Carbon-13 Nuclear Magnetic Resonance Studies of Benzocycloalkenes and Fluorobenzocycloalkenes[1]

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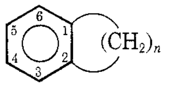
The ^{13}C NMR spectra of *o*-xylene, tetralin, indan, benzocyclobutene, and *o*-di-*tert*-butylbenzene and (excluding the latter) their 3- and 4-fluoro analogues have been obtained and assigned. In the hydrocarbon cases, aromatic carbon assignments were confirmed by examination of tactically deuterated compounds, while considerations of ^{13}C–^{19}F couplings and ^{19}F contributions to carbon screenings permitted complete assignments of all aryl and essentially all aliphatic carbon signals in the fluorobenzocycloalkenes. It is concluded that fluoro substitution in aromatic systems is manifested by sufficiently regular trends in ^{13}C–^{19}F couplings and contributions to carbon screenings as to be a useful strategy for spectral assignment of the unfluorinated aromatic. Trends in chemical shifts with the size of the fused ring ("ring strain") are discussed in the light of existing chemical shift theory, and available quantum chemical calculations for these systems. Some examination of the ^{1}H NMR spectra of the deuterated benzocycloalkenes and ^{13}C satellite spectra have been conducted and while confirming the previous proton assignments for indan demand reversal of the assignments for *o*-di-*tert*-butylbenzene and benzocyclobutene. Preliminary studies of relaxation phenomena in these systems (T_1 measurements) indicate a useful basis for spectral assignments, as C_α in all cases examined has a longer T_1 than C_β. A qualitative explanation in terms of preferred modes of molecular rotation is advanced.

Much effort has been expended in determining the chemical and physical properties of benzocycloalkenes (I) since the initial observations of Mills and Nixon some 45 years ago.[3a,b]



$n = 1, 2$

I

Changes in properties at positions in the aromatic ring are usually associated with "ring strain" effects as the size of the 1,2-fused ring decreases, and a number of explanations involving bond fixation,[3a,b] bond-order changes[4] in intermediates in electrophilic substitutions, orbital electronegativities,[5] etc., have been advanced. Direct evidence of the effects of strain on molecular properties[6] of unsubstituted benzocycloalkenes is not abundant, but Gunther's liquid crystal ^{1}H NMR studies[7] of benzocyclopropene (n = 1 in I) suggest significant distortion with internal angular increase at C_4, C_5 and decrease at C_3, C_6 in the direction of theoretical estimates. X-ray studies of related systems, e.g., benzo[1,2:4,5]dicyclobutene,[8] confirm more profound changes in structural parameters compared with an "ideal" or unstrained system.

One thorough analysis of the effects of strain in benzocycloalkenes on certain proton–proton spin coupling constants has been reported.[3b] Cooper and Manatt determined that strain exerted an ambivalent effect on $J_{1,2}$ ($^3J_{\mathrm{H,H}}$) but $J_{1,3}$ ($^4J_{\mathrm{H,H}}$) decreased and $J_{1,4}$ ($^5J_{\mathrm{H,H}}$) increased substantially, and the effects of bond length, angle, and electronegativity changes were discussed. Using CNDO/2 minimized geometries,[9] impressive agreement in trends in the various $J_{\mathrm{H,H}}$ was obtained, and indicated to the authors that the calculated geometries and charge densities by CNDO/2 were, in all likelihood, close to the truth.

In connection with an investigation of the ^{13}C NMR spectra of certain silicon analogues[10] of the benzocycloalkenes, the question of "ring-strain" effects on aryl-carbon chemical shifts arose, and we therefore commenced an examination of the spectra of the benzocycloalkenes themselves. This study seemed potentially illuminating since rather substantial variations in the aryl ^{13}C shifts were expected, and could be construed as a reflection of bond-order and charge density fluctuations at the nuclei directly in the ring. In any event, the data were of considerable importance, since they would need to be accommodated in some way by more refined theories of the ^{13}C chemical shift. Scattered pieces of data on one or two benzocycloalkenes did exist in an obscure fashion in the literature, but critical spectral assignments were not substantiated. It emerged that two other parallel investigations in the same area were being conducted and were reported,[11,12] but some of the assignments in one report[11] are now known to require modification. In our work, it became clear that strategically fluoro-substituted derivatives of the benzocycloalkenes were of much assistance in the vexing question of assignments in the hydrocarbons, but in addition afforded data of other interest. The necessity to synthesise certain deuterated derivatives stimulated a curiosity in previous suggestions[3b,13] of ^{1}H NMR assignments and our conclusions in this direction are also presented.

With the increasing appreciation of the insight available from ^{13}C relaxation measurements,[14] we have conducted such studies with some of the benzocycloalkenes, and the systematics of the results are rationalized in terms of differing contributions to relaxation from specific rotational modes.

Experimental Section

Compounds. *o*-Xylene, indan, and tetralin were commercial samples, and after distillation were of high purity as judged by vapor phase chromatography and ^{1}H NMR spectra. *o*-Di-*tert*-butylbenzene was kindly provided by Professor E. M. Arnett of the University of Pittsburgh. Benzocyclobutene was prepared as described by Oliver and Ongley.[15]

4-Deuteriobenzocyclobutene. Benzocyclobutene (10.4 g, 0.1 mol) was iodinated according to the procedure outlined for toluene

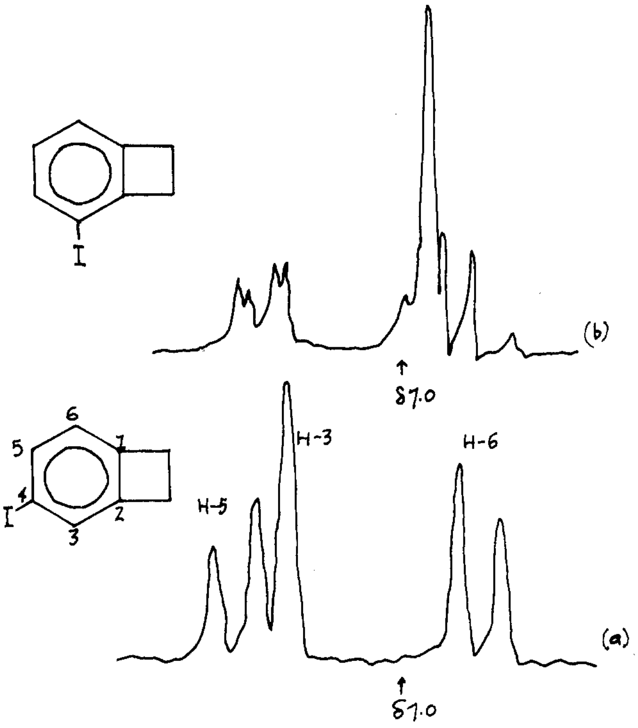


Figure 1. The aromatic portion of the 60-MHz ^{1}H NMR spectra of the separated 4-iodobenzocyclobutene (a) and 3-iodobenzocyclobutene (b) showing the characteristic pattern of the 1,2,4-proton substitution pattern in a.

by Wirth and co-workers.[16] Distillation of the crude product afforded three fractions: (a) unreacted benzocyclobutene (2 g); (b) a mixture of 3- and 4-iodobenzocyclobutenes (10 g, 56% yield based on consumed benzocyclobutene), bp 55 °C (0.01 Torr) [lit.[17] 55 °C (0.01 Torr)], n^{24}D 1.6393 (lit. 1.6395); (c) *o*-iodophenethyl acetate (1 g, 6%), bp 55 °C (0.01 Torr), n^{24}D 1.5784, ^{1}H NMR ($CDCl_3$) δ 1.98 (3 H, singlet, CH_3CO), 3.03 (2 H, triplet, J = 7 Hz, $ArCH_2CH_2OAc$), 4.23 (2 H, triplet, J = 7 Hz, $ArCH_2CH_2OAc$), and 7.0–7.82 (4 H, multiplet, Ar).

