

lengths are: experimental,³¹ 125–128 (6)°, 1.545 (5) Å, not determined; Allinger 1971, 126.9°, 1.541 Å, 1.552 Å; Allinger 1973, 128.6°, 1.546 Å, 1.548 Å; Schleyer, 126.7°, 1.540 Å, 1.551 Å; MUB-2, 122.6°, 1.541 Å, 1.552 Å.

(31) L. S. Bartell and W. F. Bradford, *J. Mol. Struct.*, **37**, 113 (1977).

(32) G. P. Hellmann, Ph.D. Thesis, Universität Frelburg, 1977, p 45.

(33) W. Klyne and V. Prelog, *Experientia*, **16**, 521 (1960).

(34) O. Bastlansen, F. N. Frltsch, and K. Hedberg, *Acta Crystallogr.*, **17**, 538 (1964).

(35) J. F. Liebman and A. Greenberg, *Chem. Rev.*, **76**, 311 (1976); cf. pp 329–330.

(36) We thank Dr. Paul Bickart for this suggestion.

(37) E. Ruch, W. Hässelbarth, and B. Richter, *Theor. Chim. Acta*, **19**, 288 (1970); W. Hässelbarth and E. Ruch, *ibid.*, **29**, 259 (1973).

(38) J. G. Nourse, *J. Am. Chem. Soc.*, **99**, 2063 (1977).

(39) For notation, cf. J. G. Nourse and K. Mislow, *J. Am. Chem. Soc.*, **97**, 4571 (1975).

(40) The conjugacy classes of S_n and the cycle structure of the wreath products necessary for L can be found in D. E. Littlewood, "The Theory of Group Characters", Clarendon Press, Oxford, 1940, pp 265–284.

(41) Note that (34)(56) yields *st*-F₂BFB₂. A representative of that double coset could equally well have been chosen to give *re*-F₂BFB₂ (e.g., (23)(45)).

Strained Small Ring Compounds. Structure of a Substituted Semibullvalene, 1-Cyanotricyclo[3.3.0.0^{2,8}]octa-3,6-diene. Geometric Evidence for Homoaromaticity in the Molecular Ground State

Gary G. Christoph* and Mark A. Beno

Contribution from the Evans Chemical Laboratories, Chemistry Department, Ohio State University, Columbus, Ohio 43210. Received September 7, 1977

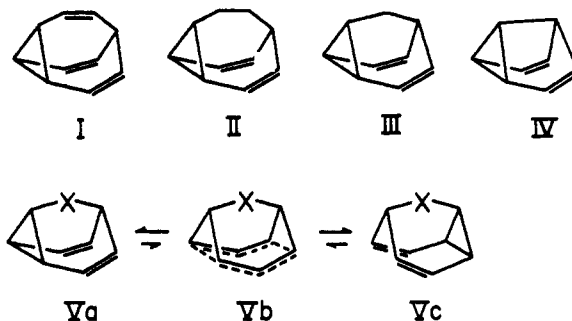
Abstract: The structure of 1-cyanosemibullvalene (1-cyanotricyclo[3.3.0.0^{2,8}]octa-3,6-diene, C₉H₇N) has been determined by high-resolution x-ray crystallographic methods at -45 °C. The molecule exists wholly in the tautomeric form possessing the cyclopropane ring C(1)–C(2)–C(8). The extraordinarily long C(2)–C(8) bond distance (1.577 Å, corrected for thermal libration) and the shortened distance between the formally nonbonded atoms C(4) and C(6) (2.35 Å), together with the lack of indication of severe repulsive strain, are evidence for a small but significant homoaromatic stabilization in the molecule. The interaction between C(4) and C(6) is accordingly deduced to be attractive, however with an estimated bond order of no more than 0.10 for the p–p σ overlap between these two atoms. 1-Cyanosemibullvalene forms colorless, prismatic crystals having the orthorhombic space group $P2_12_12_1$. The cell constants are $a = 6.693$ (2), $b = 8.301$ (3), $c = 12.393$ (4) Å (MoK α , $T = -45$ °C). There are four molecules per cell, each possessing nearly perfect noncrystallographic mirror symmetry. The final R factors for 1192 reflections are $R = 0.056$ and $R_w = 0.066$.

Introduction

Small ring hydrocarbons are particularly interesting compounds because their high energy content relative to the acyclic isomers often endows them with unusual reactivity patterns. Occasionally, such compounds are remarkably unreactive and stable, usually because rearrangement to a less highly strained system must go via an even more highly strained state or because direct rearrangements are forbidden by symmetry rules.¹ In either case, the reactivity, or lack of it, is strongly determined by the molecular structure; one is immediately led to the general question of how the "strain" inherent in these molecules is expressed; is it accumulated in one or two bonds or is it distributed throughout the molecule? Further, what is the effect on the strained system (and on its reactivity) of various substituent groups?

Sufficient numbers of small monocyclic hydrocarbons have been examined that the direct substituent effects on such compounds, if not clearly predictable, are at very least regular and understandable in terms of steric, electronic, and inductive effects. More unusual situations arise in which a small ring system is either further strained or constrained by fusion with other small rings. Abnormal molecular geometries can be generated in this fashion and the reactivity patterns of these and similar compounds have attracted much synthetic and kinetic attention.² In this and subsequent papers we will examine the structures of highly strained polycyclic hydrocarbons with the aim of finding the structural bases for their reactivities.

The bridged homotropilidenes bullvalene (I), dihydrobullvalene (II), barbaralane (III), and semibullvalene (IV) are



fluxional in the sense that internal Cope rearrangements (e.g., $Va \rightleftharpoons Vc$) are fairly facile, with calculated energies of activation on the order of 3–15 kcal/mol.³ These molecules are of considerable current interest because the transition states of such rearrangements are in theory homoaromatic, and the possibility exists of preferentially stabilizing the transition state relative to the ground state in molecules of this type with appropriate substituents⁴ and of thus isolating the first derivatives of bishomobenzene (VI).



Cheng, Anet, Mioduski, and Meinwald⁵ have recently measured the free energy of activation for the degenerate Cope

Table I. Crystal Data

1-Cyanotricyclo[3.3.0.0 ^{2,8}]octa-3,6-diene, C ₉ H ₇ N	
Mol wt	129.16
Mp	50.5–51 °C
Space group: orthorhombic, <i>P</i> 2 ₁ 2 ₁ 2 ₁ (no. 19)	
Cell constants:	
<i>a</i>	6.693 (2) Å
<i>b</i>	8.301 (3) Å
<i>c</i>	12.393 (4) Å
<i>V</i>	688.6 (4) Å ³
Density (calculated, <i>Z</i> = 4)	1.246 g cm ⁻³
Radiation: Mo Kα	λ = 0.710 69 Å
Absorption coeff: μ(Mo Kα)	= 0.803 cm ⁻¹
Transmission factors:	max 0.992, min 0.967

rearrangement of semibullvalene (IV). The value, 5.5 ± 0.1 kcal/mol, although larger than that calculated by Dewar and Schoeller³ using the MINDO/2 method, is the lowest known barrier for any compound capable of undergoing the Cope rearrangement. Hoffmann and Stohrer^{4a} predicted strong equilibrium preferences for semibullvalenes unsymmetrically substituted at the 1 or 5 position and further raised the possibility of destabilizing the ground state relative to the transition state by selective symmetrical substitution. Appropriate synthetic methods for introducing such substituents into the semibullvalene nucleus have only recently become available⁶ and we here describe the structural analysis of 1-cyanosemibullvalene, a preliminary report of which has appeared elsewhere.⁷

Experimental Section

Colorless, irregular, prismatic crystals of the title compound were sealed into thin-wall glass capillaries. Since the compound is subject to slow thermal decomposition at room temperature, all measurements were made on one crystal (0.1 × 0.1 × 0.4 mm) at -45 ± 5 °C, using an automated Syntex diffractometer equipped with a cold gas stream low-temperature device. Cell constants were determined by least-squares fit of the setting angles of eight carefully centered medium intensity reflections for which $19^\circ \leq 2\theta \leq 27^\circ$. The space group was determined to be *P*2₁2₁2₁ by inspection of the systematic absences (*h*00, *h* = 2*n* + 1; 0*k*0, *k* = 2*n* + 1; 00*l*, *l* = 2*n* + 1) after the completion of the data collection. Reciprocal space was surveyed at half-integral values of the Miller indexes to ensure that the unit cell size was correct. Cell constants and other crystal data are given in Table I.

