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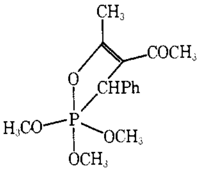

From the proton resonance spectrum data obtained by Gorenstein and Westheimer, Usher[2] determined a value of 12 kcal/mol for the free energy of activation of the exchange process. This number provides a rough estimate for pseudorotation inhibition; thus if the energy barrier for placing an O$^-$ ligand in an axial site in TBP IV is similar to that for TBP II, it will make pseudorotation unlikely.

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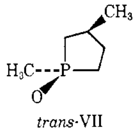
(31) NOTE ADDED IN PROOF. (1) D. Perahia, A. Pullman, and H. Berthod, *Theor. Chim. Acta*, **40**, 47 (1975), have recently carried out an ab initio study on the effect of the phosphorus 3d orbitals on some of the properties of the dimethylphosphate anion. They also concluded that omitting the phosphorus 3d orbitals does not qualitatively affect the general results obtained for most of the properties studied.

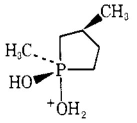
(2) We have recently carried out calculations for $R_1 = R_2 = R_3 = H$ in TBP III and TBP IV to determine which is more stable. Our results indicate that TBP IV is more stable than TBP III in agreement with the conclusions reported in the main body of this paper.

(3) In his mechanism for the acid-catalyzed interconversion of the cis and trans isomers of the phospholane oxide VII,



trans-VII

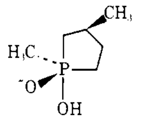
K. L. Marsi, *J. Am. Chem. Soc.*, **91**, 4724 (1969), postulates that the first step involves protonation of the phosphoryl oxygen and addition of H_2O to the oxide to form TBP VIII.



TPB VIII

This TBP then pseudorotates twice, first with the OH group as the pivot and then with the OH_2^+ group as the pivot. After the first pseudorotation, the two most electronegative groups, OH and H_2O^+, both occupy equatorial sites making this pseudorotamer a relatively unstable species. After the second pseudorotation, the OH group leaves (perhaps, after proton shift) yielding the isomer crossover.

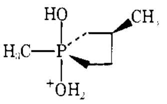
The cis and trans isomers of VII do not interconvert under basic conditions. Yet it seems likely that the mechanism postulated by Marsi would work equally well, if not better, under basic conditions. The initial TBP formed would be TBP VIII′. Under basic conditions, the phosphoryl oxygen



TBP VIII′

would not be protonated and an electropositive O$^-$ rather than an electronegative OH would occupy an equatorial site. Furthermore, the subsequent step would involve the more probable pseudorotation with an electropositive O$^-$ ligand rather than an electronegative OH ligand as the pivot. This would result in only one electronegative group (OH) being equatorial. Consequently, both pseudorotamers formed via Marsi's scheme would seem to be more stable under basic conditions.

Since the interconversion is not observed under basic conditions, it seems more probable that the initial step in the acidic reaction yields TBP



TBP IX

IX. We have shown that its analogous anionic structure is not stable; thus, interconversion via IX would be expected to go in acid but not in base.

Carbon-13 Nuclear Magnetic Resonance and Ring Currents in Vinyl Cross-Linked Annulenes

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Received October 15, 1975

Abstract: Carbon-13 NMR spectra were determined for pyracylene and several of its dihydro- and phenyl-substituted derivatives. Comparison of the data confirmed earlier indications from proton NMR spectra that pyracylene exhibits paratropism. A simple additive procedure for comparison of model compounds in determining ring current effects was developed in the course of this analysis and was applied to acepleidylene to estimate the magnitude of its diatropism. Carbon-13 NMR spectroscopy was shown to be useful for the evaluation of ring current effects when good model compounds are available.

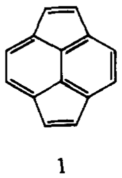
The concept of a ring current in conjugated cyclic hydrocarbons was first proposed from a purely classical viewpoint by Pauling to rationalize the large diamagnetic susceptibilities and diamagnetic anisotropies of certain molecules, such as benzene.[1,2] In 1937, London[3] offered the first quantum mechanical rationalization for ring currents by modifying the one-electron Hamiltonian of HMO theory to include the potential of the applied magnetic field, and showing that the susceptibility then depended upon the presence of closed loops of conjugated π orbitals. In 1956, Pople suggested that such a classical ring current could account for the abnormal deshielding of protons in the NMR spectrum of benzene.[4,5] In 1966, Pople and Untch[6] and Longuet-Higgins[7] pointed out that in [4*n*]annulenes and related compounds, ring currents could be paramagnetic as well as diamagnetic.

