note that the difference between eq A17 and A19 need not be interpreted as a consequence of delocalization of the $^3\Psi_{A1}$ state; instead, as outlined above, it results in this simple case from the splitting of the excited-state degeneracy in forming the correct localized $^3\Psi_s$ and $^3\Psi_{A1}$ functions. Moreover, the dependence on the exchange parameters is the same in any case. Thus the qualitative considerations of mechanisms of contact coupling do not depend on whether a sum over excited states or an average energy is employed. Which approach is better for deriving quantitative results is not clear and will require detailed calculations on simple systems for its elucidation.[50]

[50] For some discussion of the difficulties, see D. S. Bartow and J. W. Richardson, *J. Chem. Phys.*, **42**, 4018 (1965); and Y. Kato and A. Saika, *ibid.*, **46**, 1975 (1967).

Structures and Conformations of the Cyclohexadienes

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Abstract: The structures of 1,3-cyclohexadiene and 1,4-cyclohexadiene in the gas phase were determined by electron diffraction. Interatomic distances and mean-square amplitudes of vibration were evaluated. In neither molecule are the carbon atoms coplanar; the structure found for the 1,3 isomer is in good agreement with the available microwave data. Of particular interest was the magnitude of the dihedral angle in the 1,4 isomer; it was found to be 159.3°. Here the copolanar conformation was expected from estimates of nonbonded repulsions. This pair of isomers provides critical test structures for the several sets of empirically parametrized potential functions proposed for calculating strain energies of cyclic hydrocarbons.

Conclusions regarding the structure of 1,4-cyclohexadiene are contradictory. Raman and ir spectra[1] have been interpreted in terms of a conformation which deviates only slightly from planar (D_{2h}). Crystal-structure analyses of two compounds which incorporate 1,4-C_6H_8 rings have been reported. In 9,10-dihydroanthracene[2] the ring is folded about the axis through the methylene carbon atoms with a dihedral angle of about 145°. On the other hand, the crystallographic data for 9,10-dihydro-1,2:5,6-dibenzoanthracene[3] show a centrosymmetric structure which eliminates the possibility of a folded 1,4-C_6H_8 ring. Dipole moment measurements of 1,4-dichloro-1,4-cyclohexadiene[4] led to reduced values of $\mu = 0.3$ or 0.42 D, depending on the correction assumed for atomic polarization; from these, dihedral angles of 152 and 160°, respectively, were derived. Dipole moment measurements on 1,4-C_6H_8[5] suggested a small dipole moment, $\mu = 0.13$ D, but the experimental error is too large to distinguish between the planar and boat conformations. Herbstein[6] concluded from semiempirical calculations that angle strain and steric interactions (H···H only) should lead to a minimum energy at a dihedral angle of 140°.

On the basis of chemical arguments Beckett and Mulley[7] suggested a nonplanar structure for the 1,3-cyclohexadiene ring in 9,10-dihydrophenanthrene. Butcher[8] reported microwave absorption data for 1,3-cyclohexadiene, using the normal isotopic species. When he assumed generally accepted bond lengths and angles, he could deduce a torsional angle τ (the angle by which one ethylene group is rotated relative to the other ethylene group about the C_2–C_3 bond; see Figure 7). From his experimental value for $(I_a + I_b - I_c)/2$, he found $\tau = 17.5 \pm 2°$.

Experimental Section

A very pure sample of 1,4-C_6H_8 was obtained from Dr Michael Gorfinkel, Institute of Organic Chemistry, University of Novosibirsk, to whom sincere thanks are due. Additional material and the 1,3 isomer were purchased from the K & K Laboratories (99% purity for 1,3-C_6H_8 and 95–99% for 1,4-C_6H_8). Single-step distillations from samples maintained at −35 and −25°, respectively, corresponding to the sample temperatures used for the electron diffraction photographs, gave material which was better than 99%, as checked by vpc.

For each compound three sets of photographs were taken: one at low voltage (*ca.* 25 kV) and at a long sample–plate distance (*ca.* 26 cm), and two sets at high voltage (*ca.* 75 kV) at the same distance and at a shorter distance (*ca.* 13 cm). The vapor pressures were kept at 3–4 torr. With liquid nitrogen cooled cryopumps situated above the gas nozzle the ambient pressure in the diffraction chamber was maintained at about 1.5×10^{-5} torr during the exposures. The sample-plate distance (L) and wavelength (λ) were determined by a least-squares fit on six measured ring diameters of several MgO calibration photographs. The maximum standard deviation in q(ring) values was 0.0012 in the case of high voltage–short distance: $q = (40/\lambda)\sin(\theta/2)$.

Density–Intensity Calibration. Each set of photographs consisted of four plates. Two plates of each set, with a time–exposure ratio of about 1/1.5 were selected for the density–intensity calibration, following the procedure proposed by Bauer and Kimura.[9] The optical densities of the selected plates were between 0.5 and 1.5. The first two coefficients of the power series, $I = D(1 + B_1D + B_2D^2)$, where D is the optical density and I the corresponding intensity, were determined by a least-squares procedure. The B_i's

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[1] (a) H. Gerding and F. A. Haak, *Rec. Trav. Chim.*, **68**, 293 (1949); (b) H. D. Stidham, *Spectrochim. Acta*, **21**, 23 (1965).

[2] W. G. Ferrier and J. Iball, *Chem. Ind.* (London), 1296 (1954).

[3] J. Iball and D. W. Young, *Acta Cryst.*, **11**, 476 (1958).

[4] I. Miyagawa, Y. Morino, and R. Riemschneider, *Bull. Chem. Soc. Japan*, **27**, 177 (1954).