Intensity data were collected using the ω - 2θ scan technique, with a scan width which varied linearly with $\sin \theta$ to accommodate α_1 - α_2 splitting. The scan rate was adjusted between the limits of 1.0 and 12.0°/min on the basis of a quick premeasurement of peak intensity. All intensities in one octant were measured for which $0^\circ \leq 2\theta \leq 60^\circ$. The intensities of four reflections, 042, 117, 141, and 310, were remeasured periodically to monitor crystal condition and alignment, and plots of these intensities as a function of x-ray exposure time revealed no observable crystal decomposition. No absorption corrections were necessary. The intensities were reduced to F^2 's and E 's in the usual way, with the estimates of the standard errors in the scattering factor amplitudes made using the formula

$$\sigma(F^2) = \frac{r}{Lp} \{S = G^2(B1 + B2) + (pI)^2\}^{1/2}$$

where *r* is the scan rate, *Lp* is the Lorentz-polarization factor for the monochromatized beam case,⁸ *S*, *B1*, and *B2* are the scan and background counts, *G* is the ratio of scan time to total background counting time, *I* is the net intensity (= $\{S - G(B1 + B2)\}$), and *p* is a factor, chosen as 0.02, included in a term presumed to represent that component of the total error expected to be proportional to the diffracted intensity.⁹ A total of 1290 reflections were measured. After deleting systematic absences and averaging of multiply measured reflections, 1192 independent reflections remained, of which 825 were greater

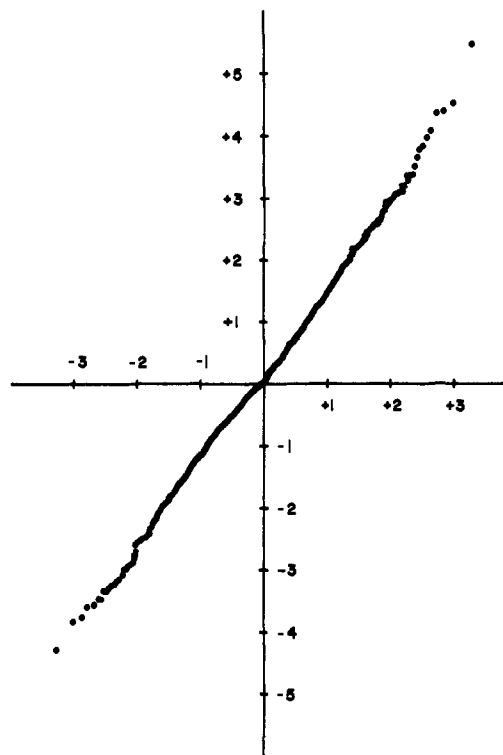


Figure 1. Normal probability plot: $(F_o^2 - F_c^2)/\sigma(F_o^2)$ vs. calculated normal deviates. The linearity indicates that the model structure accounts well for the observed data, leaving only residual normally distributed error. The slope suggests that on the average the $\sigma(F_o^2)$ were underestimated by about 40%.

than 3σ above background. The *R* factors for multiply measured reflections (principally the check reflections) were $R_1 = 0.010$ and $R_2 = 0.050$.¹⁰ The distribution of the intensity statistics and a Howells, Phillips, and Rogers plot¹¹ verified the acentric space group.

The phase problem was solved by direct methods, using the program MULTAN.¹² All nonhydrogen atoms were located on the *E* map with the highest figure of merit. After several cycles of least-squares refinement of the atomic coordinates and isotropic temperature factors, the hydrogen atoms were readily apparent on a difference map and their coordinates and isotropic thermal parameters were then also refined. Additional refinement using anisotropic thermal parameters for the nonhydrogen atoms and including a secondary extinction parameter¹³ resulted at convergence in final *R* of 0.056 and R_w of 0.066 for 1192 reflections. The final "goodness of fit" was 1.42.¹⁴ The final data-parameter ratio was 9.92. A normal probability plot¹⁷ of the quantities $(F_o^2 - F_c^2)/\sigma(F_o^2)$ vs. the expected normal deviates for 1192 points (Figure 1) shows that the $\sigma(F_o^2)$ were on the average underestimated by about 40%, but that the distribution of error was normal. The linearity of the plot is excellent, and indicates that all systematic trends in the data are satisfactorily accounted for by the derived structural model. Table II lists the final values of the parameters varied in the least-squares refinement. Tables of the observed and calculated structure factor amplitudes and $\sigma(F_o^2)$ comprise Table I of the supplementary material.¹⁸ The final difference Fourier map showed no peaks greater than +0.37 or less than -0.32 e Å⁻³. Almost all of the remaining features were located in the vicinity of the bonding regions between the atoms. The general noise level of the map was about ± 0.10 e Å⁻³.

On completion of the structure solution the program TLS¹⁹ was used to analyze the anisotropic thermal parameters and to obtain bond distances and angles corrected for rigid body librational motion. The program, which was modified to include mass weighting of the atoms,²⁰ gave essentially isotropic molecular translational root mean square amplitudes of 0.16 Å and root mean square librational amplitudes of 5.4, 2.9, and 2.2°. The largest amplitude librational motion is about a molecular axis almost exactly parallel to the normal to the plane of atoms C(3)-C(4)-C(7)-C(6). The excellent agreement between the individual atomic thermal parameters and those predicted by the librational model (root mean square error, $\{\sum \Delta u_{ij}^2/(m-s)\}^{1/2}$

