

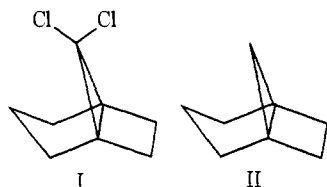
“Inverted” Tetrahedral Geometry at a Bridgehead Carbon. The X-Ray Crystal, Molecular, and Electronic Structure of 8,8-Dichlorotricyclo[3.2.1.0^{1,5}]octane (C₈H₁₀Cl₂) at -40^o^{1a}

Kenneth B. Wiberg,^{*1b} George J. Burgmaier,^{1b} Kei-wei Shen,^{1b}
Sam J. La Placa,^{1c} Walter C. Hamilton,^{1c} and Marshall D. Newton^{1c}

Contribution from the Departments of Chemistry, Yale University, New Haven, Connecticut 06520, and Brookhaven National Laboratory, Upton, New York 11973. Received December 11, 1971

Abstract: The proposed molecular structure of 8,8-dichlorotricyclo[3.2.1.0^{1,5}]octane (C₈H₁₀Cl₂), based on spectroscopic and chemical evidence, requires the normal tetrahedral arrangement about the bridgehead atoms to be “inverted” (e.g., the four interatomic vectors emanating from a bridgehead carbon to its four neighbors are all directed to one side of a plane). This unusual configuration has been authenticated by a three-dimensional single-crystal X-ray study at -40° using counter diffraction techniques. The monoclinic space group (C_{2h}²-P₂₁/m) of dimensions *a* = 6.796 (24), *b* (unique axis) = 8.721 (35), and *c* = 6.903 (25) Å, and β = 102.62 (7)° contains two molecular units, each possessing a crystallographically imposed mirror plane. The Cl-C(8)(bridge)-Cl angle is 108.7 (8)° and the C(8)-Cl bond distances average 1.761 (10) Å. Each of the two mirror-related bridgehead carbons [C(1),C(5)] is displaced only 0.093 Å from the plane defined by its three nearly trigonal nonbridgehead neighbors. The bridgehead-bridgehead bond (1.572 (15) Å) is considerably longer than the bridge-bridgehead bond (1.458 (12) Å). The electronic structure of the bonds associated with the bridgehead carbons is discussed in terms of hybrid atomic orbitals obtained from a CNDO/2 wave function. While the four C-C interatomic vectors at each bridgehead do indeed lie on one side of a plane, the angles between the corresponding bond hybrids at a given bridgehead are found to range from 101 to 116°, leading to a model more closely akin to that expected for a four-coordinate carbon atom than one might infer from simply connecting atomic centers. The remaining crystallographically independent distances are C(1)-C(7) = 1.526 (12), C(6)-C(7) = 1.512 (20) Å and C(1)-C(2) = 1.483 (12), C(2)-C(3) = 1.529 (12) Å in the four- and five-membered rings, respectively. All hydrogen atoms were unambiguously located.

The preparation of 8,8-dichlorotricyclo[3.2.1.0^{1,5}]octane (I) and its parent 8,8-dihydro compound II



have been reported.² These compounds, based on spectroscopic and chemical evidence, are believed to have an “inverted” tetrahedral arrangement about the bridgehead atoms (i.e., the four bonds emanating from this carbon, connecting nuclear centers, are all directed to one side of a plane). The bridgehead carbons and three atoms attached to them (other than the other bridgehead atom) should lie approximately in a plane. An ideal hybridization would be sp², leaving a pure p orbital to form the central bond. This is reflected in the reactivity of II. It reacts with oxygen rapidly at room temperature to give polymer. Acetic acid can undergo facile addition reaction with it across the central bond. In contrast to the behavior of II, I is relatively stable to oxygen. The white crystalline I turns to light yellow after a few weeks of standing in air at 5°. It seemed of particular interest, therefore, to determine the exact molecular structure of these com-

pounds. We wish to report the result of a low-temperature X-ray diffraction study of compound I.

Experimental Section

Preparation. 8,8-Dichlorotricyclo[3.2.1.0^{1,5}]octane (I) was prepared from the addition of dichlorocarbene, generated from ethyl trichloroacetate and sodium methoxide, to bicyclo[3.2.0]hept-1-ene.² The nmr spectrum showed only a broad multiplet, τ 6.80-7.75.² White clear crystals of I were obtained by slow sublimation at room temperature under vacuum (mp ~29-30°).

