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# NMR SPECTROSCOPY OF BENZOCYCLOBUTENE AND BIPHENYLENE[1]

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**Abstract**—NMR parameters were determined for benzocyclobutene, six substituted benzocyclobutenes and biphenylene. Values calculated for the dihedral angles between the benzylic C—H bonds of benzocyclobutene indicate that the four-membered ring is skewed. Analysis of the NMR spectrum of biphenylene shows the presence of two (and not three) ring currents.

BENZOCYCLOBUTENE[2,3] and biphenylene[4] are known to be highly strained,[5] but two questions regarding the effects of this strain on the electronic and skeletal structures of the molecules have persisted up to the present time, namely (1) the degree of aromacity of the six-membered rings in both benzocyclobutene and biphenylene and (2) the geometry of the four-membered ring in benzocyclobutene. In the present study, we have sought answers to these questions by means of NMR spectroscopy.[6]

The NMR spectra of benzocyclobutene, six substituted benzocyclobutenes, and biphenylene were determined with the Varian HR-60 or the Varian A-60 spectrometers and were analyzed by standard methods[7] with the aid of the IBM computer 7090 NMRIT and NMREN programs.[8] The chemical shifts and coupling constants of benzocyclobutene and six substituted benzocyclobutenes are listed in Table 1. The chemical shift of the benzylic hydrogens in the *trans*-1,2-dihalobenzocyclobutenes was found to be 0·4 ppm to higher field than that of the corresponding *cis* isomers. In the case of 1-bromobenzocyclobutene, the three benzylic hydrogens give rise to an ABX pattern (AB for —$CH_2$— and X for —CHBr—). On the basis of the chemical shifts found for the *cis* and *trans* dihalides, the high-field portion

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[1] Supported by the U.S. Air Force Office of Scientific Research and the National Science Foundation.

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

[3] L. Horner, W. Kirmse and K. Muth, *Chem. Ber.* **91**, 430 (1958).

[4] W. C. Lothrop, *J. Amer. Chem. Soc.* **63**, 1187 (1941).

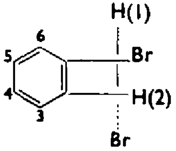
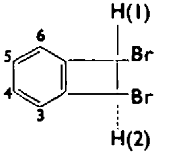
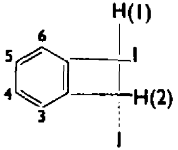
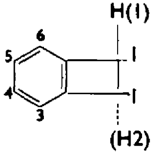
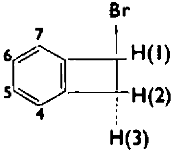
[5] Thermolysis of benzocyclobutene at 200° results in fission of the four-membered ring to give *o*-quinodimethane. The latter may be isolated as a Diels-Alder adduct [F. R. Jensen, W. E. Coleman and A. J. Berlin, *Tetrahedron Letters* No. 1, 15 (1962)]. Benzocyclobutene may be reduced catalytically to bicyclo[4.2.0]octane under conditions that do not affect *o*-xylene [M. P. Cava and M. J. Mitchell, unpublished work]. The resonance stabilization energy of biphenylene is only 17·1 kcal/mole [A. F. Bedford, J. G. Carey, I. T. Mollar, C. T. Mortimer, and H. D. Springall, *J. Chem. Soc.* 3895 (1962)]. Hydrogenolysis of the four-membered ring of biphenylene takes place with great ease in the presence of Raney nickel catalyst [W. Baker, M. P. V. Boarland and J. F. W. McOmie, *Ibid.* 1476 (1954)].

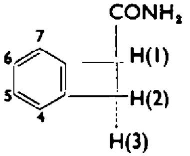
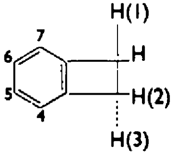
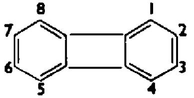
[6] NMR data have been reported for several substituted benzocyclobutenes; see A. T. Blomquist and C. H. Bottomley, *Chem. Ber.* **653**, 73 (1962).

[7] J. A. Pople, W. G. Schneider and H. J. Bernstein, *High-Resolution Nuclear Magnetic Resonance* McGraw-Hill, N.Y. p. 140*ff*; See also J. Martin and B. P. Dailey, *J. Chem. Phys.* **37**, 2594 (1962).