Fraction b was previously reported[17] to be pure 4-iodobenzocyclobutene. However, the ^{1}H NMR spectrum showed an impurity at δ 3.04 and a satisfactory integral ratio (4:3) was obtained only if the impurity signal was included in the calculation. This suggested the presence of an isomer. Combined gas chromatography–mass spectral analysis revealed two components in the ratio of 6.7:1, both exhibiting m/e 230 (M^+), and similar fragmentation patterns. The two components were separated on a 20 ft × 0.375 in. 30% SE-30 on Chromosorb W 45/60 column operating at 180°. The major component was shown to be the 4 isomer by conversion to the known[17] 4-carboxylic acid. The 4-iodo and 4-carboxyl compounds both displayed aryl ^{1}H NMR patterns requiring a 1,2,4 disposition of the protons.

The physical properties of the separated iodo isomers and the reported[17] mixture are as follows: (a) 3-iodobenzocyclobutene, bp 74 °C (0.9 Torr), n^{24}D 1.6333 (lit. 1.6335); (b) 4-iodobenzocyclobutene, bp 55 °C (0.1 Torr), n^{24}D 1.6403; (c) mixture, bp 55 °C (0.01 Torr), n^{24}D 1.6395. The aromatic regions of the ^{1}H NMR spectra are reproduced in Figure 1.

The Grignard reagent prepared from the mixture of iodobenzocyclobutenes was decomposed with D_2O (99.8%) and manipulated in the usual way to give a mixture of predominantly 4-deuteriobenzocyclobutene. The deuterium content was 67% by ^{1}H NMR and mass spectrometry.

5-Deuterioindan. Indan (100 g, 0.85 mol) was acetylated according to the method of Vaughan and co-workers.[18] Distillation of the crude product provided 5-acetylindan as a colorless oil (80.0 g, 60%), bp 80 °C (0.2 Torr) [lit.[18] 142 °C (15 Torr)], the constitution of which had been established by synthesis.[18,19] This is absolutely in agreement with the ^{1}H NMR spectrum (60 MHz, CCl_4, Me_4Si): δ 1.80–2.4 (unsymmetrical quintet, 2 H, J_{app} = 7 Hz, $-CH_2CH_2CH_2-$), 2.45 (singlet, 3 H, $COCH_3$), 2.9 (unsymmetrical triplet, 4 H, J_{app} = 7 Hz, $-CH_2CH_2CH_2-$); the aryl portion consisted of an AB pattern centered at δ 7.2 and 7.65, J_{AB} = 8.5 Hz, with the low-field resonance of the δ 7.65 pattern underlying a "singlet" (δ 7.71, br, 1 H). This aryl pattern is consistent only with a 1,2,4 disposition of the protons.

The above ketone was transformed via its oxime and amine to 5-bromoindan, bp 64–65 °C (1 Torr) [lit.[20] 113 °C (14 Torr)], by well-documented procedures. The physical properties of the intermediates encountered in this conversion are as follows: 5-indanylmethylketooxime, mp 112–113 °C (lit.[21] 114 °C); 5-acetamidoindan, mp 106 °C (lit.[22] 107 °C); 5-aminoindan, mp 35–36 °C (lit.[23] 37–38 °C).

The Grignard reagent from the bromide was prepared (in THF) in the standard way and quenched with D_2O, to provide 5-deuterioindan, bp 64 °C (15 Torr). A 70% incorporation of deuterium was indicated by ^{1}H NMR and mass spectrometry.

4-Fluoro-*o*-xylene, 6-fluorotetralin, and 5-fluoroindan have been described previously,[24] as has 4-fluorobenzocyclobutene.[25] 3-Fluoro-*o*-xylene, 5-fluorotetralin, 4-fluoroindan, and 3-fluorobenzocyclobutene were available from another investigation, and will be described elsewhere.[26]

^{13}C Spectra. The spectra were obtained for $CDCl_3$ solutions (~25% solutions) and chemical shifts are referred to internal Me_4Si. In a few cases, cyclohexane was used as internal reference and the data connected to the Me_4Si scale by using $\delta_C = 27.5 + \delta_{C_6H_{12}}$. The spectra were recorded either at 15.086 MHz (CW) using a modified[27] HA-60 spectrometer, or a Bruker HX-90 using the PFT technique. J values are considered accurate to ±0.1 Hz on small couplings and ±1 Hz on the larger one-bond couplings. Chemical shifts are accurate to ±0.1 ppm.

^{13}C spin-lattice relaxation times were determined using the PRFT method[28] on solutions containing 5% C_6D_6 for internal lock. The 90° pulse time was set beforehand on a sample of C_6H_6 and was found to be 18 μs. A recycle time at least four times the longest T_1 to be determined was used in data acquisition. At least eight τ values in the (180–τ–90°) pulse sequence were used in determining any T_1 value. Narrow spectral widths were used to ensure sufficient data points to define the line shape and thus to yield accurate values of the peak intensities at different τ settings.

^{1}H Spectra. These were determined for CCl_4 or $CDCl_3$ solutions (5–10%) with internal Me_4Si, using a JEOL MH-100 spectrometer.

Results and Discussion

Assignments. General. A number of techniques and criteria are now available and applied in a routine fashion. For example, off-resonance noise decoupling[29] is successful for identifying quaternary carbons, which in addition generally occur at substantially lower field than protonated carbons. Off-resonance decoupling is similarly useful, but of course cannot distinguish between various =CH– aryl groupings, which is the chief assignment problem in the present work. Deuterium substitution,[30] when synthetically feasible, is unambiguous and has been employed in crucial aspects of this work, but other approaches are also useful, and particular mention of Gunther's so-called "fingerprint" method[31] is warranted. The bases for our assignments are presented below.

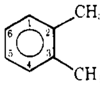
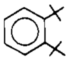
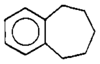
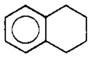
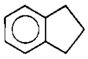
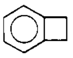
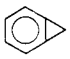
***o*-Xylene.** The spectrum has been assigned quite definitely by examination of both the 3-[10,11] and 4-deuterio[10] derivatives.