Crystallographic Data. The low melting point of the crystals necessitated capillary mounting and sealing in a 0° cold room. A crystal of approximate dimensions 0.5 × 0.5 × 0.45 mm was kept at ca. -40°, by a cooled nitrogen gas stream, during the period of data collection. The crystallographic data, as presented in Table I, require the molecule to possess a mirror plane. Nb-filtered

Table I. Crystallographic Data for 8,8-Dichlorotricyclo[3.2.1.0^{1,5}]octane

| | | | |
|--------------|------------|---|-------------------------------------|
| Mol wt | 177.09 | Space group | P ₂₁ /m |
| <i>a</i> , Å | 6.796 (24) | ζ _{calc'd} , g/cm ³ | 1.473 |
| <i>b</i> , Å | 8.721 (35) | Absent spectra | 0 <i>k</i> 0; <i>k</i> ≠ 2 <i>n</i> |
| <i>c</i> , Å | 6.903 (25) | Volume, Å ³ | 399.28 |
| β, deg | 102.62 (7) | | |
| <i>Z</i> | 2 | μ (Mo Kα) = 7.32 | |

Mo Kα radiation intensity measurements were made on a programmed G.E. Datex diffractometer equipped with a single-crystal orienter, scintillation counter, and pulse-height discriminator. Due to crystal decomposition and other experimental problems only 242 independent reflections (2θ ≤ 35°) were collected. To monitor the decomposition of the compound during data collection the 004 reflection was measured every 15 reflections. A linear correction factor was assumed between the monitored points. At the end of data collection, ~60% of initial intensity of the (004) reflection had been lost. Structure amplitudes were

(1) (a) Research performed in part under the auspices of the U. S. Atomic Energy Commission; (b) Yale University; (c) Brookhaven National Laboratory.

(2) K. B. Wiberg and G. J. Burgmaier, *Tetrahedron Lett.*, 317 (1969); K. B. Wiberg, E. C. Lupton, and G. J. Burgmaier, *J. Amer. Chem. Soc.*, 91, 3372 (1969); K. B. Wiberg, J. E. Hiatt, and G. J. Burgmaier, *Tetrahedron Lett.*, 5855 (1968).

Table II. Final Parameter Value

| Atom | x^a | y | z | β_{11}^b | β_{22} | β_{33} | β_{12} | β_{13} | β_{23} |
|-------|--------------|-------------|-------------|----------------|--------------|--------------|--------------|--------------|--------------|
| Cl(1) | 0.2234 (4) | 0.2500 | 0.5552 (5) | 0.0187 (14) | 0.0199 (9) | 0.0410 (15) | 0 | 0.0038 (10) | 0 |
| Cl(2) | 0.0949 (5) | 0.2500 | 0.1318 (5) | 0.0343 (15) | 0.0260 (9) | 0.0330 (15) | 0 | 0.0173 (10) | 0 |
| C(5) | -0.1683 (13) | 0.1599 (7) | 0.3595 (14) | 0.0113 (28) | 0.0130 (14) | 0.0160 (36) | -0.0052 (15) | -0.0018 (26) | -0.0047 (14) |
| C(4) | -0.3018 (26) | 0.1066 (17) | 0.1721 (19) | 0.0720 (45) | 0.0253 (28) | 0.0246 (43) | 0.0028 (30) | 0.0082 (41) | -0.0030 (29) |
| C(3) | -0.3668 (40) | 0.2500 | 0.0469 (34) | 0.0336 (73) | 0.0208 (47) | 0.0142 (62) | 0 | -0.0084 (49) | 0 |
| C(6) | -0.2089 (23) | 0.1633 (11) | 0.5682 (17) | 0.0285 (34) | 0.0142 (17) | 0.0198 (37) | 0.0019 (23) | 0.0014 (28) | 0.0039 (17) |
| C(8) | 0.0117 (19) | 0.2500 | 0.3566 (15) | 0.0169 (47) | 0.0109 (19) | 0.0222 (40) | 0 | -0.0064 (32) | 0 |
| H(3) | -0.472 (13) | 0.2500 | 0.004 (16) | 0.89 (3.7) | | | | | |
| H(4) | -0.351 (11) | 0.2500 | -0.095 (15) | 0.68 (2.3) | | | | | |
| H(6) | -0.243 (10) | 0.053 (7) | 0.090 (11) | 2.58 (2.2) | | | | | |
| H(5) | -0.468 (11) | 0.068 (7) | 0.211 (8) | 1.15 (2.2) | | | | | |
| H(7) | -0.324 (12) | 0.103 (8) | 0.581 (9) | 2.82 (2.1) | | | | | |
| H(8) | -0.118 (9) | 0.108 (7) | 0.664 (9) | 3.00 (1.9) | | | | | |