Probably the strongest reinforcement of organic chemists' adoption of the intuitively appealing ring-current concept derives from proton NMR spectroscopy, and in particular from the NMR spectra of annulenes.[2,8-11] However, for atoms as heavy as carbon, ring-current effects are more difficult to observe because local paramagnetic contributions dominate the shielding constant.[12,13] This does not imply that nonlocal "ring current" contributions do not exist, but their magnitudes (in parts per million) should be approximately the same for carbon nuclei as for protons,[9a] and because carbon is far more sensitive than hydrogen to such effects as steric strain and immediate electronic environment[11c,14] it is difficult to sort out the effect of the ring current. Vogel, for example, has concluded on the basis of a study of bridged [14]annulenones that ^{13}C NMR is "not suitable as a probe for the magnetic properties of cyclic π systems".[11c] Indeed, a number of other studies also lead to difficulties in interpreting the significance of the observed shifts.[16] Probably, the observations of Du Vernet and Boekelheide[9a] on the dihydropyrene systems constitute the best evidence reported to date for a diatropic ring current effect on ^{13}C chemical shifts.

The principal difficulty in using ^{13}C NMR to recognize the ring-current effects lies in obtaining suitable reference compounds with which to compare a potentially paratropic or diatropic system. A good example of the need for adequate models is the case of biphenylene. Originally, the low-field chemical shift of the cyclobutane carbons in biphenylene (151.8 ppm below TMS) was thought to demonstrate the presence of a paramagnetic ring current in the system.[17] However, by comparing the early results with a variety of related examples, Jones et al.[18] were able to show that this shift is not unusual for molecules of this type, and that the chemical shifts in biphenylene could be adequately accounted for by additivity relationships.

A second disadvantage of ^{13}C NMR relative to ^{1}H NMR for the observation of ring-current effects is the fact that the carbons around the periphery of the ring are expected to be neither strongly shielded nor strongly deshielded by the nonlocalized electron currents.[11c] In the classical current-loop model[19,20] the carbons of the ring lie between the shielding and deshielding regions. Therefore, to find ring-current effects on ^{13}C, it is necessary to observe carbons inside or outside the current loop.

Despite the gradually improving success of the use of ^{13}C NMR as a probe for diatropism, no case has yet been reported in which paratropism has clearly caused ^{13}C effects.[18] Pyracylene, **1**, a molecule for which proton NMR evidence for paratropism has been reported[21] and for which recent calculations of Mallion and Coulson[22] substantiate such an interpretation, seemed to provide a promising system in which to search for such effects. The rigidity of the tetracyclic carbon skeleton in this molecule, evident from molecular models, suggested that little geometric change should be expected between pyracylene, 1,2-dihydropyracylene (**2**), and pyracene (**3**), but any paramagnetic ring current associated with the peripheral 12-π-electron system in **1** should be absent in **2** or **3**. Furthermore, the availability of 1,2-diphenyl-substituted derivatives of these molecules[21] provided a parallel system for confirmation of the observed effects, and the geometric similarity of acenaphthene and acenaphthylene, for which ^{13}C spectra had already been analyzed,[23] promised good analogies in making the band assignments. Therefore, samples of pyracylene, 1,2-dihydropyracylene, 1,2-diphenylpyracylene, and 5,6-diphenyl-1,2-dihydropyracylene were prepared according to previously described methods[21] and their ^{13}C NMR spectra were obtained.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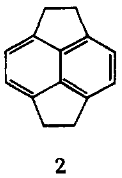
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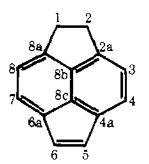
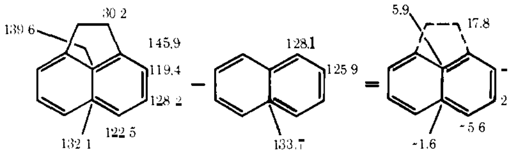


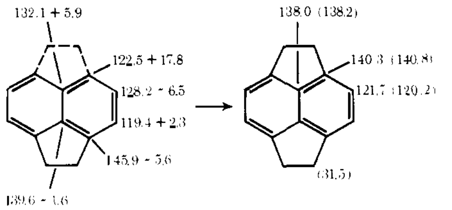
3

Carbon-13 NMR Spectra of Pyracylenes

The excellent success of additivity relationships for the prediction of chemical shifts in carbon[24] and proton[25] NMR spectroscopy prompted the application of this technique to the assignment of the ^{13}C NMR spectra of pyracylenes, using suitable derivatives as model compounds. Beginning with the known chemical shifts of naphthalene and acenaphthene, additive shift contributions for the addition of the ethano bridge were determined. Subtraction of the naphthalene chemical shifts from those of acenaphthene yielded changes to be expected in a naphthalene skeleton when such a bridge is added, as shown in eq 1. Although the chemical shifts of the reference compounds were determined in carbon disulfide or dioxane/carbon disulfide, the solvent shifts between these solvents and chloroform-*d* were expected to be on the order of 1 ppm or less,[26] and indeed, application of the shift modifications determined above to acenaphthene gave excellent agreement with the observed chemical shifts for pyracene in chloroform-*d* (eq 2). The observed chemical shifts in chloroform-*d* are shown in parentheses. These values were assigned to the indicated carbons on the basis of their spin multiplicities and apparent intensities (see Experimental Section, Table III).



