d. ***endo*-Bicyclo[2.1.0]pentane-5-methyl Tosylate.** The samples of *endo*-bicyclo[2.1.0]pentane-5-methyl tosylate used in the kinetic runs were put in excess potassium acetate after titration. The solutions were worked up as described above. The nonvolatile material solidified on cooling and was shown to be 3-cyclohexen-1-yl tosylate by comparison with an authentic sample. The volatile materials could not be separated by vpc and therefore were reduced to alcohols with lithium aluminum hydride. The alcohols could be separated on a 12 ft × 1/8 in. tris(β-cyanoethoxy)propane column at 120°, and were found to have a 45:25:30 ratio with retention times of 10.5, 11.5, and 12.3 min, respectively. The first and third were *exo*- and *endo*-2-northujanols and the second was 3-cyclohexen-1-ol.

e. ***trans*-2-Vinylcyclopentyl Tosylate.** The reaction of 2.7 g (0.01 mole) of *trans*-2-vinylcyclopentyl tosylate in 300 ml of dry acetic acid containing excess potassium acetate was allowed to proceed for 16 hr at 70°. The reaction mixture was worked up as indicated above, and in this case no internal return product was found. The product could be separated by vpc using a tris(β-cyanoethoxy)propane column at 160° giving four components in the ratio 29:25:31:15 with retention times of 4.25, 4.5, 6.25, and 7.75 min, respectively. The first two components were *trans*- and *cis*-2-vinylcyclopentyl acetates; the third component was *exo*-bicyclo[3.1.0]hexane-6-methyl acetate and the fourth component was a mixture of *exo*- and *endo*-2-norcaranyl acetates (1:4 mixture, infrared spectrum).

f. Ethanolysis. The ethanolysis experiments were carried out using 50% ethanol which was 0.5 *M* in base. After a time corresponding to ten half-lives, the reaction mixtures were worked up in essentially the same fashion as the acetolysis experiments. The alcohols formed were identified by vpc separation and comparison of spectra with those of authentic samples, giving the data cited in the text.

Kinetic Experiments. Acetolysis. Acetic acid (reagent grade) was dried by heating with a small excess of acetic anhydride, and the amount of the latter was determined by the method of Bruckenstein.[35] Typically, the concentration was about 0.05 *M*. Standard potassium acetate solution was prepared by dissolving weighed quantities of reagent grade anhydrous potassium carbonate in measured amounts of acetic acid. *p*-Toluenesulfonic acid solutions were prepared by dissolving approximately weighed quantities of reagent *p*-toluenesulfonic acid in acetic acid. The solutions were standardized by titration with the potassium acetate solution.

The reactive tosylates were studied as follows. The tosylate was weighed into a 5-ml volumetric flask, and carbon tetrachloride was added to the mark. The solution was kept at 0°. A number of test tubes were placed in a constant-temperature bath. Each was filled with measured amounts (0.1, 0.2, 0.3 ml etc.) of potassium acetate solution. To this was added five drops of bromphenol blue indicator and sufficient dry acetic acid to bring the volume to 10.0 ml. With a 250-μl Hamilton syringe, a 200-μl aliquot of the carbon tetrachloride solution was added to one of the test tubes. Immediately after injection, a timer was started. The solution was stirred vigorously. The timer was stopped and the time recorded when the yellow color of the indicator had disappeared. The procedure was repeated with each of the tubes.

The less reactive tosylates were studied by sealing 4-ml aliquots containing excess potassium acetate into ampoules. The ampoules were placed in a constant-temperature bath, and at selected intervals one was removed and quickly cooled. A 3-ml aliquot was removed and was titrated with *p*-toluenesulfonic acid solution to the bromphenol blue end point.

In each case, the rate constant was determined from a plot of ln $(V_\infty - V)$ against time. Two determinations were made for each compound and each temperature, and the rate constants generally agreed to better than ±5%.

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[35] S. Bruckenstein, Ph.D. Thesis, University of Minnesota, 1954, pp 9–11.

Concerning the Mechanism of Single-Bond Shortening. Evidence from the Crystal Structures of 1-Biapocamphane, 1-Binorbornane, and 1-Biadamantane[1]

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Abstract: The $J_{^{13}\mathrm{CH}}$ at the bridgehead carbon in norbornane is 139 Hz, indicating 28% s character. Using this number, the Dewar plot of bond length against s character (length = 1.692 − 0.0062% s) predicts a central bond length in 1-binorbornane of 1.517 A. We find this bond length to be 1.515 ± 0.005 A. We therefore agree with Dewar that the concepts of conjugation or hyperconjugation are not necessary to explain single-bond lengths in compounds such as butadiene, styrene, or propylene. A correction for two H···H repulsions in 1-binorbornane reduces the central bond length to about 1.503 A and strengthens the case against conjugation in nonaromatic hydrocarbons.

In recent years there has been considerable controversy over the effect of attached groups on carbon–carbon single-bond lengths.[2] The controversy concerns the relative importance of resonance, hybridization, and nonbonded repulsions in causing the variation observed among C–C single-bond lengths in unsaturated molecules like butadiene, biphenyl, and propylene. Stated in its simplest form, the observed fact is that lengths of C–C single bonds increase as the number (*N*) of atoms attached to the bonded carbons increases,[3,4] as shown in Table I. Similarly, heats of formation or heats of hydrogenation indicate that energies of the single bonds in this series undergo a parallel decrease.[5–7] Three different explanations have been offered.

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[1] This work was supported by the Army Research Office (Durham), Grant No. DA-ARO-D-31-124-G-602.

[2] (a) D. R. Lide, Jr., *Tetrahedron*, 17, 125 (1962); (b) R. S. Mulliken, *ibid.*, 17, 247 (1962); (c) O. Bastiensen, and M. Traeteberg, *ibid.*, **17**, 147 (1962); (d) L. S. Bartell, *ibid.*, **17**, 177 (1962); (e) I. Fischer-Hjalmars, *ibid.*, **17**, 235 (1962); see also the discussion section, pp 247–266.

[3] C. C. Costain and B. P. Stoicheff, *J. Chem. Phys.*, **30**, 777 (1959).

[4] B. P. Stoicheff, *Tetrahedron*, **17**, 135 (1962).

[5] M. J. S. Dewar and H. N. Schmeising, *ibid.*, 11, 96 (1960).

[6] M. J. S. Dewar, *ibid.*, **19**, 89 (1963).

[7] R. S. Mulliken and R. G. Parr, *J. Chem. Phys.*, **19**, 1271 (1951).

Table I[a]

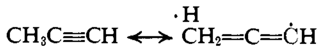
Compd	N	C–C bond length, A
$HC\equiv CC\equiv N$	2	1.378
$CH_2=CHC\equiv N$	3	1.426
$CH_3C\equiv CH$	4	1.459
$CH_2=CHCH=CH_2$	4	1.476
$CH_3CH=CH_2$	5	1.501
$CH_3CH_2CH_2CH_3$	6	1.533

[a] Taken from ref 4.

In the first proposal, by Pauling,[8] Wheland,[9] and Mulliken,[10] resonance across the central bond in, for example, butadiene

$$CH_2=CHCH=CH_2 \longleftrightarrow \cdot CH_2CH=CHCH_2\cdot$$

or hyperconjugation in, for example, methylacetylene



$$CH_3C\equiv CH \longleftrightarrow \overset{\cdot H}{CH_2=C=\dot{C}H}$$

introduces π-bond order across the single bond, decreasing its length and increasing its strength by resonance stabilization.