^a Numbers in parentheses here and in subsequent tables are estimated standard deviations in the least significant figures. ^b The general anisotropic temperature factor has the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

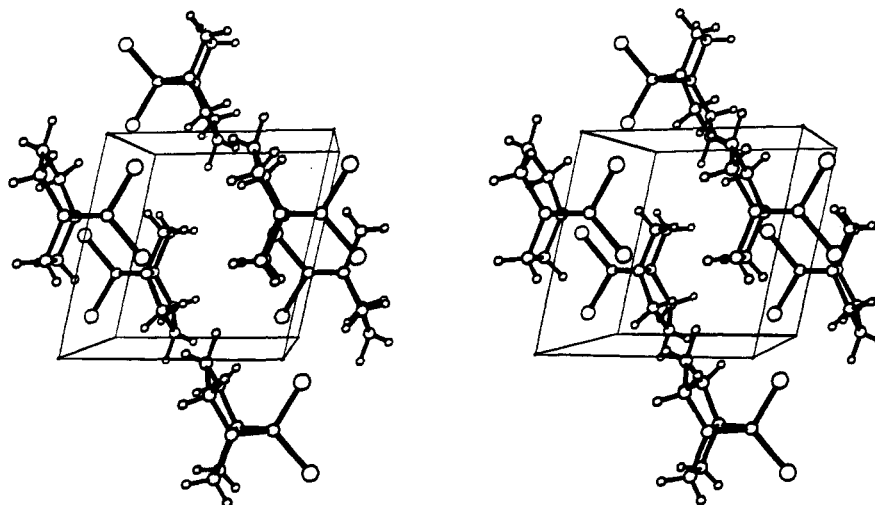


Figure 1. Molecular packing; a stereopair with the b axis of the unit cell approximately normal to the paper.

derived from the raw intensities by conventional treatment. No absorption corrections were applied.

Solution and Refinement. The structure was solved by conventional heavy atom Fourier techniques. All hydrogen atoms were subsequently unambiguously located in a difference Fourier map. The resulting structural parameters were refined by the full-matrix least-squares method minimizing the quantity $\sum w(|F_o| - |F_c|)^2$ with weights w assigned as follows: $w = [(0.10F_o)^2 + \sigma^2]^{-1}$ where σ^2 is the estimated variance of F_o^2 based on the Poisson counting statistics.

The atomic scattering factors for C and Cl were taken from the tabulation in the "International Tables for X-Ray Crystallography"^{3a} while that for H was from Stewart, Davidson and Simpson.^{3b} The chlorine and carbon atoms were refined using anisotropic thermal parameters while each hydrogen atom was refined with an individual isotropic temperature factor. The final fractional coordinates and thermal parameters together with their estimated standard deviations are listed in Table II.⁴ The conventional agreement factors are $R(F) = 0.065$ and $R'(F) = 0.067$ where $R(F) = \sum[|F_o| - |F_c|]/\sum|F_o|$ and $R'(F) = [\sum w(|F_o| - |F_c|)^2/\sum w F_o^2]^{1/2}$. The estimated standard deviation of an observation of unit weight is 1.40. An analysis of the weighting scheme at the end of this refinement revealed no unexpected trends.