***o*-Di-*tert*-butylbenzene.** We utilized the technique (reported by Günther)[31a] that the splitting patterns observed for the ^{13}C signals in the ^{1}H-*coupled* spectra of symmetrically ortho-disubstituted benzenes differ characteristically for carbons α and β, i.e., $C_{3,6}$ and $C_{4,5}$, respectively, and give rise to "fingerprints".[31b] Examination of our 22.63-MHz spectrum revealed a close similarity in forms to Günther's calculated spectra[31] and those of other symmetric ortho-disubstituted benzenes for which C_α, C_β assignments had been established. Other workers[11] arrived at the same assignments by using the coherent ^{1}H decoupling method, assuming the correctness of the ^{1}H shifts (vide infra).

This approach (i.e., the "fingerprint" method) is also the basis for the assignments of entries 3 and 7 in Table I.

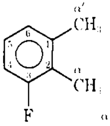
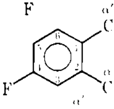
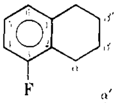
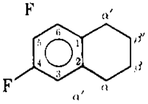
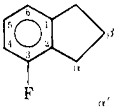
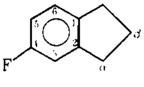
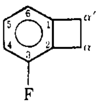
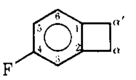
Tetralin. The assignments in Table I have been confirmed by specific deuteration, as well as the characteristic C_α, C_β "fingerprints" in the ^{1}H-coupled spectrum. It will be

Table I. Carbon-13 Assignments[a] of Benzocycloalkenes and 1,2-Dialkylbenzenes

Registry no.	Entry	Compd	Aromatic carbons						Aliphatic carbons		
			1	2	3	4	5	6	α	β	γ
95-47-6	1		136.3	136.3	129.8	126.0	126.0	129.8	19.4		
	1[b]		136.21	136.21	129.84	126.11	126.11	129.84	19.44		
1012-76-6	2		148.4	148.4	129.4	125.6	125.6	129.4	37.75[b]	35.27[b]	
	3[c]		142.7	142.7	128.7	125.7	125.7	128.7	36.6	28.2	32.6
119-64-2	4		137.0	137.0	129.2	125.2	125.2	129.2	29.7	23.6	
496-11-7	5		144.0	144.0	124.4	126.2	126.2	124.4	33.8	25.4	
694-87-1	6		145.6	145.6	122.1	126.6	126.6	122.1	29.4		
	7[c]		125.4	125.4	114.7	128.8	128.8	114.7	18.4		

[a] Numbering system for convenience only. Chemical shifts relative to Me_4Si. More positive values correspond to lower shielding. With cyclohexane as internal reference, $\delta_C = 27.5 + \delta_{C_6H_{12}}$. [b] From ref 11. [c] From 12.

Table II. Carbon-13 Assignments[a,b] of Fluorobenzocycloalkenes and Fluoro-1,2-dialkylbenzenes

Registry no.	Entry	Compd	Aromatic carbons						Aliphatic carbons			
			1	2	3	4	5	6	α	β	β′	α′
443-82-3	1		139.1	123.4	161.7	112.67	127.0	125.32	10.55			19.39
			(4.6)	(16.0)	(242.90)	(23.9)	(9.76)	(2.44)	(6.10)			(3.66)
452-64-2	2		131.6	138.2	115.9	161.5	111.9	130.4	18.9			18.0
			(2.5)	(7.2)	(21.2)	(244)	(20.3)	(7.4)	(1.5)			(n.o)
700-45-8	3		139.67	124.55	161.41	111.88	126.26	124.59	22.14	22.60	23.03	29.43
			(4.88)	(16.8)	(244.14)	(21.97)	(8.54)	(3.66)	(3.66)	(n.o)	(n.o)	(3.66)
2840-40-6	4		132.4	139.0	114.9	161.1	112.1	130.2	29.4	22.8	23.2	28.6
			(2.3)	(7.0)	(20.3)	(245.9)	(20.9)	(7.6)	(1.4)	(n.o)	(n.o)	(n.o)
57526-99-5	5		148.11	130.09	160.03	112.77	128.15	120.16	28.81	25.46		33.28
			(6.10)	(18.31)	(245.36)	(20.75)	(6.10)	(3.66)	(n.o)	(n.o)		(2.44)
37530-82-8	6		139.5	146.1	111.0	162.4	112.5	124.9	32.0	25.8		33.0
			(2.11)	(8.3)	(22.1)	(244.2)	(23.0)	(8.6)	(2.2)	(n.o)		(n.o)
51736-79-9	7		148.89	129.6	156.47	113.75	129.23	119.06	27.08			30.00
			(9.76)	(15.6)	(255.1)	(20.75)	(6.10)	(4.89)	(n.o)			(2.44)
51736-78-8	8		140.5	146.6	110.0	163.1	113.8	123.7	28.6			28.5
			(2.0)	(7.5)	(22.2)	(245.3)	(23.6)	(8.2)	(2.0)			(n.o)

[a] Chemical shifts relative to Me_4Si. More positive values correspond to lower shielding. With cyclohexane as internal reference, $\delta_C = 27.5 + \delta_{C_6H_{12}}$. [b] Values in parentheses are $^{13}C-^{19}F$ couplings. Numbering system for convenience only.

instructive to consider how the data for the fluorotetralins (entries 3 and 4 in Table II) can be scrutinized to reveal the correct assignments for tetralin itself (vide infra).

Indan. The aromatic carbons were distinguished by examination of 5-deuterioindan (D at position 4 in entry 5, Table I) which was synthesized from authentic 5-acetylindan by an unambiguous sequence. (See Experimental Section.)

The same order of aryl carbon shifts has been obtained by Günther.[12] Previously we had correctly deduced[10] these assignments from examination of the fluoroindans. Incorrect assignments have been reported,[11] based on the coherent ^1H decoupling technique, which is somewhat surprising as the ^1H chemical shifts[3b] utilized in this work have since been demonstrated to be correct (vide infra). Buchanan and Wightman,[32a] in a quite separate study, did correctly tabulate the shifts for indan, but these were unproven.[32b] Some time ago, the comparative data for indan and 1,3-dimethylindan were available,[10,33] but generally overlooked, and consideration of the γ effect (shielding) of the CH_3 group at C_α leads directly to the assignments given.

Benzocyclobutene. Deuterium introduction into benzocyclobutene was achieved via the iodo compound using standard organic transformation. Examination of a system with predominant D location at C_β confirmed the assignments in Table I. Another approach has given identical assignments.[12]

Maciel and co-workers reported[11] reversed assignments for $C_{3,6}$, $C_{4,5}$ but their coherent decoupling technique was based on an assumed correctness of the previously suggested order of the ^1H chemical shifts. Our examination of the deuterated benzocyclobutene and ^{13}C satellite studies shows that the previous suggested order of ^1H shifts[3b] need reversal, and ipso facto any soundly determined ^{13}C assignments based on these ^1H shifts. The correct set of assignments have also been reported by Jones, Garratt, and Vollhardt,[34] in another connection, apparently on the basis of differential Overhauser effects.