The second proposal, due to Dewar,[11,12] assumes that bond lengths and bond strengths of C–C single bonds depend upon the per cent s character in the hybrid atomic orbitals composing the bond. Dewar and Schmeising have plotted the bond length data tabulated above against mean per cent s character in the bond and obtained a good straight line.[12] Following Dewar, we find that the expression

$$\text{length} = 1.692 - 0.0062\,(\text{mean }\%\text{ s character}) \quad (1)$$

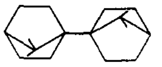
fits the bond lengths in Table I with a mean deviation of ±0.003 A. Dewar concludes from this, and from a similar correlation for stabilization energies,[5] that conjugation or hyperconjugation does not contribute to the shortening of the C–C single bonds in question.

The third proposal,[13] recently discussed by Bartell,[14] is that van der Waal's forces between neighboring atoms *lengthen* a short standard C–C single bond (*e.g.*, that in diacetylene), rather than conjugation or hybridization shortening a long standard bond. Thus, each hydrogen atom in ethane repels the opposite carbon and hydrogen atoms to lengthen the bond from 1.382 (as in diacetylene) to 1.535 A. Using reasonable repulsion potentials for H–H, H–C, and C–C, Bartell[14] was able to calculate the observed bond lengths to about the same accuracy as shown by eq 1.

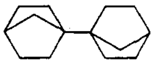
Considerable disagreement still surrounds the relative merits of these three postulates.[2] The general, but by no means unanimous, opinion seems to be that conjugation and hybridization contribute about equally to determining single-bond lengths and that repulsions are probably involved as well.[15] The reader is referred to ref 12 for a thorough discussion of the various points of view.

The crystal structure studies reported in this communication were carried out for the specific purpose of separating the effects of conjugation on the one hand from the effects of orbital hybridization or nonbonded repulsions on the other. The basic idea was to measure the central bond length in a series of saturated bridgehead dimers, each with different s character in the orbitals forming the central bond. The variation in s character would be achieved by varying the internal angles at the bridgehead in the monomer unit. As a check, the per cent s character in the orbital forming the bridgehead C–H bond in the monomer could be determined empirically from ^{13}C–H nmr coupling measurements,[16] and it is reasonable to assume that hybridization at the central bond in the corresponding dimer will not be very different. In this way, the lengths of C–C single bonds, composed of orbitals with varying s character, could be compared with predictions based upon eq 1. The interpretation would be relatively unambiguous, since there are no multiple bonds in these molecules and since the centrally bonded carbons in all of them are, in turn, bonded to three other carbon atoms. Thus, if the central bond in the bridgehead dimers is indeed found to become shorter with increasing s character, then either the Dewar hybridization mechanism or the nonbonded repulsion mechanism must be invoked.

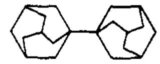
Such, at least, was the motivating logic behind the present study. As it has turned out, however, none of the three bridgehead dimers whose crystal structures are reported here is completely suitable for our purpose. The first compound, 1-biapocamphane (1,1′-bis(7,7-dimethylbicyclo[2.2.1]heptane)) (I), was chosen simply because crystals were already available at the outset of the investigation. Unfortunately the geminal dimethyl groups at C(7) cause steric complications which make it necessary to correct for nonbonded H–H repulsions before the central bond lengths can be correctly interpreted. The second compound, 1-binorbornane (1,1′-bis(bicyclo[2.2.1]heptane)) (II), would have been quite suitable sterically, but a completely satisfactory crystal structure analysis is hampered by disorder in the crystal. Nevertheless, the central bond length was determined with adequate precision for our purposes. The third compound, 1-biadamantane (1,1′-bis(tricyclo[3.3.1.1^{3,7}]decane)) (III), permits "calibration" of H–H repulsion effects, but provides only the end-point at 25% s character on the Dewar–Schmeising plot. Despite these obstacles, the three crystal structures reported here do appear to yield some conclusions relevant to the original problem.



I



II



III

Experimental Section

Preparation of Compounds and Crystal Data. A sample of 1-biapocamphane, prepared by Kolbe electrolysis of apocamphane-1-

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[8] (a) L. Pauling, L. O. Brockway, and J. Y. Beach, *J. Am. Chem. Soc.*, **57**, 2705 (1935); (b) L. Pauling, H. D. Springall, and K. J. Palmer, *ibid.*, **61**, 927 (1939).

[9] G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, pp 174–185.

[10] R. S. Mulliken, C. A. Rieke, and W. G. Brown, *J. Am. Chem. Soc.*, **63**, 41 (1941).

[11] M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **5**, 166 (1959).

[12] M. J. S. Dewar, "Hyperconjugation," The Ronald Press Co., New York, N. Y., 1962, p 53.

[13] J. B. Conn, G. B. Kistiakowsky, and E. A. Smith, *J. Am. Chem. Soc.*, **61**, 1868 (1939).

[14] (a) L. S. Bartell, *J. Chem. Phys.*, **32**, 827 (1960); (b) *Tetrahedron*, **17**, 177 (1962).

[15] E. B. Wilson, *ibid.*, **17**, 191 (1962).

[16] (a) N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 768, 1471 (1959); (b) J. N. Shoolery, *ibid.*, **31**, 1427 (1959); (c) N. Muller, *ibid.*, **36**, 359 (1962); (d) C. Juan and H. S. Gutowsky, *ibid.*, **37**, 2198 (1962).

carboxylic acid,[17] was given us by Professor H. J. Dauben, Jr. Large well-formed platelike crystals were obtained from CCl_4–MeOH solution by evaporation. The unit cell was found to be triclinic with lattice parameters:[18] $a = 6.890 \pm 0.001$ A; $b = 9.511 \pm 0.001$ A; $c = 6.579 \pm 0.001$ A; $\alpha = 112.13 \pm 0.02°$; $\beta = 65.84 \pm 0.01°$; $\gamma = 108.90 \pm 0.02°$. The crystal density measured by flotation in CsCl solution was 1.145 g cm^{-3}, from which a molecular weight of 246.3 may be calculated for one unit cell. The molecular weight of 1-biapocamphane ($C_{18}H_{30}$) is 246.4. From these data the space group was clearly either P1 or P$\bar{1}$, the correct choice depending upon whether the dimer's presumed center of symmetry is incorporated into the space group symmetry.

1-Binorbornane was prepared by electrolysis of norbornane-1-carboxylic acid. A solution of 10.5 g of norbornane-1-carboxylic acid,[19] 0.4 g of sodium methoxide, and 50 ml of anhydrous methanol was electrolyzed in a 100-ml beaker, using two cathodes and one anode, all constructed of platinum. The temperature was kept between 10 and 20° while maintaining a current of 1.0–1.5 amp. After 5.5 hr the solution became basic, indicating completion of the reaction. The methanol was distilled off and the yellow-brown residue was dissolved in 100 ml of pentane. Three successive washings with concentrated sulfuric acid removed all side products except hydrocarbons. The pentane solution was washed with water, dried over magnesium sulfate, and evaporated to dryness. Sublimation of the crude product at 80–85° (12 mm) yielded 1.25 g (9%) of 1-binorbornane, mp 111–112.5°. The nmr spectrum was consistent with the assigned structure.

Large prismatic crystals were obtained by diffusing water vapor into a concentrated solution of 1-binorbornane in acetonitrile. They were found to sublime slowly at room temperature. Precession films were consistent with any one of the three rhombohedral space groups R32, R3m, or R$\bar{3}$m, with the following lattice parameters:[18] $a = 6.695 \pm 0.001$ A; $\alpha = 99.11 \pm 0.01°$. Assuming a crystal density in the normal range for hydrocarbons, the unit-cell volume of 287.88 A^3 can accommodate only one molecule. Since a threefold axis is present in the unit cell of each of the possible space groups but not in the molecule, the crystal structure must be at least threefold disordered.