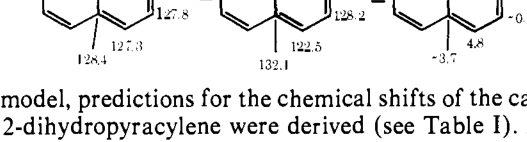
(1)



(2)

The additive shift contributions obtained and applied in this manner should represent steric, conformational, and inductive effects on the chemical shifts. Carbon-13 chemical shifts are known to be very sensitive to such effects.[11c,27]

A similar procedure was used to obtain additive shift values for the conversion of an ethano bridge into an etheno bridge by subtracting the chemical shifts of acenaphthene from those of acenaphthylene (eq 3). By applying these values to pyracene as a model, predictions for the chemical shifts of the carbons of 1,2-dihydropyracylene were derived (see Table I). Alternatively, the ethano shifts derived above were applied to ace-



(3)

Table I. Predicted and Observed ^{13}C Shifts of **1** and **3**[a]

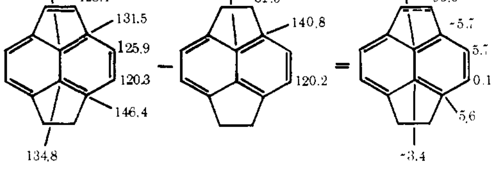
	Position							
Compd	1,2	2a,8a	3,8	4,7	4a,6a	5,6	8b	8c
3 predicted[b]		145.6	119.8	125.1	134.9	131.0	134.5	127.3
3 predicted[c]		145.1	121.3	126.6	134.4		134.3	127.1
3 obsd	32.3	146.4	120.3	125.9	135.1	128.1	134.8	126.8
1 predicted[d]	131.8	140.5	125.2	125.5	139.9		123.9	123.1
1 predicted[e]	128.9	140.7	126.0	126.0	140.7		123.4	123.4
1 obsd	132.4	142.0	124.8	124.8	142.0	132.4	131.5	131.5

[a] All chemical shifts are given in ppm downfield from TMS. [b] Calculated on the basis of ethano-etheno shifts (eq 3) applied to pyracene. [c] Calculated on the basis of ethano shifts (eq 1) applied to acenaphthylene. [d] Calculated on the basis of ethano-etheno shifts (eq 3) applied to 1,2-dihydropyracylene. [e] Calculated on the basis of shifts obtained from eq 4.

naphthylene as a model and these results are also summarized in Table I.

It is gratifying that these approaches led to predictions which are in excellent agreement with experimentally determined resonances and with each other. Together with C–H coupling data and Overhauser enhancement information (see Experimental Section, Table V), these predictions provide unequivocal assignments for all peaks in the 1,2-dihydropyracylene spectrum.

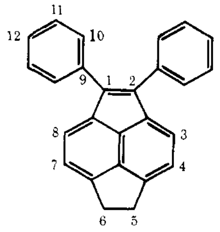
The spectrum of pyracylene itself was complicated by the presence of unavoidable impurities arising from decomposition of the sample during the time it resided in the NMR probe. In particular, the assignment of the bands for the quaternary carbons, which are expected to be weak because of long T_1's, was difficult in the noise-decoupled spectrum. Addition of ferric acetonylacetonate, a paramagnetic species, greatly enhances dipole–dipole relaxation,[28] resulting in appearance of lines corresponding to carbons with abnormally long T_1's and simultaneous elimination of NOE enhancement of lines corresponding to proton-substituted carbons in minor impurities. The net effect is the dramatic intensification of the absorptions for quaternary carbons relative to the remainder of the spectrum. To completely eliminate the effects of NOE, a spectrum of pyracylene was obtained with no decoupling field and $Fe(acac)_3$ present. Only four peaks remained in the spectrum, at 142, 132.4, 131.5, and 124.8 ppm with estimated area ratios (valid only in the absence of NOE) 2:2:1:2. The peaks at 132.4 and 124.8 ppm were split into doublets with J_{CH} of 171 and 159.3 Hz, respectively. The doublet at 132.4 was broader than that at 124.8. On the basis of this information, the observed chemical shifts in the decoupled spectra, and the assignments previously obtained for dihydropyracylene (which shows substantial distant coupling in the C-5 doublet $^1J_{CH}$ = 168.5 but less distant coupling in the C-3 and C-4 doublets of $^1J_{CH}$ = 156 and 159), the resonances of pyracylene are assigned in Table IV. Using the additive procedure described above, the pyracylene chemical shifts were predicted to be as shown in Table I when the ethano-etheno shifts were applied to dihydropyracylene. Similar predictions are obtained using dihydropyracylene and pyracene to obtain the shift differences (eq 4) and applying them to dihydropyracylene (Table I). The



