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STUDIES ON A 7-NORBORNENYL ANION, A "BISHOMOANTIAROMATIC" SYSTEM

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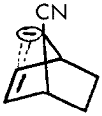
Considerable evidence has now accumulated that the cyclopropenyl anion system is antiaromatic, i.e. conjugatively destabilized.[1] Since the 7-norbornenyl cation is strongly stabilized by interaction of the positive center with the double bond, and this cation has been described as a bishomocyclopropenyl cation,[2] the stability of 7-norbornenyl anion is of interest. Just as the cation may be considered "bishomoaromatic",[3] the anion might be "bishomoantiaromatic"[3] if the interaction of the charge with the double bond were destabilizing.[4]

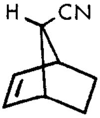
Of course, the effect might well be very small. 7-Norbornenyl cation is much less resonance stabilized than is cyclopropenyl cation, and 7-norbornenyl cation is geometrically distorted so as to increase the interaction. The 7-norbornenyl anion would certainly not distort to increase a destabilizing interaction. Thus the destabilization, if any, in 7-cyanonorbornenyl anion (I) should lead to a rate effect considerably less than the 10^4 decrease in base-catalyzed exchange rates we have observed[1] for cyanocyclopropenyl anions.[5]

We have prepared the known[5] 7-anti-cyanonorbornene (II) from NaCN and norbornenyl tosylate in hexamethylphosphoramide. The compound was purified by preparative vapor phase chromatography and had infrared, n.m.r., and mass spectra consistent with structure II and with those reported.[5] 7-Cyanonorbornane (III)[5] was obtained, m.p. 65-67°, by hydrogenation of II. Comparative deuterium exchange rates of II and III were determined by putting an equal mixture of the two in 1 M KOtBu in t-butanol-OD at 65° and removing aliquots. After separation of II and III by vapor phase chromatography, each was analyzed for deuterium by n.m.r. integration of appropriate peaks. The ratio of reactivities under these conditions, k_{II}/k_{III}, is 1.4 ± 0.2.

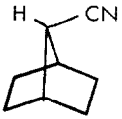
Although no net destabilization of I by "bishomoantiaromaticity" has thus been detected, one might wonder whether some such small effect is being counterbalanced by the inductive effect of the double bond in II. As a model for this we have examined the relative base-catalyzed exchange rates in cyanocyclopentane (IV) and 3-cyanocyclopentene (V). While the inductive effect of the double bond in II might be similar to that in V, bishomoconjugation in the cyclopentenyl anion system should be negligible.[6] Competitive deuteration in 1 M KOMe in methanol-OD at 90°, followed by v.p.c. separation and n.m.r. analysis of IV and V, indicate k_V/k_{IV} = 10 ± 1. Thus the double bond in V does lead to a larger increase than that in II, so anion I may have some conjugative destabilization. However, the effect is so small that other factors may also be invoked.



I

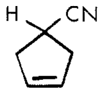


II



III

IV



V

One factor not likely to play a major role is I strain, since the C_1-C_7-C_4 angle remains 96-97° in both norbornane[7] and norbornene.[8] However, this small angle does result in slow exchange in both II and III. Thus, in 1 M KOtBu in t-butanol-OD at 50°, cyclopentyl cyanide (IV) exchanges 1.0 x 10^3 as rapidly as does norbornenyl cyanide (II). This is as expected if the transition state resembles a planar delocalized carbanion, although the magnitude of the effect (10^3 = 4.5 kcal/mole) is larger than that (2.4 kcal/mole) calculated from the simple relation:[9]

$$\text{Angle strain} = .01\ (\theta)^2\ \text{kcal/mole degree}$$

Of course, such a calculation is only approximate; furthermore, the experimental value also contains a contribution from relief of eclipsing on ionization of IV.

It is interesting that in a cyanocyclopropane the I strain effect is not dominant, and base-catalyzed exchange is actually faster than in a strainless cyano compound.[10] In the case of the three-membered ring the I strain effect on a planar anion would be quite high. Thus the carbanion is non-planar and unstrained, but much less charge is delocalized into the cyano group. However, because of the increased electronegativity of a cyclopropane carbon such a non-planar anion is of lower energy than the more delocalized anions in larger ring systems.[11]

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