[5] W. D. Kumler, R. Boikess, P. Bruck, and S. Winstein, *J. Am. Chem. Soc.*, **86**, 312 (1964).

[6] F. H. Herbstein, *J. Chem. Soc.*, 2292 (1959).

[7] A. H. Beckett and B. A. Mulley, *Chem. Ind.* (London), 146 (1955).

[8] S. S. Butcher, *J. Chem. Phys.*, **42**, 1830 (1965); also, G. Luss and M. D. Harmony, *ibid.*, **43**, 3768 (1965).

[9] K. Kimura and S. H. Bauer, *ibid.*, **39**, 3171 (1963).

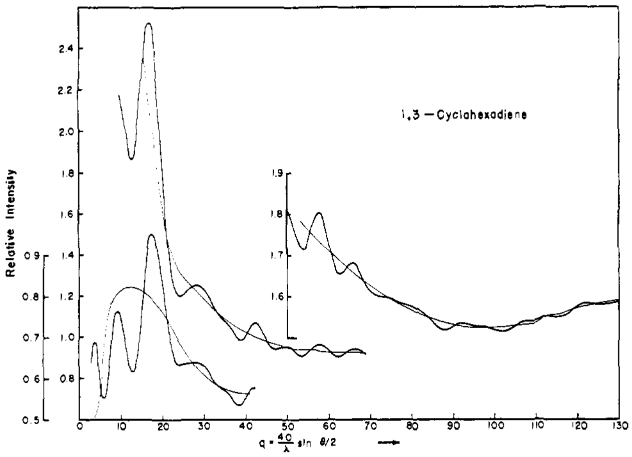

Figure 1. Reduced scattering intensity as a function of q for 1,3-cyclohexadiene derived from three sets of plates.

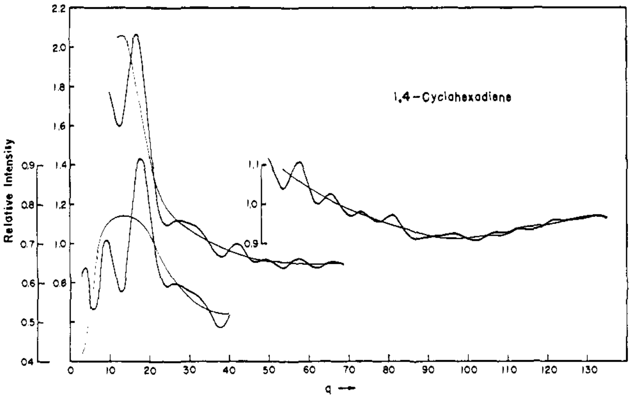

Figure 2. Reduced scattering intensity as a function of q for 1,4-cyclohexadiene derived from three sets of plates.

show a rather strong dependence on the energy of the electrons and a small dependence on the slightly varying development conditions for the photographic plates (Table I).

Table I

	kV	B_1	B_2
1,3-C_6H_8	25	0.066	0.0035
	75	0.123	0.0103
1,4-C_6H_8	25	0.077	0.0045
	75	0.135	0.0118

Scattered Intensity Curves. Photographic density traces were obtained with a modified Jarrell-Ash microphotometer. The photographic plates were rotated during recording at about 600 rpm. Transmittances are converted to densities; flatness and intensity corrections were then applied. The ranges of q values for the three sets of data were 3-41, 5-72, and 12-135 Å^{-1}. A trial background I_B was drawn in for each set (Figures 1 and 2) and the molecular intensity curves, $M(q) = (I_{\text{obsd}} - I_B)/I_B$, were spliced with an overlap region of 10 q values. These experimental molecular intensity curves and the theoretical molecular intensity curves for the final models are shown in Figure 3 for 1,3-cyclohexadiene and 1,4-cyclohexadiene.

The Radial Distribution Curves. The electronic contribution to the molecular scattering, calculated for a trial model, was subtracted from the experimental $qM(q)$, and the refined radial distribution (RDR) evaluated in the usual manner by a Fourier transform, after multiplying the nuclear contribution to the molecular scattering intensity (corrected by adding the calculated portion for q = 0-3 Å^{-1}) with the damping factor $\exp(-\gamma q^2)$, $\gamma = 0.00012$. In the initial trials, fluctuations in the RDR curves over regions below

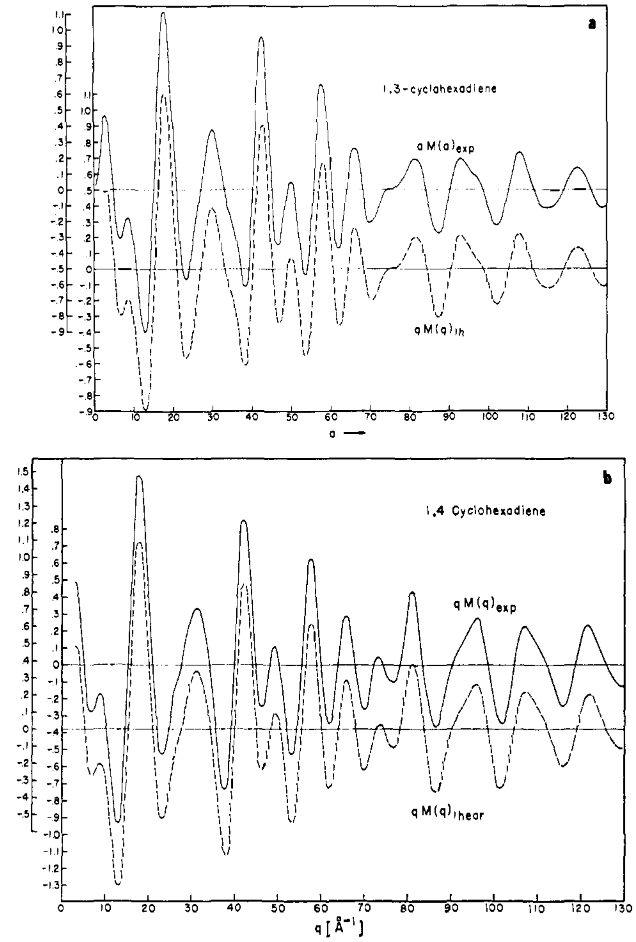

Figure 3. Comparison of experimental and theoretical (best models) molecular intensity patterns.