(4)

symmetry of the values in the final result is a consequence of using dihydropyracylene twice in the calculation. The agreement with experiment by either method is good except for the assignment for C-8b,8-c. The experimentally observed downfield shift for these carbons is attributed to the paratropism of the molecule, as described below.

A similar analysis can be performed for 1,2-diphenyl-5,6-dihydropyracylene (**4**) and 1,2-diphenylpyracylene (**5**), but



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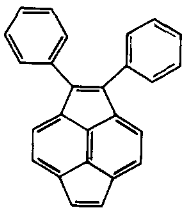


5

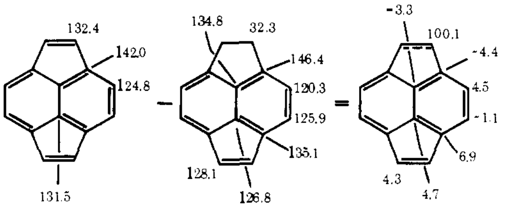
in these cases the picture is complicated by the lower symmetry of these systems as compared to pyracylene and by the presence of two more kinds of quaternary carbons. The absorptions of diphenyldihydropyracylene were assigned by comparison with dihydropyracylene and by application of the additive shifts developed for phenyl by Levy et al.[29] Treating 5-dihydropyracylenyl as phenyl and using Levy's substituent effects, the chemical shifts listed in Table II are predicted. All other resonances are assumed to be identical with the corresponding resonances in dihydropyracylene. Making use of these predictions, and of the decoupling data and estimated intensities of the undecoupled spectrum as tabulated in the experimental section, Table VI, the assignments in Table II were obtained. The assignments for C-1 and C-9 rested on the observation of a greater NOE enhancement for the resonance at 136.3 ppm,[30] and agreed with the prediction obtained above that C-1 should resonate downfield of C-9.

Like pyracylene, the diphenylpyracylene used to obtain ^{13}C spectra contained impurities that were identified by observation of their relatively large NOE enhancements. The large number of long-range C–H couplings precluded complete assignment of the undecoupled spectrum and identification of all $^1J_{CH}$ values because many broad lines overlapped one another. However, off-resonance decoupling, which removed distant couplings and partially collapsed the doublets arising from one-bond C–H couplings, permitted identification of all signals when combined with noise decoupling, addition of $Fe(acac)_3$ to promote relaxation of ^{13}C nuclei far from protons, and chemical shift predictions based on dihydropyracylene, pyracylene, and diphenyldihydropyracylene. Utilizing these compounds as models (eq 5), an approach which includes any paratropic contributions to the chemical shift, gives the values predicted in Table II. The eventual assignments are included in the table for comparison. The excellent agreement between the calculated and observed shifts, particularly for C-8b and C-8c, provides a strong confirmation of the assignments previously made for pyracylene. The appearance of some of the

Table II. Predicted and Observed ^{13}C Shifts of **4** and **5**[a]

Compd	1,2	2a,8a	3,8	4,7	4a,6a	5,6	8b	8c	9,15	*o*-Ph	*m*-Ph	*p*-Ph
4 predicted[b]	142.2								141.6	127.4	128.9	126.3
4 obsd	137.5	135.6	125.9	120.6	146.7	32.4	126.7	135.3	136.3	128.3	129.9	126.7
5 predicted[c]	141.8	142.5	124.8	125.1	142.3	132.5	131.4	132.0	136.3	128.3	129.9	126.7
5 predicted[d]	138.3	141.2	126.0	126.3	141.0	129.0	123.3	123.9	136.3	128.3	129.9	126.7
5 obsd	140.7	142.9	124.6	124.8	141.9	132.6	131.4	131.7	134.8	128.3	128.7	127.4

[a] All chemical shifts are in ppm downfield from TMS. [b] Calculated on the basis of additive shifts of Levy et al. (see text). [c] Calculated on the basis of ethano–etheno shifts derived from pyracene–pyracylene, eq 5, which includes paratropic contribution applied to **4.** [d] Calculated on the basis of ethano–etheno shifts derived from acenaphthene–acenaphthylene, eq 3, which does not include paratropic contribution applied to **4.**



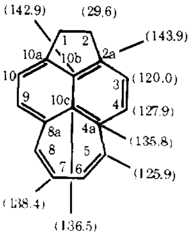
(5)

phenyl carbons (particularly C-9) upfield of their predicted locations provides further evidence for paratropism in the pyracylene molecule.