1-Biadamantane was prepared by the procedure of Reinhardt[20] and crystallized from carbon disulfide as flat prisms. The unit cell was found to be triclinic, with the following lattice parameters:[18] $a = 6.5308 \pm 0.0003$ A; $b = 6.5772 \pm 0.0007$ A; $c = 10.4571 \pm 0.0006$ A; $\alpha = 87.502 \pm 0.004°$; $\beta = 104.576 \pm 0.004°$; $\gamma = 119.861 \pm 0.007°$. Strangely, even though this molecule *does* possess a threefold axis, it is not utilized in the crystal symmetry, in a sense reversing the situation found for 1-binorbornane. As was also the case for 1-biapocamphane, the possible space groups were P1 and P$\bar{1}$, depending upon whether or not the presumed center of symmetry of the dimer is part of the crystal's space group.

X-Ray Crystallography. 1-Biapocamphane. Intensities were measured for 1-biapocamphane with a GE XRD-5 diffractometer, employing a θ–2θ scanning technique. Background corrections were made on the basis of stationary counts taken at both the start and finish of the scan.[21] Cu Kα radiation was used, a wavelength of 1.5418 A being assumed for the weighted mean of Kα_1 and Kα_2. A total of 2242 observations were made of the 1554 unique reflections within the range of the diffractometer ($2\theta < 161°$).

Intensities were corrected for Lorentz and polarization effects, but not for absorption. When a reflection was measured only once, without replication, the standard deviation of its intensity, $\sigma(I)$, was estimated from counting statistics.[22] When a reflection was measured more than once, or when a set of symmetry-related reflections were measured, the values used for I and $\sigma(I)$ were the unweighted arithmetic means of the individual results. 97% of the reflections had $I > \sigma(I)$.

The carbon atoms were located by a combination of vector coincidence and Fourier methods. Initially, a noncentrosymmetric structure in P1 was assumed, but it soon became obvious that a center was in fact present and that the space group was actually P$\bar{1}$.

Positional and thermal parameter refinement was carried out on a CDC 3600 computer using our own full-matrix, least-squares program. The quantity minimized was $\Sigma w(I - k^2F_c^{\,2})^2$, with relative weights, w, equal to $1/\sigma^2(I)$. Atomic scattering factors for carbon were obtained from "International Tables for X-Ray Crystallography"[23] and for hydrogen from Stewart, *et al.*[24] The summations were taken over all reflections except four which showed appreciable extinction effects.

After several cycles of refinement, the last three of which included anisotropic thermal parameters, the R factor had decreased from 0.37 to 0.16. A difference-Fourier computed at this stage revealed the positions of all 15 hydrogen atoms, with peak heights ranging from 0.4 to 0.7 eA^{-3}. These atoms were assigned isotropic temperature factors equivalent to those of the carbons to which they were bonded. Three cycles of refinement were computed on the hydrogen positional parameters and finally three cycles on all positional and thermal parameters, plus an over-all scale factor. The final R factor was 0.040, calculated over 1502 unextinguished reflections with $I > \sigma(I)$. In the last cycle the mean parameter shift was 0.07σ and the maximum shift was 0.39σ.

A difference-Fourier map based on all of the final refined parameters had a range of electron density from −0.15 to 0.20 eA^{-3}. It contained distinct peaks, each situated midway between two bonded carbon atoms. This effect can probably be attributed to the use of scattering factors appropriate to unbonded spherical atoms in the calculation of structure factors.[25]

The final refined values of the positional parameters and their estimated standard deviations are listed in Tables II and III. The corresponding thermal parameters are given in Table IV. The standard deviations are those output by the least-squares program.

Table II. Positional Parameters of Nonhydrogen Atoms and Their Estimated Standard Deviations for 1-Biapocamphane

Atom	$10^4x/a$	$10^4y/b$	$10^4z/c$
C(1)	4351 ± 2	4162 ± 1	4708 ± 2
C(2)	2393 ± 2	3714 ± 1	6788 ± 2
C(3)	1827 ± 2	1922 ± 1	6009 ± 2
C(4)	3460 ± 2	1517 ± 1	3565 ± 2
C(5)	2784 ± 2	1958 ± 1	1983 ± 2
C(6)	3338 ± 2	3752 ± 1	2783 ± 2
C(7)	5532 ± 2	2754 ± 1	3781 ± 2
C(8)	6396 ± 2	2573 ± 2	5462 ± 3
C(9)	7359 ± 2	2617 ± 2	1431 ± 2

Table III. Parameters of Hydrogen Atoms and Their Estimated Standard Deviations for 1-Biapocamphane

Atom	$10^3x/a$	$10^3y/b$	$10^3z/c$	Isotropic temperature factor, A^2
H(1)	436 ± 2	418 ± 1	146 ± 2	3.6 ± 0.3
H(2)	201 ± 2	420 ± 1	342 ± 2	4.2 ± 0.3
H(3)	111 ± 2	417 ± 1	711 ± 2	4.3 ± 0.3
H(4)	276 ± 2	413 ± 1	828 ± 2	3.8 ± 0.3
H(5)	364 ± 2	154 ± 2	29 ± 2	4.4 ± 0.3
H(6)	117 ± 2	153 ± 1	215 ± 2	4.2 ± 0.3
H(7)	26 ± 2	153 ± 1	603 ± 2	4.3 ± 0.3
H(8)	201 ± 2	146 ± 1	704 ± 2	4.3 ± 0.3
H(9)	663 ± 2	151 ± 2	499 ± 2	5.6 ± 0.3
H(10)	544 ± 2	279 ± 2	707 ± 3	5.3 ± 0.4
H(11)	783 ± 2	330 ± 2	548 ± 2	4.8 ± 0.3
H(12)	876 ± 2	334 ± 2	160 ± 2	4.9 ± 0.3
H(13)	705 ± 2	286 ± 1	28 ± 2	4.9 ± 0.3
H(14)	763 ± 2	157 ± 2	78 ± 2	5.7 ± 0.4
H(15)	368 ± 2	43 ± 1	297 ± 2	4.1 ± 0.3

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(17) M. A. Muhs, "Studies of the Molecular Rearrangement of Radical Intermediates in the Kolbe Electrolysis and Other Reactions," University Microfilms, Inc., Ann Arbor, Mich., 1954, pp 161–162.

(18) Standard deviations for all lattice parameters were calculated by a least-squares treatment of observed 2θ angles, measured on a GE XRD-5 diffractometer, using Cu Kα_1 radiation of wavelength 1.54051 A.

(19) W. R. Boehme, *J. Am. Chem. Soc.*, **81**, 2762 (1959).

(20) R. Reinhardt, *J. Org. Chem.*, 27, 3258 (1962).

(21) Observed and calculated structure factors have been deposited as Document No. 9717 with the ADI Auxilliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. A copy may be secured by citing the document number and by remitting $6.25 for photoprints or $2.25 for a 35-mm microfilm. Advance payment is required. Make checks or money orders payable to Chief, Photoduplication Service, Library of Congress.

(22) W. Parrish, *Philips Tech. Rev.*, 17, 206 (1956).

(23) "International Tables for X-ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 202.

(24) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(25) (a) W. Cochran, *Acta Cryst.*, **9**, 924 (1956); (b) A. O'Connell, A. Rae, and E. Maslen, *ibid.*, 21, 208 (1966).

