Acknowledgment. The authors thank Mr. William Petersen of Esso for running the mass spectrometer and Mr. Steven Szucs of Seton Hall who prepared several of the compounds while working under a National Science Foundation institutional grant for undergraduate research.

Analysis of the Proton Nuclear Magnetic Resonance Spectra of Some Strained Benzocycloalkenes and Benzocycloalkenediones. Effect of Strain on Proton–Proton, Spin–Spin Coupling Constants[1]

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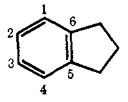
Abstract: The proton nmr spectra of some benzocycloalkenes and benzocycloalkenediones have been analyzed. The derived proton–proton spin–spin couplings have been examined for any features which might indicate partial bond fixation (the "Mills–Nixon effect") ascribable to ring strain in these series. Whereas the *ortho* couplings (^3J) exhibit no clear trends, it is found that the *meta* coupling (^4J) decreases sharply, and the *para* coupling (^5J) increases sharply with increased strain. The reasons for these changes are discussed in terms of empirical relationships found in other series, and also from a theoretical (extended Hückel molecular orbital) treatment.

Nearly 40 years ago Mills and Nixon suggested[3] that certain differences in the chemical reactivities of some indan and tetralin derivatives could be explained if the strain of fusing a five-membered ring onto the benzene nucleus caused partial fixation of the double bonds in the aromatic system. In line with the theory of aromaticity prevailing at that time they suggested that in indan the relative energies of the Kekulé structures[4] 1a and 1b were altered in favor of 1b. Further experimental work[5] showed that the original chemical evidence was ambiguous, and a theoretical study[6] of the bond-length and bond-angle strains in indan showed that 1a should be more favored, with fusion of a small alicyclic moiety serving to shorten bond 5–6 and lengthen bond 2–3.



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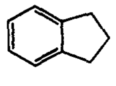

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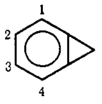

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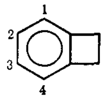

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Although the Mills–Nixon effect as originally proposed[3] has been disproved, the possibility of partial bond fixation and concomitant partial loss of aromatic character in benzocycloalkenes has continued to attract attention, and the smaller benzocycloalkenes, in particular, have recently received considerable study. Syntheses of benzocyclopropene,[7,8] 2, and benzocyclobutene,[9] 3, have been achieved, and there has been considerable discussion as to whether 2 is fully aromatic.[7,8,10] The only pertinent thermodynamic study[11] which has appeared interpreted the heat of hydrogenation of 3, *viz.* −50.3 kcal/mol compared to a value of −47.3 kcal/mol for *o*-xylene, as illustrating "the smallness of the effect of strain on aromatic resonance." Moreover, from a discussion of the properties of *o*-di-*t*-butylbenzene, in which the strain energy has been estimated[12] by a variety of methods to be *ca.* 22 kcal/mol, a value much larger than that estimated for 3 (*ca.* 3–5 kcal/mol),[11] it has been suggested that "there is no evidence from nmr, infrared, or electronic spectra or from the reactions of compounds containing the *o*-di-*t*-butylbenzene system that a nonaromatic benzene has been pro-

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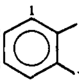
[1] This paper presents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. NAS 7-100, sponsored by the National Aeronautics and Space Administration.

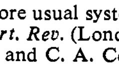
[2] NASA Resident Research Associate, 1968–1970.

[3] W. H. Mills and I. G. Nixon, *J. Chem. Soc.*, 2510 (1930).

[4] Since we shall refer both to Kekulé structures, and also to aromatic compounds where no specific bonding structure is implied, double bonds will only be used in the former case, and in the latter instance formally aromatic structures will be indicated thus



For clarity in the discussion the following numbering for *ortho*-disubstituted benzenes



will be used in place of the more usual system.

[5] See G. M. Badger, *Quart. Rev.* (London), **5**, 147 (1951).

[6] H. C. Longuet-Higgins and C. A. Coulson, *Trans. Faraday Soc.*, **42**, 756 (1946).

[7] R. Anet and F. A. L. Anet, *J. Amer. Chem. Soc.*, **86**, 525 (1964).

[8] E. Vogel, W. Grimme, and S. Korte, *Tetrahedron Lett.*, 3625 (1965).

[9] M. P. Cava and D. R. Napier, *J. Amer. Chem. Soc.*, **80**, 2255 (1958).

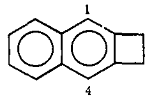
[10] E. F. Ullmann and E. Buncel, *ibid.*, **85**, 2106 (1963).

[11] R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Colburn, and M. Pomerantz, *ibid.*, **90**, 4315 (1968).

[12] E. M. Arnett, J. C. Sanda, J. M. Bollinger, and M. Barber, *ibid.*, **89**, 5389 (1967).

duced." It was observed for the latter, however, that there was "a 30% decrease (relative to benzene) in Dauben's diamagnetic susceptibility exaltation." This appears to be the only evidence for a partial loss of aromatic character. Later, however, we shall present evidence of strain from the nmr parameters of *o*-di-*t*-butylbenzene.

Unfortunately, no investigations of the structures of **2** and **3** have been published, and evidence for the nature and magnitude of strain is largely indirect. Kinetic studies of substitution reactions show[13,14] that the carbons α to the fused ring exhibit an increased acidity and reduced reactivity to electrophilic substitution. This has been explained as follows.[14] The orbitals of the aryl carbon atoms which are used to construct the strained ring have a higher p character than in an unstrained derivative. Thus the remaining orbitals (bonding to the *ortho* carbon of the aromatic system) have higher s character, and exhibit the properties of orbitals having a higher electronegativity than in the unstrained case. Consequently, the *ortho* carbon in turn becomes more electronegative. Support for this explanation has come from an epr study[15] of naphtho[*b*]cyclobutene, **4**. Relative to the unstrained 2,3-dimethylnaphthalene **5**, **4** exhibits increased hyperfine splittings (hfs) with the 1 and 4 protons, and decreased hfs elsewhere in the aromatic nucleus.



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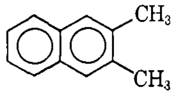

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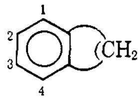
Of the other physical techniques, ir and uv spectra of **2** and **3** have been presented,[8,9] but these results have not received detailed interpretation. The C=C stretching frequency in **2** is at 1666 cm^{-1}, as against a normal range in substituted benzenes of 1590–1610 cm^{-1}. Strains in the larger benzocycloalkenes (**6**; $n \geq 3$) have recently been discussed on the basis of their uv and charge-transfer spectra, together with theoretical calculations of strain energies.[16] Proton magnetic resonance (pmr) studies of the series **6** have also concentrated on the larger members. Thus the chemical shifts of the α-methylene groups have been interpreted[17] in terms of ring currents decreased by strain. Two studies of bond fixation have appeared[18,19] in which the long-range methyl-*o*-aromatic proton–proton couplings in systems like **7** have been examined and interpreted in terms of the π-bond order of the intervening C=C bond. One group suggested[19] that such long-range couplings would not be observed unless the formal double bond was incapable of participating in an aromatic sextet. However, the other workers found such couplings in, for instance, methylnaphthalenes,[18] which demonstrates that this explanation is not correct. Studies of these long-range couplings are certainly of interest, but are of rather limited utility because of experimental factors. Thus, the couplings are often small (*ca.* 0.5–1 Hz), and it may be dangerous to deduce couplings from the first-order splittings of the methyl groups, particularly when the aromatic protons are tightly coupled. A careful study of toluene[20] has shown that the methyl group has long-range couplings to all the aromatic protons, with the couplings to the *meta* proton being of opposite sign (+0.36 Hz) to that with the *ortho* (−0.75 Hz) and *para* (−0.62 Hz) protons. This confirms an earlier report[21] on the signs of these couplings, and clarifies the situation caused by the nonobservance[22] of a coupling to the *meta* proton in acenaphthene. Many cases of splittings in methyl-group resonance signals which result from "virtual coupling"[23] or "deceptive simplicity"[24] are known, and have been discussed by Anet.[25]



