A Stable *trans*-Benzazoninyl Anion

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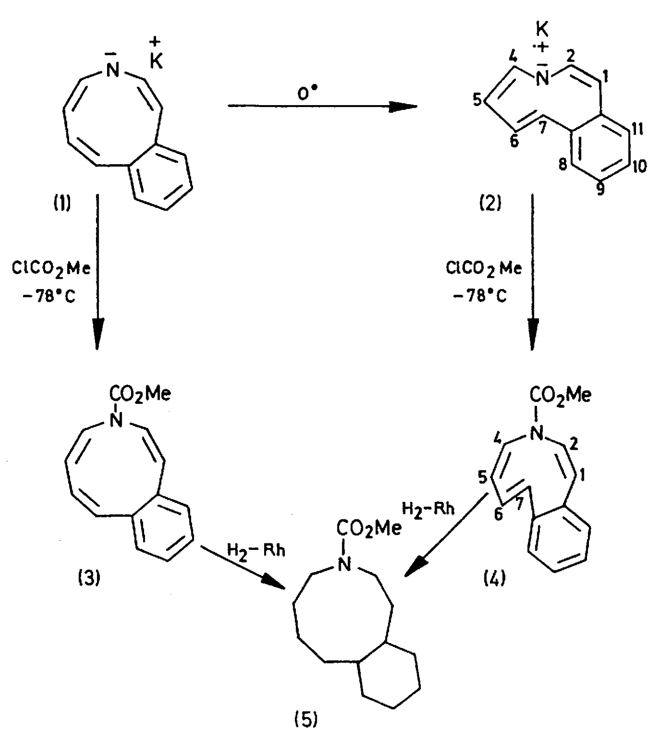
Summary The title substance (**2**) is formed on mild thermal treatment of the all-*cis* counterpart (**1**) with net relief of steric congestion and acquisition of aromatic character.

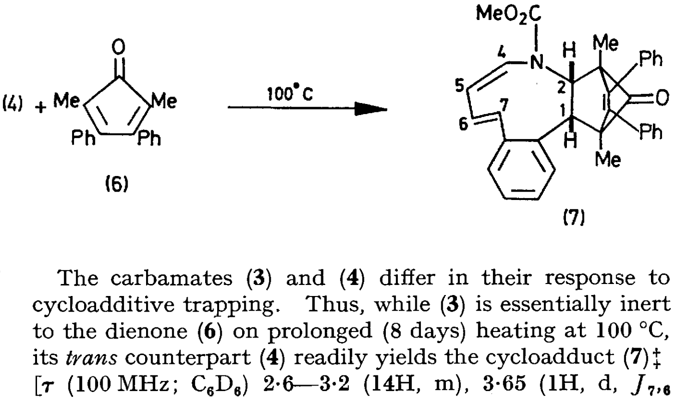
NORMALLY, medium-sized rings can meet the skeletal demands of multiple unsaturation only within an all-*cis* framework. We now report an exception which demonstrates the influence of H–H repulsions in larger medium-sized rings.[1]

We found previously[2] that the all-*cis* benzazoninyl anion (**1**) lacks aromatic character at < -35 °C and that it is thermally unstable. We have now found that (**1**) undergoes unidirectional *cis* → *trans* isomerization to (**2**). In liquid NH_3 (sealed n.m.r. tube) (**2**) is formed with k (0 °C) $8{\cdot}92 \pm 0{\cdot}95 \times 10^{-4}\ s^{-1}$, ($\Delta G^{\ddagger}$ 19·8 kcal/mol); τ 1·98 and

2·18 (each 1H, d, $J_{8,9} = J_{11,12} = 8{\cdot}0$ Hz, 8- and 11-H), 2·24 (1H, d, $J_{4,5}$ 6·5 Hz, 4-H), 2·7—3·3 (5H or 6H, m),† 4·35 (1H, dd, $J_{5,4}$ 6·5, $J_{5,6}$ 10·0 Hz, 5-H). The presence and location of the *trans* bond in (**2**) is shown by the following. Whereas (**1**) forms the known[3] all-*cis* carbamate (**3**) when treated with methyl chlorformate at −78 °C, compound (**2**) affords (**4**),‡ τ [60 MHz, $(CD_3)_2CO$] 2·72 (4H, s), 3·13 (2H, s, 1- and 2-H), 3·22 (1H, d, $J_{4,5}$ 10·5 Hz, 4-H), 3·68 (1H, d, $J_{7,6}$ 15·0 Hz, 7-H), 4·30 (1H, dd, $J_{6,7}$ 15·0, $J_{6,5}$ 7·5 Hz, 6-H), and 4·97 (1H, dd, $J_{5,4}$ 10·5, $J_{5,6}$ 7·5 Hz, 5-H). The large coupling between 6- and 7-H requires that the 6,7 double bond be *trans*, while the further splitting of 6-H indicates attachment to another ethylene group. Catalytic hydrogenation (Rh–C) of (**3**) and (**4**) gave the same perhydro derivative (**5**), showing that they are isomeric.