(3) (a) "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962, Table 3.3.1; (b) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(4) An X-ray structure factor table will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-72-7402. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

Results and Discussion

The crystal structure, described by the unit cell, space group, and the parameters of Table II, consists of the packing of individual monomeric molecules as shown in Figure 1. The bond lengths, angles, and other relevant parameters are summarized in Tables III and IV. There are no unusual intermolecular contacts. The molecular structure shown in Figures 2 and 3 is that which was previously proposed based on chemical properties and spectroscopic evidence.

The most interesting aspect of the structure is the geometry at the bridgehead. The bridgehead carbon C(1) is displaced 0.093 Å out of the plane formed by C(2), C(7), and C(8) and on the opposite side of the plane from C(5). Thus, the four interatomic vectors from C(1) (*i.e.*, the lines connecting the nuclear centers) all lie on one side of a plane.

The crystallographically imposed mirror plane requires the cyclobutane ring to be planar. Although the nonplanar conformation is considerably more prevalent, several cyclobutane rings, in simple derivatives, have been found to adopt this planar geometry.^{5,6} The cyclopentane ring is nearly planar despite the resulting increase in torsional strain. The planarity of the ring increases the angles at the bridgehead and this must

(5) T. N. Margulis, *Chem. Commun.*, 215 (1969).

(6) R. K. Bohn and Y.-H. Tai, *J. Amer. Chem. Soc.*, **92**, 6447 (1970).

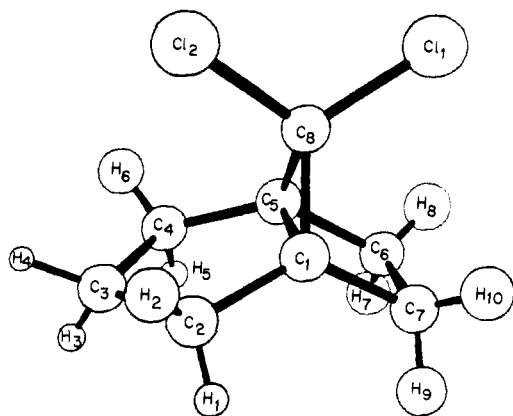


Figure 2. Atom designation (the crystallographic mirror plane contains the atoms Cl(1), Cl(2), C(8), C(3), H(4), and H(3)).

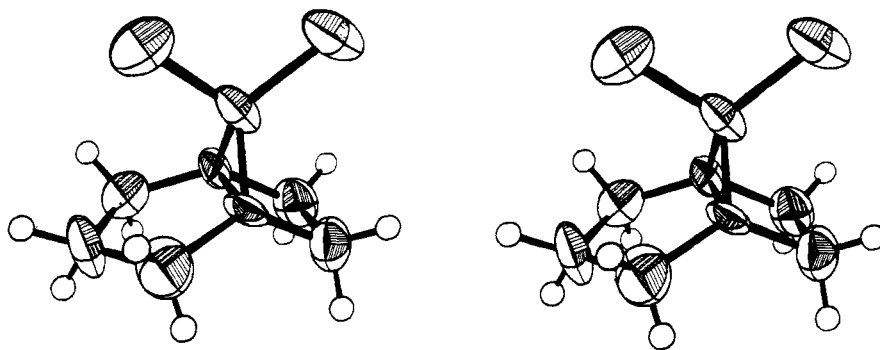


Figure 3. Stereoscopic view; thermal vibrational ellipsoids are scaled to enclose 50% probability.

