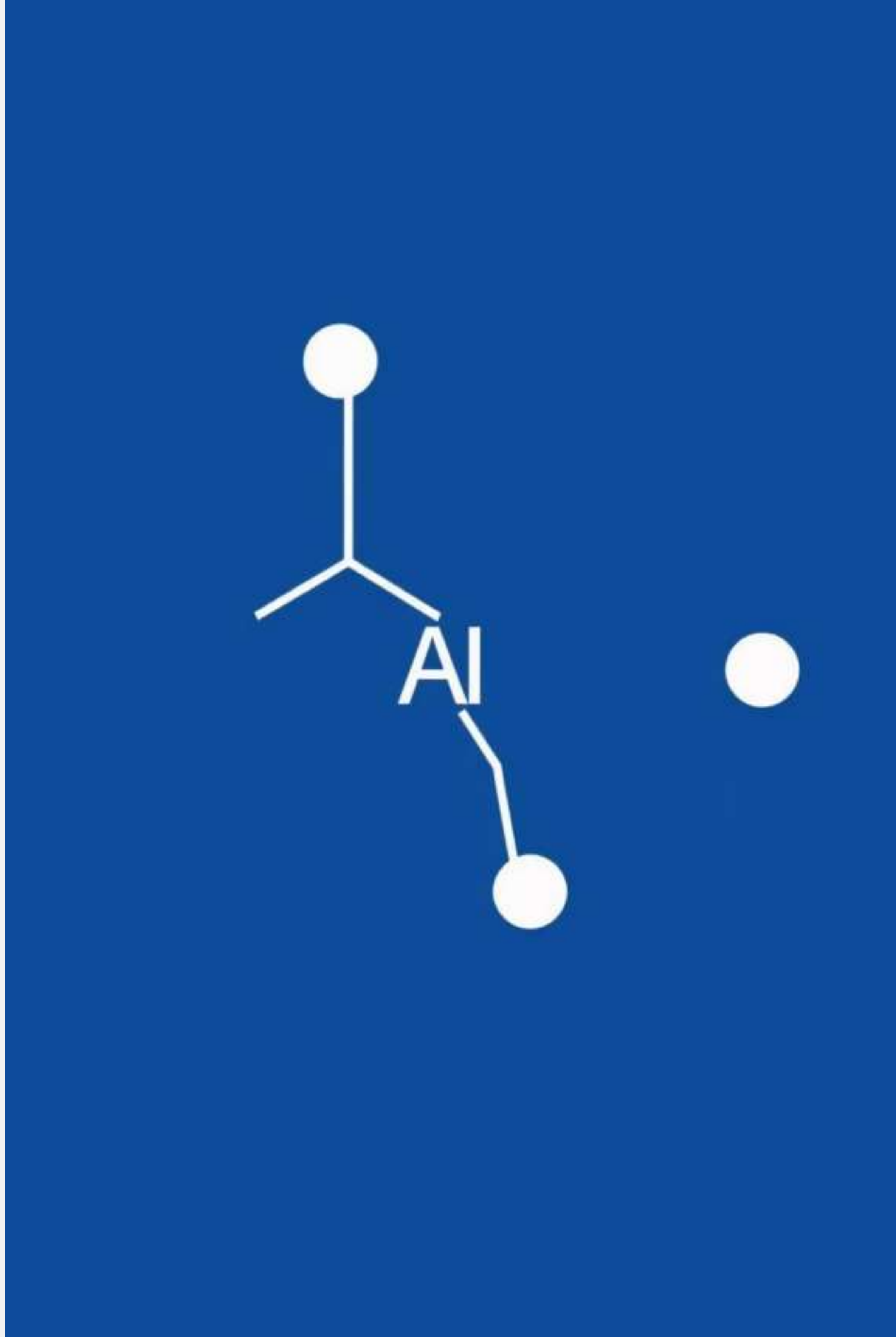
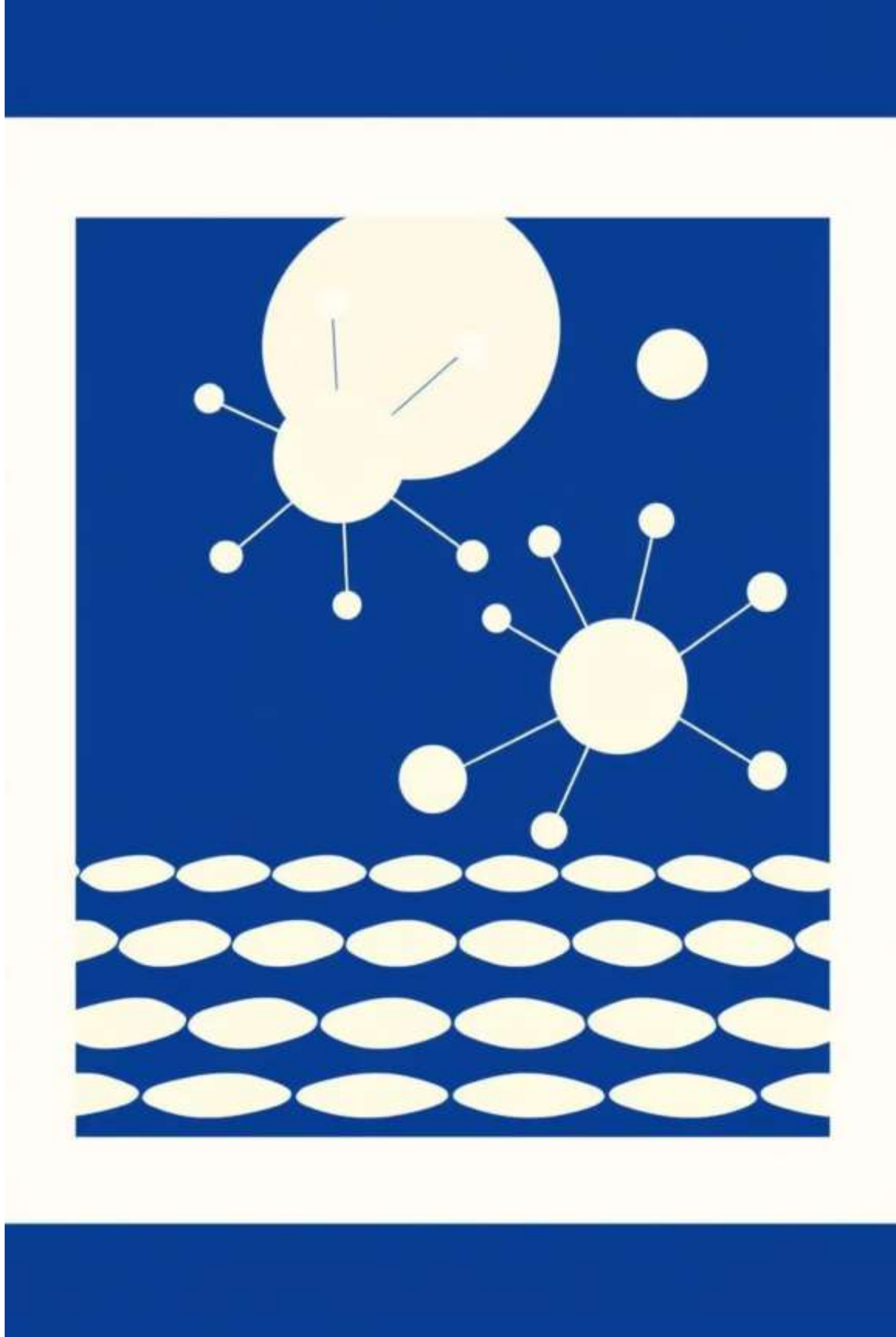
Acidity of Carboxylic Acids and Related Compounds