and above the shortest and longest distances present in the molecule are mainly due to an erroneous background, and to some extent to an incorrect trial model, as well as to errors in the experimental intensities and finite range of integration. As customary, a refined background was obtained by reinverting these extraneous fluctuations. The new background was smoothed manually and the procedure was repeated several times, concurrently with refinement of the model. The geometrical parameters and mean square amplitudes were adjusted until good agreement between the theoretical and experimental RDR was obtained. The RDR curves for 1,4-cyclohexadiene and 1,3-cyclohexadiene are shown in Figures 4 and 5, resolved in terms of the principal contributing peaks.

Least-Squares Analysis. The geometrical parameters and mean-square amplitudes from RDR analysis were used as trial values for the least-squares refinement of structures based on the reduced intensity curves. In the case of 1,4-C_6H_8 the least-squares procedures converged, fulfilling the standard requirements for convergence to a true minimum.[10] In the first minimization sequence all the geometric parameters and the l_{ij}(C···C)'s were allowed to vary, maintaining reasonable values for the l_{ij}(C···H). Then, the former set was constrained to the optimized values and the latter allowed to vary. It was found that some amplitudes for nonbonded C···H distances converged toward unreasonable magnitudes as long as the hydrogen atoms of the ethylene groups were constrained to be coplanar with the ethylenic carbons. When this constraint was released and a parameter for the out-of-plane angle of the hydrogen atoms H_1, H_2, H_4, H_5 (see Figure 6) introduced, the corresponding mean-square amplitudes assumed reasonable values (Table III). The out-of-plane angle was found to be 4.8°. The best set of values for the geometric parameters of 1,4-cyclohexadiene are listed in Table II; the l_{ij}'s are summarized in Table III and the error

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(10) J. L. Hencher, D. W. J. Cruickshank, and S. H. Bauer, *J. Chem. Phys.*, **48**, 518 (1968); J. L. Hencher and S. H. Bauer, *J. Am. Chem. Soc.*, **89**, 5527 (1967).

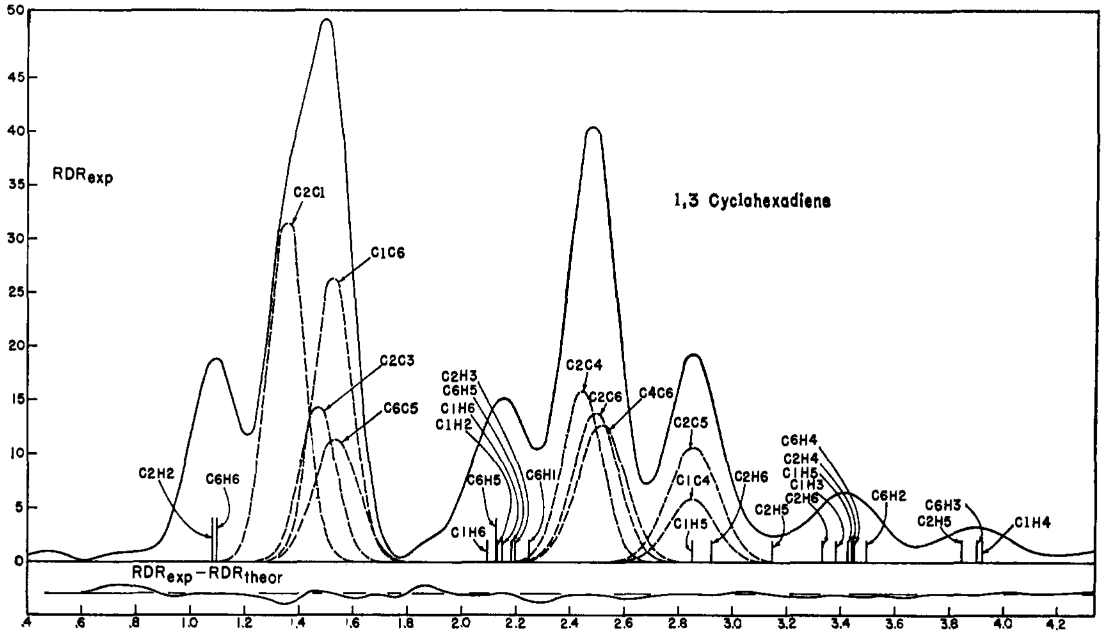

Figure 4. Refined radial distribution curve for 1,3-cyclohexadiene.

