evaporated *in vacuo* at 20° and was reevaporated with water (10 ml). The residue was recrystallized from ethanol to give the *product* (364 mg; 79%): mp 198–200°; nmr (HA-100; DMF-$d_7$) $\tau$ 8.79 (s, 9 H, $(CH_3)_3C$, Boc group), 5.47 (s, 2 H, $C_6H_5CH_2O$–, benzylserine group), 4.80 (s, 2 H, $C_6H_5CH_2N$–, benzylhistidine group), 2.98 (s, 1 H, imidazole-$H_4$) 2.70 (m, 10 H, $C_6H_5CH_2$–, benzylserine and benzylhistidine groups) 2.24 (s, 1 H, imidazole-$H_2$). Thin layer chromatography, single spot, $R_f$ 0.14 (tlc-7). $[\alpha]^{25}D$ −4.67° (*c* 1.9, DMF).

*Anal.* Calcd for $C_{41}H_{56}O_{12}N_{12}$: C, 54.18; H, 6.21; N, 18.49. Found: C, 53.99; H, 5.97; N, 18.37.

**Transesterification of *tert*-Butoxycarbonyl-L-prolyl Resin.** (i) **With Thallium Alkoxide Catalysis.** *tert*-Butoxycarbonyl-L-prolyl resin (1.5 g; 0.675 mmol of proline) was rocked for 2 days at room temperature in DMF (8 ml). The washings were discarded and the resin was suspended in a DMF–DMAE mixture (9 ml; 2:1 v/v) containing thallous 2-dimethylaminoethoxide (0.068 mmol; 0.1 equiv), and the reaction mixture was rocked for 22 hr at room temperature. The solution was separated from the resin by filtration and passed through a column (10 × 2 cm) of Amberlite IRC-50 (column poured in DMF) in order to remove the thallium salt. The resin was washed with DMF (3 × 10 ml) and the washings were passed through the ion-exchange resin column as above.

All filtrates and washings were combined and evaporated *in vacuo* at 30° to yield the product (186 mg; 96%; oil): thin layer chromatography showed a single spot; $R_f$ values (tlc-1) 0.63 and (tlc-5) 0.40; nmr (A60, DMF-$d_7$) $\tau$ 9.00 (s, 9 H, $(CH_3)_3C$–, Boc group), 8.41 (m, 4 H, –$CH_2CH_2$–, proline), 8.16 (s, 6 H, $(CH_3)_2N$–, DMAE group), 7.85 (t, 2 H, –$CH_2CH_2N$, DMAE group), 7.00 (m, 2 H, –$CH_2N$–, proline), 6.17 (m, 3 H, –$OCH_2CH_2$– and –$CH$–, DMAE group and proline). Amino acid analyses of the prolyl resin indicated 99% removal of proline from the resin.

(ii) **With Sodium Alkoxide Catalysis.** The *tert*-butoxycarbonyl-L-prolyl resin (200 mg; 0.090 mmol of proline) was stirred for 2 days in DMF (3 ml), filtered, and washed with DMF (2 × 3 ml). The washings were discarded and the resin was suspended in DMF–DMAE (3 ml; 2:1 v/v) containing sodium 2-dimethylaminoethoxide (0.03 mmol; 0.33 equiv) and the reaction mixture was stirred for 21 hr at room temperature. The solution was separated from the resin by filtration and passed through a column (10 × 1 cm) of Amberlite IRC-50 (column poured in DMF) in order to remove the sodium salt. The resin was washed with DMF (3 × 3 ml) and the washings were passed through the ion-exchange resin as above. The column was then washed with DMF (10 ml). All filtrates and washings were combined and evaporated *in vacuo* at 30° to yield the product (21.4 mg; 84%; oil). Thin layer chromatography showed one spot: tlc-3, $R_f$ 0.63; tlc-8, $R_f$ 0.40. Amino acid analysis of the prolyl resin indicated 83% removal of proline from the resin. The nmr spectrum (A60) was identical with that of the protected proline ester obtained by transesterification with thallium alkoxide catalysis.

**Cbz-L-alanyl-L-phenylalanine Benzyl Ester.** Cbz-L-alanyl-L-phenylalanyl resin (2.60 g; 1 mmol of peptide) was suspended in dry benzyl alcohol (30 ml). A solution containing sodium benzoxide [0.1 mmol) in benzyl alcohol (0.29 ml) was added and the reaction mixture was stirred for 30 min at room temperature. The mixture was filtered and the resin was washed with ether (3 × 40 ml). The filtrate and washings were combined, washed with water (50 ml), dried ($MgSO_4$), and evaporated *in vacuo* (35°; 0.1 mm Hg) to give a solid residue (259 mg) which was recrystallized from chloroform–petroleum ether to yield benzyloxycarbonyl-L-alanyl-L-phenylalanine benzyl ester (240 mg; 52%), mp 119–120°. (*Anal.* Calcd for $C_{27}H_{28}N_2O_5$: C, 70.42; H, 6.13; N, 6.08. Found: C, 70.24; H, 6.12; N, 6.09.) The resin sample from the above transesterification reaction was retreated with benzyl alcohol (30 ml) plus sodium benzoxide (0.1 mmol). The reaction mixture was stirred for 4 hr at room temperature. The isolation procedure was repeated as described above to yield a further amount of the *product* (200 mg; 43%), mp 118–119°; *i.e.*, the total recovery of protected peptide ester was 95%; nmr (A 60, $CDCl_3$) $\tau$ 8.77 (d, 3 H, $CH_3CH$–, alanine), 6.98 (m, 2 H, $C_6H_5CH_2CH$–, phenylalanine), 5.76 (m, 1 H, $C_6H_5CH_2CH$–, phenylalanine), 4.99 and 4.96 (two s, 4 H, two $C_6H_5CH_2O$–, benzyl ester and Cbz group), 2.95 and 2.76 (m and s superimposed, 15 H, three $C_6H_5$–, benzyl ester, Cbz group, and phenylalanine).