Table II. Final Values of Least-Squares Parameters

Atom	<i>x</i>	<i>y</i>	<i>z</i>	β_{11} [<i>B</i>] ²	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	0.7197 (3)	0.4258 (2)	0.1278 (1)	115 (4) [2.0]	71 (2)	31 (1)	-24 (6)	-4 (4)	-6 (3)
C(2)	0.5899 (3)	0.5670 (2)	0.0993 (2)	171 (5) [2.6]	86 (3)	40 (1)	43 (7)	-38 (5)	-9 (3)
C(3)	0.7246 (4)	0.7071 (2)	0.0953 (2)	282 (7) [3.1]	71 (3)	37 (1)	7 (8)	-2 (6)	7 (3)
C(4)	0.9058 (4)	0.6710 (2)	0.1290 (2)	231 (6) [3.1]	92 (3)	41 (1)	-97 (8)	33 (6)	-18 (4)
C(5)	0.9127 (3)	0.5006 (2)	0.1739 (1)	110 (4) [2.3]	90 (3)	41 (1)	-20 (7)	9 (4)	-36 (3)
C(6)	0.8582 (3)	0.5296 (2)	0.2911 (2)	193 (5) [2.7]	86 (3)	36 (1)	17 (7)	-45 (5)	-18 (4)
C(7)	0.6628 (3)	0.5202 (3)	0.3060 (2)	203 (5) [2.7]	93 (3)	32 (1)	29 (7)	24 (4)	-8 (4)
C(8)	0.5590 (3)	0.4709 (2)	0.2071 (2)	114 (4) [2.5]	87 (3)	48 (1)	4 (6)	32 (4)	-9 (4)
C(9)	0.7224 (3)	0.2768 (2)	0.0685 (1)	96 (4) [2.1]	86 (2)	34 (1)	-1 (6)	-14 (4)	4 (3)
N	0.7269 (3)	0.1579 (2)	0.0220 (1)	150 (4) [2.8]	89 (2)	52 (1)	11 (7)	-16 (4)	-29 (3)
H(1)	0.484 (3)	0.554 (2)	0.047 (2)	[2.8 (4)]					
H(2)	0.677 (3)	0.808 (3)	0.074 (2)	[3.2 (5)]					
H(3)	1.014 (3)	0.741 (2)	0.141 (2)	[4.0 (6)]					
H(4)	1.032 (3)	0.442 (2)	0.157 (1)	[2.2 (4)]					
H(5)	0.950 (3)	0.571 (2)	0.342 (1)	[2.1 (4)]					
H(6)	0.595 (3)	0.540 (2)	0.374 (1)	[2.8 (4)]					
H(7)	0.444 (3)	0.410 (2)	0.208 (1)	[2.2 (4)]					

^a The form of the anisotropic thermal parameter is $\exp[-2\pi(h^2\beta_{11} + k^2\beta_{22} + \dots + kl\beta_{23})]$. The *B* values given in brackets for the anisotropic atoms are the isotropic equivalent. The values in parentheses are in this and subsequent tables the estimated standard deviation in the least significant digit.

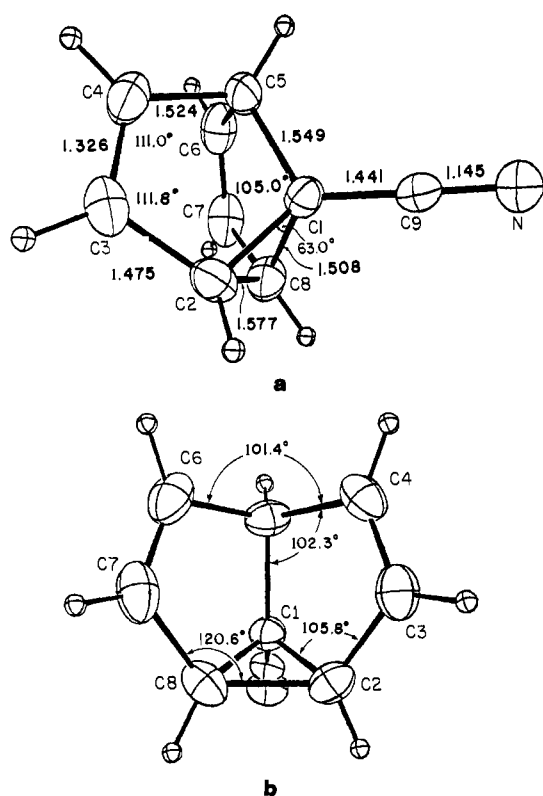


Figure 2. Thermal ellipsoid (ORTEP) diagrams showing the average values for pertinent chemically equivalent bond distances and angles, and the numbering scheme for the molecule.

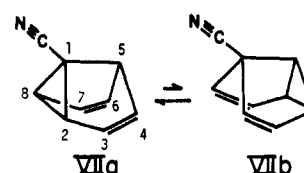
= 0.0016 Å²) indicates that the thermal motions of the atoms are predominantly of librational origin and well accounted for by the model.¹⁸ In any case, in view of the reduced data collection temperature, the resulting bond length corrections are reassuringly small.

Because of the interest in the low barrier for the Cope rearrangement, we were curious to see the effect of raising the temperature on the thermal parameters, particularly of C(2) and C(8). A second data set was therefore collected at 21 °C on the same crystal. Because of high thermal motion, thermal decomposition, or crystal decay (at completion the crystal had become nearly opaque and pale yellow in color) the data were neither extensive nor of high quality, with only 248 of the 432 reflections having $2\theta \leq 40.0^\circ$ being more than 3σ above background, for comparable counting times. Refinement using as starting coordinates the results of the -45 °C study gave physically

unrealistic results, which we attributed to the inadequate and poor-quality data, and we consequently were forced to terminate our analysis.

Description of the Structure

The molecular architecture is illustrated in Figure 2. Interatomic distances and angles, uncorrected and corrected for thermal libration effects, comprise Table III. The molecule possesses nearly perfect mirror symmetry, with the symmetry plane lying in the plane of C(1), C(5), and C(9) and bisecting the cyclopropane ring. The molecule is wholly in the tautomeric ground state VIIa; C(3)-C(4) and C(6)-C(7) are well-local-



ized double bonds and C(4) and C(6) are, at 2.35 Å apart, *apparently* (vide infra) precluded from significant bonding interaction. The cyclopropane bond lengths are inequivalent, with the C-C bonds proximal to the nitrile of normal length while the distal bond, at 1.577 Å, is substantially longer than even a normal sp^3 - sp^3 carbon-carbon bond. The cyclopentene rings are seriously puckered, the approximately planar C(2)-C(3)-C(4)-C(5) linkage being folded outward from the C(2)-C(1)-C(5) plane by 19.9°. The angle between the analogous planes on the other side of the molecule is 18.6°. Least-squares plane calculations¹⁸ show C(1) displaced from the planes of the other four atoms in each ring by about 0.3 Å. C(4) and C(6) similarly lie to the outside of their respective rings, but by only 0.05-0.06 Å, as is reflected by the small torsion angles about the two double bonds of 6.7 and 4.9°. With the exception of the bridgehead bond C(1)-C(5), and C-C bond distances in the cyclopentene rings are remarkably close to the values expected for typical bonds of appropriate hybridization (Table IV). The C≡N bond is of normal length.