If dihydropyracylene and pyracene are used instead of pyracylene and dihydropyracylene to estimate the chemical shifts of diphenylpyracylene, then contributions from paratropism in pyracylene will not be included in the chemical shift predictions. Table II also gives the predicted shifts for diphenylpyracylene using such models. These predictions permit an estimate of the paratropic contribution to the chemical shifts of C-8b and C-8c in diphenylpyracylene of 7.8 and 8.1 ppm, respectively. These values compare with an estimate of 7.6–8.4 ppm obtained from the models described above for pyracylene itself.

Recent work points out the importance of the contributions of local anisotropic effects in interpreting proton chemical shifts.[31a] Interpreting ^{13}C NMR shifts also requires consideration of whether this additivity approach accounts for changes in local paramagnetic shielding terms between the models and pyracylenes which may arise, for example, from differences in charge densities in such nonalternant hydrocarbons. Calculations reveal that differences in charge densities between acenaphthylene and pyracylene are quite small.[31b] More significantly, the shifts predicted for the peripheral carbons C-2a, 3, 4, 7, 8, and 8a of pyracylene are in excellent agreement with the observed shifts even though differences in charge density between these carbons and the corresponding ones in acenaphthylene are larger than the differences in charge density between C-8b and 8c relative to the similar carbons of acenaphthylene. Thus, the approach nicely accounts for local contributions to the chemical shift and the discrepancy between predicted and observed shifts for the latter set of carbons is attributed to nonlocal effects.

Application of Additive Shift Contributions of Acepleiadylene



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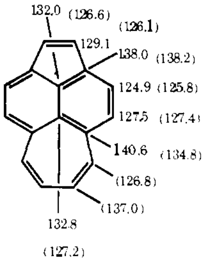


7

Application of the ethano–etheno additive shift contributions derived above to the ^{13}C chemical shift data of Jones et al.[32] leads to some interesting further insights of the spectra of acepleiadiene (**6**) and acepleiadylene (**7**). Using selective proton decoupling data, relative band intensities, and analogy to acenaphthene, Jones et al. assigned the resonances of acepleiadiene and acepleiadylene as shown in parentheses above, although they were uncertain of the assignments for C-10b and C-10c. (Their shifts were given relative to benzene, and have been converted to TMS reference.) If one applies to acepleiadiene the ethano–etheno shifts derived above from acenaphthene and acenaphthylene, one obtains the predictions shown in **7** (Jones' assigned values are in parentheses). These predictions for C-3 and C-4 are in good agreement with the observed values. The prediction for C-1 is off by 3 ppm; however, a similar large error at this position was found in the prediction for dihydropyracylene, and seems to be associated with the large chemical shift differences between sp^3- and sp^2-hybridized carbons in the two model compounds. The discrepancy in the value for C-4a is much more distressing. It is possible that a reversal in the assignment of C-2a and C-4a is necessary. The published assignment of the former is based upon comparisons to acenaphthene and acenaphthylene; the assignment of the latter is based upon the closeness of the resonance at 134.8 in **7** to the resonance at 135.8 in **6.** The resulting 6-ppm difference in the observed and calculated shifts at C-4a appears overly large, considering the excellent agreements achieved previously using this additive method, and it seems possible that the published assignments for C-2a and C-4a of **7** are reversed. Even this reversal would leave discrepancies of 3.2 and 2.4 ppm respectively between the observed and calculated values for these two carbons.

Finally, examination of the observed and calculated positions of C-10b and C-10c in **7** also proves useful. The excellent agreement between the *differences* in these shifts (0.6 ppm observed, 0.8 ppm calculated) reinforces the assignments of C-10b and C-10c in **6.** Were these assignments incorrect, the calculation would place C-10b in **7** 15.8 ppm downfield of C-10c, and such an error is far greater than the maximum so far observed with this type of calculation. However, the observed resonance positions of C-10b and C-10c are upfield of the calculated positions by 5.6 and 5.4 ppm, respectively. This effect is readily explained as a manifestation of diatropism in **7**, and will be discussed further below.