Benzocyclopropene. These data are based on the "fingerprint" criterion of Günther for C_α, C_β resonances.[12]

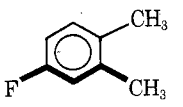
Benzosuberane. The spectrum was similarly assigned[12] and the correct assignments were suggested by Maciel,[11] on the basis presumably that the more remote $C_{4,5}$ should resemble $C_{4,5}$ in a relatively "strain-free" *o*-dialkylbenzene.

With the various approaches that have been applied to the problem of distinguishing $C_{3,6}$ (C_α) and $C_{4,5}$ (C_β) in entries 1–7 (Table I), there is no doubt that the listed aromatic assignments are correct. Regarding aliphatic carbon assignments (entries 2–5, Table I) no difference of opinion exists and considerations of one or a combination of off-resonance decoupling, selective deuteration, chemical shifts, and relative intensities, etc., yield concordant conclusions.[1,10,11,12]

^{13}C Assignments in Fluorobenzocycloalkenes (Table II). Aryl Carbons. Under conditions of broad-band proton decoupling, all aromatic carbons in Table II appear as doublets due to ^{13}C–^{19}F coupling. This apparent spectral complexity is a blessing since it has been established quite clearly that in phenyl systems this coupling declines in a regular way with the number of intervening bonds.[1,10,35] One-bond couplings usually are in the range 240–250 Hz, while coupling to secondary ortho carbons (i.e., $^2J_{C-F}$) are 20–24 Hz. A *reduced* ortho ($^2J_{C-F}$) coupling to tertiary carbons is observed (ca. 15–18 Hz), but substantially larger than coupling ($^3J_{C-F}$) to tertiary meta carbons, typical values being in the range 4–9 Hz. Coupling to secondary meta carbons is generally somewhat larger (6–10 Hz), but this similarity in values never poses a problem since the chemical shifts are quite different. Easily resolved coupling to para carbons is also observed ($^4J_{C-F}$) ranging from 2 to 4 Hz. Intensity variations are pronounced as well, and the signals of the much less intense nonprotonated carbons are assigned without difficulty. An added benefit of fluorine substitution is the pronounced effect on the chemical shift. Carbon bearing fluorine, besides having a large one-bond coupling diagnostic in itself, is quite deshielded (by ~32 ppm) whereas carbons ortho to fluorine are shifted upfield by 13–14 ppm. Carbons para to fluorine are also shielded by a lesser amount (~4–5 ppm) whereas meta carbons appear always to be deshielded by about 1–2 ppm. Considerations of these data lead generally to a unique assignment for a fluorophenyl system.[1,10,35]

Consider the assignments for the fluorotetralin (entry 3) in Table II. Six doublets at 161.41 ppm (J_{C-F} = 244.1 Hz), 139.67 (4.88), 126.2 (8.54), 124.59 (3.66), 124.55 (16.8), and 111.88 (21.97) are observed in the aromatic region. C_3 (bearing fluorine) corresponds to 161.41 (244.14) on the basis of chemical shift and coupling, and C_4 to 11.888 (21.97) since this coupling is typical of $^2J_{C-F}$ to a secondary carbon. A coupling of 16.8 Hz is too large to be $^3J_{C-F}$ but is appropriate for $^2J_{C-F}$ to a quaternary carbon. C_2 is therefore identified and confirmed by intensity considerations. The 8.54-Hz coupling is appropriate for $^3J_{C-F}$ (secondary) and locates C_5. The remaining resonances 139.67 (4.88) and 124.59 (3.66) are straightforwardly allocated to C_1 and C_6 on the basis of chemical shift and coupling constants. With these assignments for entry 3, and considering the substituent effects of fluorine in phenyl systems (vide supra), we can calculate the following aromatic shifts (parts per million) for tetralin itself: C_1, 138.17; C_2, 138.00; C_3, 129.41; C_4, 125.4; C_5, 124.76; C_6, 129.09. [In tetralin the carbon pairs are (C_1, C_2), (C_3, C_6), and (C_4, C_5)]. The agreement between these and those rigorously assigned demonstrates how regular ^{19}F contributions to carbon screenings are. Although some variations must occur depending on the particular phenyl system,[36] these seem to be minor and it is clear that these well-behaved effects of ^{19}F substitution are extremely useful for assignment purposes in the parent hydrocarbon, particularly when there is 3–4 ppm difference in shifts of contentious resonances. This can be confirmed by examining appropriate sets of other data in Tables I and II. Strategic D substitution[30] is in principle a better tactic since very minor perturbation of the system results. While carbon bearing deuterium is hence readily assigned, some care is required if adjacent carbons are to be assigned by isotope shifts, signal broadening (^{13}C–D coupling), etc., and a satisfactorily high D incorporation is required. Since fluorine can be introduced easily into aryl systems by manipulation of readily installed functionality, its use in the presently described connection is worthy of note.

Aliphatic Carbons. Chemical shifts and ^{13}C–^{19}F couplings lead to acceptable assignments in all cases, except the β,β' carbons in entries 3 and 4: for 3-fluoro-*o*-xylene (entry 1) resonances at 19.39 (3.66) and 10.55 ppm (6.10) are observed compared with 19.4 ppm for the methyl carbon in *o*-xylene. As the methyl ortho to fluorine should experience substantial shielding, the indicated assignments are arrived at. These data provide values of $^4J_{C-F}$ and $^3J_{C-F}$ of 3.66 and 6.10 Hz, respectively. In the fluorobenzocycloalkenes this latter value (i.e., $^3J_{C-F}$) depends strongly on the fused ring, and may be vanishingly small. In 4-fluoro-*o*-xylene (entry 2, Table II) the CH_3 signals are less separated and one has significant coupling (1.5 Hz). Two lines of reasoning provide the indicated assignments. α CH_3 is attached to a more electronegative aryl carbon (meta to fluorine) than is α' CH_3 (para to fluorine) and the 1.5-Hz coupling is consistent with a preferred "zigzag" array of coupled atoms and shorter internuclear path (I). In



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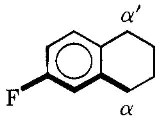

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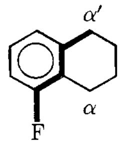

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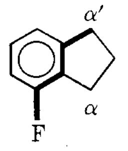
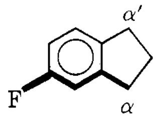