**Extent of Racemization during Transesterification of Boc-L-Leu-L-Ala-*O*-polymer with DMAE and Hydrolysis of the DMAE Ester.** The protected dipeptide resin samples (100 mg) were rocked for 24 to 48 hr in a mixture of DMAE–DMF (1:1, 2 ml). The samples were then filtered, washed with DMF, and the filtrates evaporated *in vacuo* at 30°. The crude dipeptide ester samples were dissolved in DMF (0.5 ml), water was added (2 ml), and the mixture was stirred for 24 to 68 hr at room temperature. The reaction mixtures were then evaporated *in vacuo* and reevaporated with 1 *N* HCl in water. Quantitation of diastereoisomers was performed by the method of Manning and Moore[32] using a Beckman amino acid analyzer Model 120C (59 × 0.9 cm column packed with Beckman UR-30 resin; pH 4.30; flow rate 50 ml/hr; 57°). Peak positions of the diastereoisomers were determined using DL-Leu-DL-Ala (107 and 126 ml). The extent of racemization (per cent D–L isomer) was 0.3 ± 0.1%. The time of transesterification and hydrolysis had no observable effect on the extent of racemization.

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# Microwave Structural Study of Benzvalene (Tricyclo[3.1.0.0$^{2,6}$]hex-3-ene)

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*Contribution from the Department of Chemistry, University of Kansas, Lawrence, Kansas 66044.* *Received January 5, 1973*

**Abstract:** The microwave spectra of six isotopic species of benzvalene (tricyclo[3.1.0.0$^{2,6}$]hex-3-ene) have been observed and analyzed. These data and those reported previously have permitted the determination of a complete "substitution" molecular structure. The internuclear distances are found to be (in Å): $C_1$–$C_6$ = 1.452 ± 0.001, $C_1$–$C_2$ = 1.529 ± 0.003, $C_2$–$C_3$ = 1.503 ± 0.006, $C_3$–$C_4$ = 1.339 ± 0.001, $C_1$–H = 1.078 ± 0.001, $C_2$–H = 1.082 ± 0.002, $C_3$–H = 1.078 ± 0.001; and the dihedral angle of the four-membered ring is 106.0 ± 0.3°. Isotopic labeling studies have shown an interesting internal molecular rearrangement.

In a previous communication[1] we reported the microwave spectrum and dipole moment of the normal isotopic species of benzvalene (tricyclo[3.1.0.0$^{2,6}$]hex-3-ene). These results plus those reported here for six monosubstituted isotopic species of benzvalene are sufficient for a complete structural determination. This structural study continues a series of investigations of polycyclic hydrocarbons in our laboratory,

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(1) R. D. Suenram and M. D. Harmony, *J. Amer. Chem. Soc.*, 94, 5915 (1972).

including bicyclo[1.1.0]butane,[2,3] 1-chlorobicyclo[1.1.1]-pentane,[4] and bicyclo[2.1.0]pentane.[5] The general aim of these studies is to provide a quantitative understanding of the structural properties of strained polycyclic hydrocarbons and the interrelationship of the structural features and the electronic properties of the molecule, as evidenced by chemical reactivities and other physical measurements such nmr $^{13}$C–H coupling constants, electric dipole moments, etc.

An understanding of benzvalene is particularly pertinent since it is a member of the set comprising the benzene isomers, $C_6H_6$. In addition to benzene itself, structural studies have recently been performed for fulvene[6] and hexamethyl(Dewar benzene).[7] Lemal and Dunlap[8] recently discussed qualitatively the potential surface for this isomeric system, and Christoffersen[9] has performed *ab initio* molecular orbital computations of the relative stabilities.

Our earlier microwave investigation and previous nmr studies were consistent with the $C_{2v}$ structure[10] shown in Figure 1. The principal axes and the atomic numbering scheme in the figure will be useful in the following sections.

## Experimental Section

Benzvalene samples used in this study were synthesized by the method recently reported by Katz,[11] *et al.* This method involved the reaction of the cyclopentadiene anion with methylene chloride and is therefore well suited to the preparation of monosubstituted $^{13}$C and $^{2}$H species. To form a monosubstituted benzvalene molecule one simply starts with methylene chloride enriched in $^{13}$C or $^{2}$H to obtain the corresponding monosubstituted benzvalene isomer.