An alternative additive approach to the chemical shifts of acepleiadiene and acepleiadylene uses the published data for pleiadiene[33] and naphthalene to derive additive contributions for the butadieno bridge. The pleiadiene shifts were determined in acetone-d_6 and were reported relative to external carbon-^{13}C disulfide. Lack of correction for this fact may exacerbate discrepancies between the predicted and observed shifts. Application of these shifts to acenaphthene gives estimated acepleiadiene absorptions derived in eq 6. Observed chemical shifts

Table III. Spectroscopic Data for Pyracene[a]

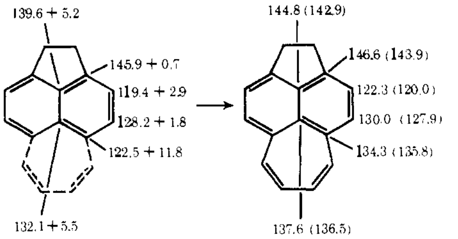
Spectrum	1	2
Cr(acac)$_3$	Yes	No
^{1}H decoupling	None	Noise
Carbon		
2a	140.8	140.7
8a	138.2	138.2
3	120.3 (157.0)	120.2
1	31.6 (131.3)	31.5

[a] Chemical shift in ppm. Numbers in parentheses are $^1J_{CH}$ in Hz.

Table IV. Spectroscopic Data for Pyracylene[a,d]

Spectrum	3[b]	4[c]	5[c]
Fe(acac)$_3$	No	No	Yes
^{1}H decoupling	Noise	None	None
Carbon			
2a	141.9 (43)		141.9
1	132.4 (108)	132.4 (171 ± 4)	132.4 (171 ± 4)
8b	131.6 (8)		131.7
3	124.7 (209)	124.7 (160 ± 4)	124.7 (159 ± 4)

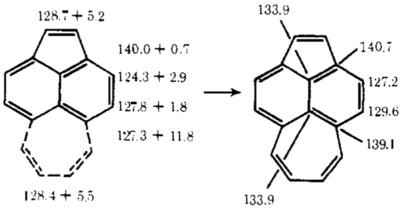
[a] Chemical shifts in ppm from TMS. [b] Numbers in parentheses are peak heights in mm. [c] Numbers in parentheses are $^1J_{CH}$ in Hz. [d] Impurity peaks appeared in spectrum 3 but not in 4 or 5 at 133.0, 130.4, 126.9, 124.9, 124.3, 123.8, 123.3, 113.2, and 55.9 ppm, and are unassigned. None had peak height greater than 13 mm.



(6)

for acepleiadiene are given in parentheses, and the predicted shifts are qualitatively correct, although the agreement is not as good as it was for pyracene and dihydropyracylene.

Application of these butadieno shifts to acenaphthylene produces the estimates for the chemical shifts of acepleiadylene in eq 7. Comparison with the results obtained by the ethano-



(7)

etheno adjustment of acepleiadiene and with the actual chemical shifts of acepleiadylene indicates reasonable agreement with the exception of the absorption for C-4a which may be in question.

The resonances for C-10b and C-10c of acepleiadylene appear upfield of their calculated positions. Utilizing different

Table V. Spectroscopic Data for 1,2-Dihydropyracylene[a]

Spectrum	6	7[d]	8[d]	9[b]	10
Fe(acac)$_3$	No	No	Yes	No	No
^{1}H decoupling	Noise	Noise	Noise	Gated noise	Single frequency δ 7.75
Carbon					
2a	146.5	146.5 (35)	146.4 (46)		146.4
4a	135.2	135.2 (37)	1351 (33)		135.1
8b		134.9 (10)	134.8 (17)		
5	128.1	128.1 (187)	128.1 (61)	128.1 (168.5 ± 1)[c]	128.1
8c		(6)	126.8 (23)		126.8
4	125.9	125.9 (196)	125.9 (50)	125.9 (158.6 ± 1)	125.9
3	120.4	120.4 (206)	120.3 (57)	120.4 (156 ± 2)	120.3
1	32.3				

[a] Chemical shifts in ppm downfield from TMS. [b] Numbers in parentheses are $^1J_{CH}$ in Hz. [c] Seco ary couplings of 3.2 and 5.1 Hz are resolvable. [d] Numbers in parentheses are relative peak integrals.