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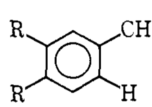

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To further probe for a clearer understanding of the relation of nuclear magnetic resonance spin–spin coupling constants to slight molecular structural variations, especially the effect of strain on aromatic rings, we have carefully determined the proton–proton coupling between aromatic protons for a series of strained benzenes. In monosubstituted benzenes[26] and polycyclic aromatics,[27] such couplings have been extensively investigated, and from an empirical standpoint their behavior seems well understood. At the time this work was begun no systematic study of these couplings in benzocycloalkenes had appeared, although values for the couplings in some benzocyclopropene[7,28] derivatives and benzocyclobutenes[29] had appeared. Indeed the large difference between the values reported for the *cis*- and *trans*-dibromobenzocyclobutenes in previous work[29] provided a considerable impetus to the present study (see later).

It has also appeared to us that a potentially very useful approach for investigating strain had been outlined by Castellano.[30] In a range of *ortho*-disubstituted benzenes where the substituents are sterically small, and do not interact, it was found[30] that the ring proton–proton coupling constants could be calculated to a high degree of accuracy (±0.05 Hz) on the basis of additive sub-

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(13) R. A. Finnegan, *J. Org. Chem.*, **30**, 1333 (1965).

(14) A. Streitwieser, G. R. Ziegler, P. C. Mowerey, A. Lewis, and R. G. Lawler, *J. Amer. Chem. Soc.*, **90**, 1357 (1968).

(15) R. D. Rieke, C. F. Meares, and L. I. Rieke, *Tetrahedron Lett.*, 5275 (1968). However, see also N. Bauld and F. Farr, *J. Amer. Chem. Soc.*, **91**, 2788 (1969).

(16) H. Meier, J. Heiss, H. Suhr, and Eu. Müller, *Tetrahedron*, **24**, 2307 (1968).

(17) H. Meier, Eu. Müller, and H. Suhr, *ibid.*, **23**, 3713 (1967).

(18) P. M. Nair and G. Gopamakur, *Tetrahedron Lett.*, 709 (1964).

(19) E. Clar, B. A. McAndrew, and M. Zander, *Tetrahedron*, **23**, 985 (1967).

(20) M. P. Williamson, R. Kostelnik, and S. M. Castellano, *J. Chem. Phys.*, **49**, 2218 (1968).

(21) G. Kotowycz and T. Schaefer, *Can. J. Chem.*, **44**, 2743 (1966).

(22) M. J. S. Dewar and R. C. Fahey, *J. Amer. Chem. Soc.*, **85**, 2704 (1963).

(23) J. I. Musher and E. J. Corey, *Tetrahedron*, **18**, 791 (1962).

(24) R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **39**, 216 (1961).

(25) F. A. L. Anet, *ibid.*, **39**, 2262 (1961).

(26) S. M. Castellano and C. Sun, *J. Amer. Chem. Soc.*, **88**, 4741 (1966).

(27) M. A. Cooper and S. L. Manatt, *ibid.*, **91**, 6325 (1969).

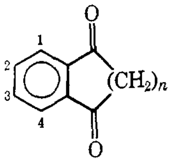
(28) E. Vogel, S. Korte, W. Grimme, and H. Günther, *Angew. Chem.*, **80**, 279 (1968); these couplings have since been refined (see later).

(29) G. Fraenkel, Y. Asahi, M. J. Mitchell, and M. P. Cava, *Tetrahedron*, **20**, 1179 (1964).

(30) S. M. Castellano and R. Kostelnik, *Tetrahedron Lett.*, 5211 (1967).

stituent constant contributions. When the substituents are bulky, or otherwise interact, *e.g.*, by hydrogen bonding, however, there may be considerable deviations from additivity, and these may be ascribed[30] to skeletal distortions produced by the interactions.

The present work set out to obtain the proton–proton couplings in the aromatic ring for some benzocycloalkenes, both to see whether a satisfactory empirical test of the strains present could be devised, and to provide a criterion against which molecular wave functions, and therefore theoretical treatments, might be tested. For experimental reasons only the smaller members of the series could be analyzed and hence the study was later extended to include the corresponding diketones **8**, and some compounds related to **6**.



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Experimental Section

Spectra were obtained on Varian HA-100 and HR-220 spectrometers, the latter instrument only being used for confirmatory work. Sweep calibration on the HA-100 was by direct frequency count, and at least three spectra were averaged to provide a set of accurate transition frequencies. Deuteriochloroform solutions were used throughout. The concentrations used were *ca.* 10–20% (v/v for liquids, wt/v for solids). When the aromatic resonances were broadened by long-range couplings to alicyclic methylenes (as in **6**), the spectra were simplified by frequency-sweep decoupling. The need for care in analyzing decoupled spectra when large decoupling fields are used has been discussed by other workers.[31] In the present case the long-range couplings are fairly small (*ca.* 1 Hz) and hence do not require a large decoupling field for their removal. Second, in many cases the aromatic protons form an AA′BB′ system, and optimum decoupling conditions may be achieved by examining the symmetry of the decoupled spectra.[32] The utility of performing highly accurate spectral analyses on decoupled spectra has recently been discussed for toluene,[20] in which the spectrum was analyzed both with and without decoupling the methyl group. The two cases gave ring couplings in very close agreement.

In all cases the parameters were refined by use of the program LAOCN3.[33] The root-mean-square (rms) error of fitting the spectra and the parameter-set errors obtained are included in the table of results. The significance of the parameter-set error has been discussed elsewhere.[27,34] The couplings are considered good to at least ±0.05 Hz.

The sample of benzocyclopropene, **2**, was kindly supplied[8] by Professor E. Vogel, Cologne, West Germany. Derivatives of benzocyclobutene, **3**, were synthesized in this laboratory with minor modification of literature methods.[9,35–37] The nmr spectra agreed with those reported.