The $^{2}$H enriched species were obtained by starting with 99% $CD_2Cl_2$ obtained from Merck Sharp and Dohme. The $^{13}$C-enriched species were obtained by using $^{13}CH_2Cl_2$ enriched to approximately 25% in $^{13}$C. The $^{13}$C-enriched methylene chloride was synthesized from $^{13}$C-enriched barium carbonate by the following reaction sequence. Carbon-13-enriched $BaCO_3$ was treated with concentrated $H_2SO_4$ on a vacuum line to liberate $^{13}CO_2$.[12] The $^{13}CO_2$ was allowed to react with $LiAlH_4$ to form $^{13}CH_3OH$,[13] which was then chlorinated with $PCl_3$. Following this, the product $^{13}CH_3Cl$ was further chlorinated with $Cl_2$ in the gas phase by photolyzing with a sun lamp. In this step, chlorine was added in an amount sufficient to completely convert $^{13}CH_3Cl$ to $^{13}CH_2Cl_2$. After the disappearance of the chlorine the reaction was stopped and the mixture subjected to preparative gas chromatography to separate $^{13}CH_2Cl_2$ from other chlorinated methanes. A 7 ft × 0.25 in. stainless steel column packed with 10% Apiezon-M on 45–60 mesh Chromosorb G was used for this purpose. It was operated at room temperature with a helium flow rate of 100 ml/min. The remaining chloromethanes were subjected to further exhaustive chlorination until only $^{13}CCl_4$ was observed by gas chromatography. The reaction mixture was again purified by gas chromatography and the resulting $^{13}CCl_4$ was reacted with two equivalents of tri-*n*-butylstannic hydride to form more $^{13}CH_2Cl_2$.[14] This liquid-phase reaction required 2 hr at 50° with magnetic stirring. The volatile products were removed from the reaction mixture by vacuum distillation into a liquid nitrogen-cooled trap and the $^{13}CH_2Cl_2$ was separated again by preparative gas chromatography. This $^{13}CH_2Cl_2$ sample was combined with that obtained from the initial chlorination of $^{13}CH_3Cl$ and was used without further purification in the reaction with lithium cyclopentadienide to form benzvalene.[11]

At the termination of the benzvalene reaction sequence, all volatile products were removed from the reaction mixture by vacuum distillation into a trap cooled to 77°K. The distillate was allowed to warm to nearly room temperature, at which point the major portion of dimethyl ether had boiled off. The remaining diethyl ether solution (approximately 0.1–0.2 *M* in benzvalene) was stored at 77°K and was then chromatographed as needed on a column similar to the one described by Wilzbach,[10] *et al.*

Since pure benzvalene is explosive,[11] only small amounts were isolated at any one time. Typically 1 ml of the ether solution was chromatographed to provide sufficient benzvalene for the microwave spectral studies (*ca.* 10 $\mu$l). Benzvalene was trapped in a U-tube containing stopcocks on both ends. When an adequate quantity had been collected, the contents of the U-tube trap were rechromatographed using a gas-phase injection system. This second pass through the vpc served to remove a small residual amount of diethyl ether. At this point it is worth mentioning that even though benzvalene decays to benzene with a half-life of several days at room temperature, we have kept the ether solutions at liquid nitrogen temperature (with periodic warming to extract samples) for 6 months with no sign of decomposition of benzvalene to benzene.

Although the reaction sequence used to produce benzvalene leads primarily to $^{13}$C or $^{2}$H labeling at the 1 position, appreciable labeling is also observed at the 2 and 3 positions. The relative enrichment at the various positions is in the order $1 > 2 > 3$ for both the $^{13}$C and $^{2}$H cases. Our qualitative observations indicate that the enrichments are invariant once the reaction has been terminated. In order to test for a thermal rearrangement of the labels, we permitted the $^{13}$C-enriched benzvalene (in ether solution) to stand for 36 hr at −30°. (These conditions should be compared with the original 3-hr reaction time at −45°.)[11] Relative intensity measurements by microwave spectroscopy showed the enrichments at the 1, 2, and 3 positions to be in the ratios 6:1.5:1, indistinguishable from that observed before the test. Moreover, small samples of both the ether solution and the neat liquid were warmed to room temperatures at various times with no evidence of a change in the isotopic distributions. Similar results were obtained for the deuterated sample, the relative distributions in the 1, 2, and 3 positions being in the ratios 5.5:1.8:1. Finally, we have no evidence indicating that label rearrangement occurs during gas chromatographic purification.

The microwave studies were carried out using a 5-kHz Stark-modulated spectrometer of conventional design.[15] The spectra of the various isotopic species were investigated in the 8–37 GHz region using both recorder and oscilloscope displays. All experiments were carried out with the microwave cell at −78° with sample vapor pressures ranging from 15 to 70 $\mu$.

## Results

**Preliminary Considerations.** Although a microwave spectrum can often be analyzed with a minimum of knowledge about the molecular structure, it is generally useful to have rough predictions of the spectrum so its general character will be more easily understood. For the isotopic species of benzvalene described here, spectral predictions were obtained using the observed spectrum of the normal isotopic species and the approximate molecular structure described in the earlier communication.[1] In this way, the low-*J* transitions were predicted within 100 MHz in most cases, making identification and assignment relatively easy.