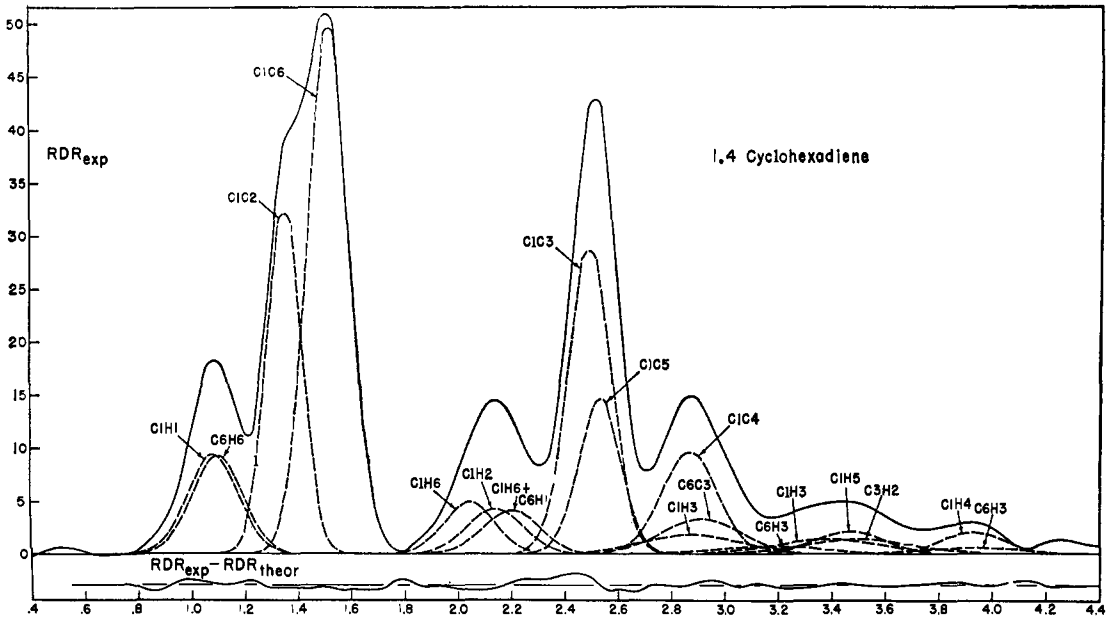

Figure 5. Refined radial distribution curve for 1,4-cyclohexadiene.

matrix[11] for the converged structure is reproduced in Table IV. The assigned error limits are justified below. The large l_{ij}'s for the C···H scattering contributions appear reasonable when compared with the corresponding distance changes which occur when the molecule flips from one folded conformation into the opposite one (Figure 7); the l_{ij}'s increase roughly linearly with the corresponding Δr_{ij}'s. The latter are far larger than any increments anticipated from shrinkage effects.

A similar procedure was followed in deducing the optimum set of parameters for the 1,3 isomer. However, in this case the correlation between some parameters, namely C_1C_6 and C_6C_5 (Figure 8), was close to unity, particularly for fixing the positions of the H atoms. This did not allow convergence. The parameters which set the positions of the H atoms were therefore constrained, and only the geometric parameters and mean-square amplitudes for the carbon ring were refined in the first step. In the second step the former parameters were in turn constrained while the parameters which fixed the positions of hydrogen atoms were refined. Here, the mean-square amplitudes for nonbonded carbon–hydrogen distances were estimated from the RDR curve. They could not be evaluated from a least-squares analysis. The geometric parameters are summarized in Table V, the l_{ij}'s are given in Table VI, and the corresponding error matrix is in Table VII.

Error Limits. The most significant sources of error arise from those inaccuracies in the experimental molecular intensity curve which extend over a region of q comparable to $\pi/\langle r_{ij}\rangle$. These may be due to unknown flats or bumps in the sector, from inadvertent mismatch in the splicing of data taken over different q ranges, or from inaccuracies in the conversion of photographic density to intensity. Errors in the scale factor which affect linearly all distances are due to improper calibration of accelerating voltage and the nozzle-plate distance. Corrections for finite sample distribution above the nozzle, the presence of small impurities in the sample, incorrect density–intensity calibration, extraneous background,

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[11] Y. Morino, K. Kuchitsu, and Y. Murata, *Acta Cryst.*, 16, A129 (1963); K. Hedberg and M. Iwaski, *ibid.*, 17, 529 (1964).

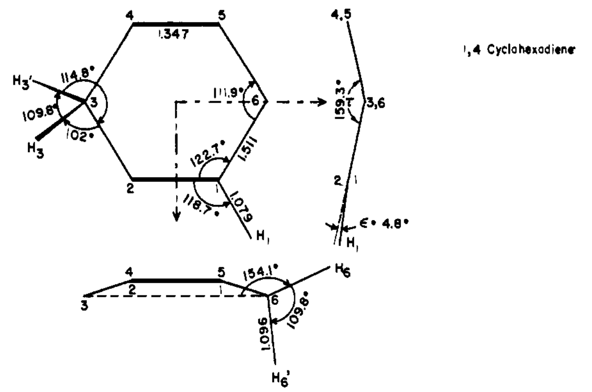

Figure 6. Projections of the structure for 1,4-cyclohexadiene.

lack of accurate form factors, etc., are difficult to estimate quantitatively. They are assumed to have little influence on the structural parameters, but they do affect the mean-square amplitudes.

