

Azo-Hydrazone Tautomerism – an Intriguing Balance

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Abstract: The preparation of the “tris(phenylazo)phloroglucinol” **4** was described by Perkin as early as in 1897. Intriguingly, the core tautomerism remains ambiguous even today, more than a century after its initial synthesis. The term “phenylazo”, which has typically been used to describe **4** and its derivatives, might adequately denote their chemical origin (from azo coupling) but incorrectly depicts the true chemical structure (see below). As shown in Scheme, the $[n,\pi]$ -conjugated core of **4** can be described as either the tris(keto-hydrazone) (commonly denoted as “hydrazone”; **4h**) or tris(azo-enol) (commonly denoted as “azo”; **4a**) form. Different theoretical methods have been applied to explain the intricate tautomeric equilibria of **1–4**.