Table VI. Spectroscopic Data for 1,2-Diphenyl-5,6-dihydropyracylene[a]

Spectrum	11	12[b]	13[c]	14
Fe(acac)$_3$	No	Yes	Yes	Yes
^{1}H decoupling	Noise	None	Noise	Off-resonance at δ −8
Carbon				
4a	146.7	146.8	146.7	146.6
1	137.5	137.5	137.5	137.5
9 (α-Ph)	136.3	136.3	136.2	136.2
2a	135.6	135.7	135.6	135.6
8c		135.5	135.3	135.2
11 (*m*-Ph)	129.9	129.9 (159 ± 4)	129.8	129.9
10 (*o*-Ph)	128.2	128.3 (160 ± 4)	128.2	128.3
12 (*p*-Ph)	126.7	126.8 (160 ± 4)	126.7	126.7
8b				126.6
3	125.9	125.9 (159 ± 2)	125.8	125.9
4	120.6	120.7 (159 ± 2)	120.6	120.7
5	32.4			

[a] Chemical shifts in ppm downfield from TMS. [b] Numbers in parentheses are $^1J_{CH}$ in Hz. [c] Proton-substituted carbons were not fully decoupled by the decoupler power used in this spectrum, and appear as broad bands.

Table VII. Spectroscopic Data for 1,2-Diphenylpyracylene[a]

Spectrum	15	16	17	18	19
$Fe(acac)_3$	No	No	Yes	No	Yes
^1H decoupling	Noise	Noise	Off-resonance at δ −8.0	Gated noise	Noise
Carbon					
2a	143.0	143.0	143.0	Unresolved	142.9
4a	142.0	142.0	141.9		141.9
1	140.8	140.7	140.8		140.7
9	134.8	134.8	134.7		134.7
5	132.6	132.6	132.6 (75.7)	132.6 (171)	132.5
8a				Unresolved	131.7
8b					131.4
11	128.7	128.6	128.6 (74.5)		128.5
10	128.2	128.2	128.1 (75.5)		128.1
12	127.4	127.4	128.5 (76.2)		127.3
4	124.9	124.9	124.9 (72.5)	127.9 (160)	124.8
3	124.7	124.7	124.7 (72.7)	124.7 (160)	124.6

[a] Chemical shifts in ppm downfield from TMS. Numbers in parentheses are $^1J_{CH}$ in Hz. [b] Benzene appears in the sample at 128.5 ppm ($J \approx 75$ Hz in spectrum 17), and unidentified impurities appear at 129.7 and 126.8 ppm in all spectra as well as at 56.1 ppm in spectrum 15 and 123.6 ppm in spectrum 16. These impurity peaks decrease substantially in intensity relative to C-8a,8b in spectrum 19.

models, Jones et al.[32] noted a 10- and 16-ppm upfield shift, respectively, for these carbons and concluded that "the shifts at C-15 (C-10b, our numbering) and C-16 (C-10c, our numbering) can only be accounted for in terms of a $4n + 2$ peripheral π electron ring current ...". Examination of the models developed here indicates that a substantial part of that shift difference can be accounted for by the addition of the C-1,2 double bond in **2**. The upfield shift of 5.4–7.3 ppm from the models herein provides the best available measure of the ring current contribution to their chemical shifts.

Conclusion

The preceding discussion has presented a formal method by which the additivity of ^{13}C chemical shift effects can be applied to obtain estimates of diatropism and paratropism in conjugated molecules. Differing levels of success from the two different approaches to estimates of the shifts in acepleiadylene have shown that good model systems are still necessary if accurate evaluations are to be achieved.

By applying this method to acepleiadylene, an estimate of about 6 ppm for the diatropic shift of the two internal carbons of this molecule was obtained. Application to pyracylene, on the other hand, confirmed proton NMR evidence for paratropism in this molecule and estimated the magnitude of the paratropic shift at the central carbons at about 8.0 ppm. It appears that ^{13}C NMR is a more useful probe for ring currents than sometimes has been attributed to it.

Experimental Section

All spectra were determined in chloroform-*d* using a Varian XL-100 spectrometer, internally locked on the deuterium of the solvent, in FT centerband mode. Chemical shifts were determined relative to internal chloroform-*d* or tetramethylsilane and are reported in parts per million downfield from TMS, calculated at 25.16 MHz by assuming that the center of the chloroform-*d* triplet occurs at 76.9 ppm.[27] $Cr(acac)_3$ or $Fe(acac)_3 \cdot H_2O$ were obtained commercially (Aldrich Chemical Co.) and were used without purification in concentrations of approximately 0.005 M.

Pyracylene, pyracene, dihydropyracylene, and diphenylpyracylene were prepared by the method of Trost, Bright, Frihart, and Brittelli.[21] Diphenyldihydropyracylene was prepared by Buhner using the published procedure.[22] Pyracylene and diphenylpyracylene were purified by column chromatography on silica gel with anhydrous ether and benzene–hexane (1:20), respectively, before use.

The data for pyracene, pyracylene, 1,2-dihydropyracylene, 1,2-diphenyl-5,6-dihydropyracylene, and 1,2-diphenylpyracylene are summarized in Tables III through VII. The assignments indicated were derived as described in the previous section. Copies of the spectra are available in the thesis of W.B.H., University of Wisconsin, 1975.