Three of the four shortest intermolecular contacts involve the cyano nitrogen atom and hydrogen atoms of C(2), C(5), and C(7) of neighboring molecules, with respective N...H contact distances of 2.61, 2.70, and 2.70 Å. The geometry of the contacts and the expected low acidity of the hydrogen atoms preclude these being interpreted as even very weak hydrogen bonds. One other contact, also essentially van der Waals

Table III. Interatomic Distances (Å) and Angles (deg)

	Uncorrected	Corrected ^a		Uncorrected	Corrected ^a
C(1)-C(2)	1.501 (3)	1.507	C(2)-C(1)-C(8)	63.0 (1)	63.0
C(1)-C(8)	1.504 (3)	1.510	C(1)-C(2)-C(8)	58.6 (1)	58.6
C(1)-C(5)	1.543 (3)	1.549	C(1)-C(8)-C(2)	58.4 (1)	58.4
C(1)-C(9)	1.438 (2)	1.441	C(1)-C(2)-C(3)	105.7 (2)	105.6
C(2)-C(8)	1.569 (3)	1.577	C(1)-C(8)-C(7)	106.1 (2)	106.0
C(2)-C(3)	1.472 (3)	1.478	C(2)-C(1)-C(5)	104.9 (2)	105.0
C(3)-C(4)	1.317 (4)	1.323	C(8)-C(1)-C(5)	104.8 (1)	105.0
C(4)-C(5)	1.521 (3)	1.526	C(2)-C(1)-C(9)	123.9 (2)	123.9
C(5)-C(6)	1.517 (3)	1.523	C(8)-C(1)-C(9)	123.8 (2)	123.8
C(6)-C(7)	1.323 (3)	1.329	C(5)-C(1)-C(9)	121.7 (2)	121.6
C(7)-C(8)	1.467 (3)	1.472	C(2)-C(3)-C(4)	111.9 (2)	112.0
N-C(9)	1.143 (2)	1.145	C(8)-C(7)-C(6)	111.6 (2)	111.7
C(3)-C(7)	3.065 (3)	3.079	C(1)-C(5)-C(4)	102.3 (2)	102.2
C(4)-C(6)	2.349 (3)	2.359	C(1)-C(5)-C(6)	102.6 (2)	102.4
C(2)-H(1)	0.97 (2)	0.97	C(4)-C(5)-C(6)	101.2 (2)	101.4
C(3)-H(2)	0.93 (2)	0.94	C(3)-C(4)-C(5)	110.8 (2)	110.9
C(4)-H(3)	0.94 (2)	0.94	C(7)-C(6)-C(5)	111.2 (2)	111.2
C(5)-H(4)	0.96 (2)	0.97	C(3)-C(2)-C(8)	120.7 (2)	120.8
C(6)-H(5)	0.94 (2)	0.94	C(7)-C(8)-C(2)	120.5 (2)	120.5
C(7)-H(6)	0.97 (2)	0.97			
C(8)-H(7)	0.92 (2)	0.92	N-C(9)-C(1)	179.0 (2)	179.0
			C(3)-C(4)-C(6)	105.1 (2)	105.0
C(1)-C(8)-H(7)	118 (1)		C(7)-C(6)-C(4)	106.4 (2)	106.4
C(2)-C(8)-H(7)	114 (1)		C(5)-C(4)-C(6)	39.3 (1)	39.2
C(1)-C(2)-H(1)	120 (1)		C(5)-C(6)-C(4)	39.4 (1)	39.4
C(8)-C(2)-H(1)	115 (1)		C(4)-C(3)-H(2)	127 (1)	
C(3)-C(2)-H(1)	121 (1)		C(6)-C(7)-H(6)	125 (1)	
C(7)-C(8)-H(7)	123 (1)		C(3)-C(4)-H(3)	128 (1)	
C(2)-C(3)-H(2)	121 (1)		C(7)-C(6)-H(5)	125 (1)	
C(8)-C(7)-H(6)	123 (1)		C(5)-C(4)-H(3)	120 (1)	
			C(5)-C(6)-H(5)	123 (1)	
			C(1)-C(5)-H(4)	114 (1)	
			C(4)-C(5)-H(4)	115 (1)	
			C(6)-C(5)-H(4)	120 (1)	

^a Corrected for thermal librational motion; see text.

Table IV. Bond Types in 1-Cyanosemibullvalene

Bond	Typical length, ^a		
	Å	Atoms	
C—C (sp ² -sp ³)	1.52	C(4)-C(5)	1.526
		C(6)-C(5)	1.523
C—C (sp ² -sp ²)	1.48	C(2)-C(3)	1.478
		C(7)-C(8)	1.472
C≡N (sp ² -sp)	1.44	C(1)-C(9)	1.441
C=C (sp ² -sp ²)	1.33	C(3)-C(4)	1.323
		C(6)-C(7)	1.329
C—C cyclopropane (sp ⁵ -sp ⁵)	1.51	C(1)-C(2)	1.507
		C(1)-C(8)	1.510

^a L. E. Sutton, "Interatomic Distances", *Chem. Soc., Spec. Publ.*, No. 11 (1958); No. 18 (1965).

in nature, between C(6) and H(3) of another molecule, is 2.68 Å. Interatomic contacts less than 3.5 Å are given in the supplementary tables;¹⁸ nearly all are hydrogen-hydrogen contacts at normal van der Waals distances. The slight nonlinearity of the nitrile group and the small deviations from molecular C₃ symmetry, all of normal magnitude, we ascribe to asymmetric packing effects.

The atomic thermal vibration amplitudes ranged from 0.14 to 0.25 Å, with the larger amplitudes primarily associated with C(4), C(6), and N(1). Rigid librational motion accounted nearly completely for the observed amplitudes. We in particular examined the residual amplitudes (observed minus librational) of C(2), C(4), C(6), and C(8) to see if there was any "extra" motion suggestive of a low-energy breathing vibration

roughly perpendicular to the cyclopentene rings, but found none.

Discussion

Both the very long C(2)-C(8) distance and the apparent normality of the bond distances in the cyclopentene rings are surprising results: C(1) is the point of attachment of the strongly π -accepting cyano group, which is expected by conjugation with the cyclopropane ring to alter its equilateral geometry, but not in the observed direction. If the low-lying unoccupied (π^*) orbitals of such a substituent are properly aligned to interact with the antisymmetric component of the highest occupied degenerate Walsh²¹ orbital pair in the cyclopropane, the net effect is a delocalization of electron density out of the cyclopropane molecular orbital and into the vicinal π system, Figure 3. Because that cyclopropane molecular orbital is primarily bonding for C(1)-C(2) and C(1)-C(8), but antibonding for C(2)-C(8), the loss of electron population from this orbital should result in an increase in the C(1)-C(2) and C(1)-C(8) bond distances (a net decrease in bond strength) and a simultaneous decrease in the C(2)-C(8) bond distance (an increase in bond strength).²² We should further expect to observe some weakening of the C≡N bond, as its empty, low-lying antibonding orbital becomes populated.

Such conjugative interactions of cyclopropanes with π substituents are amply supported by spectroscopic and chemical data²³ and structural studies.²⁴ The structure of 2,5-dimethyl-7,7-dicyanonorcaradiene^{24c} (Figure 4) is most germane to our situation: the cyclopropane bonds proximal to the dicyano substituents are ca. 0.05 Å longer, and the distal bond is ca. 0.01 Å shorter than in cyclopropane,²⁵ in agreement

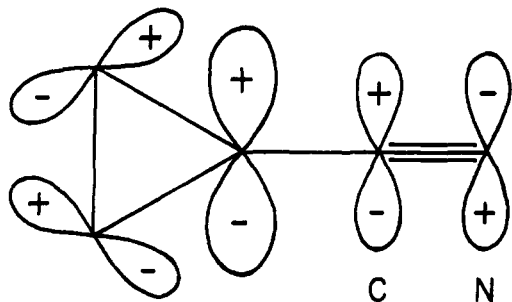


Figure 3. Interaction of cyclopropane Walsh orbital with low-lying cyanide π^* orbital (ref 22).