We believe that steric relief is responsible for the difference in thermal behaviour on warming between compound (**1**) and the carbocyclic debenzo analogue, the cyclononatetraenyl anion, which undergoes *trans*→*cis*-isomerization.[4] Upon conversion of compound (**1**) into (**2**), the 7-H–8H *peri*-interaction is removed, and the 1-H–11-H repulsion is partially alleviated by relocation of 1-H from the periphery of the nine-membered ring in (**1**) to that of the pseudo six-membered ring in (**2**). Also, 4- and 5-H in compound (**2**) show signs of aromatic character, being shifted downfield by 1·5—2 p.p.m. from their counterparts in (**1**).[2]§ Thus, benzannelation perturbs the azonine unit because of the *peri*-interaction, removal of which, *i.e.* (**1**) → (**2**), restores the aromatic character of the azonine part of the molecule.[5]



The carbamates (**3**) and (**4**) differ in their response to cycloadditive trapping. Thus, while (**3**) is essentially inert to the dienone (**6**) on prolonged (8 days) heating at 100 °C, its *trans* counterpart (**4**) readily yields the cycloadduct (**7**)‡ [τ (100 MHz; C_6D_6) 2·6—3·2 (14H, m), 3·65 (1H, d, $J_{7,6}$ 14·0 Hz, 7-H), 3·86 (1H, d, $J_{4,5}$ 8·5 Hz, 4-H) 4·33 (1H, dd, $J_{5,4} = J_{5,6} = 8{\cdot}5$ Hz, 5-H), 4·51 (1H, dd, $J_{6,5}$, 8·5, $J_{6,7}$ 14·0 Hz, 6-H), 5·25 br (1H, d, $J_{2,1}$ 8 Hz, 2-H), 5·86 (1H, d, $J_{1,2}$ 8 Hz, 1-H), 6·86 (3H, s), 8·24 (3H, s), 8·70 (3H, s)] on 3 days exposure to (**6**) at 100 °C.

Structure (**7**) follows from the appearance of 1- and 2-H as clean mutually coupled doublets in the n.m.r. spectrum showing that they are located on the isolated double bond of (**4**), and from the presence of a *trans* C=C double bond directly linked to the benzene segment of the molecule as shown by a strongly coupled (J 14 Hz) doublet at τ 3·65 (1-H).

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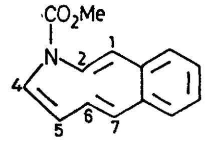
Added in proof: In the presence of shift reagent $[^2H_{27}]$-$Pr(fod)_3$, the 1-H + 2-H singlet in the n.m.r. spectrum of (**4**) undergoes the expected splitting into two mutually coupled doublets with a coupling constant ($J_{1,2}$) of *ca.* 14 Hz. This rather large value is not inconsistent with the *cis*-vicinal coupling constant expected of the isolated ethylene function of (**4**) which from an examination of Dreiding molecular models is seen to respond to the significant skeletal strain of the molecule through substantial widening of each of its C-C-H angles. This is a distortion similar to that in the all-*cis* benzocyclononatetraenyl anion whose benzylic protons are coupled to their vicinal neighbours by 14·5 Hz (A. G. Anastassiou and R. C. Griffith, *J. Amer. Chem. Soc.*, 1974, **96**, 611). However, the large



(8)

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† The spectrum also contains a high-field (τ 10·95 strongly coupled, J 16 Hz) doublet which, if real (its proximity to the solvent resonance renders the integration unreliable), must be due to the 'inner' proton 7-H. The ambiguity over this resonance is accentuated by the presence of a small amount of decomposition product with an absorption overlapping with that of the major resonance manifold thus precluding an exact estimate (5H or 6H) of its area.

‡ Compound (**4**) has m.p. 64—65 °C, (**5**) is an oil, and (**7**) has m.p. 203—203·5 °C. All afforded consistent spectral (i.r., u.v., m.s.) data and correct combustion analyses.

§ It is also interesting that the smaller value of $J_{4,5}$ in (**2**) compared to its counterpart in (**1**) (8·5 Hz)[2] appears to reflect the association of the C–C bond with an effectively smaller (pseudo five-membered) ring.

size of $J_{1,2}$ observed in the present case prevents the possibility that the 1,2-bond is *trans*, and hence that the molecule is (**8**) rather than (**4**), being excluded. It is impossible to choose between the two possibilities without using X-ray analysis but we tend to favour (**4**), since on formation of a cycloadduct with (**6**) $J_{1,2}$ changes to 8·5 Hz; this value is consistent with the *cis*-fused arrangement shown in (**7**) (1-H to 2-H dihedral angle *ca.* 0°) but not with the *trans*-fused skeleton (1-H to 2-H dihedral angle *ca.* 110°) expected to result from (**8**).

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[1] The severity of peripheral H–H repulsions in the planar larger medium-sized rings was recognized theoretically by H. E. Simmons and J. K. Williams, *J. Amer. Chem. Soc.*, 1964, **86**, 3222.

[2] A. G. Anastassiou and E. Reichmanis, *Angew. Chem.*, 1974, **86**, 410.

[3] A. G. Anastassiou, E. Reichmanis and R. L. Elliott, *Tetrahedron Letters*, 1973, 3805.

[4] G. Boche, D. Martens, and W. Danzer, *Angew. Chem. Internat. Edn.*, 1969, **8**, 984.

[5] For a review on heteronin 'aromaticity' see: A. G. Anastassiou, *Accounts Chem. Res.*, 1972, **5**, 281.