Table II. Geometric Parameters for 1,4-C_6H_8

	This work	Dallinga and Toneman[a]	(Test) planar
C_1C_2, Å	1.347 ± 0.004	1.334 {0.002}	1.347
C_1C_6, Å	1.511 ± 0.004	1.496 {0.001}	1.511
C_1H_1, Å	1.079 ± 0.010	1.103 {0.003}	1.079
C_6H_6, Å	1.096 ± 0.012	1.114 {0.003}	1.096
$\angle C_2C_1C_6$, deg	122.7 ± 0.3	123.4 {0.2}	123
Dihedral τ, deg	159.3 ± 0.7	180 (assumed)	180
$\angle C_2C_1H_1$, deg	118.7 ± 1.2	123.4 {2.7}	118.7
$\angle C_3C_6H_6$, deg	154.1 ± 4	128.5[c]	125.1
$\angle H_6C_6H_6'$, deg	109.8 ± 4	103 {2}	109.8
ϵ[b]	4.8 ± 3	0	0
$\angle C_1C_6C_5$[c]	111.9	113.3 {0.3}	114
$\angle H_3C_3C_2$[c]	102		108.3

[a] Values in braces indicate standard deviations, not error limits. [b] Out of plane, for C—H bonds on C=C. [c] Derived from above.

Table III. Mean-Square Amplitudes (Å) for 1,4-C_6H_8

$l_{C_1C_2}$	0.041 ± 0.004	$l_{C_1H_3}$	0.265 ± 0.100
$l_{C_1C_6}$	0.057 ± 0.004	$l_{C_1H_3'}$	0.112 ± 0.040
$l_{C_1C_3}$	0.062 ± 0.008	$l_{C_1H_5}$	0.090 ± 0.020
$l_{C_1C_5}$	0.067 ± 0.015	$l_{C_1H_4}$	0.091 ± 0.025
$l_{C_1C_4}$	0.077 ± 0.007	$l_{C_6H_6}$	0.080 ± 0.010
$l_{C_6C_3}$	0.090 ± 0.020	$l_{C_6H_1}$	0.092 ± 0.025
$l_{C_1H_1}$	0.080 ± 0.010	$l_{C_6H_2}$	0.090 ± 0.025
$l_{C_1H_2}$	0.084 ± 0.020	$l_{C_6H_3}$	0.277 ± 0.150
$l_{C_1H_6}$	0.116 ± 0.035	$l_{C_6H_3'}$	0.186 ± 0.120
$l_{C_1H_6'}$	0.108 ± 0.015		

The uncertainties in the parameters due to imperfect fit of the experimental molecular intensity depend on the correlation between the parameters. For 1,4-C_6H_8 the correlations between most of the parameters (off-diagonal elements in error matrix) are much smaller than unity; hence the corresponding uncertainties are small. In this case the error arising from the calibration of q is the dominant factor in the error limit of bonded distances. A maximum standard deviation of 0.0012 in the ($L\lambda$) calibration introduces an error of about ±0.002 Å for the bonded interatomic distances. We have arbitrarily set the error limits at 0.004 Å in Tables II and V, provided the standard deviations (*i.e.*, diagonal elements of error matrices) are less than this value; otherwise they were set at twice the standard deviations.

In the 1,3-C_6H_8 ring, two bonded distances, C_1C_6 and C_6C_5 (Figure 8), are of comparable length (Table V) and several nonbonded C···H distances are very close together. This introduces correlations close to unity between some of the parameters, and there are consequent large uncertainties in the least-squares refinement results. The uncertainties are larger by a factor of 15 than the corrections of the respective parameters for one cycle, as the least-squares refinement approaches the minimum. These large uncertainties appear excessive in view of the over-all consistency of the analysis. Hence those magnitudes which are limited in precision by the scale factor were assigned errors ±0.004 Å as in Table II; those distance and angles which have high correlation factors were assigned error limits 1.5 times their calculated standard deviations (Table V). The uncertainties given by the least-squares refinement do not include errors due to finite sample distribution, extraneous background, density-intensity calibration, etc. Error limits for the mean-square amplitudes of the nonbonded C···H in 1,3-C_6H_8 are listed in Table VI; they were not refined by the least-squares procedure.

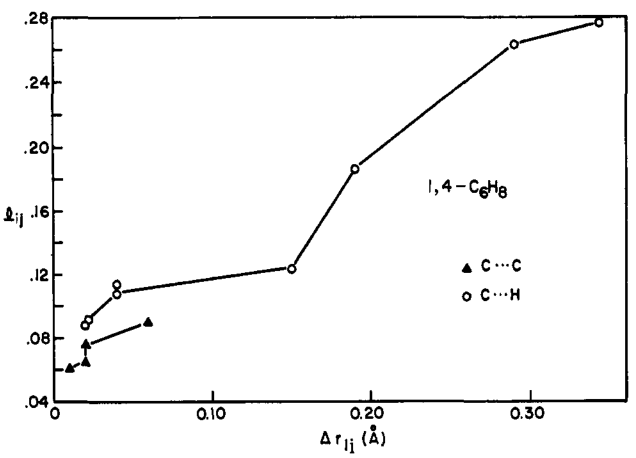

Figure 7. Observed correlation between the deduced magnitudes for various l_{ij}'s and the corresponding change in interatomic distance (Δr_{ij}) for passing from one bent conformation, through the planar structure, to the inverted conformation.

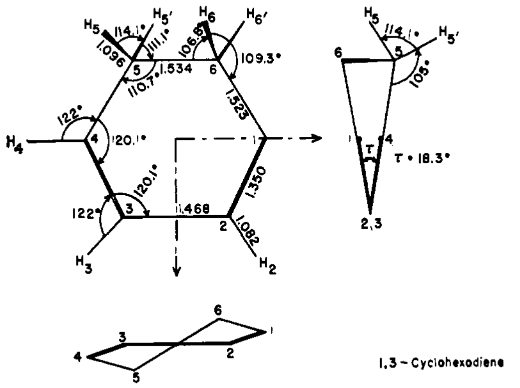

Figure 8. Projections of the structure for 1,3-cyclohexadiene.

