

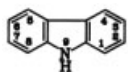
# Carbazole

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Carbazole (dibenzopyrrole) [86-74-8],  $C_{12}H_9N$ , was first found in coal tar by C. GRAEBE and C. GLASER in 1872.



## 1. Physical Properties

$M_r$  167.21;  $mp$  246 °C,  $bp$  at 101.3 kPa 354.8 °C;  $\rho$  at 18 °C 1.1035 g/cm<sup>3</sup>; plates or tables; sublimable; readily soluble in acetone, slightly soluble in ether and alcohol, barely soluble in chloroform, acetic acid, carbon tetrachloride, and carbon disulfide, soluble in concentrated sulfuric acid; heat of fusion 176.3 kJ/kg; heat of combustion  $3.719 \times 10^4$  kJ/kg at 25 °C.

## 2. Chemical Properties

The *N*-hydrogen of carbazole which is a secondary amine can be substituted with alkali metals. During halogenation, nitration, and sulfonation, substitution initially takes place at the 3- and 6-positions; the 1,3,6- and 1,3,6,8-derivatives are formed under more rigorous conditions.

Hydrogenation yields 1,2,3,4-tetrahydro-, hexahydro-, or dodecahydrocarbazole. Oxidation with chromates gives 3,3'-dicarbazyl, with permanganate 9,9'-dicarbazyl. Carboxylation with alkali and carbon dioxide gives, depending on the temperature, carbazole-3- or

carbazole-1-carboxylic acid. Alkylation yields *N*-alkylcarbazoles.

## 3. Production

High-temperature coal tar contains an average of 1.5 % carbazole. Carbazole is obtained as a co-product in the production of anthracene. Due to its higher boiling point and better solubility, it can be separated from anthracene by extraction with pyridine, ketones, benzene/methanol, *N*-methylpyrrolidone, dimethylacetamide, dialkyl sulfoxides, or dialkylformamides, or by azeotropic distillation with ethylene glycol ( $\rightarrow$  Anthracene). The chemical separation of carbazole by means of potassium hydroxide or concentrated sulfuric acid fusion has become uneconomical. Pyridine mother liquors obtained from the preparation of pure anthracene yield pure carbazole by means of concentration and recrystallization from chlorobenzene.

Carbazole can be synthesized by converting cyclohexanone azine to octahydrocarbazole and subsequent dehydrogenation [6], by reductive cyclization of 2-nitrobiphenyl [7], [8], or by dehydrogenation and cyclization of diphenylamine [9–11], *o*-aminobiphenyl [12–14], or *N*-cyclohexylideneaniline [15]. These synthetic processes are not yet of industrial significance, because sufficient quantities of carbazole can be prepared from coal tar.

## 4. Analysis

Gas–liquid chromatography is suitable for the quantitative determination of carbazole in com-

plex mixtures, such as in coal tar or coal-tar fractions [16]. Thin-layer chromatography can also be used to identify carbazole along with other compounds [17]. Purity is determined by UV spectroscopy. As little as 0.005 % carbazole in anthracene can be detected using phosphorescence spectroscopy. Small quantities of phenanthrene do not interfere with the results [18].

## 5. Uses and Economic Aspects

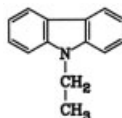
Carbazole is obtained from coal tar in amounts of several thousand t/a, primarily for dye synthesis. Co-products of anthracene recovery representing the raw material of carbazole are up to 100 000 t/a.

The blue sulfur dye Hydron Blue is commercially synthesized by condensing carbazole with *p*-nitrosophenol and subsequent sulfurization ( $\rightarrow$  Sulfur Dyes). Its 2-hydroxy-3-carboxylic acid amides (Naphtol AS-LB, -SG, -SR;  $\rightarrow$  Azo Dyes), anthraquinone vat dyes from phthaloyl carbazoles ( $\rightarrow$  Anthraquinone Dyes and Intermediates), styryl dyes from *N*-ethylcarbazole ( $\rightarrow$  Methine Dyes and Pigments), and dioxazine dyes and pigments from *N*-ethyl-3-aminocarbazole ( $\rightarrow$  Azone Dyes;  $\rightarrow$  Pigments, Organic) can also be synthesized from carbazole.

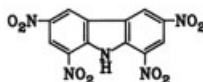
The insecticide Nirosan, 1,3,6,8-tetranitrocarbazole, has been commercially available since 1939. *N*-Vinylcarbazole is polymerized to give poly(vinylcarbazole) (Luvican, Pollectron) [19], which is thermally and chemically stable and has a high softening temperature and low dielectric loss and photoconductivity. These properties make it useful in electrical industry and for electrostatic copying methods [19–21]. Carbazole reacts with phenols and formaldehyde in the presence of acidic catalysts to give novolaks. These can be cured with hexamethylenetetramine to form highly heat-resistant polymers [22]. Concrete plasticizers are obtained by cocondensation of carbazole with phenols and formaldehyde and subsequent sulfonation [23]. Thermal condensation of 3,6-diaminocarbazole with dicarboxylic acid gives elastic and thermally stable polyamides [24].

## 6. Derivatives

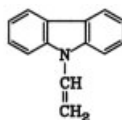
***N*-Ethylcarbazole** [86-28-2],  $C_{14}H_{13}N$ ;  $M_r$  195.27;  $mp$  68 °C; by ethylation of carbazole – potassium with diethyl sulfate [25].



**1,3,6,8-Tetranitrocarbazole** [4543-33-3],  $C_{12}H_5O_8N_5$ ;  $M_r$  347.20;  $mp$  312 °C; by nitration of carbazole with a mixture of nitric and sulfuric acid.



***N*-Vinylcarbazole** [1484-13-5],  $C_{14}H_{11}N$ ;  $M_r$  193.25;  $mp$  65 °C; from carbazole – potassium with ethylene oxide or vinyl chloride, or from carbazole and acetylene [19].



## 7. Toxicology

The  $LD_{50}$  of carbazole ranges from 200 mg/kg (intraperitoneal, mice) to more than 5000 mg/kg (oral, rats) [26], [27]. Due to this fact it can be considered as non-toxic. Folliculitis and comedos were reported by workers with carbazole contact [28]. In rats and rabbits, carbazole is glucuronized and excreted in the urine [29]. There is no evidence of carcinogenicity for carbazole.

## 8. References

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