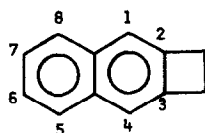


ION-PAIRING STUDIES OF NAPHTHO[b]CYCLOBUTENE

Reuben D. Rieke and Stephen E. Bales¹
 Department of Chemistry, University of North Carolina
 Chapel Hill, North Carolina 27514

(Received in USA 27 March 1972; received in UK for publication 11 May 1972)

ESR studies of pyracene², acenaphthene³ and benzocyclobutene⁴ (BCB) radical anions have provided examples of line-width alternation and nonequivalency of methylene protons as a result of ion-pairing. As a result of these studies, the naphthalene analogue of BCB, naphtho[b]cyclobutene (NBCB, shown below), was of interest due to its ethylene bridge at the 2 and 3 positions. In this communication, we would like to report the observation that under no combination of solvent and metal were we able to see any nonequivalency of the



methylene protons of NBCB. The various conditions of solvent and metal employed in generating the NBCB radical anion in this study and the hyperfine splitting constants (hfsc) obtained are shown in Table I. Reductions in DME (dimethoxyethane) or a mixture of DME and HMPA (hexamethylphosphoramide) gave virtually identical, temperature independent spectra. In these reductions ion-pairing effects are believed to be negligible. However, using Na

Table I^a

Solvent	Metal	$A_{1,4}$	$A_{5,8}$	$A_{6,7}$	A_{CH_2}	A_M	Temperature (°C)
DME	K	5.40	4.20	1.58	5.85		-50 to +25
DME/HMPA	K	5.40	4.20	1.60	5.82		-88 to 0
DME	Na	5.40	4.20	1.60	5.80		-80 to -20
THF	K	5.10	4.40	1.65	5.70		-120 to -30
THF	Na	5.35	4.23	1.60	5.80		-100 to -50
		5.10	4.20	1.55	5.75	0.75	-30
		5.00	4.00	1.50	5.50	1.10	+25
DEE	K	5.00	4.45	1.60	5.50		+25
DEE	Na	5.50	4.35	1.65	5.80	0.20	-120
		5.47	4.30	1.62	5.72	0.25	-100

^aHfsc in gauss.

and THF (tetrahydrofuran) or DEE (diethyl ether) ion-pairs were formed, as evidenced by large metal splittings. The perturbations of the hfsc (compared to the free ion case) for K in THF and DEE may also be attributed to ion-pairing, though metal splittings were not

observed for these reductions, which would suggest rapid exchange between the free ion and the ion-pair. However, the methylenes remained equivalent and alternating line widths were not observed for any of the reduction conditions shown in Table I.

This observation was quite unexpected as formally NBCB is very similar to acenaphthene and pyracene. In all these molecules, the methylene protons are situated about the same distance from the center of the 9-10 bond. There are three possible explanations for this observation. First, under all the conditions studied, we could have been in a region of fast exchange. A second possibility is that the metal ion is located in the plane of the NBCB molecule in a symmetrical position with respect to the methylene protons either close to the methylene protons or close to atoms 6 and 7. A third possibility is that the metal ion is above the π -cloud but for steric reasons is located over the ring involving atoms 5-10. We tend to favor the latter view. This stems partially from our work with benzocyclobutene⁴ but also from the finding that the metal ion is located above the plane in the case of pyracene.⁵ Also calculations on acenaphthene radical anion ion-pair indicated that the preferred position of the metal cation would be above the 9-10 bond.³

In order to gain some additional evidence on this point, HMO calculations were carried out. The effect of the metal cation was taken into account by making those positions near the cation more electronegative. HMO calculations employing different coulomb integral variations were run for three possible ion-pairs: the cation above the 9-10 bond, near the 6-7 bond, and above the center of the ring containing carbon atoms 5 through 10. The calculations indicated that the best correlation was obtained when the cation was located over the center of the ring farthest from the ethylene bridge. This configuration was calculated by making the coulomb integrals for carbons 5 through 10 more electronegative by $-0.05 |\beta_0|$ ($h_{5-10} = -0.05$) and using the coulomb integrals for carbons 1 through 4 which gave the best fits for the free ion case ($h_{1,4} = -0.2$, $h_{2,3} = 0.1$).⁶ The calculated hfsc were $A_{1,4} = 5.00$, $A_{5,8} = 4.37$, $A_{6,7} = 1.72$, and $A_{CH_2} = 4.54$. Inspection of Table I shows that these values agree quite well with the trends observed for NBCB as ion-pairing increased.

In order to determine the range over which the cation may cause nonequivalency of the methylenes, distances were calculated between the cation and ethylene bridge for the most favored ion-pair configurations. For pyracene and acenaphthene, bond lengths and angles had been determined by crystallographic studies.^{7,8} For NBCB, these values were obtained by combining the results for naphthalene⁹ and BCB¹⁰⁻¹¹, since crystallographic studies of NBCB have not been done. Using these results, the distance from the center of the 9-10 bond to the center of the ethylene bridge was 2.95 Å for acenaphthene and 2.93 Å for pyracene, while the distance from the center of the naphthalene ring with carbons 5 through 10 to the center of the ethylene bridge was 5.15 Å for NBCB. Arbitrarily placing the cation 4 Å above the ring (found to be the best position for acenaphthene³), the distance from the center of the cation to the ethylene bridge, using the most favored ion-pair configurations, was calculated to be 4.97 Å for acenaphthene, 4.96 Å for pyracene, and 6.52 Å for NBCB.

These results provide a reasonable explanation for the absence of alternating line-widths

and nonequivalency of methylenes in NBCB. Further, the calculated distances serve as a rough approximation of the range over which ion-pairing perturbations may be expected for compounds similar to those discussed in this paper.

Acknowledgements

We are grateful for partial support of this work by the National Science Foundation.

References

1. NDEA Fellow, 1967-1970; Ethyl Fellow, 1970-1971.
2. E. de Boer and E. L. Mackor, Proc. Chem. Soc. London, 23(1963); E. de Boer and E. L. Mackor, J. Amer. Chem. Soc., 86, 1513(1964); E. de Boer, Recl. Trav. Chim. Pays-Bas, 84, 609(1965).
3. M. Iwazume, M. Suzuki, T. Isobe, and H. Azumi, Bull. Chem. Soc. Japan, 40, 2754(1967).
4. R. D. Rieke, S. E. Bales, P. M. Hudnall, and C. F. Meares, J. Amer. Chem. Soc., 93, 697(1971).
5. E. de Boer, private discussion. See also A. H. Reddoch, Colloq. Int. Centre. Nat. Rech. Sci., No. 164, 419(1966).
6. Coulomb variations were made by use of $\alpha_r = \alpha_o + h_r |\beta_o|$.
7. G. L. Simmons and E. C. Lingafelter, Acta Cryst., 14, 872(1961).
8. H. W. W. Ehrlich, ibid., 10, 699(1957).
9. D. W. J. Cruickshank, ibid., 10, 504(1957).
10. G. L. Hardgrove, L. K. Templeton, and D. H. Templeton, J. Phys. Chem., 72, 668(1968).
11. F. H. Allen and J. Trotter, J. Chem. Soc. B, 916(1970).