Benzocyclohexene-1,4-dione (**8**; $n = 2$) was prepared by the method of Thomson,[38] mp 95–100°; lit.[38] 98°.

cis-**Dibromobenzocyclobutane** (**12**) had mp 95–98°; lit.[36] 101°. The assignment of the *cis* configuration follows Cava.[36]

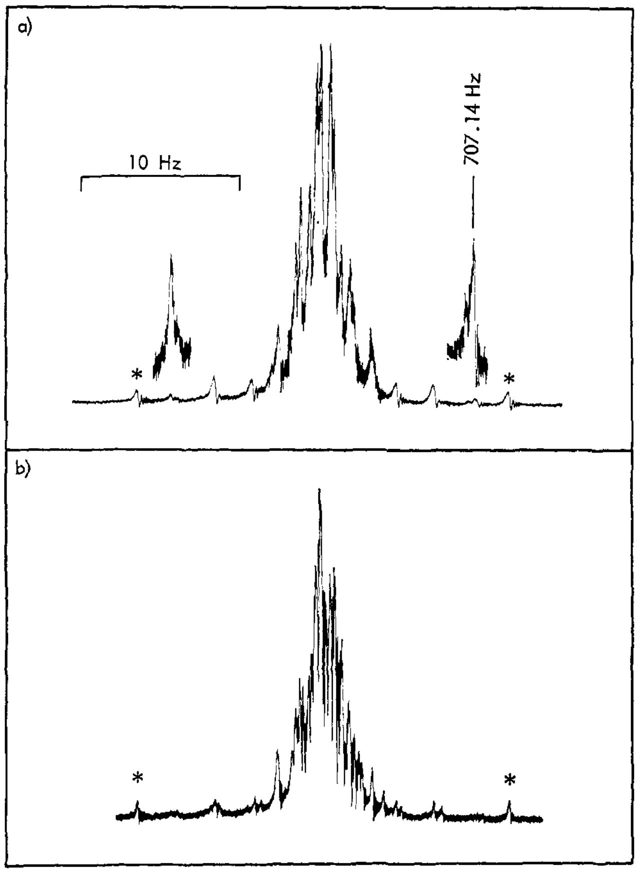

Figure 1. The nmr spectrum of benzocyclopropene (a) with and (b) without decoupling of the methylene resonance, taken at 100 MHz in $CDCl_3$ solution. Impurities are indicated by an asterisk. In (a) the sweep rate was reduced over the central portion of the sweep.

trans-**Dibromobenzocyclobutene** (**13**) had mp 40–50°; lit.[35] 55°. The pmr spectrum showed[29] that this compound contained *ca.* 5% of the *cis* isomer, but as this did not prevent a satisfactory spectral analysis from being obtained, no further purification was undertaken.

Tetrabromobenzocyclobutene had mp 114–116°; lit.[36] 117–118°.

Benzocyclobutadienequinone (**11**) had mp 128–131°; lit.[37] 132–135°.

Benzocyclobutene (**3**) was not redistilled. Its identity was assumed from its mode of preparation,[9] and from its nmr spectrum (four aromatic protons at τ 3.03; four aliphatic protons at τ 6.91; lit.[9] τ 3.00 and 6.86—CCl_4 solutions throughout).

The remaining compounds were obtained commercially and were used directly.

Analysis of Spectra

Figure 1 shows the 100-MHz spectrum of **2** with and without decoupling of the methylene resonance. The spectrum exhibits two extraneous peaks of roughly equal heights situated almost symmetrically about the midpoint of the aromatic resonances. These peaks must be assigned as impurities on the basis of the following evidence. First, the peaks are unaltered in appearance when the decoupling field is applied. Second, the peaks move linearly with applied magnet field, and at 220 MHz (Figure 2) are so far from the rest of the AA′BB′ system as to preclude being part of it. The parameters listed in the table fit the spectrum at both 100 and 220 MHz, after the chemical shift is appropriately scaled, and are in generally good agreement with the results[7] for the carbomethoxy (**9**) and 1,1-difluoro (**10**) derivatives.[39] (The newer results for **10** are rather

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(31) T. M. Connor, D. H. Whiffen, and K. A. McLauchlan, *Mol. Phys.*, **13**, 221 (1967).

(32) See J. Feeney, *Ann. Rep. Chem. Soc.*, *B*, 11 (1967).

(33) An improved version of LAOCOON II: S. M. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, **41**, 3863 (1964).

(34) S. M. Castellano, C. Sun, and R. Kostelnik, *Tetrahedron Lett.*, 5205 (1967).

(35) M. P. Cava and D. R. Napier, *J. Amer. Chem. Soc.*, **79**, 1701 (1957).

(36) M. P. Cava and K. Muth, *J. Org. Chem.*, **27**, 757 (1962).

(37) M. P. Cava, D. R. Napier, and R. J. Pohl, *J. Amer. Chem. Soc.*, **85**, 2076 (1963).

(38) R. H. Thomson, *J. Chem. Soc.*, 1737 (1950).

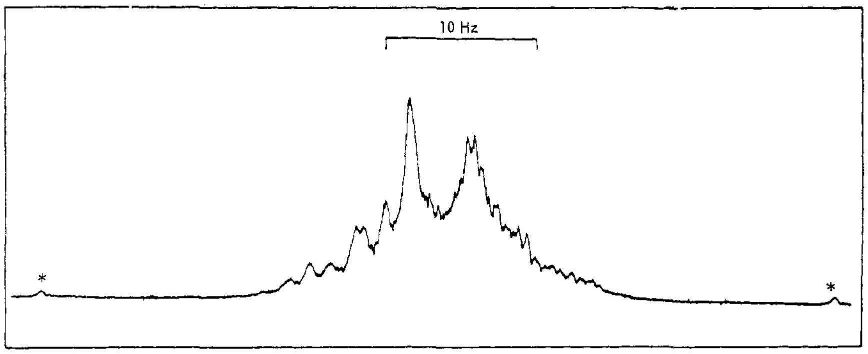


Figure 2. The nmr spectrum of benzocyclopropene at 220 MHz, $CDCl_3$ solution. Impurities are indicated by an asterisk.

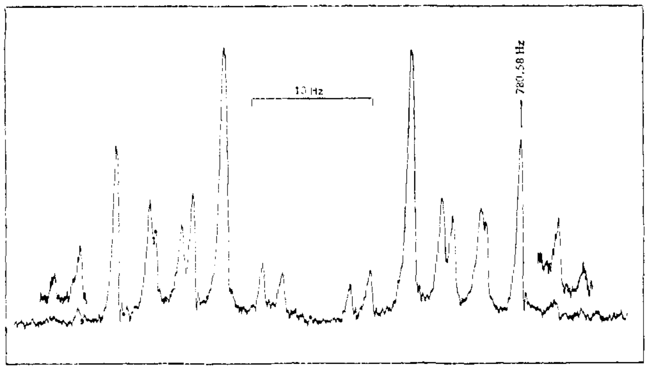
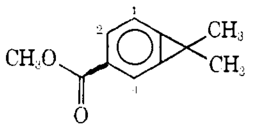


Figure 3. The nmr spectrum of benzocyclobutadienequinone, taken at 100 MHz in $CDCl_3$ solution.

different from those originally reported,[28] and together with those for **9** are included in Table I.)