[8] Kindly donated by Dr. J. Swalen, International Business Machines Corp., San Jose, Calif. We thank Mr. Kenneth Bucher, Standard Oil Co. of Ohio, Cleveland, Ohio, for help in using the IBM programs.

TABLE 1. NMR PARAMETERS FOR BENZOCYCLOBUTENES[a, b]

| Compound | Solvent | $\tau_1$ | $\tau_2$ | $\tau_3$ | $\tau_4$ | $J_{1,2}$ | $J_{1,3}$ | $J_{2,3}$ | $J_{3,4}$ | $J_{3,5}$ | $J_{3,6}$ | $J_{4,5}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | $CDCl_3$ | 4·190 | 4·190 | 2·566 | 2·752 | | | | 7·50 | 1·56 | 0·97 | 5·15 |
|  | $CDCl_3$ | 4·590 | 4·590 | 2·615 | 2·825 | | | | 7·50 | 1·17 | 0·90 | 6·04 |
|  | $CDCl_3$ | 4·040 | 4·040 | 2·596 | 2·912 | | | | 7·55 | 0·81 | 1·07 | 7·88 |
|  | $CDCl_3$ | 4·450 | 4·450 | 2·656 | 2·972 | | | | 7·55 | 0·81 | 1·07 | 7·88 |
|  | $CCl_4$ | 4·690 | 6·591 | 6·221 | 2·9[c] | 1·95 | 4·76 | ±14·6[d] | | | | |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
|  | DMSO | 5·830 | 6·742 | 6·742 | 2·64[c] | 4·00 | 4·06 | | | |
|  | $CCl_4$ | 6·863[e] | | | 3·0[c,e] | 3·5[e] | 5·0[e,f] | | | |
|  | $CDCl_3$ | 3·298 | 3·402 | | | 6·80 | 0·74 | 8·24 | 6·80 | $J_{1,4}$ = 1·08 |

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[a] Tau scale, shift of tetramethylsilane is 10 ppm, values ±0·004 ppm. Coupling constants, ±0·01 cs.

[b] Obtained by the methods of Refs. 7 and 8.

[c] Center of aromatic multiplet.

[d] The analysis is not affected by the sign of $J_{2,3}$.

[e] Parameter obtained from analysis of $C^{13}$-sideband of $CH_2$ resonance.

[f] $J_{2,3}$ could not be obtained because not all lines of the $C^{13}$ $A_2X_2$ multiplet were found.

of the methylene multiplet in the spectrum of the monobromide may be assigned to the hydrogen at $C_2$ which is *trans* to the hydrogen at $C_1$ so that $J^{trans}_{1,2} = 4\cdot75$ cs and $J^{cis}_{1,3} = 1\cdot95$ cs. The corresponding values for the two isomeric methylphenylbenzocyclobutenes are $J^{trans} = 6\cdot1$ cs (*trans*-1-methyl-2-phenylbenzocyclobutene) and $J^{cis} = 3\cdot1$ cs (*cis*-1-methyl-2-phenylbenzocyclobutene).[6] We have obtained

Table 2. Calculated dihedral angles between adjacent C—H bonds of the four-membered ring in benzocyclobutenes[a]

| Compound | Orientation | $\theta_1$ and $\theta_2$ ($\pm5°$) | |
|---|---|---|---|
| 1-Bromobenzocyclobutene | *cis* | 40 | |
| | *trans* | | 140 |
| Benzocyclobutene | *cis* | 40 | |
| | *trans* | | 120 |
| Benzocyclobutene-1-carboxamide | *cis* | 44 | |
| | *trans* | | 119 |
| 1-Methyl-2-phenylbenzocyclobutene | *cis* | 30 | |
| | *trans* | | 125 |