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[15] R. H. Hughes and E. B. Wilson, Jr., *Phys. Rev.*, **71**, 562 (1947).

**Table I.** Rotational Transition Frequencies[a] in Benzvalene

| Transition | 1-$^{13}$C |  | 2-$^{13}$C |  | 3-$^{13}$C |  | 1-$^{2}$H |  | 2-$^{2}$H |  | 3-$^{2}$H |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | Obsd | Obsd − calcd[b] | Obsd | Obsd − calcd | Obsd | Obsd − calcd | Obsd | Obsd − calcd | Obsd | Obsd − calcd | Obsd | Obsd − calcd |
| $0_{00}-1_{01}$ |  |  | 9128.34 | 0.04 |  |  | 8791.10 | 0.01 |  |  |  |  |
| $1_{11}-2_{12}$ | 16771.04 | 0.01 | 16837.64 | 0.03 | 16686.31 | 0.06 | 16378.29 | 0.01 | 16519.65 | 0.01 | 16180.80 | 0.05 |
| $1_{01}-2_{02}$ | 17648.07 | 0.01 | 17724.26 | −0.01 |  |  | 17204.03 | 0.02 |  |  | 17059.76 | 0.04 |
| $1_{10}-2_{11}$ | 19437.27 | 0.03 | 19675.74 | 0.00 | 19406.75 | 0.00 | 18786.14 | 0.05 |  |  | 18822.36 | 0.06 |
| $2_{12}-3_{13}$ |  |  | 24967.95 | −0.03 | 24772.47 | 0.08 | 24358.88 | 0.03 | 24432.66 | −0.01 | 24028.96 | 0.02 |
| $2_{02}-3_{03}$ | 25594.85 | 0.02 | 25614.64 | 0.01 | 25469.15 | −0.04 | 25055.09 | −0.03 | 24971.12 | 0.03 | 24735.81 | 0.04 |
| $2_{21}-3_{22}$ | 27156.21 | 0.02 |  |  | 27069.75 | 0.00 | 26373.27 | 0.00 | 27032.73 | −0.01 | 26252.29 | 0.00 |
| $2_{20}-3_{21}$ | 28712.56 | −0.01 |  |  |  |  | 27691.42 | −0.04 | 29094.40 | 0.00 | 27768.80 | −0.01 |
| $2_{11}-3_{12}$ | 28801.77 | −0.02 | 29089.26 | 0.00 | 28744.03 | 0.10 | 27891.80 | −0.01 | 28743.05 | 0.03 |  |  |
| $3_{13}-4_{14}$ | 32860.48 | 0.00 |  |  | 32671.53 | 0.00 |  |  |  |  | 31697.35 | −0.07 |
| $3_{03}-4_{04}$ | 33218.38 | −0.01 |  |  | 33027.60 | −0.02 |  |  | 32343.35 | −0.02 |  |  |
| $3_{22}-4_{23}$ | 35843.07 | −0.02 |  |  | 35716.11 | −0.05 |  |  |  |  | 34649.75 | −0.00 |
| $3_{31}-4_{32}$ |  |  |  |  | 36793.90 | −0.06 |  |  | 36952.09 | −0.02 | 35667.14 | 0.01 |
| $3_{30}-4_{31}$ |  |  |  |  |  |  |  |  |  |  | 36209.85 | −0.05 |
| $5_{14}-5_{33}$ |  |  |  |  |  |  | 18355.81 | −0.01 | 17049.68 | 0.02 | 18914.76 | 0.01 |
| $5_{05}-5_{24}$ |  |  |  |  |  |  | 18130.33 | 0.01 | 19517.05 | 0.04 | 19330.16 | 0.03 |
| $6_{15}-6_{34}$ |  |  |  |  |  |  | 19606.96 | 0.00 | 19776.49 | −0.06 | 20516.47 | −0.04 |

[a] All values in MHz. [b] Obtained using rotational constants of Table II.

**Table II.** Rotational Constants and Moments of Inertia[a] for Benzvalene Isotopes

|  | $^{12}$C[b] | 1-$^{13}$C | 2-$^{13}$C | 3-$^{13}$C |
|---|---|---|---|---|
| $A$ | 7389.233 ± 0.007[c] | 7334.510 ± 0.047 | 7267.656 ± 0.092 | 7344.398 ± 0.162 |
| $B$ | 5275.919 ± 0.004 | 5192.586 ± 0.004 | 5273.698 ± 0.007 | 5191.750 ± 0.011 |
| $C$ | 3889.779 ± 0.003 | 3859.480 ± 0.003 | 3854.647 ± 0.006 | 3831.499 ± 0.010 |
| $\kappa$ | −0.2077708 | −0.2327517 | −0.1684223 | −0.2255675 |
| $I_a$ | 68.3934 | 68.9037 | 69.5375 | 68.8109 |
| $I_b$ | 95.7890 | 97.3263 | 95.8293 | 97.3419 |
| $I_c$ | 129.9238 | 130.9438 | 131.1080 | 131.9001 |

|  | 1-$^{2}$H | 2-$^{2}$H | 3-$^{2}$H |
|---|---|---|---|
| $A$ | 7175.631 ± 0.004 | 6948.922 ± 0.007 | 7226.229 ± 0.007 |
| $C$ | 4997.498 ± 0.003 | 5256.549 ± 0.003 | 5035.768 ± 0.003 |
| $B$ | 3793.592 ± 0.003 | 3754.365 ± 0.002 | 3714.995 ± 0.003 |
| $\kappa$ | −0.2880613 | −0.0595558 | −0.2476869 |
| $I_a$ | 70.4293 | 72.7271 | 69.9362 |
| $I_b$ | 101.1256 | 96.1420 | 100.3571 |
| $I_c$ | 133.2181 | 134.6100 | 136.0365 |