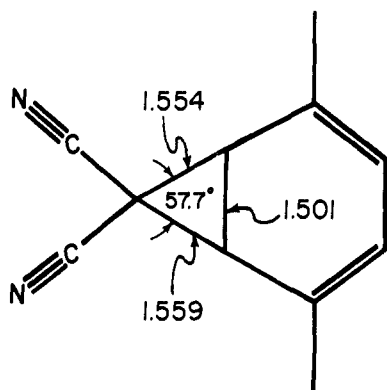


Figure 4. Effect of dicyano substitution on cyclopropane geometry; the vicinal bonds are lengthened while the distal bond is shortened in 1,1-dicyano-3,5-dimethylnorcaradiene (ref 24c).

with the above predictions. In 1-cyanosemibullvalene, however, not only do we find the proximal cyclopropane bonds, which should be most affected, to be of normal length, but the distal bond is abnormally long.

The unusual geometry of the cyclopropane ring could be interpreted as arising from steric repulsion between C(4) and C(6) forcing the cyclopentene rings apart and stretching C(2)-C(8), or, conversely, it could arise from a significant homoaromatic contribution to the molecular ground state, wherein the C(4)···C(6) contact is attractive rather than repulsive, and the C(2)-C(8) bond is lengthened, not by steric forces, but simply by increased antibonding character in compensation for the nascent bond formation between C(4) and C(6). By comparison with related structures, careful analysis will demonstrate that the observed geometry is consistent only with the C(4)···C(6) contact being attractive, rather than repulsive.

Using gas-phase electron diffraction methods, Wang and Bauer²⁶ determined the structure for the parent hydrocarbon semibullvalene, Figure 5. One is immediately tempted on the basis of their results to explain the "long" 1.577 Å C(2)-C(8) distance of 1-cyanosemibullvalene as simply the consequence of induced shortening (a la' 1,1-dicyanonorcaradiene) of the cyclopropane bond opposite the cyano substituent. This agrees well with Hoffman's prediction,²² but leaves the origin of the long C(2)-C(8) distance unexplained. The limited accuracy of Wang and Bauer's determination²⁷ makes us reluctant to use this argument; the two structures cannot be reliably compared in such fine detail. In spite of differences between some of the bonding parameters, however, the *general* conformations of the two molecules are in substantial agreement: In both cases the cyclopentene rings are puckered, with C(4) and C(6) folded outward by about 18°; the C(2)-C(8) distances in both are extraordinarily large; and the two double bonds in each case appear to be well localized and essentially planar. It is of par-

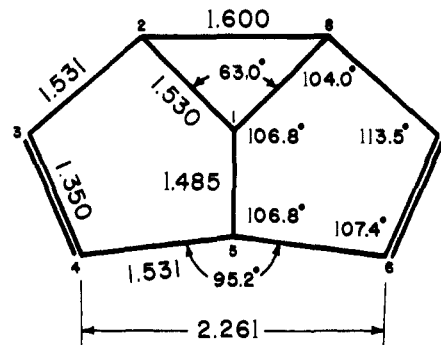
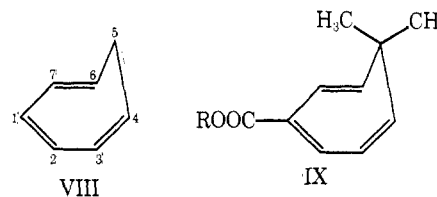


Figure 5. Structure of semibullvalene as determined by electron diffraction (ref 26). The molecule is assumed to possess mirror symmetry, and C(2)-C(3) and C(4)-C(5) are assumed to be equivalent.

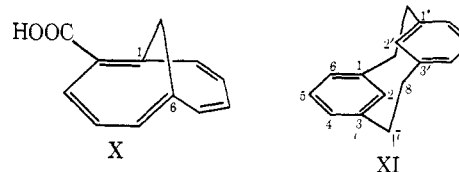
ticular interest here that the puckering of the cyclopentene rings is substantially less than the 29.0° for cyclopentene²⁸ and that, whereas steric interactions between geminal carbon atoms would be expected to increase the C(4)-C(5)-C(6) angles over the tetrahedral value, they are in both molecules much less than 109.5°. Cycloheptatriene (VIII) in the gas phase has 113° for



the value of analogous angle, and the C(4)···C(6) distance is 2.51 Å.²⁹ Slightly different results were found in IX, the structure of the *p*-bromophenacyl ester of 7,7-dimethyl-3-carboxylic acid derivative of cycloheptatriene: 106° and 2.42 Å.³⁰ The completely unstressed nonbonded distance expected for two carbon atoms each 1.525 Å from a common tetrahedral carbon center would be 2.490 Å.


Another expected consequence of steric repulsion between C(4) and C(6) would be larger than normal dihedral angles between the cyclopentene and the cyclopropane rings. In order to evaluate this more fully we compare these angles (calculated as the angle between the cyclopropane plane and the plane defined by the common and two adjacent carbon atoms of each of the cyclopentene rings) in Table V with those for similarly constituted planes in simple bicyclic systems having a cyclopropane ring fused to a five-, a six-, or a seven-membered ring, but not subject to the constraints imposed by further ring fusions. The dihedral angles for 1-cyanosemibullvalene are, although somewhat greater than the average, still well within the range of values for the unconstrained bicyclic systems, again indicative of the absence of substantial repulsive strain between the cyclopentene rings.

Very short intramolecular nonbonded C···C contacts between juxtaposed carbon atoms have been observed in a few systems, most notably in certain 1,6 methano-bridged [10]-annulenes (e.g., 2.27 Å in X³¹) and cyclophanes (2.69 Å in



XI³²). The former contain the cycloheptatriene structural unit and are similarly capable of a Cope rearrangement to a norcaradiene type structure. The ring of completely alternating double bonds in the annulene bestows considerable aromatic character on the molecule, thus providing an extra driving force

Table V. Dihedral and Bond Angles in Some Bicyclic Systems



Compd	Ring size	Dihedral angle	∠123 (∠123')	∠145 (∠145')	∠324 (∠3'24)	∠542 (∠5'42)	Ref
Africanol	7	108.0	121.0	114.8 (114.7)	119.0	116.0 (114.4)	<i>a</i>
<i>cis</i> -Bicyclo[5.1.0]-oct-4- <i>exo</i> -yl <i>p</i> -bromobenzoatesulfonate	7	111.0	121.6	121.2			<i>b</i>
<i>syn</i> -8,8-Dichloro-4-phenyl-3,5-dioxabicyclo[5.1.0]octane	7	125.4	119.0	119.5	120.5	119.5	<i>c</i>
<i>endo</i> -7-Chloro-7-phenyl-2-oxabicyclo[4.1.0]heptane	6	112.3	119.9	124.0	120.4	118.7	<i>d</i>
7-Dimethoxyphosphoryl-7-phenylnorcaradiene	6	111.1	119.8	120.3	116.8	116.5	<i>e</i>
2,5-Dichloro-7-dimethoxyphosphoryl-7-phenylnorcaradiene	6	110.4	119.6	119.0	115.5	116.2	<i>f</i>
<i>exo</i> -7-Chloro-7-phenyl-2,5-dioxabicyclo[4.1.0]heptane	6	111.1	121.1	119.8	120.5	118.9	<i>g</i>
2,5-Dimethyl-7,7-dicyanonorcaradiene	6	108.1	118.4	117.5	118.8	118.1	<i>h</i>
Axivalin hydrate	6	107.9	118.4 (116.4)	119.7	118.8 (115.8)	121.9	<i>i</i>
Benzocyclopropapyran	6	110.2	120.7 (123.4)	123.1	115.9 (116.2)	122.0	<i>j</i>
6-Oxo-3 α ,5-cycloandrostan-17-yl <i>p</i> -bromobenzoate	5	111.5	115	120 (117)	103	112 (114)	<i>k</i>
6-Oxo-3 β ,5-cycloandrostan-17-yl acetate	5	111.5	115.9	118.4 (114.6)	107.6	108.8 (129.9)	<i>k</i>
6,6-Diphenyl-3,3-diethyl-3-azabicyclo[3.1.0]hexane bromide	5	115.0	120.8	118.7	107.5	106.4	<i>l</i>
<i>exo-anti</i> -Tricyclo[3.1.1.0 ^{2,4}]heptan-6-yl <i>p</i> -bromobenzoate	5	116			100	98	<i>m</i>
<i>anti</i> -8-Tricyclo[3.2.1.0 ^{2,4}]octyl <i>p</i> -bromobenzenesulfonate	5	117	119.4	119.9			<i>n</i>
1-Cyanosemibullvalene	5	116.7	104.8	120.7	104.9	105.7	This work
	5	116.2	104.9	120.5	104.8	106.1	work