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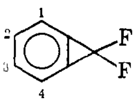

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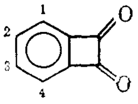
Figure 3 shows the spectrum of benzocyclobutadienequinone, **11**, which has not been reported hitherto. In contrast, analyses of some derivatives of benzocyclobutene, **3**, have appeared in the literature,[29] and the results quoted are significantly different from those found in the present work, as mentioned in the introductory statement. In particular the results for the *cis*- and *trans*-dibromobenzocyclobutenes (**12** and **13**, respectively) are now found to be almost identical, whereas in the earlier work there were significant differences. *A priori*, this was not unreasonable since the severe Br···Br interaction in **12** might well lead to considerable buckling of the cyclobutene moiety, and hence to further strain in the benzene ring, whereas this would not be so for **13**. The present results show that if this effect does occur, it is without influence on the couplings. It seems likely that the discrepancy arises because the long-range couplings to the cyclobutane protons were not removed by the earlier workers, and thereby led to broad bands instead of sharp transition frequencies. Otherwise, the spectra are very similar, and the assignment of the *cis* and *trans* configurations is that taken before. Günther[39] has informed us of his results for benzocyclobutene, and these are included in Table I; the two sets of results are in excellent agreement. For series **6**, $n \geq 4$, and also for *o*-xylene (see later), the protons *ortho* and *meta* to the methylenes have nearly identical chemical shifts, and give rise to a single band (*ca.* 1-2 Hz wide) in the variety of solvents tried and were still not analyzable at 220 MHz. For this reason the corresponding diketones **8** were examined. The carbonyl groups produce a larger chemical shift between the *ortho* and *meta* proton signals of the aromatic ring.



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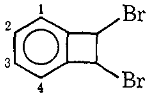

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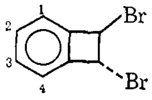
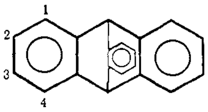


13

Analyses of triptycene,[40] **14**, fluorene,[41] **15**, and biphenylene,[29,42,43] **16**, have been given by other workers, who have discussed the assignments. The spectra of **15** and **16** have been rerun during the course of the present work, and in the case of **15** significant differences from the previous results have been found.[41] This is almost certainly due to the use of LAOCN3 in the present work, as opposed to the trial and error method for fitting the spectra in the earlier work. Accurate



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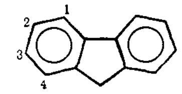

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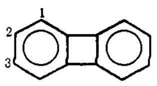

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(39) H. Günther, private communication.

(40) K. G. Kidd, G. Kotowycz, and T. Schaefer, *Can. J. Chem.*, **45**, 2155 (1967).

(41) K. D. Bartle and D. W. Jones, *J. Mol. Structure*, **1**, 131 (1968).

(42) A. R. Katritzky and R. E. Reavill, *Rec. Trav. Chim. Pays-Bas*, **83**, 1230 (1964).

(43) H. P. Figeys, *Angew. Chem. Intern. Ed. Engl.*, **7**, 642 (1968).

transition frequencies for **14** have been reported[40] and all that has been done here is to process these with LAOCN3. The new and old results exhibit differences of up to 0.1 Hz, and the reason for these discrepancies is thought to be as follows: the AA′BB′ analysis involves a 4 × 4 matrix, which cannot be diagonalized readily by hand. Hence the methods for analysis of this system which do not involve a computer depend upon the identification of spacings between the transitions, and, for example, $N(J_{AB} + J_{AB'})$ is obtained as the spacing between lines 1 and 3, in the common notation.[44] Hence any experimental errors in these lines will be directly reflected in the final value of N. Now with the computer, the matrix diagonalization is no problem, and therefore N, which determines the position of lines other than 1 and 3, is obtained as an "average value"—*i.e.*, a statistically weighted average. The advantage of using a computer even for explicit analyses, but to perform such a weighting function, does not seem to have been emphasized enough.

Since it has been demonstrated[30,45] that proton–proton couplings in disubstituted benzenes are capable of being calculated on the basis of additive substituent constant contributions to the couplings, the results for toluene,[20] *t*-butylbenzene,[30] biphenyl,[46] and acetophenone[47] have been used to give predicted (*i.e.*, strain free) results for *o*-xylene, *o*-di-*t*-butylbenzene, 2-methylbiphenyl, and *o*-diacetylbenzene. The use of these model compounds is discussed below.

The chemical shift assignment is not obtainable from an AA′BB′ analysis, but a tentative assignment can be obtained for series **6** by examining the undecoupled spectra. With the assumption that the methylene protons couple more strongly with the aromatic protons *ortho* to the methylene side chains, the region exhibiting the greatest complexity may be assigned to this *ortho* resonance. For tightly coupled systems this method did not always yield an assignment at 100 MHz, but on going to 220 MHz a decision could usually be made. Thus in Figure 2 the *ortho* resonances are seen to lie upfield.

After substitution of a carbonyl group into a benzene ring, the *ortho* protons exhibit[47] a much larger shift downfield than the *meta* or *para* protons. On this basis the *ortho* protons in series **8** would be expected to be downfield. Support for this assignment comes from a dilution experiment with **8** (n = 1) in which the $CDCl_3$ solvent was gradually replaced by C_6D_6. It was found that the upfield resonance was shifted more to high field than was the low-field resonance on changing solvent. Using the rule developed by Williams and Bhacca,[48] the upfield resonance may thus be assigned to protons 2 and 3. Shifts for the other members of the series **8** were assigned by analogy.

Discussion

The *ortho* proton–proton coupling ($^3J_{HH}$) has been extensively investigated in aromatic hydrocarbons and related compounds. It has been shown that $^3J_{HH}$ decreases with increasing carbon–carbon bond distance,[49] and with increasing H—C═C bond angle.[50–53] The electronegativity of attached groups affects the coupling, the sign of the change in $^3J_{HH}$ depending on the number of bonds separating the substituent from the coupling system.[26,54] More recently a steric effect on this coupling has been identified.[27,55]

In attempting to define the effect on the aromatic couplings of fusing a strained ring onto the aromatic system, it is necessary to isolate this strain effect. This is not an easy task, since both bond lengths and bond angles should be altered by strain. We felt that the electronegativity effect was minimized by comparison of coupling constants only in similarly substituted series such as **6** or **8**. The ideal reference compounds for **6** would be *o*-xylene, or tetralin, but as discussed above the parameters for these compounds have yet to be extracted. On the assumption of additive substituent constant contributions to the couplings, the results for toluene[20] may be used to calculate the ring couplings for *o*-xylene. Again in series **8** the results for acetophenone[47] may be used to calculate couplings for *o*-diacetylbenzene. Comparison of these calculated values with experimental results for (presumably) unstrained compounds, *viz.* 9,10-dihydroanthracene and *o*-phthalaldehyde, respectively, shows generally good agreement, especially for $^4J_{HH}$ and $^5J_{HH}$.

It is possible to obtain estimates of couplings in strain-free model compounds by empirical methods. Thus values of $^3J_{HH}$ in particular may be obtained for a (hypothetical strain-free) biphenylene from the empirical $^3J_{HH}/\pi$ bond-order relationship.[27] The Hückel π-bond orders for the 1–2 and 2–3 bonds in this molecule are 0.621 and 0.691, respectively, and these correspond to couplings J_{12} = 7.07 Hz and J_{23} = 7.88 Hz.