Table IV. Thermal Parameters of Nonhydrogen Atoms and Their Estimated Standard Deviations for 1-Biapocamphane[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	1500 ± 25	789 ± 13	1699 ± 27	142 ± 14	−532 ± 21	353 ± 15
C(2)	1776 ± 30	979 ± 15	2187 ± 34	53 ± 16	−248 ± 25	436 ± 18
C(3)	2220 ± 34	1002 ± 16	2844 ± 41	−76 ± 18	−452 ± 30	676 ± 20
C(4)	2250 ± 31	768 ± 14	2538 ± 36	122 ± 16	−812 ± 27	358 ± 18
C(5)	2643 ± 37	997 ± 16	2816 ± 40	19 ± 19	−1488 ± 32	280 ± 20
C(6)	2273 ± 32	969 ± 15	2549 ± 37	124 ± 17	−1324 ± 29	411 ± 18
C(7)	1829 ± 28	846 ± 13	2046 ± 31	267 ± 15	−591 ± 24	377 ± 16
C(8)	2892 ± 40	1152 ± 19	3404 ± 47	462 ± 22	−1453 ± 36	696 ± 23
C(9)	2241 ± 35	1115 ± 18	2550 ± 39	492 ± 20	−166 ± 29	291 ± 20

[a] β as given is defined by $T = \exp\{-10^5(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)\}$.

Table V. Positional Parameters and Their Estimated Standard Deviations for 1-Binorbornane

Atom	$10^4x/a$	$10^4y/b$	$10^4z/c$	Isotropic temperature factor, A^2
C(1)	4210 ± 3	4210 ± 3	4210 ± 3	
C(2), C(6), C(7)	2721 ± 3	2721 ± 3	5078 ± 4	
C(3), C(5)	962 ± 29	1599 ± 22	3181 ± 25	
C(4)	1718 ± 39	3014 ± 77	1718 ± 39	
H(1), H(2), H(3), H(4), H(10), H(11)	1885 ± 25	3539 ± 25	5851 ± 32	8.4 ± 0.7
H(6), H(7), H(9)	−437 ± 83	2099 ± 72	3475 ± 71	9.5 ± 2.2
H(5), H(8)	404 ± 40	404 ± 40	2821 ± 52	9.7 ± 1.5

1-Binorbornane. The collection and reduction of intensity data were carried out in the same manner as for the apocamphane dimer.[21] A total of 1884 measurements were made on 249 unique reflections. Of these 89% had $I > \sigma(I)$.

The structure solution was considerably complicated by the presence of a threefold disorder in the rotational positioning of the molecules about the C(1)–C(1′) bond. To simplify the following discussion, we anticipate its conclusion by showing, in Figure 1, one-half of the 1-binorbornane molecule in each of its three presumed rotational positions. In Figure 1a the monomer unit is viewed at right angles to the C(1)–C(1′) bond, while in Figure 1d it is viewed along that bond. In Figures 1b,e and 1c, f the monomer unit has undergone successive rotations of 120° about the C(1)–C(1′) bond. The structure at which we have arrived, by the procedure now to be described, is comprised of a disordered mixture of molecules in all three orientations, each with equal probability. It is important to note that, on the basis of X-ray diffraction experiments alone, it is impossible to decide whether the monomer units within one dimer molecule assume their three possible orientations independently or whether each dimer molecule rotates as a rigid whole.

As noted earlier, three space groups were possible on the basis of diffraction symmetry: R32, R3m, or $R\bar{3}m$. Somewhat arbitrarily it was decided to try for a solution in the centric space group $R\bar{3}m$. Fortunately, this seems to have been the correct choice since a more or less satisfactory solution was achieved and subsequent attempts to arrive at other solutions or to refine further in less symmetrical space groups all failed. The procedure by which the structure was actually arrived at is as follows. A sharpened origin-removed Patterson map was calculated and the five largest peaks were found to be consistent with the presence of a pair of atom sites, one on the threefold axis and the other on the mirror plane. As may be seen by referring to Figure 1, the first of these sites corresponds to C(1) and the second to a superposition of C(2), C(6), and C(7). A difference-Fourier map calculated with these two atom sites as input yielded only two further unique locations for the remaining three carbons of the norbornane monomer unit, one lying on a mirror plane and the second in a general position. This may be understood by referring once again to Figure 1. It will be seen that C(4) lies on the plane through C(1′), C(1), and C(7), coincident with the three mirror planes of $R\bar{3}m$ when the three molecular conformations are superimposed. Thus C(4) is responsible for the first additional atom site. The second atom site corresponds to the superposition of C(3) and C(5) in the three conformations. It will be noted that C(3) in one conformation and C(5) in another are very nearly related by a mirror plane of $R\bar{3}m$. In this way, all 14 carbon atoms of the dimer can be represented by only four sets of atom-site coordinates. Consideration of symmetry and of the numbers of atoms being superimposed at each site suggests the following relative weights per asymmetric unit (the atoms are given in parentheses): site 1, 1/6 (C(1)); site 2, 1/2 (C(2), C(6), C(7)); site 3, 1/3 (C(3), C(5)); site 4, 1/6 (C(4)). Each site was assigned the given fixed weight shown throughout the subsequent refinement.

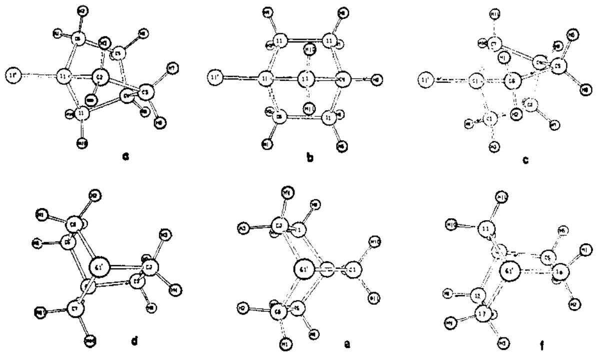

Figure 1. Two views of 1-binorbornane. In a, b, and c the view is normal to the C1–C1′ bond, while in d, e, and f it is along that bond.

Coordinates and temperature factors for the four atom sites were refined by full-matrix least-squares methods with the same program as was used for the refinement of 1-biapocamphane. The R factor was initially 0.32. After it had dropped to 0.17, a difference-Fourier map was calculated in which three peaks could be identified as originating from overlapping sets of hydrogen atoms: (1) H(1), H(2), H(3), H(4), H(10), and H(11); (2) H(6), H(7), and H(9); (3) H(5) and H(8). Six cycles of refinement were required to adjust these hydrogen positional and isotropic thermal parameters. A final six cycles including all parameters, plus an over-all scale factor, reduced the R factor to 0.061 for 221 unextinguished reflections with $I > \sigma(I)$. The mean parameter shift for the last cycle was 0.37σ, with a maximum of 0.93σ.

Final refined positional parameters with their estimated standard deviations are given in Table V Table VI lists the associated thermal parameters.

1-Biadamantane. A total of 2846 measurements of 1650 unique reflections were made on two crystals of the adamantane dimer,

Table VI. Thermal Parameters of Nonhydrogen Atoms and Their Estimated Standard Deviations for 1-Binorbornane[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	2750 ± 51	2750 ± 51	2750 ± 51	545 ± 40	545 ± 40	545 ± 40
C(2), C(6), C(7)	3925 ± 61	3925 ± 61	4179 ± 90	−589 ± 75	787 ± 42	787 ± 42
C(3), C(5)	4176 ± 400	3532 ± 489	6125 ± 403	−761 ± 549	−798 ± 316	286 ± 250
C(4)	6468 ± 1243	6468 ± 1243	9954 ± 1829	−5013 ± 988	−1212 ± 559	−1212 ± 559

[a] β as given is defined by $T = \exp\{-10^5(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)\}$.

