3,6-Extended Conjugation through Phenanthrene

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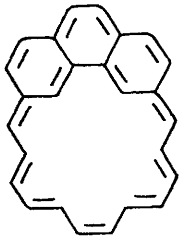
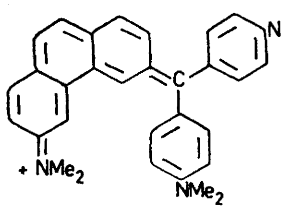
Summary Effective conjugation through phenanthrene is found in the 3,6-linked phenanthrene analogue (II) of Crystal Violet.

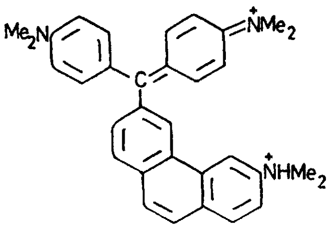
IN view of the recent finding[1] that annulenoid aromaticity is exhibited by cyclo-octadeca[*c*,*d*,*e*,*f*,*g*]phenanthrene (I), we now report the ease of 3,6-conjugation through phenanthrene observed on incorporation of the ring system into Crystal Violet.



(I)



(II)



(III)

The dye base, m.p. 102—103 °C,[†] obtained by interaction of 3-dimethylamino-6-phenanthryl-lithium with Michler's ketone gave the 3,6-linked phenanthrene analogue (II) of Crystal Violet on dissolution in either 98% acetic acid or ethanol containing 1 equivalent of hydrogen chloride. Effective conjugation of the remote nitrogen atom with the central carbon atom gives a spectrum with a single absorption band in the visible region; the absence of a second band is indicative of the relative stability of the phenanthrene dye and consistent with an even distribution of charge. The univalent ion (II) absorbs at a longer wavelength (λ_{max} 635 nm, ϵ 87,000) than Crystal Violet (λ_{max} 589 nm, ϵ 116,000) and the pronounced bathochromic shift (46 nm) is in accord with extended conjugation through the phenanthrene system; the analogous 2,6-linked naphthalene dye[2] shows a long-wavelength shift of 24·5 nm. The simplicity of the absorption spectrum of the univalent ion shows that the ground state structure (II) can be treated equally with the other two canonical structures in which the positive charge is on nitrogen. Otherwise a Malachite Green type spectrum would be found with two bands in the visible region. Absorption due to the bivalent cation (III) becomes apparent as the acidity of the acetic acid is increased by addition of water to the solvent. In 50% acetic acid a fairly close approximation to the spectrum of the bivalent ion is obtained ($\lambda_{max\,(x)}$ 629 nm, $\epsilon_{max\,(x)}$ 76,000; $\lambda_{max\,(y)}$ 446 nm $\epsilon_{max\,(y)}$ 10,000), this being shown by the correspondence between the spectrum observed and that of the related 3-phenanthryl analogue of Malachite Green.[3]

Since the extension of conjugation through polycyclic systems can be related to quinonoid stability, it is somewhat surprising that attempts to prepare 3,6-phenanthraquinone have as yet been unsuccessful.[4]

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[†] The dye base and its precursors gave satisfactory elemental analyses and spectral data.

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[2] G. Hallas and D. R. Waring, *J. Chem. Soc.* (*B*), 1970, 979.
[3] G. Hallas and R. M. Potts, *J.C.S. Perkin II*, 1974, 59.
[4] M. S. Newman and R. L. Childers, *J. Org. Chem.*, 1967, **32**, 62.