Examination of Table I shows that the most striking effects of increasing ring strain on the couplings are the monotonic decrease in $^4J_{HH}$, and the accompanying increase in $^5J_{HH}$ throughout the series studied. If these couplings are used as qualitative measures of the strain, then it appears that whereas triptycene still exhibits some strain, 9,10-dihydroanthracene is only a little more strained than *o*-xylene. Similarly, indandione still exhibits strain, while tetralindione and naphthoquinone have values of these couplings very similar to those in *o*-phthalaldehyde or *o*-diacetylbenzene, and 9,10-dihydrophenanthrene exhibits little strain relative to 2-methylbiphenyl. A complementary observation is that in the observed and "strain-free" results for *o*-di-*t*-butylbenzene, where the effect of strain is to force apart the *ortho* substituents, in contrast to the other examples where ring strain forces them together, the observed value of $^4J_{HH}$ is larger than, and $^5J_{HH}$ is smaller than the "strain-free" values.

In the case of *o*-di-*t*-butylbenzene the repulsion between the *ortho* substituents is seen to cause J_{12} to become larger than, and J_{23} smaller than, the "strain-free" values. The opposite was found[30] for *o*-nitrophenol,

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(44) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance Spectroscopy," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 147.

(45) For an extensive compilation see A. R. Tarpley, H. B. Evans, and J. H. Goldstein, *Anal. Chem.*, **41**, 402 (1969), and references therein.

(46) See Table I, footnote *k*.

(47) See Table I, footnote *j*.

(48) D. H. Williams and N. S. Bhacca, *Tetrahedron*, **21**, 2021 (1965).

(49) For a recent discussion, see ref 27.

(50) O. L. Chapman, *J. Amer. Chem. Soc.*, **85**, 2014 (1963).

(51) G. V. Smith and H. Kriloff, *ibid.*, **85**, 2016 (1963).

(52) P. Laszlo and P. von R. Schleyer, *ibid.*, **85**, 2017 (1963).

(53) For a theoretical discussion see M. Karplus, *ibid.*, **85**, 2870 (1963).

(54) T. Schaefer and H. M. Hutton, *Can. J. Chem.*, **45**, 3153 (1967).

(55) C. W. Haigh and R. B. Mallion, *J. Mol. Spectrosc.*, **29**, 478 (1969).

Table I

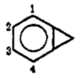
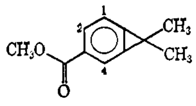
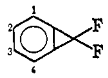
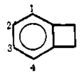
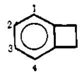
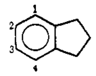
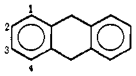
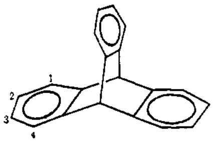
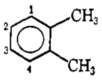
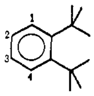
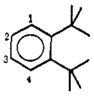
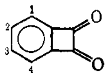
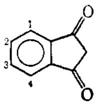
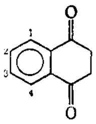
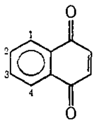
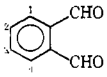
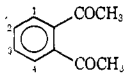
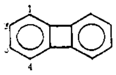
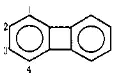
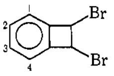
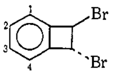
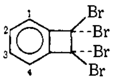
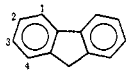
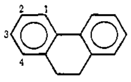
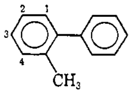
Compd	J_{12}[a]	J_{13}	J_{14}	J_{23}	δ_1[b]	δ_2	RMS	Solvent	Ref[c]
	6.04 (0.015)	0.33 (0.009)	1.85 (0.019)	7.63 (0.024)	714.92 (0.010)	718.91 (0.010)	0.037	$CDCl_3$	
	6.6	0.7 (J_{24})	1.9						*d*
	6.83	0.32	1.89	7.43					*e*
	7.36 (0.011)	1.00 (0.010)	1.03 (0.009)	7.79 (0.009)	690.69 (0.007)	676.39 (0.007)	0.026	$CDCl_3$	
	7.36	0.98	1.06	7.78					*e*
	7.59 (0.021)	1.17 (0.016)	0.48 (0.025)	7.20 (0.030)	707.30 (0.017)	699.00 (0.017)	0.035	$CDCl_3$	
	7.56 (0.017)	1.34 (0.013)	0.57 (0.027)	7.35 (0.028)	716.61 (0.014)	709.64 (0.014)	0.039	$CDCl_3$	
	7.25 (0.016)	1.18 (0.012)	0.59 (0.015)	7.62 (0.011)	433.68 (0.010)	411.30 (0.010)	0.034	CS_2 (60 MHz)	*f*
	7.61	1.38	0.54	7.50					*g*
	8.11	1.59	0.27	7.00					*h*
	7.80	1.33	0.46	7.24					*i*
	7.71 (0.012)	0.77 (0.011)	1.24 (0.010)	7.15 (0.009)	808.02 (0.007)	785.56 (0.007)	0.027	$CDCl_3$	
	7.73 (0.010)	1.05 (0.008)	0.83 (0.010)	7.34 (0.010)	796.29 (0.007)	784.50 (0.007)	0.022	$CDCl_3$	
	7.81 (0.006)	1.30 (0.005)	0.58 (0.004)	7.34 (0.005)	804.53 (0.003)	773.31 (0.003)	0.012	$CDCl_3$	
	7.81 (0.014)	1.29 (0.013)	0.54 (0.010)	7.46 (0.011)	821.81 (0.007)	790.51 (0.007)	0.030	$CDCl_3$	
	7.63 (0.011)	1.28 (0.008)	0.46 (0.009)	7.51 (0.009)	793.19 (0.006)	777.01 (0.006)	0.025	$CDCl_3$	
	7.64	1.24	0.48	7.20					*j*
	6.90 (0.005)	0.81 (0.004)	1.01 (0.007)	8.27 (0.007)	393.51 (0.004)	399.95 (0.004)	0.014	$CDCl_3$ (60 MHz)	

Table I (*Continued*)

Compd	J_{12}[a]	J_{13}	J_{14}	J_{23}	δ_1[b]	δ_2	RMS	Solvent	Ref[c]
	6.89 (0.009)	0.82 (0.008)	1.00 (0.010)	8.23 (0.009)	666.40 (0.007)	655.63 (0.007)	0.024	$CDCl_3$ (100 MHz)	
	7.58 (0.009)	0.87 (0.008)	1.05 (0.007)	7.73 (0.007)	738.24 (0.005)	719.03 (0.005)	0.020	$CDCl_3$	
	7.51 (0.013)	0.87 (0.012)	1.05 (0.010)	7.71 (0.010)	734.77 (0.007)	713.97 (0.007)	0.029	$CDCl_3$	
	7.76 (0.010)	0.83 (0.009)	1.00 (0.008)	7.60 (0.008)	750.32 (0.006)	730.30 (0.006)	0.023	$CDCl_3$	