^a R. Karlsson, *Acta Crystallogr., Sect. B*, **32**, 2609–2614 (1976). ^b R. A. Kershaw, Ph.D. Thesis, Ohio State University, 1974. ^c G. R. Clark and G. J. Palenik, *J. Chem. Soc., Perkin Trans. 2*, 194–197 (1973). ^d G. W. Henslee, J. D. Woodyard, and J. D. Oliver, *Acta Crystallogr., Sect. B*, **32**, 2880–2883 (1976). ^e G. Maas, K. Fischer, and M. Regitz, *ibid.*, **30**, 1140–1145 (1974). ^f G. Maas, K. Fischer, and M. Regitz, *ibid.*, **30**, 2853–2860 (1974). ^g J. D. Oliver, G. Henslee, and P. E. Rush, *ibid.*, **32**, 2274–2278 (1976). ^h C. J. Fritchie, Jr., *Acta Crystallogr.*, **20**, 27–36 (1966). ⁱ G. D. Anderson, R. S. McEwen, and W. Herz, *Acta Crystallogr., Sect. B*, **29**, 2783–2789 (1973). ^j L. J. Guggenberger and R. A. Jacobson, *ibid.*, **25**, 888–894 (1969). ^k R. C. Pettersen, O. Kennard, and W. G. Dauben, *J. Chem. Soc., Perkin Trans. 2*, 1929–1935 (1972). ^l F. R. Ahmed and E. J. Gabe, *Acta Crystallogr.*, **17**, 603–608 (1964). ^m S. Masamune, R. Vukov, M. J. Bennett, and J. T. Purdham, *J. Am. Chem. Soc.*, **94**, 8239–8241 (1972). ⁿ A. C. Macdonald and J. Trotter, *Acta Crystallogr.*, **18**, 243–249 (1965).

toward coplanarity of the individual π systems and a shortened C(1)–C(6) distance. Since these systems provide their own difficulties to proving whether the C(1)···C(6) contact is attractive or repulsive, the more appropriate comparison is afforded by the cyclophanes, which do not undergo such rearrangements.

The very short contacts between the directly opposed π -orbital lobes in cyclophane compounds are invariably accompanied by very severe bond distance and bond angle distortions (e.g., C(2) is displaced 0.12 Å from the plane of C(1)–C(6)–C(4)–C(3), and C(7)–C(8) is stretched to 1.568 (1) Å).³³ One could argue that the π lobes in the semibullvalenes are not opposed head-on, as in the cyclophane systems, but are angled toward a point substantially below the line of centers C(4)···C(6), as shown in Figure 6a, thus considerably reducing the magnitude of their interaction. A semiquantitative measure of the interpenetration of these p- π orbitals is provided by the size of the overlap integrals of the opposed p-orbital wave functions.³⁴ Implicit in such an overlap calculation are the assumptions that (1) the orientation of the orbitals can be accurately specified, (2) the orbitals contribute fully to the ground state molecular wave function, (3) they are fully populated, and (4) we have chosen the appropriate signs for the orbital wave functions. Assuming the validity of (1), (2), and (3)³⁵ and choosing opposite signs for the wave functions (antibonding configuration) oriented as in Figure 6, we find the value of the overlap integrals³⁶ to be –0.09 for 1-cyanosemibullvalene and –0.10 for [2.2]metacyclophane. The

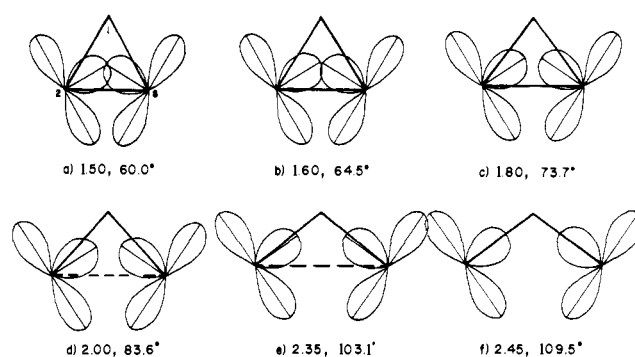


Figure 6. Position and orientation of orbitals of atoms C(2) and C(8), projected onto the plane C(1)–C(2)–C(8), as a function of the C(2)–C(8) interatomic separation. The C(2)–C(8) distance (Å) and the C(2)–C(1)–C(3) angle are given for (a) the formal structure VIIa, (b) geometry close to that observed for 1-cyanosemibullvalene, (c) a point close to the symmetric transition state, (e) the geometry observed for the C(4)–C(5)–C(6) end of 1-cyanosemibullvalene, and (f) the formal structure VIIb.

magnitudes of these numbers are comparable; that we do not observe in 1-cyanosemibullvalene the severe bond length–bond angle distortions expected for a repulsive interaction of this size, but in fact the contrary, that (1) the dihedral angles are not unusual, (2) the C(4)–C(5)–C(6) angle is compressed rather than expanded, and (3) the cyclopentene rings have less pucker than normal, lead us to conclude that rather than a

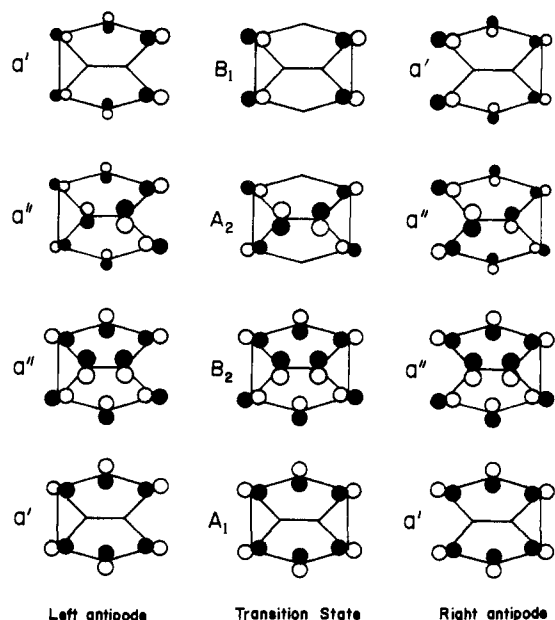


Figure 7. Highest occupied symmetry orbitals for semibullvalene. Symmetry orbitals constructed from simple basis consisting of one *p* orbital from each carbon atom: orbital lobes inside a five-membered ring should be viewed as being above the ring and roughly perpendicular to it, while lobes outside a ring are similarly below it. The transition state has C_{2v} symmetry.

repulsive, nonbonding or antibonding interaction, there exists an attractive, bonding interaction between C(4) and C(6).