[a] The rotational constants have units of megahertz. The moments of inertia are in atomic mass units square ångströms and are obtained by using the factor 505375 amu Å$^2$ MHz. [b] Taken from ref 1. [c] Standard deviation.

**Observed Spectrum and Assignment.** In the previous note[1] we reported the microwave spectrum of the normal isotopic species. We report here the spectra of three monosubstituted $^{13}$C species and three monosubstituted $^{2}$H species of benzvalene. The spectrum in each case was found to consist of *a* type R- and Q-branch transitions which were assigned easily using their Stark effects and predictions based on the normal isotopic species. The transitions in Table I were used to obtain rotational constants for each molecule. These transitions were fit statistically to the usual rigid rotor theory[16] by a standard computer program (NBS Spectral Analysis Program Version III).

All of the strong R-branch lines have a rather small dependence on the *A* rotational constant. In order to obtain a more precise experimental value for the *A* rotational constant the three Q-branch lines at the bottom of Table I were included in the statistical fit for the $^{12}$C molecule and all monodeuterated species. The corresponding transitions for the $^{13}$C species were too weak to be observed in the 25% enriched mixture of the three $^{13}$C benzvalene isotopic species. Thus the standard deviation in the *A* rotational constant is somewhat larger for the $^{13}$C species. The rotational constants obtained from the analysis of the data in Table I are presented in Table II along with the moments of inertia for each species.

**Structure.** Carbon atoms 1, 2, and 3 and hydrogen atoms 7, 8, and 9 (see Figure 1) have each been isotopically substituted so it is possible to obtain a complete $r_s$ structure for the molecule using the method of Costain[17] with the use of Kraitchman's equations.[18] In this method the coordinates of a given nucleus, with respect to the principal axis system of a reference (unsubstituted) molecule, are obtained by combining the moments of inertia of the unsubstituted molecule with those of the molecule having (only) the single nucleus of interest isotopically substituted. As an example consider the coordinates of carbon atom number 1. By combining the moments of inertia of the $^{12}$C molecule with those of the 1-$^{13}$C molecule the coordinates of carbon atom number 1 can be found. The method assumes that the nuclear coordinates are independent of the isotopic substitution. While this is

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(16) C. H. Townes and A. L. Schawlow, "Microwave Spectroscopy," McGraw-Hill, New York, N. Y., 1955.

(17) C. C. Costain, *J. Chem. Phys.*, **29**, 864 (1958).

(18) J. Kraitchman, *Amer. J. Phys.*, 21, 17 (1953).

not exactly correct, cumulative errors from the assumption are usually small (~0.003 Å) for heavy atoms. This method has the virtue that vibration–rotation effects are at least partially cancelled since only differences in moments of inertia of the two species are involved.

If the molecule is to have $C_{2v}$ symmetry, the two symmetry planes will be defined by $H_7$–$C_1$–$C_6$ and $C_2$–$C_3$–$C_4$. For an isotopic substitution in a symmetry plane the following relationship is valid for a rigid molecule

$$\Delta I_i + \Delta I_j - \Delta I_k = 0 \qquad (1)$$

where $i$ and $j$ define the plane of the substitution and $\Delta I_m$ is the difference in the moments of inertia of the $^{12}C$ molecule and the isotopically substituted molecule in question. In Table III the experimental values for the left side of eq 1 are listed for the various $^{13}C$ and $^2H$ substitutions performed in this work. As can be seen, all the values are sufficiently close to zero to confirm the $C_{2v}$ symmetry of the molecule.

**Table III.** Experimental Values for the Moment of Inertia Relationship (Eq 1)

| Substituted atom | $\Delta I_a + \Delta I_c - \Delta I_b$, amu Å$^2$ | $\Delta I_a + \Delta I_b - \Delta I_c$, amu Å$^2$ |
|---|---|---|
| 1-$^{13}C$ | 0.007 | |
| 2-$^{13}C$ | | 0.0003 |
| 3-$^{13}C$ | | 0.006 |
| 7-$^2H$ | 0.006 | |
| 8-$^2H$ | | 0.0005 |
| 9-$^2H$ | | 0.002 |