Discussion of Structures

Butcher[8] assumed values for bond distances and angles to obtain an estimate of the torsional angle (τ) in the 1,3-cyclohexadiene. His structure was inserted as the first trial model for this isomer. It is interesting to note that his assumed bond angles and his estimated torsional angle proved to be in good agreement with our final results although C_1–C_6 and C_6–C_5 are 0.02 and 0.03 Å longer, respectively, than the magnitudes he assumed. The moments of inertia calculated from this structure determination are compared with the observed microwave values and those calculated by Butcher, in Table VIII. After this report was completed, an electron diffraction study of the 1,3 isomer was published by Dallinga and Toneman.[12] Visual inspection of their $I_m(s)$ (curve a) indicates essen-

[12] G. Dallinga and L. H. Toneman, *J. Mol. Struct.*, 1, 11 (1967).

Table IV. 1,4-Cyclohexadiene Error Matrix[a]

	C_1C_2	C_1C_6	$\angle C_1C_2C_6$	τ	$\angle C_3C_6H_6$	$\angle H_6'C_6H_6$	$\angle C_2C_1H_1$	C_1H_1	C_6H_6	l_{12}	l_{16}	l_{13}	l_{15}	l_{14}	l_{63}
C_1C_2	0.0006														
C_1C_6	0.0003	0.0005													
$\angle C_1C_2C_6$	−0.0005	−0.0005	0.0024												
τ	0.0014	0.0014	−0.0031	0.0073											
$\angle C_3C_6H_6$	0.0008	0.0011	−0.0015	0.0071	0.0384										
$\angle H_6'C_6H_6$	0.0015	0.0017	−0.0024	0.0093	0.0361	0.0390									
$\angle C_2C_1H_1$	−0.0009	−0.0008	0.0013	−0.0032	−0.0126	−0.0064	0.0102								
C_1H_1	−0.0003	0.0001	0.0012	0.0019	0.0092	0.0080	−0.0036	0.0951							
C_6H_6	0.0006	0.0002	−0.0012	−0.0017	−0.0081	−0.0061	0.0033	−0.0051	0.0058						
l_{12}	0.0001	0.0003	−0.0002	0.0008	0.0007	0.0009	−0.0005	0.0003	−0.0004	0.0005					
l_{16}	−0.0003	−0.0002	0.0003	−0.0007	−0.0002	−0.0007	0.0005	0.0002	−0.0003	0.0001	0.0004				
l_{13}	0.0005	0.0004	0.0017	−0.0035	−0.0038	−0.0048	−0.0011	−0.0012	0.0014	0.0001	−0.0003	0.0036			
l_{15}	−0.0008	−0.0007	−0.0026	0.0052	0.0057	0.0072	0.0023	0.0015	−0.0019	−0.0002	0.0004	−0.0054	0.0082		
l_{14}	0.0002	0.0002	−0.0022	0.0023	−0.0027	0.0026	0.0019	−0.0013	0.0013	0.0001	−0.0001	−0.0013	0.0021	0.0034	
l_{63}	0.0001	−0.0003	−0.0035	0.0017	0.0017	−0.0065	−0.0038	−0.0022	0.0022	−0.0002	−0.0001	−0.0006	0.0016	0.0046	0.0095

[a] Units for distances in Å; for angles in radians. $\sigma_{ij} = \text{sgn}[(BJ^{-1})_{ij}][([B]^{-1})_{ij}|\chi_R/(n_q - n_p)]^{1/2}$; $[B] \equiv [J]^t[w][J]$. χ_R is the sum of the squares of the residuals. n_q is the number of observations (= 126, at integral q's). n_p is the number of variable parameters (15). $[J]$ is the Jacobian matrix. $[w]$ is the weight matrix. $w = \exp[-w_1(q_1 - q)]$ for $q < q_1 = 20$. $w = 1$ for $q_1 < q < q_2$. $w = \exp[-w_2(q - q_2)]$ for $q > q_2 = 95$. w_1 and w_2 adjusted so that $w(q_{min}) = 0.1$ and $w(q_{max}) = 0.25$.

Table V. Geometric Parameters for 1,3-C_6H_8[a]

	This work	Butcher	Dallinga and Toneman
C_2C_3, Å	1.468 ± 0.014	1.47	1.468
C_2C_1, Å	1.350 ± 0.004	1.35	1.339
C_1C_6, Å	1.523 ± 0.016	1.50	1.494
C_6C_5, Å	1.534 ± 0.020	1.50	1.510
C_2H_2, Å	1.082 ± 0.010	1.086	1.07
C_6H_6, Å	1.096 ± 0.010	1.10	1.14
$\angle C_3C_2C_1$	120.13 ± 0.6	120.16	121.6
$\angle C_2C_1C_6$	120.14 ± 0.5	120.16	118.2
$\angle C_1C_2H_2$	122.0 ± 1.4	124	121
$\angle C_6C_1H_1$	122.0 ± 1.4	122	111
$\angle C_5C_6H_6$	106.8 ± 4.5	109.5	114
$\angle C_1C_6H_6$	109.3 ± 4.5	109.5	...
$\angle C_5C_6H_6'$	111.1 ± 4.5	109.5	...
$\angle C_1C_6H_6'$	105.0 ± 4.5	109.5	112
$\angle H_6C_6H_6'$[b]	114.1	109.5	99
$\angle C_1C_6C_5$[b]	110.7	110.5	111.5
τ,[b,c]	18.34	17.5	17

[a] Angles in degrees. [b] Derived parameters. [c] Torsional angle through which one ethylene group is rotated relative to the other about the C_2C_3 bond.