Table III. Intramolecular Distances (Å) and Angles (Deg)^a

| Bond | Length, Å | Bond | Length, Å |
|------------------|---------------------|----------------------|------------|
| C(8)-Cl(1) | 1.757 (12) | C(6)-H(7) | 0.96 (7) |
| C(8)-Cl(2) | 1.764 (13) | C(6)-H(8) | 0.93 (6) |
| C(1)-C(5) | 1.572 (15) | C(4)-H(6) | 0.89 (7) |
| C(1)-C(8) | 1.458 (12) | C(4)-H(5) | 0.89 (7) |
| C(5)-C(6) | 1.526 (12) | C(3)-H(3) | 0.72 (8) |
| C(6)-C(7) | 1.512 (12) | C(3)-H(5) | 1.01 (9) |
| C(1)-C(2) | 1.483 (12) | Cl(1)···Cl(2) | 2.862 |
| C(2)-C(3) | 1.529 (13) | Cl(1)···H(8), H(10) | 2.873 |
| | | Cl(2)···H(6), H(2) | 2.831 |
| | | Cl(2)···H(4) | 3.095 |
| Angle | Deg | Angle | Deg |
| Cl(1)-C(8)-Cl(2) | 108.7 (7) | C(1)-C(5)-C(6) | 88.9 (4) |
| C(1)-C(8)-C(5) | 65.3 (8) | C(5)-C(6)-C(7) | 91.1 (4) |
| C(5)-C(1)-C(8) | 57.4 (4) | C(2)-C(1)-C(7) | 128.9 (11) |
| C(2)-C(1)-C(5) | 108.2 (6) | C(7)-C(1)-C(8) | 109.1 (8) |
| C(1)-C(2)-C(3) | 106.4 (1.4) | C(2)-C(1)-C(8) | 120.8 (10) |
| C(2)-C(3)-C(4) | 109.7 (1.7) | C(1)-C(8)-Cl(2) | 116.3 (6) |
| | | C(1)-C(8)-Cl(1) | 122.4 (6) |
| Plane 1 | Plane 2 | Dihedral angles, deg | |
| C(1)-C(5)-C(8) | C(1)-C(5)-C(6)-C(7) | 113.7 (9) | |
| C(1)-C(5)-C(8) | C(1)-C(5)-C(2)-C(4) | 115.4 (10) | |
| C(2)-C(3)-C(4) | C(1)-C(5)-C(2)-C(4) | 9.7 (27) | |

^a The estimated standard deviation (not the limit of error) appears in parentheses in units of the least significant figure.

lead to a decrease in strain which is greater than the increase in torsional strain. Within the cyclopropane ring there are two unusually short (mirror related) bridge-bridgehead bonds of 1.458 (12) Å. At first

sight this difference seemed unreasonably short, so attempts were made to refine structures with longer bonds in these positions; all converged, to within $1/2\sigma$, to the same structure.

It was thought desirable, particularly in the absence of studies on directly comparable compounds, to gain some theoretical insight into the nature of the bonds emanating from the bridgehead carbons. For this purpose we have examined the electronic structure of 1, as represented by a semiempirical CNDO/2 wave function.⁷ The calculation was based on the geometry given in Table II. As discussed in some detail by Coulson⁸ and Bent,⁹ one aspect of electronic structure especially useful in correlating bond lengths is atomic orbital hybridization. Trends in bond lengths can be related to the degree of s character and the orientation of the hybrids forming the bond. It is of particular

Table IV. Root-Mean-Square Thermal Displacements along the Principal Axes of the Thermal Ellipsoids (Å)

| Atom | Axis 1 | Axis 2 | Axis 3 |
|-------|------------|------------|------------|
| Cl(1) | 0.192 (8) | 0.277 (6) | 0.331 (6) |
| Cl(2) | 0.218 (8) | 0.308 (6) | 0.316 (6) |
| C(8) | 0.154 (28) | 0.205 (18) | 0.276 (19) |
| C(3) | 0.148 (42) | 0.283 (31) | 0.316 (25) |
| C(2) | 0.217 (26) | 0.252 (20) | 0.318 (18) |
| C(6) | 0.189 (20) | 0.250 (14) | 0.264 (16) |
| C(1) | 0.108 (31) | 0.214 (17) | 0.244 (11) |
| H(3) | 0.12 (20) | | |
| H(4) | 0.10 (14) | | |
| H(6) | 0.18 (8) | | |
| H(5) | 0.11 (13) | | |
| H(7) | 0.18 (7) | | |
| H(8) | 0.19 (6) | | |

importance for the present study to note that these correlations can also include strained rings, provided that the bent nature of the bonding density is recognized.⁹

We have obtained bond hybrids from the delocalized CNDO/2 molecular orbitals (MO's) by transformation to a set of localized two-center MO's (LMO's), which can then be decomposed into hybrid atomic orbitals. Hybrids so obtained have been usefully employed in previous studies of related bicyclic and tricyclic systems.¹⁰ The occurrence of chlorine atoms in the pres-

(7) (a) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966); (b) D. P. Santry and G. A. Segal, *ibid.*, **47**, 158 (1967).