**Table IV.** Atomic Coordinates for Benzvalene[a]

| Atom | $a$ | $b$ | $c$ |
|---|---|---|---|
| 1 | 1.0122 ± 0.0001[b] | 0 | 0.7261 ± 0.0002 |
| 2 | 0.1971 ± 0.0011 | 1.0754 ± 0.0002 | 0 |
| 3 | −1.2436 ± 0.0003 | 0.6697 ± 0.0006 | 0 |
| 4 | −1.2436 ± 0.0003 | −0.6697 ± 0.0006 | 0 |
| 5 | 0.1971 ± 0.0011 | −1.0754 ± 0.0002 | 0 |
| 6 | 1.0122 ± 0.0001 | 0 | −0.7261 ± 0.0002 |
| 7 | 1.79141 ± 0.00003 | 0 | 1.47056 ± 0.00003 |
| 8 | 0.54670 ± 0.00007 | 2.10193 ± 0.00002 | 0 |
| 9 | −2.08324 ± 0.00002 | 1.34647 ± 0.00004 | 0 |
| 10 | −2.08324 ± 0.00002 | −1.34647 ± 0.00004 | 0 |
| 11 | 0.54670 ± 0.00007 | −2.10193 ± 0.00002 | 0 |
| 12 | 1.79141 ± 0.00003 | 0 | −1.47056 ± 0.00003 |

[a] See Figure 1 for atom labeling; all values in ångströms. [b] Experimental standard deviations.

The coordinates of atoms 1–3 and 7–9 (and 4–6 and 10–12, by symmetry) have been determined by the substitution method and are tabulated in Table IV. The coordinate uncertainties in Table IV are the standard deviations, obtained by propagating the experimental errors in the rotational constants through the Kraitchman equations. They do not contain uncertainties due to nonrigid rotor behavior.

The Kraitchman equations yield only the absolute values of the coordinates and the rather small value of the $a$ coordinate of $C_2$ ($a_2$) may be subject to question as to sign choice. Also, the magnitude of the coordinate may be rather uncertain due to vibration–rotation effects. However, since we have substituted all the unique positions in the molecule, the first moment equation (eq 2) can be used to unambiguously determine the sign of this coordinate (after making obvious sign choices for the other atoms).

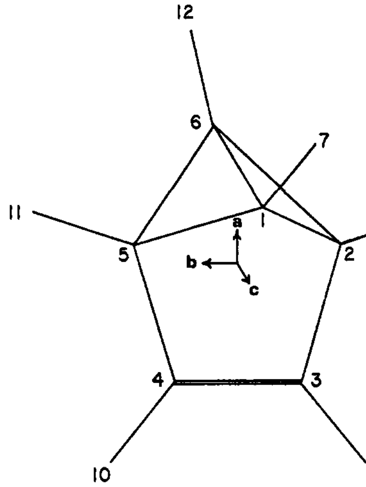

Figure 1. The benzvalene structure with principal axis and atom identifications. Atoms 1–6 are carbon, atoms 7–12 are hydrogen.

$$\sum_i m_i a_i = 0 \qquad (2)$$

When this is done the sign is found to be positive. If rigid rotor theory were precisely obeyed, the values for $a_2$ obtained from Kraitchman's equations and the first moment relation, eq 2, should be identical. In fact the value obtained from eq 2 is larger than the value from Kraitchman's equations by +0.0129 Å. This number serves in some measure as an estimate of the maximum uncertainty in this coordinate.

In Table V three sets of molecular parameters have been tabulated. Those headed I represent the complete $r_s$ structure computed from the Kraitchman coordinates of Table IV. In II we have listed the values of the parameters based on the first moment value for $a_2$, all other coordinate values being those of Table IV. Note that in this column we have listed only those parameters involving the $a_2$ value. Set III represents the average of the parameters in I and II and, as described below, probably represents the best average $r_s$ structure. The uncertainties ($\pm\sigma$) listed in column I of Table V represent the standard deviations of the parameters and thus are a measure of the experimental precision. To obtain an estimate of

**Table V.** Molecular Parameters of Benzvalene

| Parameter[a] | I[b] | II[c] | III[d] |
|---|---|---|---|
| $C_1$–$C_6$ | 1.4523 ± 0.0003[e] (0.001)[f] | *g* | 1.452 ± 0.001 |
| $C_1$–$C_2$ | 1.5324 ± 0.0007 (−0.006) | 1.5256 | 1.529 ± 0.003[h] |
| $C_2$–$C_3$ | 1.4967 ± 0.0014 (0.001) | 1.5091 | 1.503 ± 0.006 |
| $C_3$–$C_4$ | 1.3394 ± 0.0012 (0.001) | *g* | 1.339 ± 0.001 |
| $C_1$–$H_7$ | 1.0777 ± 0.0002 (−0.0004) | *g* | 1.078 ± 0.001 |
| $C_2$–$H_8$ | 1.0844 ± 0.0004 (−0.002) | 1.0803 | 1.082 ± 0.001 |
| $C_3$–$H_9$ | 1.0785 ± 0.0005 (−0.001) | *g* | 1.078 ± 0.001 |
| $\alpha$[i] | 105.68 ± 0.06 (0.62) | 106.24 | 106.0 ± 0.3 |
| $\angle C_6$–$C_1$–$H_7$ | 133.69 ± 0.01 (−0.01) | *g* | 133.7 ± 0.1 |
| $\angle C_2$–$C_1$–$H_7$ | 135.39 ± 0.01 (−0.11) | 135.24 | 135.3 ± 0.1 |
| $\angle C_1$–$C_2$–$H_8$ | 119.53 ± 0.06 (0.38) | 120.13 | 119.8 ± 0.3 |
| $\angle C_3$–$C_2$–$H_8$[j] | 124.53 ± 0.06 (−0.34) | 123.96 | 124.2 ± 0.3 |
| $\angle C_2$–$C_3$–$H_9$ | 125.40 ± 0.05 (0.05) | 125.51 | 125.4 ± 0.1 |
| $\angle C_4$–$C_3$–$H_9$[j] | 128.87 ± 0.04 (0.01) | *g* | 128.9 ± 0.1 |
| $\angle C_2$–$C_3$–$C_4$[j] | 105.62 ± 0.05 (−0.07) | 105.02 | 105.7 ± 0.1 |

