PYRACYLENE RADICAL ANION (la,b)

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Previously (2), we reported the preparation of pyracylene in solution.
This unique system appears to be best described in terms of its 4n periphery.
To provide further insight into the electronic nature of this system and to
examine the important question of variation of Q in the McConnell relation-
ship with bond angle (3,4), we undertook an e.s.r. study of the radical anion
of pyracylene.

The e.s.r. spectrum was obtained by electrolysis of a DMF solution of
pyracylene, 1,2,5,6-tetrabromopyracene, or 1,2-dibromopyracylene using tetra-
ethylammonium iodide as supporting electrolyte. Splitting constants of 2.52
(4H) and 1.88 (4H) gauss were obtained. The splitting constant ratio of 1.34
is of importance because simple Hückel theory predicts equal spin densities
at positions a and b for the radical anion of pyracylene. Fraenkel's group
(3) and Higuchi (4) have presented correlations which show Q_{CH}^{H} in the
McConnell equation should increase as the C-CH-C angle is decreased, but little
experimental data bearing on this point has been presented. Pyracylene radical
anion, although a nonalternant system, has zero spin density at the central
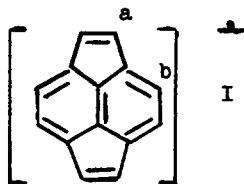
two carbons in the odd electron molecular orbital, thus leaving an alternant
periphery. Hückel calculations are expected to work well for this system.
Since the a,a' bonds of I may be somewhere between an aromatic and a single
sp^2-sp^2 bond in length, it may be reasonable to expect lower overlap between

these positions than between normal aromatic carbons. To account for this, $k_{a,a'}$ in $\beta_{ij} = k_{ij}\beta$ was varied from 1.0 to 0.7. The Longuet-Higgins and Salem equation (5) for variations of β with bond length predicts a value of about 0.70 for β_{ij} for a bond length of 1.52 Å, the maximum sp^2-sp^2 bond length known (the central bonds of biphenylene (6)); the Mulliken relation (7) gives a higher value of 0.82; and the Coulson and Golebiewski relation (8) gives a value of 0.73. The a,a' bond of I is expected to be somewhat shorter. Values of Q_{CH}^H in the McConnell equation required to fit the spectrum of pyracylene radical anion with variation of $\beta_{a,a'}$ appear in Table I. The difference in $Q_{C_aH}^H$ and $Q_{C_bH}^H$ does decrease as $\beta_{a,a'}$ is decreased, but $Q_{C_aH}^H$

TABLE I

McConnell Q_{CH}^H Values for Pyracylene Anion[+]

	Hückel Calculation				McLachlan Calculation			
$k_{a,a'}$	1.0	0.9	0.8	0.7	1.0	0.9	0.8	0.7
Position a	30.2	30.4	30.8	31.8	29.6	29.8	30.4	31.5
Position b	22.6	24.1	25.6	27.1	21.3	23.6	26.1	28.8

[+]Calculated as $Q_{CH}^H = a_1/\rho_1$

must be somewhat higher than $Q_{C_bH}^H$ for reasonable $\beta_{a,a'}$ values. Modified McConnell equations replacing Q_{CH}^H by (Q' + KX) where Q' and K are empirical constants nave been suggested. In the Colpa and Bolton modifications (9) X is the excess charge density, and in the Giacometti, Nordio, and Pavan form (10) X is the absolute sum of the bond orders to the carbon under consideration. Table II shows these modifications do not give agreement with experiment for pyracylene if equal Q' and K values are used at positions a and b. The C-CH-C angle at position a of I is estimated to be between 107° and 110°. The Fraenkel and Higuchi calculations for Q variation give values of 35-40 for this range. Clearly, these values are too high, but a $Q_{C_aH}^H$ near 30-31 is required to fit experiment.

TABLE II

Calculated Ratios of a_a/a_b

	$k_{a,a'} = 1.0$	$k_{a,a'} = 0.8$	$k_{a,a'} = 0.7$
McConnell, Hückel	1.00	1.11	1.14
McConnell, McLachlan	0.96	1.15	1.22
Colpa and Bolton[*]	0.94	1.06	1.14
Giacometti, Nordio, and Pavan[‡]	1.00	1.13	1.24
Experiment		(1.34)	

[*]$Q' = 27$, $K = 12$; [‡]$Q' = 31.5$, $K = 7$

References

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