IV



V

agreement with this, Weigert and Roberts[35] observed fluorine coupling to the methyl carbon in *m*-fluorotoluene, but not in *p*-fluorotoluene. Similar ^{13}C–^{19}F couplings across a "zigzag" path have been observed in other fluoroaliphatic compounds,[37] and the suggestion has been made that such ^{13}C–^{19}F scalar coupling is transmitted by a "back orbital" lobe on the fluorine interacting directly with the carbon orbital. Such an interaction is favored by a "zigzag" array of the coupled nuclei. The validity of this suggestion is clear from the fluorotetralin data (entry 4) where coupling to C_α but not to $C_\alpha{}'$ is observed (II). In entry 3, C_α, $C_{\alpha'}$ are distinguished by their large chemical shift difference, but again "zigzag" coupling over four bonds is similar to a less preferred geometry spanning three bonds (III). $\delta_{C_\beta,C_{\beta'}}$ in entries 3 and 4 are very similar and are not distinguished. Regarding the fluoroindans (entries 5 and 6) C_β is assigned on the basis of its similar chemical shifts (25.46, 25.8 ppm) to C_β in indan (25.4 ppm) and the lack of ^{19}F coupling. In entry 5, $C_{\alpha'}$, $C_{\alpha'}$ are allocated unambiguously on the basis of chemical shifts (C_α shielded by 5 ppm, $C_{\alpha'}$ similar to C_α in indan) and again coupling is observed to $C_{\alpha'}$ (2.44 Hz) (IV) with the favorable geometric array, but not to C_α, with one less intervening bond. In entry 6, C_α and $C_{\alpha'}$ are separated on the basis of the preferred coupling to C_α (V). Similar strategies apply to the fluorobenzocyclobutenes where zigzag coupling $^4J_{C'}$ (2.44 Hz) is observed but ^3J_C is not (entry 7) and in entry 8, α C is seen to have the requisite geometry with respect to fluorine for coupling. These geometrical dependences of $^3J_{C-F}$ and $^4J_{C-F}$ seem to have sufficient generality as to be useful considerations for assignment in fluoroarylalkyl systems.

Benzocycloalkenes. Chemical Shift Trends. Aromatic Carbons. It is useful to determine whether any trends energe in these shifts with geometrical factors, and what relation these trends may have with available theoretical parameters and explanations of "ring strain". A previous analysis of some of these shifts which indicated somewhat irregular response to strain is no longer relevant because of misassignment of key signals. Scrutiny of the data in Table I reveals the following.

$C_{1,2}$. These carbon shifts span a range of some 23 ppm (148.4 ppm for *o*-di-*tert*-butylbenzene to 125.4 ppm for benzocyclopropene) but a smooth trend is not exhibited as the size of the fused ring alters. Dissection of the shift change into a "strain" component is very difficult since α, β, γ screening effects differ with ring size. Nevertheless, with decreasing ring size and therefore more planar structures, and also less effective and essentially constant β effects, the sequence 137.0 (tetralin), 144.0 (indan), 145.6 (benzocyclobutene), and 125.4 (benzocyclopropene) must be substantially a *manifestation* of bond order, change density, and hybridization effects, rather than steric effects from the alkyl ring. Increased strain then seems to be associated with a deshielding effect at $C_{1,2}$ except for benzocyclopropene. However, in this case, $C_{1,2}$ is part of the cyclopropane ring system, and it is established that cyclopropyl carbons experience substantial shielding. Therefore a major contribution to the shielding of $C_{1,2}$ in this case must be associated with the special nature of this ring system.

$C_{3,6}$ (C_α) and $C_{4,5}$ (C_β). A clearer picture emerges here since the increasing strain is associated with increased shielding, from ca. 129 ppm for "strain-free" cases (entries 1–4, Table I) to 114.7 ppm in a regular fashion. Reduced effects operate at $C_{4,5}$ but a slight (~3 ppm) decrease in shielding occurs. Clearly $C_{4,5}$ is not very sensitive at all to ring-size effects and this is consistent with very similar reactivities at β positions in benzocycloalkenes in conventional electrophilic substitutions.[38] As rate measurements reflect details of the transition state, more meaningful comparisons may be made with ^{19}F shieldings, known to be highly sensitive to (ground-state) electron density fluctuations in aromatic systems. Relative to fluorobenzene, the ^{19}F chemical shifts of 4-fluoro-*o*-xylene, 6-fluorotetralin, and 5-fluoroindan are very similar, +5.57, +5.45, and 5.23 ppm, respectively[25] (+ indicates to higher field in ^{19}F shielding convention). Similar trends emerge in the fluorobenzocycloalkenes and attention is best focussed on entries 2, 4, 6, and 8 in Table II, i.e., the 4-fluoro series, since some nonbonded effects between fluorine and the adjacent methylene in the 3 series could occur conceivably. C_1 in this series ranges from 131.6 to 140.5 ppm, C_6 from 130.4 to 123.7 ppm, and C_5 from 111.9 to 113.8 ppm. Assuming fluorine contributions to screenings to be essentially constant, these trends are very similar to these for the hydrocarbons.

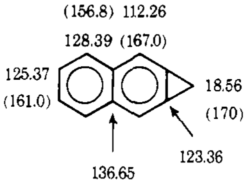
The relation between π-electron density and carbon-13 chemical shifts has been explored for some time and an early LCAO analysis concluded that there was a local charge dependence agreeing in sign and order of magnitude with experiment.[39] In substituted benzenes, for example, para-carbon shifts correlate well with other measures of substituent effects and with calculated (CNDO/2) total and π-charge density.[40] In these cases apparently other terms change in proportion with charge density, or in a minor way, so overall correlation is observed. That the situation is more complex for polycyclic aryl systems was revealed by the work of Alger, Grant, and Paul,[41] who considered other effects in their treatment. A general expression of the form

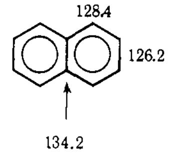
$$\delta_{13C} = \frac{1}{\Delta E}\left(A\pi\Delta Q\pi + B_\sigma\Delta Q_\sigma - C_p\Delta P\right)$$

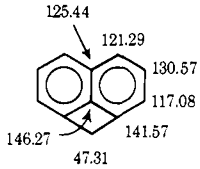
where $\Delta Q\pi$, ΔQ_σ, and ΔP are the π charge, σ charge, and total mobile bond order relative to the benzene values, was developed and applied to some alternate aromatic molecules.