Table VII. Positional Parameters of Nonhydrogen Atoms and Their Estimated Standard Deviations for 1-Biadamantane

Atom	$10^4x/a$	$10^4y/b$	$10^4z/c$
C(1)	4391 ± 1	4652 ± 1	4230 ± 1
C(2)	3155 ± 2	1973 ± 2	3867 ± 1
C(3)	1975 ± 2	1308 ± 2	2366 ± 1
C(4)	29 ± 2	2026 ± 2	1920 ± 1
C(5)	1236 ± 2	4686 ± 2	2228 ± 1
C(6)	3196 ± 2	5954 ± 2	1475 ± 1
C(7)	5136 ± 2	5228 ± 2	1927 ± 1
C(8)	6305 ± 2	5892 ± 2	3425 ± 1
C(9)	2406 ± 2	5346 ± 2	3728 ± 1
C(10)	3942 ± 3	2572 ± 2	1617 ± 1

Table VIII. Parameters of Hydrogen Atoms and Their Estimated Standard Deviations for 1-Biadamantane

Atom	$10^3x/a$	$10^3y/b$	$10^3z/c$	Isotropic temperature factor, A^2
H(1)	435 ± 3	140 ± 3	417 ± 2	4.9 ± 0.3
H(2)	184 ± 3	110 ± 3	435 ± 1	4.4 ± 0.3
H(3)	120 ± 3	−44 ± 3	219 ± 1	4.9 ± 0.4
H(4)	−77 ± 3	157 ± 3	92 ± 2	5.1 ± 0.3
H(5)	−129 ± 3	118 ± 3	240 ± 2	5.6 ± 0.4
H(6)	−2 ± 3	516 ± 3	195 ± 1	4.6 ± 0.3
H(7)	247 ± 3	557 ± 3	50 ± 2	6.0 ± 0.4
H(8)	402 ± 3	775 ± 3	163 ± 1	5.1 ± 0.3
H(9)	650 ± 3	611 ± 3	145 ± 1	4.8 ± 0.3
H(10)	717 ± 3	768 ± 3	361 ± 2	5.4 ± 0.4
H(11)	762 ± 3	547 ± 3	371 ± 1	4.8 ± 0.3
H(12)	309 ± 3	706 ± 3	391 ± 1	4.4 ± 0.3
H(13)	111 ± 3	454 ± 3	420 ± 2	4.9 ± 0.3
H(14)	528 ± 3	208 ± 3	189 ± 2	5.9 ± 0.4
H(15)	323 ± 3	216 ± 3	64 ± 2	5.3 ± 0.4

Table IX. Thermal Parameters of Nonhydrogen Atoms and Their Estimated Standard Deviations for 1-Biadamantane[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	1699 ± 32	1577 ± 29	654 ± 10	845 ± 23	274 ± 13	150 ± 12
C(2)	2788 ± 37	1624 ± 30	798 ± 11	986 ± 26	241 ± 15	114 ± 13
C(3)	3268 ± 42	1996 ± 32	839 ± 12	1183 ± 28	106 ± 17	−105 ± 14
C(4)	2393 ± 38	2699 ± 39	890 ± 12	823 ± 29	−26 ± 16	−23 ± 16
C(5)	2355 ± 36	2785 ± 38	792 ± 12	1515 ± 29	74 ± 15	121 ± 15
C(6)	3190 ± 41	2710 ± 37	745 ± 11	1466 ± 31	219 ± 16	332 ± 15
C(7)	2693 ± 38	3053 ± 40	706 ± 11	1366 ± 30	481 ± 16	255 ± 15
C(8)	1952 ± 32	2563 ± 34	726 ± 11	948 ± 26	392 ± 14	250 ± 14
C(9)	2269 ± 34	2593 ± 34	768 ± 11	1595 ± 27	189 ± 14	93 ± 14
C(10)	3948 ± 48	3393 ± 45	831 ± 12	2211 ± 38	429 ± 19	−86 ± 17

[a] β as given here is defined by $T = \exp\{-10^5(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)\}$.

following the procedure described for 1-biapocamphane;[21] 89% had $I > \sigma(I)$.

Examination of a sharpened, origin-removed Patterson map clearly indicated the expected four unique 1.5-A vectors. From this beginning it was not difficult to reconstruct the entire carbon skeleton. An initial F_c calculation, utilizing the symmetry of space group P$\bar{1}$, resulted in an R factor of 0.27. Six cycles of full-matrix, least-squares refinement of positional and thermal parameters were calculated, the last three cycles including allowance for anisotropic thermal motion. At this stage, the 15 hydrogen-atom positions were also predicted from straightforward stereochemical considerations and verified by inspection of a difference-Fourier map. Refinement was continued in the usual manner until the mean parameter shift after the last cycle was 0.09σ and the maximum shift was 0.49σ. The final R factor was 0.052 for 1582 unextinguished reflections with $I > \sigma(I)$.

Atomic parameters and their estimated standard deviations after the final refinement cycle are listed in Tables VII, VIII, and IX.

^{13}C–H Coupling in Norbornane. $J_{^{13}CH}$ at the norbornane bridgehead was measured at 60 and 100 MHz in CCl$_4$ solution, approximately 30% concentration. It was found to have a value of 139 ± 1 Hz, in agreement with an independent measurement of 140 ± 2[26a] and 142 ± 2 Hz.[26b] $J_{^{13}CH}$'s of the bridgeheads in norbornene and norbornadiene are 143 and 146 Hz,[26b] respectively. Since these structural changes bring about such small changes in $J_{^{13}CH}$, it is probably safe to assign $J_{^{13}CH} \cong 142$ Hz to the bridgehead in apobornane, the monomer corresponding to the dimer, II.

Results

Stereoscopic illustrations of the structures of 1-biapocamphane and 1-biadamantane (Figures 2 and 3) were produced on a CalComp Model 763 plotter using the program ORTEP,[27] modified to run on a CDC 3600 computer. Covalent bond lengths and angles and intramolecular approach distances are listed for the two molecules in Tables X–XV. The standard deviations were derived from the appropriate coordinate and unit-cell standard deviations. Comparable figures and tables for 1-binorbornane are not included since it is not possible to represent the disordered crystal structure clearly in a single stereoscopic illustration, nor to associate any of the atom-site distances with unique bond lengths, with the single exception of the C(1)–C(1′) bond.

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(26) (a) C. S. Foote, private communication; (b) K. Tori, R. Muneyuki, and H. Tanida, *Can. J. Chem.*, **41**, 3142 (1963).

(27) C. K. Johnson, "A Thermal Ellipsoid Plot Program for Crystal Structure Illustrations," U. S. Atomic Energy Commission Publication ORNL-3794, 1965.

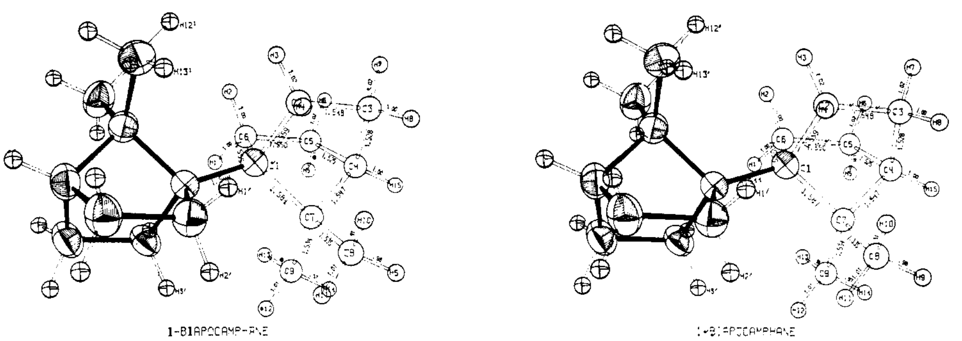

Figure 2. Stereoscopic projection of 1-biapocamphane.