[a] See Figure 1 for labeling. Bond lengths are in ångströms and angles are in degrees. [b] From Kraitchman coordinates of Table IV. [c] With $a_2$ coordinate from first moment equation. [d] Average of I and II. [e] Standard deviation; obtained by propagating the errors from the rotational constants. [f] Estimated changes in parameters produced by vibration–rotation effects. See text for discussion. [g] Same as in column I. [h] Difference between parameters of I and II divided by 2. [i] Dihedral angle of four-membered ring. [j] Redundant parameters.

the magnitude of the uncertainties due to vibration–rotation effects, we have computed the changes in the parameters that would arise from the Kraitchman equations if the C–C and C–H bond lengths decreased by $5 \times 10^{-5}$ and $1 \times 10^{-4}$ Å, respectively, upon substitution.[19] These values are listed in parentheses following the experimental uncertainties in column I and serve as estimates of the uncertainty of the $r_s$ structure due to neglected vibration–rotation effects.

It should be noted that the precision of the experimental data fitting for the $r_s$ structure (I) is very high, the largest bond distance uncertainty being ±0.0014 Å. The estimated vibration–rotation effects listed in column I are in general several times larger than the experimental uncertainties and probably represent a more valid measure of the bond length uncertainty from a theoretical point of view. The small $a_2$ coordinate makes structure II attractive, since the first moment equation should suffer less from uncancelled vibration–rotation effects. However, it is certainly not true that *only* $a_2$ suffers from vibration–rotation effects, so that the structure II must represent an extreme view to some extent. Consequently, we believe that the average $r_s$ structure III is perhaps the most satisfactory. It is particularly pleasing that structure III is essentially within the range defined by the vibration–rotation errors given for structure I. The uncertainties listed for structure III are of a hybrid type. For those parameters not involving $a_2$, the uncertainties are the experimental ones of column I, except we take 0.001 Å and 0.1° as the *lowest* uncertainties. For the parameters involving $a_2$, we take the uncertainty to be one-half the difference between the column I and column II values. In the following section our structural discussion will be based on the column III values.

## Discussion

The tricyclic species benzvalene presents a number of interesting structural features. First, Table V indicates that the bridgehead CH bonds are short compared with aliphatic species (CH = 1.096 and 1.091 Å in propane)[20] but are somewhat longer than the bridgehead CH bond (1.071 Å) in bicyclobutane.[3] In general this shortening of CH bonds correlates with increased acidity and in a simple chemical bonding scheme implies an increased s character in the carbon-bonding orbital. Note that the $C_1$–$H_7$ bond is the same length as the vinyl bond, $C_3$–$H_9$, which is itself longer than the vinyl CH in ethylene or cyclopropene (1.070 Å).[21]

The bicyclobutane skeleton of benzvalene has undergone rather appreciable changes in comparison with free bicyclobutane. Thus, the bonds in bicyclobutane corresponding to $C_1$–$C_6$ and $C_1$–$C_2$ have the values 1.497 and 1.498 Å, respectively.[3] The bridgehead $C_1$–$C_6$ bond has shortened very considerably, a fact which correlates with increased p character in this bond.[22] At the same time $C_1$–$C_2$ has lengthened appreciably. The *average* C–C bond length in each cyclopropyl ring is, however, 1.503 Å, which is very similar to the average value (1.498 Å) in bicyclobutane. As pointed out previously,[5] the average CC distances in the cyclopropyl moiety in polycyclic species are relatively constant, clustering about the value for cyclopropane[23] itself, 1.510 Å. Thus we see a very clear case of a *push-pull* effect in cyclic systems; namely, if one or more bonds shorten, one or more other bonds must lengthen in such a way that the *average* length remains essentially constant.[5] *Ab initio* and semiempirical molecular orbital computations indicate a very close quantitative correlation of this phenomenon with changes in s and p character in the C–C bonds.[24]

The perturbation of the bicyclobutane ring is also apparent from the dihedral angle, $\alpha$, which is 16° smaller than the 121.7° value in free bicyclobutane.[3] Although it seems reasonable that the bridging of an ethylene group across the bicyclobutane ring should

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(19) See V. W. Laurie and D. R. Herschbach, *J. Chem. Phys.*, 37, 1687 (1962). We have chosen the slightly larger value for the C–H bond shortening since the $5 \times 10^{-5}$ value would probably underestimate the vibration–rotation uncertainties of the C–H bond.

(20) D. R. Lide, Jr., *J. Chem. Phys.*, 33, 1514 (1960).