In the present cases of the benzocycloalkenes, contributions from both charge densities and bond-order changes with ring size presumably occur. Fortunately, careful scrutiny of the data for the tetralin and indan systems provides the key to a meaningful analysis of the problem. Compared with fluorobenzene, ^{19}F shieldings of +5.03, +6.12, and +5.42 ppm are observed[26] for 3-fluoro-*o*-xylene, 5-fluorotetralin, and 4-fluoroindan, respectively, indicating modest charge density and C–F π-bond order differences at C_α for the tetralin–indan duo. The values of $J_{^{13}C_\alpha-H}$ for the pair are also essentially identical.[12] In impressive contrast, the less sensitive $^{13}C_\alpha$ probe registers a −4.8 ppm difference (i.e., to higher field) for the same pair (Table I). These results seem to demand that some factor very modestly (if at all) affecting the ^{19}F shifts is having a substantial effect on the related $^{13}C_\alpha$ shifts. The direction of this effect is to higher field, opposite to that expected on the basis of diminished charge density at C_α.[40] We therefore conclude that the ΔP term above must exercise a decisive influence on the resultant C_α shieldings and it is possible to extrapolate in a qualitative way from the proposal of Streitweiser[5] regarding these systems. As the "ring strain" increases the decreasing angles about carbon in the fused ring are associated with higher "p character" in these carbon orbitals, and hence the orbitals directed toward C_α have higher "s character". This increase in orbital electronegativity causes a polarization of electrons away from C_α which becomes more electronegative. This ground-state change accounts for $J_{C_\alpha-^1H} > J_{C_\beta-^1H}$ in benzocyclobutene[12] and increased acidity at the α positions.[5,6] As pointed out above, it does not rationalize the shift trends if charge density alone is invoked. However, there must also be changes in p-bond orders about C_α and the bridgehead carbons, and as strain increases, this term must increase between bridgehead carbons, but decrease between these carbons and C_α. This would suggest decreased shielding for bridgehead carbons, but increased shielding for C_α.

"Strain" has significant effects on ^{13}C shifts in naphtho systems also. Naphtho[*b*]cyclopropene has been examined and the fully proton-coupled spectrum[12] provides the assignments shown below. (Values in parentheses are $^1J_{C-H}$.)

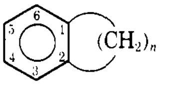






On comparison with naphthalene, fusion of the strained ring has consequences very similar to those observed in the benzocyclopropene case. C_α experiences substantial shielding (−16.14 ppm) while C_β (now the quaternary carbon) is deshielded (+2.45 ppm). The assignments recently listed for 1,8-methanonaphthalene (1*H*-cyclobuta[*de*]-naphthalene) have been reproduced above, and confirm 1,8 bridging to have serious effects also.

Quantitative assessment of the situation in terms of the theory is difficult for several reasons. Firstly, as described by Alger, Paul, and Grant,[41] and polarization and bond-order coefficients A_π, B_δ, etc., are functions of the assumed overlap integrals, and the character of the wave functions chosen. Secondly, accurate structural data for the lower members of the benzocycloalkenes are lacking, as are refined MO calculations for these molecules. However, Cheung, Cooper, and Manatt[9] have applied the CNDO/2 semiempirical method to these cases, and it is of interest to summarize their findings. Regarding bond orders, both the C_{2s} and $C_{2p\pi}$ components to the C_5–C_6 bond decrease, yielding a substantial decrease in bond order while the C_{2s} component to the C_1–C_6 bond increases but also does the $C_{2p\pi}$ component.



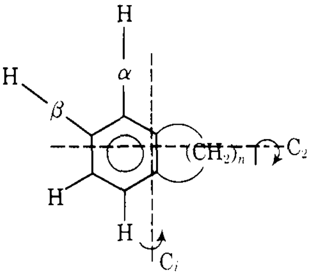
I

This latter result is surprising in view of the p-orbital reorganization toward the fused ring. The effect of increasing strain is to increase total electron density at C_5 and C_6 (largely because of changes in $2p\pi$ density with irregular C_{2s} contributions) while at C_1, total charge density decreases with strain, as does the C_{2s} component, but the $C_{2p\pi}$ portion fluctuates. While there are some encouraging aspects in these result, and some accord with experimental findings, it is necessary to point out that others considered the CNDO/2 approach somewhat crude, with drastic and unreal assumptions, to contribute anything meaningful to the interpretation of strain in these molecules. This is because the semiempirical methods (CNDO, INDO, MINDO) are parameterized with respect to nonstrained systems, but Streitweiser recently established[43] that ab initio methods confirm the earlier qualitative proposal that compression of bond angles results in enhanced acidity of adjacent C–H bonds. Accurate molecular geometries are required for n = 1, 2 to allow more refined theoretical treatment of these molecules. However, the ^{13}C data reported herein do confirm that special care is required in interpreting such shifts in cases where bridgehead carbons and substantial bond-order fluctuations occur, and the simple correlations with π or total charge may break down.

^{13}C–^{19}F Couplings. Most features of the spectra of the fluorobenzocycloalkenes have been outlined but there are trends in ^{13}C–^{19}F couplings with ring size that are worthy of note. In the 4-fluoro derivatives (entries 2, 4, 6, and 8, Table II) the one-bond J_{C-F} are 245 ± 1 Hz, suggesting rather minor variations in C–F bond character and effective nuclear charge. However, in the 3-fluoro derivatives, a wider range is encountered from 244.0 Hz (entry 3, Table II) to 255.1 Hz for the benzocyclobutene (entry 7, Table II). One other aromatic J_{C-F} in excess of 255 Hz (255.3 Hz) has been reported[44] (for 1,8-difluoronaphthalene) and steric effects were regarded as the likely cause of the exalted value. In the present case, the steric environment of the 3-fluorine does not seem congested enough to explain completely this large exaltation, and the altered s character and effective nuclear charge at C_α is probably largely responsible.[45] Some other variations with ring size in $^nJ_{C-F}$ in the aryl ring are also evident but in view of the poor understanding of factors responsible for $^{n>1}J_{C-F}$, discussion of these trends is not pursued here, although possible factors are outlined elsewhere.[46]

Relaxation (T_1) Measurements. As a further possible aid to the ^{13}C chemical shift assignments and in order to investigate the microdynamics of this type of molecule in solution we have measured the ^{13}C T_1 values of the protonated carbons. (We have excluded from discussion the T_1 values of the methyl carbons because of the additional effect of internal motion.[47]) There is convincing evidence from previous studies[48] that the relaxation mechanism of protonated carbons in compounds of this type will be dominated by the ^{13}C–^1H dipolar interactions. We assume this to be so in the following discussion.

Inspection of the results in Table III shows that for the benzocycloalkenes and *o*-xylene, the T_1 of C_α is always *longer* than that of C_β. We ascribe this behavior to anisotropic rotational reorientation of the molecule. Although the theoretical description of the situation is often difficult to treat quantitatively, that such a result is reasonable can be appreciated in a qualitative way from inspection of models of these compounds and consideration of the relative magnitudes of the reorientation rates about the various principal axes.



We have depicted above what we believe is a reasonable approximation to the principal reorientation axes of the molecules. Not drawn is the rotation axis perpendicular to the plane of the molecule. Grant[49] has applied Woessner's treatment of an ellipsoidal tumbler to analyze motion in some near-ellipsoidal molecules such as *trans*-decalin and has demonstrated a good correlation between the ellipticity about a rotation axis and the reorientation rate about the same axis and this treatment predicts $R_2 > R_i$, where R_2 and R_i are the reorientation rates about the appropriate axes shown above. (An alternative approach would involve consideration of relative moments of inertia about C_2 and C_i axes.) The effect these rates have on the various ^{13}C T_1

Table III. Carbon-13 Spin-Lattice Relaxation Times[a] for the Protonated Carbons of *o*-Xylene and Benzocycloalkenes

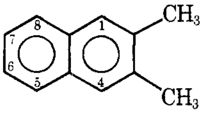
Compd	T_1, s			
	Ar–C_α	Ar–C_β	α-CH_2	β-CH_2
o-Xylene	10.8	8.9		
Tetralin	7.1	5.7	3.7	3.6
Indan	10.1	8.0	5.3	6.4
Benzocyclobutene	10.5	8.9		

[a] Determined using PRFT method as per Experimental Section.