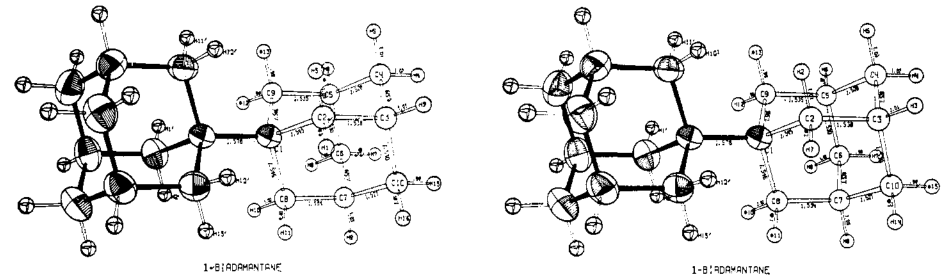

Figure 3. Stereoscopic projection of 1-biadamantane.

It must be emphasized that the tabulated standard deviations relate to the precision of the structural parameters, and not to their accuracy. In fact, bond lengths obtained from any given crystallographic structure determination may be systematically in error by an appreciable amount that is difficult to estimate accurately as a result of anisotropic thermal motion.[28] For the central bridgehead atoms, however, we have found that the thermal ellipsoids are approximately spherical and of approximately the same shape and size in all three structures. Thus any correction that might be applied to the central bond lengths would be approximately the same for all three and a valid comparison among them may be made. Our standard deviations are smaller than usual, probably because of centrosymmetry, the absence of atoms heavier than carbon, low *R* factors (4–6%), and low and almost spherical temperature factors (2.2–4.6 A^2).

Table X. 1-Biapocamphane. Bond Lengths of Covalent Bonds and Their Estimated Standard Deviations

Bond	Length, A
C(1)–C(1′)	1.544 ± 0.002
C(1)–C(2)	1.559 ± 0.001
C(1)–C(6)	1.555 ± 0.002
C(1)–C(7)	1.584 ± 0.002
C(4)–C(7)	1.547 ± 0.002
C(2)–C(3)	1.548 ± 0.002
C(5)–C(6)	1.550 ± 0.002
C(3)–C(4)	1.528 ± 0.002
C(4)–C(5)	1.525 ± 0.003
C(7)–C(8)	1.535 ± 0.003
C(7)–C(9)	1.534 ± 0.001
C(2)–H(3)	1.02 ± 0.02
C(6)–H(2)	1.00 ± 0.01
C(2)–H(4)	1.01 ± 0.01
C(6)–H(1)	1.00 ± 0.01
C(3)–H(7)	1.02 ± 0.01
C(5)–H(6)	1.02 ± 0.01
C(3)–H(8)	1.00 ± 0.02
C(5)–H(5)	1.01 ± 0.01
C(4)–H(15)	1.00 ± 0.01
C(8)–H(9)	0.98 ± 0.02
C(9)–H(14)	0.97 ± 0.02
C(8)–H(10)	0.97 ± 0.01
C(9)–H(13)	0.99 ± 0.02
C(8)–H(11)	1.01 ± 0.01
C(9)–H(12)	1.01 ± 0.01

Table XI. 1-Biapocamphane. Bond Angles for Covalent Bonds[a]

Angle	Degrees
C(2)–C(1)–C(1′)	114.8
C(6)–C(1)–C(1′)	115.0
C(7)–C(1)–C(1′)	119.6
C(2)–C(1)–C(6)	104.0
C(6)–C(1)–C(7)	100.5
C(2)–C(1)–C(7)	100.5
C(1)–C(2)–C(3)	104.7
C(1)–C(6)–C(5)	104.9
C(2)–C(3)–C(4)	102.9
C(4)–C(5)–C(6)	102.7
C(3)–C(4)–C(7)	103.0$_5$
C(5)–C(4)–C(7)	103.0
C(3)–C(4)–C(5)	107.7
C(1)–C(7)–C(4)	93.7
C(8)–C(7)–C(9)	107.2
C(1)–C(7)–C(8)	116.4
C(1)–C(7)–C(9)	116.5
C(4)–C(7)–C(8)	111.2
C(4)–C(7)–C(9)	111.4

[a] The estimated standard deviation is 0.1° for all angles in the table.

1-Biapocamphane. It is encouraging to note that the high precision indicated by the least-squares stan-

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(28) (a) Thus the H···H approach distance might be 0.1 A shorter than indicated: D. W. J. Cruickshank, *Acta Cryst.*, **9**, 757 (1956); (b) D. W. J. Cruickshank, *ibid.*, **14**, 896 (1961); (c) G. S. Pawley, *ibid.*, **16**, 1204 (1963); (d) W. R. Busing and H. A. Levy, *ibid.*, 17, 142 (1964).

Table XII. 1-Biapocamphane. Hydrogen–Hydrogen Approach Distances[a]

Approach	Distance, A
H(1)–H(4′)	2.13
H(2)–H(11′)	2.18
H(3)–H(12′)	2.18
H(4)–H(13′)	2.63
H(1)–H(10′)	2.65
H(4)–H(10)	2.29
H(8)–H(10)	2.29_5
H(1)–H(13)	2.28
H(5)–H(13)	2.27
H(2)–H(3)	2.26
H(6)–H(7)	2.36_5

[a] The primes refer to the centrosymmetrically related half of the dimer. The estimated standard deviations are ±0.03 A for all distances listed.

Table XIII. 1-Biadamantane. Bond Lengths of Covalent Bonds and Their Estimated Standard Deviations

Bond	Length, A
C(1)–C(1′)	1.578 ± 0.002
C(1)–C(2)	1.545 ± 0.001
C(1)–C(9)	1.546 ± 0.002
C(1)–C(8)	1.546 ± 0.001
C(2)–C(3)	1.538 ± 0.002
C(5)–C(9)	1.535 ± 0.001
C(7)–C(8)	1.534 ± 0.001
C(3)–C(4)	1.529 ± 0.002
C(3)–C(10)	1.530 ± 0.002
C(5)–C(6)	1.530 ± 0.002
C(7)–C(10)	1.527 ± 0.002
C(6)–C(7)	1.529 ± 0.002
C(4)–C(5)	1.528 ± 0.002
C(2)–H(1)	1.01 ± 0.02
C(2)–H(2)	1.01 ± 0.02
C(9)–H(12)	0.99 ± 0.02
C(9)–H(13)	0.99 ± 0.02
C(8)–H(10)	1.02 ± 0.02
C(8)–H(11)	1.00 ± 0.02
C(3)–H(3)	1.00_5 ± 0.02
C(5)–H(6)	0.99 ± 0.02
C(7)–H(9)	1.03 ± 0.02
C(4)–H(4)	1.02 ± 0.01_5
C(4)–H(5)	1.01 ± 0.02
C(10)–H(14)	1.05 ± 0.02
C(10)–H(15)	0.99 ± 0.01_5
C(6)–H(7)	0.99_5 ± 0.02
C(6)–H(8)	1.02 ± 0.02

dard deviations is confirmed by comparing structurally identical but crystallographically unrelated bond lengths and angles within the molecule. Four pairs of C–C bonds are related by the molecular mirror plane through C(1), C(7), and C(4). None of these pairs shows differences of greater than 0.004 A in their bond lengths. Similarly there are seven pairs of related C–C–C angles among which there are no differences greater than 0.1°.