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Oxidation of Polycyclic Arenes in SbF_5/SO_2ClF. Formation of Arene Dications and Observation of Electron Exchange with Radical Cations Based on ^{13}C Nuclear Magnetic Resonance Studies[1]

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Abstract: A series of aromatic hydrocarbons was examined for formation of arene dipositive ions in SbF_5/SO_2ClF solution. Arenes with low ionization potentials as predicted in simple Hückel π-electron molecular orbital calculations are oxidized to dications, which were detected by ^{13}C NMR spectroscopy. The ^{13}C spectra of picene and 1,2,3,4-dibenzanthracene dications show nonuniform line-broadening due to electron exchange between the dications and the radical cations. Arenes predicted to have high ionization potentials formed solid products in SbF_5/SO_2ClF, probably via the radical cations. Naphthalene was not oxidized to a dication, but a dication was observed for octamethylnaphthalene.

Introduction

Polycyclic aromatic hydrocarbons have been the subject of an extraordinary amount of research, undoubtedly due in part to the early development of π electronic theories. The carcinogenic activity of many polycyclic arenes has also been a stimulus to research in this area. Evidence has been accumulating that most chemical carcinogens are either strongly electrophilic agents per se or are converted in vivo to electrophilic agents by metabolic action.[3,4] Thus, as part of our continuing investigations of carbocationic species, we were interested in possible chemical conversions of polycyclic arenes to carbocations which obviously are potential electrophiles. In this paper, we report our observations on the chemical oxidation of polycyclic arenes to stable dipositive ions. The oxidations were carried out using SbF_5 in SO_2ClF and the dications were detected by ^{13}C NMR spectroscopy. Simple Hückel π-electron molecular orbital theory is used as a background for presenting our experimental results.

Dipositive ions of aromatic systems have been observed in electrochemical oxidations,[5] and have been implicated as intermediates in reactions of radical cations[6-8] and in ESR studies of stable radical cations.[9] The generation of arene dications from arenes in strong acid media has been reported for naphthacene by SO_3 in dimethyl sulfate,[10] for naphthacene and 1,2-benzanthracene by FSO_3H-SbF_5,[11] and for naphthacene, perylene, anthracene, and some substituted anthracenes by SbF_5 in SO_2ClF, FSO_3H, or H_2SO_4.[12] The unusual hexachlorobenzene dication has been generated in SbF_5-Cl_2 at low temperatures.[13] We now report the oxidation of an extensive series of arenes to dipositive ions, including a naphthalene dication, and we also report our observations on systems with ionization potentials too high to permit full ionization to the dication stage. ^{13}C NMR is used to demonstrate the existence of the dications because of the sensitivity of ^{13}C chemical shifts to charge development; no previous ^{13}C data are available for arene dications.

Experimental Section

All polycyclic arenes were commercially available compounds of the highest purity, with the exception of octamethylnaphthalene, which was a generous gift of Professor Harold Hart, Michigan State University. SbF_5 was distilled twice prior to use and SO_2ClF was distilled directly from a storage cylinder into the reaction flask. The typical procedure for generation of dications was to add 100–150 mg of the solid arene, in small portions, directly to a vigorously stirred (Vortex mixer) solution of 1.5 ml of SbF_5 in 2 ml of SO_2ClF kept at -10 to -40 °C by periodic cooling in an ice-salt or dry ice-acetone bath. Depending on the molecular weight of the arene, SbF_5 was present in 40- to 100-fold excess on a mole-to-mole basis. The dication solutions were transferred immediately into the NMR tubes used for ^{13}C NMR analysis. About 0.5 ml was removed by precooled pipet for examination by ^1H NMR, and then returned to the ^{13}C NMR tube if signals were detected in the ^1H NMR spectrum. ^{13}C NMR spectra were obtained on a Varian Associates Model XL100-15 spectrometer operated in the pulsed Fourier transform mode. Ion concentrations were dilute and required 1000–4000 transients for acceptable signal-to-noise ratios. The spectra were recorded at 5000–7000 Hz spectral width. Chemical shifts were measured from the Me_4Si signal of a 1.75-mm capillary of 5% ^{13}C-enriched Me_4Si. The temperature at which the spectra were measured was -10 °C except as follows (ion, temp): **16**, $-30°$; **17**, $-25°$; **18**, $-40°$; and **19**, $-40°$.

Results and Discussion

Eighteen unsubstituted aromatic hydrocarbons were examined, using ^{13}C NMR, for the formation of stable dipositive ions when dissolved in SbF_5/SO_2ClF. The results are summarized in Table I. The arene systems in Table I are listed in the order of increasing energy level of the highest occupied π