Table VI. 1,3-C_6H_8 Mean-Square Amplitudes

C_2C_3	0.045 ± 0.017	C_2H_6	0.095 ± 0.020
C_2C_1	0.044 ± 0.004	C_2H_5	0.100 ± 0.020
C_1C_6	0.051 ± 0.020	C_2H_6'	0.105 ± 0.020
C_6C_5	0.065 ± 0.020	C_2H_5'	0.100 ± 0.020
C_2C_4	0.055 ± 0.007	C_1H_6	0.085 ± 0.020
C_2C_6	0.066 ± 0.020	C_1H_5	0.100 ± 0.020
C_2C_5	0.079 ± 0.008	C_1H_6'	0.095 ± 0.020
C_1C_4	0.069 ± 0.010	C_1H_5	0.100 ± 0.020
C_4C_6	0.074 ± 0.017	C_1H_4	0.100 ± 0.020
C_2H_2	0.077 ± 0.010	C_6H_4	0.105 ± 0.020
C_2H_3	0.100 ± 0.020	C_6H_5	0.090 ± 0.020
C_2H_4	0.100 ± 0.020	C_6H_5'	0.095 ± 0.020

tial agreement with the reduced experimental molecular intensity curve [$qM(q)$], shown in our Figure 3a, except for $s < 5$, where significant differences appear between their experimental and theoretical curves. Our $qM(q)_{theor}$ is in better over-all agreement with our $qM(q)_{exp}$ and their curve a than is their curve b. The two electron diffraction structures and that proposed from the incomplete microwave data are compared in detail in Table V. One should note that Dallinga and Toneman tested many combinations of constraints on the structural parameters to deduce the most acceptable values by least-squares analysis of their data. Their final structure was obtained by inserting the microwave magnitudes of the moments of inertia in their program. For compatibility they introduced a scale factor which proved to be greater than unity, contrary to all previous correlations between electron diffraction and microwave scales,[13] and contrary to the anticipated difference between the two types of averaging intrinsic in these methods for structure determination.

At a somewhat later date, Dallinga and Toneman published their electron diffraction structure of 1,4-cyclohexadiene.[14] Again, most of the reduced experimental molecular intensity curves are in good agreement, but in this case there are significant differences not only in the low s region but also at $20 < s < 25$ (in Figure 3b; this corresponds to $60 < q < 80$). The

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(13) D. R. Lide, *Tetrahedron*, 17, 125 (1962).

(14) G. Dallinga and L. H. Toneman, *J. Mol. Struct.*, 1, 117 (1967).

Table VI 1,3-Cyclohexadiene Error Matrix

	C_2C_3	C_2C_1	C_1C_6	C_6C_5	$\angle C_3C_2C_1$	$\angle C_2C_1C_6$	l_{23}	l_{21}	l_{65}	l_{16}	l_{24}	l_{26}	l_{25}	l_{14}	l_{46}
C_2C_3	0.0096														
C_2C_5	0.0014	0.0004													
C_1C_6	−0.0192	0.0015	0.0111												
C_6C_5	0.0167	−0.0022	−0.0228	0.0130											
$\angle C_3C_2C_1$	−0.0145	−0.0015	0.0128	−0.0086	0.0080										
$\angle C_2C_1C_6$	0.0047	−0.0012	−0.0057	0.0056	−0.0013	0.0055									
l_{23}	0.0177	−0.0005	−0.0193	0.0186	−0.0126	0.0051	0.0088								
l_{21}	0.0041	0.0005	−0.0044	0.0039	−0.0030	0.0012	0.0043	0.0008							
l_{65}	−0.0212	0.0025	0.0245	−0.0248	0.0142	−0.0067	−0.0210	−0.0039	0.0146						
l_{16}	0.0187	−0.0013	−0.0200	0.0189	−0.0134	0.0053	0.0178	0.0037	−0.0232	0.0097					
l_{24}	0.0086	−0.0007	−0.0103	0.0108	0.0048	−0.0068	0.0088	0.0020	−0.0113	0.0091	0.0035				
l_{26}	0.0170	−0.0006	−0.0192	0.0193	0.0039	−0.0114	0.0168	0.0038	−0.0210	0.0174	0.0120	0.0111			
l_{25}	−0.0075	−0.0008	0.0054	0.0030	0.0103	−0.0079	−0.0061	−0.0016	0.0062	−0.0066	0.0047	0.0069	0.0044		
l_{14}	0.0099	0.0005	−0.0099	0.0085	−0.0080	0.0022	0.0092	0.0022	−0.0110	0.0096	0.0045	0.0094	−0.0080	0.0055	
l_{46}	−0.0129	0.0014	0.0162	−0.0175	−0.0072	0.0100	−0.0137	−0.0030	0.0177	−0.0140	−0.0104	−0.0193	−0.0067	−0.0082	0.0088

Table VIII. Moments of Inertia for 1,3-Cyclohexadiene

	Obsd	Butcher, calcd	This work
I_a	99.86	99.02	100.02
I_b	99.63	99.44	99.68
I_c	187.12	186.10	186.33

reasons for these discrepancies are not clear: they may be due to perturbations in the sectors as cut and to difficulties in drawing in appropriate backgrounds. Dallinga and Toneman reported that their least-squares reductions for three nonplanar models failed to converge completely. They then *assumed* that the structure was planar (D_{2h}) and refined it by testing various parameter constraints. For comparison their final interatomic distances are listed in Table II. In this isomer there is close agreement with respect to the bonded distances, but there are substantial differences with respect to bond angles. Our least-squares structure has C_{2v} symmetry (boat conformation) with $\tau = 159°$.