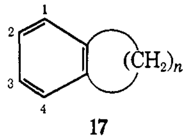
Compd	J_{12}	J_{13}	J_{14}	J_{23}	J_{24}	J_{34}	δ_1	δ_2	δ_3	δ_4	RMS	Solvent	Ref
	7.58 (0.023)	1.22 (0.024)	0.80 (0.015)	7.34 (0.019)	1.15 (0.020)	7.47 (0.020)	764.79 (0.010)	725.46 (0.017)	718.63 (0.019)	738.80 (0.012)	0.037	$CDCl_3$	
	7.64 (0.021)	1.52 (0.024)	0.61 (0.024)	7.40 (0.022)	1.32 (0.019)	7.47 (0.020)	753.87 (0.012)	710.44 (0.018)	703.70 (0.020)	701.12 (0.020)	0.040	$CDCl_3$	
	7.81	1.40	0.57	7.42	1.34	7.53							k

[a] Coupling constants in hertz. Values in parentheses are parameter set errors from LAOCN3. [b] Chemical shifts downfield from TMS in hertz; 100 MHz unless otherwise stated. [c] Results obtained in present work unless otherwise stated. [d] Reference 7. [e] Reference 39. [f] Data of K. G. Kidd, G. Kotowycz, and T. Schaefer (*Can. J. Chem.*, **45**, 2155 (1967)) reworked. [g] Calculated couplings, from data for toluene, ref 20, assuming additive substituent constant contributions (see text). [h] Experimental values, ref 30. [i] Calculated values, using values for *t*-butylbenzene, ref 30. [j] Calculated values, using values for acetophenone (K. Hayamizu and O. Yamamoto, *J. Mol. Spectrosc.*, **25**, 422 (1968)). [k] Calculated values, using values for biphenyl (R. E. Mayo and J. H. Goldstein, *Mol. Phys.*, **10**, 301 (1966)) and toluene, ref 20.

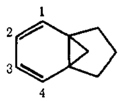
where a strong intramolecular hydrogen bond between the substituents causes them to come together, and produces a strain not unlike that in the benzocycloalkenes. A similar effect in biphenylene is seen when the reference values of $^3J_{HH}$ derived from π-bond orders are compared with experimental values. In series **6** and **8**, however, no such trends are apparent. In **8**, J_{12} and J_{23} are virtually constant at 7.7 ± 0.1 Hz and 7.3 ± 0.15 Hz, respectively. The variations in **6** are rather larger, but there is no clear trend in J_{23}. In **2**, J_{12} is significantly smaller than in the other molecules, but the general conclusion is that $^3J_{HH}$ is largely insensitive to ring strain in these molecules.

At this point it is pertinent to discuss to what degree the observed variations in the couplings accord with current theory. To this end the couplings will be discussed in terms both of empirical correlations and a molecular orbital treatment. The separation of the effects present into specific contributions, *e.g.*, "bond-length variations" and "electronegativity differences" which we make here, is not fully realistic in that such effects will not be mutually independent. However, such an approach is intuitively useful. Because the effects found in series **6** and **8** and the smaller number of miscellaneous examples are consistent, we shall restrict our discussion to cover **6**, but with the implication that the same considerations apply to the other molecules.

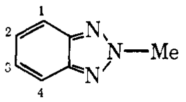
Bond Length. The treatment of Longuet-Higgins and Coulson[6] indicated that bond-length distortions in a small benzocycloalkene should tend toward the structure **17**. Thus with increasing strain the trend should be to increase J_{12} relative to J_{23}. It is relevant at this point to mention that several studies in the literature have discussed the effect of delocalization on proton–proton couplings.[56,57] Not always has care been taken to isolate this factor from other variables, however. Günther has discussed the couplings in the molecules **18**, **19**, and **20**, in terms of separate σ- and π-electron mechanisms to the couplings, and these results are shown in Table II. The effect of increasing delocalization is to increase J_{23} and J_{13} and decrease J_{12} and J_{14}. Thus returning to our discussion of **17**, partial bond fixation would be expected to increase J_{14} and decrease J_{13}, and these trends are those observed for these couplings, whereas no clear trends are seen in J_{12} and J_{23}. Comparison of the values of J_{13} and J_{14} in benzocyclopropene with those in **18**, however, shows that bond



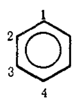
17



18



19



20

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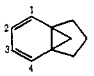
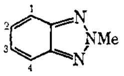
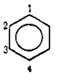
(56) H. Günther and H.-H. Hinrichs, *Ann.*, **706**, 1 (1967).

(57) H. Günther, *Tetrahedron Lett.*, 2967 (1967), and references therein.

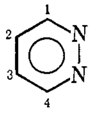
Table II[a]

	Compd	J_{12}	J_{13}	J_{14}	J_{23}
	**18**	9.25	0.58	1.31	5.94
	**19**	8.65	1.04	1.03	6.79
	**20**	7.56	1.38	0.68	7.56

[a] Values taken from ref 57.

fixation can hardly be the only or predominant effect, as otherwise we should have to conclude that benzocyclopropene exhibits the greater amount of bond fixation.

Electronegativity. From empirical evidence[14] it has been proposed that with increasing strain the bridge carbons become more electronegative. The amount of this change is hard to estimate quantitatively, for example on the Pauling scale. The direction of the changes to be expected may be estimated for our purposes from the couplings in pyridazine,[58] **21**. Com-

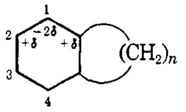


$J_{12} = 5.07$ Hz; $J_{14} = 1.38$ Hz
$J_{13} = 1.88$ Hz; $J_{23} = 8.34$ Hz

21

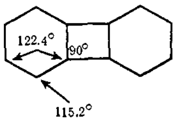
pared to the couplings in benzene (Table II) J_{13}, J_{14}, and J_{23} in **21** exhibit increases of 0.5–0.8 Hz, whereas J_{12} has decreased very sharply (2.5 Hz). It is noteworthy that in the case of all the couplings except J_{14}, these changes are in the opposite sense to those expected from bond-fixation models.

Bond-Angle Changes. Longuet-Higgins and Coulson[6] showed that the signs of angular distortions in benzocycloalkenes could be predicted with reasonable confidence, even though the magnitudes of these changes were open to doubt. In a small benzocycloalkene the deviations in C–C–C angles from 120° were shown[6] to be in the sense of **22**.



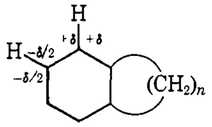
22

Experimental support for this suggested distortion was provided by an X-ray structure determination on biphenylene,[59] where the ring angles are found to be as in **23**.



23

In the absence of severe steric repulsions from the cycloalkene moiety, the C–H bonds of the aromatic system will bisect the corresponding C–C–C angle, and hence the C–C–H bond angles will differ from 120° as shown in **24**.



24

The values of $^3J_{HH}$ are very sensitive to changes in these bond angles,[50–53] and for an increase in δ as small as 1° the changes in J_{12} and J_{23} may be estimated[27] as −0.3 and +0.5 Hz, respectively. The effect of these changes on J_{13} and J_{14} is very hard to assess, as there is sparse experimental or theoretical evidence available on this point.[60] The tentative results we have available from molecular orbital theory (see later) suggest that these couplings are much less affected than J_{12} and J_{23} by small skeletal distortions.