[a] For the method of calculation, see Ref. 9

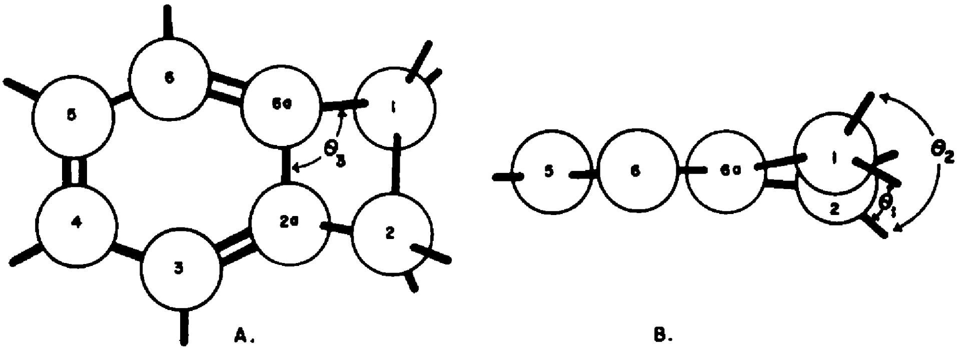

Fig. 1. Ball-and-stick models of benzocyclobutene (A, side view; B, top view), showing the skewed alicyclic ring.

values for the coupling constants of benzocyclobutene-1-carboxamide and benzocyclobutene itself (the latter by analysis of the $C^{13}$-satellite multiplets).

Karplus has described the theoretical dependence of the coupling constant for two hydrogens bonded to adjacent carbon atoms in ethanes on the dihedral angle between the C—H bonds.[9] Using Karplus' equation, we calculate the dihedral angles between adjacent C—H bonds on the four-membered ring of the benzocyclobutenes (Table 2). Since the original Karplus equation is a zero-order approximation, the angles in Table 2 have only a qualitative significance. Nevertheless, the results clearly indicate that the four-membered ring is a non-planar, i.e. skewed, in all of the benzocyclobutenes studies (Fig. 1). Some of the skew may be attributed to steric

[9] M. Karplus, *J. Chem. Phys.* 30, 11 (1959). See also H. Conroy, *Advances in Organic Chemistry*, Vol. 2, p. 265. Interscience, N.Y. (1960). Coupling is affected by the electronegativity of substituents, by bond hybridization and bond lengths. K. L. Williamson, *J. Amer. Chem. Soc.* **85**, 516 (1963); M. Karplus, *Ibid.* **85**, 2870 (1963).

interaction of the benzylic substituents, particularly in *cis*-1,2-disubstituted benzocyclobutenes, but it is interesting to note that the effect persists even in benzocyclobutene itself.[10] From this and the fact that the junction angle ($\theta_3$) of the four-membered ring must be at least as large as 90°, it follows that the single bond between the two methylene carbon atoms ($C_1$—$C_2$) is of lower order (longer) than the normal carbon-to-carbon single bond. Additional evidence is provided by the $C^{13}$, H coupling constant. The coupling constant $J_{C^{13}H(2)}$ for benzocyclobutene is 138 cs, corresponding to 27·7% *s*-character for the C—H bond.[11] The constant $J_{C^{13}H(3)}$ for *o*-xylene is 126 cs.

It is possible that the benzocyclobutene ring system does not exist in a rigid conformation but undergoes rapid "flipping" between two skew-conformers. If this is the case, the observed vicinal coupling constant of benzocyclobutene will be average values of the coupling constants of the two ground-state conformations. That this is *not* the case is indicated by the following considerations: (a) Molecular models of *cis* and *trans*-1,2-diiodobenzocyclobutene show that there is considerable steric strain in the *cis* isomer due to mutual crowding of the two halogen substituents and, hence, that a relatively high energy-barrier must be involved in the flipping process of the *cis* compound. (b) The chemical shifts observed for both the *cis*- and *trans*-diiodobenzocyclobutenes and, indeed, for monobromobenzocyclobutene and for *cis*- and *trans*-dibromobenzocyclobutene as well, are all of a high order of consistency. These considerations imply that flipping, if it occurs, is not appreciable, at least not in the case of the halogen-substituted benzocyclobutenes.

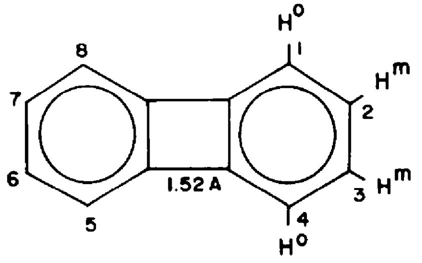

FIG. 2. Biphenylene.

