

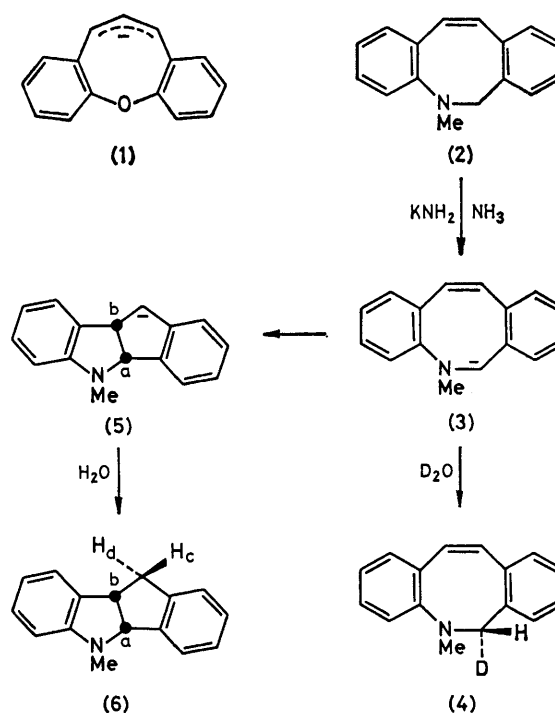
Generation and Thermal Reorganization of a Linearly-fused *N*-Methyldibenzoazocinyl Anion

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Summary The potentially 'aromatic' (18π), π -excessive title substance (**3**) was generated in liquid ammonia and was found to undergo ring closure exclusively to the dibenzobicyclic frame of the anion (**5**).

In recent work¹ on the generation and direct observation of the symmetrically diannulated oxocinyl anion (**1**) we used spectroscopic data to show that the central ring of this potentially 'aromatic' 18π -electron substance is largely atropic (¹H n.m.r. chemical shifts) and distinctly buckled (¹³C-H coupling constants). In an attempt to show that the lack of aromaticity in (**1**) is mainly due to a periphery-induced ('peri' H-H interactions) skeletal inability of the central ring to adopt the necessary planar geometry, we examined the dibenzoheterocinyl anion (**3**). The choice of (**3**) was dictated by the nature of its benzannulation and type of heteroatomic lone pair, both of which are distinctly different from those of the previously studied anion (**1**), as well as the availability of its direct progenitor (**2**).²

The anion (**3**) was obtained from compound (**2**) under conditions similar to those used for the anion (**1**),¹ namely exposure to KNH₂ in liquid ammonia at *ca.* -35 °C; the formation of the anion (**3**) was established by rapid D₂O quench at *ca.* 0 °C to yield the monodeuterio-analogue (**4**) (¹H n.m.r.). On the other hand, when the ammonia solution containing (**3**) was allowed to warm gradually to *ca.* 0 °C,† ¹H n.m.r. revealed the presence of the rearranged anion (**5**)



† It was necessary to warm the NH₃ solution to 0 °C in order to determine the ¹H n.m.r. spectrum.

and not (3). The structure of (5) was established by the ^1H n.m.r. spectrum which, except for the anticipated shift of the anion centre, is characterized by an absorption pattern which is virtually superimposable on that of the conjugate acid (6), obtained on exposure of (5) to H_2O at 0°C . Compound (6) is a white, crystalline substance, m.p. $79.5\text{--}80^\circ\text{C}$; ^1H n.m.r. (60 MHz, $[\text{D}_6]\text{acetone}$) δ 6.4–7.6 (8 H, m), 5.05 (1 H, H_a , d, J_{ab} 8.4 Hz), 4.15 (1 H, H_b , dt, $J_{ba} = J_{bc}$ 8.4 Hz, J_{bd} 5.2 Hz), 3.52 (1 H, H_c , dd, J_{cb} 8.4 Hz, J_{cd} 15.4 Hz), \ddagger 3.00 (3 H, Me, s), and 2.97 (1 H, H_d , dd, J_{db} 5.2 Hz, J_{dc} 15.4 Hz); ^{13}C n.m.r. (80 MHz, tetramethylsilane; H-coupled, $[\text{D}_6]\text{tetrahydrofuran}$) δ 104–143 (8 C, 'sp²' centres), 75.15 (1 C, C_a , d), 45.13 (1 C, C_b , d),

39.22 (1 C, CH_2 , t), and 32.12 p.p.m. (1 C, Me, q); u.v. (hexane) λ_{max} 256 (ϵ 10 200) and 306 nm (3 600); m/e (70 eV) 221 (M , 100%).

In conclusion, we note that whereas our failure to observe directly the desired anion (3) precludes the determination of the presence or absence of ring anisotropy, the rapid rearrangement into (5) indicates that the linearly benzannulated azocinyl anion (3) distinctly lacks the type of π -frame stability normally associated with 'aromatic' systems. \S

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\ddagger The specific stereochemical assignments of H_c and H_d given were made on the basis of the magnitude of coupling constants J_{bc} and J_{bd} taken in conjunction with the dihedral angles $\text{H}_b\text{--H}_c$ (ca. 0°) and $\text{H}_b\text{--H}_d$ (ca. 110°) as measured from a 'Dreiding' molecular model of (6).

\S It is pertinent to note that although the molecular reorganization of (3) to (5) had not been observed previously, the low kinetic acidity of (2) relative to those of appropriate models was interpreted to mean that the incipient anion (3) is not endowed with 'appreciable aromatic stability' (ref. 2).

¹ A. G. Anastassiou and H. S. Kasmai, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 393.

² R. M. Coates and E. F. Johnson, *J. Am. Chem. Soc.*, 1971, **93**, 4016.