This presentation will explore the factors influencing the acidity of carboxylic acids, amides, and esters, their significance in organic chemistry, and practical qualitative tests for their identification.



What Determines Acidity in Carboxylic Acids?

The strength of a carboxylic acid is quantified by its pKa value, typically ranging from 4 to 5. Acidity is fundamentally determined by the stability of its conjugate base, the carboxylate ion. The greater the stability of this ion, the stronger the acid.



Resonance Stabilization of Carboxylate Ion

The key to a carboxylic acid's strength lies in the **resonance stabilization** of its conjugate base. The negative charge in the carboxylate ion is delocalized over both oxygen atoms, dispersing the charge and lowering the overall energy of the ion.

This delocalization significantly stabilizes the conjugate base, making it easier for the carboxylic acid to donate a proton. This is why carboxylic acids are significantly stronger acids (pKa ~4-5) compared to alcohols (pKa ~15-18), which lack this effective resonance stabilization.

$$R-COO^- \leftrightarrow R-C(=O)O^-$$

Inductive Effect: Electron-Withdrawing and Donating Groups

The **inductive effect** plays a crucial role in modifying acidity. Electron-withdrawing groups (EWGs) pull electron density through sigma bonds, stabilizing the conjugate base and increasing acidity (lowering pKa).

Conversely, electron-donating groups (EDGs) push electron density towards the carboxylate, destabilizing the conjugate base and thereby decreasing acidity.

Electron-Withdrawing Groups (EWG)

Pull electron density, stabilize carboxylate, **increase acidity**.

Electron-Donating Groups (EDG)

Push electron density, destabilize carboxylate, **decrease acidity**.

Effect of Substituents on Acidity: Examples

Consider **Trifluoroacetic acid** (CF_3COOH), with a pKa of ~0.59. The three highly electronegative fluorine atoms strongly withdraw electron density, making it significantly more acidic than **acetic acid** (CH_3COOH) with a pKa of ~4.76.

The cumulative effect of multiple EWGs is also observed: dichloro- and trichloroacetic acids show progressively stronger acidity. Importantly, the inductive effect rapidly diminishes over distance, becoming negligible beyond three sigma bonds.

Carboxylic Acid	Approx. pKa
Trifluoroacetic Acid	0.59
Trichloroacetic Acid	0.70
Dichloroacetic Acid	1.48
Chloroacetic Acid	2.86
Acetic Acid	4.76

Qualitative Tests for Carboxylic Acids

Identifying carboxylic acids in the lab often involves simple qualitative tests:

Litmus Test

Blue litmus paper turns red, indicating an acidic solution ($pH < 7$).

2

Sodium Bicarbonate Test

Upon addition of $NaHCO_3$, effervescence (gas bubbles) due to CO_2 release confirms the presence of a carboxylic acid.

3

Solubility & Smell

Many short-chain carboxylic acids are water-soluble and have distinct, often pungent, odors (e.g., acetic acid's vinegar smell).

Qualitative Tests for Amides

Amides behave differently from carboxylic acids in qualitative tests, reflecting their neutral character:

- **Neutral pH:** Amides are generally neutral and do not react with sodium bicarbonate, unlike carboxylic acids.
- **Infrared (IR) Spectroscopy:** A strong characteristic C=O stretch appears near 1650 cm^{-1}, distinguishing them from other carbonyl compounds.
- **Hydrolysis:** Amides can be hydrolyzed under harsh acidic or basic conditions, yielding a carboxylic acid and an amine. This process often requires heating.

Qualitative Tests for Esters

Esters are recognizable by their distinct properties and spectroscopic signatures:

- **Fruity Odors & Solubility:** Many esters are known for their pleasant, fruity aromas and are generally soluble in organic solvents.
- **Hydrolysis Test:** Esters undergo hydrolysis (acid or base catalyzed cleavage) to produce a carboxylic acid and an alcohol. This reaction can be used for identification.
- **IR Spectroscopy:** Esters exhibit a strong C=O stretch near 1735 cm^{-1} in their IR spectrum, and importantly, lack the broad -OH stretch seen in alcohols or carboxylic acids.

Summary of Key Points

Understanding the factors influencing acidity and how to differentiate these functional groups is foundational in organic chemistry.

Acidity Drivers

Carboxylic acid acidity is primarily governed by **resonance stabilization** and the **inductive effect**.

Substituent Impact

Electron-withdrawing groups increase acidity, while **electron-donating groups** decrease it.

Qualitative Differentiation

Specific qualitative tests (litmus, bicarbonate, hydrolysis, IR) effectively distinguish carboxylic acids, amides, and esters.

Conclusion

A deep understanding of acidity, substituent effects, and qualitative tests for carboxylic acids, amides, and esters is indispensable for any organic chemist. These concepts not only help predict chemical reactivity but also guide the design and synthesis of new organic compounds with desired properties. Mastery of these fundamentals is key to success in organic synthesis and analysis.