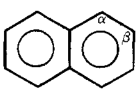
values depends on the angle the C–H vector makes with these axes. If the angle is zero (as is the case of the C_α–H vector and C_i axis) then motion about this axis will not contribute to the relazation as no change in the C–H vector occurs. As an approximation, the larger the angle the more influence reorientation about the axis has on T_1.

Consider motion about the C_2 axis: the C_α–H vector makes an angle of 90° while the C_β–H vector makes an angle of 30°. Thus, fast motion about the C_2 axis will have a larger influence on the C_α T_1 than on the C_β T_1. As a consequence, the T_1 of C_α will be longer given the inverse relation between T_1 and the correlation time. A similar result has been observed[50] in substituted biphenyls where the para carbon has the shortest T_1, internal motion of the phenyl groups not having any influence on the relaxation processes of this carbon.

The effect described above is operative in other compounds with the appropriate symmetry level and this technique, if applied correctly, may be generally useful for spectral assignments, e.g.



$T_1(C_1, C_4) = 5.2$
$T_1(C_5, C_8) = 5.2$
$T_1(C_6, C_7) = 4.1$

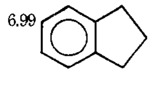


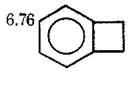
$T_1(C_\alpha) = 9.2$
$T_1(C_\beta) = 8.5$

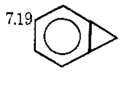
The pattern of the T_1 values (Table III) for the protonated aromatic carbons is in accord with rigorously established assignments presented in this paper, and those in the literature for naphthalene[41] and 2,3-dimethylnaphthalene.[52]

The variation of the T_1 values between the aromatic and aliphatic carbons is interesting. They are not related simply to the number of attached protons, the aliphatic carbon T_1's being somewhat longer than expected. There is no difference in the T_1's for these carbons in tetralin (nonplanar fused ring) and only a slight variation for indan (planar fused ring). It appears that anisotropic reorientation has less of an influence on the relaxation processes of these carbons.

^1H Chemical Shifts. The necessity to synthesize certain deuterium-labeled benzocycloalkenes prompted examination of their ^1H NMR spectra, since it seemed that positive conclusions would result. Previously Mannatt and Cooper,[3b] in their thorough study of ^1H–^1H coupling in these molecules, had analyzed the AA′BB′ system of the aromatic protons, but δ_A and δ_B are not explicit from such an analysis. It was suggested that the broadened half of the AA′BB′ pattern corresponded to H_α, on the basis of preferred coupling (over H_β) to the methylene protons. In this way, suggested assignments for indan, benzocyclobutene, and benzocyclopropene were presented, and shown below (δ from Me_4Si).





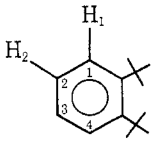


Subsequently, Maciel[11] was guided by these assignments in his approach to the corresponding ^{13}C assignments, which were contrary to ours and Günther's[12] for $n = 1, 2, 3$. It was therefore a matter of interest whether the ^1H assignments were in error, and therefore the major cause of the discrepancies in the ^{13}C data. It should be made clear that the main thrust of Mannatt and Cooper's work concerned the variation of ^1H–^1H couplings with structural factors, and the order of ^1H assignments was not necessary for any of their conclusions.

We have utilized two approaches to distinguish H_α, H_β in the ^1H spectra of indan and benzocyclobutene. The first is unambiguous, and involves careful examination and integration of the tactically deuterated analogue. 5-Deuterioindan (~70% D) was examined and it was quite clear that the higher field part of the AA′BB′ system (270 Hz sweep width at 100 MHz) had suffered an intensity loss. The same system has also been examined by Günther,[52] with concordant conclusions. The assignments suggested by Manatt and Cooper[3b] for indan are therefore established. At the time that we were examining approaches for assignment of ^1H and ^{13}C frequencies in some AA′BB′ spectra, Günther kindly disclosed[53] a very useful technique, which is based on observation of the ^{13}C satellite pattern. The overall width must be larger for β protons than α protons, as $(2J_o + J_m) > (J_o + J_m + J_p)$. We applied this technique to the ^{13}C satellites of indan, but the very similar values of $J_{^{13}C-H_\alpha}$ and $J_{^{13}C-H_\beta}$ and small δ_α–δ_β resulted in some overlapping. Nevertheless, the higher field portion of the complete low-field satellite pattern was more spacious, corresponding to H_β at higher field, as already rigorously established.

Deuteriobenzocyclobutene was synthesized from a mixture of 4-iodo- (87%) and 3-iodobenzocyclobutene (13%) (as indicated in the Experimental Section) resulting in overall 67% D incorporation (mass spectrum). The relative intensities of H_α:H_β signals in the ^1H spectrum should be ca. 1.25–1.30. Scrutiny of the spectral trace (540 Hz sweep width, 100 MHz) (Figure 2a,b) shows quite definitely the lower field portion to be of reduced intensity, and several integrations confirm this ($H_\alpha/H_\beta \sim 1.35$). H_β is therefore at lower field, contrary to the previous suggestion. The high- and low-field ^{13}C satellite patterns for benzocyclobutene are relatively easy to identify, and it is quite clear (Figure 2c,d) that the more spacious patterns are associated with the lower field resonance, i.e., H_β at lower field, in agreement with the conclusion above.

o-Di-*tert*-butylbenzene was of particular interest, since although both reported assignments[1,11] of the ^{13}C spectrum were in agreement (vide supra), that of Maciel[11] was based on the application of coherent ^1H decoupling to the reported (now shown to be incorrect) aryl ^1H assignments. Castellano and Kostelnik[13] in a study of the various ^1H–^1H couplings in substituted benzenes, analyzed the AA′BB′ pattern of *o*-di-*tert*-butylbenzene, and reported without comment the following shifts.



$\delta_1 = 418.35$ Hz $= 6.97$ ppm
$\delta_2 = 446.8$ Hz $= 7.44$ ppm (Me_4Si)
$\Delta = 28.45$ Hz (60 MHz)

Molecular models indicate substantial steric (nonbonded) interactions between the $-C(CH_3)_3$ group and H_1, and in the light of present knowledge, "steric deshielding"[54] would be consistent with a reversed order of these chemical shifts. This also yields a chemical shift for H_2 (6.97 ppm) almost identical with that for H_2 in tetralin (6.99 ppm).