One of the most striking things to be seen upon examining Figure 2 is the extent to which intramolecular crowding has distorted the structure. For example, in the apocamphane monomer one would expect to find the bond lengths C(1)–C(7) and C(7)–C (4)to be equal. In this structure they are found to be 1.584 and 1.547 A, respectively. It will be noted that the average length of these two bonds, 1.565 A, is very close to 1.57 A found for the corresponding bond length in norbornadiene.[29]

Table XIV. 1-Biadamantane. Bond Angles for Covalent Bonds[a]

Angle	Degrees
C(2)–C(1)–C(1′)	111.8
C(9)–C(1)–C(1′)	111.7
C(8)–C(1)–C(1′)	111.5
C(2)–C(1)–C(9)	107.3
C(2)–C(1)–C(8)	107.1
C(8)–C(1)–C(9)	107.2
C(1)–C(2)–C(3)	111.5
C(1)–C(9)–C(5)	111.6_5
C(1)–C(8)–C(7)	111.8
C(2)–C(3)–C(4)	109.7
C(2)–C(3)–C(10)	109.6
C(4)–C(5)–C(9)	109.5
C(6)–C(5)–C(9)	109.9
C(8)–C(7)–C(10)	109.7
C(6)–C(7)–C(8)	109.7
C(3)–C(4)–C(5)	109.1
C(4)–C(5)–C(6)	109.4
C(5)–C(6)–C(7)	109.0
C(6)–C(7)–C(10)	109.4
C(3)–C(10)–C(7)	109.0
C(4)–C(3)–C(10)	109.6

[a] The estimated standard deviation is 0.1° for all angles in the table.

Table XV. 1-Biadamantane. Hydrogen–Hydrogen Approach Distances[a]

Approach	Distance, A
H(1)–H(12′)	2.16
H(2)–H(10′)	2.14
H(13)–H(11′)	2.14
H(2)–H(13)	2.53
H(2)–H(5)	2.52
H(5)–H(13)	2.51
H(1)–H(11)	2.58
H(1)–H(14)	2.57
H(11)–H(14)	2.54
H(10)–H(12)	2.59
H(8)–H(10)	2.54
H(8)–H(12)	2.57
H(4)–H(15)	2.53_5
H(7)–H(15)	2.52
H(4)–H(7)	2.53_5

[a] The primes refer to the centrosymmetrically related half of the dimer. The estimated standard deviation is ±0.02 A for all distances listed.

Further, the bonds C(1)–C(2) and C(1)–C(6) are about 0.02 A longer than normal C–C bonds. They are in fact even longer, by about 0.01 A, than the comparable bonds in hexamethylethane[30] and norbornadiene,[29] where the equivalent distances are 1.544 ± 0.002 and 1.549 ± 0.005 A.

Angular distortion about C(1) is evidenced by the increase in the angles C(1′)–C(1)–C(2) and C(1′)–C(1)–C(6) from the 111.1° observed for the corresponding structural features of hexamethylethane[30] to 114.8 and 115.0°, respectively.

There is also evidence of crowding at the methyl groups, C(8) and C(9), causing them to be bent away from the center of the dimer molecule. This is most readily seen if it is assumed that, in the hypothetical undistorted structure, the bisector of the angles C(1)–C(7)–C(4) would lie in the plane formed by atoms C(7), C(8), and C(9). In fact, it is found that the latter plane has been tilted backward by 5.4° from its expected position.

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(29) T. W. Muecke and M. I. Davis, *Trans. Am. Cryst. Assoc.*, 2, 173 (1966).

(30) L. S. Bartell, *ibid.*, 2, 134 (1966).

These distortions can probably be traced to the six nonbonded hydrogen interactions between the two halves of the molecule. The ring hydrogens H(1) and H(4′) and the symmetrically equivalent H(1′) and H(4) are separated by only 2.1 A, or 0.3 A less than the normal van der Waals contact distance. The other four repulsions involve hydrogens on the two methyl groups, where an approach distance of 2.2 A is found between the four pairs H(2)–H(11′), H(3)–H(12′), H(11)–H(2′), H(12)–H(3′). (Average deviations for H–H distances are about ±0.03 A. However, see ref 28a.)

In light of the preceding observations, we can now consider the central bond—its observed length and the length that might be expected if nonbonded repulsions were negligible. The essential point to be made is that the observed C(1)–C(1′) distance of 1.544 ± 0.002 A must be appreciably stretched by intramolecular nonbonded repulsions. A rough measure of the extent of this stretching may be obtained by comparison with the central bond in hexamethylethane. An electron diffraction study by Bartell[30] has shown that the central bond length in this molecule is 1.573 ± 0.004 A. This represents the stretching of 0.04 A when compared with the normal sp^3–sp^3 distance of 1.534 A. We have obtained similar results with 1-biadamantane. In 1-biapocamphane, where rather similar geometry is involved, and where other molecular distortions clearly indicate the presence of repulsions tending to stretch the C(1)–C(1′) bond, it may be assumed that this bond has also lengthened by about 0.04 A.[31] Therefore, we tentatively conclude that the central C(1)–C(1′) bond distance would be 1.50–1.51 A in the absence of nonbonded repulsions.

1-Binorbornane. The determination of the crystal structure of this molecule was carried out in order to verify the above conclusion. Of the six nonbonded hydrogen repulsions presumed to cause stretching of the central bond in the apocamphane dimer, only the two interactions H(1)–H(4′) and H(4)–H(1′) are also present in the norbornane dimer. Thus the central bond in the latter should be approximately 0.03 A shorter than in the former molecule.

Unfortunately, the problem of disorder has prevented a conventional structure solution. Nevertheless, it appears that we have been able to determine the central bond length with some precision. In agreement with prediction, this length is 1.515 ± 0.005 A. It will, however, be evident that the C(1)–C(1′) bond is unique in that it is coincident with the axis of rotational disorder. None of the other atom-site to atom-site distances represent true bond lengths, since the atom-site coordinates are, in fact, nothing more than mean coordinates for groups of two or more atoms. For the sake of the record, we note that these distances lie between 1.44 and 1.58 A.

1-Biadamantane. Solution of the crystal structure of this molecule was intended to provide a basis for comparing the preceding results with those for a presumably normal sp^3–sp^3 bond in a similar environment. As in the apocamphane dimer, the central bond in this molecule is also distorted by six hydrogen nonbonded repulsions: H(1)–H(12′), H(2)–H(10′), H(11)–H(13′), H(1′)–H(12), H(2′)–H(10), and H(11′)–H(13). The hydrogen–hydrogen approach distances are about the same as those observed for the apocamphane dimer, namely, 2.1–2.2 A. As expected, the central bond has been stretched by 0.04 A to a length of 1.578 ± 0.002 A, in agreement with the equivalent bond distance seen in hexamethylethane.[30]

Other features of the adamantane dimer are unexceptional. The bonds from C(1) to C(2), C(8), and C(9) appear to have been lengthened by 0.01 A and there is compensating shortening by approximately 0.005 A of the six bonds furthest removed from the center of the molecule. This phenomenon is more strikingly displayed in 1-biapocamphane. In both cases the changes may be attributed to hybridization differences resulting from geometrical distortions. For example, as the internal angles at the C(1) bridgehead in 1-biapocamphane are decreased, the hybridization in the 1,2 bond increases in p character with a corresponding increase in C(1)–C(2) bond length. At the C(4) position the internal angles are larger, the C(3)–C(4) bond has more s character at C(4), and the bond length is shorter than that at C(1)–C(2). The 1-biadamantane structure may be explained similarly.