In cases where the side chains are sterically bulky, *e.g.*, *o*-di-*t*-butylbenzene, there will be a further effect related to skeletal distortion, produced by the steric repulsion between the *t*-butyl groups and protons 1 and 4. The net result of this would be expected to increase J_{12},[27,55] and decrease J_{23}.[61]

To summarize this discussion, it appears that fusing a small cycloalkene ring onto a benzene nucleus gives rise to small bond length, bond angle, and electronegativity differences in the aromatic ring. The effect of such changes on $^4J_{HH}$ and $^5J_{HH}$ is not fully known, but it certainly appears that the net result would be an increase in the latter with increasing ring strain, in agreement with experiment. The trend observed in $^4J_{HH}$ seems to suggest that the effect of electronegativity is smaller than that of bond length. In the case of $^3J_{HH}$ these effects produce contributions of opposite signs to the couplings, such that, depending on the relative magnitudes of these terms, the resultant effect might be rather small—as found experimentally.

Theoretical Considerations. Although at the present time no appropriate structural information is available, and many questions still exist regarding theoretical treatments of couplings, we nonetheless feel it is useful to consider the coupling constants in the strained members of series **6** using extended Hückel molecular orbital theory.[62] This theory has been criticized for being too gross an oversimplification,[63,64] but it seems that within a series of closely related molecules it is capable of providing useful insight into, for example, hydrocarbon conformations,[62] mechanistic intermediates,[65] and nmr spin-spin coupling constants.[66–69]

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(58) V. M. S. Gil and A. J. L. Pinto, *Mol. Phys.*, **16**, 623 (1969).

(59) J. K. Fawcett and J. Trotter, *Acta Crystallogr.*, 20, 87 (1965).

(60) M. Barfield and B. Chakrabarti, *Chem. Rev.*, **69**, 757 (1969).

(61) M. A. Cooper and S. L. Manatt, unpublished work.

(62) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963). The authors are grateful to Professor Hoffmann for a copy of his program.

(63) M. J. S. Dewar in "Aromaticity," Special Publication No. 21, The Chemical Society, London, 1967.

(64) R. L. Flurry, Jr., "Molecular Orbital Theories of Bonding in Organic Molecules," Marcel Dekker, Inc., New York, N. Y., 1968, pp 270–275.

(65) J. E. Baldwin and W. D. Foglesong, *J. Amer. Chem. Soc.*, **90**, 4311 (1968).

(66) R. C. Fahey, G. C. Graham, and T. L. Piccioni, *ibid.*, **88**, 193 (1966).

(67) M. A. Mainster and J. D. Memory, *J. Chem. Phys.*, **49**, 3992 (1968).

(68) A. H. Cowley, W. D. White, and S. L. Manatt. *J*, *Amer. Chem. Soc.*, **89**, 6433 (1967).

Indeed, in a previous study[68] we suggested that the extended Hückel method appears "generally the most satisfactory" of three common methods (extended Hückel, SCF-MO program, and extended Hückel with complete neglect of differential overlap) for calculation of coupling constants which were tested, although that work was rather different from the present in that only directly bonded coupling constants were under investigation. A comparison[69] of the extended Hückel treatment with the widely applied Pople–Santry method[70–72] has shown the former to be more reliable—at least for ${}^2J_{\mathrm{HH}}$ and ${}^3J_{\mathrm{HH}}$. Thus we have used the extended Hückel method in the present work.

The values of the input parameters for the program were taken to be the same as used by previous workers interested in coupling constants.[66,67] The Coulomb integrals were taken as H, −13.6 eV; C_{2s}, −21.4 eV; C_{2p}, −11.4 eV. The Slater exponents used were C, 1.625 and H, 1.2. For bond lengths the standard values of C═C (aromatic) = 1.40 Å; C–C (aliphatic) = 1.54 Å, and C–H = 1.10 Å were taken. In the absence of detailed structural information, regular hexagonal geometry was initially assumed for the aromatic rings. The cyclobutene and cyclopentene rings of benzocyclobutene and indan were assumed coplanar with the benzene ring.

The proton–proton coupling constants were calculated from the expression for the Fermi contact term given by Pople and Santry,[70] *viz.*

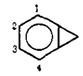
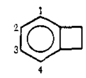
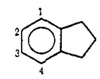
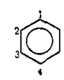
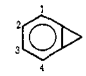
$$J_{\mathrm{AB}} = \frac{64}{9}\beta^2\gamma_{\mathrm{A}}\gamma_{\mathrm{B}}h(S_{\mathrm{A}}|\delta(r_{\mathrm{A}})|S_{\mathrm{A}})(S_{\mathrm{B}}|\delta(r_{\mathrm{B}})|S_{\mathrm{B}}) \times \sum_{i}^{\mathrm{occ}}\sum_{j}^{\mathrm{unocc}}(\epsilon_i - \epsilon_j)^{-1} \times C_{i\mathrm{S_A}}C_{j\mathrm{S_A}}C_{j\mathrm{S_B}}C_{i\mathrm{S_B}}$$

where the symbols have their usual meanings.[68]

Terms involving two-center integrals, which have been included by some authors,[66,67] were ignored. It has been suggested[69] that these terms are small for proton–proton couplings over three or more bonds, and hence this omission should not affect the general conclusions—particularly in considering a similar series such as **6**. A more serious omission is the neglect of any coupling mechanism *via* the π-electron system, which is undoubtedly important[60] for ${}^4J_{\mathrm{HH}}$ and ${}^5J_{\mathrm{HH}}$. A recent treatment[73] of the couplings in ethylene, using a LCAO self-consistent field treatment both with and without configuration interaction, has suggested that inclusion of the latter significantly affects the value of ${}^3J_{\mathrm{HH}}$.

The calculated ring coupling constants, together with the total net charges (in electrons) of the ring carbon atoms are shown in Table III. It is seen that whereas C_6 becomes rapidly more negative with increasing strain, C_1 becomes slightly more positive. This is interesting in that it implies that, at this level of approximation, the increasing electronegativity of C_6 does not cause a corresponding increase in the electronegativity of C_1, in contrast to the suggestion made by Streitwieser and discussed earlier.[14] Rather there is a charge alternation, which has been suggested by other theoretical studies[74] of inductive effects.

Table III

	Calculated couplings (Hz)				Net calculated charges (e)		
Molecule	12	13	14	23	C_1	C_2	C_6
	4.74	−0.60	1.78	3.21	0.023	0.058	0.082
	4.31	−0.51	1.47	3.52	0.064	0.064	0.009
	3.99	−0.50	1.22	3.67	0.078	0.066	−0.032
	3.80	−0.47	1.15	3.80	0.047	0.047	0.047
 (distorted)	4.31	−0.59	1.76	3.83	0.023	0.058	0.075

Pronounced trends in ${}^3J_{\mathrm{HH}}$ are predicted, and it is of interest that these are in the same direction as those suggested by the bond-length alternation picture of Longuet-Higgins and Coulson.[6] However, no bond-length or bond-angle changes were allowed in the initial calculations. The predicted and observed trends for ${}^5J_{\mathrm{HH}}$ are in substantial agreement, while it is predicted that ${}^4J_{\mathrm{HH}}$ (for which a numerically wrong sign is obtained) should become only slightly more negative with ring strain, in contrast with the quite substantial shift observed in this direction. In the absence of an estimate of the π-electron contribution to these couplings, however, these results for ${}^4J_{\mathrm{HH}}$ and ${}^5J_{\mathrm{HH}}$ must be treated with caution.