(21) P. H. Kasai, R. J, Myers, D. F. Eggers, and K. B. Wiberg, *J. Chem. Phys.*, 30, 512 (1959).

(22) See, for example, K. B. Wiberg, *Tetrahedron*, 24, 1083 (1968).

(23) O. Bastiansen, F. N. Fritsch, and K. Hedberg, *Acta Crystallogr.*, 17, 538 (1964).

(24) To be published.

produce some angular distortion, it is not immediately clear why both $\alpha$ and $\angle C_2C_3C_4$ (105.7°) decrease markedly from normal values. A decrease in these particular bond angles should lead to an increase in total energy because of the angle distortions involved. On the other hand, increasing these bond angles would require a decrease in $\angle C_1C_2C_3$ which would be energetically unfavorable also. Thus the equilibrium structure of strained polycyclic species such as benzvalene represents a delicate balance between numerous opposing forces.

The five-membered ring system in benzvalene also presents interesting contrasts with other similar systems. Table VI presents a comparison of corresponding bonds and angles in several molecules using the benzvalene numbering system. The C–C single bonds are appreciably shorter in benzvalene than in cyclopentene[25] or the bicyclic species.[26,27] The C═C bond is relatively invariant, but the $\angle C_2C_3C_4$ is, as mentioned above, distorted significantly. Cyclopentene is a rather flat molecule with a dihedral angle of 151.2°. In the two bicyclic species of Table VI this angle is determined primarily by the constraints of the cyclobutane ring and is consequently much smaller. In benzvalene, the dihedral angle of the cyclopentene moiety is determined by the constraints of the more highly puckered bicyclobutane ring system, and consequently this angle returns more closely to the cyclopentene value.

**Table VI.** Structural Parameters[a] in Five-Membered Rings

| | Benzvalene[b] | Cyclopentene[c] | Bicyclo-[2.1.1]-hexane[d] | Bicyclo-[2.1.1]-hexene[e] |
|---|---|---|---|---|
| $C_1$–$C_2$ | 1.529 | 1.546 | 1.544 | 1.549 |
| $C_2$–$C_3$ | 1.503 | 1.519 | 1.565 | 1.537 |
| $C_3$–$C_4$ | 1.339 | 1.342 | | 1.332 |
| $\angle C_2C_3C_4$ | 105.7 | 111.0 | 102.1 | 108.4 |
| Dihedral angle | 138.3 | 151.2 | 117.5 | 118.2 |

[a] Distances in ångströms and angles in degrees. [b] Present study. [c] Reference 25 in text. [d] Reference 27 in text. [e] Reference 26 in text.

One final structural feature concerning the bridgehead proton ($H_7$ and $H_8$) orientations bears discussion. We have observed earlier[3] that the bicyclobutane bridgehead protons are oriented such that the three HCC bridgehead angles are nearly equal (128.3 and 130.3°). It was suggested that such a result was physically reasonable, since the bridgehead proton should experience roughly equivalent nonbonded interactions with the adjacent carbon atoms. Thus the proton would find its equilibrium position at the equipotential point, which would be given approximately by the equal angle orientation. In benzvalene we see that this idea is preserved, the corresponding angles for $H_7$ from Table V being 133.7 and 135.3°. The same principles might be expected to apply also to the orientation of $H_8$. As seen in the table, $\angle C_1C_2H_8$ and $\angle C_3C_2H_8$ differ by 4.4°, which is not too great a discrepancy. Indeed, since $C_2$ is a vinyl carbon center, its interaction with $H_8$ should differ from the $C_1$ and $C_6$ interactions so the nonequality of the angles is reasonable.

The $^2H$ and $^{13}C$ enrichments were performed primarily for structural analysis purposes. However, some valuable mechanistic data arises from these experiments also. The available evidence indicates that the rearrangement of the labels occurs in the primary reaction mixture and ceases when the reaction is terminated by low-temperature vacuum distillation of the benzvalene product and other volatile components (primarily dimethyl and diethyl ether and methylene chloride).[11] Our speculation is that the observed isotope distribution ratios are the result of a process of the general form $R \rightarrow P_1 \rightleftarrows P_2 \rightleftarrows P_3$, where R represents reactants and $P_1$, $P_2$, and $P_3$ the 1-, 2-, and 3-$^{13}C$ or -$^2H$ products. If this were the case, a distribution ratio of 1:1:1 would be expected after equilibrium had been reached, since all positions have equal statistical probability. The correctness of this suggestion, and the detailed nature of the mechanism (perhaps involving metal ion catalysis),[28] must await further studies.

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(26) D. L. Zebelman, S. H. Bauer, and J. F. Chiang, *Tetrahedron*, **28**, 2727 (1972).

(27) J. F. Chiang, *J. Amer. Chem. Soc.*, **93**, 5044 (1971).

(28) For recent studies of molecular rearrangements promoted by transition-metal ions, see P. G. Gassman and F. J. Williams, *J. Amer. Chem. Soc.*, **94**, 7733 (1972); L. A. Paquette, S. E. Wilson, R. P. Henzel, and G. R. Allen, *ibid.*, **94**, 7761 (1972). In our case, the only metal ion present is $Li^+$, but there may be analogies.