Agreement between bond lengths related by the three noncrystallographic mirror planes is as good as that noted for the apocamphane dimer, again indicating satisfactory precision. The maximum difference is 0.004 A for C–C bonds and 0.6° for C–C–C angles.

The above results can be summarized as follows.

1. The central C(1)–C(1′) bond length in 1-binorbornane is 1.515 ± 0.005 A, or 0.020 A shorter than the standard C–C single bond length. This is so in spite of the probable existence of two H–H nonbonded repulsions at about 2.1–2.2 A tending to stretch the central bond. This fact is to be correlated with the observed value of 139 Hz for the bridgehead ^{13}C–H coupling constant in norbornane, corresponding[16] to 28% s character in the orbitals forming the central bond of the dimer.

2. The central C(1)–C(1′) bond length in 1-biapocamphane is 1.544 ± 0.002 A, or 0.034 A shorter than the central bond length of 1.578 ± 0.002 A in 1-biadamantane. The two are comparable because six H–H repulsions at about 2.1–2.2 A, tending to stretch the central bond, are present in both dimer molecules. This fact is to be correlated with the observation that, like 1-binorbornane, the orbitals composing the central bond of 1-biapocamphane should also have about 28% partial s character, whereas 1-biadamantane is composed of monomer units with classical tetrahedral hybridization at the bridgehead.

Discussion

Although the effects described above are small, they must be considered significant. The bond shortenings observed are, respectively, four standard deviations in 1-binorbornane and ten standard deviations in 1-biapocamphane. Increased s character (to 28%) of the bridgehead orbitals forming the central bond in these two dimers, expected because the other bonds are bent backward, away from the center, is confirmed by ^{13}C–H coupling measurements at the bridgehead in norbornane. In addition, the corresponding average ^{13}C–H coupling

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(31) Actually the vector components of the H–H repulsion forces parallel to the C(1)–C(1′) bond in biapocamphane are 0.90, 0.87, and 0.87, whereas the corresponding vector components for biadamantane are 0.96, 0.97, and 0.97. Thus the stretching of the C(1)–C(1′) bond in biapocamphane is a few per cent less than 0.04 A.

constant for all hydrogens in adamantane has been determined by Fort and Schleyer[32a] and found to be 120 ± 1 Hz. This gives an average of 24% s character at the C–H bonds in adamantane,[32b] further helping to confirm expectations based on geometrical considerations. We suggest that these results support the Dewar hypothesis, that C–C single bond shortenings observed in compounds like those listed in Table I are *also* caused by increased s character in the bond orbitals. However, it must be emphasized that decreasing the angles at the bridgehead in going from III to I results in decreased repulsions between, *e.g.*, C(2) and C(2′) carbons. Thus the present results will not differentiate between the hybridization and the nonbonded repulsion theories for bond lengths.

Quantitative Comparison with Eq 1. Since there are six H–H repulsions at 2.1–2.2 A stretching the central bond in both 1-biapocamphane (I) and 1-biadamantane (III), the bond lengths may be compared directly. The observed shortening is 0.034 A. From ^{13}C–H couplings, the calculated partial s character in the bond orbitals is 4% greater for I than for III. Thus $\Delta l/\Delta s = 8 \times 10^{-3}$, even greater than the slope of 6.3×10^{-3} predicted from eq 1.

Another test of eq 1 can be made if it is assumed that the central bond of III has been stretched by 0.043 A, from a normal single bond length of 1.535 A to the observed 1.578 A, by the six H–H repulsions. The reasonableness of this assumption, on a rough quantitative basis, will be discussed below. Using this figure to correct the central bond length of 1-binorbornane (II) to its hypothetical length in the *absence* of the similar set of six H–H repulsions found in the latter dimer molecule, we obtain an estimated bond length of 1.544 − 0.043 = 1.501 A. Since II most probably has just two such repulsions instead of six, its hypothetical unstretched bond length is approximately 1.515 − (2.6)(0.043) = 1.501 A also. We conclude that a reasonable estimate for the unstretched bond length for a C–C single bond composed of orbitals with 28% s character is 1.501 A. Equation 1 predicts a bond length of 1.519 A. The agreement is probably satisfactory, in view of the assumptions. Nevertheless, that the observed bond lengths are shorter than predicted by eq 1 despite the absence of multiple bonds shows that conjugation need not be invoked as a cause of single-bond shortening.

Internal H–H Repulsions. If we take the C–C stretching force constant[33] to be 320 kcal mole^{-1} A^{-2}, then the 0.04 A stretching in 1-biadamantane requires a force of 30 kcal mole^{-1} A^{-1}. Since this force is supplied by six H–H repulsions, the contribution from each is ~5 kcal mole^{-1} A^{-1}, which ought to correspond to the slope of the van der Waals curve at 2.15 A. Agreement with the potentials given by Mason and Rice[34] or Haigh[35] is satisfactory.

Hybridization at the C(1)–C(1′) Bonds. We have assumed that orbital hybridization at the bridgehead in the dimers, RR, is the same as that in RH and that this hybridization is given by the empirical relation[16] % s = $J_{^{13}CH} \times 0.2$. The former is justified by the small distortions possible in such bicyclic systems and by the observation that $J_{^{13}C_1{}^{13}C_2} \propto J_{^{13}C_1H} \times J_{^{13}C_2H}$ in a number of hydrocarbons R_1R_2, R_1H, and R_2H.[36]

Foote[37] has noted a linear correlation of $J_{^{13}CH}$ with internal angle in cycloparaffins and Mislow[38] has extended this correlation to include bicyclic compounds. In addition, several other properties attributed to changes in s character have been observed to change in bridgehead compounds as predicted by $J_{^{13}CH}$. Among these are hydrocarbon acidities,[39] bridgehead carbanion,[40] and radical[41] stabilities and C–H stretching frequencies.[42] The extension of the relationship between $J_{^{13}CH}$ and per cent s character to strained bridgeheads in hydrocarbons therefore seems justified.[43]

Conclusions

We have demonstrated that the single-bond lengths in bis-bridgehead compounds (R–R) correlate with several properties of the RH bond in the monomer in the same way that single-bond lengths in "conjugated" dimers (R′–R′) correlate with the properties of the R′H bond. This encourages us to believe that there is a common basis for these correlations. We note that the admittedly rather artificial concept of hybridization supplies this common basis, in agreement with the sugges tion of Dewar and Schmeising.

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[32] (a) R. C. Fort, Jr., and P. von R. Schleyer, *J. Org. Chem.*, **30**, 789 (1965). (b) Clearly the $J_{^{13}CH}$ measured for adamantane is that for the more numerous methylene hydrogens since all the hydrogens in adamantane have about the same chemical shift. The $J_{^{13}CH}$ for tertiary positions in, *e.g.*, isobutane are difficult to measure and have not been reported. However, purely tetrahedral carbon–hydrogen bonds give $J_{^{13}CH}$ = 124–125 Hz whether they are primary or secondary.[16] Therefore, we are making the reasonable assumption that tertiary carbon hydrogen bond will have the same coupling constant if the carbon is purely tetrahedral as in adamantane.

[33] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, Inc., New York N. Y., 1965, p 447.

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[39] See D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, p 49.

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[41] D. F. Applequist and L. Kaplan, *ibid.*, **87**, 2194 (1965).

[42] T. L. Brown and J. C. Puckett, *J. Chem. Phys.*, **44**, 2238 (1966).

[43] As an alternative to $J_{^{13}CH}$ we have used our measured angles and the relationship of Mislow[38] to calculate 28% s in the central bond of I and 25.5% s in the central bond of III.