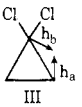
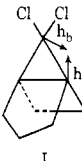
(8) C. A. Coulson, "Valence," Oxford University Press, London, 1952, Chapter 8.

(9) H. A. Bent, *Chem. Rev.*, **61**, 275 (1961).

ent case raises two additional points. We have not included 3d orbitals on the chlorine atoms, since previous studies suggest that molecular geometries are rather insensitive to their omission.^{7b} Secondly, we have used the CNDO/2 method instead of the INDO method,¹¹ since extensive parameterization and testing of the latter method have not been carried out for the second row of the periodic table.^{11b} Although the two methods may yield somewhat different hybridization parameters, they both yield the same relative trends in most cases tested so far.^{12, 15}

We first examine the unusually short (1.458 ± 0.012 Å) bridge-bridgehead bond of I. The relevant hybrids (denoted as h_a and h_b) are presented in Table V along with the corresponding hybrids for two refer-

Table V

| Molecule | Hybrid | Bond length, Å |
|--|------------------------------------|----------------|
|  | $h_a sp^{4.76}$ $h_b sp^{4.76}$ | 1.510 (2) |
|  | $h_a sp^{5.03}$ $h_b sp^{3.42}$ | 1.532 (4) |
|  | $h_a sp^{3.26}$ $h_b sp^{2.73}$ | 1.458 (12) |

ence systems—cyclopropane and 1,1-dichlorocyclopropane (III), both of which are found to have reasonably “normal” C–C single bond lengths (1.52 ± 0.01 Å).¹⁷ We are in effect comparing the cyclopropane ring in three different environments. In all cases, the hybrids h_a and h_b deviate by a roughly constant

(10) (a) M. D. Newton and J. M. Schulman, *J. Amer. Chem. Soc.*, **94**, 767 (1972); (b) M. D. Newton and J. M. Schulman, *ibid.*, **94**, 773 (1972); (c) the work in ref 10a and 10b employed hybrids obtained from INDO wave functions; see ref 12.

(11) (a) J. A. Pople, D. M. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967). (b) An INDO approach for interhalogen molecules was recently reported by B. M. Deb and C. A. Coulson, *J. Chem. Soc. A*, 958 (1971).

(12) (a) M. D. Newton, unpublished results. (b) In certain cases, generally associated with multiple bonds or multiple lone pairs, the localization of CNDO/2 wave functions by the Edmiston–Ruedenberg criterion¹³ used here leads to indeterminate solutions.¹⁴ This accounts for some of the previously noted¹⁵ differences between CNDO/2 localized orbitals¹⁶ and those obtained by the INDO method. In the present case, there is no unique solution for the chlorine lone pairs, but the solutions for all other localized orbitals in I are unique and well behaved.

(13) (a) C. Edmiston and K. Ruedenberg, *J. Chem. Phys.*, **43**, S97 (1965). (b) One should note that the hybrids obtained by this method are not constrained to be orthogonal. Overlap between hybrids on the same center is generally found to be < 0.1 .

(14) M. D. Newton, unpublished work, and E. Switkes, R. M. Stevens, W. N. Lipscomb, and M. D. Newton, *J. Chem. Phys.*, **51**, 2085 (1969).

(15) W. England and M. S. Gordon, *J. Amer. Chem. Soc.*, **91**, 6864 (1968).

(16) C. Trindle and O. Sinanoglu, *ibid.*, **49**, 65 (1968); *J. Amer. Chem. Soc.*, **91**, 853 (1968).

(17) (a) Cyclopropane: O. Bastiensen, F. N. Fritsch, and K. Hedberg, *Acta Crystallogr.*, **17**, 538 (1964); (b) 1,1-dichlorocyclopropane: W. H. Flygare, A. Narath, and W. D. Gwinn, *J. Chem. Phys.*, **36**, 200 (1962); (c) a microwave structure for the related species, cyclopropyl chloride, has been reported by R. H. Schwendeman, G. D. Jacobs, and T. M. Krigas, *ibid.*, **40**, 1022 (1964).