Two brief reports on the conformation of 1,4-cyclohexadiene have appeared recently. Garbisch and Griffith[15] have evaluated the allylic–allylic proton coupling constants for this isomer. Assuming a molecular geometry as close to classical as possible and the applicability of Karplus's theory[16] for σ–π interactions, they concluded that the molecule was nearly planar ($\tau \approx 172°$). A more substantive argument is based on an analysis of an absorption band assigned to the B_{2u} ring-puckering mode, at 108 cm^{-1}, by Laane and Lord.[17] From the structure of the Q branch they concluded that either the lowest energy conformation is planar and the out-of-plane potential function is a superposition of a negative quartic term on a quadratic function, or, if the out-of-plane conformation has the lowest energy, the barrier for inversion is relatively high (greater than 4 kcal/mole).

The nonplanarity of the 1,3-C_6H_8 ring is a consequence of the balance between minimization of bond angle strain, of torsional strain about the C_6–C_5 bond, and nonbonded repulsions. To make $\tau > 0$, rotation occurs about C_5–C_6, but in this motion the C_6H_5/C_5C_6, etc. distances remain essentially unaltered. Concurrently, conjugation is lost in the 1,3-butadiene group. The latter factor is not significant, but it possibly has some influence on ring conformation. The nonplanarity of 1,4-C_6H_8 also follows from balance of the above factors. Angle strain would be zero for near-tetrahedral values at C_3 and C_6 and 120° at the other carbon atoms; in such a structure the dihedral angle would be about 141°.

A number of empirical procedures have been proposed for estimating the magnitudes of energies involved in distorting molecules from specified "normal" structures. These may be used to compare the relative contributions for bond angle distortions and the nonbonded interactions between H···H, C···H, and C···C atom pairs for the nonplanar and planar conformations. The results depend sensitively on the potential functions used in the calculations, and in ring

[15] E. W. Garbisch, Jr., and M. G. Griffith, *J. Am. Chem. Soc.*, **90**, 3590 (1968).

[16] M. Karplus, *J. Chem. Phys.*, **33**, 1842 (1960).

[17] J. Laane and R. C. Lord, prepublication note; R. C. Lord, Abstracts, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, No. P-074.

compounds, on the assumed distribution of angle distortion between the C═C—C and C—C—C angles. During the past year four "second-generation" prescriptions have been proposed for estimating empirically the magnitudes of energies ascribed to bond stretching and angle distortions, nonbonded interactions, and torsional strains. Two of these[18,19] restricted their calculations to the parent and alkyl-substituted cycloalkanes, C_6 rings and higher; Allinger and coworkers[20] checked their method with a long list of alkanes and cycloalkanes. Parameters appropriate to alkenes were proposed by Jacob, Thompson, and Bartell,[21] but their scheme has not been tested on cycloalkenes. The question remains whether any of the proposed prescriptions adequately accounts for the observed conformations of the cyclohexadienes.

The equations proposed by Bartell, *et al.*,[21] were programmed to compute the energies individually allocated to bond stretching, angle bending, nonbonded interactions, and torsional strain for several specified cyclohexadiene structures. Table IX brings to light a number of very interesting features. First, according to this scheme, the magnitudes of bond stretching and nonbonded interactions are very large; these are not observable directly; only differences between conformations should be considered. However, a high premium is thereby placed in the accuracy of the parameters, since the observables correspond to small differences between large calculated quantities. Second, as anticipated, differences between the nonbonded interactions are much larger than those between the angle-strain terms. In the 1,4 isomer this clearly favors the planar conformation, contrary to our experimental result. On the basis of Bartell's procedure, the structure proposed by Dallinga and Toneman for 1,4-cyclohexadiene has the lowest strain energy, but this is not necessarily the minimum energy conformation.

There are two independent checks on the validity of the prescription for calculating total strain energies. The potential barrier for inversion of the nonplanar conformation is, in principle, measurable *via* the temperature dependence of its nmr spectrum, at low temperatures.

Table IX. Strain Energy for 1,4-Cyclohexadiene (kcal/mole)

	Planar (Dallinga and Toneman)	(Test) planar	Non-planar
Bond stretching[a]	52.09	50.83	50.83
Nonbonded repulsions	94.67	100.41	106.39
Angle bending	3.18	1.85	3.10
Torsion	6.00	6.00	5.24
Total	155.95	159.09	165.56

Strain Energy of 1,3-Cyclohexadiene

	Nonplanar	(Test) planar
Bond stretching	49.98	49.98
Nonbonded repulsions	99.46	99.79
Angle bending	0.11	0.95
Torsional	3.26	6.00
Total	152.81	156.72

[a] Double bond length was assumed fixed and was not included in the calculations. In the planar models the bond distances were taken to be equal to those found experimentally; the angles, as near to those found as possible, except for 1,4: $\angle H_3C_3C_2 = 108.3°$ (see Table II).

The second and more direct test for these empirical energy calculations is the estimation of isomerization energy from 1,3- to 1,4-cyclohexadiene. Indirect estimates[22] based on equilibrium product distributions for isomerization of substituted derivatives in DNSO by KO-*t*-Bu suggest that ΔH_{isom} is quite small. The measured heats of hydrogenation are 53.6 and 53.9 kcal/mole for the 1,3 and 1,4 isomers, respectively.[23] In contrast, the calculated difference in strain energies for the structures as observed is 12.7 kcal/mole (Table IX). Our conclusion is that potential energy parameters appropriate for cycloalkadienes have yet to be proposed. Analysis of electron diffraction photographs for cyclohexene is now underway; that structure will also serve as a test for strain-energy calculations.

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