It remains to be shown that the very long C(2)–C(8) bond is a consequence of the nascent bond formation between C(4) and C(6). Intuitively, one can see that this is likely to be so by considering the observed structure to be resonance combination of, say, 90% of the formal structure VIIa and 10% of the formal structure VIIb. This viewpoint is especially attractive because VIIa and VIIb are of course the antipodes of the internal Cope rearrangement, and such an argument is consistent with the ease of the rearrangement. Since the bishomoaromatic transition state can be viewed as the resonance average of VIIa and VIIb, then the observed geometry for 1-cyano-semibullvalene can be interpreted as a molecular configuration at some point along the reaction path between the formal structure VIIa and the symmetrical transition state. To the extent that the observed structure is along the Cope rearrangement path toward the transition state, then to that extent it must possess homoaromatic character.

Quantitative assessment of the magnitude of the homoaromatic, or "through-space", stabilization, analogous to the resonance stabilization energy in aromatic compounds, is difficult because hyperconjugative, through-bond effects are also operative, and only the net result, namely, the magnitude of the splitting of otherwise degenerate molecular energy levels, can be measured spectroscopically.³⁷ An alternative index of the extent of homoaromatic character would be the "bond order" for the C(4)–C(6) interaction. Empirical bond order–bond length curves are unfortunately unreliable for highly strained or small ring systems because of the unusual orientations of the bonding orbitals. Although we are confident of a significant homoaromatic contribution in 1-cyano-semibullvalene, the high degree of localization of the C(3)–C(4) and C(6)–C(7) double bonds argues for an upper limit of perhaps 0.1 (viz., our overlap calculation) for the C(4)–C(6) "bond order".

Both the magnitude of the through-space effect and the C(4)–C(6) bond order can be calculated³⁸ given accurate molecular orbital wave functions for the molecule. The only reported calculations are those of Hoffmann and Stohrer⁴ and

Dewar,^{4b,39} the former at the extended Hückel level and the latter at the MINDO/2 and MINDO/3 levels of approximation. The Hückel calculations were based on assumed or only partially optimized geometries and the full details of the geometry optimization and wave functions of the MINDO studies were not reported. We have consequently begun examining the 1-cyano- and semibullvalene rearrangement pathways using the minimum basis PRDDO method⁴⁰ and the observed x-ray coordinates for the initial geometry. Full geometry optimization of the ground state satisfyingly reproduces the observed structure.

Although this work is not complete, some qualitative statements can be made about the changes that occur in the course of the rearrangement and how these reflect on our understanding of the ground-state geometry. For the purpose of illustration we can conveniently, and reasonably accurately, consider all of the carbon atoms to be sp^2 hybridized. Movement along the reaction pathway consists principally of concerted displacements of C(4) and C(6) toward each other and of C(2) and C(8) outward, causing the five-membered rings to become somewhat more planar as the transition state is approached and the C(3)–C(4) and C(6)–C(7) double bonds to delocalize into two strongly interacting allylic systems. The reorientations of the involved orbitals as the reaction progresses are more subtle but equally important: initially aligned in classical Walsh orbital fashion, toward the center of the cyclopropane ring, the sp^2 lobes of C(2) and C(8) rotate about the C(2)–C(3) and C(8)–C(7) bonds so as to point toward C(1) (Figure 6). The dissolution of the exocyclic cyclopropane Walsh orbital overlaps is compensated by the formation of conventional sp^2 – sp^3 σ bonds to a rehybridized C(1), and by the incipient formation of the allylic systems. The orientations of C(4) and C(6), being coupled with C(2) and C(8), change simultaneously but in the opposite directions. It can be seen from purely symmetry arguments that the p_z orbital involvements of C(3) and C(7) in the top two HOMO's (and consequently the extent of localization of the double bonds) are critically sensitive to the position along the reaction path, being zero at the transition state and opposite in sign at the antipodes of the rearrangement (Figure 7). Why then do we not find significant changes in the C(2)–C(3) and C(3)–C(4) bond distances in the 1-cyano-semibullvalene crystal structure? The answer is that the C(2)–C(8) and C(4)–C(6) distances are simply much more sensitive functions of the bond order; the bond distance–bond order relationship is strongly nonlinear in the range $0 < \text{B.O.} < 1$. In very crude fashion we can estimate the C–C distances by taking the average of the distances of the formal resonance structures, weighted with the percent contribution of each. Since we have estimated an upper limit of 9–10% of form VIIb, let us take the weights as 0.91 for structure VIIa and 0.09 for VIIb:

C(2)–C(8)	1.59 Å	$(1.51 \times 0.91 + 2.45 \times 0.09)$
C(4)–C(6)	2.36 Å	$(2.45 \times 0.91 + 1.51 \times 0.09)$
C(2)–C(3)	1.33 Å	$(1.32 \times 0.91 + 1.48 \times 0.09)$
C(3)–C(4)	1.47 Å	$(1.48 \times 0.91 + 1.32 \times 0.09)$

The distances are remarkably close to the observed values, and the differences between the values predicted for C(2)–C(3) and C(3)–C(4) and their "normal" values are comparable with the error of the measurements.

Finally, we wish to note that, although we hesitate to call the C(4)–C(6) interaction in 1-cyano-semibullvalene a bond because of its very fragility, it would, in more favorable circumstances (e.g., a C–C distance of 2.0 Å), be technically correct to do so, inasmuch as it is a simple extension of the term "bond" to fractional orders less than unity. Where it is warranted, the term "partial bond" seems to us most appropriate. Since "partial bonds" are common to every bond-making or bond-breaking event, the careful study of such unusual cases

in stable molecules is well justified, and with the results of theory should lead to a better understanding of the geometrical changes in chemical reactions. Further accurate studies on a number of related molecules are currently in progress.

Acknowledgments. We thank Professor L. A. Paquette for his generous gift of the crystals of the title compound, the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their support, and the Ohio State University Instruction and Research Computer Center for their generous gift of computer time.

Supplementary Material Available: Tables of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