amount ($\sim 32 \pm 3^\circ$) from the C–C bond vectors. Furthermore, examination of the localized MO's indicates that the C–C bonds of interest are essentially homopolar—*i.e.*, ionic contributions to the C–C bonding can be ignored. Looking first at cyclopropane and III, we find that while the 1,1-dichloro substitution results in a significant increase in the s character of one of the bond hybrids (h_b), a rehybridization in the *opposite* sense (though smaller in magnitude) is induced in the other hybrid (h_a) of the bond. Thus, at least qualitatively, we can understand why the C₁–C₂ bond lengths are similar in the two molecules. That such a second-order inductive effect would tend to resist changes in C–C bond lengths caused by halogen substitution was anticipated by Bent.⁹ In the 1,2-dichloro isomer, symmetry would prevent such a compensating effect and one might expect a significantly shortened C₁–C₂ bond in this molecule, a prediction which remains to be tested. We note that the reported microwave C–C bond length for III is actually slightly *longer* than the electron-diffraction value reported for cyclopropane. Any explanation of such an effect, which incidentally is not observed in the case of the monochloro derivative of cyclopropane,^{17c} would presumably require more than a hybrid orbital analysis (perhaps invoking partial C–Cl π bond formation). At any rate, the effect is quite small relative to the major shortening observed in going from III to I.

Turning now to the system of principal interest, I, we observe (Table VI) the dramatic effect of converting the C₂–C₃ bond of III into the bridgehead–bridgehead bond of I: *both* hybrids of the bridge-bridgehead bond in I [*cf.* the C₁–C_{2,3} bonds of III] have considerably greater s character than the C–C bond hybrids of cyclopropane. The increase in the s content of h_a in going from III to I arises from an apparently^{10, 18, 19} general property of bridgehead carbon atoms in polycyclic systems in which two or three small rings share a common single bond (*e.g.*, [1.1.0]bicyclobutane,^{10a, 18} [1.1.1.0^{1,3}]tricyclopentane,^{10b} and [2.2.2.0^{1,5}]tricyclooctane,¹⁹ as well as I). In such molecules, the bridgehead hybrids not involved in the bridgehead–bridgehead bond prefer a high degree of s character (relative to that in the corresponding isolated small rings), while the bridgehead–bridgehead bonds are formed from nearly pure p orbitals. Thus, the increase in s character (compared to cyclopropane) of *both* of the hybrids in the bridge-bridgehead bonds of I is the result of the independent actions of their respective local influences (chlorine substitution on the one hand, the nature of bridgehead position on the other). The significant shortening of the bridge-bridgehead bond with respect to cyclopropane is accordingly attributed to the fact that the s character in *both* pertinent hybrids is enhanced. Merely increasing the s content of one of the hybrids, as in III, leads to little effect on bond length, since in the absence of stronger influences, a slight rehybridization in the opposite sense is induced at the other carbon atom.

We have just argued that the high s character of the hybrids in the bridgehead–bridge bond of I is due to the general nature of the environment of the participating

(18) J. M. Schulman and G. J. Fisanick, *J. Amer. Chem. Soc.*, **92**, 6653 (1970).

(19) M. D. Newton and J. M. Schulman, *ibid.*, **94**, 773 (1972).

carbon atoms. This high s character is *consistent* with the observed shortness of the bond. Conversely, one might ask what happens to the hybrids if the bridge-bridgehead bond is artificially lengthened, say, to the distance observed in III, by moving the $C_8Cl_1Cl_2$ moiety and adjusting its bond lengths and angles to match those in III, with all other atoms kept in their original positions. Clearly, if this distortion resulted in hybrids similar to those in III, we would then have an equally *consistent* basis for arguing that the bridge-bridgehead bond should have a *normal* length. Fortunately, such a circularity does not arise since calculations on III with the distorted geometry just described lead only to small changes in the s content of the hybrids. Correspondingly, the hybrids of III are not strongly affected when a calculation is carried out using the geometry of the 1,1-dichlorocyclopropane moiety of I. Thus, the difference in C-C bond lengths in I and III reflects the intrinsic difference in the types of hybridization in the two systems.