The aromatic hydrogens in the benzocyclobutene dihalides give rise to $A_2B_2$ patterns. The lines due to the benzylic hydrogens and those in the upfield half of the $A_2B_2$ multiplet are both slightly broadened, probably as a result of coupling between the *ortho* aromatic hydrogens and the benzylic hydrogens. Hence, we assign the upfield portion of the $A_2B_2$ multiplet to the *ortho* aromatic hydrogens. Long-range interaction between the *ortho* aromatic hydrogens and the benzylic hydrogens was found in each of the benzocyclobutenes studied, but the coupling constant could not be obtained.

Finally, we analyzed the NMR spectrum of biphenylene (Table 1, and Figs 2 and 3). The chemical shift between the two kinds of hydrogens (*ortho* and *meta*) is

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[10] The strain inherent in the benzocyclobutene nucleus is reflected in its UV spectrum, in which the absorption maxima of the benzene chromophore are shifted to higher wavelengths and are more intense than the corresponding maxima in the spectrum of *o*-xylene. *cis*-1,2-Disubstituted benzocyclobutenes almost invariably have slightly larger extinction coefficients than the *trans* isomers.

[11] M. Muller and B. E. Pritchard, *J. Chem. Phys.* **31**, 768 (1959); *Ibid.* **31**, 1471 (1951); H. S. Gutowsky and C. Juan, *Disc. Faraday Soc.* **34**, 58 (1962).

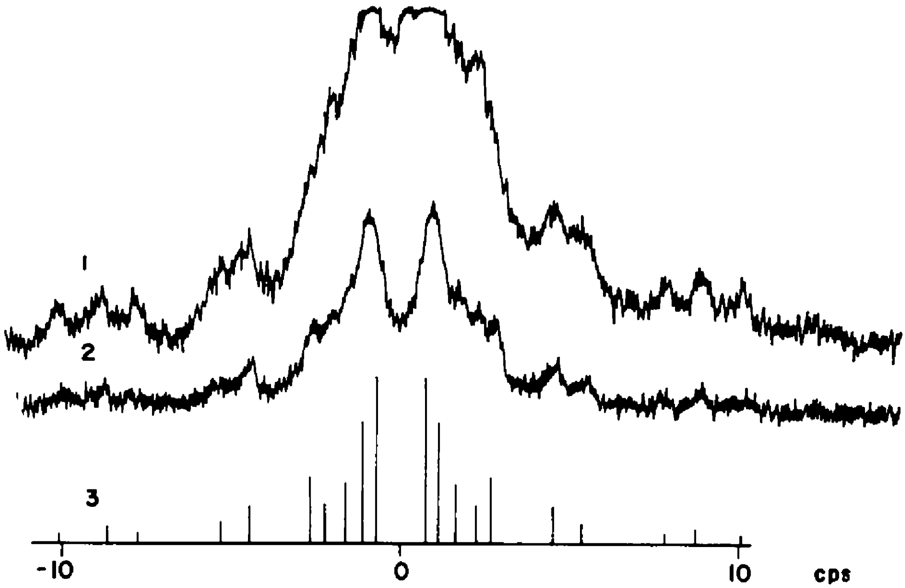

FIG. 3. NMR spectra (60 Mc) of biphenylene (5% in deuteriochloroform): (1) High gain, (2) Low gain, and (3) Calculated.

0·104 ppm. Taking into consideration the fact that the molecule is planar and that the two six-membered rings are known to be 1·52 Å apart[12,13] and assuming that the charge density around the molecule is uniform, we calculated the chemical shifts between the *ortho* and *meta* hydrogens due only to ring currents in two cases, i.e., two ring currents (0·13 ppm) and three ring currents (0·34 ppm). The chemical shift for the two ring-current case is in good agreement with the experimentally determined value (0·105 ppm), but it should be borne in mind that ample physical chemical evidence exists to show that the six-membered rings are not entirely independent electronic systems.[14]

[12] J. Waser and C.-S. Lu, *J. Amer. Chem. Soc.* **66**, 2035 (1944).

[13] T. C. W. Mak and J. Trotter, *J. Chem. Soc.* 1 (1962).

[14] D. Ginsburg, ed., *Non-Benzenoid Aromatic Compounds* pp. 73–76 and 80–83. Interscience, N.Y. (1959).