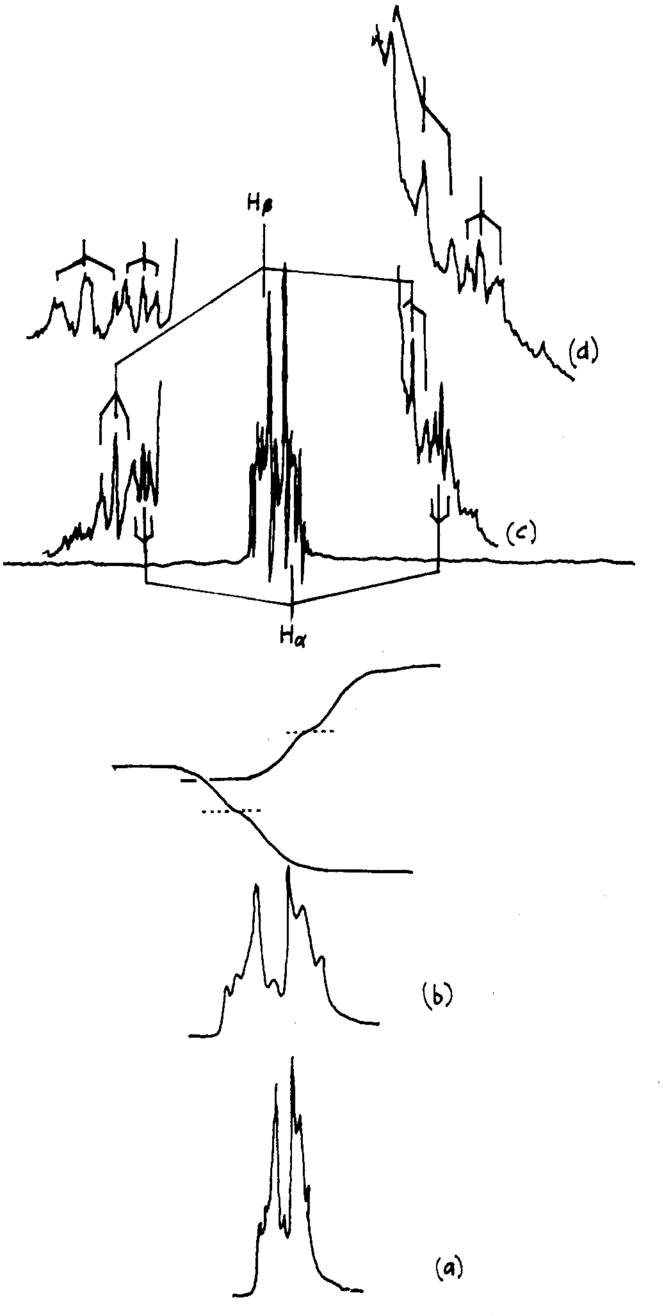


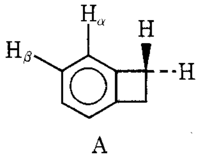
Figure 2. The aromatic portion of the 100-MHz ^{1}H NMR spectrum of benzocyclobutene selectively deuterium enriched at the 4 position on 1080-Hz sweep width (a) and 540-Hz sweep width (b). Integral traces for b are shown. (c) High-gain spectrum (1080-Hz sweep width) showing ^{13}C satellite patterns about H_α (higher field) and H_β. (d) As in c but 540-Hz sweep width.

This is expected, since H_2 is remote from the region of steric congestion.

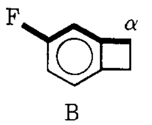
Our proton-*coupled* ^{13}C spectrum of *o*-di-*tert*-butylbenzene, in addition to settling the C_β, C_β assignments (vide supra), provides values of $J_{^{13}C-H_1}$ = 154.8 and $J_{^{13}C-H_2}$ = 160.5 Hz (see numbering above). The difference in these coupling constants (5.7 Hz) is small in comparison with the chemical shift difference between H_1 and H_2 at 100 MHz (47.4 Hz), confirming that no "crossover" of the ^{13}C satellite patterns could occur. From the data of Kostelnik and Castellano,[13] it can be shown that the ^{13}C satellites about H_1 should have a total spacing of ca. 9–10 Hz, while those about H_2 should be ca. 16–17 Hz wide. In the 100-MHz ^{1}H spectrum of *o*-di-*tert*-butylbenzene, the low-field satellites about H_1 and H_2 were identified, and were separated by ca. 45.5 Hz [calculated $47.4 - \frac{1}{2}(160.5 - 154.8) = 44.6$ Hz]. (Slight impurities to the high-field side of the main aryl ^{1}H spectrum prevented identification of the high-field satellites.) The lowest field satellite pattern had a "spread" of ca. 10 Hz while the higher field one had a total spacing of ca. 16 Hz, demanding that H_1 be at lower field than H_2, as deduced from the chemical shift difference above. The suggestion of Kostelnik and Castellano[13] therefore requires reversal.

The spectrum of *o*-bis(trimethylsilyl)benzene also exhibits[55] a substantial chemical shift difference (ca. 0.4 ppm) for the sets of aromatic protons. Although no analysis was reported, chemical shifts of ca. δ 7.1 and 7.5 appear to apply, and it would seem that protons ortho to $Si(CH_3)_3$ are also sterically deshielded in this system, as expected. No studies of the ^{13}C satellite spectra were reported.

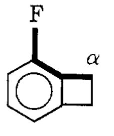
There are two aspects relating to the orders of ^{1}H and ^{13}C shifts now established in this series of molecules. Firstly, the ^{13}C shifts faithfully reflect the ^{1}H shifts within a molecule, and this type of correlation in substituted benzenes has been noted widely, particularly for para-carbon shifts.[40,56–58] In the present cases, a lack of correlation at the α position would not have been surprising, in view of the possible additional perturbations that might operate in this vicinity. Secondly, the ^{1}H assignments now established for benzocyclobutene indicate that the preferential broadening of one-half of the AA′BB′ aromatic pattern (the criterion used by Manatt and Cooper[3b] in their suggested H_α, H_β assignments) must involve H_β and the methylene protons, where a preferable geometry presumably exists. This is reminiscent of the situation in the fluorobenzocyclobutenes B and C, where observable $^4J_{C_\alpha-F}$ is observed (B, 2.0 Hz), but not $^3J_{C_\alpha-F}$ (C). While many factors affecting longer range proton–proton and carbon–fluorine coupling are undoubtedly different,[46] the geometry of the coupled nuclei is clearly of importance.



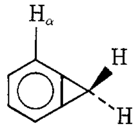
A



B



C



D

The situation for benzocyclopropene is unclear, as the aryl ^{1}H assignments have not been established, e.g., by selective deuteration. It would not be surprising, however, if H_α was more strongly coupled to the methylene protons than H_β since the geometry is now different (D) from the benzocyclobutene case.[59] Special electronic effects associated with the cyclopropyl ring may also be important.

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Registry No.—*o*-Iodophenethyl acetate, 57527-00-1; 3-iodobenzocyclobutene, 38122-16-6; 4-iodobenzocyclobutene, 1004-07-5; 5-acitylindan, 4228-10-8.

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