The other bridgehead bonds in I also deserve some comment. The side bond in the five-membered ring (C_1-C_2) is almost as short ($1.483 \pm 0.012 \text{ \AA}$) as the bridge-bridgehead bond. The key to understanding the C-C₂ bond length lies in noting the similarity of its $sp^{1.73}$ bridgehead hybrid (the C₂ hybrid is $sp^{2.83}$) and that found for the bridgehead C-H bond in [1.1.0]bicyclobutane ($sp^{1.58}$).²⁰ The latter C-H bond has been referred to as acetylenic, and is noted for its acidic nature.^{10,18,21} Therefore it is not surprising that the C₁-C₂ bond length in I approaches that found for the

single bond of methylacetylene (1.459 \AA),²² the bond hybrids for the latter molecule being $sp^{1.10}$ ($-C\equiv$) and $sp^{2.78}$ (CH_3-).^{12a}

As noted above, the bridgehead-bridgehead bond is formed from two essentially pure p orbitals ($sp^{2.9,4}$). This bond is probably the bond least amenable to a simple analysis because it is the one most subject to the constraints imposed by the other bridgehead bonds. It is interesting to note that it is considerably longer ($1.572 \pm 0.015 \text{ \AA}$) than its counterpart in [1.1.0]bicyclobutane ($1.497 \pm 0.003 \text{ \AA}$),²³ also formed from p hybrids.^{10a,18} Part of the difference may lie in the fact that the p orbitals in [1.1.0]bicyclobutane deviate from the bridgehead-bridgehead vector by $\sim 33^\circ$, compared to only a 21° deviation for I. A similar analysis in terms of hybrid orientation has been invoked by Bent⁹ to account for the different C-C bond lengths in cyclopropane (1.510 \AA)^{17a} and cyclobutane (1.584 \AA).²⁴ The side bond of I in the five-membered ring seems to be the most normal. The slight shortening relative to cyclobutane is presumably related to the s content ($sp^{2.28}$) of the bridgehead hybrid.

In conclusion it should be noted that while the four C-C *interatomic vectors* at each bridgehead do indeed lie on one side of a plane, the same is not true for the corresponding *bond hybrids*. The six interhybrid angles at a given bridgehead range from 101 to 116° ,^{13b} leading to a model more closely akin to that expected for a four-coordinate carbon atom than one might infer from simply connecting atomic centers.

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Mechanism of Azoalkane Thermolysis. Concerted or Nonconcerted?

Robert J. Crawford* and Kunihiko Takagi

*Contribution from the Department of Chemistry,
University of Alberta, Edmonton, Alberta, Canada. Received March 6, 1972*

Abstract: The synthesis and gas-phase thermolysis of the unsymmetrical azo compounds, methylazo-3-propene (**6**), 1-propylazo-3'-propene (**7**), and *tert*-butylazo-3-propene (**8**), are described. The nitric oxide inhibited rates of thermolysis of **6**, **7**, and **8** at 122.3° are compared with the rate of thermolysis of azo-3,3'-propene (**5**). It is concluded that the azoalkanes undergo thermolysis in the gas phase to produce two fragments in the rate-determining step. The secondary deuterium kinetic isotope effect of methylazo-3-propene-3,3-*d*₂ was determined, and the value obtained, $k_H/k_D = 1.28$ at 126.0° ($\Delta\Delta G^\ddagger$ per deuterium, $98 \pm 15 \text{ cal mol}^{-1}$), is consistent with the formation of two fragments for both **5** and **6**.

Azoalkanes have been used for many years as a convenient source of alkyl radicals, but there remains some doubt as to the nature of the initial mechanistic step involved in their thermolysis. The earliest work addressed directly to this matter was that of Ramsperger¹ who compared the activation parameters of **1**, **2**, and **3** and was led to conclude that "The heat of activation

(1) H. C. Ramsperger, *J. Amer. Chem. Soc.*, **51**, 2134 (1929).

of **3** is intermediate between that for dimethyl diimide (**1**) and di-isopropyl diimide (**2**)... If the reaction occurs by the simultaneous rupture of both bonds, then we may expect an intermediate heat of activation, and this is the experimental result." The activation energy is $47.5 \text{ kcal mol}^{-1}$ for **3**, being slightly larger than the arithmetic mean of the then accepted values of 51.2 and $40.9 \text{ kcal mol}^{-1}$ for **1** and **2**. Subsequent