Finally, an estimate of the effect of molecular framework distortions on the couplings has been made. The calculations for benzocyclopropene were redone keeping the same parameters, except that instead of regular hexagonal geometry for the aromatic ring, angles C_1–C_2–C_3 and C_1–C_6–C_5 were increased[6] to 122°, and C_2–C_1–C_6 was decreased to 116°, *i.e.*, $\delta = 2°$ in **22**. From Table III it is seen that whereas ${}^4J_{\mathrm{HH}}$ and ${}^5J_{\mathrm{HH}}$ were unaffected by this change, J_{12} decreases by 0.43 Hz and J_{23} increases by 0.62 Hz. Thus such changes in geometry may well counterbalance other effects and leave ${}^3J_{\mathrm{HH}}$ in this series almost unaffected by strain, as discussed above from an empirical standpoint.

Chemical Shifts. We have concentrated on the coupling constants in these molecules largely because the theory of these is better developed than that of chemical shifts, but also because no attempt has been made to extrapolate the shifts to infinite dilution in an inert solvent such as carbon tetrachloride. Moreover, the geometry of these systems is not well established. It is noteworthy that in each of the series considered the shifts lie in a fairly narrow range (*ca.* τ 2.8–3.3 for **6** and τ 1.9–2.3 for **8**). These shifts are characteristically "aromatic" rather than "dienic." Thus in **6**, for

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(69) W. H. DeJeu and G. P. Beneder, *Theor. Chim. Acta*, **13**, 349 (1969).

(70) J. A. Pople and D. P. Santry, *Mol. Phys.*, **8**, 1 (1964).

(71) J. A. Pople and D. P. Santry, *ibid.*, **9**, 311 (1965).

(72) J. A. Pople and A. A. Bothner-By, *J. Chem. Phys.*, **42**, 1339 (1965).

(73) E. A. G. Armour and A. J. Stone, *Proc. Roy. Soc.*, *A*, **302**, 25 (1967).

(74) J. A. Pople and M. Gordon, *J. Amer. Chem. Soc.*, **89**, 4253 (1967).

example, the shifts may be compared with those for the vinyl protons in cyclohexa-1,3-diene (τ 4.21) and *o*-xylene (τ 3.00), both in dilute $CDCl_3$ solution.

Conclusion

In the introductory statement, a survey of the evidence for strain in the benzocycloalkenes was given, and it was seen that there was little to suggest a partial loss of aromaticity in these compounds. The work in this paper has presented the first systematic examination of the proton–proton coupling constants between the aromatic protons in the strained benzocycloalkenes and a number of related molecules. It is found that the *ortho* couplings ($^3J_{HH}$) are insensitive to the strain, whereas $^4J_{HH}$ shows a significant decrease, and $^5J_{HH}$ a significant increase with strain. It should be emphasized that lack of thermochemical data means that only a qualitative estimate of strain energy can be made. The changes observed in $^4J_{HH}$ and $^5J_{HH}$ are in contrast to the insensitivity to strain of many other physical properties of these molecules.

A satisfactory qualitative explanation of these changes in the couplings may be given on the basis of empirical arguments which take into account the bond length, bond angle, and electronegativity changes thought to occur in these strained molecules. Many previous studies on "bond fixation" do not seem to have stressed enough the possible interplay of these factors. The results from an extended Hückel molecular orbital theory have also been presented in an attempt to describe the observed changes of these couplings on a reasonable theoretical basis. In view of the trends found for $^4J_{HH}$ and $^5J_{HH}$ in the present work, it would be of great interest to examine the ring-proton coupling constants in other strained aromatic compounds, for example, the cyclophanes.[75]

Before any more sophisticated theoretical treatment of these strained benzocycloalkenes is undertaken, it would seem necessary to obtain the molecular geometries, for example by X-ray or electron diffraction techniques. These values would also serve as a yardstick against which to test the success of geometries predicted using the method of Coulson and Longuet-Higgins,[6] or more recent theories.[76]

Acknowledgments. We thank Dr. H. Günther (Cologne, West Germany) for supplying results prior to publication, and both him and Dr. R. D. Rieke for helpful discussion. Professor E. Vogel (Cologne, West Germany) is most gratefully thanked for the generous sample of benzocyclopropene and for his interest. We thank Mr. J. H. Prestegard, Department of Chemistry, Caltech, for assistance in obtaining the 220-MHz spectra.

(75) For a review of the properties of these molecules, see: B. H. Smith, "Bridged Aromatic Compounds," Academic Press, New York, N. Y., 1964.

(76) See N. L. Allinger, J. A. Hirsch, M. A. Miller, I. J. Tyminski, and F. A. Van-Catledge, *J. Amer. Chem. Soc.*, 90, 1199 (1968), and references therein.

The Molecular Structure of Bicyclo[1.1.1]pentane

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Abstract: This article reports on a molecular structure investigation of bicyclo[1.1.1]pentane by electron diffraction in the vapor phase. The data support a D_{3h} conformation, with dihedral angles of the cyclobutane rings fixed at 120°. The "best" structural parameters were obtained by applying a least-squares analysis to the experimental molecular intensities. These are: $C\text{–}C = 1.545 \pm 0.006$ Å, $\langle C\text{–}H\rangle_{av} = 1.100 \pm 0.010$ Å, $\angle C_1C_2C_3 = 73.3 \pm 1.0°$, $\angle HCH = 103.9 \pm 5.0°$. The separation between the bridgehead carbon atoms is 1.845 Å, the shortest nonbonded $C \cdots C$ distances on record, in complete agreement with the value found by X-ray diffraction for the 2-hydroxy-2-phenyl disubstituted derivative.

The structure of bicyclo[1.1.1]pentane presents interesting features of strained, fused four-membered ring systems. The dihedral angle for the cyclobutane rings is restricted to 120° by molecular symmetry. It appears evident that nonbonded carbon–carbon interactions are strong in this molecule. The present measurements of its molecular geometry in the gas phase by electron diffraction provide quantitative parameters for a theoretical treatment of this unusual structure.

Experimental Section

A purified sample of bicyclo[1.1.1]pentane was supplied by Dr. F. Uno and Professor J. Meinwald of the Department of Chemistry, Cornell University. Sectored electron diffraction patterns were taken with our new apparatus using a 70-kV electron beam, at 129- and 262-mm nozzle-to-plate distances. The sample was kept at 0° during the exposures. MgO patterns were recorded concurrently to establish the (λ L) scale factor. The diffraction patterns were microphotometered with a double beam Jarrell–Ash microdensitometer interfaced with a digital recorder. The procedure for data reduction and structure analysis has been described in several previous publications.[1]

Analysis and Results

The total experimental intensity curves for the two sets of data, along with the refined background, are plotted in Figure 1.[2] The reduced experimental $qM(q)$

(1) (a) J. L. Hencher and S. H. Bauer, *J. Amer. Chem. Soc.*, 89, 5527 (1967); (b) W. Harshbarger, G. Lee, R. F. Porter, and S. H. Bauer, *Inorg. Chem.*, 8, 1683 (1969); (c) R. L. Hilderbrandt and S. H. Bauer, *J. Mol. Structure*, 3, 825 (1969).