References and Notes

- Hoffmann and R. B. Woodward, *Science*, **167**, 825–831 (1970).
- For example, D. Ginsburg, *Acc. Chem. Res.*, **5**, 249–256 (1972); J. Haywood-Farmer, *Chem. Rev.*, **74**, 315–350 (1974).
- M. J. S. Dewar and W. W. Schoeller, *J. Am. Chem. Soc.*, **93**, 1481–1482 (1971).
- (a) R. Hoffmann and W. D. Stohrer, *J. Am. Chem. Soc.*, **93**, 6941–6948 (1971), (b) M. J. S. Dewar and D. H. Lo, *ibid.*, **93**, 7201–7207 (1971).
- A. K. Cheng, F. A. L. Anet, J. Mioduski, and J. Meinwald, *J. Am. Chem. Soc.*, **96**, 2887–2891 (1974).
- L. A. Paquette and W. E. Volz, *J. Am. Chem. Soc.*, **98**, 2910–2917 (1976).
- L. A. Paquette, W. E. Volz, M. A. Beno, and G. G. Christoph, *J. Am. Chem. Soc.*, **97**, 2562–2563 (1975).
- U. W. Arndt and B. T. M. Willis, "Single Crystal Diffraction", Cambridge University Press, New York, N.Y., 1966, p 287.
- W. R. Busing and H. A. Levy, *J. Chem. Phys.*, **26**, 563–568 (1957).
- $R_1 = \frac{\sum |F_o| - |F_{av}|}{\sum |F_o|}$, $R_2 = \frac{\sum [(F_o^2 - F_{av}^2)^2 / \sigma^2 (F_o^2 - F_{av}^2)]}{\sum [F_{av}^4 / \sigma^2 (F_o^2 - F_{av}^2)]^{1/2}}$
- E. R. Howells, D. C. Phillips, and D. Rogers, *Acta Crystallogr.*, **3**, 210–214 (1950).
- G. Germain, P. Main, and M. M. Woolfson *Acta Crystallogr., Sect. B*, **26**, 274–285 (1970).
- A. C. Larson, *Acta Crystallogr.*, **23**, 664–665 (1967).
- The function minimized in the least-squares refinement was $\sum \{F_o^2 - F_c^2\}^2 / \sigma^2 (F_o^2)$, $R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$, $R_w = \frac{\sum w(F_o^2 - F_c^2)^2}{\sum w F_o^4}^{1/2}$ where $w = 1/\sigma^2(F_o^2)$. The "goodness of fit" is defined as $\{\sum w(F_o^2 - F_c^2)^2 / (n_o - n_p)\}^{1/2}$. Atomic form factors for C and N were taken from the International Tables,¹⁵ and that for hydrogen from Stewart, Davidson, and Simpson.¹⁶
- "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, 1962, pp 202–203.
- R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175–3187 (1965).
- S. C. Abrahams and E. T. Keve, *Acta Crystallogr., Sect. A*, **27**, 157–165 (1971).
- See paragraph at end of paper regarding supplementary material, which consists of (I) observed and calculated structure factor amplitudes; (II) thermal motion librational model parameters; (III) results of least-squares planes calculations; and (IV) interatomic contacts of less than 3.5 Å.
- V. Schomaker and K. N. Trueblood, *Acta Crystallogr., Sect. B*, **24**, 63–76 (1968).
- R. F. Picone, M. T. Rogers, and M. Newman, *J. Chem. Phys.*, **61**, 4808–4813 (1974).
- A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179–190 (1949).
- W. A. Bennett, *J. Chem. Educ.*, **44**, 17–24 (1967); R. Hoffmann, *Tetrahedron Lett.*, 2907–2909 (1970).
- For example, M. Charton in "The Chemistry of Alkenes", Vol. II, J. Zabricky, Ed., Wiley-Interscience, New York, N.Y., 1970, Chapter 10, pp 511–610.
- (a) R. E. Long, H. Maddox, and K. N. Trueblood, *Acta Crystallogr., Sect. B*, **25**, 2083–2094 (1969); (b) A. Hartman and F. L. Hirschfeld, *ibid.*, **20**, 80–82 (1966); (c) C. J. Fritchie, *ibid.*, **20**, 27–36 (1966).
- O. Bastiansen, F. N. Fritsch, and K. Hedberg, *Acta Crystallogr.*, **17**, 538–543 (1964).
- Y. C. Wang and S. H. Bauer, *J. Am. Chem. Soc.*, **94**, 5651–5657 (1972).
- The complexity and low symmetry of the molecule did not permit optimization of all the independent geometry parameters simultaneously in their study; indeed, constraints on two or more parameters were required for convergence of their least-squares procedure to be achieved at all. Ten models, differing in which 2 of 14 parameters were constrained, each were found to give satisfactory agreement with the observed radial distribution function. The constraints consisted chiefly of the imposition of equality on the bond distances C(1)–C(5), C(1)–C(2), and C(4)–C(5) or C(2)–C(3). We are consequently inclined to view the results as approximate. No estimates of the errors in the derived structure were given. However, a measure of the reliability of their results is suggested by the range of values of the bonding parameters for the ten models: C₁–C₅, 0.030 Å; C₁–C₂, 0.030 Å; C₄–C₅, 0.031 Å; C₂–C₃, 0.046 Å; and C₂–C₆, 0.032 Å. These ranges recommend esd's of at least 0.015 Å for the distances in Figure 5.
- M. I. Davis and T. W. Muecke, *J. Phys. Chem.*, **74**, 1104–1108 (1970).
- M. Traetteberg, *J. Am. Chem. Soc.*, **86**, 4265–4270 (1964).
- R. E. Davis and A. Tullinsky, *J. Am. Chem. Soc.*, **88**, 4583–4588 (1966).
- M. Doblér and J. D. Dunitz, *Helv. Chim. Acta*, **48**, 1429–1440 (1965).
- C. J. Brown, *J. Chem. Soc.*, 3278–3285 (1953).
- (a) D. J. Cram and J. M. Cram, *Acc. Chem. Res.*, **4**, 204–213 (1971), (b) Y. Kai, N. Yasuoka, and N. Kasai, *Acta Crystallogr., Sect. B*, **33**, 754–762 (1977).
- L. A. Paquette, T. G. Wallis, T. Kempe, G. G. Christoph, J. P. Springer, and J. Clardy, *J. Am. Chem. Soc.*, **99**, 6946–6954 (1977).
- The double bonds C(3)–C(4) and C(6)–C(7) are well localized and essentially planar; the geometry recommends fully occupied p–π lobes perpendicular to the C(2)–C(3)–C(4)–C(5) and C(5)–C(6)–C(7)–C(8) planes. For [2.2]-metacyclophane the orientations of the p orbitals are probably accurate, but the hybridization and orbital population are certainly somewhat altered (see ref 33) due to the alterations from normal benzene geometry. The assumptions (2) and (3) are thus likely to be less accurate for [2.2]metacyclophane than for 1-cyanosemibullvalene.
- R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, **17**, 1248–1267 (1949).
- R. Askani, R. Gleiter, E. Hellbronner, V. Hornung, and H. Musso, *Tetrahedron Lett.*, 4461–4466 (1971).
- E. Hellbronner and A. Schmelzer, *Helv. Chim. Acta*, **58**, 936–967 (1975).
- R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1294–1301 (1975).
- T. A. Halgren and W. N. Lipscomb, *J. Chem. Phys.*, **58**, 1569–1591 (1973).

Mechanism of Formation of Grignard Reagents

E. A. Vogler,* R. L. Stein, and J. M. Hayes¹

Department of Chemistry, Indiana University,
Bloomington, Indiana 47401. Received November 11, 1977

Abstract. Experiment shows that there is no carbon kinetic isotope effect in the formation of CH₃MgI from CH₃I ($k_{12}/k_{13} = 0.9992$, $\sigma = 0.0005$). Calculations indicate that an observable isotope effect should accompany this reaction if it proceeds by an inner-sphere electron-transfer mechanism in which breakage of the carbon-halogen bond must be involved in the rate-determining step. Accordingly, it is proposed that the alternative mechanism must be followed, with the rate-determining step involving formation of a radical-ion pair by outer-sphere electron transfer from the magnesium to the organic halide.

The formation of the Grignard reagent from alkyl halide and magnesium is of continued mechanistic interest.^{2–8} It is generally concluded from stereochemical, kinetic, and CIDNP studies that alkyl radicals are intermediates. However, the route by which radicals are formed and the relevance of such

an intermediate to the formation of the Grignard reagent remains largely undefined.

Two alternative rate-determining steps can be envisioned. One involves electron transfer from the magnesium surface (here represented in monomeric form for simplicity) to the